MEASUREMENT AND COMPUTATION OF PHASE EQUILIBRIUM AT INFINITE DILUTION

By

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ABSTRACT

In this study, a presentation of vapour-liquid equilibrium measurement and computation is made. The problem was to find infinite dilution activity coefficients (γ^{∞}) of volatile organic compounds in water and silicone oils. These were then compared to find a thermodynamically better absorbent for the effective removal of volatile organic compounds from contaminated air streams. Experimentally, the infinite dilution activity coefficients were obtained using chromatographic methods namely Static headspace and the dynamic Gas Liquid Chromatography (GLC) techniques. When the static determined activity coefficients were compared with the GLC results, a good agreement was observed and these compare very well to those in literature, hence suitable, reliable and accurate techniques were used. The internal agreements of the static and GLC experiments were found to be ±3% and ±1% respectively. Using the γ^{∞} as a measure of solubility, silicone oil was found to be a better absorbent, for example in the case of heptane the following mole fraction based activity coefficients were obtained 0.385 and 607 000 in silicone oil and water respectively. To confirm experimental work, original, modified and effective UNIFAC methods were used to estimate γ^{∞}. Compared to experimentally obtained results, reasonable predictions were obtained in water and they were found to be wrong in oil leading to the conclusion that the UNIFAC procedure is not suitable for studying solvent-polymer solution thermodynamics.

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NOMENCLATURE

a	Interfacial area of the packing
a_i	Activity of component *i* in a mixture, dimensionless
a_T	Reference volume intercept in the GCLF theory at temperature T, $m^3/kmol$
a_{mn}	Group interaction parameter between groups m and n.
A_{wk}	Van der Waals surface area
A_i	Antoine coefficient A of component *i*
$B(T)$	Second virial coefficient
B_{33}	Second Virial coefficient
B_{13}	Second cross virial coefficient
B_i	Antoine coefficient C of component *i*
b	Liquid phase cross sectional area in column
C_{133}	Third cross virial coefficient
C_i	Antoine coefficient C of component *i*
D_g	Gas diffusity, m^2/s
d_f	Effective thickness of liquid film
d_p	Particle diameter
$e_{km,T}$	Group characteristic interaction energy between groups *k* and *m* at temperature T, $kJ.mol^{-1}$
f_i^v	Fugacity of component *i* in the vapour phase
f_i^l	Fugacity of component *i* in the liquid phase
F	Volume fraction in column
F_o	Carrier-gas flow rate
G^E	Molar excess Gibbs free energy
h^E	Molar excess enthalpy
H	Henry's law constant, dimensionless
H_C	Henry's law constant, $length^3$.pressure/mole
HTU_G	Height of gas-phase transfer unit, length
HTU_L	Height of a liquid-phase transfer unit, length
HTU_{OG}	Height of an overall gas-phase transfer unit, length

HTU_{OL}	Height of an overall liquid phase transfer unit, length
J_3^2, J_3^4	Pressure drop corrections
k^o	Zero pressure partition coefficient
k_G	Gas-phase mass transfer coefficient, kmol/s.bar.m^3
K_G	Overall gas-phase mass transfer coefficient, kmol/s.bar.m^3
k_L	Liquid phase mass transfer coefficient, kmol/s.bar.m^3
K_L	Overall liquid-phase mass transfer coefficient, kmol/s.bar.m^3
L	Liquid volumetric flow rate, m^3/s
	Length of column
M_i	Molecular mass of component *i*
n_i	Number of mole of component *i*
n	Total number of moles
N	Number of molecules in the ensemble, dimensionless
N_h	number of holes in the lattice, dimensionless
N_i	Number of molecules of type *i* in the system, dimensionless
N_q	total number of interaction sites available in the system, dimensionless
N_{av}	Avogadro's number, kmol^{-1}
NTU	Number of transfer units
p_i, p_o	Column inlet and outlet pressure
p	Pressure, Pa
p_i^o	Pure component vapour pressure
p_F	Flowmeter pressure
P^*	characteristic pressure, Pa
$\widetilde{P}$	Reduced pressure of the mixture dimensionless
$\widetilde{P}_i$	Reduced Pressure of component *i*, dimensionless
P_o	Athermal contribution to the vapour pressure, Pa
P_i^s	Vapour pressure of component *i*
q	Effective chain length or surface area parameter for the mixture, dimensionless
q_i	Effective chain length or surface area parameter for component *i*, dimensionless
Q_k	UNIFAC surface area parameters, dimensionless

Q_n	Amount of solute in the nth plate
r	Number average chain length for the mixture, dimensionless
r_i	Number of segments in a molecule of type i, dimensionless
r_{ij}	Distance between atoms i and j
R_k	Volume of group k
R	Universal gas constant, $J.kmol^{-1}.K^{-1}$
R_{ij}	The ratio of headspace concentration
S	The solubility of a gas in a liquid
t_R, t_M	Retention times, (minutes)
T_F	Flowmeter temperature
T	Temperature
T^*	Characteristic temperature, K
$\tilde{T}_i$	Reduced temperature of component i in the mixture, dimensionless
$\tilde{T}$	Reduced temperature of the mixture, dimensionless
u	Linear gas velocity
u_{jj}	Interaction energy between atoms i and j
U_{mn}	Interaction energy between groups m and n
v	molar volume, m^3/kmol; volume per segment, m^3
$\tilde{v}$	Reduced volume of the mixture, dimensionless
v_h	Volume of lattice site, m^3/kmol
$\tilde{v}_i$	Reduced volume of component i $\left(v/v^*\right)$, dimensionless
v_i^*	Characteristic volume for component i, m^3/kmol
v_i^o	Pure component molar volume
$\bar{v}_{12}^{\infty}$	Partial molar volume at infinite dilution
V	Volume
V_m	Gas hold up volume
V_h	Effective volume of each plate
V_R	Uncorrected retention volume
V_N	Net retention volume
V_g	Specific retention volume
V_2	Solvent volume
V^*	Reference volume, m^3/kmol

ΔV	Volume change of mixing, m^3
V^E	Molar excess volume
V_{wk}	Van der Waals volume
w_i	Weight fraction of component *i*
x_i	Mole fraction of component *i* in the liquid phase
X_m	Mole fraction of group m in the solution
y_i	Mole fraction of component *i* in the gas phase
Z	Co-ordination number, dimensionless, a constant set equal to ten
	Packing height in column, m
	Compressibility factor

Greek letters:

α	Iteration number
α_h	Characteristic surface area of a lattice site, dimensionless
β	Coefficient, $1/kT$, J^{-1}
γ_i	Activity coefficient of component i
Γ_k	Residual activity coefficient of group k in solution
Γ_k^i	Residual activity coefficient of group k in pure component i
Γ_{km}	Nonrandomness parameter for *k-m* contacts on a hole-free basis, dimensionless
δ_i	Flexibility parameter for component i, dimensionless
δ_{ij}	Binary interaction parameter between molecule *i* and *j*, dimensionless
ξ	Coefficient
ε_{ij}	Characteristic energy of interaction between a segment of molecule *i* and a segment of molecule *j*, $kJ.kmol^{-1}$
θ	Surface fraction of the mixture, dimensionless
θ_i	Surface area fraction of molecule *i* in the solution
θ_k	Surface area fraction of group *k* in the solution

$\theta_{i,p}$	Surface area fraction of component at the same temperature and pressure as the mixture, dimensionless
$\Theta_k^{(i)}$	Surface area fraction of group k in component i using UNIFAC surface area parameters, dimensionless
μ^L	Liquid phase chemical potential, J.kmol^{-1}
μ^V	Vapour phase chemical potential, J.kmol^{-1}
μ_i	Chemical potential of component i, J.kmol^{-1}
$\Delta\mu_i$	Change in chemical potential upon mixing for component i, J.kmol^{-1}
v_k^i	Number of groups of type k in a single molecule i, dimensionless
$\rho^{sat,liq}$	Saturated liquid molar density, kmol/m^3
ρ_l	Liquid phase density, kmol/m^3
ρ_v	Vapour phase density, kmol/m^3
σ_i	Symmetry parameter of component i, dimensionless
ϕ_i	Fugacity coefficient of component i, dimensionless
	Volume fraction of molecule in the solution
$_{mn}$	Group interaction parameter between groups m and n
Ω_i	Weight fraction activity coefficient of component i, dimensionless

Subscripts:

I, 2,	Component identification
i, o	Inlet and outlet
g	gas
l	Liquid
k,m,n	Functional groups

Superscripts:

o	Pure component or zero pressure
*	Experimental value

C	Combinatorial
E	Excess property
fv	Free volume
L	Liquid phase
R	Residual
s	At the saturation state
V	Vapour phase
∞	At infinite dilution

Dimensionless Numbers:

Re_L	Reynolds number
Sc_G	Schmidt number

CHAPTER ONE

INTRODUCTION

CHAPTER 1: INTRODUCTION

1.1 Summary

This work was sponsored by the National University of Science and Technology, Zimbabwe. All research activities were carried out at the school of chemical engineering, University of Birmingham. The subject of this thesis is fluid phase equilibrium thermodynamics aimed at describing quantitatively the distribution of solutes (volatile organic compounds) among the liquid phase (silicone oil or water) and the vapour phase. The quantity used to describe this distribution is the infinite dilution activity coefficient.

Infinite dilution activity coefficients are of great importance in that in many separation processes, the system behaviour in the very dilute regions is crucial in obtaining high-purity products and this is usually the most expensive and difficult part of the separation. The greatest deviation from ideal behaviour is usually exhibited in the dilute regions. Therefore it is reasonable to suggest that experimental measurement in the dilute regions should be given prominence. Infinite dilution activity coefficients γ^{∞}, usually represent the most accurate characterization of system behaviour in the dilute regions. In this work measurement of infinite dilution activity coefficients is considered important because environmental concerns, the focus of this research, usually centre on the extremely dilute regions for example parts per million (ppm) in the gas phase. Also another crucial consideration is that measurement of γ_i saves a lot of time and effort as compared to the determination of a full set of vapour-liquid equilibrium (VLE) data, say over the entire composition range.

In various separation processes such as distillation, absorption and extraction, separation is based on the differential change in concentration developed in two phases usually flowing in counter current. The maximum attainable separation occurs when the two phases are significantly far away from equilibrium. Separation factors are calculated from vapour liquid equilibrium data. Therefore knowledge of vapour-liquid equilibrium is essential in the design and operation of the equipment handling these operations. In this work, great effort was made to provide such data for the absorption and stripping processes involving volatile organic compounds and water or silicone oil systems.

Experimental determination of phase equilibrium is a tedious and expensive process, and sometimes it is very difficult to perform. To overcome this burden, the use of group contribution methods such as UNIFAC in the computation of vapour-liquid equilibrium is suggested. However it is important not to underestimate the value of having a few good measurements in order to generate a sound and reliable model. Therefore it is necessary to maximise the information and understanding gained from a minimum amount of experimentation.

1.2 Objectives

This work was carried out with the following aims;

1. To investigate the ability of chromatographic methods in the study of aqueous and solvent–polymer solution thermodynamics.
2. To measure infinite dilution activity coefficients of acetone, chloroform, cyclohexane, diethylether, ethylmethlketone, isobutylmethylketone, n-heptane, n-hexane, n-pentane, toluene, triethylamine and xylene in silicone oils and water.

3. To consider the effectiveness of silicone oils and water as absorbents in the removal of volatile organic compounds from contaminated air streams.
4. To perform sample manual calculations of activity coefficients of some volatile organic compounds in both water and silicone oils using the original UNIFAC, modified UNIFAC and effective UNIFAC. Vapour-liquid equilibrium computations can play crucial roles in the preliminary design of separation processes.

1.3 Measurement of infinite dilution activity coefficients

A number of methods can be used to measure infinite dilution activity coefficients. The most commonly used methods are differential ebulliometry, differential static apparatus, gas chromatographic methods and inert gas stripping. The static headspace and the dynamic gas-liquid chromatographic techniques were used to measure the infinite dilution activity coefficients of thirteen volatile organic compounds studied in this work.

The first phase of the experimental work was to use an improved and modified apparatus for the simple headspace technique in the measurement of infinite dilution activity coefficients. This enclosed system consisted of a conical flask with a side glass arm and sealed from the atmosphere by a rubber bung. Measurements were performed at atmospheric pressure and the temperature was varied from 303 to 333K.

In the second phase, a gas-liquid chromatographic technique was used to measure the infinite dilution activity coefficients of volatile organic compounds in poly(dimethylsiloxane) (PDMS) in the temperature range 303 to 423K. With the GLC

method, results can be obtained directly at infinite dilution, thus eliminating conventional extrapolation. The other advantage with this technique is that several types of information can be obtained from one chromatographic measurement. The effect of experimental variables, namely, liquid loading, sample size, temperature, vapour pressure and carrier gas flow rate on the solute specific retention volumes was investigated by the gas –liquid chromatographic technique using PDMS as the stationary phase.

Although the GLC was developed mainly as a highly efficient analytical technique, its capabilities in the study of the thermodynamics of solutions were duely foreseen by the inventors, Martin (1955, 1956, 1957). The theory of chromatographic operation as presented by Martin and Synge (1941) laid the foundation for a new approach to the study of solution behaviour.

1.4 Phase equilibrium computation

The universal functional-group activity coefficient (UNIFAC) method developed by Fredenslund et al (1975, 1977, 1977a) was used in the later stages of this work to calculate activity coefficients of some volatile organic compounds in both water and silicone oils. The results of this work show that the original UNIFAC procedure is not good for studying solvent-polymer solution thermodynamics.

1.5 Volatile organic compounds abatement technology

The growth in environmental legislation, the increasing influence of public opinion and the inception of the "permit to operate" principle are placing increasing pressure on industry to avoid and minimise gaseous emissions. Several techniques are available for

the control of volatile organic compounds and odours. Considering whether organic compounds are destroyed or extracted for later recovery, two main types of removal technologies can be distinguished under the destruction type. Incineration and biological oxidation are the most common while absorption, adsorption and condensation are used as recovery techniques. Gas absorption processes are described in detail in appendices A and B while other technologies are only surveyed.

1.6 Thesis Overview

Presented in table 1.1 is an executive summary of the thesis. The thesis is divided into nine chapters, in addition to this an appendix section is also included.

Table 1.1 Thesis overview

CHAPTER	CONTENTS
1. Introduction	Thesis highlights including objectives
2. Phase equilibrium measurements	Literature survey material explaining the two experimental techniques, the static headspace and the glc methods.
3.Phase equilibrium computations	Activity coefficient and equations of state based group contribution methods are outlined. Molecular simulation of phase equilibrium is introduced.
4. Experimental work	Infinite dilution activity coefficients measurements
5. Results	Results are presented in tabular and graphic forms.
6. Discussion	Comments on the important findings, the chapter is divided into three parts; simple headspace method, the glc and group contribution methods.
7. Conclusion	A summary of achievements, failures and interesting findings of this research.
8. Recommendations	A list of short term and long term future plans. This covers future work on gas absorption and vapour-liquid equilibrium prediction using group contribution methods and simulation procedures.
9. List of references	References used in this work are listed.
Appendices	Additional material including VOC abatement techniques, experimental raw data and calculations.

CHAPTER TWO

PHASE EQUILIBRIUM MEASUREMENTS

CHAPTER 2: PHASE EQUILIBRIUM MEASUREMENTS

2.1.The Headspace Method

The dilute solution has played a very important role in the developments of concepts in physical chemistry. The study of very dilute solutions has been given prominence both in theory and experiment. The various laws of infinitely dilute solutions are thermodynamically deducible from one another, Adamson (1979).

The values of Henry's law constants (*H*) are required in

(i) The prediction of the behaviour of volatile organic compounds in the environment.

(ii) The design and performance models of air stripping processes for the renovation of organic solvent contaminated waters.

(iii) Transport models that attempt to describe the movement of volatile organic compounds in the saturated zone of the subsurface environments.

(iv) The design of absorption equipment that try to prevent the release of high organic concentration gas / air streams from chemical plants.

In literature, Henry's law constant (*H*), La Grega, Buckingham and Evans (1994); Tchobanoglous and Burton (1991); Hansen and others (1995); Gosset (1994); Yaws, Yang and Pan (1991), is conveniently expressed as the ratio of the partial pressure P_i in the vapour phase (in various units such as Pa, atm, torr) to concentration C_i in the liquid phase (also in various units such as mole fraction and mass or mole concentration)

$$H = P_i / C_i \quad \text{.....} \quad (2.1.1)$$

There is a growing interest in the study of Henry's law constants, which describe the equilibrium partitioning between a liquid and a gas phase to predict the fate of volatile organic compounds in the environment Bukhard, Andren and Armstrong (1985). Therefore Henry's law constant, referring to the gas / liquid equilibrium is one of the most important parameters governing the distribution of chemicals in the environment. A knowledge of Henry's law constant is essential in calculating the rate and direction of transfer Mackay, Shiu and Sutherland (1979).

Henry's law represents a limiting behaviour for any gas / solvent system as the partial pressure approaches zero. The law breaks down when (i) the partial pressure exceed 5 – 10 atmospheres and (ii) the dissolved concentration exceed approximately 3 mole % Mackay, Shiu and Sutherland (1979).

Mackay and Shiu (1981) presented a comprehensive review of the common methods which can be used to measure H. The review also gives the merits and deficiencies of each method. Mackay and Shiu cited three basic methods

(i) use of vapour pressure and solubility data

(ii) direct measurements of the air and aqueous concentrations in a system at equilibrium

(iii) measurement of relative changes in concentration within one phase, while affecting a near equilibrium exchange with another phase.

In the first method, Henry's law constant for a solute with a low aqueous solubility is the ratio of the vapour pressure to aqueous solubility. This method suffers from the lack of

reliable solubility and vapour pressure data. This is sometimes due to analytical difficulties Lawrence and co-workers (1985).

The second one is a thermodynamic method where the gas and liquid concentrations of a compound are determined under equilibrium conditions and H is calculated as their ratio Mackay and Wilkoff (1981). Bukhart *et. al.* (1985) discussed the validity and limitations of this approach. It is quite useful to have measurements at different temperatures to to allow temperature variation of the physical properties of the organic compound to be evaluated. This method depends on the fact that after the establishment of equilibrium in a closed system, the fugacity of any material is the same in each of the phases present (Mackay (1979, 1981) The establishment of equilibrium is dependent upon experimental apparatus and the operating conditions for example gas flow rates and liquid depths. If equilibrium is not attained the measured value of H will be too low. This is difficult to carry out with accuracy at the low concentrations typical of environmental levels.

Finally, the third method is a kinetic one based on the rate of loss of a compound from a solution by gas stripping Doskey and Andren (1981) and Atlas, Foster and Giam (1982). It suffers from the experimental deficiencies in achieving adequate approach to equilibrium Lincoff and Gosset (1984).

Poly(dimethylsiloxane)

Silicone oil, chemically known as poly(dimethylsiloxane) can be used as an absorption medium in waste air scrubbing. It is highly suitable for removing solvent vapours from waste air, especially for absorbing alcohol, esters, chlorinated hydrocarbons, hydrocarbons, aromatics and ketones. Owing to its high boiling point and its stability

temperatures in excess of 150 ^{0}C, it can be desorbed at standard pressure for the recovery of the substances.

In assessing the solubility of gases and vapours in solutions the crucial factor alongside the vapour pressure of the pure substance is the activity coefficient γ_i of the dissolved substance. Activity coefficients are correction factors that can be applied to Raoult's and Henry's laws to allow for deviations from ideal and ideal dilute behaviour respectively. There is an inverse of proportionality between the solubility and the activity coefficient of a chemical. In absorption operations low activity coefficients are highly desirable.

Raoult's law

$$p_i = x_i p_i^o = y_i \phi_i P \quad \text{..... (2.1.2)}$$

Dalton's law

$$p_i = y_i P = x_i \gamma_i p_i^o \quad \text{..... (2.1.3)}$$

2.1.1. The Simple Method.

The simple method Evanson (1999) is a static head space concentration in a closed system. It was developed to determine the effect of Sodium hypochlorite on the vapour – liquid equilibrium of styrene monomer and water. It is a common method for measuring Henry's law constants for volatile organics. This method makes use of a calibration curve for the calculation of headspace concentration of a volatile compound.

2.1.2. The Equilibrium Partitioning in Closed Systems (EPICS)

The method requires no special apparatus and obtains results from measurement of gas headspace concentration ratios from pairs of sealed bottles identical in all respects except liquid volumes. Calibration curves are not needed since the relative rather than the absolute concentrations are required. It is based upon the addition of equal masses of solute to two sealed bottles. The resulting ratio of the two headspace concentrations is used to compute Henry's constant. The principle requirement for the successful application of this method is that the instrument response must be linear throughout the concentration range of interest and can be correlated with a temperature regression equation. The modified EPICS version of the original formulation by Gosset and Lincoff (1984) can be used. The modified version eliminates the assumption of equal solute masses in the individual bottles comprising an EPICS system. Differences in mass due to imperfect, volumetric additions are accounted for through gravimetric means.

The total moles (M) of volatile solute added to a serum bottle will be partitioned at equilibrium according to

$$M = C_l V_l + C_g V_g$$

Since

$$H_c = \frac{C_g}{C_l}$$

$$M = C_g\left(V_l / H_c\right) + C_g V_g$$

$$M = C_g\left[\left(V_l / H_c\right) + V_g\right] \quad \text{..... (2.1.4)}$$

where C_l is the concentration of the solute in the liquid (mol/L), C_g is the concentration of the solute in the gas phase, V_l is the volume of liquid in bottle (L), V_g is volume of headspace in the bottle/flask. H_c is the dimensionless Henry' law constant. If two bottles are prepared with differing liquid volumes V_{l1} and V_{l2}, equation (2.1.4) hold for each and one can write

$$M_1 = C_{g1}\left[\left(V_{l1}/H_c\right)+V_{g1}\right] \quad \text{.....(2.1.5)}$$

$$M_2 = C_{g2}\left[\left(V_{l2}/Hc\right)+V_{g2}\right] \quad \text{.....(2.1.6)}$$

The original EPICS formulation, $M_1 = M_2$ is assumed. However, one may refrain from this assumption and instead divide equations (2.1.5) and (2.1.6) by M_1 and M_2 respectively. The left - hand sides of each will be equal to unity. This allows the two equations to be equated.

$$\left(C_{g1}/M_1\right)\left[\left(V_{l1}/H_c\right)+V_{g1}\right]=\left(C_{g2}/M_2\right)\left[\left(V_{l2}/H_c\right)+V_{g2}\right] \quad \text{.....(2.1.7)}$$

Solving for H_c yields

$$H_c = \frac{\left[\left(C_{g1}/M_1\right)/\left(C_{g2}/M_2\right)\right]V_{l1}-V_{l2}}{V_{g2}-\left[\left(C_{g1}/M_1\right)/\left(C_{g2}/M_2\right)\right]V_{g1}} \quad \text{.....(2.1.8)}$$

$$H_c = \frac{V_{l2}-rV_{l1}}{rV_{g1}-V_{g2}} \quad \text{.....(2.1.9)}$$

where

$$r = \left(C_{g1}/M_1\right)/\left(C_{g2}/M_2\right) \quad \text{.....(2.1.10)}$$

The original EPICS formulation was merely a simplification of equation (2.1.10) for a special situation in which $M_1 = M_2$ and $r = C_{g1}/C_{g2}$. Evaluation of H_c using equation (2.1.9) does not actually require that M_1 and M_2 be known, only their ratio is required. This is an important point because if a stock solution of solute is used to prepare EPICS samples, the actual concentration of the solute need not to be known. The gravimetric

measure of the relative quantity of the stock solution added to the EPICS bottles suffices. Volumetric measures are far less precise than gravimetric ones. If one attempts to inject equal volumes of the stock solution to the bottles, gravimetric analysis of the stock masses injected via weighing of a syringe or bottle just before or after injection, will detect the differences.

2.1.2.1 Measurement of Activity Coefficients.

A further modification of the EPICS procedure allows the measurement of activity coefficients of volatile solutes. Suppose two sealed bottles are prepared with identical liquid volumes one containing liquid water plus solute and another containing the solute in a mixture for which the solute's activity coefficient is desired. Equation (2.1.5) is applicable and rearranging it yields

$$(V_l/H_c)+V_g = r^*\left[(V_l/H_c^*)+V_g\right] \quad \text{..... (2.1.11)}$$

where

$$r^* = (C_{g1}/M_1)/(C_{g0}/M_0) \quad \text{..... (2.1.12)}$$

Where C_{g1} and C_{g0} are the gas – phase concentrations in the bottles with the non ideal and ideal solutions respectively (mol/L), M_1 and M_0 are quantities of volatile solutes added to the non ideal and ideal bottles respectively (mol), H_c is the dimensionless Henry's constant for the ideal system, H_c^* is the effective dimensionless Henry's constant in the non ideal system ($H_c^* = \gamma H_c$), and γ is the applicable activity coefficient for the non ideal system. Making the substitution of $H_c^* = \gamma H_c$ and rearranging yield

$$\gamma = r^* V_w/\left[V_w + (1-r^*)H_c V_g\right] \quad \text{..... (2.2.13)}$$

Equation (2.2.13) allows the determination of activity coefficients for a solute in several different, non ideal systems yielding different values of (C_{g1}/M_1), with a single reference ideal system giving (C_{g0}/M_0).

2.2 Gas – Liquid ChromatographicTechnique

2.2.1 A Brief Historical Review of Chromatography

The first published work on chromatography was in 1906 by Tswett although the word chromatography was employed as early as 1731. Tswett was the first to recognise that the chromatographic process consists of sequential sorption – desorption interactions. This was visualised in his original experiments in which plant pigments were separated into coloured bands by elution with petroleum ether through a bed of powdered calcium carbonate. The name chromatography was suggested for this separation method.

After Tswett's experiments nothing was done until 1931 when Kuhn, Winterstein and Lederer rediscovered the same technique when resolving plant carotene into its components. This technique called liquid – solid chromatography was further developed between 1940 to 1946 mainly by Tiselius and Claesson.

Wilson (1940) was the first to describe the chromatographic process mathematically assuming complete solute sorption – desorption equilibria. The elution process was then treated as the passage of a concentration profile through the chromatographic system. He also recognised that bandwidth phenomena were most likely dependent on column void space, diffusion, and finite rates of sorption – desorption.

The most important development in the history of chromatography was in 1941 when Martin and Synge (1941) developed a theory based on packed column distillation for liquid – liquid chromatography. Equilibration of a solute between the mobile and stationary phases in each plate was assumed to be complete. Plate to plate diffusion was

said to be negligible and the ratio of solute concentration in the phases (partition coefficient) was taken to be a constant irrespective of the amount of solute present (linear isotherm). De Vault (1943) offered a promising improvement to Wilson's earlier treatment by correcting several of the physical impossibilities, which developed from the theory. De Vault's treatment was superior to that of Martin and Synge in that it was based on the continuous distribution of solute between the stationary and mobile phases along the length of the column. Thus avoiding the hypothetical discontinuity of the plate model. This treatment was also confirmed later by Weiss (1943).

Thomas (1944) made an important contribution to the continuous distribution model. He examined ion exchange process in flowing systems and demonstrated that if the flow rate is slow enough the rate – controlled sorption – desorption column processes will approach equilibrium and then can be treated with mathematical precision. Investigations of rate controlled kinetic processes such as diffusion and mass transfer were carried out by many workers. Laidus and Amundson (1952) developed a mathematical model that introduced explicitly concepts of eddy and longitudinal diffusion and mass transfer non equilibrium contributions. These studies formed the basis of the well – known treatments of, Zuiderweg, van Deemter, Klinkenberg and Sjenitzer (1956). These workers simplified the mathematics of Lapidus and Amundson and as a result clarified and popularised what is known as the rate theory of chromatography.

After the publication of the successful experiments of James and Martin, GLC received great response as the simple and powerful technique in separation and analysis work. The gas – liquid Chromatography technique has progressed rapidly in theory and practice

since 1952. Important contributions to GLC are due to James and Martin (1952), James and Phillips (1953), Ray (1954), Bradford, Harvey and Chalkey (1955).

Golay (1957) introduced a new version of GLC in 1957 by replacing the packed chromatographic column with high efficiency capillary column in which the liquid phase is supported by the inside wall of the capillary tube. He developed a theory for the capillary column based on an electrical analogy of resistors and condensers.

In this work the interest is on gas – liquid chromatography of packed column type. On investigating various experimental parameters, James and Martin (1952) found that under constant conditions of flow and temperature the volume of gas required to elute each substance from a given column (the retention volume) was constant. And that for a homologous series of compounds the retention volumes of the members bore a simple relation to their molecular weights.

2.2.2 Solute Polymer Interactions:

A gas chromatographic column is usually filled with a solid support material, which is coated with a stationary phase. The retention of a moving solute then depends on the partition of the solute between the stationary phase and the moving gas phase. This partition is dependent mainly on the saturation vapour pressure of the solute at the column temperature and on the tendency of the stationary phase to sorb the solute molecules. In this study the carrier gas is assumed to behave ideally, thus any imperfections in the gas are disregarded, also any corrections for the interactions between the solute molecules and solute – carrier gas molecules are neglected. These assumptions are more valid when hydrogen or helium is the carrier gas and the operating pressure of the column is low.

Taking poly (dimethylsiloxane) as an ordinary liquid, the main mechanism for the sorption of solutes is the absorption of solutes in the bulk polymer phase. This mechanism allows the quantitative treatment of the data obtained from glc work. When the solute is held back by absorption only, the retention volume is directly proportional to the amount of polymer on the column loading.

When absorption in the bulk of the polymer is the dominating mechanism, the theory of gas liquid partition chromatography may be applied to the results to calculate various thermodynamic quantities. The vapour pressure p_i of compound i above a binary solution can generally be expressed as

$$p_i = \gamma_i x_i P_i^o \quad \text{..... (2.2.1a)}$$

where γ_i is the activity coefficient.

x_i is the mole fraction of component 1 (the injected solute)

P_i^o is the saturation vapour pressure of the solute.

In ideal solutions γ_i equals unity, in real solutions γ_i is different from unity and depend on x_i----x_n. The concentration of the solute in the gas chromatographic column is not known and is often so low that Henry's law, stating that γ_i is a constant independent of x_i explains the results. Such behaviour cannot be expected if polymers are used as a stationary phase. Experiments are done with different sample sizes and extrapolation to zero concentration is done using the following relationship.

$$P_i = \gamma_i^{\infty} x_i P_i^o \quad \text{..... (2.2.1b)}$$

Where γ_i^{∞} is the activity coefficient at infinite dilution

Many treatments of gas liquid retention theory have been reported in literature. These differ mainly in the procedure used for extrapolating measured retention data to zero

carrier gas pressure. The GLC technique allows the determination of activity coefficients of a non -electrolyte solute (component 1) at very low concentrations (E-03 to E-06) mole fraction in a solvent (component 2). The technique is applicable to ternary systems in which component 3 is a carrier gas that is relatively insoluble in the solvent. The solvent is usually a non - volatile, non- electrolyte, but the technique can be modified for volatile solvents.

2.2.3. Significance of Infinite Dilution Studies.

Infinite dilution is important as the concentration region for linear chromatography where all solute molecules behave independently. At infinite dilution there is no interaction between solute molecules and the property under investigation varies linearly with concentration. Infinite dilution is often the most important region in studying phase interactions because this region normally exhibits the greatest deviation from ideal solution behaviour. Solutions can be categorised by specifying the infinite dilution activity coefficients of all components. From these values predictions can be made for the complete composition dependence of the activity coefficients using the Van Laar or other correlation equations. The accuracy of prediction from infinite dilution values is often quite good. The GC is unrivalled as a good technique of measuring infinite dilution activity coefficients and is potentially of great value in process design.

2.2.4. Theories of Chromatography.

Several mathematical methods have been developed to describe the chromatographic phenomena. For gas-liquid chromatography the applicable methods can be divided into two basic theories. One of these theories is based on equilibrium and is called the plate

theory, while the other, the rate theory is based on the kinetics. Their descriptions are as follows

2.2.4.1. The 'plate' theory

Martin and Synge (1941) introduced the plate theory for the first time by applying the 'theoretical plate' concept of distillation to a liquid – liquid chromatographic column. In 1947 this theory was expanded by Mayer and Tomplains who showed how the number of theoretical plates could be calculated. Later James and Martin modified the theory in 1952 by deriving a correction factor for the compressibility of the carrier gas in the case of gas liquid chromatography.

The theory makes the following assumptions:

1. Instantaneous equilibrium takes place on the first and on each successive theoretical plate.
2. The distribution isotherm is linear, that is at equilibrium the distribution ratio of one solute between the two phases is independent of both the absolute value of its concentration and the presence of other solutes.
3. The diffusion effects of the solute along the length of the column are negligible.
4. The solute volume is negligibly small.
5. The molecules of the solute are distinguishable in the carrier gas.
6. The pressure is constant throughout the column.
7. The support material is completely inert and exerts no adsorption effect

According to the plate theory the GLC column is considered to consist of a number of thin layers and each is such that true equilibrium exists between the mean concentration of the solute in the stationary phase in that layer and its vapour in the gas phase leaving the

layer. Consequently, each layer is equivalent to one theoretical plate. The height of each plate is called the height equivalent to the theoretical plate (H.E.T.P).

The passage of a solute through the column can be treated mathematically by making a material balance around each plate during the continuous flow. A binomial expansion is developed to express the amount of solute left in each plate after successive infinitesimal volumes of the gas phase have passed. The Gaussian distribution is used to approximate the binomial distribution through the use of Bernoulli's theorem. This treatment finally leads to the following expression of the shape of the elution curve in a column of n plates:

$$Q_n = \frac{1}{\sqrt{2\pi n}} \left(\frac{V}{V_m + KV_L}\right)^{ne^n - \frac{V}{V_h}} \quad \text{..... (2.2.2)}$$

where Q_n is the amount of solute in the n^{th} plate when V of gas phase has passed.

V_m is the volume of gas hold – up in the column.

V_L is the liquid phase volume

K is the partition coefficient defined as the ratio of the solute concentration per unit volume in the liquid phase to that in the gas phase.

V_h is the effective volume of each plate which is equal to $h(a + Kb)$ where h is the height equivalent to a theoretical plate, a and b are the cross sectional areas of the gas and liquid phases respectively.

At maximum concentration

$$Q_n = \frac{1}{\sqrt{2\pi n}}$$

$$n = \frac{V}{V_h}$$

and V being the volume of the gas used to elute the maximum peak of the solute through the column and this is by definition equal to the retention volume V_R

Therefore

$V_R = V_M + KV_L$ ..... (2.2.3)

A correction factor (j) derived by James and Martin is used to account for the change in the volume of the carrier gas due to pressure drop across the column.

$V_N = jV_R^0$ ..... (2.2.4)

Where V_N is the net retention volume

V_R^0 is the adjusted retention volume and is equal to V_R - V_M.

P_i is the inlet pressure

P_o is the outlet pressure

j is the carrier gas compressibility factor given by $\frac{3}{2}\left[\frac{\left(P_o/P_i\right)^2 - 1}{\left(P_o/P_1\right)^3 - 1}\right]$

Equation (2.2.3) is the fundamental equation in GLC through from which thermodynamic functions can be calculated. The number of theoretical plates can be derived by making use of equation (2.2.2) Ambrose (1961). The two points of inflection of the Guassian curve of the equation are at $V = (2 \pm \sqrt{n})V_h$ and the intersections with the base line of the tangents to these points are at $V = (n \pm 2\sqrt{n})V_h$. The section of the baseline between these two points of intersection is the peak width V_p (shown in figure 2.1) and is calculated as follows

$V_p = (n + 2\sqrt{n})V_h - (n - 2\sqrt{n})V_h = V_h\sqrt{n}$ ..... (2.2.5)

The number of theoretical plates (n) which is essentially a measure of peak sharpness and can be calculated from measurements of the volume of gas corresponding to peak maximum (V_R) and the peak width (V_p) of the chromatogram in the following way

$$\frac{V_R}{V_P} = \frac{nV_h}{4V_h\sqrt{n}} = \frac{1}{4}\sqrt{n}$$

or

$$n = 16\left(\frac{V_R}{V_p}\right)^2 \quad \text{..... (2.2.6)}$$

The height equivalent to a theoretical plate (HETP) is given by

$$\text{HETP} = \frac{L}{n} \quad \text{..... (2.2.7)}$$

Where L is the length of the column.

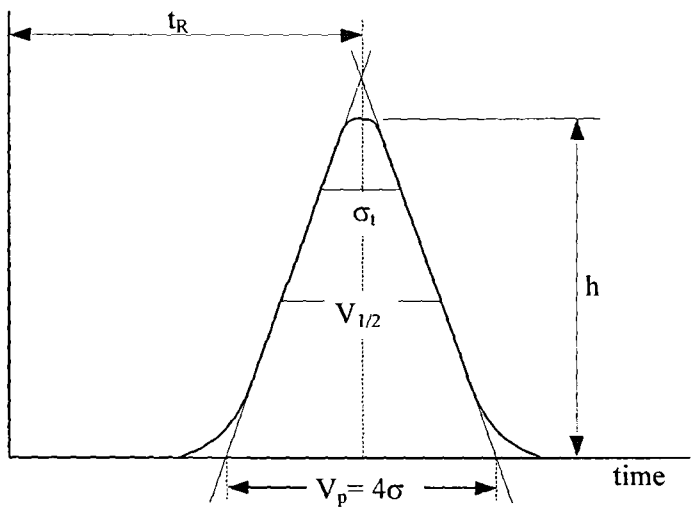


Figure 2.1. Measurement of N

2.2.4.2 The "rate" theory.

Van Deemeter *et al.* developed the rate theory for linear isotherm, by taking the chromatographic column as a continuous medium and also taking into account diffusional operations of mass transfer. The theory shows that the distribution curve of a single solute can be approximated by a Gaussian curve of the same type as that of the "plate" theory.

According to the rate theory as presented by Van Deemeter *et al*, the phenomena-taking place in chromatographic columns are described by the following factors

1. Eddy diffusion caused by the irregular paths of gas molecules, which result from the presence of packing material.
2. Molecular diffusion of the solute in the vapour phase takes place longitudinally. Molecular diffusion in the liquid phase is very small and can be neglected.
3. Equilibrium between the two phases does not take place instantaneously because of resistance to mass transfer.

The relationship between the above factors and the height equivalent to theoretical plate is given as

$$\text{HETP} = 2\lambda d_p + 2MD_g/u + \frac{8k'}{\pi^2(1+k')^2} \times \frac{d_f^2}{D_L}u \quad \text{..... (2.2.8)}$$

Where λ is a quantity characteristic of the packing and is a measure of packing irregularities.

M is a correction factor for the toruosity of the interparticle spaces.

D_g is the diffusion coefficient in the gas phase.

u is the linear gas velocity.

k' is the factor given by KF_l/F_g where K is the partition coefficient, F_l and F_g are volume fractions of liquid and gas phase in the column.

d_f is the effective thickness of liquid film on the support.

D_L is the diffusion coefficient in the liquid phase.

Equation (2.2.8) can simply be expressed using three constants only as follows

$$HETP = A + B/u + C_s\bar{u} \quad \text{.....} \quad (2.2.9)$$

This is the abbreviated form of the well known equation referred to as the Van Deemeter equation. Where A, B, $C_s\bar{u}$ are the eddy diffusion, molecular diffusion and mass transfer terms.

The "rate" theory as represented by equation (2.2.8) was tested experimentally and found to be essentially correct DeWet and Pretorius (1958) and Bohemen and Purnell (1958). However Bohemen and Purnell indicated that the eddy diffusion term is not independent of flow rate but inversely proportional to it. The Van Deemeter equation (2.2.8) was also modified by including the fourth term to account for the resistance to mass transfer in the gas phase Knox (1962).

The "plate" theory is the simpler of the two theories and is suitable in describing the shape of the elution curves and in calculating the number of theoretical plates and the HETP. The combination of the "plate" and "rate" theories can be made through the HETP of equation (2.2.8). The HETP is calculated from the "plate" and "rate" theories by equations (2.2.7) and (2.2.8) respectively and then expressed by three terms of equation (2.2.9). The resulting equation is very useful in discussing the various factors affecting GLC operation.

2.2.5. Activity and Activity coefficients

2.2.5.1 Defining Equations

The activity of a component (a_i) is defined as the ratio of its fugacity (f_i) in the given state to that in the standard state (f_i^o).

$$a_i = \frac{f_i}{f_i^o} \quad \text{..... (2.2.10)}$$

The standard state is taken as that of the pure component at the pressure and temperature of the system. The fugacity (f) was defined by Lewis (1958) in terms of the chemical potential (μ) as

$$\mu = RT\,\ell n f_i + B \quad \text{..... (2.2.11)}$$

where

$$\lim_{P \to o}\left(\frac{f}{p}\right) = 1$$

B is a constant at a single temperature and p is the pressure.

Combining equations (2.2.10) and (2.2.11) yields

$$\mu_i - \mu_i^o = RT \ln \frac{f_i}{f_i^o} = RT\, ln\, a_i \quad \text{..... (2.2.12)}$$

Equation (2.2.12) indicates that the activity is a measure of the difference between the chemical potential in the given state and that in the standard state.

The activity coefficient (γ) of a component is defined as the ratio of its activity to its mole fraction. Thus the activity coefficient of component i in a liquid phase is

$$\gamma_i^l = \frac{a_i^l}{x_i} = \frac{f_i^l}{f_i^{ol} x_i} \quad \text{..... (2.2.13a)}$$

In the vapour phase

$$\gamma_i^v = \frac{a_i^v}{y_i} = \frac{f_i^v}{f_i^{oV} y_i} \quad \text{..... (2.2.13b)}$$

Where subscripts l and v refer to the liquid and gas phase respectively, x and y refer to liquid and vapour phase mole fractions.

Provided the above defining equations of activity coefficient are related to the definition of ideal solution as suggested by Lewis (1958) the activity coefficient will then be a measure of the deviation from ideal solution. Lewis' definition of an ideal solution is represented by the following equations.

For the vapour phase

$$f_i^v = f_i^{oV} y_i \quad \text{..... (2.2.14a)}$$

For the liquid phase

$$f_i^l = f_i^{ol} x_i \quad \text{..... (2.2.14b)}$$

When both liquid and vapour phases are in equilibrium, the equilibrium criteria require that the chemical potential of a component, and therefore its fugacity must be the same in the two phases.

$$f_i^V = f_i^l = \gamma_i^v f_i^{oV} y_i = \gamma_i^l f_i^{ol} x_i$$

Therefore

$$\gamma_i^l = \frac{f_i^V}{f_i^{ol} x_i} \quad \text{..... (2.2.15)}$$

The activity coefficient of equation (2.2.15) is the liquid phase activity coefficient of component i when:

(a) the pure vapour does not obey the ideal gas law

(b) the vapour mixture is a non – ideal solution

(c) the liquid mixture is a non ideal solution

If the vapour phase is assumed to obey the ideal gas law, the fugacity of component *i* in the vapour phase will be equal to its partial pressure. By applying the equation of state of an ideal gas together with Dalton's law of partial pressure to the vapour phase, it can be shown that the partial pressure (P_i) will be equal to

$$P_i = f_i^V = Py_i$$

where P is the total pressure and so equation (2.2.15) becomes

$$\gamma_i = \frac{y_i P}{f_i^{ol} x_i} \quad \text{..... (2.2.16)}$$

Under conditions of low pressure, the effect of pressure on the fugacity of liquids is very small so that the fugacity of component *i* in the pure liquid state at the temperature and pressure of the system (f_i^{ol}) is taken to be the same as its fugacity at the system temperature and its own vapour pressure (f_i^o)

Therefore equation (2.2.16) becomes

$$\gamma_i = \frac{y_i P}{f_i^o x_i} \quad \text{..... (2.2.17)}$$

Provided that the vapour pressure is not too high, it can be taken to be equal to the fugacity of the pure component Hala (1958). Under these conditions equation (2.2.17) becomes

$$\gamma_i^o = \frac{y_i P}{x_i P_i^o} \quad \text{..... (2.2.18)}$$

Where P_i^o is the vapour pressure of pure component *i*.

Equation (2.2.18) is Raoult's law applied to non-ideal liquid solution. It involves two main assumptions:

(a) The vapour mixture obeys the ideal gas law and so it is an ideal solution.

(b) The fugacity of the pure liquid component is equal to its saturated vapour pressure.

2.2.5.2 Activity coefficients from conventional GLC

When the solute concentration is low in gas liquid chromatography, the gas phase is usually assumed to obey the ideal gas law so that equations (2.2.17) and (2.2.18) are applicable. Neglecting a small change in the volume of the liquid –phase due to the solubility of the solute, the concentrations (moles per unit volume) of solute in both vapour and liquid phases (c_1 and c_2) of a gas chromatographic column can be expressed as

In vapour – phase

$c_1 = P_i/RT = y_iP/RT$

In liquid phase

$c_2 = x_i\rho_l/M_l$

By definition the partition coefficient of solute is given as

$K = c_2/c_1$ ..... (2.2.19)

From equations (2.4.11) and (2.4.12) the activity coefficient can be expressed as

$$\gamma_i = \frac{RTN_i}{f_i^o K} \quad \text{..... (2.2.20)}$$

or

$$\gamma_i^o = \frac{RTN_i}{P_i^o K} \quad \text{..... (2.2.21)}$$

Where N_i is the number of moles of liquid phase per unit volume and is equal to

ρ_l / M_l .The partition coefficient is determined from GLC data by the fundamental equation.

$$K = \frac{j(V_R - V_M)}{V_L} = \frac{jV_R'}{V_L} = \frac{V_N}{V_L} \quad \text{..... (2.2.22)}$$

Rewriting equation (2.2.1b) so as to express the activity coefficient in terms of gas chromatographic data and saturation vapour pressure yields

$$\gamma_i^{\infty} = \frac{273.15R}{V_g^o P_1^o M_2} \quad \text{..... (2.2.23)}$$

where R is the universal gas constant

M_2 is the molecular weight of the solvent in the stationary phase.

V_g is the specific volume (per gram of solvent) reduced to the standard state

(0^0, 1atm)

2.2.5.3. Corrections for vapour phase deviation from ideality.

To correct for the vapour phase deviation from ideal behaviour, one can conveniently make use of the second virial coefficient (B) defined in the following way

$$B = \lim_{P \to 0} \left(V - \frac{RT}{P} \right) \quad \text{..... (2.2.24)}$$

Where V is the molar volume and P is the pressure. Corrections involving terms beyond the second virial coefficient are negligible at pressures of a few atmospheres. Taking corrections for the vapour phase deviation from ideality into account the activity coefficient at infinite dilution can be expressed as follows

$$\ln \gamma^{\infty} = \ln \left[\frac{273.15R}{P_i^o V_g^o M_2} \right] - \frac{P_i^o}{RT} (B_{11} - V_1) \quad \text{..... (2.2.25)}$$

Where B_{11} is the gas – state second virial coefficient of component 1 and V_1 is the liquid state molar volume.

When the carrier gas is helium at no more than 6 psi above atmospheric pressure (corresponding to 10 – 50 cm^3min^{-1} flow rate), the solute-carrier gas virial corrections are negligible.

If the activity coefficients of the volatile organic compounds in water are to be measured using the GLC technique, the calculation and graphical procedure of Newsham and Barr (1987) can be used to obtain the desired data. Newsham and Barr used equation (2.2.26) due to Cruickshank *et al* (1966) which shows the relationship between V_N and p_o for real gases at moderate carrier - gas pressures and allows for the non-ideality of the solute vapour, the solute / carrier gas molecular interactions and the pressure dependence of the partition coefficient.

$$\ln V_N = \ln\left(k^o V_2\right) + \beta p_o J_3^4 + \xi\left(p_o J_3^4\right)^2 \quad \text{.....(2.2.26)}$$

where

$$J_3^4 = \frac{3}{4}\left[\frac{(p_i/p_o)^4 - 1}{(p_i/p_o)^3 - 1}\right] \quad \text{.....(2.2.27)}$$

and V_2 is the volume of the solvent on the chromatographic support material.

The first three coefficients in equation (2.2.26) can be identified as follows

$$\ln k^o = \ln\frac{RT}{\gamma_1^\infty v_2^o p_1^o} - \frac{B_{11} - v_1^o}{RT} p_1^o \quad \text{.....(2.2.28)}$$

$$\beta = \left(2B_{13} - \bar{v}_{12}^{\infty}\right)/RT \quad \text{.....(2.2.29)}$$

$$\xi = (3C_{133} - 4B_{13}B_{33})/2(RT)^2 \quad \text{.....(2.2.30)}$$

In the above equations k^o is the zero pressure partition coefficient which is related to the activity coefficient through equation (2.2.28). B_{11} is the solute second virial coefficient, p_1^o the saturation vapour pressure of pure component 1, v_1^o is the molar volume of the pure solute and v_2^o is the molar volume of the pure solvent. B_{33} is the second virial coefficient of the carrier gas. $\bar{v}_{12}^{\infty}$ is the partial molar volume of solute infinitely dilute in the solvent (where this information is not available then v_1^o is used as an approximation). B_{13} and C_{133} are, respectively, the second and third cross virial coefficients between the solute and the carrier gas.

Barr and Newsham (1987) also stated that for solute samples of < 2 μmol admitted to packed columns of 4 mm internal diameter, equation (2.2.26) can be reduced to equation (2.2.31) if certain conditions are met. Thus carrier gas pressure p_o < 2 MPa, carrier gas not appreciably soluble in the solvent at the column temperature, $|B_{13}|$ < 180 $cm^{-3}mol^{-1}$ and $(p_i - p_o) < 200KPa$.

$$\ln V_N = \ln(k^o V_2) + \beta p_o J_3^4 \quad \text{..... (2.2.31)}$$

Thus a plot of $\ln(V_N / V_2)$ against $p_o J_3^4$ should give a straight line from which γ_1^{∞} and B_{13} can be found.

2.2.6 Definition of retention volumes.

2.2.6.1 Gas Holdup Volume (V_m)

The gas hold up volume is a measure of the total volume of space available to the mobile phase in the system, that is column dead / void volume, injector and detector volumes and the volumes of any connecting tubing for example from column to detector.

$V_m = Ft_m$ ..... (2.2.32)

In a well-designed system, the extra column dead volume is small compared to the column void volume. The column itself is not filled completely with stationary phase; the fraction of free (non-solid) space within a certain volume element of a porous material is called its porosity which is a measure of the space available to the mobile phase. Gas occupies both the space between particles where its moving and pores within particles, where it is stagnant. A non-sorbed molecule will spend part of its time in each type of space and will sometimes be flowing and sometimes be stopped. The time t_M the average molecule takes to reach the end of the column is the sum of these times. Hence V^0_M, the compressibility corrected gas hold up comprises both interparticle and intraparticle gas space.

2.2.6.2 Retention Volume (uncorrected) V_R

This is the mobile phase volume required to elute the sample from the column and is usually referred to as the retention volume without any qualification though it is properly called the uncorrected retention volume V_R.

Where

$V_R = Ft_R$ ..... (2.2.33)

2.2.6.3 Adjusted Retention Volume.

The retention time t_R is made up of t_m, the time a solute spends in the mobile phase and time t_s, the time the solute spends in the stationary phase. Separations are due to different times solutes spend in the stationary phase. The adjusted retention time is the time the solute molecule spends in the stationary phase t_s, which is usually given by the symbol $t`_R$, where $t`_R = t_R - t_M$

Therefore the adjusted retention volume V'_R is given by

$$V'_R = Ft`_R$$

$$= V_R - V_M \quad \text{..... (2.2.34)}$$

2.2.6.4 Corrected Retention Volume V^0_R

This takes into account the compressibility of the gaseous mobile phase and is given by

$$V^0_R = j\,V_R \quad \text{..... (2.2.35)}$$

The term j is called the compressibility factor and it is expressed as follows

$$j = \frac{3}{2}\left[\frac{\left(p_i/p_o\right)^2 - 1}{\left(p_i/p_o\right)^3 - 1}\right] \quad \text{..... (2.2.36)}$$

Where p_i/p_o is the ratio of inlet and outlet pressures.

2.2.6.5 Net Retention Volume V_N

This is the adjusted retention volume corrected for the compressibility of the gaseous mobile phase and is given by

$$V_N = j\,V'_R$$

$= j\,(V_R - V_M)$ ..... (2.2.37)

2.2.6.6 Specific Retention Volume V_g.

The specific retention volume is defined as the net retention volume per gram of stationary phase at 0^0C. This is very important because it allows the comparison of retention data obtained at different temperatures and with different weights of the same stationary phase. It is given by

$V_g = 273.16V_N / W_s T_c$ ..... (2.2.38)

Where W_s, T_c, V_N are weight of the stationary phase, column temperature and the net retention volume corresponding to that measured at column temperature, corrected for gas hold-up in the column and for pressure drop from inlet to outlet of the column respectively.

2.2.7.Mobile Phase Compressibility and Partition Coefficient

2.2.7.1 Mobile Phase Compressibility

Under the conditions used in liquid chromatography, the liquid mobile phase is considered to be incompressible and this is not the case with gases. The mass flow rate of a gas measured in cm^3s^{-1} is constant throughout the column, but because of the

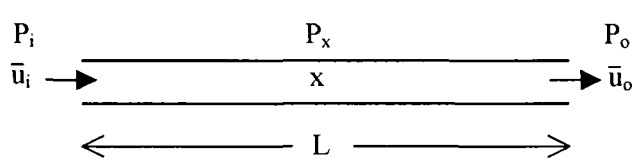


Figure 2.2: Column presentation to show change of linear flow rate.

compressibility of the gas its flow rate must change along the column in such a way that its higher at the column outlet than the inlet. The column may be represented as shown in figure 2.2.

Where P_i – inlet pressure

P_o - outlet pressure

$\bar{u}_i$ - inlet linear velocity

$\bar{u}_o$ - outlet linear velocity

P_x – is the pressure at distance x down the column of overall length L

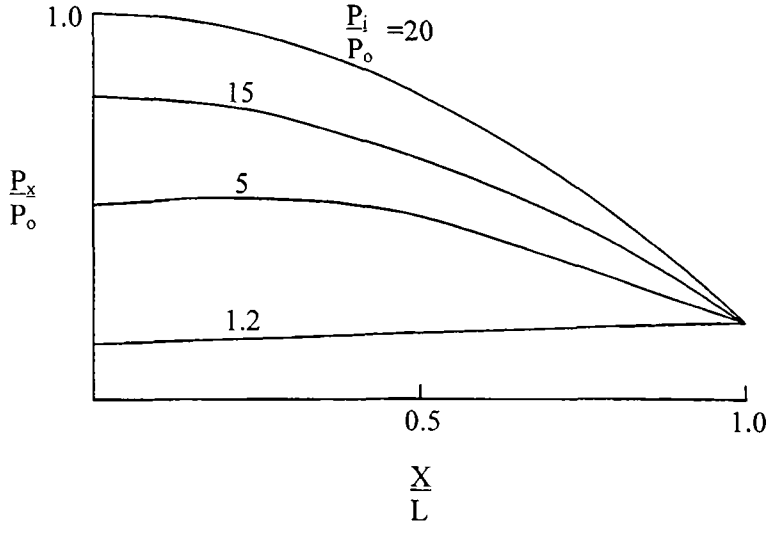


Fig 2.3: Variation of pressure along the column.

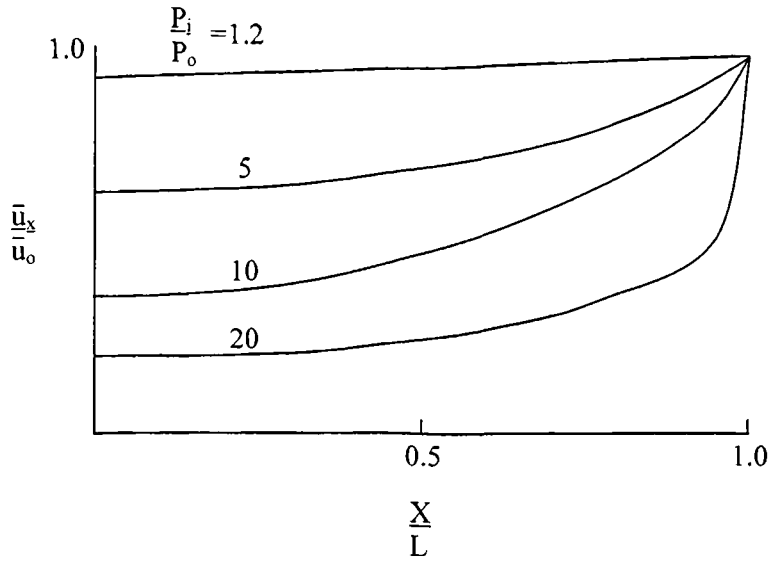


Fig 2.4: Variation of flow rate along the column.

It can be seen that the linear flow rate changes more rapidly along the column when the ratio P_i / P_o is high and that the region of most rapid change is at the end of the column. It is important to operate as much of the column as possible in the optimum region. Irrespective of the actual value of the optimum flow rate, figure 2.4 shows that the ratio P_i / P_o should be close to unity since the value P_i / P_o = 1.2 gives the most constant value of the flow rate through the column.

2.2.7.2 The Partition Coefficient.

The retention volume may be related to a physico-chemical property of the solute – solvent system, the partition coefficient K. This is defined as

K = wt. of solute per ml of stationary phase / wt. of solute per ml of mobile phase

K is a measure of the vapour pressure of the solute above a solution, and its value is determined by both the vapour pressure of the pure solute and the extent of its interaction with the solvent. Partition coefficients have been determined from gas chromatographic measurements, the agreement between these values and those obtained from static

equilibrium studies is a good indication of the soundness of the chromatographic treatment.

2.2.7.3 Relation Between the Partition coefficient and the Retardation Factor.

The dependence of the retention volume upon the partition coefficient can be seen from the simplified description below

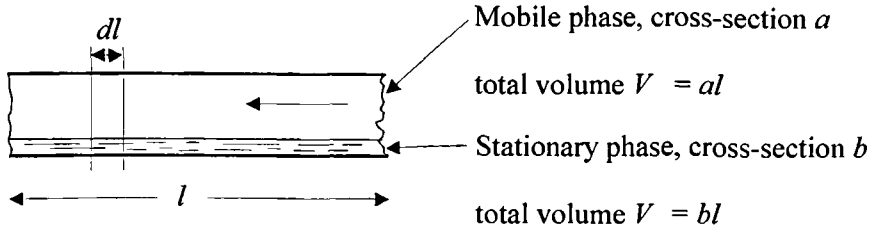


Figure 2.5: Simplified picture of column to explain partition action.

In the above diagram the gas is shown as passing continuously along the tube of uniform bore of length ℓ, over a layer of liquid. The inert support on which the liquid is held merely reduces the effective bore and may be ignored. The cross sections of the two phases are a and b, and there are therefore different volumes of gas and liquid in the column, and in a short length of the column dl in which we consider equilibrium to be reached. When expressing equilibrium conditions in the column the partition coefficient must be adjusted accordingly

Defining the capacity ratio K'

$$K' = KV_L / V_G = K / \beta \quad \text{..... (2.2.39)}$$

Where $\beta = V_G / V_L$ is the phase ratio or the capacity ratio

K' = weight of solute in the stationary phase / weight of solute in the mobile phase

A sample passing down the column will be distributed between the two phases. Only those molecules in the gas phase move, those in the stationary phase remain stagnant until the concentration in the gas falls, when they evaporate. As the sample moves over fresh liquid surface, molecules from the gas phase dissolve and the passage of the sample consists of a continuous series of infinitesimal equilibrations between the phases. The time required for the sample to pass along the column depends upon the ratio of the number of molecules in the stationary phase to those in the mobile phase that is the capacity ratio. Average molecules will spend K' times as long in the stationary phase than in the mobile phase. Considering a length of column *dl*, the time taken by carrier gas molecules to pass through it is dt_G and for average molecules of a sample is dt_R. Then dt_R is the sum of the time spent by average molecules in the moving and stationary phases, and

$$dt_R = dt_G (1 + K') \quad \text{..... (2.2.40)}$$

This leads directly to the retardation factor R_F, which is the ratio of the velocities of the sample and mobile phase.

Then

$$R_F = dt_G / dt_R = 1/(1 + K') \quad \text{..... (2.2.41)}$$

2.2.7.4 The Pressure – gradient correction factor: Relationship between Retention Retention Volume and Partition coefficient.

When we sum the infinitesimals *dt* over the whole column to find the retention times t_G and t_R and hence the retention volumes, the compressibility of the carrier gas comes into play.

Therefore there is a pressure drop along the column, and the velocity $u = f(l)$. According to Darcy's law we can put

$$u = -\frac{kdp}{ndl} \quad \text{..... (2.2.42)}$$

Where k, n and p are the constant, viscosity and pressure respectively. From the gas law we know that

$$aup = au_o p_o = a\bar{u}\bar{p} \quad \text{..... (2.2.43)}$$

Where u_o - velocity at the column outlet

$\bar{u}$ - averaged velocity over the whole length of column

p_o - pressure at the outlet of the column.

$\bar{p}$ - averaged pressure over the whole column length

Then

$$d\ell = -\frac{kdp}{nu} = -\frac{kpdp}{np_o u_0} \quad \text{..... (2.2.44)}$$

By definition

$$\bar{p}\int_{=l}^{l=0} dl = \int_{=l}^{l=0} pdl$$

$$\frac{\bar{p}\left(p_i^2 - p_o^2\right)}{2} = \frac{p_i^3 - p_o^3}{3}$$

$$\bar{p} = \frac{2}{3}\left[\frac{p_i^3 - p_o^3}{p_i^2 - p_o^2}\right] = \frac{2p_o}{3}\left[\frac{\left(p_i/p_o\right)^3 - 1}{\left(p_i/p_o\right)^2 - 1}\right]$$

Then if we put

$$j = \frac{3}{2}\left[\frac{\left(p_i/p_o\right)^2 - 1}{\left(p_i/p_o\right)^3 - 1}\right]$$

We have

$$\bar{p} = \frac{p_o}{j}$$

But $F_c = au_o$ and $V_G = al$

Then

$$_G = \frac{l}{u} = \frac{l\bar{p}}{u_o p_o} = \frac{al\bar{p}}{au_o p_o} = V_G / F_c j \quad \text{..... (2.2.45)}$$

From equqtions 2.2.40 and 2.2.45.

$$t_R = t_G\left(1 + K'\right) = V_G\left(1 + K'\right)/ F_c j$$

$$V_R = t_R F_c = V_G\left(1 + K'\right)/ j$$

$$V_M = t_G F_c = V_G / j \quad \text{..... (2.2.46)}$$

Any contribution of the apparatus to V_M can be neglected assuming perfect apparatus.

Then

$$V'_R = V_R - V_M = K' V_G / j \quad \text{..... (2.2.47)}$$

Taking the definition

$$V_N = j V'_R$$

$$V_N = K' V_G = K V_L$$

and

$$V_g = 273V_N/W_LT = 273KV_L/W_LT = 273K/\rho_LT \quad \text{.....} \quad (2.2.48)$$

2.2.8 Effect of State Variables on Activity Coefficients

The effects of pressure, temperature and composition on the activity coefficients are briefly explained below.

2.2.8.1 Effect of pressure

When temperature and composition are constant, the effect of pressure on activity coefficient is given by the expression below Hala (1958)

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{1}{RT}\left(\bar{V}_i - V_i^o\right) \quad \text{.....} \quad (2.2.49)$$

Where $\bar{V}_i$ is the partial molar volume of component *i*.

V_i^o is the molar volume of component *i* in the pure state.

Ellis and Bourne (1960) calculated the integral molar volume change of mixing $[\sum x_i\left(\bar{V}_i - V_i^o\right)]$ for several hydrocarbons and concluded that the effect of pressure on the activity coefficients was negligible. At low pressures, constant composition and temperature the activity coefficient can be assumed to be independent of pressure.

2.2.8.2 Effect of Temperature

When pressure and composition are constant, the effect of temperature on the activity coefficient is given by the following expression.

$$\left(\frac{\partial \ln \gamma_i}{\partial \ln T}\right)_{P,x} = -\frac{\left(\bar{H}_i - H_i^o\right)}{RT^2} \quad \text{..... (2.2.50)}$$

Where $\bar{H}_i$ is the partial molar enthalpy of component i in the pure state. To correct for the effect of temperature on activity coefficient, equation (2.2.50) is written as follows

$$\left(\frac{\partial \ln \gamma_i}{\partial \frac{1}{T}}\right)_{P,x} = \frac{\bar{H}_i - H_i^o}{R} = \frac{\bar{L}_i}{R} \quad \text{..... (2.2.51)}$$

where $\bar{L}$ is the partial molar heat of solution for component i and $\sum x_i L_i = L$ integral. A plot of log γ_i versus 1/T is constructed at constant composition and values of γ_i are interpolated from the plot at the required temperatures. In most cases the plot is approximately linear and can be extrapolated to a near temperature. This method will probably be used in this work for the interpretation of the infinite dilution activity coefficients at the required temperatures from values of other temperatures.

The well-known rule of T logγ_i = constant at constant composition has been used to correct for the effect of temperature on activity coefficients. This rule is only true if the heat of solution is constant. Colburn and Schoenborn (1945) investigated this rule with various organic systems showing both negative and positive deviations from Raoult's law at 0.5 mole fraction, at 0 to 100^oC and found satisfactory agreement with the rule. Bourne (1959) plotted the 'end-values' for several organic systems exhibiting positive deviations and found that the rule applied satisfactorily. This rule failed when water was one of the components Clark (1958).

2.2.8.3. Effect of Composition

The effect of composition on activity coefficient can be expressed by the Isothermal – Isobaric Gibbs – Duhem Equation Hala (1958)

$$x_1 \frac{\partial \ln \gamma_1}{\partial x_1} + x_2 \frac{\partial \ln \gamma_2}{\partial x_2} + ... + x_n \frac{\partial \ln \gamma_n}{\partial x_n} = 0 \qquad ..... (2.2.52)$$

A number of mathematical solutions to this equation have been proposed giving expressions relating activity coefficients to concentration and containing various numbers of constants. The resulting equations have been used in testing thermodynamic consistency as well as in correlating and predicting vapour - liquid equilibrium data. Equations with constants related to infinite dilution activity coefficients have been found to be very useful in predicting vapour – liquid equilibria. These predicting equations will be discussed in the next chapter.

2.2.9 Effect of Experimental Variables on Retention Volume.

2.2.9.1 Effect of Temperature.

It has been found experimentally Smidrod and Guillet (1969) that plots of the logarithm of specific retention volume (or partition coefficient) against the reciprocal of the absolute temperature are frequently approximately linear and this fact can be related to the thermodynamics of the systems. Applying Dalton's and Henry's laws for equilibrium between vapour and liquid, one can write

$$y_i P = \gamma_i x_i p_i^o \qquad ..... (2.2.53)$$

where γ_i - the activity coefficient

x_i - the mole fraction of the solute in the stationary phase

y_i - the mole fraction of the solute in the mobile phase

P - the total pressure of the gas phase which is considered to be ideal

p_i^o - the vapour pressure of the pure solute

The amount of solute in each volume of stationary phase is given by the product of the mole fraction and the molar density that is the number of moles per ml in the phase. For the liquid phase this is ρ_L / M where ρ_L is the density of the liquid and M is the molecular weight and for gas phase we have P/RT

Then

$$K = \frac{\left(x\rho_L / M\right)}{\left(yP / RT\right)}$$

$$K = RT\rho_L / \gamma P^o M$$

$$K = RT\rho_L / \gamma_1 P^o M \qquad \text{.....} \quad (2.2.54)$$

Therefore

$$\ln(K / T\rho_L) = \ln(R / M) - \ln P^o$$

The effect of temperature on vapour pressure and activity coefficient is known

$$\ln P^o \alpha - \Delta H_e / RT$$

and

$$\ln \gamma \alpha \Delta H_d / RT$$

therefore

$$\ln(K / T\rho_L) = [(\Delta H_e - \Delta H_d) / RT] + k_1 \qquad \text{.....} \quad (2.2.55)$$

substituting the term

$V_g = 273V_N / W_L T = 273KV_L / W_L T = 273K / \rho_L T$

into the equation (2.2.55) above yields

$\log V_g = \Delta H / 2.3RT + k_2$ ..... (2.2.56)

where k_1, k_2 are appropriate values of constants for each of these and subsequent equations. Plots of log K/T or log V_g against $1/T$ will therefore be linear if ΔH is a constant.

It should be noted that the treatment given above, in which the gas phase has been assumed to be ideal, must be refined to take into account of its non ideality if the gas chromatography is being used as a physico – chemical tool for the determination of activity coefficients Martire and Pollara (1965) and Conder (1968). It has been assumed that the choice of the carrier gas does not affect retentions. This has been shown not to be always true and developments are being reported of separation carried out at high pressures in which the carrier gas enters significantly into the phase equilibrium Giddings and others (1968); Karayannis and coworkers (1968); Sie, Bleumer and Rijnders (1969).

2.2.9.2 Effect of Vapour Pressure.

When the accuracy within which retention data are normally determined and the small temperature range of most practical interest in gas chromatography are taken into account, the assumption of constant values of ΔH term is frequently justified. When the equation for variation of vapour pressure with temperature log p^o = Constant - ΔH_e / 2.3RT, is combined with equation (2.2.56), the following relation is obtained

Log V_g = K_3 - $(\Delta H / \Delta H_e) \log p^o$ ..... (2.2.57)

When values of p^o and Vg are obtained at the same temperature, plots of $\log V_g$ against log p^o are therefore linear with a slope of $-\Delta H / \Delta H_e$. For ideal solutions

$\Delta H_d = 0$, and $\Delta H = \Delta H_e$ and the slope is -1. Slopes other than -1 are a measure of departure from ideality of the solution.

Use of the Antoine Equation.

Exact measurements may reveal curvature in the log V_g against 1/T plots and this means that ΔH is not a constant. This fact can most readily be allowed for by using an Antoine type equation and putting

$$\text{Log } V_g = A - B / (\theta + C) \quad \text{..... (2.2.58)}$$

Where θ is temperature in degrees centigrade, K etc, A, B and C are constants which can be evaluated by simple graphical trial and error. The use of other values of C other than 273 enable allowances to be made for the variation in ΔH. The constant B can be related to ΔH at any particular temperature by the equation

$$\Delta H = 2.3RBT^2 / (\theta + C)^2 \quad \text{..... (2.2.59)}$$

Where R ($Jkmol^{-1}$) = 8.314 gives ΔH ($Jmol^{-1}$)

2.2.9.3 Effect of Sample Size.

The term sample size is usually taken to refer to the total amount of solute injected whether measured in μmol, μl, mg or other units. If exact retention volumes are required, the variation with sample size must be found by measuring the peak positions for several small sized samples so that an extrapolation to the position of a vanishingly small sample may be made. Calculations of sample size at which several concentration dependent effects become significant concluded that for infinite dilution studies samples should be

limited to about 0.1mg (0.1μl liquid) in GLC. It is very wise to attempt a few runs with smaller samples to check that retention or plate height does not change. An investigation of the effect of sample size on retention is always advisable in any case. Unexpected results for example maxima and minima in plots of retention against sample size may mean that adsorption or reaction effects are present in addition to the retention mechanism under study. When reporting results it is essential to include some statement of sample size. Without such information very little confidence can be placed in the results.

2.2.9.4. Effect of flow rate

The equation below gives the relationship between the retention time of a compound to the mobile phase flow rate.

$$t_R = \frac{L}{\bar{u}_m}\left(1 + K\frac{V_s}{V_m}\right) \quad \text{..... (2.2.60)}$$

It has been reported in the literature that there is no significant change observed on the retention volumes by varying flow rates, Lictenthaler, Newman and Prausintz (1973); Pollard and Hardy (1957); Porter, Deal and Stross (1956). This is mainly because the retention time is inversely proportional to the flow rate thus if the mobile phase flow rate is doubled the retention time will be halved with no net effect on the retention volume.

2.2.10. Band Broadening Processes

There are three main contributions to band broadening; eddy diffusion (or the multiple path effect), longitudinal molecular diffusion and mass transfer. The variances of each of the band broadening processes are additive to give the overall variance for the system, and this is a measure of column efficiency. It is expressed in terms of H (the plate height)

rather than σ^2, the two being related by the column length, L. The overall value of H is a function of the average linear velocity of the mobile phase, $\bar{u}$, the general equation being expressed in the form;

$$H = \left(\frac{1}{A} + \frac{1}{C_m \bar{u}} \right)^{-1} + \frac{B}{u} + C_s \bar{u} + C_{sm} \bar{u} \quad \text{..... (2.2.61)}$$

In the above equation, each term represents a contribution to band broadening due to diffusion and / or mass transfer effects.

2.2.10.1.The Multiple Path Effect (Eddy Diffusion) – The A Term

The flow pattern through a bed of granular material is very tortuous as solute and mobile phase species take path of least resistance to fluid flow. The velocity of a single particle through the packed bed will fluctuate between wide limits, and the total distances travelled by individual particles will also vary. These fluctuations are random because the structure of the bed which causes them is random. Particles travelling through open pathways will move more rapidly than those in narrow pathways. The simple theory of eddy diffusion assumes that a particle will remain in a single flow path. In practice this is not so because there is nothing to stop the particle from diffusing laterally from one flow path to another. This process is called coupling and it averages out the two flow paths and reduces the amount of band broadening so that the final bandwidth, although still greater than the initial bandwidth, is less than if coupling had not occurred.

The contribution to the overall plate height, H, from multiple paths effect is expressed as follows;

$$A = 2\lambda d_p \quad \text{..... (2.2.62)}$$

where λ is the packing constant (≈ 0.5 for a well packed column) and d_p is the particle diameter.

2.2.10.2. Longitudinal (Molecular) Diffusion

As the solute band moves through the column, diffusion in the direction of flow (longitudinal or axial) also occurs. Besides occurring in the fluid phase, this diffusion also takes place at interfaces between surfaces. The plate height contribution of longitudinal diffusion is given by

$$B = 2\gamma D_M \quad \text{..... (2.2.63)}$$

In the above equation γ is an obstruction factor, which accounts for the fact that diffusion is hindered by the column packing. For packed columns, typical values range from 0.6 – 0.8. D_M is the coefficient of diffusion of the solute species in the mobile phase.

2.2.10.3. Mass Transfer – The C Terms

Mass transfer relates to the rates at which solute species are sorbed and desorbed, and diffuse within each phase. This rate is governed by two mechanisms;

(i) Sorption – desorption kinetics

This refers to the intermittent capture and release of solute species by the stationary phase

(ii) Diffusion controlled kinetics

This may originate in either the liquid stationary or the mobile phase. The mass transfer effects are divided into stationary and mobile phase mass transfer terms, C_s and C_m respectively.

Stationary phase mass transfer, C_s: The rate at which solute species transfer into and out of the stationary phase makes a significant contribution to band broadening. The rate is

controlled mainly by diffusion in a liquid stationary phase. Because of statistical fluctuations, individual solute species will spend different times in the stationary phase. Those particles, which spend most time in/on the stationary phase will, when they re-enter the mobile phase, have been left behind and the solute band would have been broadened. The contribution to the overall plate height, H is given by

$$C_s = \frac{d_f^2}{D_s} \frac{k'}{(1+k')^2} \quad \text{..... (2.2.64)}$$

Where k', d_f and D_s are the capacity factor, liquid film thickness and the rate of diffusion respectively. The liquid film thickness should be small and the liquid stationary phase should be chosen to give high solute diffusion coefficients. Film thickness is controlled both by the amount of liquid stationary phase used and the surface area of the support material.

Mobile phase mass transfer terms C_m and C_{sm}: The mobile phase mass transfer may be divided into contributions from the moving mobile phase and those from the stagnant mobile phase.

(a) **Moving mobile phase**

The solute species in the same flow path do not move with the same velocity. One reason for this is that those in the centre will move more rapidly than those at the column walls, which are influenced by frictional forces and this results in band broadening. The contribution to the overall plate height, H is given by:

$$C_m = \Omega d_p^2 / D_M \quad \text{..... (2.2.65)}$$

where Ω is function of the packing structure, d_p the particle diameter and D_M is the coefficient of diffusion of the solute species in the mobile phase.

(b) **Stagnant mobile phase:**

If the stationary phase involves a porous material, the pores (the intra-particle void volumes) are filled with the mobile phase at rest and there is very little interchange between this 'stagnant' mobile phase contained in the pores and the moving mobile phase in the outside of the pores, i.e. the interparticle void volume. To reach the stationary phase, solute particles will have to diffuse into this stagnant pool of fluid. Like in the stationary phase itself some particles will diffuse deeper into the stagnant pool than others and will consequently be left behind. When they finally join the main stream again, a broadening of the chromatographic band results.

The contribution to the overall plate height, H, from this stagnant mobile phase effect in porous spherical particles is

$$C_{sm} = \frac{\left(1-\phi+k'\right)^2 d_p^2}{30(1-\phi)\left(1+k'\right)^2 \gamma D_M} \quad \text{..... (2.2.66)}$$

Where ϕ is the fraction of the total mobile phase in the inter-particle space.

2.2.11. Preparation of Packed Columns

In physico-chemical work the major need is to know accurately the amount of stationary phase loaded into the column rather than the art of packing the column attached to the analytical GC. A liquid stationary phase is coated on the support with the aim to achieve the percentage loading accurately and a uniform distribution of stationary phase on the support.

2.2.11.1 Liquid Loading

In GLC the term liquid loading is defined in two different ways. Usually it is taken to refer to the ratio.

λ = mass of stationary liquid phase/mass of (support + stationary liquid phase)

This is usually expressed on a percentage basis but a more useful ratio is however

λ = mass of stationary liquid phase/mass of support.

This ratio is linearly proportional to the amount of liquid present.

2.2.11.2 Selection of Solid supports

The choice of a suitable solid support for a liquid phase is governed by two principal requirements, which are inertness and adequately large surface area. Inert support in most context means one which does not significantly adsorb the solute when coated with a liquid stationary phase. The reference to the liquid phase is very important because uncoated supports are invariably adsorptive and the activity is often suppressed partly or totally by the liquid coating.

By far the most commonly used supports are those based on diatomaceous silica. These come in two different types (i) pink – from diatomite fire brick (ii) white – from diatomite filter aids. Examples of pink supports are Sil - O – Cel C 22, Chromosorb P, Gas – Chrom R, Sterchamol and Anachrom P. Examples of white supports are celite 545, Chromosorb W, Gas – Chrom CL, Embacel and Celatom. Pink supports have greater surface area and an average pore diameter of 0.7 μm, compared with 5μm for white supports. Pink supports therefore give a higher column efficiency (lower HETP). All diatomite supports need as gentle and as little handling as possible to minimise attrition and production of

fines. Treating the surface with a silanizing agent, for dimethylchlorosilane (DMCS), considerably reduces the adsorptivity of diatomaceous supports. Supports can either be bought silanized or can be treated in the laboratory. DMCS is said to be the most effective silanizing agent especially when the treatment is preceded by acid washing, Kirkland (1963) and Ottenstein (1968).

Table 2. 1 Physical Properties of Supports

Property	Pink Diatomite type e.g. Chromosorb P	White Diatomite type e.g. Chromosorb W
Surface area a, m^2/g	2 - 4	0.8 - 1.2
Pore volume, cm^3/g	1.1	2.8
Mean pore diameter, μm	0.77	5
True density g / cm^3	2.2	2.2
Packed density, g / cm^3	0.5 - 0.6	0.25 - 0.3
Interparticle voidage	0.4	0.4
Inter- + intra- particle voidage	0.6 - 0.8	0.85 - 0.9
pH[b]	6.7	8 - 10
Friability (% breakdown from 30 to 60 mesh in 10 min)[b]	28	53

2.2.11.3 Preparation of Packing

The two objectives when packing a column as stated in section 2.2.11 can be achieved by the following procedure. The stationary phase is dissolved in a suitable solvent, mixed with the support and evaporates off the solvent.

2.2.11.4 Packing the column

Despite the presence of a liquid coating on the support, GLC packings are normally free flowing and may be poured into the column. Packings become sticky only at high percentage loading, the value depending on the support and its specific surface area. Loading as high as 30 percent on pink diatomaceous supports yield a completely free flowing material. In packing a column the common practice is to add the packing to the column in small quantities at a time, tapping and vibrating the column to settle and consolidate its contents. In doing this, a lot of care is put into consideration because excessive mechanical consolidation is deleterious since diatomaceous support materials tend to break down.

Column configuration depends on the space available in the thermostated oven. U- shaped columns are packed after bending the tube to shape. Coiled columns can be packed in U configuration before completing the coiling. The small amount of compression produced in the second case probably does not significantly change the properties of the packing, nor its adsorptive character.

2.2.11.5 Leak Testing

After the column has been installed in the chromatograph the presence of any leaks can be tested by pressurising the system with the carrier gas, closing the exit and noting if the pressure falls over a period of time. If it does, the leak is located by checking all connections in the flow line with a soap solution or a leak testing device.

2.2.11.6 Conditioning and Running the Column

A freshly made GLC column contains a small amount of solvent remaining from the coating process, along with water and other volatilities. The column is conditioned by placing it in the chromatograph and heating for a number of hours in a stream of carrier gas until the contaminants are removed as indicated by the attainment of a stable baseline. The conditioning process also helps to achieve a more even distribution of liquid on the support.

2.2.12 Determinations and Measurements.

2.2.12.1 Measurement of retention time.

Retention time is measured from the point of injection to the maximum of the chromatographic peak. For very sharp peaks the maximum is easily determined but for broad peaks it helps to draw tangents to the peak and take the point of intersection as shown in figure 2.6. It is sometimes preferable to use the retention volume V_R, where $V_R = Ft_R$. The use of V_R makes it easier to compare results obtained under different flow conditions, V_R is independent of F, whereas t_R is dependent on F.

The measurement of t_m requires a solute that has a distribution coefficient $K = 0$. Since the value of K is dependent on temperature, a change in column temperature will produce a change in t_R unless $K = 0$. A temperature change of a about 30^0C is usually sufficient to observe this.

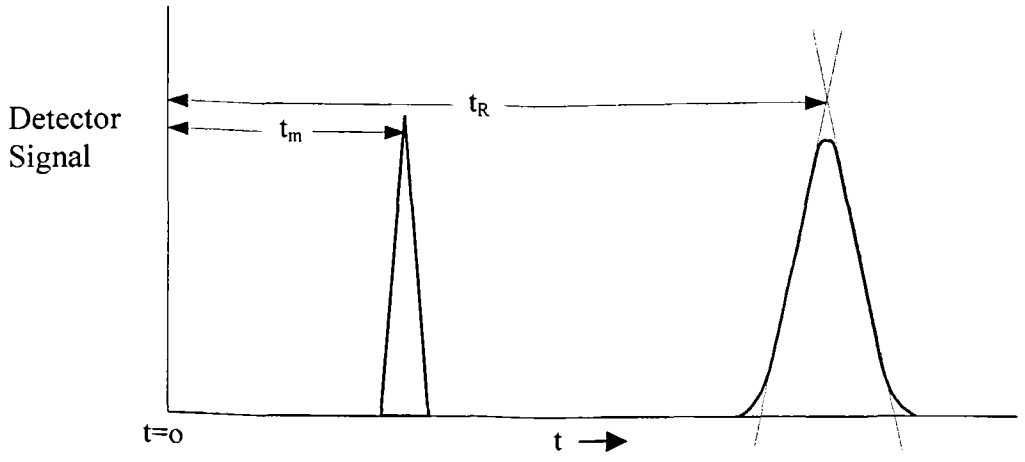


Figure 2.6. Measurement of retention times

2.2.12.2 Pressure Measurement

Provision of pressure measurement is not often included in analytical gas chromatographs. For purposes of physical measurement, the pressures at both inlet and outlet of the column must be known in order to calculate the gas compressibility correction factor. The apparatus must be designed so that the pressures measured are the pressures at the inlet and outlet of the columns. The column outlet pressure is usually assumed to be atmospheric, though a small correction may be needed if the detector, flow meter or any connecting tubing presents more than the usual resistance to flow. It is also important to note that there is an appreciable pressure drop across the jet of a flame ionisation detector so that the outlet pressure will not be atmospheric. Even the Katharometer assembly may have constrictions, which cause the column outlet pressure to differ from that measured at the outlet of the detector. Either pressure gauges or mercury manometers can be used for pressure measurement. The manometers should not be less than 8 mm in diameter in order to minimise capillary error due to non uniformity of the bore.

2.2.12.3 Flow Rate Measurement

A soap film bubble flow meter is undoubtedly the best instrument for measuring gas flows in the region of 1 – 1000ml /min. Rotameters are too inaccurate for the purpose, unless they are calibrated against a soap film meter. A soap – film meter is an absolute instrument requiring no calibration. It gives a routine precision of 1 percent and can also achieve a 0.25 per cent precision under well-controlled conditions with gases that do not dissolve in the soap film. It has also a distinct advantage of being very simple and cheap to construct from an ordinary burette.

When measuring with a soap film flow meter, the walls should be well wetted, if necessary by sending many bubbles completely through the burette before measuring. Any dryness of the walls will lead to unproducible flow rate determinations because the carrier gas in the burette is not saturated with water vapour. The observed flow rate is corrected for the saturation vapour pressure of water, which is little affected by the presence of the detergent.

If F is the flow rate of the saturated gas determined from the flow meter at pressure p, F_m the flow rate of dry gas and p_w the vapour pressure of water at the temperature of the flow meter. Then F_m is expressed as follows

$$F_m = \frac{F(p - p_w)}{p} \quad \text{.....} \quad (2.2.67)$$

The flow rate will normally be determined at room temperature and must be corrected to obtain the flow rate at the column temperature. Accurate measurement of flow rate is less easy with the flame ionisation detector, which dilutes or consumes the gas stream unlike other detectors.

2.2.12.4 Determination of Gas Hold-up

In gas – liquid columns, the gas hold-up contributes 1 to 10 percent of the total retention volume. The accuracy of measurement required for the gas hold up is very variable and an accuracy of about 10 percent, which will often lead to an accuracy in the region of 0.1 – 1 percent in net retention volume is adequate for many applications. The gas holdup can be measured by implementing one of the following methods; air peak, homologous or geometrical calculation methods. Though the air peak is the simplest and commonest means, the homologous series method was used in this work because of the desirable high sensitivity of the flame ionisation detector at low concentrations of the organic compounds. The three methods are briefly described below:

2.2.12.4.1 Air Peak Method

The "air peak" or "inert gas peak" method is the most often used on account of its simplicity. It involves injecting the sample of air or other non-sorbed gas whose retention volume is then taken as the gas hold up. The type of gas used depends on the detection system. With a Kathorometer, one can actually use any gas such as air, hydrogen, helium or methane. The gas used should have a thermal conductivity different from that of the carrier gas. When hydrogen or helium are used as carriers, it is convenient to include a small volume of air with the sorbed solute in a 1μl syringe. In the case of nitrogen as the carrier gas, hydrogen can be used to provide the inert gas peak. Air can also be used though it needs to be injected in a separate run with a larger (say 100 μl to 1ml syringe). This is because the difference between the thermal conductivities of nitrogen and oxygen is only 2 percent. The flame ionisation detector does not normally respond to inorganic materials and this has led most workers to use methane for the inert gas peak.

2.2.12. 4.2 Homologous Series Method

This relies on the accepted generalisation that the logarithm of the adjusted retention time (t_R - t_M) is a linear function of the carbon number in any homologous series. Thus

$$\log (t_R - t_M) = an + b \quad \text{..... (2.2.68)}$$

where a and b are constants for the solute class (e.g. monohydric alcohols) and stationary phase. A known gas hold-up time t_M can be determined as the value, which will linearise a plot of this equation. A mixture of three successive members of any homologous series is injected into the column. The gas hold-up is calculated from the equation (2.2.69) below which is derived from equation (2.2.68) above.

$$t_M = \frac{t_{R_1} t_{R_3} - t_{R_2}^2}{t_{R_1} + t_{R_3} - 2t_{R_2}} \quad \text{..... (2.2.69)}$$

Equation (2.2.69) is also valid for homologous members of carbon numbers n, (n + k) and (n + 2k) where n and k are integers. Also, any three members not necessarily successive members of a homologous series can be used. In this case, the gas hold up is calculated from the iterative solution of the equation

$$\frac{\log \frac{t_{R_2} - t_M}{t_{R_1} - t_M}}{n_2 - n_1} = \frac{\log \frac{t_{R_3} - t_M}{t_{R_1} - t_M}}{n_3 - n_1} \quad \text{..... (2.2.70)}$$

Whichever form of the method used, its success depends on the linear relationship (2.2.68) being obeyed. In some cases the plots may not be linear anyway because sometimes the lowest homologues depart from linear behaviour.

2.2.11.4.3 Geometrical Calculation Method

The gas hold up is obtained from a knowledge of the volume of an empty column and of the true (absolute) solid density determined under a liquid such as water or kerosene, which wets the support or solid adsorbent. The method depends on the assumption that the liquid occupies the whole of the intraparticle pore space. There is considerable variation in the results obtained in this manner compared with those from other methods. This puts a lot of doubt on their reliability and a low value of the geometrical gas holdup would be expected if, in solid density measurements, the kerosene fails to penetrate the finest pores.

2.2.13 Previous Work on Equilibrium Data from GLC.

A review of the important work on the evaluation of equilibrium data such as partition constants, equilibrium constants and activity coefficients is presented in this section. The review is divided into two parts; the first covers the work when solvents (stationary phases) are non-volatile and the second when the solvents are volatile.

2.2.13.1 When Solvents are Non- Volatile

James and Ray (1952) found that plots of log relative retention volumes versus solute carbon number were linear for a wide variety of homologous series. Hoare and Purnell (1956) demonstrated that vapour pressures, boiling points, heats of vaporisation, solution and mixing and activity coefficients could be measured by GLC.

Porter, Deal and Stross (1956) established that partition coefficients obtained from gas – liquid chromatography were essentially identical to those obtained from static

measurements. They showed that column properties and operating conditions did not have significant effects on the partition coefficients. By using diisodocylphthalate as solvent, they determined partition coefficients of paraffins and alcohols at 150^0C. The reliability of partition coefficients obtained from GLC data was also investigated by Anderson (1956) and Anderson and Napier (1957). They determined activity coefficients of benzene and cyclohexane in polyethelene glycol at 80 to 131^0C using columns of different properties. They compared the results with those obtained from static measurements and concluded that partition coefficients obtained from GLC data were true equilibrium quantities.

The specific retention volumes were introduced by Littlewood *et al.* (1955) and he also suggested their use in place of partition coefficients in vapour identification. Measurement of specific retention volumes for a series of alcohols, aromatic hyrocarbons and esters in silicone 702-fluid and tritolyl phosphate was carried out. Keulemans (1959) calculated infinite dilution activity coefficients of n- paraffins, aromatics, n- alcohols, ketones and acetates at 100^0C in three solvents namely polyethylene glyol 400, methoxy-polyethylene glycol 350 and polyethylene glycol 425 using partition coefficients published by Adlard (1957). From the partition coefficients published by Porter *et al.* (1956), Keulemans also calculated infinite dilution activity coefficients of paraffins, alcohols and cyclo hydrocarbons in diisodo cyclopthalate at 75 - 135^0C.

Kwantes and Rijnders (1958) measured infinite dilution activity coefficients for non-polar solvents and of polar solutes in polar solvents. Their results compared very well with those estimated from Bronsted relationship and published results from static measurements. Good agreement was obtained in all cases except for polar solutes in polar solvents. Adsorption effects of packing materials (sterchamol, silocel, pumice, alumina,

and burnt gypsum) were thought to be accountable for this exceptional case. The partition coefficient published by Kwantes and Rijnders were used by Preston (1959) to calculate equilibrium constants (K – Values).

The validity of the GLC technique in determining infinite dilution activity coefficients was investigated by Everett and Stoddart (1961). They measured infinite dilution activity coefficients for several hydrocarbons in dinonylphthalate at 30^0C and made corrections for the non-ideality of the vapour phase. They also studied the effects of sample size and flow rates on retention volumes. Adlard *et al.* (1960) determined accurate values of infinite dilution activity coefficients of c6 hydrocarbons in di 3,5,5-trimethylhexyl phthalate in the temperature range 48 - 110^0C. The non-ideal behaviour of the vapour phase was correctly accounted for.

Desty and Goldup (1962) studied the effects of the nature of carrier gas and column pressure on retention data. These effects were accounted for by calculating the changes in gas imperfections. They used hydrogen, helium, nitrogen, argon, oxygen, carbon monoxide and carbon dioxide as carrier gases at column pressures of 2-5 atmospheres. Partition coefficients of paraffins, cyclic – hydrocarbons and benzene in squaline were measured at 25^0C.

Infinite dilution activity coefficients of carbon tetrachloride and ethanol in dinonylphthalate at 20 - 45^0C with capillary columns were measured by Adlard *et al.* (1962). Corrections for vapour phase imperfections were made. The results agree with those that these same authors obtained from packed GLC columns. The results compared

far much better to those obtained by Fregnard and Stock (1962) than those of Hardy (1959).

Kobayashi and Mellado (1960) measured infinite dilution activity coefficients of C – 4 hydrocarbons in furfural at various temperatures and the results did agree very well with those in the literature. Pollard and Evered (1960) determined activity coefficients for some alkanes, alkylnitrates, nitroalkanes, and alcohols in squalane and dinonylphthalate. Martire and Pollara (1965) obtained equilibrium data for 39 solutes in 7 non-volatile solvents.

Barker and Lloyd (1963) measured partition coefficients of benzene, cyclohexane and methylcyclohexane at infinite dilution in polyoxyethelene 400 diricinoleate at temperatures between 15 – 97^{0}C. Partition coefficients at finite concentration were also determined but the calculations did not take into account the indistinguishibility of solute molecules from others in the elution gas. Stalkup and Deans (1963) presented a mathematical analysis for the GLC process when solute molecules were indistinguishable from those present in the carrier gas. Helfferich and Patterson (1963) derived equations for a binary elution gas containing a continuous stream of solute vapour.

Chueh and Ziegler (1965) presented an equation relating the retention volume of a solute to the equilibrium solute concentration when the elution gas is a binary mixture of solute vapour and inert gas. Using this equation, activity coefficients at finite concentrations of benzene in diethylene glycol at 50, 70 and 90^{0}C and of n – hexane in
1, 2 ,4-trichlorobenzene at 30^{0}C were determined. A ±5% agreement was found between these results and those obtained by static methods (1965).

Smidsrød and Guillet (1968) investigated the interaction of acetic acid, butyl alcohol, ∝ - chloronaphthalene and hexadecane with poly(N-isopropylacylamide) by gas chromatography using the polymer as the stationary phase. Their columns were 0.25 in, aluminium tubing and approximately 5ft long. The solid support was chromosorb G, which was acid washed and treated with dimethylchlorosilane. Specific retention volumes were determined using an Aerograph Autorep 700 gas chromatograph equipped with flow meter, pressure gauge and thermal conductivity detector. Temperature control was obtained by a means of circulating air oven. In all their injections the retention volume depended significantly on the amount of solute injected. They found that for acetone and ethanol the retention volume decreased with increasing sample size, this corresponds to an increase in γ with an increase in sample size. Thus these solutes show negative deviations from Raoult's law and a positive deviation was found in the case of hexadecane.

Smidsrød and Guillet pointed out that qualitative information concerning the type of deviation may also be obtained directly by inspecting peak asymmetry (Purnell, 1962). A comparative study of their work shows that for acetone, butyl alcohol and ethanol, the specific retention volumes at zero peak height are independent of the liquid loading. Such results strongly indicate that these solutes are held back exclusively by absorption in the bulk polymer phase. On the other hand, hexadecane gave specific retention volumes with no dependence on liquid loading suggesting an adsorption mechanism.

Patterson, Tewari and Schreiber (1970) considered the application of Gas – liquid chromatography to the thermodynamics of polymer solutions. The primary interest was the determination of thermodynamic quantities using this technique. This was prompted

by comments from several workers who noted the difficulty of applying the usual thermodynamic equations of the G.L.C, which yield γ_i^{∞}, the activity coefficient of component 1 at infinite dilution. This is because the equations require an exact molecular weight value of component 2, thus making their use difficult for polymer systems. Their main objective was to resolve the problem and also stressed the utility of the technique in providing data with which to test contemporary theories of polymer solution thermodynamics, Flory and Eichinger (1968), Patterson (1968)

Lichtenthaler, Newman and Prausnitz (1972) measured specific retention volumes from gas – liquid chromatography for Poly(dimethylsiloxane) – hydrocarbon systems as part of a more extensive study of polymer solvent interactions. The carrier gas was helium; measurements were made at 25, 40, and 55^0C. A lot of attention was paid to controlling and determining the system temperature accurately. Poly(dimethysiloxane) (average molecular weight, $\bar{M}_n$ of 150 000) was coated into chromosorb P or W, AW – DMCS, from a solution in n – hexane or toluene. Details of the column preparation are shown in table 2.2 below

Table 2.2: Chromatographic columns.

Column No.	Wt of PDMS (g)	Support (g)	Coverage ratio	Support	Solvent	Length (m)	i.d (cm)
1	1.7998	12.9948	0.139	Chrom P	n-hexane	1.5	0.635
2	1.9810	12.7800	0.155	Chrom P	n-hexane	1.5	0.635
3	3.1810	12.6853	0.251	Chrom P	Toluene	1.5	0.635
4	1.0096	8.0130	0.126	Chrom P	n-hexane	1.5	0.635

Tables 2.3 and 2.4 show the experimental specific retention volumes at the temperatures considered. The carrier gas flow rate ranged from 18 to 120 cm^3 per minute and the flow rate was found to have no effect on the specific retention volumes.

Table 2.3: Specific Retention Volumes for Poly(dimethylsiloxane) – Hydrocarbon system at 40^{0}C.

Solute	$V_g^o(cm^3/g)$					
	Column					
	1	2	3	4	5	Average
n-pentane	48.20	48.60	47.10	47.30	46.79	47.60
n-hexane	124.2	126.8	123.0	124.5	122.5	124.2
benzene	201.3	203.3	196.2	199.0	198.7	199.7
toluene	520.3	525.1	504.8	517.0	515.8	516.6

Table 2.4: Specific retention volumes for Poly(dimethylsiloxane) – Hydrocarbon system at 25 and 55^{0}C.

Solute	$V_g^o(cm^3/g)$			
	Temperature -25^{0}C			Temperature - 55^{0}C
	Column - 1	Column – 2	Average	Column - 5
n – pentane	81.01	80.31	80.66	29.80
n – hexane	230.4	225.0	227.7	70.50
benzene	380.0	370.2	375.1	112.5
toluene		1032	1032	269.2

Summers, Tewari and Schreiber (1972) obtained specific retention volumes for polydimethylsiloxane – hydrocarbon systems from gas – liquid chromatography. A single

PDMS column with an average molecular weight 500 000 was used. The polymer was coated onto chromosorb W support (60 – 80 mesh acid washed, DMCS treated) from solutions in n-hexane. The coated support was re-sieved and packed into 4 – ft, 0.25 in o.d copper tubing which had previously been washed in methanol to clean it. A total of 4 columns were prepared and their details are presented in table 2.5 below.

Table 2.5: Description of Columns.

Column code →	1	11	111	1V
Length, ft	4	4	4	4
Chromosorb W, g	5.3400	5.9308	6.4317	6.2128
PDMS, g	0	0.3703	0.4953	0.7505
Wt % PDMS	0	6.21	7.70	10.78
HETP		560	680	910

Column 1 (uncoated support) was used to monitor interactions between solutes and support, while columns 11 – 1V were used to study the elution effects in PDMS – hydrocarbons and to detect possible changes in retention volume due to varying liquid loading. The calculated height equivalent to theoretical plate (HETP) was based on elution peaks for 2 – methylhexane using Van Deemter's procedure (Purnell 1962).

Summers, Tewari and Schreiber (1972) used a dual column G.L.C apparatus consisting of a Perkin Elmer hot wire thermal conductivity detector. Temperature control was achieved by means of a water bath and it was regulated to $\pm 0.05^{0}$C. Experimental temperature was varied from 25 to 70^{0}C and in this range, the solvent polymer vapour pressure is negligible. Helium was used as the carrier gas, thus minimising solution effects in the

solvent Desty, Goldup and Swanton (1962). Summers and co-workers measured flow rates in the range of 70 to 120 ml/min at room temperature at the detector outlet using a soap bubble flow meter. The rate was chosen so as to indicate any flow rate dependence of the elution peaks and also leading to convenient operation of the columns. Inlet pressures were generally in the range 900 – 1200mm, while the outlet pressure was always atmospheric. Uniformly symmetrical elution peaks were obtained and they were considered to confirm the infinite dilution approximation Conder (1969) thus representing solvent - solute interactions. Summers, Tewari and Schreiber concluded that peak asymmetry is not a necessary condition for surface adsorption effects thus agreeing with Conder (1971). The absence of asymmetry in their work resolved difficulties of choice in defining a suitable working value of the retention volume. Recommendations of Cruickshank, Windsor and Young (1966) were followed in defining the retention volume by the elution peak maximum. The solute specific retention volumes reported in table 2.6 below were calculated from peak retention times and column operating conditions, using the well known expression of Littlewood and co-workers (1955).

Table 2.6: Specific Retention Volumes for PDMS – hydrocarbon systems.

Solute	$V_g^o(cm^3/g)$, from columns 111 and 1V			
	25°C	40°C	55°C	70°C
n-pentane	74.76	43.65	27.43	18.33
n-hexane	211.1	114.8	66.45	41.05
n-heptane	587.6	290.8	157.8	89.54
n-octane	1626.6	740.9	367.1	194.9
2-methylpentane	149.9	83.9	51.63	32.21
2-methylhexane	420.9	211.4	119.6	70.04
2-methylheptane	1138.0	534.7	275.8	150.1
2, 2, 4-trimethylpentane	510.0	260.9	145.8	84.66
benzene	340.4	181.2	105.4	63.43
toluene	959.6	463.7	251.4	141.3
p-xylene	2654.6	1187.5	586.5	307.4
ethylbenzene	2365.7	1090.5	541.2	286.4

Patterson *et al* (1974) also studied thermodynamic interactions in polymer systems by gas – liquid chromatography. The dual column GLC apparatus used was similar to that of Summers, Tewari and Schreiber (1972). All the columns were made of 0.25 in o.d copper tubing, methanol washed prior to use. The supporting solid was chromosorb W (60 –80 mesh, acid washed and DMCS treated). The following stationary phases were studied: n-C_{24}, DOP, PDMS (L) a 50- cs Dow Corning silicones fluid and n-C_{24} – DOP and n-C_{24}-PDMS (L) mixtures. All the stationary phases were coated onto chromosorb from solutions of n-hexane. After removing excess hexane, the coated support was dried in a vacuum evaporator and finally oven dried at 100°C for several hours to remove traces of hexane. Details of the column composition used by Patterson *et al.* are given in table 2.7 below

Table 2.7: Column Description.

Stationary phase	Wt of support, g	Mass of stationary phase	Wt Composition Stationary Phase		
			n-C_{24}	DOP	PDMS
n-C_{24}	7.4707	12.00	1.000	-	-
DOP	4.4896	10.65	-	1.000	-
PDMS (L)	5.1373	10.22	-	-	1.000
n-C_{24} – DOP	5.7416	17.69	0.405	0.595	-
n-C_{24} – PDMS (L)	5.6515	13.93	0.440	-	0.560

Table 2.8: Specific Retention Volumes, ($V_g^o(cm^3/g)$, for Two and Three Component Systems:

Probe	n-C_{24}	DOP	PDMS (L)	n-C_{24} - DOP	n-C_{24}-PDMS(L)
Column Temp(K)	333	348	333	348	333
n-pentane	43.27	15.46	24.76	25.49	41.64
n-hexane	115.25	39.14	60.91	61.65	93.09
n-heptane	298.53	90.68	144.30	147.68	234.42
n-octane	761.55	208.15	332.14	352.40	580.61
n-nonane		470.53	765.38		
2-methylpentane	86.21	29.98	46.96	47.07	72.36
3-methylpentane	98.65	34.14	52.65	53.79	80.46
2-methyhexane	216.25	69.57	107.76	110.33	
2,4-dimethylpentane	152.13	49.79	98.97	80.03	122.19
cyclohexane	207.45	77.49	106.14	112.82	162.24
carbon tetrachloride	180.07	98.92	105.71	117.15	
benzene	169.65	120.20	105.46	126.10	145.22

Ashworth and co-workers (1984) reported replicate gas – liquid chromatographic based specific retention volumes, activity coefficients and interaction parameters of ten solutes

with poly(dimethylsiloxane) (PDMS) solvent at 303K. Static determined activity coefficients and interaction parameters are also reported and compared with the GLC results. These workers commented that, the activity and partition coefficient data derived from the GLC method do in fact agree to well within experimental errors arising with more traditional (static) apparatus of various designs Purnell and others (1965). The PDMS used in this work were supplied by Dow Corning Ltd and had a number average molecular weight of 89 000. The high precision GLC apparatus used were essentially identical with those discussed and described by Purnell (1978). The polymer was coated into chromosorb G (60-80 mesh, acid washed and treated with dimethylsiloxane). Their results, mainly specific retention volumes and infinite dilution activity coefficients are presented in table 2.9 and 2.10 respectively. The internal agreement of the GLC based data was found to be a factor of 2 superior compared to the static experiments.

Table 2.9: Specific Retention Volumes ($V_g^o(cm^3/g)$) with PDMS solvent at 303K.

Solute	Column A	Column B	Column C	Average	% std deviation
n-pentane	67.05	64.90	66.37	66.11±1.10	1.66
n-hexane	181.6	177.9	180.2	179.9±1.8	1.04
n-heptane	484.4	480.1	483.1	482.5±2.2	0.46
n-octane	1305	1286	1280	1290±13	1.02
cyclohexane	316.4	213.8	315.2	315.1±1.3	0.41
methylcyclohexane	575.0	566.2	567.7	569.6±4.7	0.83
benzene	291.2	289.7	290.4	290.4±0.7	0.26
toluene	797.5	785.0	790.5	791.0±0.7	0.79
dichloromethane	78.89	78.03	79.23	78.72±0.62	0.79
chloroform	183.0	179.8	182.2	181.7±1.6	0.93

Table 2.10: Comparison of Static with Gas –Chromatographic Solute Mole – and Weight Fraction Based Activity Coefficients and Interaction Parameters at Infinite Dilution with Poly(dimethylsiloxane) solvent at 303K.

Solute	Static					GLC		
	${}^{w}\gamma_i^{\infty}$							
	run A	run B	average	$10^3({}^{x}\gamma_i^{\infty})$	$x_{i(s)}$	${}^{w}\gamma_i^{\infty}$	$10^3({}^{x}\gamma_i^{\infty}$	$x_{i(s)}$
n-pentane	6.082	6.049	6.066	4.918	0.356	6.092	4.938	0.360
n-hexane	5.991	6.014	6.003	5.812	0.398	6.023	5.832	0.402
n-heptane	6.128	6.090	6.109	6.878	0.454	6.135	6.907	0.458
n-octane						6.342	8.139	0.456
cyclohexane	5.386	5.339	5.363	5.071	0.454	5.378	5.085	0.262
methylcyclohexane						4.712	4.937	0.752
benzene	6.448	6.370	6.409	5.625	0.753	6.404	5.620	0.748
toluene						6.457	6.684	0.901
dichloromethane						4.937	4.712	0.640
chloroform						3.366	4.515	

2.2.13.2. When Solvents are Volatile

Kwantes and Rijnders (1958) were the first to determine infinite dilution activity coefficients of solutes in volatile solvents by the G.L.C technique. They determined values for several non-polar solutes in n-octane and n-decane at 303 and 333K. The carrier gas was pre-saturated with liquid solvent. Their results were in good agreement with those predicted from the Bronsted relationship.

Their work was later extended to include polar systems, Hofstee, Kwantes, Rijnders (1960). They encountered difficulties in their method of detecting solute vapours. This was because the thermal conductivity detectors failed in some cases to respond to solute

vapours. Adsorption effects of inorganic support materials interfered and produced diffused peaks with erratic results. Improvement in the results was realised when finely granulated tetrafluoroethene (20-30 mesh) were used as support materials.

Hilmi (1965) presented the details and construction of a G.L.C apparatus suitable for the measurement of activity coefficients at infinite dilution for volatile systems. The apparatus included an accurate method of measuring flow rates based on the laminar flow of gases through capillary tubes. Both the hydrogen flame ionization and katharometer were used in detecting the solute vapours. A direct "air- peak" method of measuring the gas hold-up of chromatographic columns when using the flame ionization detector was also found. The end-values of the isothermal ternary system n-propanol, 1,2-dichloroethane and toluene were evaluated at 65^0C from the retention volumes. Also determined were the "end-values" of n-propanol and toluene in 1, 2-dichloroethane at 30, 40 and 50^0C. Hilmi also measured the activity coefficients at infinite dilution of carbon tetrachloride in benzene at 40^0C. No significant effect on the retention volumes was found whether solutes were injected as pure components or as mixtures.

Barr and Newsham (1987) measured activity coefficients at infinite dilution for six chlorinated alkane / water mixtures in the temperature range 293-323K using the gas – liquid chromatography. Their experiments also provided estimates of the second cross virial coefficients of chlorinated alkane / nitrogen mixtures. The gas – liquid chromatographic apparatus used was originally designed and constructed at the National Physical Laboratory (Teddington, U.K). A mixture of methane marker gas and solute vapour was continuously injected through the gas-sampling loop. The eluted solutes were detected with a flame ionization detector, which was of course insensitive to the water

vapour that was present in the carrier gas stream. The chromatographic columns used by Barr and Newsham were made from 1.2m length of soft annealed 7mm copper tubing. These columns were packed with either Diatomite S 60 – 72 mesh or chromosorb G/AW/DMCS (45 – 60 mesh) and coated uniformly with water in the loading range of 45 – 50%. They weighed the columns after each day's work and the amount of water in the column at meantime of each experiment was determined by linear interpolation.

Cooling (1987) measured infinite dilution activity coefficients for benzene, chlorobenzene, 1,2-dihloroethene and trichloroethene in water using the gas – liquid chromatographic technique. The columns used in this work were constructed from soft annealed copper tubing (O.D 6.4mm, I.D 4.8mm) wound into a coil of 20cm radius. Two column lengths were used (1.2 and 2.0) depending on the solute volatility. The columns were packed with an inert diatomaceous earth, Diatomite 'S' (60-72 BSS mesh). The carrier gas was oxygen free nitrogen, with a quoted purity of 99.99% (British Oxygen Company Ltd). Infinite dilution activity coefficients were determined at four different temperatures; 293.15, 303.15, 313.15 and 333.15K.

Cooling, Khalfaoui and Newsham (1992) measured activity coefficients for very dilute mixtures of water with benzene, chlorobenzene, 1,1-dichloroethene, trans- 1,2-dichloroethene and trichloro-ethene in the temperature range 285-323K. The authors used the results of this work to update parameters in the UNIFAC model of (Fredenslund et al, 1975). The experimental method consisted of determining the solute retention time, the nitrogen carrier gas flow rate and the column inlet and outlet pressures. Typical values of these were as follows solute retention time, 45-65s; carrier gas flow rate, 0.65 – 0.85

cm^3s^{-1}; column inlet pressure, 140-690Kpa; column outlet pressure 115-660KPa. Measurement of these values permit the calculation of the retention volume V_N and the derived values of γ_1^∞ and the zero partition coefficients are presented in table 2.11.

Table 2.11: Activity coefficients at infinite dilution (γ_1^∞) and zero pressure partition coefficients (k^0) for organic solvent (solvent (1) and water mixtures – Cooling *et al* (1992)

Compound	T (K)	γ_1^∞	γ_2^∞	k^0
Benzene	293.15	2505	245.4	5.418
	303.15	2570	-	3.446
	308.15	-	170.0	-
	313.15	2535	-	2.396
	323.15	2465	135.5	1.686
Chlorobenzene	293.15	12960	329.7	8.898
	303.15	10280	-	6.479
	308.15	-	243.2	-
	313.15	7450	-	5.494
	323.15	4952	201.3	5.274
Trichloroethene	293.15	5450	400.5	3.153
	303.15	6061	-	1.859
	308.15	-	354.2	-
	313.15	5943	-	1.294
	323.15	5893	282.1	0.930
Trans-1,2-Dichloroethene	285.15	-	385.6	-
	293.15	1216	215.5	3.196
	303.15	1435	-	1.865
	308.15	-	185.3	-
	313.15	1477	-	1.276
	323.15	1509	-	0.889
1,1-Dichloroethene	285.15	-	890.3	-
	293.15	-	461.4	-

2.2.14 Comparison of GC and Static Methods: Advantages and Limitations

GC instrumentation is generally easy to build (or in the case of commercial instruments they are inexpensive to buy), operate and maintain. Demands on experimental skills are therefore minimal compared with other techniques. Chromatographic methods are generally more rapid than conventional techniques because the rate of approach to equilibrium of solute and stationary phase is greater. Results can be obtained directly at infinite dilution, obviating the conventional extrapolation; but finite concentrations can also be studied chromatographically. The oven temperature of the GLC can be varied and therefore activity coefficients are obtained over a wide temperature band. One chromatogram gives several quite different types of information. Also, high purity samples are not always needed because only a few milligrams of a sample and a few grams of stationary phase are required. This allows the characterisation and study of rare, expensive research chemicals.

Gas chromatography is not limited solely to infinite dilution studies. Solution and adsorption data can in fact be obtained over widely extended mole fraction ranges. Due to these advantages little time is lost researching the instrumentation and purity of the reagents. In general gas chromatography can be used to study a wide variety of physicochemical phenomena quickly, simply and accurately.

Beside its numerous advantages, gas chromatography has limitations that may necessitate the choice of other techniques. It is limited to the study of interactions that occur on solids, liquids, mobile gas phase and their interfaces. But in certain cases it can be used to acquire intrinsic information such as boiling points, ionisation potentials and molecular

weights provided the possibility of correlating the property of interest to retention behaviour exist.

Another drawback associated with the GC is the temperature limit of the stationary phase in the normal elution mode. Liquid phases are limited normally to the operation at temperatures at which their vapour pressure is less than 0.01 torr at the column temperature. This enables one to ensure that the amount of stationary phase in the column remains constant over a reasonable period. The use of volatile materials is not impossible but if there is a finite pressure drop across a column such phases will be stripped even if saturators and pre-columns are present. Employing coarse packing, small pressure gradients and internal standards can be a temporary remedy to the above problem.

CHAPTER THREE

PHASE EQUILIBRIUM COMPUTATION

CHAPTER THREE
PHASE EQUILIBRIUM COMPUTATION

3.1 Introduction

A reliable knowledge of the phase equilibrium as a function of temperature, pressure and composition is required in:

(i) The synthesis and design of separation processes.

(ii) The choice of suitable selective solvents.

(iii) The choice of optimum separation sequence.

(iv) The conditions for the different separation columns.

Since chemical process design is often concerned with the separation of fluid mixtures, design engineers must frequently estimate liquid phase activity coefficients. This is because the real behaviour of fluid mixtures can be calculated with the help of activity or fugacity coefficients. In those fortunate cases where phase equilibrium data are at hand, such estimates can usually be made with ease. In many other cases where the required experimental data are not available, it is difficult to make rough estimates on a rational basis. For polymer – solvent systems, the predictive ability of engineering models describing such mixtures is rather limited. As a result there is a growing theoretical and practical interest for better understanding of the thermodynamics of mixtures composed of large and small molecules.

One obvious method for estimating activity coefficients for process design is to use correlations and theoretically based models. Models contain adjustable parameters, which can be obtained by fitting few experimental data points. However there is major drawback in that available experimental data, particularly for long chain solutes or polymers are

either of poor quality or not available at all. For liquid mixtures of components with similar volatilities, the infinite dilution activity coefficients for the components involved can be obtained by differential ebulliometry, Nicolaides and Eckert (1978), Lobien and Prausnitz (1982). When the mixture components differ greatly in volatility, gas-liquid chromatography is often used to obtain the infinite dilution activity coefficients for more volatile components Parcher et al (1975). In this technique, the chromatograph is used as the equilibrium cell; the heavy component is the substrate and an inert carrier gas flows over that substrate. A small amount of the light component is injected and the important measured quantity is the retention time that the light component is retained as result of its contact with the heavy component.

Another convenient available experimental method for obtaining activity coefficients at infinite dilution is by headspace analysis, Hackenburg and Schmidt (1976), Kieckbusch and King (1979), Kolb and Ettre (1997). In this method, a chromatograph is used as an analytical tool to determine the vapour-phase concentration of a trace component in equilibrium with a liquid phase of known composition.

Several factors such as non-equilibrium effects, and liquid or solid surface adsorption may cause complications. In addition to this, chromatographic techniques cannot be used to measure the infinite dilution activity coefficient for the heavy component. Kniaz (1991) obtained experimental data for activity coefficients of long chain solutes in short chain solvents from solid – liquid equilibrium measurements. Activity coefficients were estimated from thermal properties for the long chain solute, such as the enthalpy change on melting. Kniaz's resulting activity coefficient values are subject to significant measurement uncertainties.

3.2 Thermodynamic models

The criteria for phase equilibrium requires the equivalence of temperature (thermal equilibrium), pressure (mechanical equilibrium) and chemical potential (material equilibrium) for every particle in the coexisting phases. Equations of state and activity coefficient approaches can be used to model vapour-liquid equilibrium (VLE). A brief discussion of these approaches is given by Al-Hayan (1999).

In the activity coefficient approach, activity coefficients are used to describe the real behaviour in the liquid phase while fugacity coefficients are needed to account for the real behaviour in the vapour phase. In the equation of state approach, the real behaviour is described with the help of fugacity coefficients. The PVT behaviour of the vapour and liquid as a function of composition must be known for the whole pressure range in order to calculate the required fugacity coefficients. The behaviour can be described using equations of state like the further developments of the van der Waals equation of state such as the Soave-Redlich Kwong, Soave (1972) or the Peng-Robinson equation of state, Peng and Robinson (1976).

Both the activity coefficient and equation of state model approaches allow the calculation of phase equlibria of multicomponent nonelectrolyte systems using binary parameters. Comparing the two approaches, there are great advantages for the equations of state, since with this approach it is possible not only to calculate phase equilibria but also other important properties such as enthalpies, entropies, densities etc, for a given temperature, pressure and composition. As no standard fugacity is required it is not limited to

subcritical systems. Also equations of state can be used to describe the PVT behaviour for both vapour and liquid phases.

In the two approaches, the equality of the fugacity of each component in the two phases is the starting point.

$$f_i^v = f_i^l \quad \text{.....(3.1)}$$

where f_i^v and f_i^l represent the fugacities of component *i* in the vapour and liquid phases respectively.

The fugacity of a pure liquid at a pressure above the saturation pressure (P^{sat}) is given by

$$f_i^L = f_i^{sat} \exp\left[\frac{1}{RT}\int_{P_i^{sat}}^{P} V_i^L dP\right] \quad \text{.....(3.2)}$$

The exponential term is the Poynting correction. It is small at low pressures but increases rapidly at high pressures or low temperatures. Calculations done by Prausnitz et al. (1986) for a hypothetical component for which $V_i^L = 100\text{cm}^3/\text{gmol}$ (assumed constant) at 300K gave the following values of the Poynting correction 1.004, 1.04, 1.50 and 57 at the pressures of 1, 10, 100 and 1000 bar respectively.

For an incompressible liquid (V_i^L assumed independent of pressure), equation (3.2) becomes

$$f_i^L = \phi_i^{sat} P_i^{sat} \exp\left[\frac{V_i^L (P_i - P_i^{sat})}{RT}\right] \quad \text{.....(3.3)}$$

Using the basic equation for vapour liquid equilibrium ($\hat{\phi}_i^V y_i P = \gamma_i x_i f_i^0$) and replacing f_i^0 by f_i^L, the following is obtained

$$y_i = \frac{x_i \gamma_i \phi_i^{sat} P_i^{sat} \exp\left[\frac{V_i^L (P - P_i^{sat})}{RT}\right]}{\hat{\phi}_i^V P} = \frac{x_i \gamma_i P_i^{sat}}{P \Phi_i} \quad \text{..... (3.4)}$$

where $\Phi_i = \frac{\hat{\phi}_i}{\phi_i^{sat}} \exp\left[\frac{-V_i (P - P_i^{sat}}{RT}\right]$

The above is a general equation relating liquid and vapour mole fractions (the principal phase equilibrium equation) and is based on the assumption that the liquid is incompressible between the limits of system pressure, P_i^{sat}.

3.3 Group Contribution Methods:

3.3.1 Summary

This section gives a review of the ways in which the activity coefficients of simple organic compounds can be estimated using the intuitively attractive idea of characteristic structural group contributions. These can be used for estimation when no data is available and for assessing data for new systems in terms of data for related systems. This supplements traditional thermodynamic consistency tests. The group contribution method has been used to estimate various physico – chemical properties of pure compounds such as densities, heat capacities and critical constants.

In group contribution methods, a molecule is divided arbitrarily into functional groups. Molecular interactions are considered to be properly weighted sums of group-group interactions. For a multifunctional component in a multicomponent system, group contribution methods assume that each functional group behaves in a manner independent of the molecule in which it appears. Quantitative information on the necessary group-group interactions is obtained from reduction of experimental data for binary systems.

Once such data is available, it becomes possible to calculate molecular interactions for molecular pairs where no experimental data are available. The fundamental advantage of the group contribution method is that when attention is focussed on typical mixtures of non-electrolytes, the number of possible distinct functional groups is much smaller than the number of distinct molecules. Thus the number of distinct group-group interactions is very much smaller than the number of possible distinct molecule-molecule interactions.

By assuming that a physical property of a fluid is the sum of the contributions made by the molecule's functional groups, a possible technique for correlating the properties of a very large number of fluids in terms of much smaller number of parameters which characterise the contributions of individual groups is obtained. For example activity coefficients for systems involving alcohols and alkanes can be obtained by taking the liquid solution as made up of CH_3 / CH_2 and OH groups. This method for predicting activity coefficients of components in liquid mixtures using group contribution is referred to as the Solution of Groups Model and is discussed in section 3.3.4.

In dealing with mixtures of molecules in terms of their constituent groupings of atoms / molecules, one should consider the effect of:

(1) Interactions of various groups occurring in solutions and pure liquids.

(2) The restrictions imposed on these interactions by the organisation of the groups into molecules.

(3) The organisation of the molecules within solution and pure liquid.

The detailed theories of mixtures take these effects into account in terms of some particular model and attempt to estimate the result by statistical mechanical procedures.

No completely satisfactory models have yet been developed due to the complexity that arise even in simple molecules. Detailed theories enhance greater understanding of solutions but fail to fulfil the applied needs. Therefore it is important to have detailed and simple models which take the above mentioned effects into account.

3.3.2 A Review of Group Contribution Methods

Calculation of activity coefficients from group contributions was suggested in 1925 by Langmuir. His suggestion was not practical until a large database and readily accessible computers became available. A detailed review of group contribution concept starting with Langmuir's principle of "independent surface action", through the works of Symthe and Engel (1929), Butler et al (1935), Bronsted and Koefed (1946) and Pierotti (1956) is found in both the work of Al-Hayan (1999) and Cooling (1987).

Derr and Deal (1969, 1973) established the analytical solution of groups (ASOG) method. A similar but more convenient method called the UNIFAC) (UNIQUAC functional group activity coefficients) Gmehling, Tiegs and Knipp (1990), based on the UNIQUAC equation was developed by Fredenslund, Jones and Prausnitz (1975). Since the publication of the original UNIFAC, numerous modifications and extensions have appeared Oishi and Prausnitz (1978), Skjold-Jorgensen et al (1979), Rasmussen et al. (1980), Kikic et al. (1980), Nagata and Katoh (1981), Gmehling (1982, 1986,), Fredenslund and Rasmussen (1985), Larsen et al. (1987) and Weidlich and Gmehling (1987). In both the ASOG and UNIFAC methods, the required activity coefficient is calculated by the combinatorial and residual parts.

3.3.3 Group Interaction model

Based on the success of the group contribution approach, Redlich, Derr and Pierotti (1959) derived a group interaction model for heats of mixing determination. This was based on the assumption that the interaction energy could be represented as the sum of the contributions of the pairs of interacting groups present in the solution. In this model, an assumption is made that the contribution of each group pair is independent of the nature of the present molecules. Thus, each pair of groups was given a characteristic 'interaction coefficient' and this accounted for different group sizes through assigning each a characteristic 'cross section' parameter. The results of testing the group interaction model on available data of binary hydrocarbons solutions, Papadopolous and Derr (1959), showed that the model predicted the relative partial molar heat contents of components to well within experimental errors of the limiting heat data for dilute binary systems which widely deviated from Raoult's law.

3.3.4 Solution of Groups

According to the solution of groups of Wilson and Deal (1962), the activity coefficient for a wide concentration range could be estimated on the basis of group contributions. The assumptions and equations that they presented are now the basis for most group contribution methods in the prediction of liquid phase activity coefficients. The assumptions are as follows:

1. The liquid solution is considered to be a solution of groups which make up the components of the mixture. The groups are chosen to be convenient structural units such as OH, CCl_2, CH_2O, CO etc.
2. The excess Gibbs free energy of a solution is considered to be the sum of two

Contributions; namely, the combinatorial and residual parts. The combinatorial part captures major entropic contribution as determined by the sizes and shapes of the constituent molecules and their mole fractions. The residual part depends on the intermolecular forces that lead to finite enthalpies of mixing. The combinatorial contribution requires only pure component properties while the residual part requires two binary interaction parameters. As a result of this assumption, the logarithm of the activity coefficient may be written as

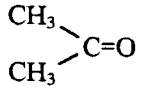
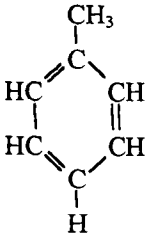
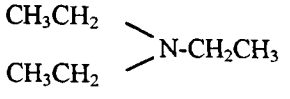
$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R$$

where γ_i^c is the combinatorial (entropy) part and γ_i^R is the residual (enthalpy) part.

3. The residual part, resulting from group interactions, is assumed to be the difference between the sum of the individual contributions of each solute group in the solution and the sum of the individual contributions in the pure component environment.
4. The individual group contributions in any environment are treated as a function of group concentrations and temperature only. Group contribution methods are attractive because they are based on this assumption of group independence. A typical assumption is that the properties of a carbonyl (CO) group in a monoketone are the same as those in a diketone and that the properties of this carbonyl group in a linear ketone, say hexanone, are the same as those in a cyclic ketone like cyclohexanone.

Examples of group assignments in components considered in this work are shown in table 3.1.

Table 3.1. Typical group assignments

Component	Molecular formula	Molecular structure	Group assignment
Acetone	C_3H_6O		$2CH_3$, 1CO
Diethyl ether	$C_4H_{10}O$	CH_3-CH_2-O-CH_2-CH_3	$2CH_3$, $2CH_2$, 1O
Pentane	C_5H_{12}	CH_3-CH_2-CH_2-CH_2-CH_3	$2CH_3$, $3CH_2$
Toluene	C_7H_8		5ACH, 1ACCH
Triethyl amine	$C_6H_{15}N$		$3CH_3$, $3CH_2$, 1N

3.3.5 Analytical Solution of Groups (ASOG)

The analytical solution of groups (ASOG) procedure was developed by Derr and Deal (1969), Ronc and Ratcliff (1971) and Palmer and Smith (1972), thus leading to the universal applicability of this model. The ASOG methods correlates the interaction of functional groups and any given combination with characteristic interaction parameters which are independent of composition. The interaction parameters for a combination of groups can be calculated and then used for other mixtures containing the same group combination. Activity coefficients were predicted as the sum of the interactions between the groups in the mixture less the interactions between groups of the pure components. The two parameter equation developed by Wilson (1964) was used to correlate each

interaction between groups as if it were a mixture of two pure components. The effect of differences in molecular size was added to these interaction contributions.

The molecular activity coefficient was divided into two parts, the first part gave the contribution due to molecular size and shape differences while the other part provided the contribution due to the molecular interactions. The first and second parts of the molecular activity coefficients were estimated using the athermal Flory – Huggins equation, Flory (1941) and Huggins (1942), and the Wilson equation (1964) applied to functional groups respectively. The fundamental equations of the Analytical Solutions of Groups are presented in appendix C.2.

Since the ASOG equation is not limited to the prediction of activity coefficient at infinite dilution, it can be used to study the effect of concentration on activity coefficients. Palmer (1975) presented the introduction to ASOG and a large number of parameters for its use were reported by Derr and Deal (1962). As an alternative to ASOG, Fredenslund *et al.* (1975) proposed a group contribution method called UNIFAC (UNIQUAC Functional Group Activity Coefficients). The UNIFAC and ASOG models are similar in principle, but do differ in detail.

3.4. The UNIFAC Group Contribution Method

3.4.1 Introduction

The fundamental idea of the solution of groups model is to utilize existing phase equilibrium data to predict data for systems for which no experimental data are available. In concept, the UNIFAC model follows Derr and Deal's ASOG model, where the activity coefficients in mixtures are related to interactions between structural groups. The method

involves (a) a suitable reduction of experimentally obtained activity coefficient data to obtain parameters characterising interactions between pairs of structural groups in non electrolyte systems (b) the use of these parameters to predict activity coefficients for other systems which have not been studied experimentally but which contain the same functional groups. The UNIFAC method in conjunction with its modifications, the effective UNIFAC and the modified UNIFAC with a modified Staverman Guggenheim combinatorial part are presented in this section.

3.4.2 The UNIFAC Procedure

The UNIFAC model combines the UNIQUAC model with the solution of groups approach of Wilson and Deal (1962). Fredenslund *et al.* (1975) developed and presented the original UNIFAC model. By combining the solution of groups concept with the UNIQUAC equation, much of the arbitrariness in the ASOG method is removed. Firstly the UNIQUAC model contains a combinatorial part which is essentially due to differences in size and shape in the mixture and the residual part due to energetic interactions. Secondly functional group sizes and interaction surface areas are introduced from independently obtained pure – component data. Based on the assumption in the solution of groups approach that the logarithm of the activity coefficient is the sum of the two contributions, combinatorial and residual parts, for a multi-component mixture the following equation can be written

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad \ldots\ldots (3.5)$$

where $\ln \gamma_i^C$ and $\ln \gamma_i^R$ are the combinatorial and residual parts respectively.

The distinction between the two components is very crucial because the liquid phase non-idealities cannot be associated only with group energetic interactions.

3.4.2.1 The Combinatorial Component

In the UNIFAC method, the combinatorial part can be calculated using the Staverman – Guggenheim function as used in the UNIQUAC model. The combinatorial part is given by

$$\ln \gamma_i^C = \left\{ \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} \right\} - \frac{zq_i}{2} \left\{ \ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right\} \quad \text{..... (3.6)}$$

where

$$\phi_i = \frac{r_i x_i}{\sum r_j x_j} \quad \text{..... (3.7)}$$

$$\theta_i = \frac{q_i x_i}{\sum q_j x_j} \quad \text{..... (3.8)}$$

For j =1, 2, 3 - - - - - -n, and n is the number of components. In the three equations above, x_i is the mole fraction of component i and the summation includes all components. The parameters θ_i and ϕ_i represent molecular surface area fraction and segment fraction (similar to molecular volume fraction) respectively. The coordination number, z can be considered as 10 after Fredenslund *et al.* (1975), r_i and q_i are pure component parameters representing van der Waals volume and surface area respectively. These are calculated by summing the group volume and area constants, R_k and Q_k in the following way

$$r_i = \sum v_k^{(i)} R_k \quad \text{..... (3.9)}$$

$$q_1 = \sum v_k^{(i)} Q_k \quad \text{..... (3.10)}$$

In equations (3.9) and (3.10) $v_k^{(i)}$ is an integer and stands for the number of groups of type k in molecule i. The group parameters R_k and Q_k are obtained from atomic and molecular structure data, the van der Waals group volume and surface areas, V_k and A_k can be obtained from Bondi (1968).

$$R_k = {V_k}/{15.17} \quad \text{..... (3.11)}$$

$$Q_k = {A_k}/{2.5x10^9} \quad \text{..... (3.12)}$$

The normalisation factors 15.17 and $2.5x10^9$ are those derived by Abrams and Prausnitz.

3.4.2.2 The Residual Component

The assumption in the solution of groups method, that the contribution from group interactions is equal to the sum of the individual contributions of each solute in the solution minus the sum of the individual contributions in pure component situation can be written as

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \quad \text{..... (3.13)}$$

where Γ_k and $\Gamma_k^{(i)}$ stand for residual activity coefficients of group k in a mixture solution and in a solution containing only molecules of i respectively. The term $\ln \Gamma_k^{(i)}$ is very important in order to reach the normalisation that γ_i becomes unity as x_i tends to 1.0.

The terms Γ_k and $\Gamma_k^{(i)}$ are functions of group concentrations and temperature only, both can be calculated from an expression similar to the one used for the residual activity coefficient in the UNIQUAC model.

$$\ln \Gamma_k = Q_k \left\{ 1 - \left(\ln \sum_m \theta_m \psi_{mk} \right) - \sum_m \left(\frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}} \right) \right\} \quad \text{..... (3.14)}$$

NB $\ln \Gamma_k^{(i)}$ can also be calculated from the same equation.

The parameter θ_m represents the surface area fraction of group m and is calculated in the same manner as θ_i in equation (3.8).

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad \text{.....(3.15)}$$

Here the summation covers all the groups and X_m is the mole fraction of group m in the mixture and it is given by

$$X_m = \frac{\sum v_m^{(j)} x_j}{\sum_n \sum_j v_n^{(j)} x_j} \quad \text{.....(3.16)}$$

where j = 1, 2, 3 ----------M (number of components) and

n = 1, 2, 3 ----------N (Number of groups)

ψ is the group interaction parameter and this can be calculated from the expression below

$$\psi_{mn} = \exp\left(-a_{mn}/T\right) = \exp\left[-(U_{mn} - U_{nm})/RT\right] \quad \text{.....(3.17)}$$

where U_{mn} is a measure of the interaction energy between groups m and n. The group interaction parameters, a_{mn}, must be calculated from phase equilibrium data. Since a_{mn} is not equal to a_{nm}, it means that, there are two parameters for a binary mixture.

3.4.3 Modification of UNIFAC

3.4.3.1 Modified UNIFAC

Kikic *et al.* (1980) developed the modified UNIFAC by proposing a modification to the volume fraction in the Staverman – Guggenheim combinatorial term while the residual term remained unchanged.

The modified combinatorial term is given by

$$\ln \gamma_i^C = \left\{\ln \frac{\psi_i}{x_i} + 1 - \frac{\psi_i}{x_i}\right\} - \frac{zq_i}{2}\left\{\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}\right\} \quad \text{.....(3.18)}$$

where ψ_i is calculated from

$$\psi_i = \frac{x_i r_i^{\frac{2}{3}}}{\sum_j x_j r_i^{\frac{2}{3}}} \quad \text{..... (3.19)}$$

or

$$\psi_i = \frac{x_i \left(v_i^o\right)^{\frac{2}{3}}}{\sum_j x_j \left(v_j^o\right)^{\frac{2}{3}}} \quad \text{..... (3.20)}$$

The comparison of experimental data for large numbers of mixtures of aliphatic hydrocarbons led to the empirical evaluation of exponent (2/3).

Like in the UNIFAC method, no additional information is needed in the evaluation of ψ_i in equation (3.19) but the van der Waals volume is calculated from group volumes and, hence present a problem in distinguishing between certain isomers. Making use of equation (3.20) overcome the difficulty because the modified volume fraction is related to pure component molar volumes and these must be known.

3.4.3.2 Effective UNIFAC

In their modification, Nagata and Koyabu (1981) chose not to change the Staverman - Guggenheim combinatorial term of the UNIFAC. They modified the residual term and this is expressed in the following manner.

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} \left\{ \ln \Gamma_k - \ln \Gamma_k^{(i)} \right\} - \left\{ \ln \frac{\theta_i}{x_i} + 1 - \frac{\theta_i}{x_i} \right\} \quad \text{..... (3.21)}$$

In the effective UNIFAC method, the residual activity coefficients, Γ_k and $\Gamma_k^{(i)}$, are calculated by

$$\ln \Gamma_k = 1 - (\ln \sum_m X_m \psi_{mk}) - \sum_m \left(\frac{X_m \psi_{km}}{\sum_n X_n \psi_{nm}} \right) \quad \text{..... (3.22)}$$

Unlike the original UNIFAC expression, in the above equation the group mole fraction X_m, is used instead of the group surface area fraction. Also the group interaction parameters are modified by making use of the ratio of the group surface area parameters in the following way

$$\psi_{mn} = \frac{Q_m}{Q_n} \exp\left(\frac{-a_{mn}}{T} \right) \quad \text{..... (3.23)}$$

3.4.4 Extension of UNIFAC to Polymer solutions

In 1978, Oishi extended the use of UNIFAC model to polymer solutions by adding a free volume contribution. Here, the suggestion of Prigogine-Flory Patterson theory, Prigogine (1957); Flory (1965, 1970) and Patterson (1969, 1970) of accounting for the free-volume difference between polymer and solvent molecules was applied. It is important to realise that while this difference is usually insignificant for the liquid mixtures of small molecules, it is of importance in polymer solvent systems.

Holten-Andersen *et al.* (1987) presented another extension of UNIFAC to polymer solutions and obtained the free volume from an equation of state similar to that based on the perturbed-hard chain (PHC) theory of Beret (1975) and Donohue (1978). This equation of state contains a simplified attraction term that contains a UNIQUAC-like expression for mixtures.

Goydan *et al.* (1989) performed a comparative study of the predictions of the UNIFAC free volume model of Oishi and Holten-Andersen equation of state for solvent activities in

a variety of polymer solutions. Their conclusion was that the Holten-Andersen correlation is more accurate while Oishi's model is more widely applicable.

Elbro et al (1990) proposed to include free-volume contributions in a simple way. The combinatorial and free volume terms were combined for an athermal solution to give

$$\frac{s^{E,fv}}{R} = -\frac{g^{E,fv}}{RT} = -\sum_i x_i \ln \frac{\Phi_i^{fv}}{x_i} \quad \text{..... (3.24)}$$

Where fv and Φ_i^{fv} represent the free-volume and free volume fraction of component i. The free-volume fraction is given by

$$\Phi_i^{fv} = \frac{x_i\left(v_i - v_i^*\right)}{\sum_j x_j\left(v_j - v_j^*\right)} \quad \text{..... (3.25)}$$

In the above equation v_i and v_i^* are, respectively, the pure-component molar volumes and the hard core volumes; x_i is the mole fraction of component i.

In the case of the activity coefficient of an athermal solution, Elbro obtained

$$\ln \gamma_i^{fv} = \ln\left(\frac{\Phi^{fv}}{x_i}\right) + 1 - \frac{\Phi^{fv}}{x_i} \quad \text{..... (3.26)}$$

Then to obtain the total activity coefficient, the residual term was added.

Other group-contribution methods for polymer/solvent systems were presented by Chen *et al.* (1990), High and Danner (1990a) and Lee and Danner (1996, 1996a, 1996b, 1997).

3.5. Equation of State Models for Polymer Solution Thermodynamics

In phase equilibria calculations, equations of state models are preferred over activity coefficient models because equations of state can describe all phases and pressure dependency. From the various equations of state that have been developed, the chemical industry makes use of further developments of the cubic van der Waals equations of state such as the Soave-Redlich, Soave (1972) and Peng-Robinson equation of state, Peng and Robinson (1976).

Lee and Danner (1996) described an equation of state that is capable of predicting pure component and mixture properties of low and high molecular weight compounds. They developed the predictive model using the group contribution approach. This approach assumes that the interaction energy between groups will be constant regardless of the overall molecular structure.

High and Danner (1989) and High (1990) originally developed the group – contribution lattice fluid equation of state (GCLF – EOS) which can be used for vapour – liquid equilibria involving polymer – solvent solutions. Their model generally predicted well the activities of non-polar solvents in various polymers but it was not adequate for some solvent-polymer systems. Typical examples were the consistently poor predictions for a variety of solvents in polyisobutylene. In 1990, High and Danner suggested that the poor predictions for polyisobutylene were a result of the inaccurate group contribution values used for the quaternary carbon atom found in polyisobutylene. Also reported in their work were the predictions obtained with the original GCLF – EOS for solutions of acetone or methyl ethyl ketone in polystyrene. Their conclusion was that for polar solvents a non-zero binary interaction parameter was necessary. Also noted was that the original GCLF –

EOS systematically under predicted solvent activities for many polar solvent systems, and polar solvents as well.

By modifying the original GCLF – EOS, Lee and Danner (1996) developed an improved model that is capable of predicting the equilibrium thermodynamic behaviour of pure polymers and polymer solutions for a large number of polymer- solvent systems. The predictability power of the model was improved by making several modifications such as the addition of new groups, thus expanding model applicability. Also developed were more accurate temperature dependencies for the interaction energy and reference volume parameters. All the group contribution values were revised. For a mixture, a binary interaction parameter was introduced into the combining rule and group contribution mixing rule for this parameter was developed. Pure component and binary mixture equilibrium properties of low molecular weight compounds were used to obtain all the group parameters. The modified GCLF – EOS can be applied to the prediction of vapour-liquid equilibria in both dilute and concentrated polymer solutions to any homopolymer, random copolymer or alternating copolymer which can be constructed from available contributions.

3.5.1 Group – Contribution Lattice - Fluid Equation of State

3.5.1.1 Equation of state for pure components

The theory in which the polymer - solvent system is modelled as a lattice structure was developed independently by Flory (1941,1942) and Huggins (1942). The various possible ways in which the polymer and solvent molecules could be arranged on the lattice sites were used to calculate the combinatorial contributions to thermodynamic mixing functions. The 1976 Sanchez and Lacombe EOS is based on the lattice – hole theory and

assumes that a random mixing combinatorial term is sufficient to describe the fluid. Equations for both pure components and mixtures that correct for the non random mixing caused by the interaction energies between molecules was developed by Panayioutu and Vera (1982). In the Panayioutu - Vera theory the volume of the lattice is fixed to a value of 9.75×10^{-3} m^3/kmol. In the Sanchez-Lacombe model the volume of the lattice site is a variable quantity regressed from experimental data. The Sanchez-Lacombe fluid Equation of state (1976) is expressed as follows

$$\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{1}{r} - \left[1 + \tilde{v}\ln\left(1 - \frac{1}{\tilde{v}}\right)\right] - \frac{1}{\tilde{v}\tilde{T}} \quad \text{.....(3.27)}$$

The reduced (~) and characteristic (*) temperature and pressure are defined as follows

$$\tilde{P} = \frac{P}{P^*} = \frac{P}{z\varepsilon/2v^*} \quad \text{.....(3.28)}$$

$$\tilde{T} = \frac{T}{T^*} = \frac{T}{z\varepsilon/2k} \quad \text{.....(3.29)}$$

The characteristic parameters P^*, v^* and T^* obey the equation

$$P^*v^* = kT^* \quad \text{.....(3.30)}$$

The lattice hole theory is different from the lattice model of Flory - Huggins because in the former, the density of the mixture is allowed to vary by increasing the fraction of holes in the lattice. The Flory - Huggins treatment considers every site as occupied by a solvent molecule or polymer segment. The holes present in the lattice act as a means of varying the density of the fluid and are analogous to the free volume in the generalised van der Waals models.

The lattice-fluid equation of state for pure components is based on the well-established lattice statistical model of Guggenheim (1952). Panayiotou and Vera (1982) and High

(1990) gave a detailed derivation of the equation of state. For pure components the equation is expressed in terms of reduced variables as

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\bar{v}_1}{\bar{v}_1 - 1}\right) + \frac{z}{2}\ln\left(\frac{\bar{v}_1 + \left(\bar{q}_1/\bar{r}_1\right) - 1}{\bar{v}_1}\right) - \frac{\theta_1^2}{\bar{T}_1} \quad \text{..... (3.31)}$$

$$\tilde{P}_1 = \frac{P}{P_1^*} = \frac{2P_{v_h}}{z\epsilon_{11}} \quad \text{..... (3.32)}$$

$$\tilde{T} = \frac{T}{T_1^*} = \frac{2RT}{z\epsilon_{11}} \quad \text{..... (3.33)}$$

$$\tilde{v}_1 = \frac{v}{v_1^*} = \frac{v_h\left(N_h + r_1 N_1\right)}{v_1^* N_i} \quad \text{..... (3.34)}$$

$$\theta_1 = \frac{q_1 N_1}{N_q} \quad \text{..... (3.35)}$$

$$zN_q = z\left(N_h + q_1 N_1\right) \quad \text{..... (3.36)}$$

$$zq_1 = (z-2)r_1 + 2 \quad \text{..... (3.37)}$$

$$r_1 = \frac{v_1^*}{v_h} \quad \text{..... (3.38)}$$

$$N_h = r_1 N_1\left(\tilde{v}_1 - 1\right) \quad \text{..... (3.39)}$$

where ϵ_{11} is the molecular interaction energy, v_1^* is the molecular reference volume, z is the co-ordination number (10), v_h is the volume of the lattice site, r_1 is the number of lattice sites occupied by a molecule of type 1 in the system, zq_1 is the number of interaction sites available to molecules of type 1, θ_1 is the surface area fraction of pure component 1, N_h is the number of holes in the lattice, and zN_q is the total number of interaction sites in the lattice. The above equation of state contains two adjustable

parameters: molecular interaction energy, ϵ_{11} and molecular reference volume, v_1^*. Once one has established these two parameters, all the remaining parameters in equation (3.31) can be determined from equation (3.32) through to (3.39) for a given temperature and pressure. The system properties can be determined by solving equation (3.31) with respect to reduced volume. During the derivation of equation (3.31) it was assumed that the molecules and holes are randomly placed in the lattice.

The characteristic interaction molecular energy, ϵ_{11}, is taken as an average over the length of the molecule. Structural elements of the molecule with large interaction energies are averaged with other structural elements with less or zero interaction energy. Averaging the interaction energy over the length of the molecules does not correspond to the exact statistical mechanical definition of the mean field approximation. Also this is most likely to cause poor predictions for strongly associating systems.

Intermolecular interactions result from dispersion forces. Electrons moving within a molecule produce a fluctuating dipole in all molecules, polar and non-polar. Polar molecules also posses permanent dipoles. Both types of dipoles induce other dipole (induced dipoles) in neighbouring molecules. The induced dipoles are attracted to the original dipoles and this attraction lowers the energy of the system. The energy is lowest when the dispersive forces are exactly balanced by the repulsive forces between the cores; the decrease in energy is called the interaction energy and is responsible for the cohesion of liquids and molecular crystals. This energy is larger for polar molecules than for non-polar molecules.

The interaction energy for a pure substance i is expressed by means of the cohesive energy density, e_i, the energy needed to separate the molecules in 1ml. This is experimentally achieved through vaporization. Therefore e_i is related to the molar enthalpy of vaporization of substance i, $\Delta h_{vap,i}$

$$e_i = (\Delta h_{vap,i} - RT)/V_i \quad \text{..... (3.40)}$$

Here RT reflects the volume work and V_i is the molar volume.

3.5.1.2 Equation of State for Binary Mixtures:

Based on the same assumption that the holes in the mixture mix randomly as in pure component cases, the equation of state for the mixture is derived. In the case of the mixture, the molecules are not assumed to mix randomly. Local compositions of the molecules are calculated using Guggenheim's quasi-chemical theory and the resultant mixture equation of state is

$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) + \frac{z}{2}\ln\left(\frac{\tilde{v}+\left(q/r\right)-1}{\tilde{v}}\right) - \frac{\theta^2}{T} \quad \text{..... (3.41)}$$

The reduced variables in equation (3.41) are defined by

$$\tilde{P} = \frac{P}{P^*} = \frac{2Pv_h}{z\epsilon^*} \quad \text{..... (3.42)}$$

$$\tilde{T} = \frac{T}{T^*} = \frac{2RT}{Z\epsilon^*} \quad \text{..... (3.43)}$$

$$\tilde{v} = \frac{v}{v^*} = \frac{v_h(N_h + rN)}{v^* N} \quad \text{..... (3.44)}$$

The following simple combining rules are used for other parameters

$$v^* = \sum x_i v_i^* \quad \text{..... (3.45)}$$

$$r = \frac{v^*}{v_h} = \sum x_i r_i \quad \text{..... (3.46)}$$

$$q = \sum x_i q_1 \quad \text{..... (3.47)}$$

$$\theta = \sum \theta_i \quad \text{..... (3.48)}$$

Where x_i is the mole fraction of component i in the mixture and θ_i is the molecular surface fraction including holes in the mixture.

$$\theta_i = \frac{zq_i N_i}{z\left(N_h + \sum q_j N_j\right)} = \frac{q_i N_i}{N_h + qN} \quad \text{..... (3.49)}$$

The interaction energy, $\in_{11}$, for a binary mixture is given by

$$\in^* = \bar{\theta}_1 \in_{11} + \theta_2 \in_{22} - \bar{\theta}_1 \bar{\theta}_2 \Gamma_{12} \dot{\Delta} \in \quad \text{..... (3.50)}$$

where

$$\Delta \in = \in_{11} + \in_{22} - 2 \in_{12} \quad \text{..... (3.51)}$$

$$\theta_1 = \frac{zq_i N_i}{z\sum q_j N_j} = \frac{q_i N_i}{qN} = \frac{x_i q_i}{q} \quad \text{..... (3.52)}$$

Since $N_h = rN\left(\tilde{v} - 1\right)$ from equation (3.44), equation (3.49) becomes

$$\theta_1 = \frac{x_i q_i}{q + r\left(\tilde{v} - 1\right)} \quad \text{..... (3.53)}$$

The non randomness parameters Γ_{ij} are related by

$$\bar{\theta}_1 \dot{\Gamma}_{11} + \bar{\theta}_2 \dot{\Gamma}_{12} = \bar{\theta}_2 \dot{\Gamma}_{22} + \bar{\theta}_1 \dot{\Gamma}_{12} = 1 \quad \text{..... (3.54)}$$

$$\dot{\Gamma}_{12} = \frac{2}{1 + \sqrt{1 - 4\bar{\theta}_1 \bar{\theta}_2 (1 - \dot{G})}} \quad \text{..... (3.55)}$$

$$\dot{G} = \exp\left(\frac{\theta\left(\in_{11} + \in_{22} - 2 \in_{12}\right)}{RT}\right) = \exp\left(\theta \frac{\Delta \in}{RT}\right) \quad \text{..... (3.56)}$$

When the molecules are randomly mixed, $\Delta \in = 0$, $\dot{\Gamma}_{11} = \dot{\Gamma}_{22} = \dot{\Gamma}_{12} = 1$. In a mixture the holes are assumed to mix randomly as in a pure component situation but the molecules are not assumed to mix randomly. The quasi-chemical theory of Guggenheim (1952) is used to calculate local compositions of the molecules.

3.5.1.3 Weight Fraction Activity Coefficient

The pure component chemical potential $\mu_i^{(P)}$ as given by Panayiotou and Vera (1982b), High (1990) is expressed as follows

$$-\frac{\mu_i^{(P)}}{RT} = \ln\frac{\delta_1}{\sigma_1} + \ln q_1 + \ln\frac{(1-\theta_1)^{r_1}}{\theta_1} + \frac{\theta_1}{\tilde{T}_1}\left(q_1 + r_1\tilde{v}_1\theta_1\right) \quad \text{..... (3.57)}$$

where the subscript 1 in $\tilde{T}_1$ and $\tilde{v}_1$ stands for a pure component. Pressure and volume are implicitly involved in the parameters θ_i, q_i, r_i and $\tilde{v}$, which must be determined by solving the equations of state, (3.31) and (3.57) simultaneously in the calculation of chemical potential. In the derivation of this expression of chemical potential, it was assumed that the molecules and holes are distributed randomly throughout the lattice. The chemical potential of component *i* in a binary mixture, $\mu_i^{(M)}$ is represented as follows:

$$-\frac{\mu_i^{(M)}}{RT} = \ln\frac{\delta_i}{\sigma_i} + \ln q_i \ln\frac{(1-\theta)^{r_1}}{\theta_i} + q_i\theta\left(\frac{1}{\tilde{T}_i} + \frac{1}{\tilde{T}}\right) + \frac{\theta^2(r_i - q_i)}{\tilde{T}} - \frac{1}{2}zq_i\ln\dot{\Gamma}_{ii} \quad \text{..... (3.58)}$$

δ_i and σ_i are volume – independent parameters accounting for flexibility and symmetry of molecule *i*. As a result these parameters do not appear in the equation of state and will not influence equilibrium calculations. The activity of a component in a mixture is given by

$$\ln a_i = \frac{\Delta\mu_i}{RT} = \frac{\mu_i^{(M)} - \mu_i^{(P)}}{RT} \quad \text{..... (3.59)}$$

Where $\frac{\Delta\mu_i}{RT}$ is the change in chemical potential between the species i in the mixture and pure component i and is calculated from the equation below.

$$\frac{\Delta\mu_i}{RT} = \ln\phi_i + \ln\frac{\tilde{v}_i}{\tilde{v}} + q_i \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\frac{\tilde{v}_i-1}{\tilde{v}_i}\right) + q_i\left(\frac{2\theta_{i,p}-\theta}{\tilde{T}_i} - \frac{\theta}{\tilde{T}}\right) + \frac{zq_i}{2}\ln\dot{\Gamma}_{ii} \quad \text{..... (3.60)}$$

The weight fraction activity coefficient (WFAC) is given by the following expression

$$\Omega_i = \frac{a_i}{w_i} \quad \text{..... (3.61a)}$$

$$\ln\Omega_i = \ln a_i - \ln w_i = \frac{\Delta\mu_i}{RT} - \ln w_i \quad \text{..... (3.61b)}$$

Also, by combining equations (3.60) and (3.61b), the WFAC of component i in a mixture can be shown to be

$$\ln\Omega_i = \ln\phi_i - \ln w_i + \ln\frac{\tilde{v}_i}{\tilde{v}} + q_i \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\frac{\tilde{v}_i-1}{\tilde{v}_i}\right) + q_i\left(\frac{2\theta_{i,p}-\theta}{\tilde{T}_i} - \frac{\theta}{\tilde{T}}\right) + \frac{zq_i}{2}\ln\dot{\Gamma}_{ii} \quad \text{..... (3.62)}$$

Where ϕ_i and w_i are the volume and weight fractions of component i in the mixture respectively, $\theta_{i,p}$ being the area fraction of pure component i at the same temperature and pressure as the mixture.

In polymer – solvent situations, which is of interest in this study, the equation of state must be solved for the pure solvent, the polymer and the solvent-polymer mixture. The solvent is the only component available in the vapour phase, hence the iso-chemical potential condition does not have to be solved. Therefore equation (3.61b) is directly used to calculate the weight fraction activity coefficient of the solvent.

3.5.1.4 Conclusion

The GCLF-EOS was developed by High and Danner (1990) through determining group contributions for the adjustable parameters in the Panayiotou – Vera EOS. While the Panayiotou – Vera formulation gives a correlation method, the GCLF-EOS model is capable of predicting polymer – solvent equilibria. The advantage of the GCLF – EOS is that, the only input required is the structure of the polymer and solvent molecules. The use of mixing rules in the calculation of molecular interaction energies is found in the work of Lee and Danner (1996), High and Danner (1989) and Byung Chul (1996).

3.6 Summary of Group Contribution Methods.

In this work infinite dilution activity coefficients are estimated primarily using the UNIFAC group contribution method. In addition to solvent – polymer solutions, activity coefficients of volatile organic compounds of interest in water are also predicted. Where appropriate the experimental and predictions results of this study can be compared to the work of Barr and Newsham (1987), Cooling and Newsham (1992) and Al – Hayan (1999). The work of these authors is discussed in detail in other sections because their experimental and modelling work were inspirational to this study.

In the process of reviewing the various group contribution methods, the UNIFAC procedure proved to be the most developed, most widely used and offers a lot of promises for future improvements and modifications of the available models. Also of great importance is that group-group interaction parameter tables are available, for example those by Hansen *et al.* (1993), Gmehling *et al.* (1993) and Fredenslund and Sorensen (1994). The UNIFAC model is successful for semi-quantitative predictions of vapour-liquid equilibria for a wide variety of mixtures, those containing polymers included. The

above reasons led to the decision of using the UNIFAC model, along with its two modifications, effective UNIFAC and modified UNIFAC in this work.

The original UNIFAC model often results in large deviations from experimental data when applied to athermal polymer – solvent systems. Empirical modifications of the UNIFAC model by Kikic *et al.* (1980), Larsen *et al.* (1987) proposed to overcome the tendency to overestimate the degree of non-ideality, but many of the important features of polymer solutions behaviour still can not be explained. For example, the existence of lower critical solution temperatures (LCST) suggests that in addition to the combinatorial term, there are other factors that play a role in polymer solution thermodynamics. One possibility is free volume dissimilarity as suggested by Patterson (1969, 1982). Free volume deals with "voids" in a polymer melt or glass that can accommodate small molecules or segments of larger molecules without much distortion to the structure of the polymer.

Activity coefficient models that take into account both size and free volume effects Elbro *et al.* (1990), Prausnitz, 1978) can perform a better job in the prediction of solvent activity coefficients Kontogeogis *et al.* (1994). The fundamental basis for previously discussed existing group contribution methods for polymer solutions is the lattice theory of Flory (1970) and Huggins (1942) with variations of Guggenheim (1952), Orifino and Flory (1957), Koningsveld *et al.* (1971). However it is well known that the Flory – Huggins theory is based on severe simplifying assumptions which have been overcomed in part by the much-improved lattice – cluster theory of Freed and co-workers (1991).

Freed's theory for a mixture of athermal chains and monomers is mathematically complicated but the results can be well approximated using a mathematical simplification introduced by Hu *et al.* (1991,1993, 1996). The theory contains only a single binary parameter $\in_{12}$ and does not take into consideration both the orientation as found in hydrogen bonded liquids and compressibility (free volume effects). Hu *et al.* (1991, 1993) introduced a secondary lattice, which in effect assigns theoretical temperature dependence to the binary parameter $\in_{12}$ so as to include the effects of oriented forces.

3.7. Molecular Simulation of Phase Equilibria

The application of molecular theory to the study of phase equilibria and thermodynamic properties involves two steps (a) determination of intermolecular potential energy between molecules or ions in the system (b) solution of the equations of statistical mechanics for the system with this potential. The problem of how to calculate the properties of a system containing a large number of molecules (macroscopic) from the individual molecules, is the province of statistical mechanics.

Molecular simulation is a generic term including both Monte Carlo (MC) and Molecular Dynamics (MD) computing methods. The primary aim and desire for molecular simulation is the provision of exact results for statistical mechanical problems in preference to approximate solutions. Molecular simulation differs from other computing methods and approximations in that the molecular co-ordinates of a system are evolved in accordance with a rigorous calculation of intermolecular energies or forces. One can suitably describe molecular simulation as computational statistical mechanics. It enables the determination of macroscopic properties by evaluating exactly the theoretical model of molecular behaviour using a computer program. The results of the simulation are

affected solely by the nature of the theoretical model implemented. Therefore comparison of simulation results with experimental data is an ambiguous test of the accuracy of the model. As a result any discrepancies between accurate experimental measurements and molecular simulation data can be attributed unambiguously to the failure of the model to represent molecular behaviour.

The history of molecular simulation parallels that of the computer. As pointed out by Yu *et al.* (1995) molecular simulations can act as a bridge between direct experimental measurements and engineering models. They also reported that, a possibility of giving data for the validation purposes of approximate techniques for well-defined model systems. However, the details and methods of simulations are not considered in this work, as this will be done at some stage as part of the future work. It looks to be an attractive idea to study phase equilibrium of solvent-polymer systems using this technique and then compare the results with those from experiment, equations of state and activity coefficient models. Al-Hayan (1999) discussed the application of molecular theory to phase equilibria calculation.

CHAPTER FOUR

EXPERIMENTAL WORK

CHAPTER 4: EXPERMENTAL WORK

4.1. Introduction

In order to test the effectiveness of silicon oils in the removal of volatile organic compounds from contaminated air streams, it was necessary to understand the phase equilibrium involved. Therefore it was the goal of this work to find a simple, rapid and accurate method for studying phase equilibrium between volatile organic compounds and silicon oils. The simple static headspace and the dynamic gas-liquid chromatographic techniques are presented as methods of measuring activity coefficients of VOCs in water and silicone oils. The effectiveness and reliability of the experimental methods were later tested using some group contribution methods such as the UNIFAC. However, there is a general agreement in literature that the GLC is "a means, perhaps the easiest for studying the thermodynamics of the interaction of a volatile solute with a non volatile solvent", Martin (1956).

The experimental work was divided into two stages.

The first phase was performed using shaker flasks, with four main objectives;

1. To determine the solubility of organics in silicone oil.
2. Finding an alternative method for calibration instead of the commonly used air bags.
3. Studying the accuracy and reproducibility of the data obtained using this method.
4. Establishing a very simple and cheap method for determining Henry's law constants and infinite dilution activity coefficients in the laboratory.

The second stage of the experimental work involved the use of the gas-liquid chromatographic technique to study phase equilibrium between the organics and silicone oils. The objectives for carrying out this study were;

1. Establishing a fast, rapid and accurate method for determining infinite dilution activity coefficients of solvent-polymer solutions.
2. To provide a lot of phase equilibrium data for solvent-polymer systems.
3. To study the effect of experimental variables such as temperature, pressure and concentration on the infinite dilution activity coefficients.
4. Finding a suitable and simple technique for packing columns.
5. Minimising the use of large quantities of both organics and silicone oils in the study of phase equilibrium as in the first phase, thus minimising costs.
6. To compare the data obtained in this study with that in literature using the same method and predicting equations.

4.2. The Simple Static Headspace Method

4.2.1. Equipment and Procedure

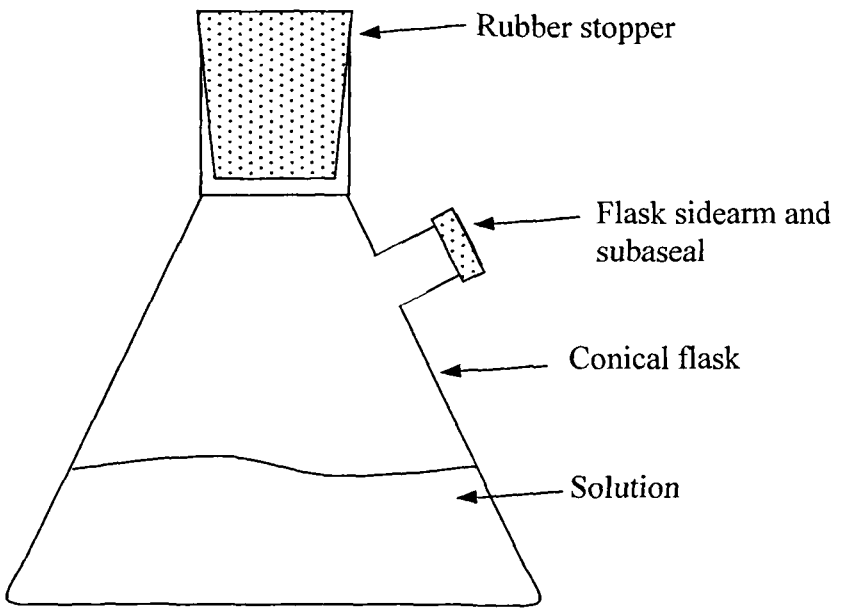


Figure 4.1. Simple headspace apparatus

The equipment consisted of an enclosed system of a 500ml conical flask (figure 4.1) with a glass sidearm. The flask was sealed from the atmosphere by a rubber bung. The initial VOC injection and gas sampling were done through the sidearm subaseal.

At start up, a fixed volume of silicone oil (200ml) and different volumes of the VOC were added to each flask. Afterwards, they were placed in the water bath shaker at constant temperature. The reciprocal shaker ensures good mixing within the flask and the required temperature could be maintained. Five flasks were used for each VOC concentration and two injections were made from each flask after 30 minutes of shaking time.

4.2.2. Sample Analysis

The gas samples were analysed by a Perkin – Elmer Gas Chromatography equipment. A gas tight syringe was used to take a sample from the flask. A gas sample volume of 0.5ml was injected into the GC. The GC conditions were as follows;

- Flame ionisation detector (FID)
- Carrier gas was helium at a flow rate of 35ml/min
- Injector and detector temperature at 250^0C
- Column was a 1/8 inch diameter stainless steel packed with a 30% Carbowax 20M in Chromosorb P 60-80 mesh.

4.2.3.Calibration Curves

The simple headspace method relies on the availability of accurate and reproducible calibration equations in order to determine the concentrations in both the gas and liquid phases. The shaker flasks were thoroughly cleaned and dried. Known volumes of VOC corresponding to the required parts per million were injected into the flasks. The VOC was allowed to vaporise in a water bath shaker at the desired temperature. Gas samples were withdrawn using a gas tight syringe and injected into the GC. The procedure was repeated for all concentrations of interest. Calibration curves were obtained by plotting concentrations in kg/m^3 against peak area in units. The calibration data and curves for this work are shown in appendix E.

4.3.The Gas-Liquid Chromatographic Technique

4.3.1.Theoretical background

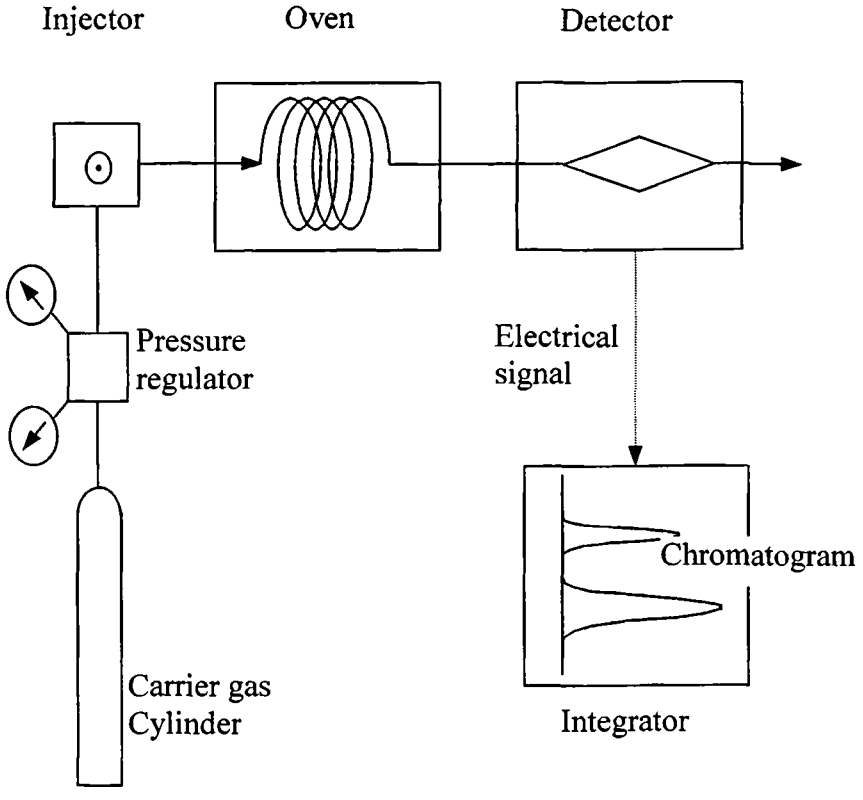


Figure 4.2 Typical gas chromatography

The essential parts are:

1. Carrier gas supply at constant pressure. This is obtained from a commercial cyclinder fitted with a pressure reducing valve, followed with a drying tube.
2. Needle valve or precise pressure regulator for fine adjustment of flow rate.
3. Manometer or pressure gauges
4. Sample introduction system
5. Chromatographic column
6. Thermostat

7. Detector, the output of which is normally fitted to the recorder
8. Flow meters

Apparatus effectiveness depends on the attention paid to the preparation of the column and the introduction of the sample. The sample must be vaporised rapidly so that equilibrium between the two phases occurs as quickly as possible. This is frequently achieved by provision of a special flasher heater at the point of injection. Temperatures should not be too high so as not to decompose the sample.

The liquid used as the stationary phase must satisfy the following requirements as far as possible:

(i) low volatility

(ii) low viscosity

(iii) thermal stability

(iv) chemical inertness except when some chemical interactions are used to achieve separation.

The above conditions are well satisfied by poly(dimethylsiloxane).

4.3.1.1. Column performance optimum conditions

Below is a summary of factors, that contribute to high column efficiency

1. Low ratio of inlet to outlet pressure
2. Operation at maximum practical gas velocity found by the determination of column performance as the function of the gas flow rate in terms of HETP.

3. The use of a dense carrier gas although there may be practical reasons as to why a light gas might be preferred.
4. Small column diameters
5. A small proportion of the stationary phase, so that the film thickness is reduced.
6. Because of condition 5 above, a small sample size say less than 5% of the stationary phase should be used.
7. A small range of particle sizes for the support and fines should be removed.
8. Study of the apparatus and techniques to ensure that their contributions to zone spreading are minimal, a correct injection technique is very important.

4.3.1.2. Operating conditions for good measurements

(a) Equipment

The apparatus should be free of major dead spaces, the detector and recorder time constants should be negligible in relation to the expected retention time. The pressure drop between the points at which the inlet and outlet pressures are measured and the actual inlet and outlet should be very small. Linear detector response is an essential requirement for accurate measurements. Linearity of response can be confirmed by calibrating the known volumes of solute injected.

(b) Gas flow rate

Optimum flow rates are often in the region 20-60ml/min.

(c) Sample size

As mentioned in section 2.2.3 for infinite dilution studies samples should be limited to about 0.1mg (0.1μl liquid in GLC).

4.3.1.3. Packed column design

(a) Tubing

Chromatographic columns may be made from any suitable tubing. The materials most frequently used are glass, copper, stainless steel and, for moderate temperatures, nylon. Internal diameters range from 3 to 6 mm, and for general analyses a length of 1 to 2 m is adequate. Normally, for convenience, the column is bent, usually into the form of a U, W, helix or spiral (in commercial instruments). A helical or spiral column is difficult to pack and for this shape, a metal tube which may be packed when straight and then bent may be convenient, copper being probably the easiest material to use. The helical shape offers the advantage of being relatively compact for a given length of column and is therefore the easiest to heat at an even temperature in an air filled oven. The air filled oven is the equipment most frequently supplied commercially for temperature control of the column. A draw back that can be associated with copper tubing columns is that they may sometimes react with components of samples being analysed or exert a catalytic effect on decomposition and in such circumstances stainless steel tubing is usually the most preferred.

Glass as column tubing has the advantages of being chemically inert and of allowing inspection of the state of the packing both during the preparation of the column and subsequently after use. If the configuration is more complex than a simple U, the column is probably best prepared as a series of Us or straight lengths, which are joined together after packing. Connection should be made of metal, which is joined, to the glass. It is possible for the sections to be joined by glass capillaries, which, with practice may be fused to the columns without blowing. Capillary connectors are used so that empty space

in the column is kept to a minimum otherwise the efficiency of the column will be greatly affected. Whenever a column is made in sections which are subsequently joined together, care must be taken that all joints are leak free.

In a helical column the outside path is longer than the inside. If this difference is excessive some loss of efficiency is expected. However, diffusion across the column tends to counteract this effect and no serious deterioration in efficiency is likely to arise if the diameter of the helix is large in comparison with the diameter of the tubing, say larger by a factor of twenty.

(b) Support

The aim in the column is to provide a thin liquid film with as large an interface as possible between the gas and liquid phases so as to facilitate partition between them. The support for the liquid should have a high specific surface area if a good performance, that is sharp separations, is to be obtained from the column. Many solids of high specific surface area exhibit adsorptive effects, which would interfere with the partition and lead to peaks of unsatisfactory shape. The support should therefore have a low adsorptive activity in addition to a large surface area. It is quite desirable for the individual particles to be as nearly as possible of the same size.

Reduction of adsorption maybe done in the following ways

(i) By choosing a stationary phase which itself contains suitable functional groups for the formation of hydrogen bonds with the support. This is usually achieved by the incorporation in the stationary phase of a tailing reducer.

(ii) By removing the adsorption sites through a chemical reaction with the silanol group. Supports can be treated with trimethylchlorosilane or dimethylchlorosilane. An easier and equally effective reagent to use is hexamethyldisilazane.

(iii) The adsorptive sites can be removed with acid or alkali. The support may be washed with hot hydrochloric or nitric acids and then with water. An alkaline wash is carried out with sodium hydroxide in methanol, followed by methanol and then water.

(iv) By coating the support with a solid which will cover the adsorption sites.

(c) Column Packing

The support should be dried at 100 – 150^{0}C before it is added to the stationary phase. If the stationary phase is a liquid at room temperature, it is dissolved in a sufficient volatile solvent to form a slurry with the support. The slurry is then poured into a flat dish as a thin layer and the solvent is gently evaporated. Alternatively, the evaporation may be carried out in a large flask, which is warmed while a current of dry air is passed through it. Before being packed, the empty tubing should be cleaned to remove any residual contaminants from the manufacturing process or the previous packing. In loading the column, an even packing is desirable so that the gas flow does not vary either across the column or regularly along its length. A funnel is attached to one end of the column by rubber tubing while the other end is plugged with a wad of glass or silica wool. Sufficient packing to fill 5-10 cm of the column is placed in the funnel after a final sieving and is agitated so that it moves down into the column. Various means can be implemented to achieve this agitation including manual tapping. The packing should be carried near to the end of the column and then plugged with glass or silica so that no dead space is left, but care must be taken that the wool plugs do not introduce any undue resistance to gas flow.

In some cases, the coating with the stationary phase may be deferred until after the column has been packed. A solution of the stationary phase is forced by gas pressure through the column. The volatile solvent remaining is then removed in a stream of gas from the part of the solution that has been absorbed by the support. This method seems to offer most advantage for packings, such as those made from glass beads, that do not flow freely when coated.

In packing the column, the aim is a high efficiency accompanied by a low pressure drop and the highest efficiencies are to be obtained with the finest particles which, however, naturally have the greatest resistance to flow of the mobile phase. The necessary skill in packing columns may be acquired by practice. Various methods can be used and the efficiencies of the columns obtained compared in order to obtain the best method. There is an optimum degree of consolidation achieved by the right degree of agitation. The greatest danger appears to lie in excessive vibration as this may cause the packing to be less dense than it would otherwise be, and may also cause breakdown of the particles.

A newly packed column should be conditioned before being put into use by passing carrier gas through it at the intended highest operating pressure. This will remove volatile contaminants (water, solvent used in making up the packing, low boiling point components of the stationary phase) which otherwise would affect the detector and cause movement of the baseline. Conditioning may also lead to chemical reaction between components of the stationary phase, which will help to stabilise its performance. If this operation is done in the chromatograph, a steady baseline will show when conditioning is complete. It is important to keep columns sealed during storage and if they contain

material sensitive to oxygen, they should be allowed to cool with carrier gas flowing before they are plugged.

(d) The carrier gas

Nitrogen, helium, hydrogen and argon are the most frequently used carrier gases. They are drawn from cylinders in which they are stored at pressures in excess of 100 atm, and pass through the column at low controlled flow rates (20 – 50 ml/min).

Purity

In general, gases of sufficient purity are obtainable commercially but care must be taken that dust particles, water and other volatile materials are excluded from the lines. Cylinders must be assumed to contain water and it is a good practice always to dry the issuing gas. This is most frequently done by including a tube containing adsorbat in the flow line immediately after the cylinder. The molecular sieve is the most suitable reagent and this should be reactivated after every change of cylinder by heating to 250 – 300^{0}C overnight in a stream of carrier gas. The higher the sensitivity of the detector, the higher are the requirements for purity in the carrier gas, and avoidance of organic impurities in the lines is of special importance when ionisation detectors are and at high temperatures it is important that there should be no oxygen in the carrier gas. Oxygen may easily be removed by passing the gas through a tube at 450^{0}C containing copper oxide which has been reduced to the metal in hydrogen.

Flow control

Constancy of flow of the carrier gas is important if a stable baseline in the output from the detector is to be achieved and also to ensure reproducibility of peak sizes. Controlled variation of the flow is required to obtain the best conditions of operation. Small variations in the carrier gas flow rate will affect column performance and retention times. Therefore to achieve optimum separation, good accuracy and precision, it is necessary to keep the flow rate constant. Good regulation is therefore required to obtain a pulse free gas flow at pre-set pressures and flow rates. Flow control is important since if the carrier gas pressure remains constant during temperature programming of the column, the flow rates will change as the viscosity of the carrier gas varies with temperature. This will result in a decrease in the flow rate, which will in turn affect the performance. The simplest control consists of a pressure regulator and gauge, but this really only suitable for straightforward isothermal chromatography. Column flow rates are generally checked using a soap bubble flow meter and a stopwatch.

(e) Column oven and column temperature

The separation process occurring in the column involves an equilibrium established by the solute between the stationary phase and the mobile phases. The partition coefficient involved is dependent on solute vapour pressure and thermodynamic properties of the solute and is function of temperature as related in the Clausius - Clapeyron equation

$$\ln p = {}^{\Delta h}/_{RT} + C \quad \text{..... (4.1)}$$

where p is the solute vapour pressure, h the molar heat of solution and C a constant. Thus the relative retention α for an adjacent pair (A and B) will be dependent on column temperature T and is given by

$$\ln \alpha = (\Delta h_A - \Delta h_B)/RT + C \quad \text{..... (4.2)}$$

The component with longer retention time will have a higher heat of solution in the stationary phase. Relative retention of the two components will decrease as the stationary phase (column) temperature increases. Packed columns with larger amounts of stationary phase on the support material will require higher temperatures to obtain elution times equivalent to lower stationary phase loading. It is important to note that decreasing the amount of stationary phase and reducing the column temperature results in peaks first eluted having poorer separation. A balance of stationary loading is therefore required, 10 – 15 % w/w is used for small molecules up to C_8 and up to 3 – 5% for C_9 – C_{20}. After choosing a column, the variables, which can be modified to optimise the separation of components, are temperature and carrier gas flow rate. Control of column temperature is required if reproducible chromatograms are to be obtained.

A GC oven can be set to operate from about 10^0C above ambient temperature, up to 450^0C with a reproducibility better than 0.1^0C. Also accurate temperature control is also important in isothermal analyses where the retention times are being measured. In order to avoid problems of the least volatile components in a mixture taking too long to elute and hence forming broad – tailing peaks, the column temperature can be progressively increased while the flow rate is kept constant.

4.3.1.4. Retention values

To assist in the assessment of their accuracy and relevance to other experimental results, any published set of values should be accompanied by the following details of experimental conditions;

1. Nature and particle size range of support
2. Nature, concentration and amount of liquid phase in the column.

3. Sample size
4. Column dimensions (length and internal diameter)
5. Column inlet and outlet pressures
6. Flow rate of carrier gas and method of measurement.
7. Column temperature and accuracy of temperature control
8. Description of detector, for example type of sensing element cell geometry, cell volume and response time.

4.3.2. A Brief Description of Equipment

The Perkin Elmer Model 8500 used in this work is a dual channel, microprocessor based gas chromatograph. The instrument has flexibility in configuration with many options and accessories. It has a wide range of operating conditions, enabling it to be set to suit specific requirements. The instrument is made up of two main units (i) analysis and keyboard unit (ii) visual display unit (VDU). The analyser unit is made up of an analytical oven, electronics and pneumatic compartment. The visual display unit together with the keyboard on the chromatograph are used to set the instrument in accordance with the type of analysis required. Because of the availability of screen graphics, the resultant chromatograms were displayed.

4.3.2.1. Packed column injector.

For complete flash vaporization, the temperature of the injector should be set to approximately 50 degrees centigrade above the boiling point of the highest boiling component in the sample. In order to make sure that the sample is deposited in the hottest part of the injector, the samples were injected using a micro syringe that has a 710mm needle. To ensure leak free operation the septum was changed regularly. Although the life

of the septum depends on the number of injections performed, it was changed on a daily basis in most cases.

4.3.2.2. Detector Types

Detectors may be divided into two main classes:

(i) Those that respond to the total mass of material emerging from the column for example the automatic titration system and these are called integral detectors.

(ii) Those that respond to the concentration of the vapour in the carrier gas at any instant, for example the Hot wire detector, and these are called differential detectors.

Detectors of the first type have obvious advantage in quantitative analysis since this only requires the measurement of step heights. However the two types of detectors are limited in their application.

Several types of detectors are used in gas chromatography such as the hot wire detectors (HWDs), flame ionisation detectors (FIDs), flame photometric detectors (FPDs) and the electron capture detectors (ECDs). The main purpose of the detector is to identify the components by means of their retention times and to measure their concentrations. Selection of detectors depends on many factors, for example, sensitivity (minimum detection), stability (linearity), selectivity (signal –to- noise ratio), response time and the components involved. The flame ionisation and hot wire detectors will be discussed in detail while only a brief description of the other types will also be presented.

Thermal conductivity detectors have been widely used in the chromatographic determination of thermodynamic data. They are simple in construction and permit direct

determination of the gas hold-up of the chromatographic column by the timing of an air peak. However since their response depends on the difference between the thermal conductivity of the organic solute and that of the carrier gas, this response is reduced considerably when there is a constant bleed of pure volatile organic solvents into the detector. For volatile solvents, thermal conductivity detectors are therefore expected to be limited in applicability to systems where thermal conductivities of solvent and solute vapours are different. A more suitable detector would be a flame ionisation detector. One drawback in the use of flame ionisation detectors in the accurate determination of retention data has been the elaborate and indirect method of measuring the column gas hold-up. This is because the detector is insensitive to air under the conditions prevailing in a conventional column. The other drawback associated with flame ionisation detectors when volatile solvents are used is the decrease in sensitivity of the detector due to the increase in ion concentration between the electrodes. This eventually leads to complete insensitivity when the condition of ion saturation is reached. However, since non-volatile solvents (silicon oils) were used in this work, this drawback was eliminated. FIDs are very useful in the detection of volatile organic compounds in very low concentrations, say down to the 1ppm range. It was therefore decided to use the flame ionisation detector.

4.3.2.2.1. The flame ionisation detector (FID)

(a) Principle of operation

McWilliam and Dewar (1958) developed this type of detector and it is based on the principle that the electrical conductivity of a flame burning hydrogen and oxygen mixture increases when the organic molecules enter the flame. This is because of the difference in the ionisation potentials of the gas (15.8-24.5ev) and organic molecules (9-12ev).

However, the ionisation of the organic molecules that takes place in the flame is not well understood. The increase in conductivity of the flame is much more than that would be expected from the normal ionisation potential of the organic compounds. The organic potentials or organic molecules are in the range 9-12ev while the effective ionisation potential of carbon is about 5ev. One explanation, as postulated by Stern (1958), could be the formation of carbon aggregates within the flame and their subsequent ionisation. This explanation is strengthened by the fact that the ionisation potential of solid carbon is 4.6ev and the detector response is essentially proportional to the number of carbon atoms in the organic molecules. Under the conditions prevailing in the conventional chromatographic column, the flame ionisation detector is insensitive to air, carbon dioxide, water vapour and hydrogen sulphide.

(b) Lighting the detector flame

No attempt was made to light the detector flame until the detector temperature was at least 100^0C. Below this temperature, water condensation can take place inside the detector producing a noise signal. In lighting the detector flame, the following procedure was followed. The first step was to ensure that the combustion gases (air and hydrogen) were turned on at the cylinders. The cylinder pressure regulators for air and hydrogen were set to 280 kPa and 84 kPa respectively. Sufficient time was allowed for the hydrogen to purge the plumbing and the supply at pneumatics panel was turned off. This was followed by setting the air pressure to 138 kPa and the optimum air pressure was found by experiment. The next step was to remove the lower oven door cover. Then, the igniter was held against the FID chimney, the hydrogen supply was turned on and the flame was lit. A distinct "pop" sound was heard as the flame ignites. A precaution was taken to make sure that the igniter filament was glowing before turning on the hydrogen, this ensured that the

combustion takes place at the jet and not above the collector. Checking whether the filament was lit was done by holding a cool shiny object against the end of the detector. Water from the flame should condense onto the cold surface.

(c) FID optmisation

The hydrogen and air flow rates were set to values within the ranges in the table below

Table 4.1 FID optimisation flow rates

GAS	FLOW(ml/min)	APPROXIMATE INLET PRESSURE	
		kPa	Psig
Air	430	152	22
Hydrogen	33	83	12

The optimum pressure was determined by measuring the flow rate at the manifold at the bottom of the oven door with a soap film bubble flow meter.

4.3.2.2.2. Hot wire detectors (Katharometers)

(a) Principle of operation

The word katharometer, meaning pure in Greek, was originally given by Shakespeare (1921) to an instrument he devised for the measurement of the purity of hydrogen gas by thermal conductivity. The katharometer as used in the GLC is a type of detector, which works on the principle that the resistance of a heated wire placed in a flowing gas changes according to the thermal conductivity of the gas components.

When heated filaments are placed in a flowing carrier gas, they maintain a definite temperature and resistance. If the resistance of the carrier gas changes due to eluted solute sample, its thermal conductivity also changes. This will alter the rate of heat loss from the heated filaments and thus the temperature and resistance will change. Usually a pair of matched filaments are used, one being exposed to the carrier gas and called the "reference filament" and the other to the column, called the "sample filament". The reference and sample filaments are incorporated in a Wheatstone bridge, the out of balance potential passing to the recorder. The schematic view of the hot wire detector is shown in figure 4.3.

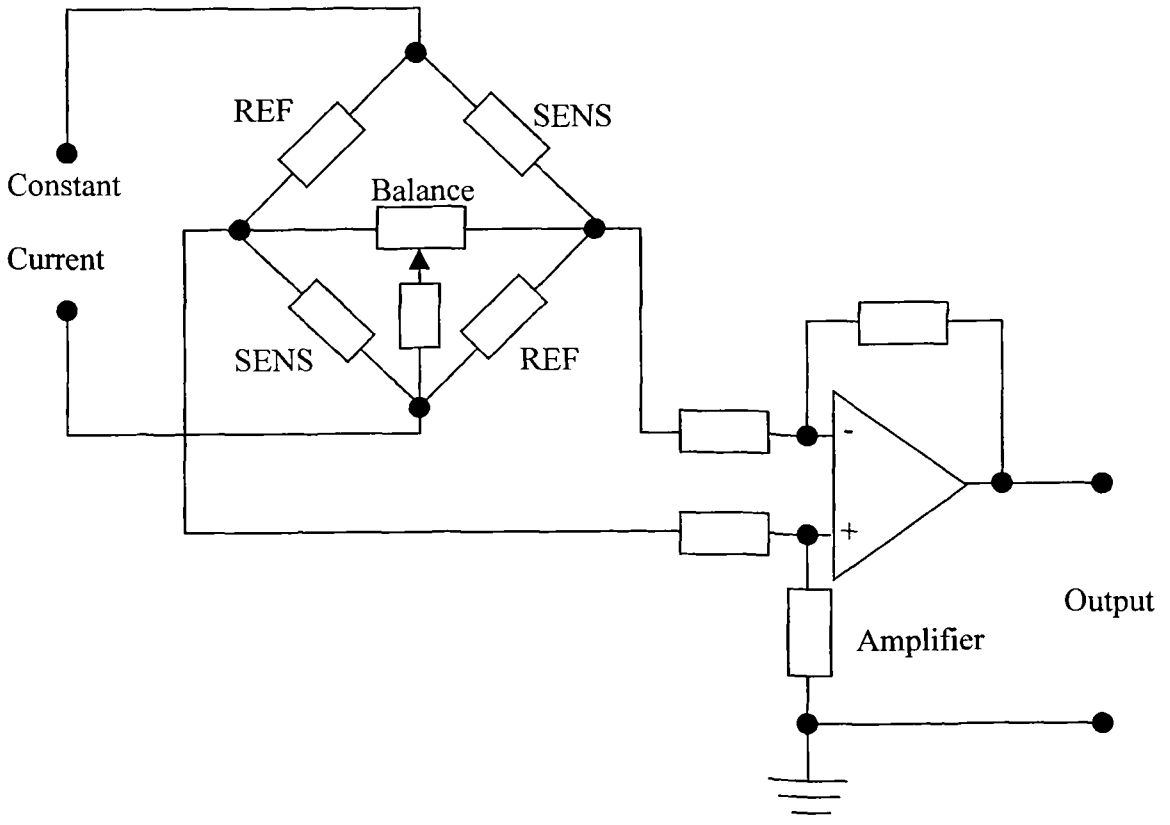


Figure 4.3. Schematic view of the hot wire detector.

As shown in figure 4.3, four tungsten rhenium filaments are connected as a bridge circuit, two filaments being located in each channel. The presence of a sample component in the

carrier gas flowing in a channel changes the resistance of the filament in that channel, unbalancing the bridge and producing a signal related to the sample concentration from which the chromatogram is plotted. The detector is mounted on a standard cylindrical detector module and is mounted in the lower part of the oven door with the amplifier board positioned below it. The detector has two heated zones, the detector block and the interface, which are separately controlled but are always set at the same temperature.

(b) **Choice of carrier gas**

Helium is the recommended carrier gas for use with a hot wire detector because of its high thermal conductivity. The use of helium is avoided when helium or hydrogen content of the sample is being analysed. The use of hydrogen is a possibility, but great care must be taken because of its high flammability. Therefore, it is very necessary to make sure that all the connections inside the oven are leak free. In the event of the helium or hydrogen content of the sample being analysed, nitrogen or argon may be used as the carrier gas. When nitrogen or argon is used, positive or negative peaks are obtained depending on whether the thermal conductivity of the particular sample content is smaller or larger than the thermal conductivity of argon. Sometimes samples containing hydrogen may show anomalous behaviour resulting in M-shaped peaks when helium is used as the carrier gas. This can be eliminated if a helium/ hydrogen mixture containing between 8 and 9 % by volume of hydrogen is used as the carrier gas Pollard and Hardy (1957).

4.3.2.2.3. Flame Photometric Detectors (FPD)

They are similar to the flame ionisation detectors. They are a combination of the FID and an optical system, which has a very high selectivity with adequate sensitivity towards phosphorus and sulphur. They detect sulphur compounds down to ppb levels.

4.3.2.2.4. Electron Capture Detectors (ECD)

These are the most sensitive detectors available for the non-destructive detection of electrophilic substances, such as chlorinated hydrocarbons. They are very useful for pesticide residue determinations. They depend on the ability of the compounds to capture electrons. Many compounds have high electron affinities thus allowing their detection with this system.

4.3.2.2.5. Nitrogen Phosphorus Detector (NPD)

This is a thermionic detector that is sensitive to organically bound nitrogen and phosphorus. It can be operated in either two modes, NP mode in which both nitrogen and phosphorus are detected and quantified and the P mode in which the phosphorus is the only component to be detected and quantified. The action of the NPD destroys the sample being analysed.

4.3.2.2.6. Choice of detector

In summary the ideal detector should possess the following properties;

1. A high sensitivity which allows small amounts of impurities to be detected, small samples to be analysed, and low column temperature to be used.
2. A small internal volume, which ensures that the resolution of the components, which are only just separated by the column, is not, lost, and the shape of the peaks is not distorted by the detector.
3. A temperature of use such that no appreciable amount of the eluted vapours condenses in it.

4. Insensitivity to changes in the rate of flow of the carrier gas and in the temperature.
5. A rapid and reproducible response, produced by simple ancillary electrical equipment, accompanied by stability of the baseline.
6. For qualitative analysis –a response which can be adjusted so that identification is assited.
7. For quantitative analysis – linear response with concentration or amount of component so that the compositions may be calculated.
8. A response to all substances, whatever their chemical nature which depends upon a simple law so that calibration may be reduced to a minimum.
9. Cheapness and reliability

It is important to note that no detector fulfils all the desirable characteristics. For some problems however there will be reasons for choosing one detector rather than another. For instance, ionisation detectors will almost always be preferred for work with open tubular and packed columns containing only a small loading of stationary phase because of the need for high sensitivity. In a flame ionisation detector the sample is destroyed, while it can be recovered from the gas stream after it has passed through others. This is a disadvantage of the flame ionisation detector if further examination of the sample is planned. However, except for work with open tubular columns, it is probably not a big drawback as the effluent from a large column can be split, and a part only passed to the detector. A more important limitation of the flame – ionisation detector is its lack of response to permanent gases. The Katharometer, which can easily be made to give response to any substance, is more often chosen for gas analysis. For high boiling materials the temperature of the detector must be raised and the sensitivity of the katharometer falls when the temperature is above 100 – 150^{0}C Pollard and Hardy (1957).

4.3.3. Equipment and Procedure

4.3.3.1. Support preparation and column packing

All glassware used in this work was cleaned before use with soap and water, and finally dried with acetone. Four PDMS polymers, supplied by Dow Corning Ltd. were used as stationary phases in this work. The polymers differed in their viscosity average molecular weight, which ranged from 760 to 13000. With the exception of column 1V, which was prepared by Perkin Elmer where the PDMS was coated into chromosorb W, in the other three columns, PDMS was coated into chromosorb P support (60-80 mesh, acid washed, dimethylchlorosilane treated) from a solution in chloroform. The columns were made of stainless steel, 3.33 feet long and ¼ inch diameter and all the columns used in this work were purchased from Perkin Elmer.

The following procedure was followed in preparing the support and packing the column.

1. Calculation of the approximate weight of the stationary phase and solid support required to give the percentage loading.

   Percent loading = (wt. of stat. phase x 100)/(wt of stat phase + wt of support)
2. The support was weighed roughly in a small beaker and any aggregated lumps were removed. The support was dried over night at 150^0C and allowed to cool in a desicator.
3. The stationary phase was weighed into the flask and great attention was paid to knowing accurately the amount of liquid added to the flask.
4. A suitable amount of chloroform was added to dilute the stationary phase to a total volume, which will completely cover the support when the liquid and solid are mixed at a later stage. The flask was swirled gently to dissolve the stationary phase.

5. The support was reweighed quickly and accurately in its vessel. It was then transferred to the stationary phase beaker. The flask was agitated slightly to ensure that all the support was covered by the liquid. The use of a stirring rod was avoided for fear of breaking the support and introducing uncertainty into the weight of the stationary phase present. The beaker originally containing the support was re-weighed with any support remaining in it.
6. The solvent was then evaporated in a water bath.
7. The particles were then dried on a magnetic stirrer heater at a temperature of 120^0C to constant weight or rather until no odour remained in the effluent. The amount of polymer on the support was found by weighing.
8. The column tubing was cleaned by pushing acetone impregnated wads of cotton wool through it with a clean wire, until no more oil material appeared in the wads. The column was then dried by passing nitrogen from the cylinder through it for a few seconds until acetone odours disappeared.
9. The column was bent into a U-shape round a metal cylinder of appropriate diameter. The column was weighed on a balance and then clamped on a retort stand.
10. The prepared and coated support was transferred into a small beaker (1/4 or ½ full capacity) and weighed accurately. Using a small funnel attached to a short length of rubber tubing, the column was filled with a small amount of packing through each end of the column alternately. Both limbs of the column were tapped both during and between the pouring process. Great care was taken not to spill any of the packing. A gap of 1-cm to be occupied by glass wool was left on each end of the column.
11. Very small glass wool plugs were inserted into each end of the column using only light pressure to avoid obstructing gas flow.

4.3.3.2. Column pre-treatment and performance

The packed column was then subjected to final cleansing treatment prior to installation. The treatment removed the residual boiling materials before they could contaminate the detector, this contamination can be seen by an unstable baseline. The column was maintained at the recommended maximum temperature for 12 to 24 hours with carrier gas passing through it continuously at about 10 to 20 ml/min. This was done by mounting the column in the oven with inlet gas connected, but no connection was made at the outlet end to the detector.

Column mounting, column packing and correct sample injection are all the factors, which affect the performance of columns. The column was mounted in the column oven with the coil held vertically so that should further packing down occurs during use, channelling is minimised and column efficiency is not impaired. The column was packed leaving only a 1 cm gap at the exit so that eluted components pass directly into the detector. Injection of liquid samples was made by inserting micro-syringe needle in the injection head cap hole. The tip of the needle pierced the rubber septum and enters the column packing. This ensured that the sample was brought into immediate contact with the stationary phase, thus minimising diffusion during evaporation.

4.3.3.3. Care of columns

The columns were stored in a dry place with ends sealed by means of caps. They were held vertically with straight sections pointing upwards in order to prevent tracking, that is the creation of small passages along the sides of the packing material. The columns were handled with great care to prevent abrasion of the support particles.

Table 4.2 Typical packing information data (50 cS PDMS column)

Material	Mass (g)
Beaker	90.174
Support	7.200
Support + beaker	97.374
Beaker after removing support	90.174
Flask	111.173
Stationary phase + flask	111.978
Stationary phase	0.805
Flask + stationary phase + support before packing	119.178
Flask after packing	118.188
Support + stationary phase in column	7.99
Stationary phase in column	0.804

Details of the columns used in this work are presented in table 4.3 below.

Table 4.3: Description of columns

Code	1	11	111a	111b	111c	1V
Length, m	**1**	**1**	**1**	**1**	**1**	**1**
Chromosorb W or P, g	**6.158**	**7.291**	**7.186**	**7.200**	**6.914**	**4.86**
PDMS	**0.688**	**0.825**	**0.804**	**1.8**	**2.97**	**0.54**
Wt % PDMS	**10.05**	**10.16**	**10.06**	**20**	**30**	**10**
Viscosity of PDMS, cS	**5**	**10**	**50**	**50**	**50**	**500**
RMM of PDMS	**760**	**1000**	**3200**	**3200**	**3200**	**13000**

4.3.3.4. Techniques for improving reproducibility

(a) Filling the syringe

The syringe and plunger were cleaned before filling using the following simple procedure. A cold chromic acid solution was pumped through the syringe with the plunger. The syringe and plunger were rinsed with distilled water. The syringe was dried by blowing air through it and the plunger was carefully wiped with a lint free tissue. Care was taken not to touch the plunger shaft with the fingers. To ensure accurate measurements, the interior surface (barrel and plunger) were wetted with the sample by pumping the plunger before filling. The syringe was then overfilled in the sample bottle, moved from the bottle and the plunger moved to the desired calibration line. The syringe graduation was read from the same angle each time the syringe was filled. The recommended practice is to read the sample at the top (flange end) of the calibration line because this provided an accurate visual check and reduced the problems of line thickness. An attempt was made to develop a smooth, uniform loading operation to minimise slight involuntary errors. The syringe was then inspected for bubbles or foreign matter in the sample. The needle was wiped clean with a lint free tissue in a quick motion before injection. Great care was taken not to wipe the sample out of the needle or transfer body heat from the fingers to the needle.

(b) Injecting the sample

A rhythm in motion was developed and this was used each time when injections were made. This included doing the same things in the manner at the same time. The rhythm was smooth so as to inject the sample both quickly and accurately. The syringe was held as close to the flange as was possible thus preventing heat transfer that occurs when the needle or barrel is held with the fingers. Also the plunger was handled by the bottom, not

the plunger shaft. This was done to reduce the possibility of damage or contamination. For greater accuracy, the maximum capacity of the syringe was not used.

4.3.3.5. Flow rate measurement

The flow rate of a carrier gas is one important quantity that has to be measured with great accuracy for reliable retention data. Several methods of measuring flow rates are conventionally available. The choice of a method for flow rate measurement must meet two essential requirements, namely, the method must be non-destructive and accurate for small flow rates without causing any disturbance to the flow. It was decided that a suitable flow meter that would fulfil these requirements would be a soap film bubble flow meter.

The soap film bubble flow meter was made of a 100ml calibrated burette having a small glass jet attached to its base. The burette was thoroughly cleaned with chromic acid and rinsed with distilled water before it was assembled. The level of the soap solution around the jet was adjusted so that when the carrier gas from the GC entered the jet it created a thin soap film travelling up the vertical burette. The rate of travel of a soap film was timed with a stopwatch. The walls of the soap film flow meter were well wetted by sending many bubbles completely through the burette before measuring. Any dryness of the walls will lead to irreproducible flow rate determinations because the carrier gas in the burette would not be saturated with water vapour. The observed flow rate was corrected for the saturation vapour pressure of water, which was slightly affected by the presence of a detergent. This correction procedure was explained in section 2.2.11.3. The flow rate was determined at room temperature and then corrected to obtain the flow rate at the column temperature. Accurate measurement of the flow rate was easy with the flame ionisation

detector because it diluted the gas streams. A diagram of the soap film bubble flow meter used in this work is shown in figure 4.4.

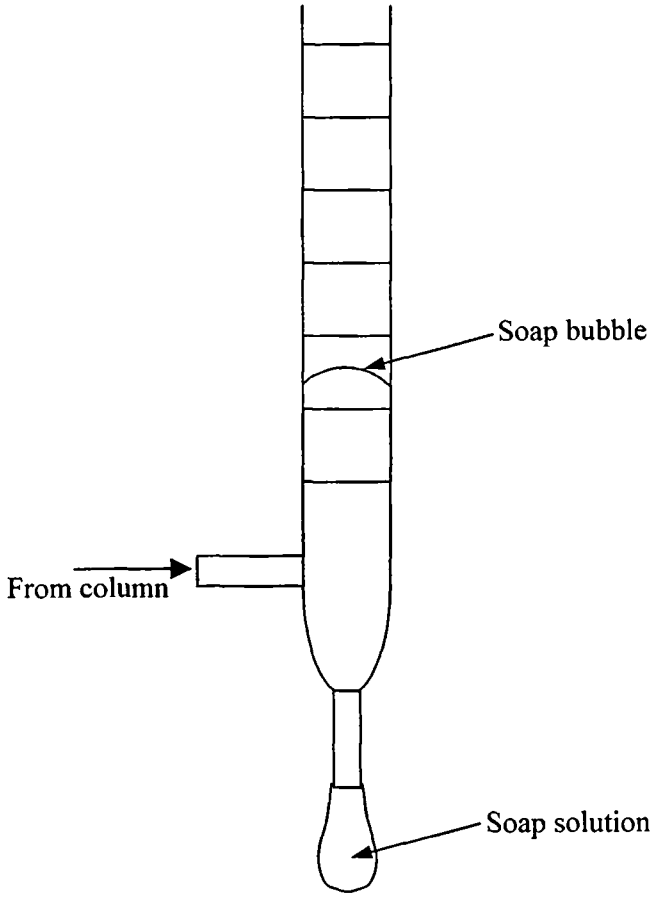


Figure 4.4. Soap film bubble flow meter.

4.3.3.5.1. Flow rate calibrations.

The soap bubble flow meter was connected to the column outlet by the side arm and soap bubbles are introduced into the gas stream by squeezing the bulb at the bottom. The bubbles move up the calibrated tube and the time taken for a bubble to travel between the calibrations marks say 10ml was measured. For example when the GC set was at 90ml /

min, the time taken by the bubble to travel through two calibration marks (10ml) in a 5 cS PDMS – column 1 was on average 16.68 seconds (0.278 mins).

Therefore flow rate (ml/min) = 10 ml/0.278 min

= 35.97 ml / min

The GC flow rate calibrations for the columns used in this work are shown in tables 4.4 to 4.9 below.

Table 4.4: GC flow rate calibrations (5 cS PDMS – column 1)

GC set (ml/min)	40	50	60	70	80	90
Time, t, (sec) to pass through two marked positions	34.89	28.63	24.55	21.17	19.09	17.05
	34.77	28.57	24.49	21.06	19.10	16.97
	34.90	28.49	24.48	21.23	19.02	16.78
	34.84	28.42	24.52	21.09	18.99	16.75
	34.72	28.53	24.47	21.08	18.89	16.82
	34.89	28.48	24.32	21.13	18.71	16.72
	34.61	28.41	24.68	21.07	18.70	16.71
	34.77	28.46	24.34	21.06	18.74	16.68
	34.83	28.45	24.42	21.09	18.70	16.64
Average t, sec	34.84	28.48	24.48	21.08	18.70	16.68
Actual flow rate (ml/min)	17.22	21.07	25.51	28.44	32.09	35.97

Table 4.5: GC flow rate calibrations (10 cS PDMS – column 11)

GC set (ml/min)	40	50	60	70	80	90
Time, t, (sec) to pass through two marked positions	60.04	48.02	40.06	34.18	30.18	26.61
	60.00	48.07	40.08	34.38	30.38	26.61
	60.03	47.97	40.04	34.28	30.24	26.66
	60.01	47.98	40.10	34.20	30.32	26.62
	60.02	48.06	40.02	34.36	30.28	26.67
	60.02	48.03	40.05	34.25	30.29	26.68
	60.03	48.01	40.07	34.31	30.27	26.63
	60.00	48.10	40.09	34.30	30.33	26.70
	60.01	49.92	40.03	34.26	30.23	26.58
Average t, sec	60.02	48.16	40.06	34.28	30.28	26.64
Actual flow rate (ml/min)	10.00	12.46	14.98	17.50	19.82	22.52

Table 4.6: GC flow rate calibrations (50 cS PDMS – column 111a)

GC set (ml/min)	40	50	60	70	80	90
Time, t, (sec) to pass through two marked positions	36.13	29.52	24.58	21.32	19.15	17.32
	36.03	29.52	25.01	21.42	19.15	17.24
	36.02	29.48	24.92	21.82	19.16	17.26
	36.06	29.36	24.90	21.92	19.14	17.32
	36.12	29.52	24.94	22.24	19.13	17.30
	36.02	29.38	24.90	22.13	19.15	17.28
	36.01	29.36	25.44	22.01	19.17	17.27
	36.02	29.34	25.91	21.82	19.16	17.23
Average t, sec	36.02	29.48	24.92	21.82	19.16	17.26
Actual flow rate (ml/min)	16.66	20.35	24.08	27.50	31.32	34.76

Table 4.7: GC flow rate calibrations (50 cS PDMS – column 111b)

GC set (ml/min)	40	50	60	70	80	90
Time, t, (sec) to pass through two marked positions	36.24	29.84	25.02	21.64	19.24	17.38
	36.18	29.82	25.03	21.63	19.22	17.37
	36.28	29.85	25.01	21.62	19.21	17.38
	36.25	29.83	25.02	21.64	19.23	17.39
	36.23	29.84	25.04	21.63	19.20	17.38
	36.24	29.83	25.02	21.64	19.22	17.38
	36.22	29.85	25.03	21.65	19.20	17.40
	36.25	29.84	25.01	21.66	19.23	17.37
Average, t, sec	36.24	29.84	25.02	21.64	19.22	17.38
Actual flow rate (ml/min)	16.56	20.11	23.98	27.73	31.22	34.52

Table 4.8: GC flow rate calibrations (50 cS PDMS – column 111c)

GC set (ml/min)	40	50	60	70	80	90
Time, t, (sec) to pass through two marked positions	36.43	30.28	25.64	22.30	19.32	17.24
	36.62	30.41	25.62	22.32	19.20	17.24
	36.52	30.32	25.54	22.30	19.24	17.22
	36.58	30.26	25.62	22.36	19.32	17.23
	36.48	30.31	25.63	22.32	19.30	17.18
	36.54	30.32	25.67	22.26	19.31	17.24
	36.54	30.33	25.70	22.31	19.24	17.29
	36.53	30.30	25.61	22.32	19.32	17.30
Average t, sec	36.54	30.32	25.67	22.32	19.32	17.21
Actual flow rate (ml/min)	16.42	19.79	23.42	26.88	31.06	34.80

Table 4.9: GC flow rate calibrations (500 cS PDMS –column 1V)

GC set ml/min	40	50	60	70	80
Time, t, (sec) to pass through two marked positions	29.48	24.02	20.11	17.14	14.99
	29.94	24.03	20.04	17.10	15.03
	29.99	24.01	20.07	17.16	14.99
	29.96	24.06	20.10	17.11	14.97
	30.03	23.98	20.08	17.12	15.03
	29.98	24.04	10.10	17.13	14.97
	30.00	23.99	20.06	17.16	15.02
	29.96	23.98	20.07	17.10	14.96
	29.99	24.05	20.09	17.13	15.04
Average, t (sec)	29.98	24.02	20.08	17.13	14.99
Actual flow rate ml/min	20.01	24.98	29.88	35.02	40.01

4.3.3.6. Measurement of the column hold-up

The measurement of the absolute and the relative retention data requires the knowledge of the column gas hold-up. Errors in the measurement of the gas hold-up can introduce serious errors in the retention data especially when the latter are comparatively small. When using detectors such as katharometers, which respond to permanent gases, the gas hold-up can be directly measured from the air peak corresponding to the elution of a non-absorbed air sample. Since ionisation detectors are insensitive to permanent gases the direct "air peak" method is not applicable under the conditions prevailing in the conventional GLC apparatus. Therefore an indirect method was proposed based on the linear relationship of the logarithm of the corrected retention time and the carbon number of a homologous series. Using this linear relationship the gas hold-up was evaluated as a "mathematical air peak" and as "calculated dead time" from the retention times of three members of a homologous series, namely, pentane, hexane and heptane. No attempt was

made to use the direct method of "methane peak" because it is unreliable as a generally applicable method because of the small solubility of methane in organic solvents.

A sample containing pentane, hexane and heptane was injected into the GC at a particular flow rate and desired temperature. The retention times of the three solutes were then used to calculate the gas hold-up volumes. The gas hold-up volumes for 4 of the six columns used in this work are shown in the following tables.

Table 4.10: Gas hold-up volume for column 1 (F = 35.97ml/min)

Temp (K)	Mean retention time t_R			Mathematical air retention time t_M (min)	Gas hold-up V_M (ml)
	Pentane	Hexane	Heptane		
303	1.75	4.38	11.44	0.19	6.834
313	1.39	3.22	7.83	0.19	6.834
323	1.12	2.36	5.25	0.19	6.834
333	0.85	1.69	3.60	0.19	6.834

Table 4.11: Gas hold-up volume for column 11 (F = 18.86 ml/min)

Temp (K)	Mean retention time t_R			Mathematical air retention time t_M (min)	Gas hold-up V_M (ml)
	Pentane	Hexane	Heptane		
303	4.95	12.39	32.43	0.56	10.561
313	3.93	9.13	22.36	0.56	10.561
323	3.03	6.53	14.99	0.56	10.561
333	2.43	4.99	10.44	0.56	10.561

Table 4.12: Gas hold-up volume for column 111a (F = 34.76 ml/min)

Temp (K)	Mean retention time t_R			Mathematical air retention time t_M (min)	Gas hold-up V_M (ml)
	Pentane	Hexane	Heptane		
303	2.61	6.76	17.98	0.17	5.909
313	1.97	4.64	11.28	0.17	5.909
323	1.51	3.30	7.48	0.17	5.909
333	1.16	2.39	5.15	0.17	5.909

Table 4.13: Gas hold-up volume for column 1V (F = 40.01 ml/min)

Temp (K)	Mean retention time t_R			Mathematical air retention time t_M (min)	Gas hold-up V_M (ml)
	Pentane	Hexane	Heptane		
303	1.62	3.77	9.49	0.33	13.203
313	1.27	2.68	6.21	0.33	13.203
323	1.03	1.98	4.22	0.33	13.203
333	0.84	1.50	3.00	0.32	12.803

4.3.3.7. Measurement of retention data

(a) Solutes

The thirteen solutes namely acetone, butylacetate, chloroform, cyclohexane, diethylether, ethylmethylketone, isobutylmethylketone, heptane, hexane, pentane, toluene, triethylamine and xylene purchased either from Merck Ltd or Sigma Aldrich Company, Supelco UK, were used as received for chromatographic work. The solutes represent the following families of organic compounds; esters, ketones, alkanes, aromatics, cycloalkanes, halogenated alkanes and amines. The purities of these compounds were above 99%. The physical properties of the solutes at the various temperatures including their second virial coefficients are presented in appendix D. For simplicity the solutes are coded numerically according to the scheme of table 4.14.

Table 4.14: Solute description and code

Code no.	Compound	Code no.	Compound
1	n-pentane	8	butylacetate
2	n-hexane	9	diethylether
3	n-heptane	10	chloroform
4	triethylamine	11	acetone
5	toluene	12	ethylmethylketone
6	xylene	13	isobutylmethylketone
7	cyclohexane		

(b) Measurement of retention times

The retention time of each solute was automatically measured by the instrument clock from the point of injection to the peak maximum. To increase the accuracy of the measurements, two stop watches were also used to measure each peak. The first stop watch was started and when a known period of time had elapsed the sample was injected. The first stop watch was stopped and the second one started simultaneously at the point halfway up the peak. The second watch was stopped at the same position from the axis of symmetry on the other half of the peak. When two stop watches were used, the retention time was taken as the time recorded by the first watch plus half the time recorded by the second watch. This method required that the peaks were symmetrical and of reasonable size.

(c) Reproducibility of results

The reproducibility of the results was tested by measuring the retention times of chloroform in column 1 at 303K. These were measured at a constant flow rate of 35.97ml/min and the results are shown in table 4.15.

Table 4.15: Retention volumes of chloroform at 303K

Run no.	Flow rate ml/min	Retention volume at 303K (ml)
1	35.97	146.04
2	35.96	146.03
3	35.97	146.04
4	35.97	146.04
5	35.96	146.02

The coefficient of variation and the mean of the deviation of the net retention volumes were 0.00869 % and 0.0072ml respectively.

(d) Effect of liquid loading

The effect of liquid loading was studied by varying the amount of PDMS. Three columns were used for this purpose with the following liquid loadings 10, 20 and 30%. A sample size of 0.1μl was used and the carrier gas flow rate was also kept constant. The results for this work are presented in chapter 5.

(e) Effect of sample size

The retention volumes of pentane, acetone, diethyl ether, chloroform and ethyl methyl ketone were measured at a constant flow rate of 40.01 ml/min and variable sample sizes ranging from 0.1μl to 10μl in column 1V. The results are presented in table 5.2.9 and plotted in figure 5-12.

(f) Effect of flow rates

To study the effect of flow rates on the retention data, retention volumes of acetone, pentane, chloroform, diethyl ether and cyclohexane with a constant sample size of 0.1μl were measured at variable flow rates ranging from 20 to 40 ml/min. The results of this work are shown in table 5.2.10 and plotted in figure 5.13.

CHAPTER FIVE

RESULTS

CHAPTER 5: RESULTS

5.1: Static Headspace Method

5.1.1 Original Equipment

Table 5.1.1.1: γ and H for various volumes of Acetone in 50 cS PDMS at 303K

Solute volume (ml)	Peak area (units)	x	y	γ	H (k Pa m^{-3} mol^{-1})
0.0005	0.4526	0.000103	0.0000388	0.968	0.122
0.001	0.7284	0.000210	0.0000624	0.817	0.0963
0.002	1.4148	0.000421	0.0002120	0.792	0.163
0.005	3.2562	0.001059	0.0002790	0.725	0.0854
0.01	5.8432	0.002130	0.0005000	0.646	0.0761
0.025	13.0641	0.005344	0.0011800	0.576	0.0761
0.05	24.1781	0.010673	0.0020673	0.533	0.0716
0.06	25.8775	0.012850	0.0022120	0.474	0.0628
0.08	33.6415	0.017079	0.0028740	0.464	0.0558
0.1	37.3762	0.021354	0.0031920	0.412	0.0546
0.2	73.9860	0.041840	0.0069720	0.415	0.0485
0.3	104.6914	0.061599	0.0088920	0.398	0.0468
0.4	140.6914	0.080459	0.0119100	0.408	0.0481
0.5	170.2536	0.099694	0.0143780	0.401	0.0472

Table 5.1.1.2: γ and H for various volumes of Acetone in 10 cS PDMS at 303K

Solute volume (ml)	Peak area (units)	x	y	γ	H (k Pa m^{-3} mol^{-1})
0.01	4.5434	0.000686	0.000389	1.563	0.0575
0.02	8.5069	0.001384	0.000728	1.449	0.0533
0.03	11.7296	0.002082	0.001004	1.328	0.0489
0.04	15.3218	0.002776	0.001131	1.299	0.0478
0.05	17.8607	0.003477	0.001513	1.198	0.0441
0.06	20.3995	0.004176	0.001745	1.150	0.0423
0.07	22.8620	0.004876	0.001955	1.104	0.0406
0.08	25.3245	0.005574	0.002165	1.070	0.0394
0.09	27.6991	0.006272	0.002368	1.040	0.0383
0.1	30.0734	0.006969	0.002569	1.015	0.0374

Table 5.1.1.3: γ and H for various volumes of Acetone in 5 cS PDMS at 303K

Solute volume (ml)	Peak area (units)	x	y	γ	*H* (k Pa m^{-3} mol^{-1})
0.005	1.4815	0.000273	0.000127	1.282	0.0358
0.01	2.8182	0.000546	0.000241	1.215	0.0334
0.02	5.4291	0.001089	0.000465	1.175	0.0329
0.04	10.2761	0.002185	0.000880	1.109	0.0310
0.06	14.4157	0.003239	0.001234	1.048	0.0293
0.08	18.3695	0.004372	0.001571	1.010	0.0277
0.1	22.1232	0.005464	0.001892	0.953	0.0267
0.2	43.3728	0.010874	0.003702	0.940	0.0262
0.4	87.9396	0.021971	0.007478	0.937	0.0262
0.6	115.6185	0.030278	0.009809	0.893	0.0249

Table 5.1.1.4: γ and H for various volumes of Toluene in 50 cS PDMS at 303K

Solute volume (ml)	Peak area (units)	x	y	γ	*H* (k Pa m^{-3} mol^{-1})
0.005	0.9464	0.000777	0.000026	0.682	0.107
0.01	1.8828	0.000153	0.000051	0.678	0.1077
0.05	8.3142	0.007722	0.000225	0.602	0.00943
0.06	10.5971	0.009247	0.000286	0.640	0.0100
0.1	17.5966	0.015318	0.000475	0.642	0.01001
0.2	23.4616	0.030253	0.000633	0.433	0.00679
0.5	59.3357	0.072344	0.001599	0.408	0.00717
1	92.6396	0.135065	0.002495	0.383	0.00599
2	162.5091	0.238081	0.004369	0.380	0.00595
4	324.5625	0.384610	0.008688	0.448	0.00733
8	638.5969	0.555553	0.016952	0.632	0.00989
10	733.1328	0.609826	0.094266	0.660	0.0501

Table 5.1.1.5: γ and H for various volumes of Toluene in 10 cS PDMS at 303K

Solute volume (ml)	Peak area (units)	x	y	γ	*H* (k Pa m^{-3} mol^{-1})
0.01	1.4229	0.000497	0.000038	1.591	0.00779
0.02	2.5964	0.000994	0.000070	1.460	0.00715
0.03	3.6102	0.001491	0.000098	1.354	0.00663
0.04	4.7886	0.001987	0.000129	1.347	0.00658
0.05	5.7262	0.002483	0.000155	1.289	0.00633
0.06	6.4993	0.002979	0.000176	1.220	0.00599
0.07	7.5257	0.003474	0.000203	1.211	0.00592
0.08	8.5324	0.003968	0.000230	1.202	0.00587
0.09	9.3249	0.004463	0.000252	1.168	0.00572
0.1	10.2291	0.004856	0.000276	1.154	0.00576

Table 5.1.1.6: γ and H for various volumes of Acetone in 5 cS PDMS at 303K

Solute volume (ml)	Peak area (units)	x	y	γ	*H* (k Pa m^{-3} mol^{-1})
0.025	0.5047	0.000700	0.000014	0.290	0.00108
0.050	0.9894	0.001938	0.000027	0.286	0.00106
0.075	1.4641	0.002904	0.000040	0.282	0.00105
0.1	1.9207	0.003868	0.000058	0.278	0.00115
0.2	3.6414	0.007706	0.000098	0.264	0.00098
0.5	6.5089	0.019050	0.000175	0.191	0.00071
0.75	9.2563	0.028306	0.000249	0.183	0.000679
1	11.9818	0.037390	0.000323	0.180	0.000666
1.5	16.3865	0.055078	0.000442	0.167	0.000618
2	20.6235	0.072009	0.000556	0.160	0.000595

5.1.2: Modified Equipment

Table 5.1.2.1: Effect of Test Volume on Henry's constants and activity coefficients at 303K.

PDMS volume (ml)	Peak area (units)	y	x	γ	H (k Pa m^{-3} mol^{-1})
200	4.6422	0.000398	0.002207	0.0496	0.0058
250	3.7254	0.000319	0.01776	0.0495	0.0058
300	3.1242	0.000268	0.01485	0.0496	0.0058
350	2.6855	0.00023	0.01277	0.0496	0.0058
400	2.3608	0.000202	0.0112	0.0497	0.0059
450	2.0901	0.000179	0.00997	0.0495	0.0058
500	1.8942	0.000162	0.00898	0.0497	0.0059

Table 5.1.2.2: Effect of PDMS Molecular Weight on Activity Coefficients at 303K.

Compound	PDMS Molecular Weight					
	760		1000		3200	
	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$
Acetone	1.353	17.711	1.026	17.669	0.302	16.632
Chloroform	0.561	3.572	0.425	3.557	0.112	2.994
Hexane	0.751	6.624	0.503	5.833	0.140	5.196
Toluene	0.746	6.157	0.560	6.080	0.173	5.998

Table 5.1.2.3: Effect of shaking time on Henry's law constants and activity coefficients (Acetone).

Time (hrs)	Peak area (units)	y	x	γ	H (k Pa m^{-3} mol^{-1})
0.5	4.6423	0.0003975	0.0220670	0.0496	0.0058
1	4.6423	0.0003975	0.0220670	0.0496	0.0058
2	4.6421	0.0003976	0.0220670	0.0496	0.0058
4	4.6418	0.0003975	0.0220670	0.0496	0.0058
6	4.6418	0.0003975	0.0220670	0.0496	0.0058
8	4.6412	0.0003975	0.0220670	0.0496	0.0058
10	4.6406	0.0003974	0.0220670	0.0496	0.0058
12	4.6394	0.0003973	0.0220670	0.0496	0.0058
14	4.6371	0.0003971	0.0220670	0.0496	0.0058
16	4.6341	0.0003969	0.0220671	0.0495	0.0058
18	4.6322	0.0003987	0.0220671	0.0495	0.0058
20	4.6294	0.0003965	0.0220672	0.0495	0.0058
24	4.6243	0.0003960	0.0220674	0.0494	0.0058

Table 5.1.2.4: Comparison of Static and GLC Solute Mole and Weight - Fraction Based Activity Coefficients at Infinite Dilution with PDMS (MW-1000).

Compound	Headspace Static Methods		GLC Technique	
	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$
Pentane	0.388	5.384	0.384	5.323
Hexane	0.503	5.833	0.458	5.317
Heptane	0.539	7.340	0.539	5.382
Triethylamine	0.525	5.187	0.392	3.878
Toluene	0.560	6.080	0.585	6.354
Xylene	0.805	7.587	0.617	5.808
Cyclohexane	0.397	4.720	0.399	4.378
Butylacetate	0.860	7.401	0.748	4.350
Diethylether	0.624	8.413	0.359	4.489
Chloroform	0.425	3.557	0.374	3.133
Acetone	1.026	17.669	0.865	14.895
Ethylmethylketone	0.532	7.381	0.739	10.245
Isobutylmethylketone	1.096	10.942	0.841	8.396

Table 5.1.2.5: γ and H for various volumes of Pentane in 10 cS PDMS at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction (x)	Gas Phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.01	3.4324	0.0004522	0.00014201	0.388	0.0318
0.02	5.2379	0.0009098	0.0002167	0.294	0.0241
0.03	6.7349	0.0013680	0.0002786	0.252	0.0206
0.04	8.2043	0.0018259	0.0003394	0.230	0.0188
0.05	9.8929	0.0022826	0.0004092	0.222	0.0182
0.06	11.2129	0.0027401	0.0004368	0.209	0.0172
0.07	12.4583	0.0031975	0.0005153	0.199	0.0163
0.08	13.3561	0.0036557	0.0005524	0.187	0.0125
0.09	14.4066	0.0041129	0.0005958	0.179	0.0147
0.1	15.0496	0.0045711	0.0006224	0.168	0.0138

Table 5.1.2.6: γ and H for various volumes of Hexane in 10cS PDMS at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction (x)	Gas phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.01	1.4586	0.0004033	4.6323E-05	0.503	0.0116
0.02	2.8446	0.0008066	9.0338E-05	0.491	0.0114
0.03	4.1121	0.0012098	1.3059E-05	0.473	0.0109
0.04	5.2231	0.0016131	1.6586E-05	0.450	0.0104
0.05	6.3254	0.0020160	2.0086E-05	0.436	0.0101
0.06	7.3425	0.0024189	2.3315E-05	0.422	0.00976
0.07	8.3879	0.0028214	2.6633E-04	0.414	0.00956
0.08	9.4561	0.0032235	3.0024E-04	0.408	0.00944
0.09	10.4166	0.0036256	3.3073E-04	0.400	0.00924
0.1	11.3386	0.0040275	3.5599E-04	0.392	0.00905

Table 5.1.2.7: γ and H for various volumes of Heptane in 10cS PDMS 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction (x)	Gas phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.002	0.1229	7.19E-05	3.05E-06	0.539	0.00429
0.005	0.2632	0.00018	6.53E-06	0.462	0.00368
0.01	0.4386	0.00036	1.09E-05	0.385	0.00306
0.02	0.7627	0.00072	1.89E-05	0.334	0.00267
0.03	1.0629	0.001079	2.64E-05	0.311	0.00248
0.04	1.3399	0.001439	3.33E-05	0.294	0.00234
0.05	1.6438	0.001798	4.08E-05	0.289	0.00229
0.06	1.8775	0.002157	4.66E-05	0.275	0.00219
0.07	2.1134	0.002516	5.25E-05	0.265	0.00211
0.08	2.3426	0.002878	5.82E-05	0.257	0.00205
0.09	2.5411	0.003233	6.31E-05	0.248	0.00198
0.1	2.7420	0.003591	6.81E-05	0.241	0.00192

Table 5.1.2.8: γ and H for various volumes of Triethylamine in 10cS PDMS at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction (x)	Gas phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.01	0.8784	0.0003814	2.5916E-05	0.525	0.00689
0.02	1.2387	0.0007638	5.1255E-05	0.518	0.00679
0.03	1.7653	0.0011455	7.3044E-05	0.492	0.00646
0.04	2.1032	0.0015274	8.7024E-05	0.440	0.00577
0.05	2.4833	0.0019088	1.0275E-04	0.416	0.00577
0.06	2.7644	0.0022903	1.1438E-04	0.386	0.00545
0.07	3.1105	0.0026712	1.2869E-04	0.372	0.00506
0.08	3.3351	0.0030522	1.3799E-04	0.349	0.00488
0.09	3.4556	0.0034332	1.4297E-04	0.322	0.00422
0.1	3.5689	0.0038138	1.4766E-04	0.299	0.00392

Table 5.1.2.9: γ and H for various volumes of Toluene in 10cS PDMS at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction (x)	Gas phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.01	0.3541	0.0004951	1.3386E-05	0.560	0.00274
0.02	0.6012	0.0009900	2.2727E-05	0.475	0.00233
0.03	0.7842	0.0014847	2.9645E-05	0.413	0.00202
0.04	1.0222	0.0019787	3.8641E-05	0.404	0.00198
0.05	1.2104	0.0024724	4.5755E-05	0.383	0.00188
0.06	1.3257	0.0029678	5.0113E-05	0.350	0.00171
0.07	1.5259	0.0034584	5.7681E-05	0.345	0.00169
0.08	1.6819	0.0039507	6.3578E-05	0.333	0.00163
0.09	1.8698	0.0044424	7.0679E-05	0.329	0.00161
0.1	2.0148	0.0049338	7.6160E-05	0.320	0.00156

Table 5.1.2.10: γ and H for various volumes of Xylene in 10cS PDMS 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction (x)	Gas phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.005	0.1457	0.000215	2.3900E-06	0.805	0.00113
0.01	0.2394	0.00043	3.9271E-06	0.661	0.000925
0.02	0.4054	0.00086	6.6501E-06	0.559	0.000783
0.03	0.5415	0.00129	8.8826E-06	0.498	0.000698
0.04	0.6542	0.00172	1.0731E-06	0.452	0.000632
0.05	0.7999	0.00215	1.3121E-05	0.442	0.000619
0.06	0.9037	0.00258	1.4824E-05	0.416	0.000583
0.07	0.9643	0.00301	1.5818E-05	0.381	0.000533
0.08	1.0596	0.00343	1.7381E-05	0.366	0.000513
0.09	1.1812	0.00386	1.9376E-05	0.363	0.000508
0.1	1.2945	0.00428	2.1234E-05	0.358	0.000502

Table 5.1.2.11: γ and H for various volumes of Cyclohexane in 10cS PDMS 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction (x)	Gas phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.005	0.3448	0.0002451	1.6309E-05	0.397	0.00674
0.01	0.6124	0.0004903	2.8966E-05	0.353	0.00599
0.02	1.0396	0.0009809	4.9171E-05	0.299	0.00506
0.03	1.3554	0.0014714	6.4107E-05	0.260	0.00442
0.04	1.6849	0.0019614	7.9690E-05	0.243	0.00412
0.05	1.9099	0.0024513	9.0331E-05	0.220	0.00373
0.06	1.2014	0.0029405	1.0416E-04	0.211	0.00359
0.07	2.5282	0.0034290	1.1957E-04	0.208	0.00353
0.08	2.8134	0.0039172	1.3306E-04	0.203	0.00344
0.09	3.1487	0.0044048	1.4891E-04	0.202	0.00343
0.1	3.4218	0.0048921	1.6183E-04	0.197	0.00335

Table 5.1.2.12: γ and H for various volumes of Butyl acetate in 10 cS PDMS 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction (x)	Gas phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.01	0.5645	0.0004021	8.4635E-06	0.860	0.00213
0.02	0.8614	0.0008042	1.2915E-05	0.656	0.00163
0.03	1.1074	0.0012060	1.6603E-05	0.563	0.00139
0.04	1.3597	0.0016076	2.0386E-05	0.518	0.00129
0.05	1.6267	0.0020087	2.4389E-05	0.496	0.001230
0.06	1.8439	0.0024096	2.7645E-05	0.469	0.00116
0.07	2.0487	0.0028103	3.0716E-05	0.447	0.00111
0.08	2.1963	0.0032106	3.2928E-05	0.419	0.00104
0.09	2.3692	0.0036106	3.5521E-05	0.402	0.000997
0.1	2.4749	0.0040104	3.7105E-05	0.378	0.000938

Table 5.1.2.13: γ and H for various volumes of Diethylether in 10 cS PDMS at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction (x)	Gas phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.01	7.7244	0.0004875	0.0002592	0.624	0.633
0.02	15.2242	0.0009751	0.0005108	0.615	0.625
0.03	22.3327	0.0014633	0.0007491	0.601	0.613
0.04	28.9658	0.0019524	0.0009714	0.584	0.599
0.05	35.6093	0.0024409	0.0011939	0.574	0.590
0.06	41.6906	0.0029307	0.0013975	0.560	0.578
0.07	47.8333	0.0034198	0.0016031	0.550	0.570
0.08	53.8226	0.0039087	0.0018034	0.542	0.563
0.09	59.4467	0.0043982	0.0019915	0.532	0.554
0.1	65.0519	0.0048873	0.0021788	0.523	0.547

Table 5.1.2.14: γ and H for various volumes of Chloroform in 10 cS PDMS at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction (x)	Gas Phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.01	2.3586	0.0006507	0.0000983	0.425	0.0153
0.02	4.161	0.0013024	0.0001734	0.375	0.0135
0.03	4.1578	0.0019562	0.0002145	0.309	0.0111
0.04	6.4565	0.0026080	0.0002690	0.290	0.0105
0.05	7.7984	0.0032588	0.0003249	0.281	0.0101
0.06	8.9772	0.0039094	0.0003740	0.269	0.0097
0.07	10.0761	0.0045594	0.0004198	0.259	0.00933
0.08	11.4420	0.0052076	0.0004767	0.258	0.00927
0.09	12.2482	0.0058569	0.0005102	0.245	0.00883
0.1	13.1535	0.0065050	0.0005479	0.237	0.00853
0.2	21.7245	0.0129417	0.0009046	0.197	0.00708
0.3	31.4726	0.0192914	0.0013100	0.191	0.00688
0.4	39.1817	0.0255668	0.0016304	0.179	0.00646
0.5	47.2329	0.0317698	0.0019647	0.174	0.00927
0.6	55.4559	0.0378769	0.0023059	0.171	0.00617
0.7	63.3907	0.0439179	0.0026351	0.169	0.00608
0.8	70.7369	0.0498831	0.0029395	0.166	0.00597
0.9	77.7575	0.0557765	0.0032304	0.163	0.00587
1	85.1757	0.0615959	0.0035374	0.162	0.00582

Table 5.1.2.115: γ and H for various volumes of Acetone in 10 cS PDMS at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction (x)	Gas phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.01	3.0502	0.000701	0.000261	1.026	0.474
0.02	6.0402	0.001402	0.000517	1.016	0.470
0.03	8.9456	0.002102	0.000766	1.003	0.466
0.04	11.7697	0.002801	0.001007	0.990	0.461
0.05	14.5074	0.003501	0.001241	0.977	0.456
0.06	17.2327	0.004199	0.001474	0.967	0.453
0.07	20.1113	0.004895	0.001720	0.968	0.453
0.08	22.8534	0.005592	0.001954	0.962	0.451
0.09	25.5345	0.006288	0.002182	0.956	0.449
0.1	28.1872	0.006983	0.002409	0.950	0.447

Table 5.1.2.16: γ and H for various volumes Ethylmethylketone in 10cS PDMS at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction (x)	Gas phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.002	0.2371	0.000119	0.000011	0.532	0.00909
0.005	0.5371	0.000297	0.000024	0.482	0.00823
0.01	1.0009	0.000593	0.000045	0.449	0.00766
0.02	1.9207	0.001186	0.000086	0.431	0.00736
0.04	3.5525	0.002371	0.000159	0.399	0.00681
0.06	4.7102	0.003554	0.000211	0.353	0.00602
0.08	6.0679	0.004734	0.000272	0.341	0.00582
0.1	7.3095	0.005912	0.000328	0.329	0.00562
0.2	13.3126	0.011759	0.000597	0.301	0.00514
0.4	23.8636	0.023256	0.001069	0.273	0.00466
0.6	33.9088	0.034489	0.001519	0.261	0.00446
0.8	43.2951	0.045469	0.001938	0.253	0.00432

Table 5.1.2.17: γ and H for various volumes of Isobutylmethylketone in 10 csS PDMS at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas Phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
0.005	0.2645	0.000212	7.88424E-06	1.052	0.00377
0.01	0.5076	0.000423	1.51305E-05	1.010	0.00362
0.02	0.9349	0.000847	2.78670E-05	0.930	0.00334
0.04	1.3165	0.001693	3.92411E-05	0.655	0.00235
0.06	1.7284	0.002538	5.15181E-05	0.573	0.00206
0.08	2.1188	0.003382	6.31539E-05	0.528	0.00189
0.1	2.3838	0.004224	7.10521E-05	0.475	0.00170
0.2	3.8633	0.008416	1.15145E-04	0.387	0.00139
0.4	6.5079	0.016694	1.93952E-04	0.328	0.00118
0.6	9.2509	0.024835	2.75678E-04	0.314	0.00113
0.8	10.5351	0.032846	3.13935E-04	0.270	0.00097

Table 5.1.2.18: Effect of temperature on H and γ (Acetone).

Temperature (K)	Peak area (units)	Liquid phase mole fraction (x)	Gas phase mole fraction (y)	γ	H (k Pa m^{-3} mol^{-1})
298	4.0516	0.022079	0.000347	0.0433	0.0051
303	4.6423	0.022067	0.000398	0.0496	0.0058
308	5.4230	0.022050	0.000464	0.0580	0.0068
313	6.0240	0.022037	0.000516	0.0645	0.0076
318	6.9017	0.022018	0.000591	0.0739	0.0087
323	7.5263	0.022005	0.000644	0.0806	0.0095

Table 5.1.2.19: γ and H for various volumes of Pentane in water at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.01	131.5667	9.9211E-08	0.005415	67500	99.5
0.02	261.2334	3.1049E-07	0.010694	42500	62.8
0.03	385.9946	8.1111E-07	0.015722	2400	35.5
0.04	511.5223	1.2665E-06	0.020728	20200	29.8
0.05	632.5891	1.9851E-06	0.025509	15900	23.4
0.06	746.2229	3.1419E-06	0.029954	11800	17.4
0.07	852.3579	4.7412E-06	0.034069	9000	13.1
0.08	951.4118	6.7581E-06	0.037879	6900	10.2
0.09	1028.2448	1.0086E-05	0.040813	5000	7.4
0.1	1098.4962	1.3801E-05	0.043479	3900	5.7

Table 5.1.2.20: γ and H for various volumes of Hexane in water.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.01	150.6245	7.5139E-08	0.004761	277000	115.5
0.02	300.0056	2.0657E-07	0.009438	200000	83.3
0.03	448.5624	3.7531E-07	0.014046	163000	68.3
0.04	596.2493	5.8344E-07	0.018585	139000	58.1
0.05	743.3254	8.1922E-07	0.023064	123000	51.3
0.06	888.3425	1.1482E-06	0.027440	104000	43.6
0.07	1030.8564	1.5905E-06	0.031702	87000	36.4
0.08	1169.4561	2.2100E-06	0.035812	70000	29.6
0.09	1305.2388	2.9571E-06	0.039809	58000	24.6
0.1	1431.3386	4.1425E-06	0.043483	45000	19.1

Table 5.1.2.21: γ and H for various volumes of Heptane in water at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.01	130.8554	8.7645E-08	0.004206	607000	87.5
0.02	261.2506	1.9646E-07	0.008362	539000	77.6
0.03	390.9887	3.3550E-07	0.012462	470000	67.7
0.04	519.6487	5.2414E-07	0.016496	398000	57.4
0.05	646.3284	8.0387E-07	0.020435	321000	46.4
0.06	771.2512	1.1644E-06	0.024288	264000	38.0
0.08	1022.6512	1.8140E-06	0.031953	223000	32.1
0.1	1262.2512	3.0065E-06	0.039146	164000	23.7
0.2	2472.5877	8.4010E-06	0.073908	111000	16.0
0.3	3608.3224	1.7227E-05	0.104314	77000	11.04
0.4	4702.2502	2.7976E-05	0.131772	60000	8.6

Table 5.1.2.22: γ and H for various volumes of Triethylamine in water in water at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.01	1.5688	6.4274E-06	4.6285E-05	55.6	0.730
0.02	2.2173	1.2893E-05	9.1745E-05	54.9	0.721
0.03	3.1599	1.9347E-05	1.3074E-04	52.2	0.685
0.04	3.7647	2.5815E-05	1.5576E-04	46.5	0.611
0.05	4.4451	3.2279E-05	1.8391E-04	44.0	0.577
0.06	4.9482	3.8751E-05	2.0472E-04	40.8	0.535
0.07	4.5679	4.5218E-05	2.3034E-04	39.3	0.516
0.08	5.9698	5.1693E-05	2.4697E-04	36.8	0.484
0.09	6.1676	5.8178E-05	2.5515E-04	33.9	0.444
0.1	6.3883	6.4661E-05	2.6428E-04	31.6	0.4141

Table 5.1.2.23: γ and H for various volumes of Toluene in water at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.005	21.6294	2.5692E-06	0.001167	8900	0.828
0.01	41.8436	5.2474E-06	0.002255	8500	0.784
0.02	81.2118	1.0685E-05	0.004367	8000	0.745
0.04	153.5664	2.2052E-05	0.008225	7700	0.680
0.06	213.8611	3.4347E-05	0.011418	7300	0.606
0.08	260.1964	4.7715E-05	0.013857	6900	0.529
0.1	290.5499	6.2314E-05	0.015448	6400	0.452
0.2	458.6332	1.3404E-04	0.0241698	6000	0.329
0.4	721.6792	2.8309E-04	0.035712	5600	0.242
0.6	924.2082	4.3676E-04	0.0475389	5400	0.199
0.8	1127.784	5.9029E-04	0.0574092	5300	0.177
1	1308.982	7.4551E-04	0.0660240	5100	0.162

Table 5.1.2.24: γ and H for various volumes of Xylene in water at 303K.

Water volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.001	13.0089	4.2488E-07	0.000213	36000	0.916
0.002	22.8749	9.2324E-07	0.000375	29400	0.741
0.005	46.9303	2.5479E-06	0.000769	21800	0.551
0.01	76.7945	5.4948E-06	0.001258	16500	0.418
0.05	279.6697	2.9912E-05	0.004567	11000	0.278
0.1	517.5706	6.0798E-05	0.008419	10000	0.253
0.2	897.7994.1	1.2480E-04	0.014537	8400	0.212
0.4	601.8949	2.5409E-04	0.025605	7200	0.184
0.6	2174.0202	3.8644E-04	0.000386	6400	0.163
0.8	2679.9596	5.2029E-04	0.000520	5800	0.148
1	2998.6221	6.5849E-04	0.000658	5100	0.129

Table 5.1.2.25: γ and H for various volumes of Cyclohexane in water 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.001	8.4532	1.2179E-07	0.000500	24400	7.481
0.002	16.7242	2.5894E-07	0.000988	22800	6.958
0.005	40.9464	7.2016E-07	0.002415	20000	6.116
0.01	80.8456	1.5286E-06	0.004757	18600	5.676
0.05	366.2548	1.0843E-05	0.021196	16700	3.565
0.1	675.1222	2.6521E-05	0.038385	8600	2.640
0.2	1286.0032	5.8453E-05	0.070663	7200	2.205
0.4	2384.0233	1.3274E-04	0.123542	5600	1.698
0.6	3512.4412	2.0445E-04	0.171963	5000	1.534
0.8	4725.6554	2.6901E-04	0.218388	4900	1.481
1	5879.1114	3.3859E-04	0.257943	4500	1.389

Table 5.1.2.26: γ and H for various volumes of Butyl acetate in water.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.005	0.5276	3.3978E-06	7.9103E-06	95.1	0.00425
0.01	0.8305	6.8004E-06	1.2452E-05	74.8	0.00334
0.02	1.5264	1.3604E-05	2.2885E-05	68.7	0.00307
0.04	2.7701	2.7213E-05	4.1531E-05	62.3	0.00278
0.08	4.9452	5.4437E-05	7.4139E-05	55.6	0.00248
0.1	5.8364	6.8053E-05	8.7498E-05	52.5	0.00235
0.2	9.6408	1.3614E-04	1.4453E-04	43.4	0.00194
0.4	16.2307	2.7231E-04	2.4329E-04	36.5	0.00163
0.6	19.8969	4.0850E-04	2.9823E-04	29.8	0.00133
0.8	23.6511	5.4466E-04	3.5448E-04	26.6	0.00119
1	26.2657	6.8080E-04	3.9365E-04	23.6	0.00106

Table 5.1.2.27: γ and H for various volumes of Diethyl ether in water at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.01	15.4488	7.8828E-06	0.000518	77.2	0.119
0.02	30.4488	1.5787E-05	0.001021	75.9	0.118
0.03	44.6658	2.3728E-05	0.001497	74.1	0.115
0.04	28.9658	3.3101E-05	0.001892	72.5	0.154
0.05	70.6093	3.9731E-05	0.002365	69.9	0.109
0.06	82.1206	4.7801E-05	0.002748	67.5	0.109
0.07	94.8333	6.3832E-05	0.003173	66.8	0.103
0.08	107.4232	7.1835E-05	0.003593	66.1	0.102
0.09	120.3365	7.1835E-05	0.004023	65.8	0.099
0.1	130.6897	7.9961E-05	0.004368	64.1	0.098

Table 5.1.2.28: γ and H for various volumes of Chloroform in water 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.001	1.0536	7.4016E-07	0.000263	1000	0.649
0.002	1.9596	1.5329E-06	0.000490	900	0.583
0.005	4.3831	4.0162E-06	0.001095	770	0.497
0.01	7.4065	8.5169E-06	0.001849	600	0.396
0.02	12.6391	1.7809E-05	0.003151	500	0.323
0.05	26.8361	4.6217E-05	0.006666	400	0.263
0.1	49.3316	9.3977E-05	0.012186	370	0.237
0.2	86.2613	1.9236E-04	0.021116	300	0.200
0.3	120.0028	2.9185E-04	0.029135	280	0.182
0.4	154.6265	3.9101E-04	0.037228	270	0.174
0.5	180.8672	4.9313E-04	0.043273	250	0.160
0.6	213.8300	5.9284E-04	0.050759	240	0.156

Table 5.1.2.29: γ and H for various volumes of Acetone in water at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.01	0.3339	1.2201E-05	2.8606E-05	6.456	0.00428
0.02	0.5624	2.4414E-05	4.8181E-05	5.434	0.00359
0.04	0.8978	4.8855E-05	7.6913E-05	4.335	0.00287
0.06	1.2638	7.3291E-05	1.0826E-04	4.068	0.00269
0.08	1.5747	9.7733E-05	1.3489E-04	3.801	0.00252
0.1	1.7361	1.2219E-04	1.4872E-04	3.351	0.00222
0.2	2.9816	2.4441E-04	2.5538E-04	2.877	0.0191
0.5	5.5733	6.1104E-04	4.7727E-04	2.151	0.00143
1	8.7589	1.2216E-03	7.4986E-04	1.690	0.00112
1.5	12.1589	1.8314E-03	1.0406E-03	1.565	0.00104
2	15.7035	2.4405E-03	1.3436E-03	1.516	0.00100

Table 5.1.2.30: γ and H for various volumes of Ethylmethylketone in water at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.005	2.0187	4.9257E-06	9.0538E-05	109.1	0.0335
0.01	3.8082	9.8661E-06	1.7078E-04	102.8	0.0316
0.02	9.7951	1.9592E-05	4.3915E-04	93.1	0.0309
0.04	12.2364	3.9655E-05	5.4855E-045	82.1	0.0253
0.06	15.9549	5.9634E-05	7.1513E-04	71.2	0.0219
0.08	19.2575	5.9634E-05	8.6303E-04	64.3	0.0198
0.1	22.5194	7.9639E-05	1.0091E-03	60.1	0.0185
0.2	39.5542	9.9647E-05	1.7710E-03	52.7	0.0162
0.4	72.7915	1.9963E-04	3.2543E-03	48.4	0.0149
0.6	103.3354	3.9957E-04	4.6136E-03	45.7	0.0141
0.8	131.0955	5.9961E-04	5.8457E-03	43.4	0.0133
1	153.2659	7.9975E-04	6.8276E-03	40.5	0.0125

Table 5.1.2.31: γ and H for various volumes of Isobuty lmethyl ketone in water at 303K.

Solute volume (ml)	Peak area (units)	Liquid phase mole fraction(x)	Gas phase mole fraction (y)	γ	*H* (k Pa $m^{-3}mol^{-1}$)
0.02	1.4238	0.000014	0.000042	83.7	0.00541
0.04	2.6448	0.000029	0.000079	77.7	0.00502
0.06	3.6654	0.000043	0.000109	71.8	0.00463
0.08	4.4526	0.000057	0.000133	65.4	0.00422
0.1	5.2838	0.000072	0.000157	62.1	0.00401
0.2	8.9854	0.000143	0.000268	52.7	0.00341
0.4	15.9236	0.000287	0.000474	46.7	0.00302
0.6	21.5688	0.000430	0.000643	42.2	0.00272
0.8	26.2683	0.000574	0.000782	38.5	0.00249
1	30.5216	0.000717	0.000909	35.8	0.00231

5.2.1: Gas – Liquid Chromatographic Technique Results

Table 5.2.1: Flow rate calibrations for 5 cS PDMS column (10 % Loading).

GC Set (ml/min)	Time, t (sec)	Flow meter Flow rate, F (ml/min)	Averages	
			Time, t (sec)	F (ml/min)
40	34.78	17.25		
	34.90	17.19	34.84	17.22
	34.87	17.21		
	34.82	17.23		
	34.83	17.23		
50	28.49	21.06		
	28.47	21.07	28.48	21.07
	28.45	21.09		
	28.50	21.05		
	28.49	21.06		
60	24.10	24.90		
	24.18	24.81	24.14	24.86
	24.19	24.80		
	24.10	24.90		
	24.13	24.87		
70	21.13	28.40		
	21.07	28.48	21.10	28.44
	21.15	28.37		
	21.06	28.49		
	21.09	28.45		
80	18.74	32.02		
	18.72	32.05	18.70	32.09
	18.64	32.19		
	18.73	32.03		
	18.68	32.10		
90	16.72	35.89		
	16.64	63.06	16.68	35.97
	16.74	35.84		
	16.63	35.08		
	16.67	35.99		

Table 5.2.2: Flow rate calibrations for 10 cS PDMS column (10 % Loading).

GC Set (ml/min)	Time, t (sec)	Flow meter Flow rate, F (ml/min)	Averages	
			Time, t (sec)	F (ml/min)
40	63.63	9.43		
	63.56	9.44	63.63	9.43
	63.70	9.42		
	63.65	9.43		
	63.61	9.43		
50	50.96	11.77		
	50.90	11.79	50.93	11.78
	50.91	11.79		
	50.96	11.77		
	50.95	11.78		
60	42.46	14.13		
	42.40	14.15	42.43	14.14
	42.39	14.15		
	42.48	14.12		
	42.47	14.13		
70	36.32	16.52		
	36.40	16.48	36.36	16.5
	36.33	16.51		
	36.37	16.50		
	36.36	16.50		
80	31.75	18.89		
	31.87	18.83	31.81	18.86
	31.78	18.88		
	31.86	18.83		
	31.84	18.85		
90	28.26	21.23		
	28.32	21.19	28.29	21.21
	28.30	21.20		
	28.26	21.23		
	28.31	21.19		

Table 5.2.3: Flow rate calibrations for 50 cS PDMS column (10 % Loading).

GC Set (ml/min)	Time, t (sec)	Flow meter Flow rate, F (ml/min)	Averages	
			Time, t (sec)	F (ml/min)
40	35.98	16.68		
	36.06	16.64	36.02	16.66
	36.08	16.63		
	35.96	16.69		
	36.01	16.66		
50	29.41	20.40		
	29.56	20.30	29.48	20.35
	29.44	20.38		
	29.49	20.35		
	29.51	20.33		
60	24.94	24.06		
	24.90	24.10	24.92	24.08
	24.86	24.14		
	24.93	24.07		
	24.97	24.03		
70	23.53	24.50		
	23.51	24.52	23.52	27.51
	23.52	25.51		
	23.50	25.53		
	23.54	25.49		
80	19.17	31.30		
	19.15	31.33	19.16	31.32
	19.14	31.35		
	19.16	31.32		
	19.17	31.30		
90	17.24	34.80		
	17.27	34.74	17.26	34.76
	17.27	34.74		
	17.23	34.82		
	17.28	34.72		

Table 5.2.4: Flow rate calibrations for 50 cS PDMS column (20 % Loading).

GC Set (ml/min)	Time, t (sec)	Flow meter Flow rate, F (ml/min)	Averages	
			Time, t (sec)	F (ml/min)
40	36.23	16.56		
	36.24	16.56	36.23	16.56
	36.22	16.57		
	36.25	16.55		
	36.21	16.57		
50	29.80	20.13		
	29.86	20.09	29.84	20.11
	29.87	20.09		
	29.86	20.09		
	29.83	20.11		
60	24.98	24.01		
	25.06	23.94	25.02	23.98
	25.08	23.92		
	24.97	24.02		
	25.01	23.99		
70	21.60	27.78		
	21.66	27.70	21.63	27.73
	21.68	27.68		
	21.59	27.79		
	21.62	27.75		
80	19.25	31.17		
	19.19	31.27	19.22	31.22
	19.26	31.15		
	19.21	31.23		
	19.19	31.27		
90	17.36	34.56		
	17.40	34.48	17.38	34.52
	17.32	34.64		
	17.43	34.42		
	17.39	34.50		

Table 5.2.5: Flow rate calibrations for 50 cS PDMS column (30 % Loading).

GC Set (ml/min)	Time, t (sec)	Flow meter Flow rate, F (ml/min)	Averages	
			Time, t (sec)	F (ml/min)
40	36.54	16.42		
	36.56	16.41	36.54	16.42
	36.52	16.43		
	36.58	16.40		
	36.51	16.43		
50	30.34	19.78		
	30.30	19.80	30.32	19.79
	30.27	19.82		
	30.28	19.82		
	30.36	19.76		
60	25.58	23.46		
	25.66	23.38	25.62	23.42
	25.59	23.45		
	25.61	23.43		
	25.65	23.39		
70	22.30	26.91		
	22.33	26.87	22.32	26.88
	22.34	26.86		
	22.27	29.94		
	22.35	26.85		
80	19.32	31.06		
	19.34	31.02	19.32	31.06
	19.32	31.06		
	19.28	31.12		
	19.35	31.01		
90	17.23	34.82		
	17.25	34.78	17.24	34.80
	17.20	34.88		
	17.27	34.74		
	17.28	34.72		

Table 5.2.6: Flow rate calibrations for 500 cS PDMS column (10 % Loading).

GC Set (ml/min)	Time, t (sec)	Flow meter Flow rate, F (ml/min)	Averages	
			Time, t (sec)	F (ml/min)
40	29.98	20.01		
	29.94	20.04	29.98	20.01
	29.99	20.01		
	29.96	20.01		
	30.03	19.98		
50	24.02	24.98		
	24.04	24.96	24.02	24.98
	23.99	25.01		
	23.98	25.02		
	24.05	24.94		
60	20.11	29.84		
	20.04	29.94	20.08	29.88
	20.10	29.85		
	20.07	29.90		
	20.08	29.88		
70	17.14	35.01		
	17.10	35.09	17.13	35.02
	17.16	34.97		
	17.11	35.07		
	17.12	35.05		
80	15.04	39.89		
	14.99	40.03	14.99	40.01
	14.97	40.08		
	15.03	39.92		
	14.97	40.08		

Table 5.2.7: Effect of liquid loading on retention volumes (50 cS PDMS column)

% liquid loading	Compound	Net retention volume (V_N)	Specific retention volume (V_g)
10	Pentane	28.59	29.17
	Hexane	64.12	65.42
	Heptane	143.83	146.75
	Diethyl ether	29.46	30.06
	Acetone	26.28	26.82
	Chloroform	66.72	68.07
20	Pentane	63.39	28.89
	Hexane	138.54	63.13
	Heptane	314.36	143.26
	Diethylether	59.95	27.32
	Acetone	50.77	23.14
	Chloroform	140.55	64.05
30	Pentane	98.02	27.06
	Hexane	222.65	61.47
	Heptane	505.73	139.63
	Diethylether	89.93	24.83
	Acetone	72.29	19.96
	Chloroform	219.76	60.67

Table 5.2.8: Effect of temperature and solute vapour pressure on V_g (5 cS PDMS column).

Compound	Temperature (K)	Vapour pressure (k Pa)	Specific retention volumes V_g (ml/g)
Chloroform	303	32.80	159.00
	313	48.85	106.91
	323	70.13	70.90
	333	101.33	50.60
Pentane	303	81.97	61.09
	313	115.62	45.49
	323	159.15	34.17
	333	217.85	23.16
Hexane	303	24.94	164.09
	313	37.25	114.87
	323	53.33	80.46
	333	76.35	55.23
Heptane	303	7.79	440.58
	313	12.33	289.65
	323	18.88	185.89
	333	28.08	132.20
Acetone	303	36.80	52.09
	313	53.33	44.36
	323	79.99	28.89
	333	119.72	18.89
Toluene	303	4.89	737.05
	313	7.89	483.37
	323	12.28	295.74
	333	18.52	181.38
Cyclohexane	303	16.23	337.98
	313	24.62	219.51
	323	36.24	148.05
	333	51.89	100.85
Xylene	303	1.37	2443.19
	313	2.52	1116.50
	323	4.15	858.57
	333	6.59	512.07

Diethylether	303 313 323 333	86.30 122.83 170.25 233.05	61.49 46.25 30.49 27.44
Butylacetate	303 313 323 333	1.92 3.32 5.52 8.89	1293.16 800.70 484.94 315.01
Isobutylmethylketone	303 313 323 333	3.56 5.80 9.17 14.11	627.39 393.90 249.08 159.64
Triethylamine	303 313 323 333	13.12 20.49 31.16 46.17	413.95 264.62 168.63 111.18
Ethylmethylketone	303 313 323 333	18.30 25.33 37.73 53.33	150.78 100.47 68.33 49.35

Table 5.2.9: Effect of sample size on retention volume (500 cS PDMS column)

Compound	Sample size (µl)	t_R (mins)	V_N (ml)	V_g (ml/g)
Pentane	0.10	0.89	18.617	28.280
	0.50	0.88	18.284	27.775
	1.00	0.83	16.622	25.250
	5.00	0.67	11.303	17.170
	10.00	0.50	5.652	8.585
Acetone	0.10	0.83	16.622	25.250
	0.50	0.82	16.290	24.745
	1.00	0.77	14.627	22.220
	5.00	0.61	9.308	14.140
	10.00	0.44	3.657	5.5555
Chloroform	0.10	1.57	41.223	62.621
	0.50	1.56	40.891	62.116
	1.00	1.53	39.893	60.601
	5.00	1.42	36.236	55.046
	10.00	1.31	32.579	49.491
Diethylether	0.92	0.92	19.614	29.795
	0.90	0.90	18.949	28.785
	0.86	0.86	17.619	26.765
	0.71	0.71	12.633	19.190
	0.58	0.58	8.3111	16.625
Ethylmethylketone	0.10	1.46	37.566	57.066
	0.50	1.45	37.234	56.561
	1.00	1.42	36.236	55.046
	5.00	1.27	31.250	47.471
	10.00	1.11	25.931	39.390

Table 5.2.10: Effect of carrier gas flow rate on specific retention volumes (500 cS PDMS column).

Compound	Flow rate (ml/min)	t_R (mins)	V_N (ml)	V_g (ml/g)
Acetone	20.01	1.37	17.291	26.267
	24.94	1.17	17.407	26.443
	29.88	1.02	17.131	26.023
	35.02	0.93	17.459	26.521
	40.01	0.85	17.287	26.260
Pentane	20.01	1.42	18.123	27.530
	24.98	1.21	18.236	27.702
	29.88	1.06	18.124	27.532
	35.02	0.96	18.332	27.847
	40.01	0.88	18.284	27.775
Chloroform	20.01	2.71	39.571	60.111
	24.98	2.24	39.644	60.222
	29.88	1.93	39.724	60.343
	35.02	1.69	39.573	60.115
	40.01	1.52	39.561	60.096
Diethyl ether	20.01	1.42	18.123	27.530
	24.98	1.21	18.265	27.746
	29.88	1.06	18.124	27.532
	35.02	0.96	18.332	27.847
	40.01	0.88	18.284	27.775
Ethyl methyl ketone	20.01	4.43	68.168	103.552
	24.98	3.61	68.079	103.418
	29.88	3.07	68.027	103.338
	35.02	2.67	68.090	103.433
	40.01	2.38	68.151	103.526

Table 5.2.11: Solute Description and Code.

Code no.	Compound	Code no.	Compound
1	chloroform	8	xylene
2	n-pentane	9	diethylether
3	n-hexane	10	butylacetate
4	n-heptane	11	isobutyl methyl ketone
5	acetone	12	triethylamine
6	toluene	13	ethyl methyl ketone
7	cyclohexane		

Table 5.2.12: Chloroform retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	4.25	4.06	146.04	121.34	159.00
	313	2.98	2.79	100.36	83.39	105.77
	323	2.16	1.97	70.86	58.88	72.37
	333	1.58	1.39	50.00	41.54	49.53
	353	1.05	0.86	27.60	22.93	25.79
	373	0.66	0.47	15.08	12.53	13.34
	393	0.53	0.34	10.91	9.07	9.16
	423	0.37	0.18	5.78	4.80	4.50
10	303	11.55	10.99	207.27	172.22	188.20
	313	8.55	7.99	150.69	125.21	132.45
	323	6.08	5.52	104.11	86.50	88.67
	333	4.68	4.12	77.70	64.56	64.20
	353	1.33	0.77	14.52	12.07	11.32
	373	0.87	0.31	5.85	4.86	4.31
	393	0.68	0.12	2.26	1.88	1.58
	423	0.47	0.09	1.16	1.12	1.25
50	303	6.29	6.12	212.73	176.76	198.20
	313	4.36	4.19	145.64	121.02	131.36
	323	3.12	2.95	102.54	85.20	89.62
	333	2.26	2.09	72.65	60.36	61.59
	353	1.26	1.09	37.89	31.48	30.30
	373	0.86	0.69	23.98	19.93	18.15
	393	0.64	0.47	16.34	13.57	11.74
	423	0.45	0.28	9.73	8.09	6.50
500	303	11.55	11.22	448.91	373.00	622.72
	313	8.55	8.22	328.88	273.27	441.64
	323	6.08	5.75	230.06	191.15	299.37
	333	4.68	4.35	174.04	144.61	219.68
	353	0.98	0.65	26.01	21.61	30.97
	373	0.78	0.45	18.00	14.96	20.29
	393	0.58	0.25	10.00	8.31	10.70
	423	0.44	0.11	4.40	3.66	4.37

Table 5.2.13: Pentane retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	1.81	1.62	58.27	48.42	63.44
	313	1.38	1.19	42.80	35.97	45.11
	323	1.12	0.93	33.45	27.80	34.17
	333	0.89	0.7	25.18	20.92	24.94
	353	0.7	0.51	16.37	13.60	15.29
	373	0.54	0.35	11.23	9.33	9.93
	393	0.45	0.26	8.34	6.93	7.00
	423	0.36	0.17	5.46	4.53	4.25
10	303	4.95	4.39	82.80	68.79	75.18
	313	3.93	3.37	63.56	52.81	55.86
	323	3.03	2.47	46.58	38.71	39.68
	333	2.43	4.87	35.27	29.30	29.14
	353	0.81	0.25	4.72	3.92	3.67
	373	0.68	0.12	2.26	1.88	1.67
	393	0.52	0.08	1.58	1.75	1.42
	423	0.41	0.05	1.23	1.22	0.96
50	303	2.58	2.41	83.77	69.61	78.05
	313	1.97	1.8	62.57	51.99	56.43
	323	1.51	1.34	46.58	38.70	40.71
	333	1.16	0.99	34.41	28.59	29.17
	353	0.74	0.57	19.81	16.46	15.84
	373	0.54	0.37	12.86	10.69	9.73
	393	0.44	0.27	9.39	7.80	6.74
	423	0.38	0.21	7.30	6.07	4.87
500	303	4.95	4.62	184.85	153.59	256.41
	313	3.93	3.6	144.04	119.68	193.42
	323	3.03	2.7	108.03	89.76	140.57
	333	2.43	2.1	84.02	69.81	106.05
	353	0.68	0.35	14.00	11.64	16.67
	373	0.57	0.24	9.60	7.98	10.82
	393	0.46	0.13	5.20	4.32	5.56
	423	0.38	0.05	2.00	1.66	1.99

Table 5.2.14: Hexane retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	4.62	4.43	159.35	132.40	173.49
	313	3.48	3.29	118.34	98.33	124.73
	323	2.44	2.25	80.93	67.25	82.66
	333	1.84	1.65	59.35	49.31	58.80
	353	1.28	1.09	34.98	29.06	32.69
	373	0.85	0.66	21.18	17.60	18.73
	393	0.63	0.44	14.12	11.73	11.85
	423	0.45	0.26	8.34	6.93	6.51
10	303	12.39	11.83	223.11	185.39	202.58
	313	9.13	8.57	161.63	134.30	142.07
	323	6.53	5.97	112.59	93.55	95.90
	333	4.86	4.3	81.10	67.38	67.00
	353	1.51	0.95	17.92	14.89	13.96
	373	1.03	0.47	8.86	7.37	6.54
	393	0.8	0.24	4.53	3.76	3.17
	423	0.52	0.12	2.11	1.75	1.49
50	303	6.52	6.35	220.73	183.40	205.65
	313	4.64	4.47	155.38	129.10	140.14
	323	3.31	3.14	109.15	90.69	95.39
	333	2.39	2.22	77.17	64.12	65.42
	353	1.42	1.25	43.45	36.10	34.75
	373	0.92	0.75	26.07	21.66	19.73
	393	0.68	0.51	17.73	14.73	12.73
	423	0.5	0.33	11.47	9.53	7.66
500	303	12.39	12.06	482.52	400.93	669.34
	313	9.13	8.8	352.09	292.55	472.80
	323	6.53	6.2	248.06	206.11	322.80
	333	4.86	4.53	181.25	150.60	228.77
	353	1.02	0.69	27.61	22.94	32.87
	373	0.78	0.45	18.00	14.96	20.29
	393	0.6	0.27	10.80	8.98	11.55
	423	0.44	0.11	4.40	3.66	4.37

Table 5.2.15: Heptane retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	11.98	11.79	424.09	352.37	461.73
	313	7.96	7.77	279.49	232.23	294.57
	323	5.41	5.22	187.76	156.01	191.77
	333	3.76	3.57	128.41	106.70	127.22
	353	2.31	2.12	68.03	56.53	63.58
	373	1.47	1.28	41.08	34.13	36.33
	393	0.99	0.8	25.67	21.33	21.55
	423	0.62	0.43	13.80	11.47	10.76
10	303	32.43	31.87	601.07	449.43	545.75
	313	22.36	21.8	411.15	341.62	361.38
	323	14.99	14.43	272.15	226.13	231.80
	333	10.44	9.88	186.34	154.83	153.95
	353	2.88	2.32	43.76	36.36	34.10
	373	1.78	1.22	23.01	19.12	16.97
	393	1.26	0.7	13.20	10.97	9.24
	423	0.7	0.14	2.64	2.19	1.72
50	303	17.06	16.89	587.10	487.82	546.99
	313	11.28	11.11	386.18	320.88	348.30
	323	7.48	7.31	254.10	211.13	222.08
	333	5.15	4.98	173.10	143.83	146.75
	353	2.73	2.56	88.99	93.74	71.16
	373	1.57	1.4	48.66	40.43	36.83
	393	1.06	0.89	30.94	25.71	22.22
	423	0.7	0.53	18.42	15.31	12.29
500	303	32.43	32.10	1284.32	1067.14	1781.57
	313	22.36	22.03	881.42	732.37	732.37
	323	14.99	14.66	586.55	487.36	763.26
	333	10.44	10.11	404.50	336.10	510.56
	353	1.72	1.39	55.61	46.21	66.22
	373	1.18	0.85	34.01	28.26	38.12
	393	0.82	0.49	19.60	16.29	20.97
	423	0.55	0.22	8.80	7.31	8.75

Table 5.2.16: Acetone retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	1.72	1.53	55.03	45.73	59.92
	313	1.32	1.13	40.65	33.77	42.84
	323	0.96	0.77	27.70	23.01	28.29
	333	0.72	0.53	19.06	15.84	18.89
	353	0.66	0.47	15.08	12.53	14.10
	373	0.58	0.35	11.23	9.33	9.93
	393	0.48	0.29	9.31	7.73	7.81
	423	0.36	0.17	5.46	4.53	4.25
10	303	4.84	4.28	80.72	67.07	73.29
	313	3.58	3.02	56.96	47.33	50.06
	323	2.76	2.2	41.49	34.48	35.34
	333	2.24	1.68	31.68	26.33	26.18
	353	0.7	0.88	2.64	2.19	2.06
	373	0.58	0.41	0.38	0.31	0.28
	393	0.47	0.32	0.29	0.19	0.18
	423	0.39	0.17	0.15	0.11	0.12
50	303	2.18	2.01	69.87	58.05	65.09
	313	1.52	1.35	46.93	38.99	42.32
	323	1.1	0.93	32.33	26.86	28.25
	333	0.88	0.71	24.68	20.51	20.92
	353	0.66	0.49	17.03	14.15	13.62
	373	0.56	0.39	13.56	11.26	10.26
	393	0.45	0.28	9.73	8.09	6.99
	423	0.33	0.16	5.56	4.62	3.71
500	303	4.84	4.51	180.45	149.93	250.31
	313	3.58	3.25	130.03	108.04	174.61
	323	2.76	2.43	97.22	80.78	126.52
	333	2.24	1.91	76.42	63.50	96.46
	353	0.59	0.26	10.40	8.64	12.39
	373	0.49	0.16	6.40	5.32	7.21
	393	0.41	0.08	3.20	2.66	3.42
	423	0.36	0.03	1.20	1.00	1.19

Table 5.2.17: Toluene retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	20.22	20.03	720.48	598.65	784.43
	313	12.72	12.53	450.70	374.49	475.03
	323	8.24	8.05	289.56	240.59	295.74
	333	5.28	5.09	183.09	152.13	181.38
	353	2.96	2.77	88.89	73.86	83.07
	373	1.91	1.72	55.19	45.86	48.82
	393	1.27	1.08	34.66	28.80	29.09
	423	0.79	0.6	19.25	16.00	15.02
10	303	47.07	46.51	877.18	728.85	796.45
	313	30.54	29.98	565.42	469.81	496.98
	323	22.35	21.79	410.96	341.47	350.03
	333	12.96	12.4	233.86	194.32	193.21
	353	4.05	3.49	65.82	54.69	51.30
	373	2.28	1.72	32.44	26.95	23.93
	393	1.52	0.96	18.11	15.04	12.67
	423	0.89	0.33	6.22	5.17	4.05
50	303	25.28	25.11	872.82	725.23	813.19
	313	16.12	15.95	554.42	460.67	500.04
	323	10.19	10.02	348.30	289.40	304.41
	333	6.12	5.95	206.82	171.85	175.33
	353	3.28	3.11	108.10	89.82	86.45
	373	2.01	1.84	63.96	53.14	48.41
	393	1.63	1.46	50.75	42.17	36.45
	423	0.78	0.61	21.20	17.62	14.15
500	303	47.07	46.74	1870.07	1553.84	2594.10
	313	30.54	30.21	1208.70	1004.31	1623.11
	323	22.35	22.02	881.02	732.04	1146.45
	333	12.96	12.63	505.33	419.88	637.82
	353	2.43	2.1	84.02	69.81	100.04
	373	1.49	1.16	46.41	38.56	52.30
	393	1.04	0.71	28.41	23.60	30.38
	423	0.68	0.35	14.00	11.64	13.91

Table 5.2.18: Cyclohexane retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	8.82	8.63	310.42	257.93	337.98
	313	5.98	5.79	208.27	173.05	219.51
	323	4.22	4.03	144.96	120.45	148.05
	333	3.02	2.83	101.80	84.58	100.85
	353	2.05	1.86	59.69	49.59	55.78
	373	1.36	1.17	37.55	31.20	33.21
	393	0.89	0.7	22.46	18.66	18.86
	423	0.61	0.42	13.48	11.20	10.51
10	303	21.3	20.74	391.16	325.01	355.16
	313	14.69	14.13	266.49	221.43	234.23
	323	10.19	9.63	181.62	150.91	154.70
	333	7.62	7.06	133.15	110.64	110.01
	353	1.65	1.09	20.56	17.08	16.02
	373	1.37	0.81	15.28	12.69	11.27
	393	0.92	0.36	6.79	5.64	4.75
	423	0.66	0.1	1.89	1.57	1.23
50	303	10.95	10.78	374.71	311.35	349.11
	313	7.75	7.58	263.48	218.93	237.64
	323	5.38	5.21	181.10	150.48	158.28
	333	3.91	3.74	130.00	108.02	110.21
	353	2.09	1.92	66.74	55.45	23.37
	373	1.25	1.08	37.54	31.19	28.41
	393	0.89	0.72	25.03	20.80	17.98
	423	0.55	0.38	13.21	10.98	8.82
500	303	21.3	20.97	839.01	697.13	1163.85
	313	14.69	14.36	574.54	477.39	771.53
	323	10.19	9.86	394.50	327.79	513.35
	333	7.62	7.29	291.67	242.35	368.15
	353	1.36	1.03	41.21	34.24	49.07
	373	0.92	0.59	23.61	19.61	26.60
	393	0.67	0.34	13.60	11.30	14.55
	423	0.47	0.14	5.60	4.65	5.57

Table 5.2.19: Xylene retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	62.32	62.13	2234.82	1856.91	2433.19
	313	33.64	33.45	1203.20	999.74	1268.15
	323	20.56	20.37	732.71	608.81	748.35
	333	14.56	14.37	516.89	429.48	512.07
	353	6.44	6.25	200.56	166.65	187.44
	373	3.48	3.29	105.58	87.72	93.38
	393	2.42	2.23	71.56	59.46	60.07
	423	1.12	0.93	29.84	24.80	23.28
10	303	157.56	157.00	2961.02	2460.31	2688.50
	313	88.32	87.76	1655.15	1375.27	1454.81
	323	42.36	41.8	788.35	655.04	671.41
	333	27.96	27.4	516.76	429.38	426.93
	353	8.3	7.74	145.98	121.29	113.77
	373	4.25	3.69	69.58	57.83	51.33
	393	2.56	2.00	37.72	31.34	26.41
	423	1.31	0.75	14.15	11.75	9.20
50	303	81.86	81.69	2839.54	2359.38	2645.55
	313	36.21	36.04	1252.75	1040.91	1129.87
	323	26.35	26.18	910.02	756.13	795.35
	333	17.69	17.52	609.00	506.01	516.27
	353	8.06	7.89	274.26	227.88	219.33
	373	4.51	4.34	150.46	125.35	114.17
	393	2.69	2.52	87.60	72.88	62.92
	423	1.34	1.17	40.67	33.79	27.14
500	303	157.56	157.23	6290.77	5227.00	8726.37
	313	88.32	87.99	3520.48	2925.17	4727.48
	323	42.36	42.03	1681.62	1397.26	2188.25
	333	27.96	27.63	1105.48	918.54	1395.33
	353	4.66	4.33	173.24	143.95	206.28
	373	2.49	2.16	86.42	71.81	97.38
	393	1.58	1.25	50.01	41.56	53.49
	423	0.94	0.61	24.41	20.28	24.25

Table 5.2.20: Diethylether retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	1.76	1.57	56.47	46.92	61.49
	313	1.31	1.12	40.29	33.47	42.46
	323	1.02	0.83	29.86	24.81	30.49
	333	0.84	0.65	23.38	19.43	23.16
	353	0.63	0.44	14.12	11.73	13.20
	373	0.54	0.35	11.23	9.33	9.93
	393	0.44	0.25	8.02	6.67	6.73
	423	0.32	0.13	4.17	3.47	3.25
10	303	5.04	4.48	84.49	70.21	76.72
	313	4.06	3.5	66.01	54.85	58.02
	323	3.1	2.54	47.90	39.80	40.80
	333	2.54	1.98	37.34	31.03	30.85
	353	0.78	0.22	4.15	3.45	3.24
	373	0.63	0.14	1.32	1.28	0.97
	393	0.5	0.09	1.13	1.12	0.75
	423	0.4	0.04	1.11	0.9	0.52
50	303	2.51	2.34	81.34	67.58	75.78
	313	1.78	1.61	55.96	46.50	50.47
	323	1.38	1.21	42.06	34.95	36.76
	333	1.09	0.92	31.98	26.57	27.11
	353	0.71	0.54	18.77	15.60	15.01
	373	0.6	0.43	14.95	12.42	11.31
	393	0.48	0.31	10.78	8.95	7.74
	423	0.34	0.17	5.91	4.91	3.94
500	303	5.04	4.71	188.45	156.58	261.41
	313	4.06	3.73	149.24	124.00	200.40
	323	3.1	2.77	110.83	92.02	144.22
	333	2.54	2.21	88.42	73.47	111.61
	353	0.62	0.29	11.60	9.64	13.82
	373	0.52	0.19	7.60	6.32	8.57
	393	0.44	0.11	4.40	3.66	4.71
	423	0.36	0.03	1.20	1.00	1.19

Table 5.2.21: Butyl acetate retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	33.21	33.02	1187.73	986.88	1293.16
	313	19.12	18.93	680.91	565.77	717.67
	323	11.39	11.2	402.86	334.74	411.47
	333	7.03	6.84	246.03	204.43	243.74
	353	3.66	3.47	111.35	92.52	104.06
	373	1.98	1.79	57.44	47.73	50.80
	393	1.12	0.93	29.84	24.80	25.05
	423	0.79	0.6	19.25	16.00	15.02
10	303	93.09	92.53	1745.12	1450.02	1584.50
	313	51.96	51.4	969.40	805.48	852.06
	323	34.92	24.36	648.03	538.45	551.96
	333	22.81	22.25	419.64	348.67	346.69
	353	6.77	6.21	117.12	97.32	91.28
	373	3.16	2.6	49.04	40.74	36.17
	393	1.86	1.3	24.52	20.37	17.16
	423	0.94	0.38	7.17	5.95	4.66
50	303	49.58	49.41	1717.49	1427.06	1600.15
	313	29.63	29.46	1024.03	850.87	923.59
	323	18.38	18.21	632.98	525.94	553.22
	333	11.56	11.39	395.92	328.97	335.64
	353	6.25	6.08	211.34	175.60	169.01
	373	3.36	3.19	110.88	92.13	83.92
	393	1.98	1.81	62.92	52.28	45.19
	423	0.89	0.72	25.03	20.80	16.70
500	303	93.09	92.76	3711.33	3083.74	5148.24
	313	51.96	51.63	2065.72	1716.40	2773.95
	323	34.92	34.59	1383.95	1149.92	1800.90
	333	22.81	22.48	899.42	747.33	1135.25
	353	3.62	3.29	131.63	109.37	156.73
	373	1.89	1.56	62.42	51.86	70.33
	393	1.2	0.87	34.81	28.92	37.23
	423	0.65	0.32	12.80	10.64	12.72

Table 5.2.22: Isobutyl methyl ketone retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	16.21	16.02	576.24	478.80	627.39
	313	8.58	8.39	301.79	250.76	318.08
	323	5.33	5.14	184.89	153.62	188.83
	333	3.57	3.38	121.58	101.02	120.45
	353	2.33	2.14	68.67	57.06	64.18
	373	1.36	1.17	35.55	32.20	33.21
	393	0.84	0.65	20.86	17.33	17.51
	423	0.52	0.33	10.59	8.80	8.26
10	303	45.12	44.56	840.40	698.29	763.06
	313	29.12	28.56	538.64	447.56	473.44
	323	19.14	18.58	350.42	291.16	298.47
	333	12.48	11.92	224.81	186.80	185.73
	353	3.52	2.96	55.83	46.39	43.51
	373	2.34	1.78	33.57	27.89	24.76
	393	1.42	0.86	16.22	13.48	11.35
	423	0.77	0.21	3.96	3.29	2.58
50	303	24.68	24.51	851.97	707.90	793.76
	313	15.64	15.47	537.74	446.81	484.99
	323	10.08	9.91	344.47	286.22	301.07
	333	6.56	6.39	222.12	184.56	188.30
	353	3.36	3.19	110.88	92.13	88.68
	373	2.08	1.89	65.70	54.59	49.72
	393	1.33	1.16	40.32	33.50	28.96
	423	0.77	0.6	20.86	17.33	13.92
500	303	45.12	44.79	1792.05	1489.01	2485.87
	313	29.12	28.79	1151.89	957.10	1546.81
	323	19.14	18.81	752.59	625.33	979.33
	333	12.48	12.15	486.12	403.92	613.58
	353	2.11	1.78	71.22	59.17	84.80
	373	1.27	0.94	37.61	31.25	42.38
	393	0.91	0.58	23.21	19.28	24.82
	423	0.38	0.05	2.00	1.66	1.99

Table 5.2.23: Triethylamine retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	10.76	10.57	380.20	315.91	413.95
	313	7.17	6.98	251.07	208.61	264.62
	323	4.78	4.59	165.10	137.18	168.63
	333	3.31	3.12	112.23	93.25	111.18
	353	1.96	1.77	56.80	47.19	53.08
	373	1.21	1.02	32.73	27.20	28.95
	393	0.82	0.63	20.22	16.80	16.97
	423	0.48	0.29	9.31	7.73	7.26
10	303	26.62	26.06	491.49	408.38	446.26
	313	18.12	17.56	331.18	275.18	291.09
	323	12.6	12.04	227.07	188.68	193.41
	333	8.82	8.26	155.78	129.44	128.70
	353	2.62	2.06	38.85	32.28	30.28
	373	1.69	1.13	21.31	17.71	15.72
	393	1.24	0.68	12.82	10.66	8.98
	423	0.68	0.12	2.26	1.88	1.47
50	303	14.71	14.54	505.41	419.95	470.88
	313	9.67	9.5	330.22	274.38	297.83
	323	6.48	6.31	219.34	182.25	191.70
	333	4.58	4.41	153.29	127.37	129.95
	353	2.51	2.34	81.34	67.58	65.05
	373	1.68	1.51	52.49	43.61	39.72
	393	1.09	0.92	31.98	26.57	22.97
	423	0.6	0.43	14.95	12.42	22.97
500	303	26.62	26.29	1051.86	873.99	1459.11
	313	18.12	17.79	711.78	591.42	955.81
	323	12.6	12.27	490.92	407.91	638.83
	333	8.82	8.49	339.68	282.24	428.75
	353	1.53	1.2	48.01	39.89	57.17
	373	0.95	0.62	24.81	20.61	27.95
	393	0.70	0.37	14.80	12.30	15.83
	423	0.45	0.12	4.80	3.99	4.77

Table 5.2.24: Ethyl methyl ketone retention times and volumes

Viscosity of PDMS (cS)	Temp (K)	Mean values (five measurements were made)				
		t_R	t'_R	V_R	V_N	V_g
5	303	4.04	3.85	138.48	115.07	150.78
	313	2.84	2.65	95.32	79.20	100.47
	323	1.99	1.8	64.75	53.80	66.13
	333	1.37	1.18	42.44	35.27	46.21
	353	1.32	1.13	36.26	30.13	33.89
	373	0.99	0.8	25.67	21.33	22.71
	393	0.82	0.63	20.22	16.80	16.97
	423	0.54	0.35	11.23	9.33	8.76
10	303	10.54	9.98	188.22	156.39	170.90
	313	7.9	7.34	138.43	115.02	121.68
	323	5.7	5.14	96.94	80.55	82.57
	333	4.22	3.66	69.03	57.36	62.67
	353	1.25	0.69	13.01	10.81	10.14
	373	0.78	0.22	4.15	3.45	3.06
	393	0.66	0.11	1.89	1.57	1.32
	423	0.49	0.09	1.51	1.21	1.19
50	303	5.73	5.56	193.27	160.58	180.06
	313	4.31	4.14	143.91	119.57	129.79
	323	3.02	2.85	99.07	82.31	86.58
	333	2.18	2.01	69.87	58.05	59.23
	353	1.24	1.07	37.19	30.90	29.74
	373	0.79	0.62	21.55	17.91	16.31
	393	0.58	0.41	14.25	11.84	10.24
	423	0.39	0.22	7.65	6.35	5.10
500	303	10.54	10.21	408.50	339.42	566.66
	313	7.9	7.57	302.88	251.66	406.72
	323	5.7	5.37	214.85	178.52	279.58
	333	4.22	3.89	155.64	129.32	215.90
	353	0.92	0.59	23.61	19.61	28.11
	373	0.7	0.37	14.80	12.30	16.68
	393	0.52	0.19	7.60	6.32	8.13
	423	0.4	0.07	2.80	2.33	2.78

Table 5.2.25: Volatile Organic Compounds Specific Retention Volumes at 303.15K.

Solute code	Poly(dimethylsiloxane viscosity)				Literature values
	5 cS	10 cS	50 cS	500 cS	
1	159.00	188.20	198.20	190.97	181.7 (2)
2	61.09	75.18	78.05	69.91	66.11 (2)
3	173.49	202.58	205.65	191.98	179.9 (2)
4	461.73	545.75	546.99	508.25	482.5 (2)
5	59.92	73.29	65.09	68.80	
6	782.02	796.45	813.19	852.27	791.1 (2)
7	337.98	355.16	349.11	336.80	315.10 (2)
8	2443.19	2688.50	2645.55	2452.52	2654.60 (1)
9	61.49	76.72	75.78	79.80	
10	1293.16	1584.50	1600.15	1703.99	
11	627.39	763.06	793.76	814.55	
12	413.95	446.26	470.88	469.14	
13	150.78	170.90	180.06	173.57	

Table 5.2.26: Volatile Organic Compounds Specific Retention Volumes at 313.15K.

Solute code	Poly(dimethylsiloxane) viscosity				Literature values
	5 cS	10 cS	50 cS	500 cS	
1	105.77	132.45	131.36	126.23	
2	45.11	55.86	56.43	47.81	43.65(2) 47.60(4)
3	124.73	142.07	140.14	126.23	114.8(1) 124.2(4)
4	294.57	361.38	348.30	301.34	290.8(1)
5	44.36	50.06	42.32	48.34	
6	471.24	496.98	500.04	529.08	463.7(1) 516.6 (4)
7	219.51	234.23	158.28	230.43	
8	1268.15	1454.81	1129.87	1223.61	1187.50
9	42.46	58.02	50.47	55.33	
10	717.67	852.06	923.59	912.60	
11	318.08	473.44	484.99	503.30	
12	264.62	291.09	297.83	306.53	
13	100.47	121.68	129.79	124.77	

Key 1- Summers, Tewari and Schreiber (1972) 2-Ashworth et al (1984)
3- Deshpande, Patterson, Schreiber and Su (1974)
4- Lictenthaler, Newman, Prausnitz (1973) 5- Galin (1977)

Table 5.2.27: Volatile Organic Compounds Specific Retention Volumes at 323.15 K.

Solute code	Poly(dimethylsiloxane) viscosity				Literature values
	5 cS	10 cS	50 cS	500 cS	
1	72.37	88.67	89.62	85.88	
2	34.17	39.68	40.71	35.39	
3	82.66	95.90	95.39	87.97	
4	191.77	231.80	222.08	201.96	
5	28.89	35.34	28.25	35.39	
6	300.15	350.03	304.41	370.60	269.20 (3)
7	148.05	154.70	158.28	144.18	
8	858.57	671.47	795.35	688.64	
9	30.49	40.80	36.76	39.04	
10	411.47	551.96	553.22	588.70	
11	188.83	298.47	301.07	314.55	
12	168.83	193.41	191.70	201.32	
13	66.13	82.57	86.58	88.73	

Table 5.2.28: Volatile Organic Compounds Specific Retention Volumes at 333.15K.

Solute code	Poly(dimethylsiloxane) viscosity				Literature values
	5 cS	10 cS	50 cS	500 cS	
1	49.53	64.20	61.59	59.05	
2	24.94	29.14	29.17	26.79	24.76 (5)
3	58.80	67.00	65.42	57.05	60.91(5)
4	127.22	153.95	146.75	134.31	144.30 (4)
5	18.89	26.18	20.92	26.25	
6	199.20	193.21	175.33	201.45	
7	100.85	110.01	110.21	103.40	106 (5)
8	512.07	426.93	516.27	403.40	536.50 (4)
9	23.16	30.85	27.11	27.77	
10	243.74	346.69	335.64	367.55	
11	120.45	185.73	188.30	193.37	
12	111.18	128.70	129.95	131.70	
13	46.21	62.67	65.09	59.89	

Table 5.2.29: Volatile Organic Compounds Specific Retention Volumes at 353.15K.

Solute code	Poly(dimethylsiloxane) viscosity				Literature values
	5 cS	10 cS	50 cS	500 cS	
1	25.79	33.51	34.47	33.35	
2	15.29	15.87	15.84	16.67	
3	32.69	32.63	34.75	30.49	
4	63.58	74.67	69.17	66.22	
5	14.10	13.23	11.95	12.39	
6	95.37	92.90	95.35	100.04	
7	55.78	56.15	57.82	56.69	
8	187.38	179.03	213.77	203.42	
9	13.20	18.67	16.12	16.67	
10	104.06	141.84	137.60	150.06	
11	64.18	86.72	85.90	88.61	
12	53.08	62.62	64.21	64.79	
13	33.89	41.04	34.19	38.59	

Table 5.2.30: Volatile Organic Compounds Specific Retention Volumes at 373.15K.

Solute code	Poly(dimethylsiloxane) viscosity				Literature values
	5 cS	10 cS	50 cS	500 cS	
1	13.34	17.81	18.15	17.58	
2	9.93	9.74	10.79	10.37	
3	18.73	19.06	18.42	18.48	
4	36.33	37.42	35.52	35.62	
5	9.93	7.65	8.42	7.21	
6	50.24	49.94	51.30	52.30	
7	33.21	31.44	32.62	32.01	
8	93.38	94.06	111.81	95.58	
9	9.93	11.96	10.26	10.37	
10	50.80	67.19	65.24	70.33	
11	33.21	42.43	42.62	44.18	
12	28.95	33.66	34.73	36.52	
13	22.71	31.30	25.52	28.40	

Table 5.2.31: Volatile Organic Compounds Specific Retention Volumes at 393.15K.

Solute code	Poly(dimethylsiloxane) viscosity				Literature values
	5 cS	10 cS	50 cS	500 cS	
1	9.16	12.54	11.74	12.41	
2	7.00	6.07	7.74	7.27	
3	11.88	11.62	11.74	10.70	
4	21.55	21.65	22.22	20.97	
5	7.81	4.49	5.24	4.28	
6	28.82	28.12	36.45	30.38	
7	18.86	17.82	18.73	18.40	
8	60.07	48.19	57.68	49.64	
9	6.73	8.19	6.74	7.27	
10	25.05	34.06	33.46	37.23	
11	17.51	23.63	23.72	24.39	
12	16.97	18.22	19.48	18.83	
13	16.97	22.97	18.48	19.26	

Table 5.2.32: Volatile Organic Compounds Specific Retention Volumes at 423.15K.

Solute code	Poly(dimethylsiloxane) viscosity				Literature values
	5 cS	10 cS	50 cS	500 cS	
1	4.50	6.87	6.50	6.76	
2	4.25	3.93	4.41	4.37	
3	6.51	6.38	6.50	6.76	
4	10.76	11.16	12.29	10.73	
5	4.25	2.21	2.78	1.99	
6	14.52	14.11	14.15	15.11	
7	10.51	9.69	10.21	9.94	
8	23.28	21.83	26.21	22.26	
9	3.25	4.42	3.71	3.98	
10	15.02	20.24	19.72	21.07	
11	8.26	11.28	11.37	11.93	
12	7.26	7.61	8.12	7.95	
13	8.76	12.51	9.98	10.73	

Table 5.2.33: Static and GLC Solute Mole- and Weight – Fraction Based Activity Coefficients at Infinite Dilution with PDMS at 303.15K.

Solute	Static 10 cS PDMS	GLC							
		Column 1 5 cS PDMS		Column 11 10 cS PDMS		Column 111 50 cS PDMS		Column 1V 500 cS PDMS	
	$^{w}\gamma_1^{\infty}$	$^{x}\gamma_1^{\infty}$	$^{w}\gamma_1^{\infty}$	$^{x}\gamma_1^{\infty}$	$^{w}\gamma_1^{\infty}$	$^{x}\gamma_1^{\infty}$	$^{w}\gamma_1^{\infty}$	$^{x}\gamma_1^{\infty}$	$^{w}\gamma_1^{\infty}$
1	3.557	0.583	3.708	0.374	3.133	0.111	2.975	0.028	3.088
2	5.384	0.599	6.308	0.384	5.323	0.116	5.127	0.032	5.724
3	5.833	0.704	6.208	0.458	5.317	0.141	5.237	0.037	5.610
4	7.340	0.839	6.361	0.539	5.382	0.168	5.369	0.045	5.779
5	17.669	1.392	18.219	0.865	14.895	0.304	16.772	0.071	15.868
6	6.080	0.785	6.472	0.585	6.354	0.179	6.224	0.042	5.938
7	4.720	0.551	4.979	0.399	4.738	0.127	4.820	0.032	4.996
8	7.587	0.893	6.391	0.617	5.808	0.205	6.186	0.052	6.367
9	8.413	0.590	6.050	0.359	4.849	0.114	4.909	0.027	4.662
10	7.401	1.205	7.885	0.748	6.435	0.231	6.372	0.053	5.984
11	10.942	1.346	10.212	0.841	8.396	0.253	8.072	0.061	7.865
12	5.187	0.557	4.181	0.392	3.878	0.116	3.676	0.029	3.689
13	7.381	1.102	11.612	0.739	10.245	0.219	9.724.	0.056	10.088

Table 5.2.34: GLC Solute Mole- and Weight- Fraction Based Activity Coefficients at Infinite Dilution with PDMS at 313.15K.

Solute	Column 1 5 cS PDMS		Column 11 10 cS PDMS		Column 111 50 cS PDMS		Column 1V 500 cS PDMS	
	$^{x}\gamma_1^{\infty}$	$^{w}\gamma_1^{\infty}$	$^{x}\gamma_1^{\infty}$	$^{w}\gamma_1^{\infty}$	$^{x}\gamma_1^{\infty}$	$^{w}\gamma_1^{\infty}$	$^{x}\gamma_1^{\infty}$	$^{w}\gamma_1^{\infty}$
1	0.591	3.763	0359	3.005	0.113	3.030	0.029	3.153
2	0.604	6.364	0.371	5.139	0.115	5.087	0.033	6.004
3	0.660	5.823	0.441	5.113	0.140	5.183	0.038	5.754
4	0.833	6.321	0.516	5.152	0.167	5.369	0.048	6.179
5	1.307	17.105	0.880	15.157	0.325	17.929	0.070	15.696
6	0.809	6.677	0.583	6.331	0.181	6.292	0.042	5.947
7	0.562	5.076	0.400	4.757	0.123	4.689	0.031	4.835
8	0.939	6.720	0.622	5.857	0.214	6.462	0.057	6.964
9	0.605	6.204	0.337	4.540	0.121	5.219	0.027	4.761
10	1.257	8.222	0.804	6.925	0.232	6.389	0.058	6.466
11	1.633	12.395	0.834	8.327	0.254	8.129	0.060	7.833
12	0.560	4.205	0.387	3.823	0.118	3.736	0.028	3.630
13	1.198	12.625	0.752	10.424	0.220	9.773	0.056	10.166

Table 5.2.35: GLC Solute Mole- and Weight- Fraction Based Activity Coefficients at Infinite Dilution with PDMS at 323.15K.

Solute	Column 1 5 cS PDMS		Column 11 10 cS PDMS		Column 111 50 cs PDMS		Column 1V 500 cS PDMS	
	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$
1	0.605	3.851	0.375	3.143	0.116	3.110	0.030	3.246
2	0.587	6.187	0.384	5.328	0.117	5.193	0.033	5.974
3	0.700	6.174	0.459	5.321	0.144	5.350	0.038	5.801
4	0.840	6.372	0.528	5.272	0.172	5.502	0.047	6.051
5	1.348	17.645	0.838	14.425	0.328	18.045	0.064	14.404
6	0.819	6.756	0.534	5.793	0.192	6.661	0.039	5.472
7	0.569	5.139	0.414	4.918	0.126	4.807	0.034	5.277
8	0.843	6.038	0.820	7.721	0.216	6.518	0.061	7.528
9	0.616	6.313	0.350	4.717	0.121	5.236	0.028	4.930
10	1.319	8.632	0.747	6.435	0.233	6.420	0.054	6.033
11	1.744	13.234	0.839	8.373	0.260	8.301	0.061	7.945
12	0.581	4.363	0.385	3.804	0.121	3.838	0.028	3.654
13	1.229	12.954	0.748	10.375	0.223	9.894	0.054	9.654

Table 5.2.36: GLC Solute Mole- and Weight- Fraction Based Activity Coefficients at Infinite Dilution with PDMS at 333.15K.

Solute	Column 1 5 cS PDMS		Column 11 10 cS PDMS		Column 111 50 cS PDMS		Column 1V 500 cS PDMS	
	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$
1	0.616	3.922	0.361	3.026	0.118	3.154	0.030	3.289
2	0.596	6.272	0.388	5.371	0.121	5.366	0.032	5.842
3	0.694	6.124	0.463	5.374	0.148	5.504	0.042	6.311
4	0.857	6.499	0.538	5.370	0.176	5.634	0.047	6.156
5	1.398	18.297	0.767	13.022	0.300	16.522	0.059	13.167
6	0.821	6.769	0.643	6.979	0.195	6.769	0.047	6.694
7	0.588	5.306	0.409	4.864	0.128	4.855	0.033	5.175
8	0.892	6.386	0.813	7.660	0.229	6.901	0.066	8.106
9	0.603	6.179	0.344	4.639	0.122	5.278	0.029	4.930
10	1.384	9.054	0.739	6.365	0.239	6.575	0.054	6.004
11	1.785	13.547	0.880	8.786	0.271	8.666	0.065	8.439
12	0.599	4.499	0.393	3.886	0.122	3.849	0.029	3.798
13	1.254	13.211	0.702	9.742	0.211	9.379	0.057	10.194

Table 5.2.37: GLC Solute Mole- and Weight- Fraction Based Activity Coefficients at Infinite Dilution with PDMS at 353.15K.

Solute	Column 1 5 cS PDMS		Column 11 10 cS PDMS		Column 111 50 cS PDMS		Column 1V 500 cS PDMS	
	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$
1	0.671	4.2736	0.393	3.288	0.119	3.197	0.030	3.304
2	0.596	6.282	0.437	6.052	0.137	6.063	0.032	5.761
3	0.685	6.042	0.522	5.053	0.153	5.684	0.043	6.478
4	0.858	6.506	0.555	5.540	0.176	5.637	0.048	6.247
5	1.098	14.361	0.889	13.306	0.308	16.945	0.073	16.343
6	0.825	6.803	0.643	6.984	0.196	6.804	0.046	6.462
7	0.606	5.470	0.457	5.434	0.139	5.277	0.035	5.382
8	1.018	7.291	0.812	7.646	0.212	6.403	0.055	6.729
9	0.653	6.700	0.351	4.737	0.127	5.486	0.030	5.305
10	1.328	8.686	0.740	6.373	0.238	5.569	0.054	6.023
11	1.544	11.713	0.868	8.669	0.274	8.752	0.065	8.484
12	0.622	4.673	0.401	3.961	0.122	3.863	0.030	3.828
13	1.216	12.819	0.764	10.594	0.286	12.707	0.062	11.258

Table 5.2.38: GLC Solute Mole- and Weight- Fraction Activity Based Coefficients at Infinite Dilution with PDMS at 373.15K.

Solute	Column 1 5 cS PDMS		Column 11 10 cS PDMS		Column 111 50 cS PDMS		Column 1V 500 cS PDMS	
	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$
1	0.691	4.399	0.393	3.295	0.121	3.234	0.031	3.338
2	0.595	6.266	0.461	6.388	0.130	5.766	0.033	6.000
3	0.715	6.310	0.534	6.201	0.173	6.416	0.045	6.723
4	0.821	6.226	0.606	6.045	0.186	5.929	0.049	6.350
5	0.924	12.091	0.912	15.695	0.259	14.260	0.074	16.653
6	0.826	6.816	0.632	6.857	0.192	6.675	0.046	6.547
7	0.577	5.213	0.463	5.507	0.140	5.307	0.035	5.409
8	1.082	7.746	0.818	7.702	0.215	6.478	0.062	7.578
9	0.562	5.763	0.555	4.785	0.129	5.577	0.031	5.518
10	1.304	8.531	0.749	6.450	0.241	6.643	0.055	6.162
11	1.495	11.344	0.889	8.879	0.277	8.839	0.066	8.527
12	0.618	4.640	0.404	3.991	0.122	3.868	0.031	3.921
13	1.388	14.629	0.765	10.615	0.293	13.019	0.065	11.699

Table 5.2.39: GLC Solute Mole - and Weight- Fraction Based Activity Coefficients at Infinite Dilution with PDMS at 393.15K.

Solute	Column 1 5 cS PDMS		Column 11 10 cS PDMS		Column 111 50 cS PDMS		Column 1V 500 cS PDMS	
	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$
1	0.714	4.547	0.396	3.321	0.132	3.547	0.031	3.356
2	0.590	6.216	0.517	7.168	0.127	5.621	0.033	5.985
3	0.720	6.353	0.560	6.495	0.173	6.429	0.043	6.535
4	0.818	6.204	0.619	6.176	0.188	6.017	0.049	6.376
5	0.723	9.467	0.956	16.467	0.256	14.110	0.077	17.275
6	0.831	6.851	0.647	7.021	0.195	6.787	0.046	6.499
7	0.596	5.378	0.479	5.692	0.142	5.416	0.036	5.513
8	0.872	6.242	0.833	7.842	0.217	6.552	0.062	7.613
9	0.566	5.807	0.354	4.772	0.130	5.631	0.031	5.375
10	1.341	8.777	0.750	6.455	0.239	6.571	0.053	5.906
11	1.587	12.041	0.894	8.922	0.278	8.888	0.067	8.644
12	0.597	4.483	0.423	4.175	0.123	3.905	0.031	4.040
13	1.388	14.628	0.779	10.807	0.303	13.433	0.071	12.889

Table 5.2.40: GLC Solute Mole- and Weight- Fraction Based Activity Coefficients at infinite Dilution with PDMS at 423.15K.

Solute	Column 1 5 cS PDMS		Column 11 10 cS PDMS		Column 111 50 cS PDMS		Column 1V 500 cS PDMS	
	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	${}^{x}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$
1	0.805	5.125	0.401	3.357	0.132	3.548	0.031	3.411
2	0.602	6.343	0.495	6.658	0.138	6.112	0.035	6.225
3	0.744	6.561	0.577	6.695	0.177	6.571	0.045	6.716
4	0.850	6.499	0.623	6.218	0.191	6.013	0.050	6.467
5	0.668	8.742	0.976	16.812	0.243	13.365	0.083	18.671
6	0.836	6.897	0.654	7.097	0.192	6.667	0.047	6.628
7	0.588	5.309	0.485	5.758	0.144	5.465	0.036	5.614
8	1.018	7.290	0.839	7.905	0.218	6.584	0.063	7.752
9	0.640	6.565	0.358	4.827	0.133	5.751	0.031	5.361
10	1.350	8.835	0.762	6.556	0.244	6.729	0.056	6.298
11	1.632	12.385	0.908	9.069	0.282	8.997	0.066	8.575
12	0.583	4.381	0.423	4.180	0.124	3.917	0.031	4.001
13	1.477	15.567	0.786	10.900	0.308	13.664	0.070	12.709

5.3 Figures

This section presents all the results in graphic form. All the graphs will be explained and discussed in the next chapter (chapter six – discussion).

Figure 5.1: Effect of test volume on Henry's law constants and activity coefficients

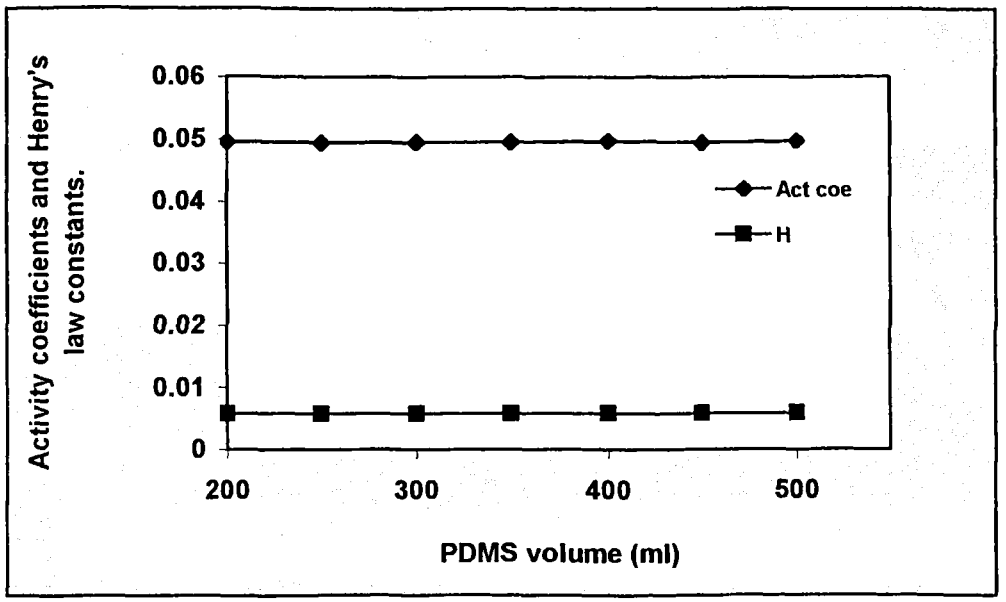


Figure 5.2: Effect of shaking time on Henry's law constants and activity coefficients

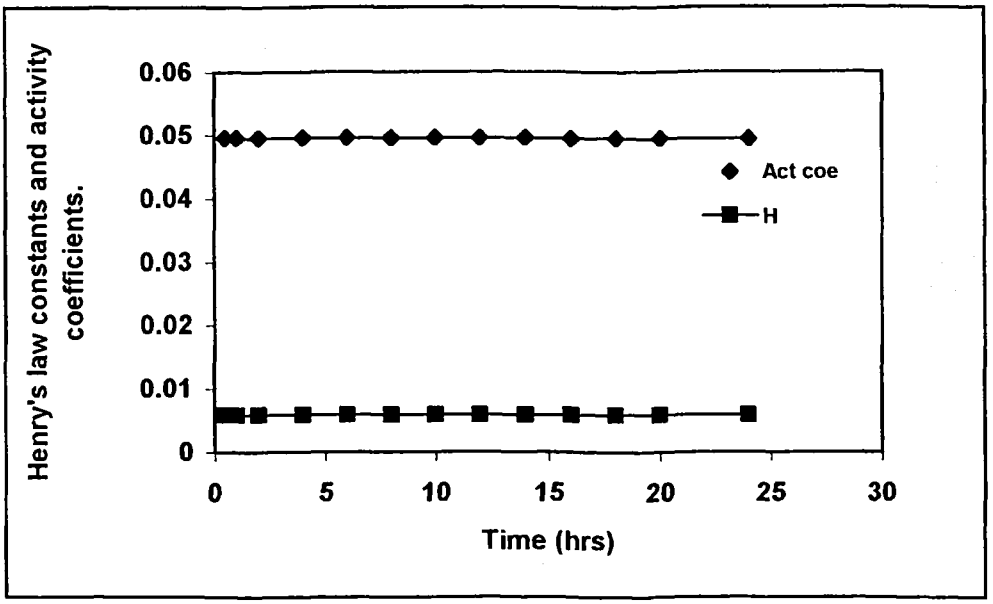


Figure 5.3: Typical Van't Hoff plot for acetone

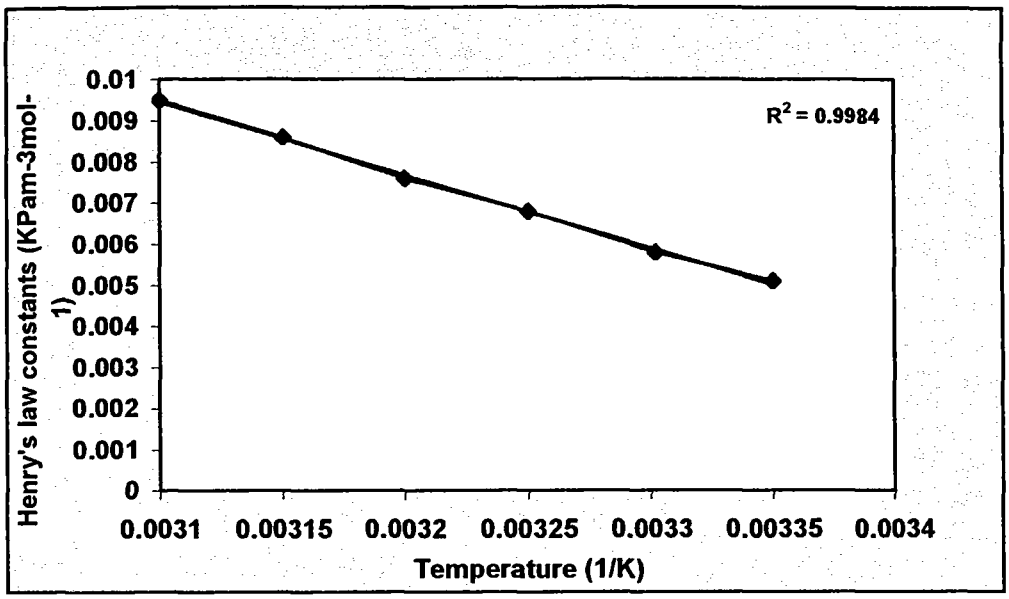


Figure 5.4: Flow rate calibration for 5 cS PDMS column (10 % loading)

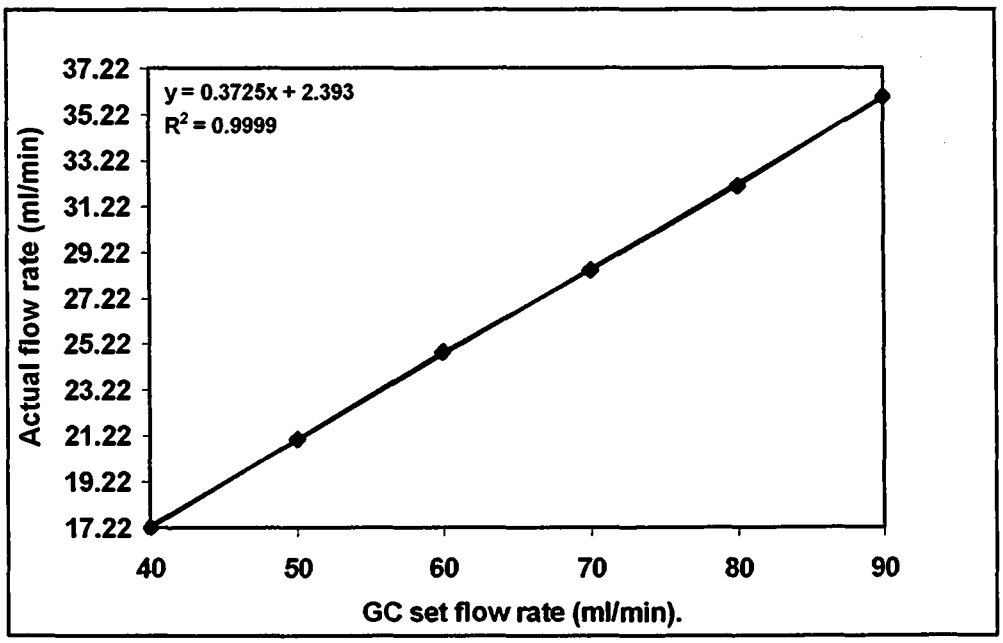


Figure 5.5: Flow rate calibration for 10cS PDMS column (10% Loading).

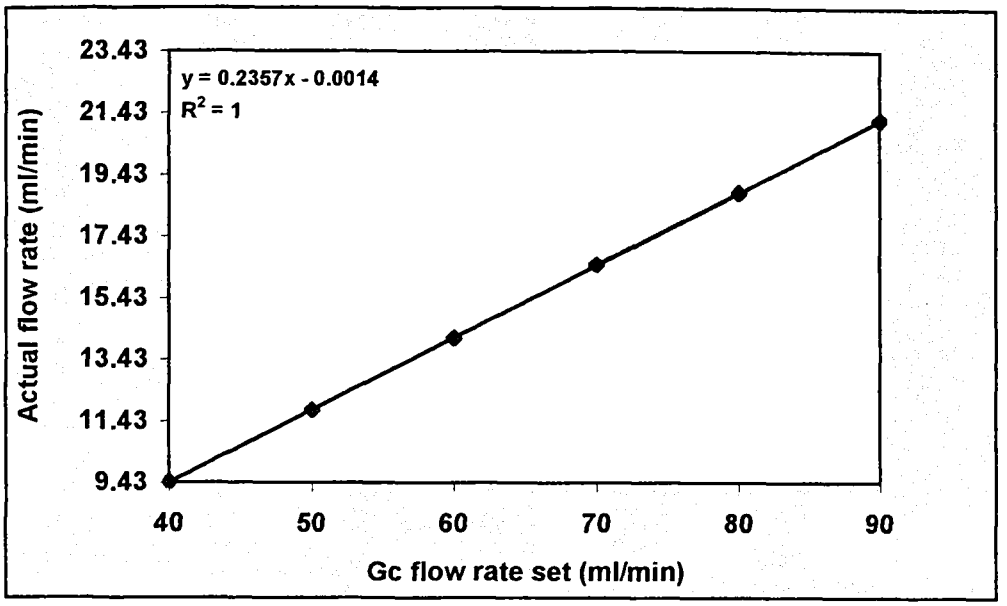


Figure 5.6: Flow rate calibration for 50cS PDMS column (10 % loading)

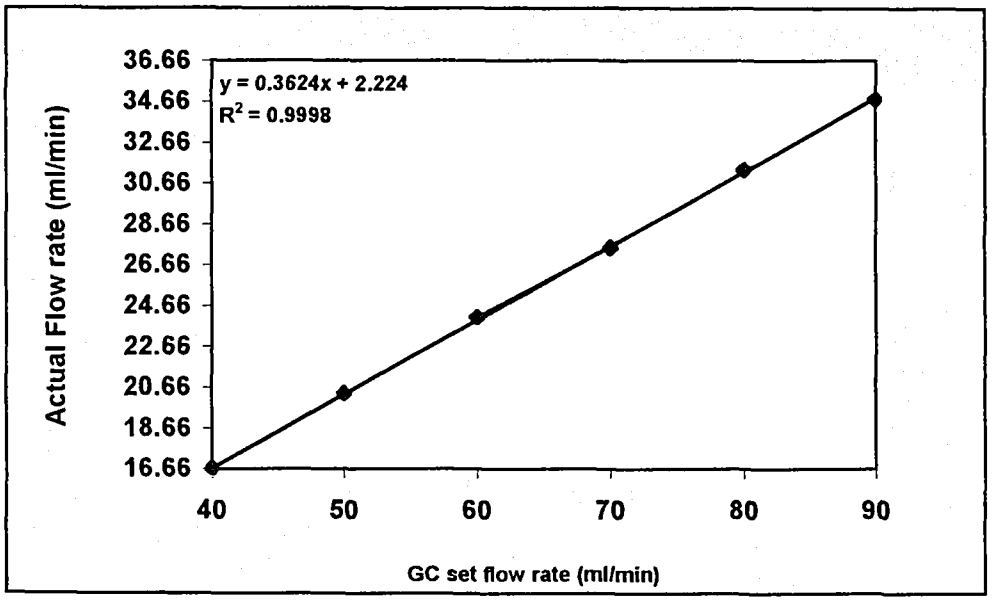


Figure 5.7 Flow rate calibration for 50 cS PDMS column (20% loading)

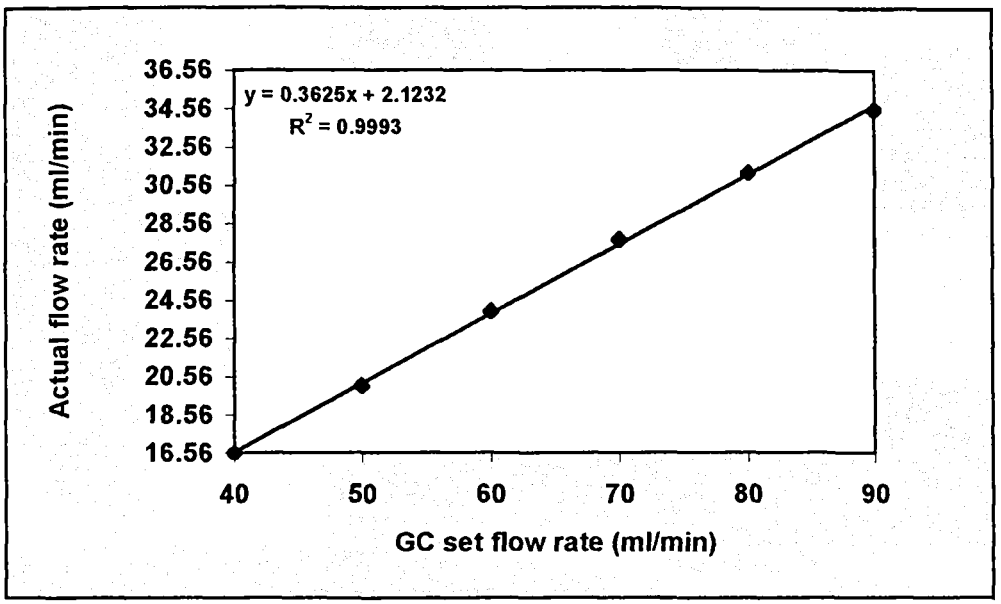


Figure 5.8 Flow rate calibration for 50 cS PDMS column (30% loading)

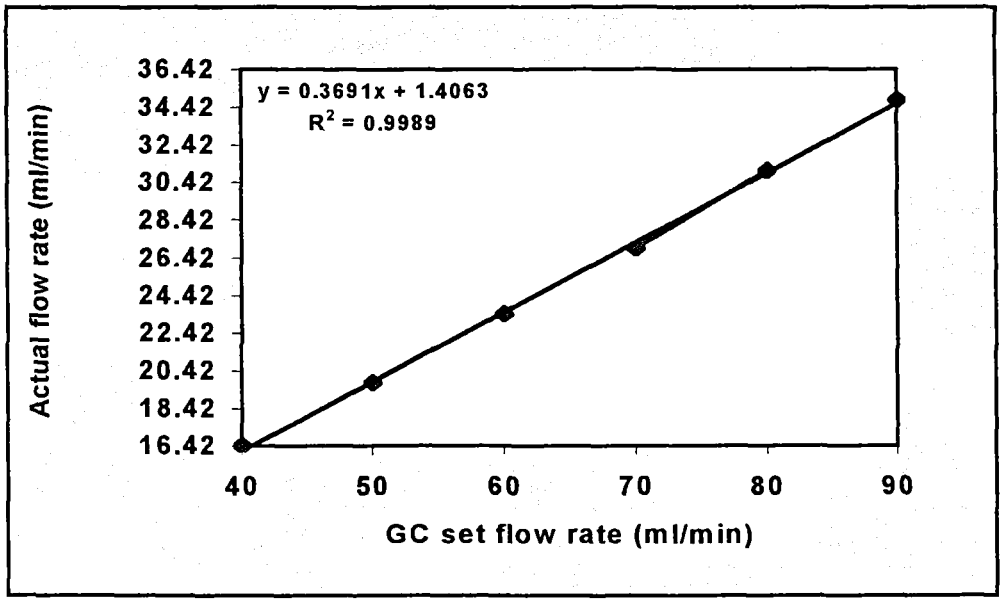


Figure 5.9: Flow rate calibration for 500 cS PDMS column (10% loading

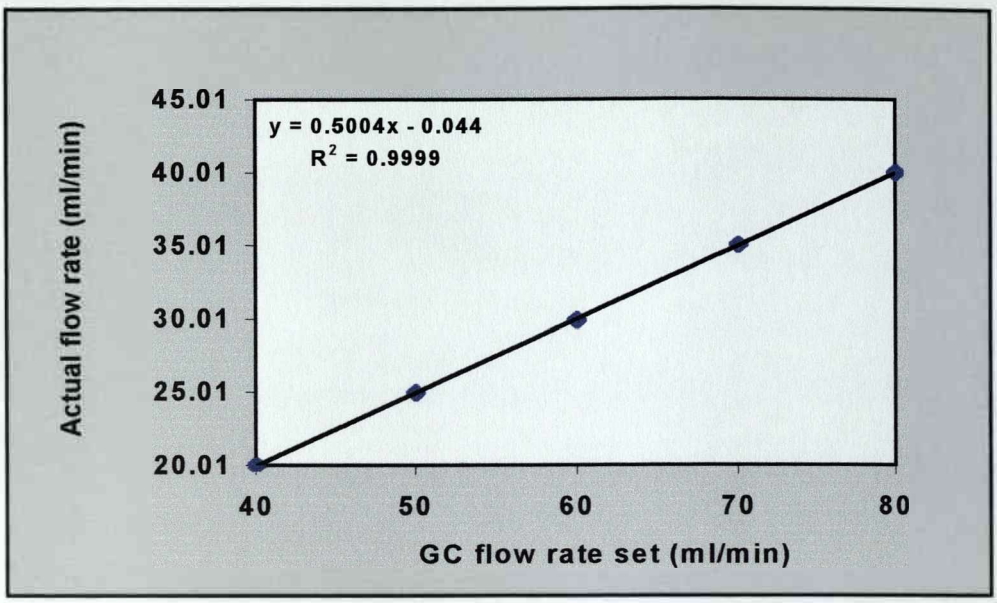


Figure 5.10: Effect of liquid loading on the net retention volume

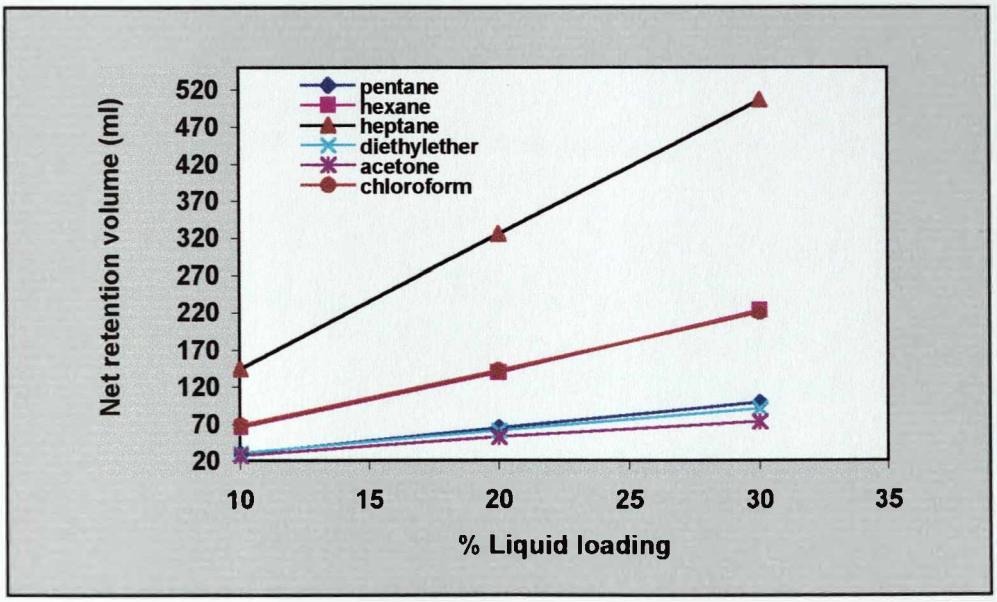


Figure 5.11: Effect of liquid loading on specific retention volume

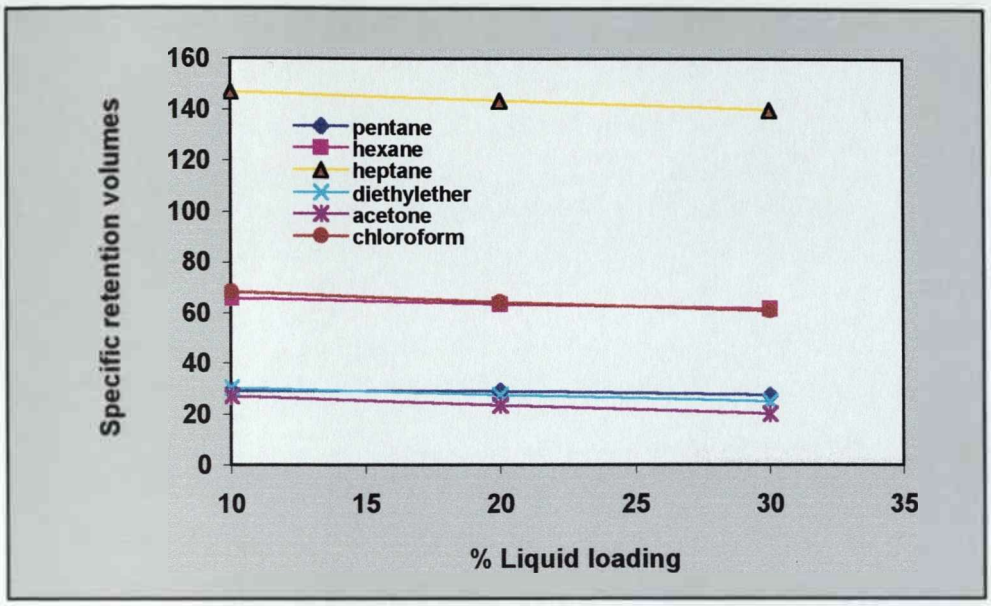


Figure 5.12: Effect of sample size on retention volume

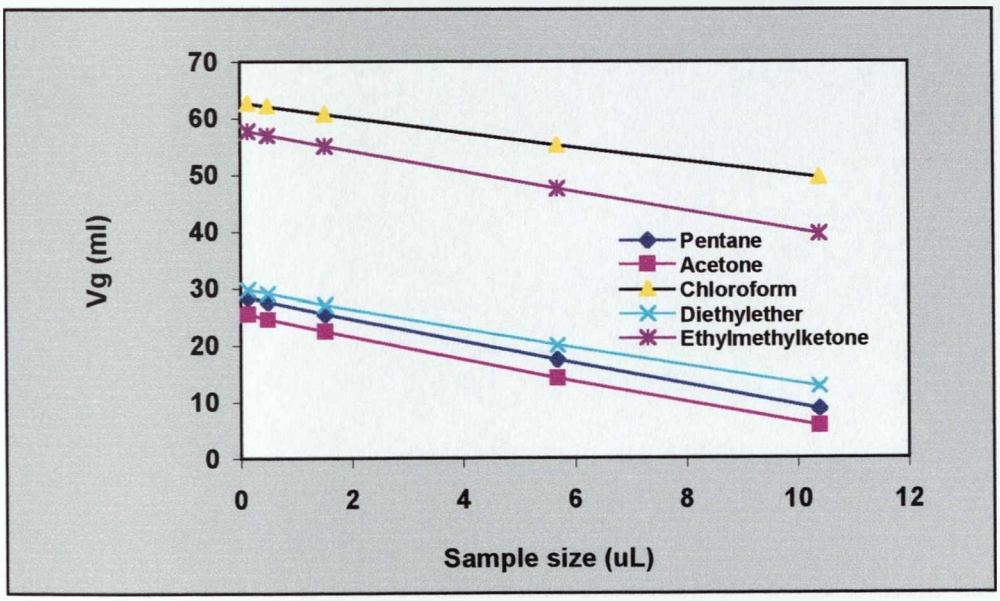


Figure 5.13: Effect of carrier gas flow rate on specific retention volumes

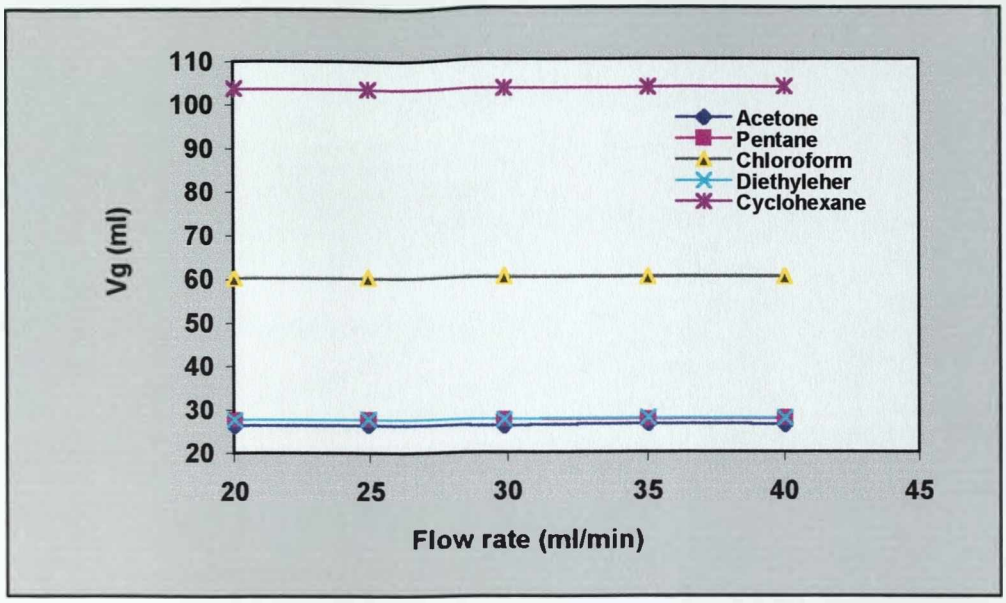


Figure 5.14a: Effect of temperature on specific retention volumes (5 cS PDMS column)

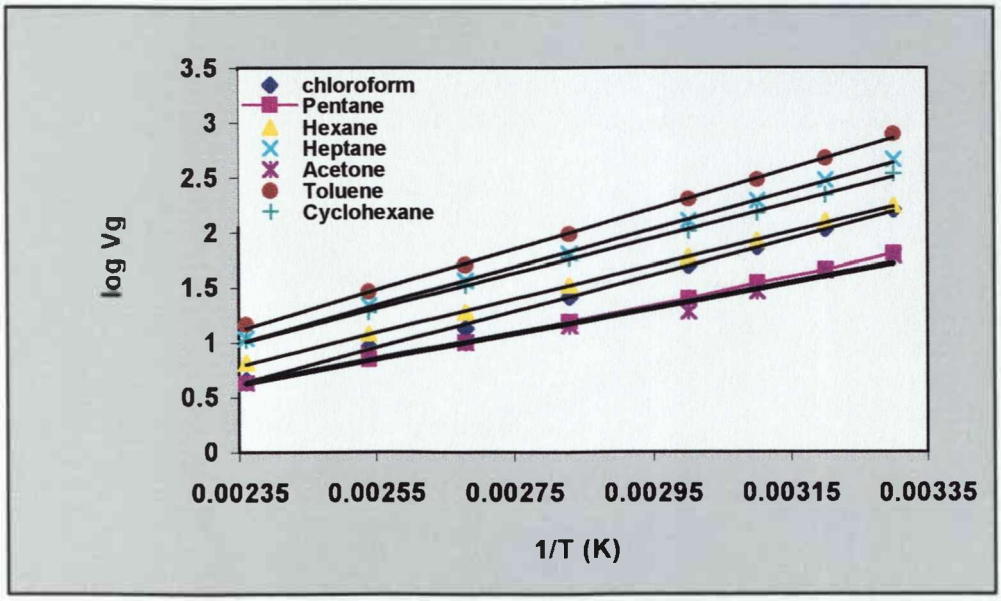


Figure 5.14b: Effect of temperature on specific retention volumes (5 cS PDMS column)

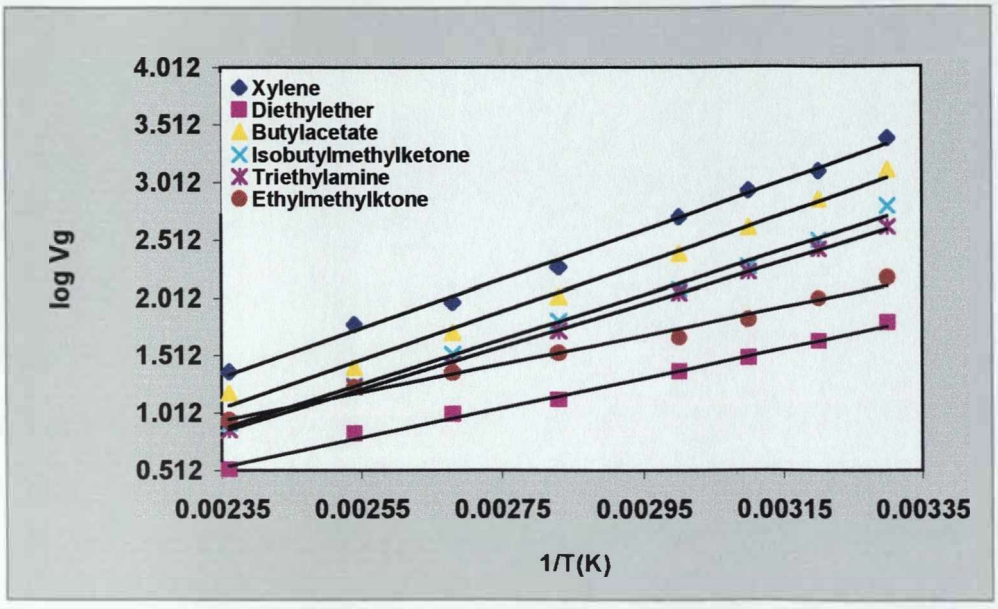


Figure 5.15a: Effect of temperature on specific retention volumes (10 cS PDMS column)

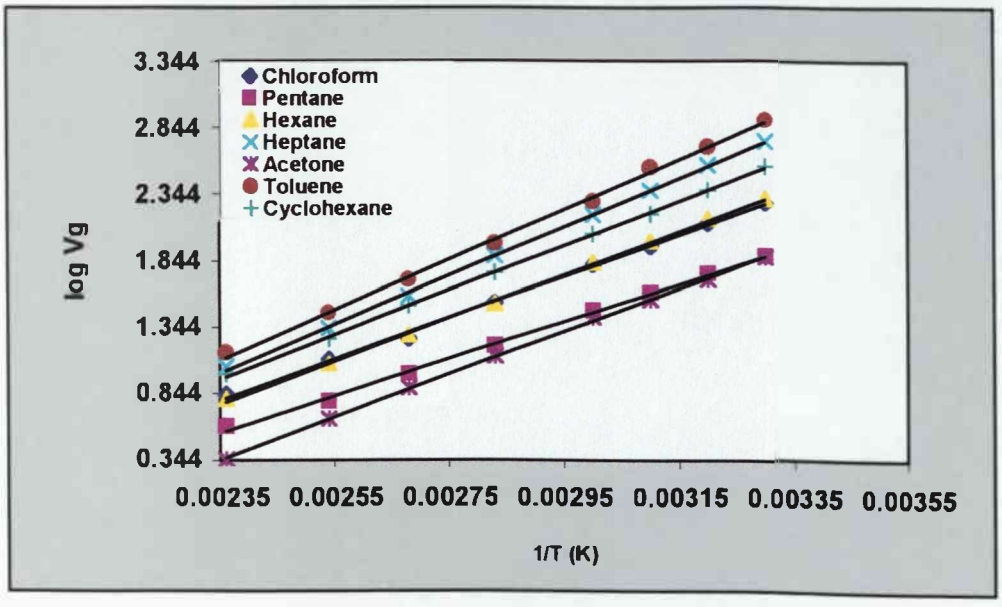


Figure 5.15b: Effect of temperature on specific retention volumes (10 cS PDMS column)

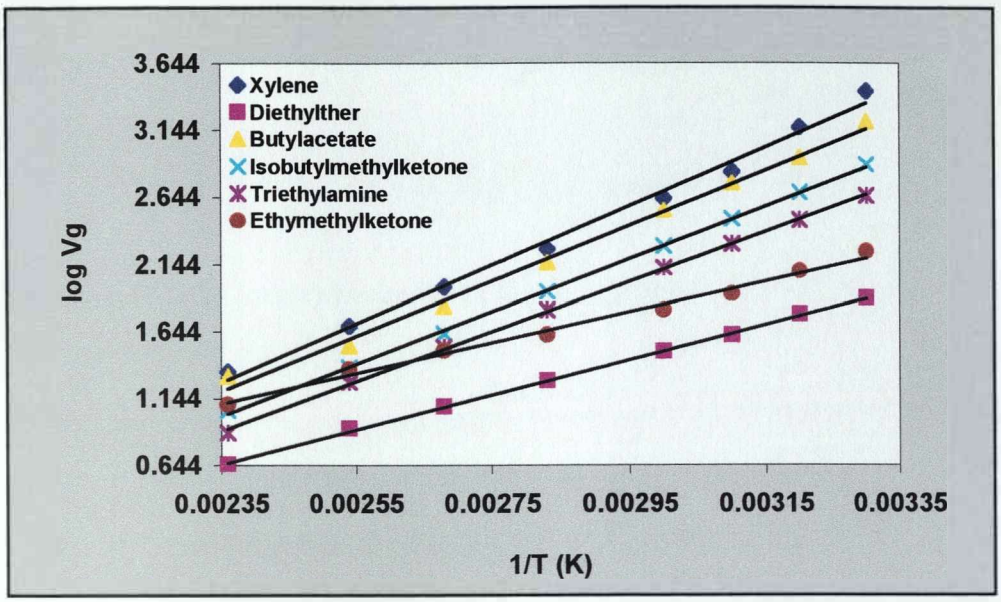


Figure 5.16a: Effect of temperature on specific retention volumes (50 cS PDMS column)

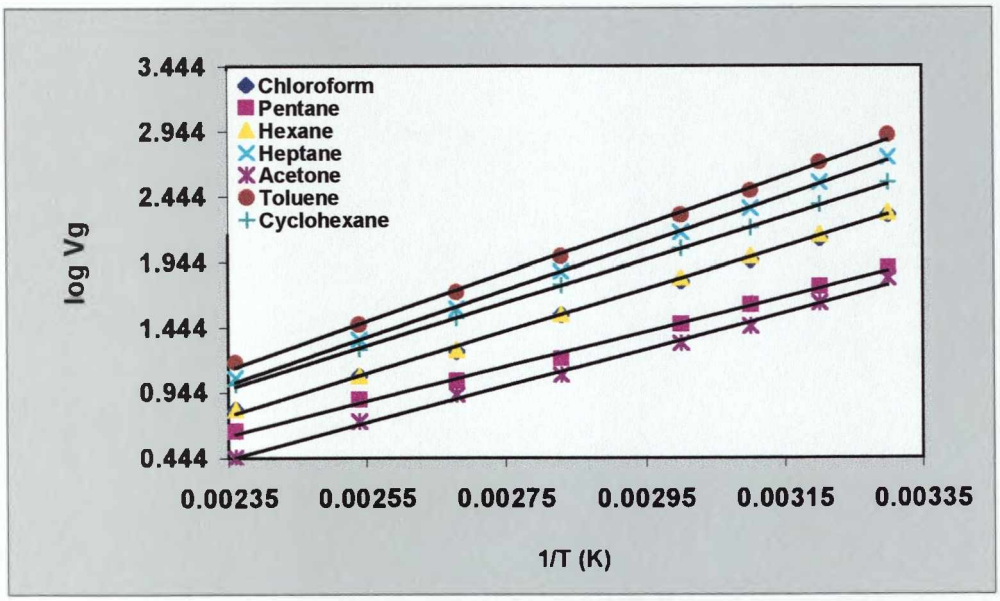


Figure 5.16b: Effect of temperature on specific retention volumes (50 cS PDMS column)

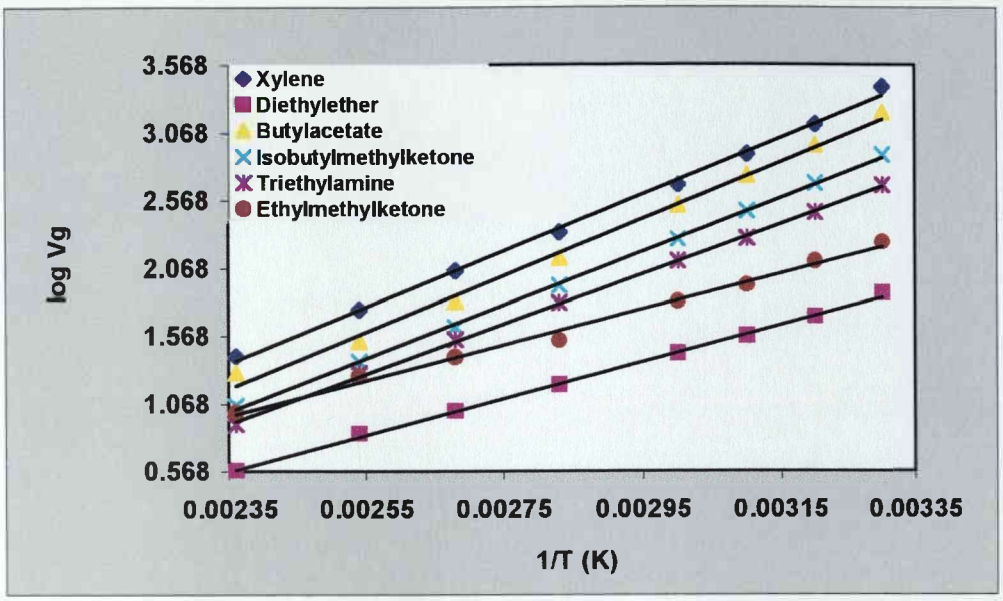


Figure 5.17a: Effect of temperature on specific retention volumes (500 cS PDMS column)

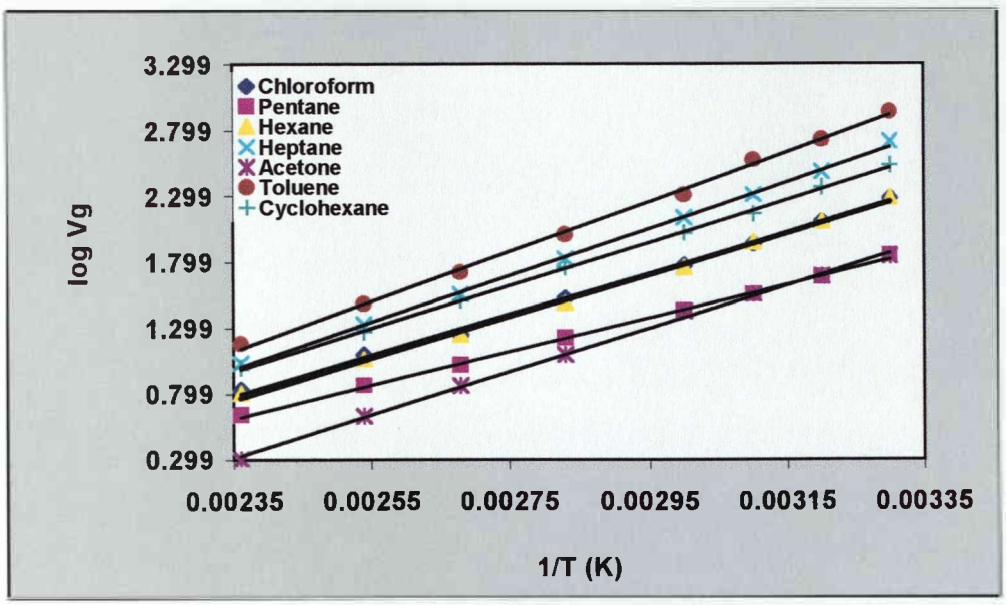


Figure 5.17b: Effect of temperature on specific retention volumes (500 cS PDMS column)

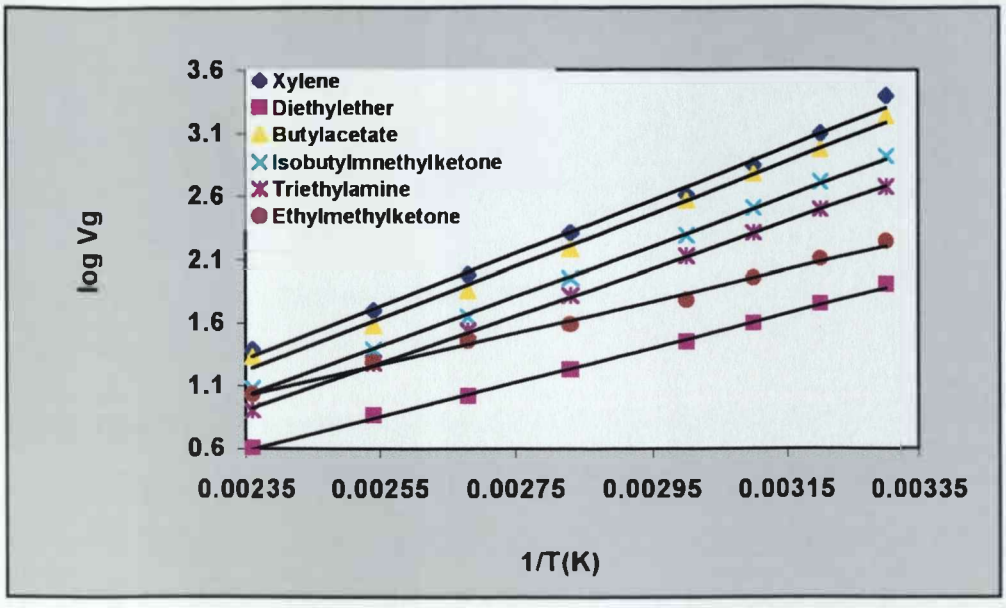


Figure 5.18a: Effect of temperature on activity coefficients (5 cS PDMS column)

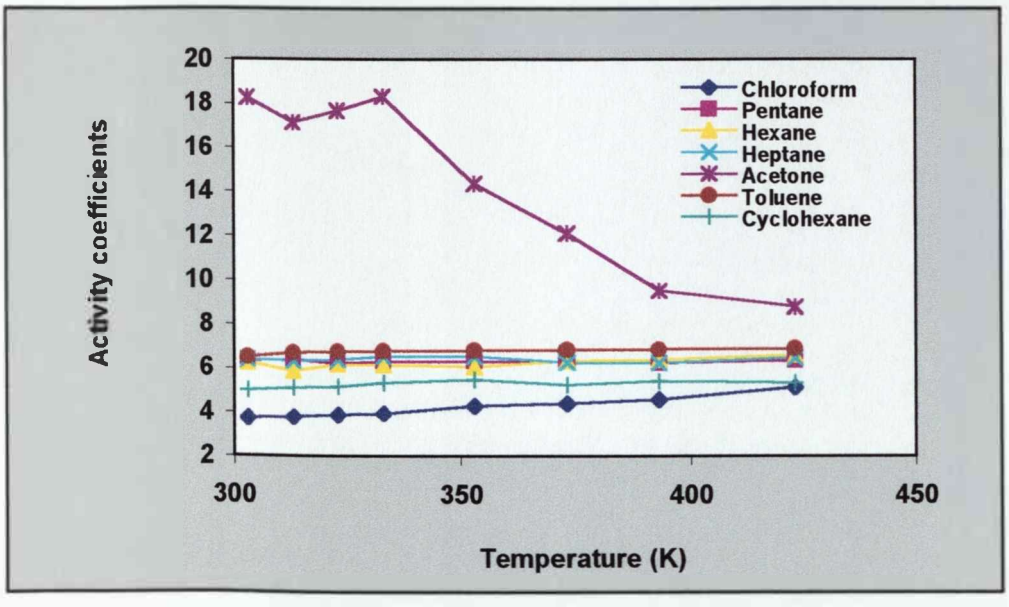


Figure 5.18b: Effect of temperature on activity coefficients (5 cS PDMS column)

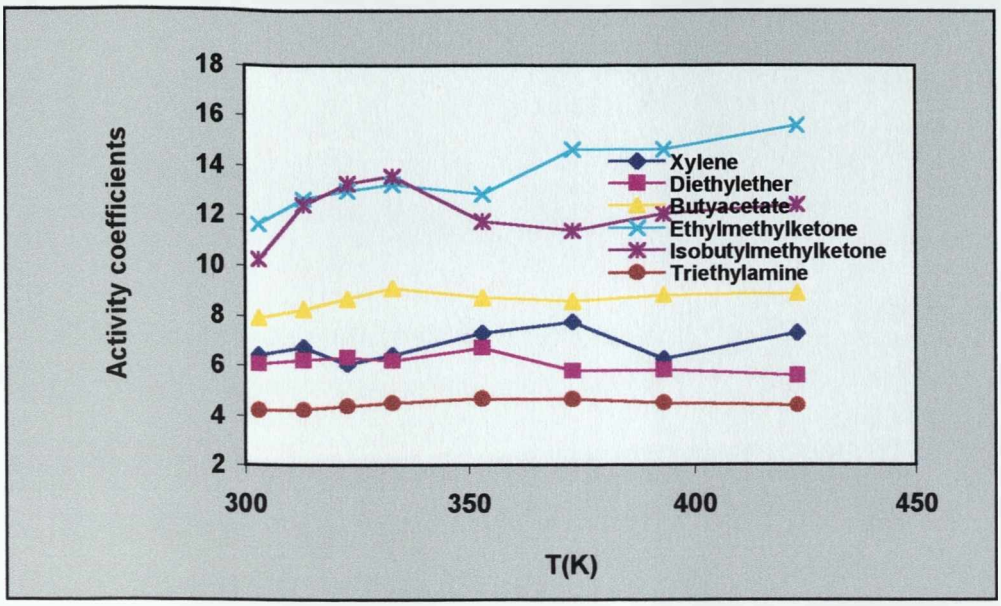


Figure 5.19a: Effect of temperature on activity coefficients (10 cS PDMS column)

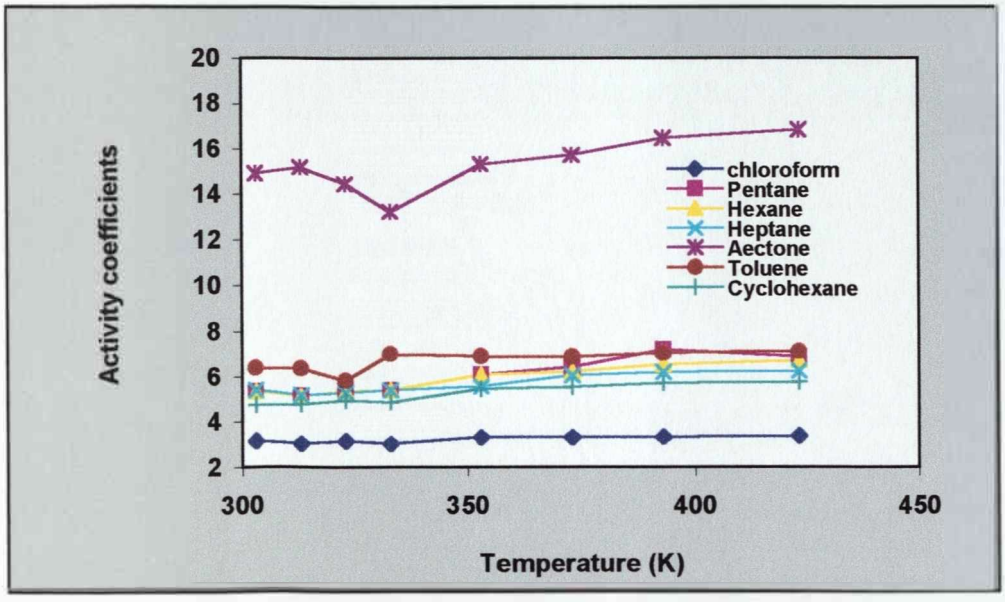


Figure 5.19b: Effect of temperature on activity coefficients (10 cS PDMS column)

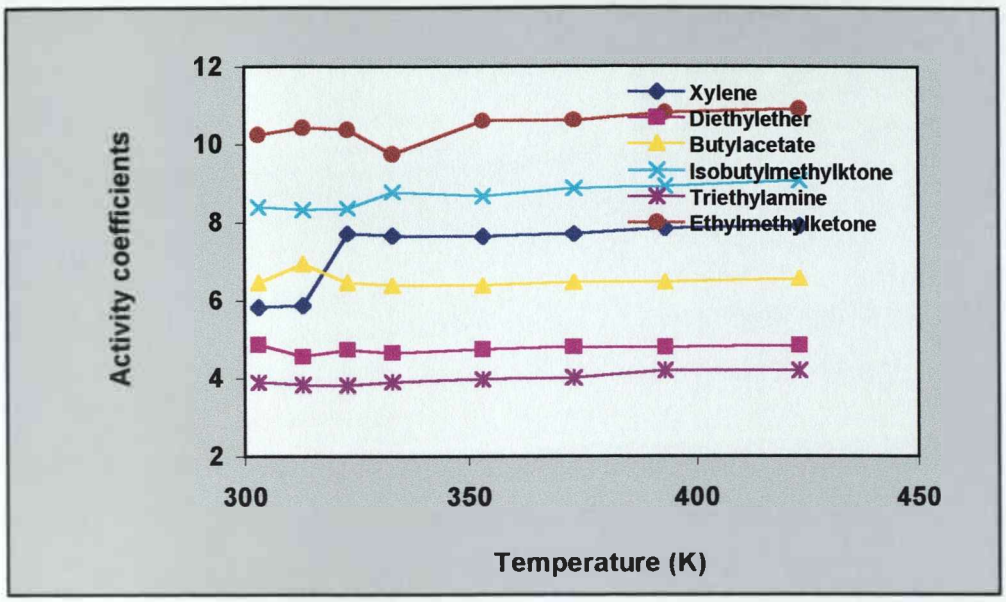


Figure 5.20a: Effect of temperature on activity coefficients (50 cS PDMS column)

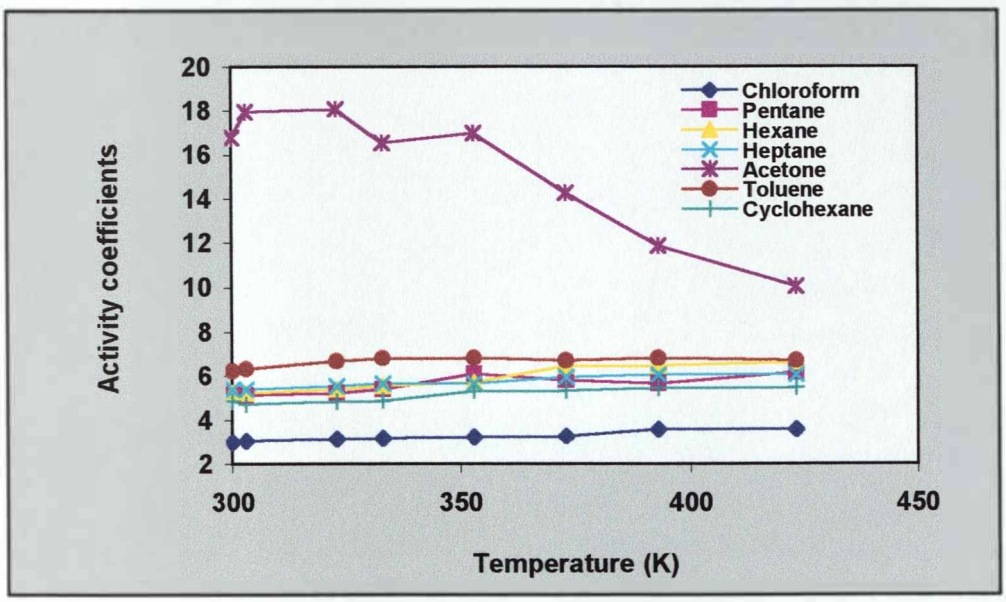


Figure 5.20b: Effect of temperature on activity coefficients (50 cS PDMS column)

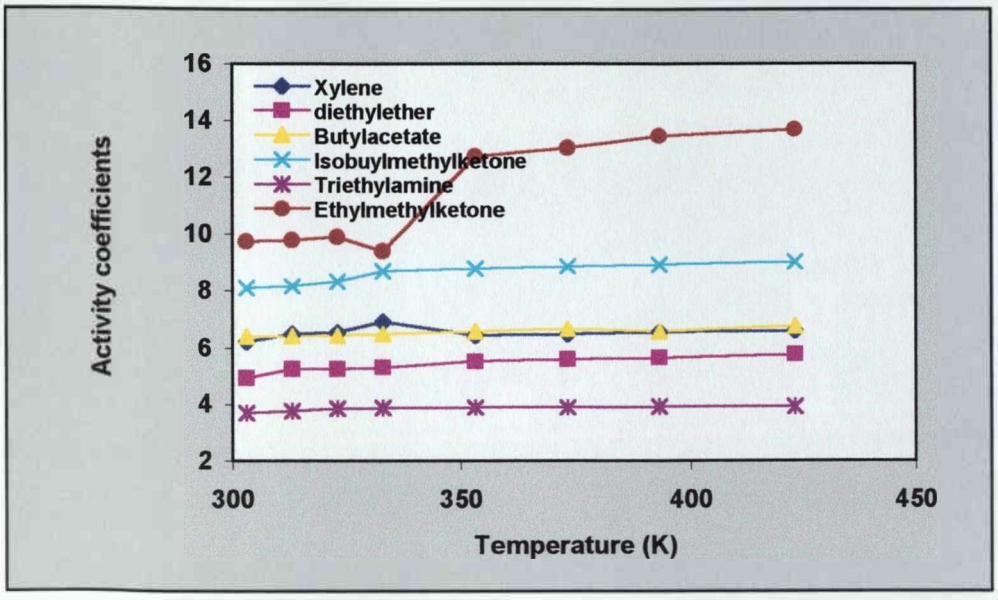


Figure 5.21a: Effect of temperature on activity coefficients (500 cS PDMS column)

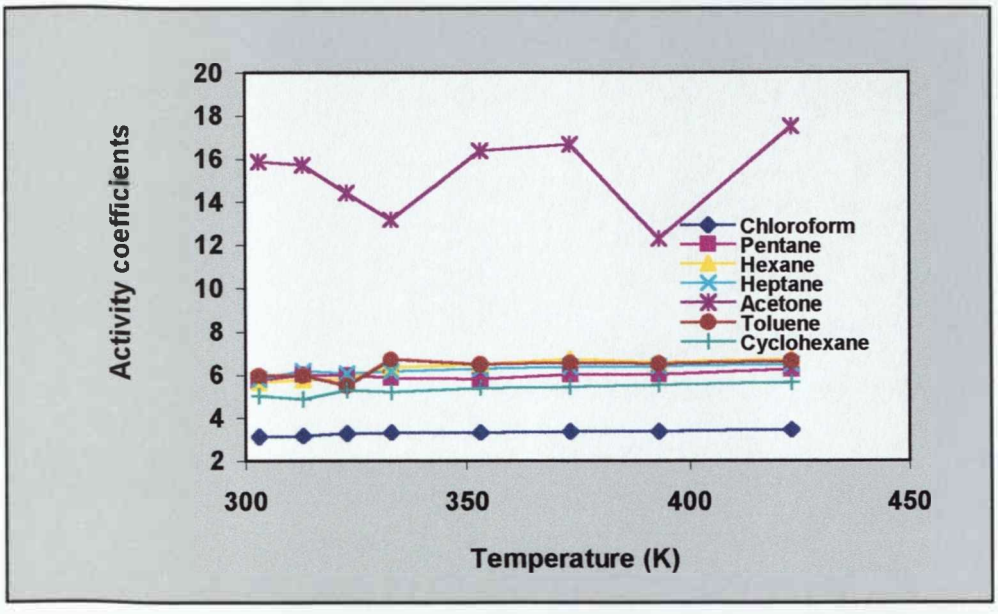


Figure 5.21b: Effect of temperature on activity coefficients (500 cS PDMS column)

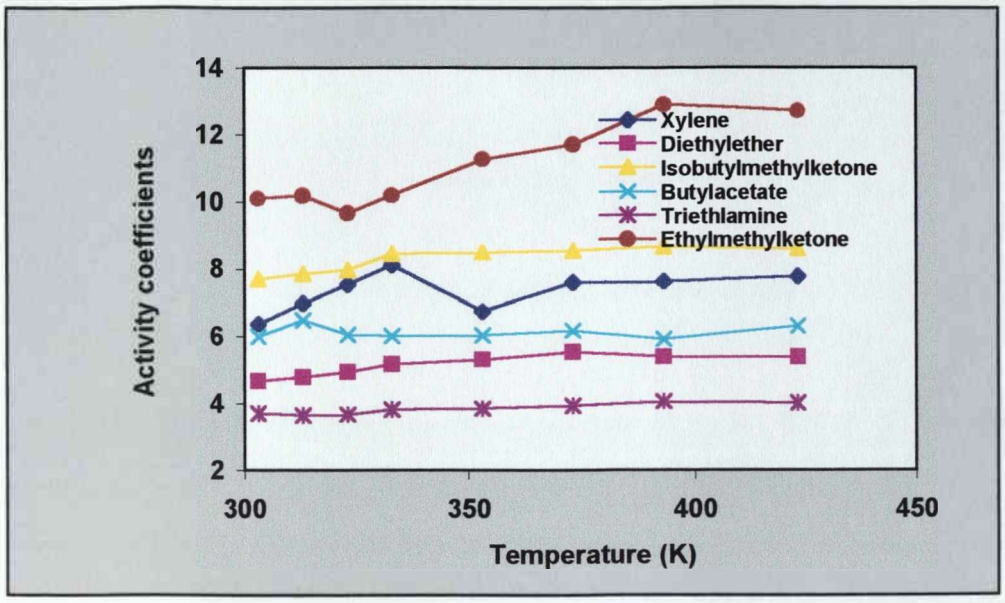


Figure 5.22: Effect of solute vapour pressure on specific retention volumes (chloroform)

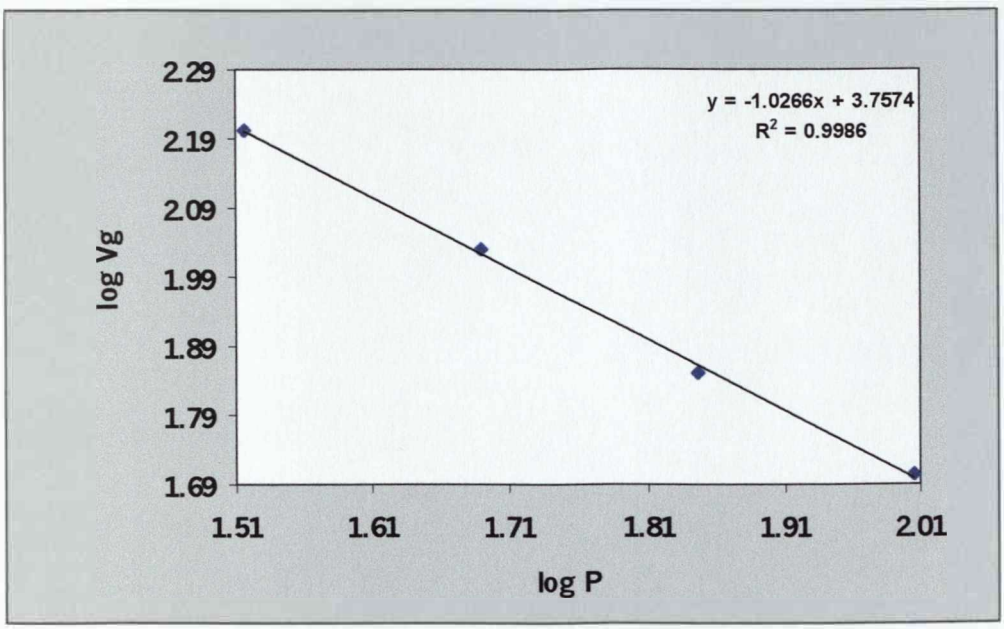


Figure 5.23: Effect of solute vapour pressure on specific retention volumes (pentane)

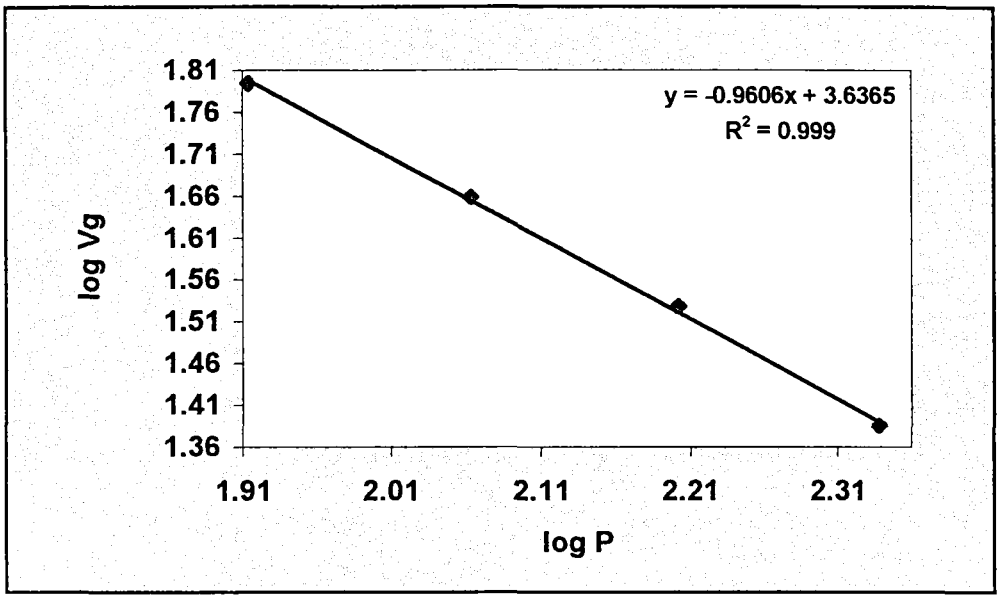


Figure 5.24: Effect of solute vapour pressure on specific retention volumes (hexane)

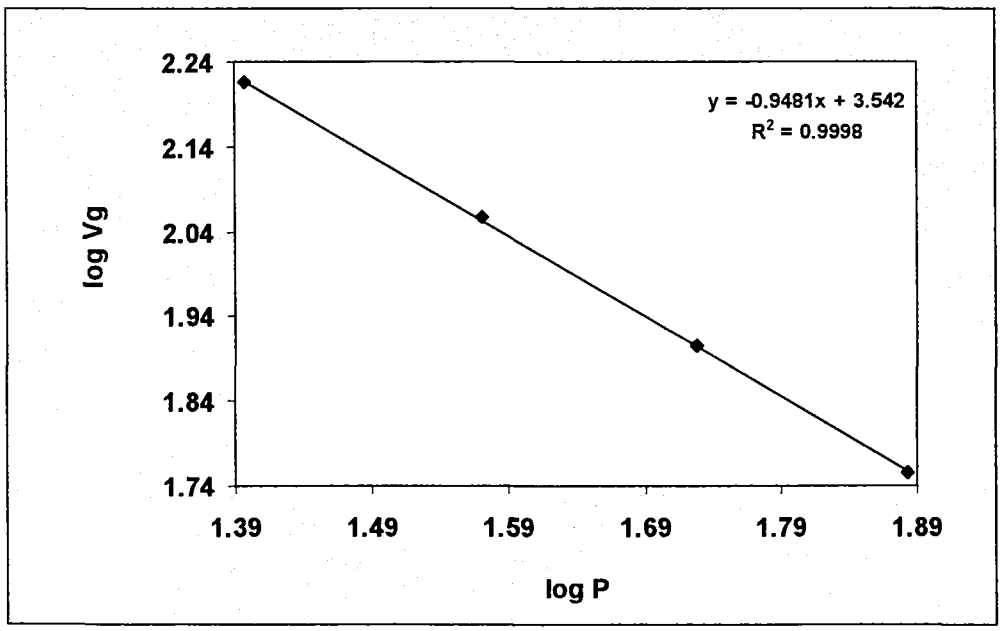


Figure 5.25: Effect of solute vapour pressure on specific retention volumes (heptane)

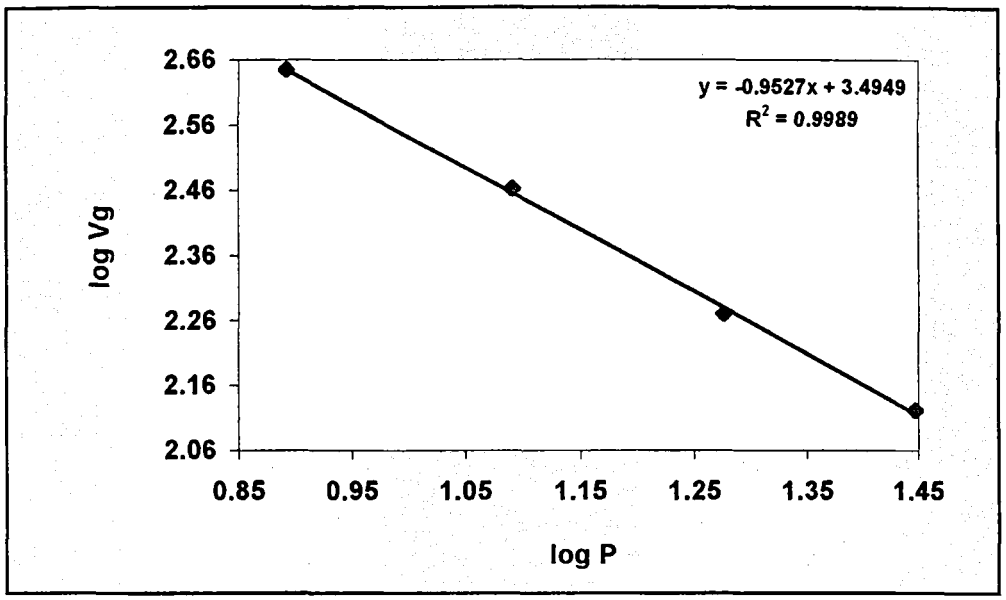


Figure 5.26: Effect of solute vapour pressure on specific retention volumes (acetone)

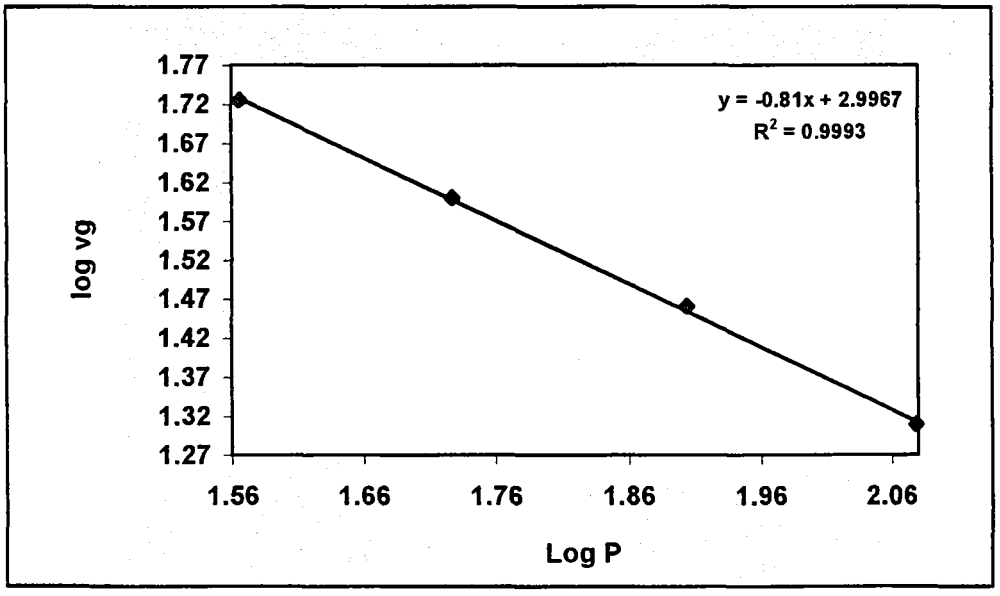


Figure 5.27: Effect of solute vapour pressure on specific retention volumes (toluene)

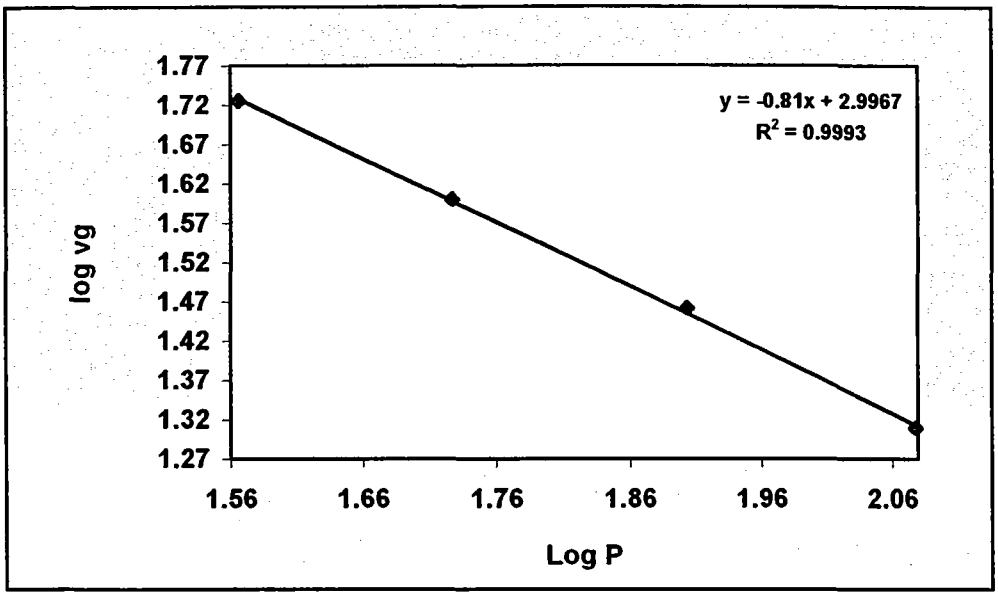


Figure 5.28: Effect of solute vapour pressure on specific retention volumes (cyclohexane)

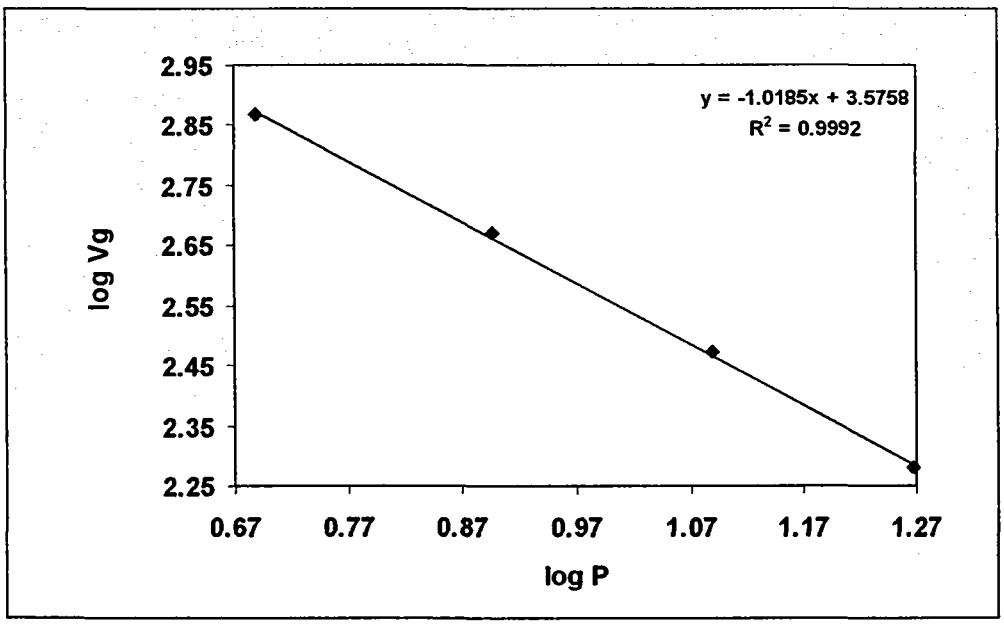


Figure 5.29: Effect of solute vapour pressure on specific retention volumes (xylene)

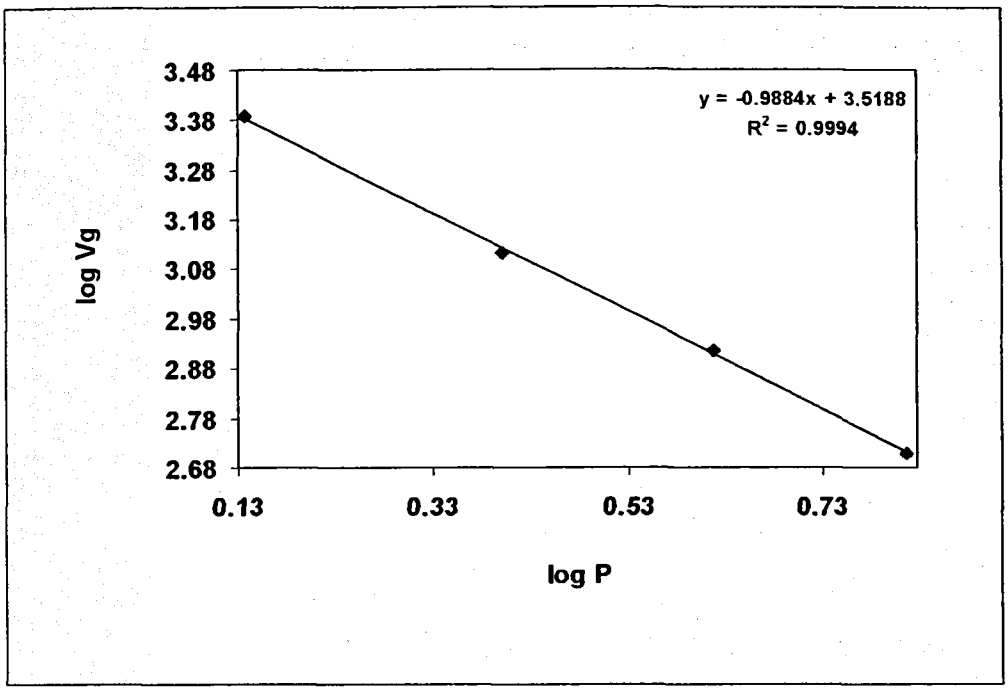


Figure 5.30: Effect of solute vapour pressure on specific retention volumes (diethyl ether)

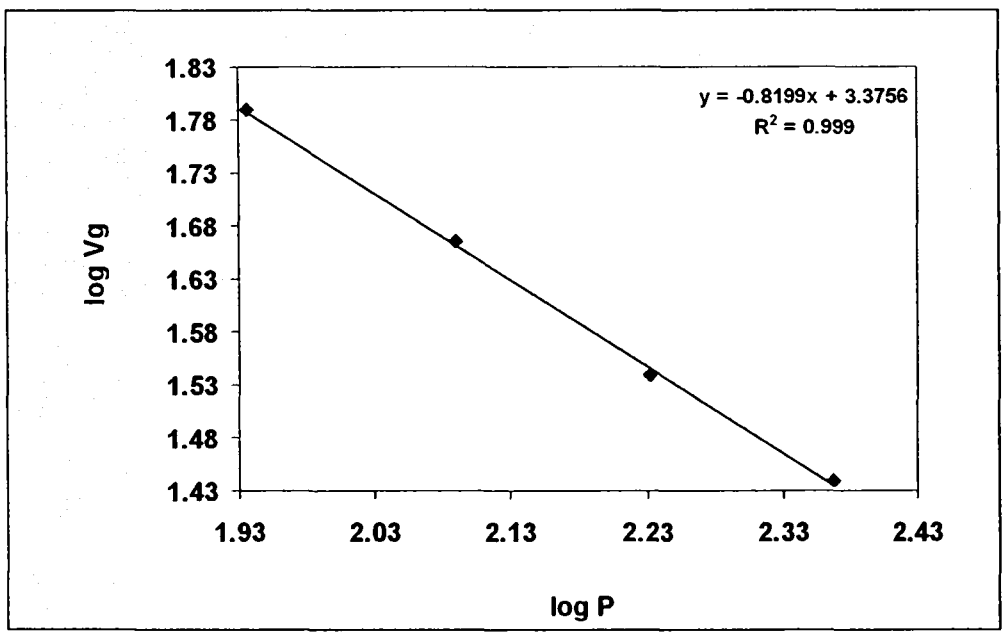


Figure 5.31: Effect of solute vapour pressure on specific retention volumes (butylacetate)

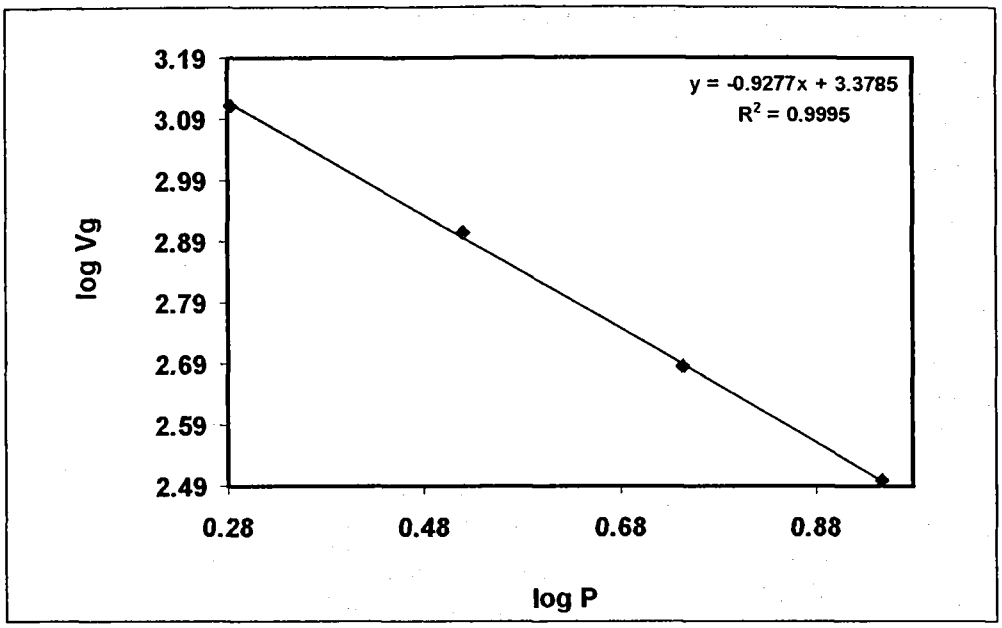


Figure 5.32: Effect of solute vapour pressure on specific retention volumes (isobutylmethylketone)

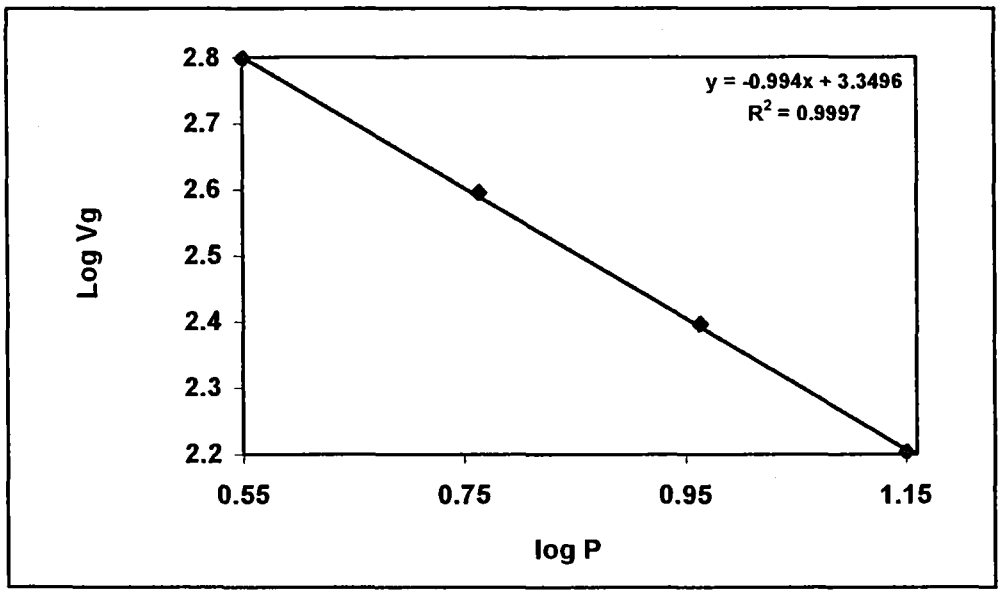


Figure 5.33: Effect of solute vapour pressure on specific retention volumes (triethylamine)

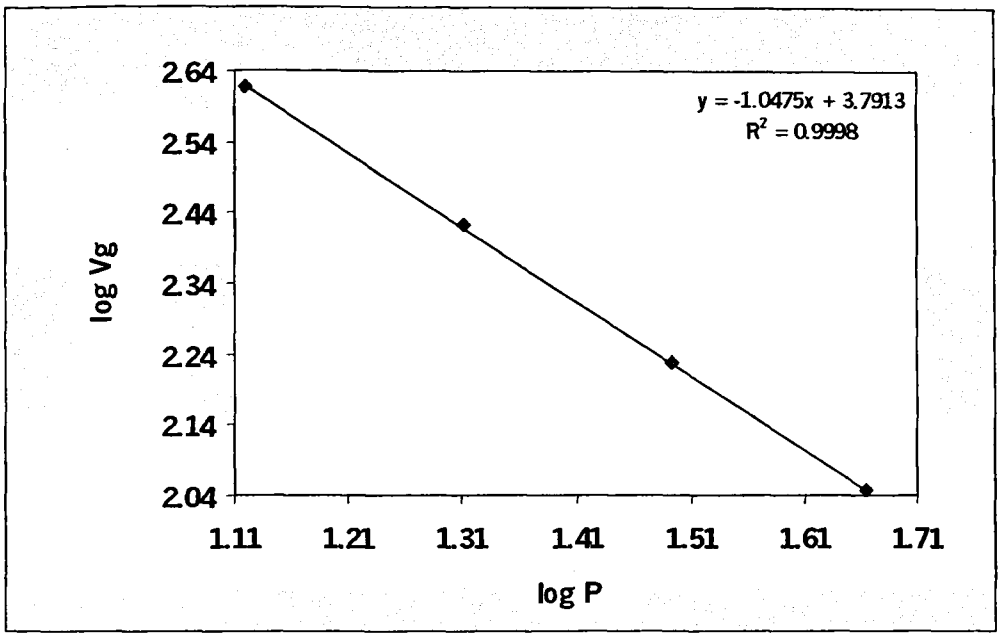
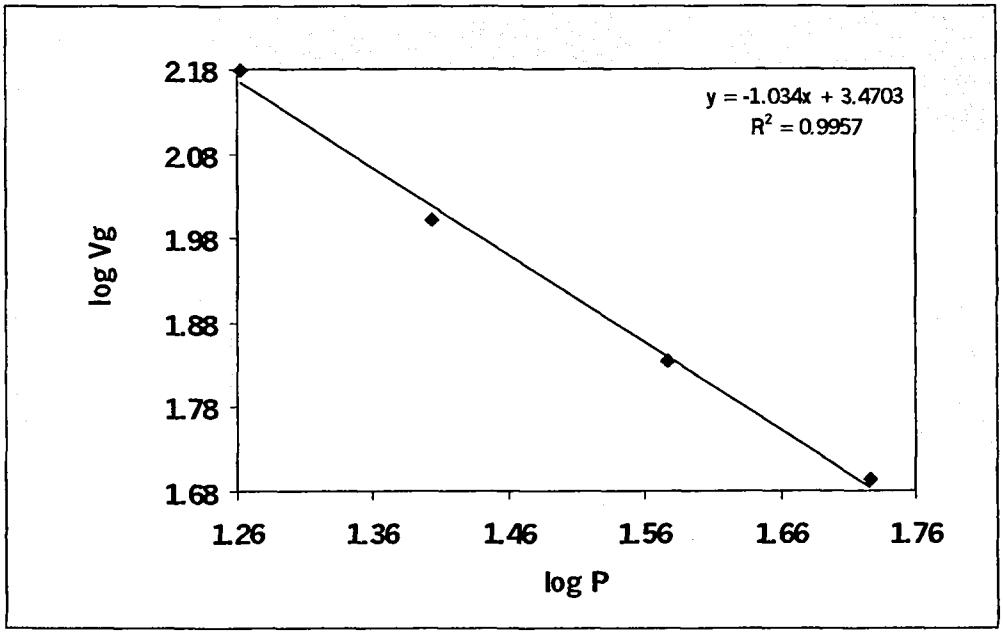


Figure 5.34: Effect of solute vapour pressure on specific retention volumes (ethyl methyl ketone)



CHAPTER SIX

DISCUSSION

CHAPTER 6: DISCUSSION

6.1 Simple Headspace Method

6.1.1 Calibration curves

The simple headspace method relied very much on the availability of accurate and reproducible calibration curves. The calibration for the thirteen volatile organic compounds investigated in this study are shown in table 6.1 below.

Table 6.1: Volatile organic compounds calibration equations

Compound	Calibration equation	R^2 Value
n-pentane	Y = 0.00012x – 0.00005	0.9998
n-hexane	Y = 0.00011x – 0.00001	0.9997
n-heptane	Y = 0.00013x – 0.00042	0.9999
triethylamine	Y = 0.00012x – 0.00041	0.9995
toluene	Y = 0.00014x – 0.00150	0.9993
xylene	Y = 0.00007x – 0.0014	0.9995
cyclohexane	Y = 0.00016x – 0.00049	0.9997
butylacetate	Y = 0.00007x – 0.0001	1.0000
diethylether	Y = 0.00010x – 0.0001	0.9994
chloroform	Y = 0.00020x – 0.0004	1.0000
acetone	Y = 0.00020x – 0.0014	0.9996
ethymethylketone	Y = 0.00013x – 0.00156	0.999
isobutylmethylketone	Y = 0.00012x – 0.0003	0.9998

The above calibration equations were obtained using modified equipment where silicon rubbers where used instead of red rubbers. In these equations Y is the concentration in kgm^{-3} and x is the peak area from the chromatograph. The shaker flasks produced curves with a high degree of linearity and the calibration data characterised by a high degree of reproducibility. The equations fit the data very well since the R^2 values are greater than

0.99 in all cases. The calibration equation for toluene was used to test the reliability of the calibration method by finding Henry's law constants of toluene in water. A value of 0.792 kPa $m^3 mol^{-1}$ was obtained and it compared very well with the value of 0.768 kPa m^3 mol^{-1} $KPam^3mol^{-1}$ also obtained at 28.5^0C by Hansen et al (1993). The result gave a 3.1 % variation from the literature value. The calibration equations were obtained both graphically and using the least squares method. Also the calibration equation of toluene was found to be the same as that of Yoswathana (2000) obtained using the Equilibrium partitioning in closed system (EPICS) bottles and calibration bags.

6.1.2 Original equipment data

The results shown in tables 5.1.1.1 to 5.1.1.6 were obtained using the original equipment where red rubbers were implemented. The suba seals were also used more than once and the resultant activity coefficients values differed very much from those obtained by other workers using the GLC method. If activity coefficients against mole fraction graphs are drawn, they are not realistic, no solution behaviour trend. For example the activity coefficient of acetone in 5cS viscosity silicone oils ranged from 0.893 at a mole fraction of 0.030278 to 1.282 at a mole fraction of 0.000273. This was found to be really worrying as it was difficult to characterise the trend of results as either positive or negative deviations from ideal thermodynamic behaviour. Activity coefficients of toluene in the three silicon oils differ very much. For example when 0.1ml of toluene was added to each flask, the following values were obtained 0.642, 1.154 and 0.278 in 50cS, 10cS and 5cS silicone oils respectively. The abnormality led to critical study of the experimental procedures, set up and equipment materials. It was found that the low values in peak areas were due to VOC adsorption onto the red rubbers. The sudden increase in γ values was due to the use of both new and already pierced suba seals. The

volatile organic compounds escaped through pierced holes. When a new suba seal was used, it obviously gave a greater value than expected since there was no material loss.

The drawbacks associated with the original equipment were identified. The rest of the experimental work concerning the Simple method was carried out using the modified procedure where silicon and neoprene rubbers were used instead of the red rubbers.

6.1.3 Modified equipment

6.1.3.1 Effect of test volume on Henry's law constants and activity coefficients.

Using various volumes of silicone oil from 200ml to 500ml tested the effect of liquid volume on the phase equilibrium. The same amount of solute was injected in the various flasks similar in all respects except silicone oil volume. These tests were carried out at 303K. The results were found to be the same in all cases as shown in table 5.1.2.1 and figure 5.1 and therefore a volume of 200ml was used for economic reasons and ease of handling. This means that the activity coefficients obtained in this work do not depend on the volume of silicone oil used. This is good for the Simple method since the question with regards to the use of 200ml of silicone oil was answered.

6.1.3.2 Effect of PDMS molecular weight on activity coefficients

Table 5.1.2.2 shows the effect of PDMS molecular weight on activity coefficients. The activity coefficients of acetone, chloroform and hexane were measured in the three silicone oils supplied by Dow Corning. The weight fraction based activity coefficients are reasonably comparable while those based on the mole fraction were found to decrease with the increase in molecular weight. This decrease could be due to the high values of molecular weights used in the calculation.

6.1.3.3 Effect of shaking time on Henry law constants and activity coefficients.

To ascertain equilibrium establishment activity coefficients of acetone were determined for various shaking times from 0.5 to 24 hours. The results for this are shown in table 5.1.2.3 and figure 5.2 and they are almost the same for all the shaking times applied. The slight decrease in Henry's law constants may be due to the slight adsorption of the organic compound on the experimental apparatus with time. Since an approach to equilibrium can be achieved within 30 minutes of shaking, the simple method can be rapidly used in the study of phase equilibrium between solvents and polymeric materials.

6.1.3.4 Comparison of Static and GLC Solute Mole- and Weight- Fraction Based Activity coefficients with PDMS (MW-1000)

Presented in table 6.2 are the Static and GLC solute mole- and weight- fraction based activity coefficients found using silicone oil of 10cS viscosity with a corresponding average molecular weight of 1000. The activity coefficients for pentane, heptane, hexane, toluene and cyclohexane showed a variation of less than 10%. However in the other compounds such as heptane, triethylamine, diethyl ether, and butyl acetate a variation of more than 10% was observed. These results show that although not very accurate the static method can be used for a quick check on the solubility of compounds in certain solvents. In the calculation, a mean of ten measurements for each VOC concentration was used.

Table 6.2 Comparison of Static and GLC Solute Mole- and Weight- Fraction Based Activity Coefficients with PDMS (MW-1000)

Compound	Mole fraction based γ			Weight fraction based		
	Static	GLC	% Variation	Static	GLC	% Variation
Pentane	0.388	0.384	1.042	5.384	5.323	1.146
Hexane	0.503	0.458	9.825	5.833	5.317	9.705
Heptane	0.539	0.539	0	7.340	5.382	36.381
Triethylamine	0.525	0.392	33.925	8.187	3.878	28.652
Toluene	0.560	0.585	4.274	6.080	6.354	4.312
Xylene	0.805	0.617	30.470	7.587	5.808	30.630
Cyclohexane	0.397	0.399	0.501	4.720	4.378	7.812
Butylacetate	0.860	0.748	14.973	7.401	4.350	70.138
Diethylether	0.624	0.359	73.816	8.413	4.489	87.413
Chloroform	0.425	0.374	13.636	3.557	3.133	13.533
Acetone	1.026	0.865	18.613	17.669	14.895	18.624
Ethylmethylketone	0.532	0.739	28.011	7.381	10.245	27.955
Isobutylmetylketone	1.096	0.841	30.321	10.942	8.396	30.324

6.1.3.5 Comparison of solute activity coefficients in water and silicone oil (10 cs PDMS)

Activity coefficients of the thirteen volatile organic compounds were also determined in water. This was done so as to compare the activity coefficients as solubility indicators in the two absorbents. The comparisons of the mole fraction based activity coefficients are shown in tables 6.3 to 6.15. As can be seen from the tables, silicone oil is better absorbent of organic compounds as compared to water. For example in the case of pentane, the activity coefficient in water is 1.4×10^6 times greater than that in silicon oil. Water can be used as an absorbent for the removal of acetone because the difference in activity coefficients is not very large compared to the other compounds.

Table 6.3 Pentane activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.01	0.388	67 500	173 969
0.02	0.294	42 600	144 897
0.03	0.252	24 000	95 238
0.04	0.230	20 200	87 826
0.05	0.222	15 900	71 621
0.06	0.209	11 800	56 459
0.07	0.199	8 900	44 724
0.08	0.187	6 900	36 898
0.09	0.179	5 000	27 933
0.1	0.168	3 900	23 214

Table 6.4 Hexane activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.01	0.503	277 000	550 696
0.02	0.491	200 000	407 332
0.03	0.473	163 000	344 608
0.04	0.450	139 000	308 888
0.05	0.436	123 000	282 150
0.06	0.422	104 000	246 445
0.07	0.414	87 000	210 114
0.08	0.408	70 000	171 568
0.09	0.400	58 000	125 000
0.1	0.392	45 000	114 796

Table 6.5: Heptane activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.01	0.385	607 000	1 576 624
0.02	0.334	539 000	1 613 772
0.03	0.311	470 000	1 511 254
0.04	0.294	400 000	1 360 544
0.05	0.289	320 000	1 107 266
0.06	0.275	264 000	960 000
0.07	0.265	240 000	905 660
0.08	0.257	220 000	856 031
0.09	0.248	180 000	725 800
0.1	0.241	164 000	680 498

Table 6.6: Triethylamine activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.01	0.525	55.6	105
0.02	0.518	54.9	105
0.03	0.492	52.2	118
0.04	0.440	46.6	104
0.05	0.416	44.0	105
0.06	0.386	40.8	105
0.07	0.372	39.3	105
0.08	0.349	36.9	105
0.09	0.322	33.9	105
0.1	0.299	31.6	105

Table 6.7: Toluene activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.01	0.560	8900	15 892
0.02	0.475	8500	17 894
0.03	0.413	8000	19 370
0.04	0.404	7700	19 059
0.05	0.383	7300	19 060
0.06	0.350	6900	19 714
0.07	0.345	6400	18 286
0.08	0.333	6000	18 018
0.09	0.329	5600	17 021
0.1	0.320	5100	15 938

Table 6.8: Xylene activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.01	0.661	16500	24 962
0.02	0.559	16400	29338
0.03	0.498	14300	28 714
0.04	0.452	12900	28 540
0.05	0.442	11000	24 889
0.06	0.416	11000	26 442
0.07	0.381	10800	28 346
0.08	0.366	10600	28 962
0.09	0.363	10300	28 375
0.1	0.358	10000	27 933

Table 6.9: Cylohexane activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.01	0.353	18500	52 408
0.02	0.299	16400	54 849
0.03	0.260	14400	55 385
0.04	0.243	12600	51 440
0.05	0.220	11700	52 727
0.06	0.211	11000	52 133
0.07	0.208	10400	50 000
0.08	0.203	9600	47 290
0.09	0.202	9000	44 554
0.1	0.197	8600	43 655

Table 6.10: Butylacetate activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.01	0.860	74.8	86
0.02	0.656	68.7	104
0.03	0.563	65.6	116
0.04	0.518	62.4	110
0.05	0.496	60.7	122
0.06	0.469	58.8	125
0.07	0.447	57.2	128
0.08	0.419	55.6	133
0.09	0.402	53.5	133
0.1	0.378	52.4	138.6

Table 6.11: Diethylether activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.01	0.624	77.2	123
0.02	0.615	75.9	123
0.03	0.601	74.1	123
0.04	0.584	72.5	124
0.05	0.574	69.9	121
0.06	0.560	67.5	120
0.07	0.550	66.7	121
0.08	0.542	66.1	122
0.09	0.532	65.8	124
0.1	0.523	64.1	123

Table 6.12: Chloroform activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.01	0.425	610	1 435
0.02	0.375	490	1 306
0.03	0.309	450	1 456
0.04	0.290	400	1 423
0.05	0.281	400	1 424
0.06	0.269	390	1 450
0.07	0.259	390	1 506
0.08	0.258	380	1 473
0.09	0.245	370	1 510
0.1	0.237	360	1 519

Table 6.13: Acetone activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.01	1.026	6.456	6.3
0.02	1.016	5.434	5.3
0.03	1.003	4.885	4.9
0.04	0.990	4.335	4.4
0.05	0.977	4.202	4.3
0.06	0.967	4.068	4.2
0.07	0.968	3.935	4.1
0.08	0.962	3.801	4.0
0.09	0.956	3.576	3.7
0.1	0.950	3.351	3.5

Table 6.14: Ethylmethylketone activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.005	0.482	109	226
0.01	0.449	102	227
0.02	0.431	93	216
0.04	0.399	82	205
0.06	0.353	71	201
0.08	0.341	64	188
0.1	0.329	60	182
0.2	0.301	52	172
0.4	0.273	48	175
0.6	0.261	45	172
0.8	0.253	43	170

Table 6.15: Isobutylmethylketone activity coefficients in water and silicone oil compared

Solute volume injected (ml)	Activity coefficients		Factor
	Silicone oil	Water	
0.01	1.010	85.8	85
0.02	0.930	83.7	90
0.03	0.793	80.4	101
0.04	0.655	77.8	118
0.05	0.614	74.2	120
0.06	0.573	71.8	125
0.07	0.551	68.4	124
0.08	0.528	65.4	124
0.09	0.502	63.5	126
0.1	0.475	62.1	130

6.1.3.6 Variation of Solute Activity Coefficients from Literature values

(a) In silicone oils

The variation of activity coefficients obtained using the Simple headspace method and those in the literature are shown in table 6.16. The results obtained in this study do compare very well to those obtained by other workers using the GLC, Static and Group contribution methods such as UNIFAC. A variation as small as 1.7% was obtained in the case of hexane. This shows that when full attention is paid to the experimental set-up and procedures, the simple headspace method can be of value in phase equilibrium studies. In order to obtain each value of the activity coefficient, five flasks were used and two injections made from each flask. Therefore the peak area used in the calculation is an average of ten (10) measurements. As a result of the successful comparison, the activity coefficients of triethyl amine, butyl acetate, diethyl ether, acetone, ethyl methyl ketone and Isobutyl methyl ketone can be considered to be correct and accurate. Besides the

work recorded in this thesis no other worker has attempted to determine infinite dilution activity coefficients for the above compounds in silicon oils.

Table 6.16: Solute activity coefficients in Poly(dimethylsiloxane) at 303K

Compound	Activity Coefficients		%Variation	Source
	This work	Literature		
Pentane	5.384	6.066 (static)	11.2	1
		6.092 (GLC)	11.6	1
		5.523 (GCLF-EOS)	2.5	2
		6.134 (UNIFAC)	12.2	2
Hexane	5.833	6.003 (static)	2.8	1
		6.023 (GLC)	3.2	1
		5.679 (GCLF-EOS)	2.7	2
		5.932 (UNIFAC)	1.7	2
Heptane	7.340	6.109	20.2	1
		6.135	19.6	1
		6.109	20.2	2
		5.895	24.5	2
Triethyl amine	5.187	-	-	-
Toluene	6.080	5.363 (Static)	13.4	1
		6.457 (GLC)	5.8	1
Xylene	7.587	-	-	-
Cyclohexane	4.720	5.378 (GLC)	12.2	1
		5.363 (GCLF-EOS)	11.9	2
		4.245 (UNIFAC)	11.2	2
Butyl acetate	7.401	-	-	-
Diethyl ether	8.413	-	-	-
Chloroform	3.557	3.366	5.6	1
Acetone	17.669	-	-	-
Ethyl methyl ketone	7.381	-	-	-
Isobutyl methyl ketone	10.942	-	-	-

Referenes:- 1. Ashworth, Chien, Furio and Hooker (1984), 2. Hand (1994)

(b) In water

The variation of activity coefficients and Henry's law constants obtained in this work and those in the literature are shown in tables 6.17 and 6.18. The values do agree well especially those for acetone and diethyl ether with variations from literature findings of 1.2% and 5.6% respectively.

Table 6.17: Solute activity coefficients in water at 303K

Compound	Activity Coefficients		%Variation	Source
	This work	Literature		
Pentane	67 400	-	-	-
Hexane	277 000	-	-	-
Heptane	607 000	-	-	-
Triethyl amine	56	-	-	-
Toluene	8 800 5.187	10400 (exp) 7 000 (UNIFAC)	14.5 27	1 1
Xylene	16 500	-	-	-
Cyclohexane	18 500	20 400 (exp) 4 960 (UNIFAC)	9.3	1 1
Butyl acetate	75	-	-	-
Diethyl ether	77	72.9 (exp) 163 (UNIFAC)	5.6 52.3	1 1
Chloroform	611	821 (exp) 921 (UNIFAC)	25.5 50.7	2 2
Acetone	7	-	-	-
Ethyl methyl ketone	109	-	-	-
Isobutyl methyl ketone	86	-	-	1

References:- 1. Nielsen and Olsen ; 2. Barr and Newsham (1987)

Table 6.18: Solute Henry's law constants in water at 303K.

Compound	Henry's law constants ($KPam^3mol^{-1}$)		%Variation	Source
	This work	Literature		
Pentane	100	128	22	2
Hexane	115	130	11	2
Heptane	88	95	7.5	1
Triethyl amine	0.730	-	-	-
Toluene	0.828	0.768	7.2	2
Xylene	0.915	0.981	6.7	1
Cyclohexane	7.481	19.500	61.7	2
Butyl acetate	0.00425	-	-	-
Diethyl ether	0.120	-	-	-
Chloroform	0.649	0.570	13.8	2
Acetone	0.00428	0.00433	1.2	2
Ethyl methyl ketone	0.035	-	-	-
Isobutyl methyl ketone	0.00541	-	-	-

References:- 1. Hansen et al (1993); 2. Yaws, Yang and Pan (1991).

6.1.3.7 Effect of temperature on Henry's law constants

The temperature dependence of the Henry's law constants was studied using the typical Van't Hoff relation of the form

$$\ln H = \frac{A}{T} + B \quad \text{.....} \quad (6.1)$$

Linear behaviour was obtained in all cases and Henry's law constants were found to increase with increase in temperature. Typical Van't Hoff plot for acetone is shown in figure 5.3. The R^2 value is greater than 0.95 which means that the data fit the model very

well. The large temperature effect on the vapour pressure is the principal cause of the temperature dependence of H.

6.1.3.8 Significance of the Solutes activity coefficients in water and silicone oils.

The basic theory for the absorption and stripping cycles is based on Raoult's law, modified for non ideality

$$p_i = \gamma_i x_i p_i^o$$

The mole fraction based activity coefficients of the volatile organic compounds obtained in this work are less than unity in silicone oils and more than unity in water. Thus a mixture of any organic compound and silicone oil exhibit negative deviations while that of any organic compound and water show positive deviations from Raout's law.

Negative deviation occurs when the species generate mutually attractive forces. The tendency to escape into the vapour phase will decrease and therefore the vapour pressures will be less than those predicted by Raoult's law. Silicone oils hold the organic molecules in the liquid phase and this promotes much easier absorption. However the stripping part of the cycle will be more difficult with silicone oils. Therefore, for stripping purposes activity coefficients above unity as those shown in water are desirable.

Positive deviations occur if the two species generate a net repulsive force in the liquid phase. This will increase their tendency to vaporise and they will thus exert vapour pressures greater than those predicted by Raoult's law. Since the activity coefficients of the volatile organic compounds in water are greater than unity, it means that the absorption part will be more difficult while stripping can be accomplished easily.

The choice between water and silicone oils is a matter of an economic balance. One has to weigh the advantages and disadvantages that can be associated with each system.

Figures 6.1, 6.2 and 6.3 show positive deviation, negative deviation and ideal systems based on Raoult's law. Systems involving volatile organic compounds in water will be presented by figure 6.1 and those of organic compounds in silicone oils by figure 6.2.

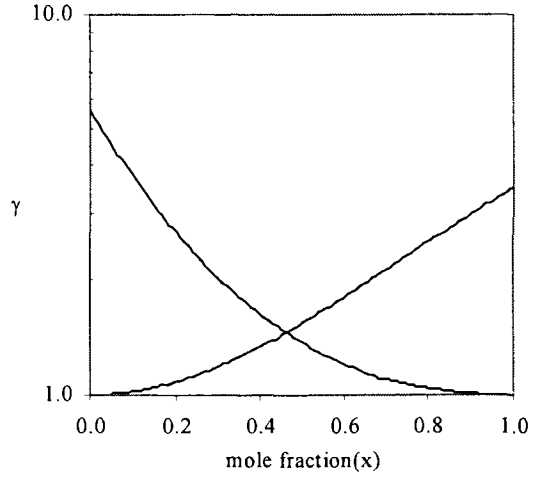


Figure 6.1. Positive deviation system (say pentane and water)

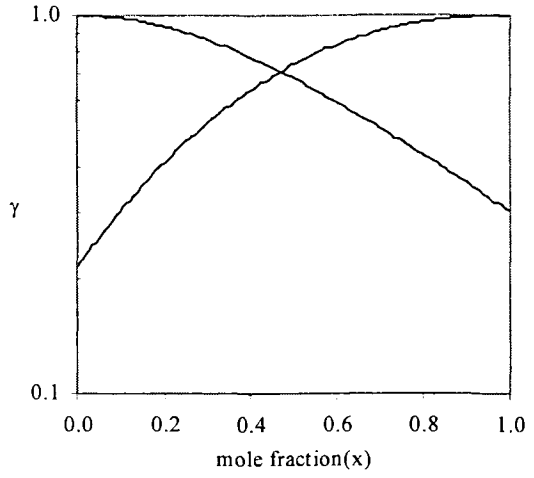


Figure 6.2. Negative deviation system (say Toluene and silicone oil)

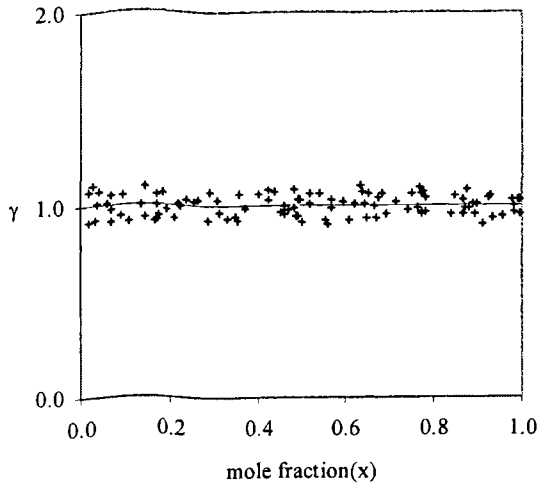


Figure 6.3. An ideal system

6.1.3.9 Water versus silicone oil as absorbents: a general summary.

In absorption work it is desirable that the absorbent be of low volatility. Whilst there are many organic compounds of low volatility, the majority are oils of relatively high viscosity and therefore mass transfer between gas and liquid would be so poor that the column height required would not be practical. It is essential that the absorbent should have a low viscosity and water satisfies this condition very well. Although the activity coefficients obtained in silicon oils indicate that absorption will be much easier as compared to water, silicon oils are more likely to present mass transfer and flow problems in columns.

The stripping process normally involves distillation or steam stripping at an elevated temperature. The absorbent needs to be thermally stable over the operating temperature range. Comparing water and silicone oil, the latter will be very desirable since it is quite stable up to 150^0C. Since the activity coefficients of volatile organic compounds in silicone oils are still low at high temperatures say 423K, the stripping part will be very difficult.

Water is frequently used, as many solvents are water-soluble. Moreover water is cheap and plentiful and its use also makes a simpler plant. However, as relatively large volumes of water are needed to achieve low levels of VOC concentration in the exhaust air stream, the resulting low concentration in the water makes solvent recovery unlikely. Unlike water, silicone oils are expensive and their use would lead to a complex plant.

6.2 Gas-liquid Chromatographic Technique

The advantage of the gas chromatographic technique compared to classical static equilibrium methods for obtaining thermodynamic data for the mixing of polymer and solutes lies mainly in the speed of obtaining the data.

6.2.1 Injection of Solute mixtures

The injection of solute mixtures instead of pure solutes was studied to see if such a technique would affect the results. In some cases injection of solutes as a mixture would save experimental time. Retention volumes of the mixtures of pentane, hexane and heptane in the four silicone oils investigated in this work at temperatures varying from 303 to 423K were measured. The specific retention volumes obtained were compared with those determined when solutes were injected as pure components. No significant difference in the results of the two procedures could be detected. This suggests that the presence of molecules of another component does not interfere with the retention data of the solute. This is one of the assumption of the GLC theory and in this case it was found to be true. It is also important to note that the injection of a solute mixture is not always advantageous. It is only useful when the retention volumes of the solutes are not too similar for the peak overlapping or two different to cause diffusion of one of the peaks.

6.2.2 Effect of Liquid Loading on Retention Volumes

The effect of liquid loading on retention volumes was studied with three columns with 10%, 20% and 30% liquid loading. The specific retention volumes of pentane, hexane, heptane, diethyl ether, acetone and chloroform were measured in the three columns at 303K. This investigation was carried out because high polymers lie somewhere between conventional crystalline solids and ordinary liquids with respect to viscosity and diffusity

of small molecules in the polymer phase, hence there are two possible mechanisms for solute sorption. These are absorption of the solutes in the bulk of the polymer phase and adsorption in the polymer surface. In order to treat the data obtained from the GLC quantitatively, one must be sure that absorption is the dominant mechanism. When the solute is held back by absorption only, the retention volume is directly proportional to the amount of polymer in the column. The results shown in table 5.2.7 and figures 5.10 and 5.11 indicate that a direct proportionality existed between the retention volume and the liquid loading. Both plots of specific retention volumes against liquid loading and net retention volumes against liquid loading produced linear relationships. Therefore the application of the theory of gas-liquid partition chromatography to the results to calculate the activity coefficients is justified. In addition to this, adsorption on the column wall and non-covered parts of the solid support surface can be ruled out.

6.2.3 Effect of carrier gas flow rate

Retention volumes of acetone, pentane, chloroform, diethyl ether and cyclohexane were measured in a 500cs PDMS column. A constant sample size of 0.1μl was injected in all cases and the flow rate was varied from 20ml/min to 40ml/min. The results for this are shown in table 5.2.10 and plotted in figure 5.13. The results do not show any well defined trend in the variation of retention volumes with flow rates. Thus increasing the flow rate up to 40ml/min did not affect the rate of approach to equilibrium in the column. These findings are in accordance with literature findings where no significant change was observed on the retention volumes by varying flow rates. Lictenthaler (1973) Pollard and Hardy (1957) and Porter, Deal and Stross (1956). This is mainly because the retention time is inversely proportional to the flow rate thus if the mobile phase flow rate is doubled the retention time, t_R will be halved with no net effect on the retention volume.

6.2.4 Effect of sample size

The retention volumes of pentane, acetone, chloroform, diethyl ether and ethyl methyl ketone were measured at a constant flow rate of 40.01ml/min, column temperature of 333K and variable sample sizes ranging from 0.1 to 10µl in 500cS PDMS column. The results for this work are presented in table 5.2.9 and plotted in figure 5.12. A trend towards earlier peak elution was observed with increasing sample size. The peaks broadened and became more asymmetrical as the injection volume increased from 0.1µl to 10µl. In all cases the retention volume decreased with increasing sample size. This corresponds to an increase in γ as reported by Purnel (1962) and therefore negative deviations from ideal behaviour is exhibited by the solutes. The asymmetry of the peaks was also inspected in order to obtain qualitative information as regards deviation from Raoult's law Desty, Goldup, Luckhurst and Swanton (1962). All the compounds gave sharp leading and diffuse tails indicating negative deviations from ideality. The absence of maxima and minima in the plots means that adsorption and reaction effects are not present. Extrapolation to zero sample size will be linear and therefore very accurate. Also uniformly symmetrical peaks obtained by injecting small samples can be considered to confirm the infinite dilution approximation, thus representing solvent-solute equilibrium interactions Locke (1977). Keeping with Conder's (1969) admonition peak asymmetry is not a necessary condition for surface adsorption effects for this could be due to poor sample introduction and excessive sample size as was observed in this work.

6.2.5 Effect of temperature and vapour pressure

Specific retention volumes of chloroform, pentane, hexane, heptane, acetone, toluene, cyclohexane, xylene, diethyl ether, butyl acetate, Isobutyl methyl ketone, triethyl amine and ethyl methyl ketone were measured by injecting a constant amount of sample of 0.1µl

into column 1 (5cS PDMS). Measurements were done at a constant mean flow rate of 35.97ml/min and the temperature was varied from 303 to 333K. The results for this work are shown in table 5.2.8 and figures 5.22 to 5.34. The plots of log V_g against log p^o gave slopes other than –1 as expected from equation 2.2.57 which indicated some deviation from ideal behaviour. Since vapour pressure is directly related to temperature, a similar effect was observed on the solute specific retention volumes. The specific retention volumes decreased when either of these two variables was increased.

6.2.6 Specific retention volumes

The solute specific retention volumes reported in tables 5.2.12 to 5.2.21 were calculated from corrected peak retention times and column operating conditions, using the well known expression of Littlewood and co-workers (1955). The retention time used in the calculation of specific retention volumes was an average of five measurements. Individual values of retention times were found to vary by no more than 1% in all cases. The specific retention volumes obtained in this work compare very well with those found in the literature as shown in table 6.19.

Table 6.19: Variation of Specific retention volumes from literature findings

Compound	Temp (K)	Specific retention volumes		% Variation	Source
		This work	Literature		
chloroform	303	188.20	181.7	3.4	1
n-pentane	303	69.91	66.11	5.7	1
	313	47.81	47.65	0.3	1
	333	24.94	24.76	0.7	5
n-hexane	303	191.98	179.2	7.1	2
	313	126.23	124.2	1.6	4
	333	58.80	60.91	3.5	5
n-heptane	303	508.25	482.5	5.3	2
	313	294.57	290.8	1.3	3
	333	146.75	144.30	1.7	4
toluene	303	796.45	791.1	0.7	1
	313	529.08	516.6	2.4	2
	323	300.15	269.20	11.5	2
cyclohexane	303	336.80	315.10	6.9	2
	333	103.40	106	2.5	5
xylene	303	2645.55	2654.60	0.3	3
	313	1223.61	1187.50	3	2
	333	516.27	536.50	3.8	4

Source: 1. Ashworth et al (1984); 2. Lictenthaler; Newman R.D; Prausnitz J.M (1973); 3. Deshpande and others (1974); 4. Summers, Tewari and Schreiber (1972); 5. Smidsrod and Guillet (1969).

As can be seen from table 6.19, small variations were observed especially in the case of n-heptane, toluene, xylene and hexane.

6.2.7 Infinite dilution activity coefficients

Infinite dilution activity coefficients for the thirteen volatile organic compounds in the four silicone oils studied are shown in tables 5.2.20 to 5.2.27. The effect of temperature

on activity coefficients is also shown in figures 5.18a to 5.21b. With the exception of acetone in 5cs and 10cs PDMS, activity coefficients were generally found to increase with increase in temperature. In some cases a fall and increase in activity coefficients as the temperature was increased was also observed. This behaviour is in agreement with the findings of Hand (1994) and Galin (1977).

The infinite dilution activity coefficients were calculated using the relationships below

Mole fraction based activity coefficients

$$\ln {}^{x}\gamma_1^{\infty} = \ln \frac{273.16R}{V_g P_1^o M_s} - \frac{P_1^o\left(B_{11} - \bar{v}_1^o\right)}{RT} \quad \text{.....(6.1)}$$

Weight fraction based activity coefficients

$${}^{w}\gamma_1^{\infty} = \frac{{}^{x}\gamma_1^{\infty} M_s}{M_1} \quad \text{.....(6.3)}$$

6.2.8. Summary

By using equation (6.4) an estimated accuracy of ±5% can observed.

$$\gamma_i^{\infty} = \frac{n_2^L RT}{V_N P_i^{sat}} \quad \text{.....(6.4)}$$

According to Letcher (1980), the accuracy can be improved to ±0.4% by making use of refined theory and measurement as reflected in equation (6.5).

$$\ln \gamma_{12}^{\infty} = \ln \frac{n_2 RT}{V_N P_i^{sat}} - \frac{\left(B_{11} - V_1^*\right)P_1^{sat}}{RT} + \frac{\left(2B_{12} - V_1^{\infty}\right)j_2^3 P_0}{RT} \quad \text{.....(6.5)}$$

Possible problems with the GLC technique are surface adsorption and stationary phase stripping. To eliminate the latter problem, the carrier gas can be presaturated with stationary phase although this is not a desirable method of operation. Stationary phase stripping can be identified and quantified by weighing the column before and after an experimental run. However, this difficulty was not encountered in this work because of the low vapour pressure of silicone oils. This problem is likely to be encountered when the GLC technique is used to measure the activity coefficients of volatile organic compounds in water. Newsham and Barr (1987) also observed this behaviour in their study of phase equilibria in very dilute mixtures of water and chlorinated hydrocarbons. These authors weighed the column after each day's work and the amount of water in the column at the mean time of each experiment was obtained by linear interpolation.

6.3 Predictions using the UNIFAC Procedure

This section gives a summary of activity coefficients obtained from manual calculations using the original UNIFAC, Fredenslund *et al.* (1975, 1977); modified UNIFAC, Kikic *et al.* (1980) and effective UNIFAC, Nagata and Koyabu (1981). The detailed calculation procedures are shown in appendix G while the group volume, surface area and interaction parameters are presented in appendix H.

Table 6.20 Solute Predicted activity coefficients in water and silicon oil

Compound	Expt (Static)	Original UNIFAC	Modified UNIFAC	Effective UNIFAC
	Water			
Heptane	607 829	75 963	478 702	7 093
Toluene	9 400	10 524	33 784	5 440
Acetone	6.5	834	1 333	578
	Silicon oil			
Heptane	0.539	1.2318	1.3877	0.4216
Toluene	0.560	1.9725	-	-

It can be seen from table 6.20 that, although reasonable predictions are possible with the UNIFAC procedure, they are not very accurate and reliable for process design. The original UNIFAC model often results in large deviations from experimental measurements when applied to athermal polymer-solvent systems. Comparing the predictions in water and oil, the deviations are wrong in the latter. The experimental mole fraction based activity coefficients in silicone oil were found to be less than one (negative deviation) while the predicted ones are above one (positive deviation). Athermal solutions are those with zero enthalpy of mixing when mixed at constant temperature and pressure because they neither liberate nor absorb heat. It is important to note that athermal behaviour is never observed exactly but those mixtures of components that are similar in their chemical characteristics despite size differences approximate the behaviour very well. Typical examples are the mixtures of toluene with polystyrene and polydimethylsiloxane with hexamethyldisiloxane. Therefore the wrong deviations in silicone oil could be due to free volume dissimilarity as suggested by Patterson (1969, 1982). The limitations of the UNIFAC procedure including its failure in systems involving polymers as found in this work are given and discussed in the work of Fredenslund and Sorensen (1984) and Al-Hayan (1999).

Therefore in engineering design, prediction procedures in particular group contribution methods find much application in the preliminary design / feasibility studies. This is because it is almost always easier to make a calculation than to perform an experiment. In addition to this a computation can be performed in a very short time, no financial input in the case of manual calculations or a one off expense in the case of computerised predictions. These are sound advantages of prediction procedures as compared to

experimental work. Performing an experiment takes a lot of time and in some cases a significant financial input is required. Therefore in this work it is suggested that in the preliminary design or feasibility studies of separation processes, prediction procedures should be implemented while accurate fluid phase equilibrium data should be obtained from experiment.

CHAPTER SEVEN

CONCLUSION

CHAPTER 7: CONCLUSIONS

A. Simple Headspace Method

1. An improved and modified experimental apparatus for the Simple headspace technique was developed for the measurement of vapour-liquid equilibrium of volatile organic compounds in water and silicone oils.
2. The experimental design confirmed that equilibrium could be approached within a reasonable time period.
3. Measurements were reproducible with the relative standard deviation and coefficient of variation of 1.3E-03 and 1.3 respectively.
4. Static determined activity coefficients using shaker flasks are reasonably comparable to those obtained using the GLC technique.
5. The Simple headspace method is reasonably accurate and uses the standard gas chromatographic headspace analysis and the data obtained in this study do agree with literature findings as explained in chapter six.
6. An advantage that can be associated with this technique is that it does not require any special apparatus.
7. The technique is quite tiresome and laborious, and therefore it is not the easiest for studying the thermodynamics of the volatile solute with a non-volatile solvent.
8. Shaking time and test volumes were found to have no significant effect on Henry' law constants.
9. Compared with water, silicone oil does absorb volatile organic compounds far much better. See table 7.1 showing activity coefficients of the volatile organic compounds in the two absorbents.

Table 7.1: Summary of activity coefficients in water and silicone oils by the Simple headspace method.

Compound	Water		Silicone oil	
	${}^{x}\gamma^{\infty}$	${}^{w}\gamma^{\infty}$	${}^{x}\gamma^{\infty}$	${}^{w}\gamma^{\infty}$
n-pentane	67 000	935 000	0.388	5.378
n-hexane	277 600	3 221 000	0.503	5.837
n-heptane	607 800	6 066 000	0.539	5.379
triethyl amine	55	544	0.525	5.188
toluene	9 404	102 000	0.560	6.078
xylene	36 300	342 400	0.805	7.583
cyclohexane	95	1128	0.397	4.717
butyl acetate	77	662	0.860	7.403
diethyl ether	1 000	13 500	0.624	8.419
chloroform	6	50	0.425	3.559
acetone	10	172	1.026	17.665
ethyl methyl ketone	109	1 500	0.532	7.378
isobutyl methyl ketone	84	839	1.052	10.503

B. The gas-liquid chromatographic technique

1. The greater rate of approach to equilibration of solute and stationary phase makes chromatographic methods generally more rapid than conventional techniques.
2. Results were obtained directly at infinite dilution, thus eliminating conventional extrapolation.
3. Several different types of information can be obtained from one chromatographic measurement.
4. The use of high purity samples is not always required, only a few milligrams of sample and few grams of stationary phase are required to characterise the expensive research chemicals being studied.
5. Infinite dilution was found to be important as the concentration region for linear chromatography because solute molecules behave independently. In this region there is

no interaction between solute molecules and the property under investigation varies linearly with concentration.

6. Close agreement was found between the infinite dilution activity coefficients obtained by the simple, rapid and accurate dynamic GLC and simple headspace methods. The successful comparison should promote a rapid compilation of thermodynamic data of compounds of interest through the GLC method. In addition the results suggests that for non-volatile stationary phases the GLC method is of great value as compared to the tedious, and laborious static experiments in the measurement of the thermodynamic properties of polymer solutions.
7. Complete coverage of supporting surfaces by the stationary phase is necessary if elution data are to be free of influence from adsorption effects. In this case PDMS on chromosorb W or P.
8. Uniformly symmetrical elution peaks obtained by injecting small volumes of solutes were considered to confirm the infinite dilution approximation and thus to represent solvent – solute equilibrium interactions.
9. Absorption was found to be the main sorption mechanism since a direct proportionality existed between retention volume and liquid loading. Thus the application of the gas-liquid partition chromatographic theory to the results in the calculation of various thermodynamic quantities is justified. Also absorption on the column wall and non-covered parts of solid support can be ruled out.
10. Plots of log V_g against $\log p^o$, a qualitative analysis of peak asymmetry and calculated mole fraction based activity coefficients showed that all the solutes exhibit negative deviations from Raoult's Law.

10. The measurements were highly reproducible with relative standard deviation and coefficient of variation in the determination of specific retention volumes of 1.3E-04 and 0.013 respectively.
11. The internal agreement of the static experiments is on average ±3% while that of the data obtained from the GLC technique is ±1%.
12. The low activity coefficients obtained suggested that silicon oils are suitable for the effective removal of volatile organic compounds from contaminated air streams.
13. The control of the operating conditions as indicated by the stability of the baseline and the shapes of the peaks obtained indicated that the equipment was working properly. The close agreement of the activity coefficients obtained in this study with those reported in literature proved that a sound technique was used.

C. Vapour-liquid equilibrium computations.

1. For rough estimates of activity coefficients group-contribution methods such as UNIFAC can be used. For accurate engineering design data, it is recommended that the desired vapour-liquid equilibrium data be obtained experimentally.
2. It is easier and faster to obtain activity coefficients through predictions than experiment.
3. The Manual UNIFAC calculations are laborious, tedious and time consuming.

CHAPTER EIGHT

RECOMMENDATIONS

CHAPTER 8: RECOMMENDATIONS FOR FUTURE STUDY

1. Equilibrium Partitioning in Closed Systems

Although the Simple headspace method seems suitable for the measurements of Henry's law constants and activity coefficients, it is susceptible to a number of uncertainties or rather source of errors. The main drawbacks are the need for calibration curves and polymer molecular weight in the calculation. The above two drawbacks can be overcom by making use of the equilibrium partitioning in closed systems (EPICS) method.

The method requires no special apparatus and obtains results from the measurement of gas headspace concentration ratio from pairs of sealed bottles identical in all respects except liquid volumes. Calibration curves are not needed since relative rather absolute concentrations are required. The resulting ratio of the two headspace concentrations is used to compute Henry's constant. The only requirement for the successful application of the method is that the instrument response should be linear throughout the concentration range of interest. The molecular weight of the polymer is not involved in the calculation and also differences due to imperfect, volumetric additions are accounted for through gravimetric means.

2. Simple Method

To increase the reliability of the results from the simple methods, both the reproducibility and repeatability tests should be done on them. This means experimental work have to be done a number of times in one day and then repeated say once every week for a certain period of time.

3. Computing vapour-liquid equilibrium

In future it will be necessary to calculate activity coefficients at infinite dilution using the equation of state models. Then the results will be compared with those obtained from activity coefficient models and experiments. More work on vapour-liquid equilibrium prediction is suggested as it offers opportunities for improving both the activity coefficient and equation of state approach models. As a result of the failure of the UNIFAC procedure in accurately predicting vapour-liquid equilibrium data for solvent-polymer systems, it is suggested to consider group contribution methods for solvent-polymer systems. Typical examples of these are those presented by Chen et al (1990), High and Danner (1990a), Lee and Danner (1996, 1996a, 1997), Oishi (1978) and Holten-Andersen (1987). Of these group contribution methods the UNIFAC free volume models of Oishi and Holten Andersen will be tried in the computation of activity coefficients of the volatile organic compounds in silicone oils.

Vapour-liquid equilibrium can be predicted from measured heats of mixing (h^E) and this procedure is of considerable potential. The possibility of using this procedure is strengthened by the fact that there is large H^E database in particular the extensive compilation by Christensen et al (1982). Developments in micro flow calorimeters for H^E data can be measured more rapidly than VLE data and the accuracy can be equal to that of the best methods for VLE measurement, Raal and Muhlbauer (1998).

Considering that the manual UNIFAC calculations are tiresome and laborious, the use of a thoroughly tested computer program is suggested.

Molecular simulation can be performed to study the activity coefficients of volatile organic compounds in polymeric materials. Molecular simulation can provide an intermediate layer between direct experimental measurements and engineering models. This can provide a direct comparison of the predictions of engineering models with simulation data for the activity coefficients in polymer solvent systems.

4. Absorption and Stripping Work

Since the ultimate overall aim of this research is to use silicone oils in the removal of volatile organic compounds from contaminated gaseous streams, absorption and stripping work at pilot plant scale is recommended. This work will provide information as regards absorption performance and the desired subsequent removal of the VOC from the absorbent in this case silicone oils.

5. Photographic work to study flow characteristics

This involves taking photographs of the flowing fluid. The use of a colorant can be implemented to ease flowing pattern identification. The work will involve the following;

(i) an observation of the flow characteristics such as channelling

(ii) a study of the effect of the initial distribution on the performance of the columns in terms of wetted area.

(iii) a study of the effect of varying liquid and/or gas flow rates on overall distribution or wetting.

6. Packed column performance studies

The author proposes a detailed study of the variation of efficiency in packed columns under different operating conditions. These conditions are as follows; composition,

liquid-gas ratio, packing material and surface nature, packing orientation, surface tension, interfacial area, liquid hold-up, initial liquid distribution and maldistribution. Testing various types of packing will provide information as far as the most suitable packing for mass transfer studies involving silicon oils are concerned.

7. Activity Coefficients in water using G.L.C

To achieve full comparison of the activity coefficients in water and those in silicone oils it is necessary to determine activity coefficients of the volatile organic compounds in water using the simple, rapid and accurate gas-liquid chromatographic technique.

9. Testing other oils

From the obtained phase equilibrium data, silicone oils sound favourable for the removal of volatile organic compounds from contaminated air streams. However there is a possibility that the oil can present flow or mass transfer problems in columns. To overcome this, it might be necessary to determine activity coefficients of the VOCs in other oils such as glycol, polyethylene, dibutyl phthalate and Shell. This broadens the data bank that can be used in the selection of a suitable absorbent to cover phase equilibrium and mass transfer properties. The measurement of activity coefficients in other oils will be easy and fast with the established G.L.C technique.

CHAPTER NINE

LIST OF REFERENCES

CHAPTER 9: LIST OF REFERENCES

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APPENDICES

APPENDIX A: VOC ABATEMENT BY ABSORPTION SYSTEMS

A.1. Introduction

Absorption involves the removal of a volatile organic compound from gas streams by contacting the contaminated air with a suitable absorption fluid. Absorption systems can be split into two categories, those in which the interface transfer is by purely physical processes and those in which a chemical reaction occurs between the component being absorbed and the absorbent.

A.2. Physical Absorption Systems

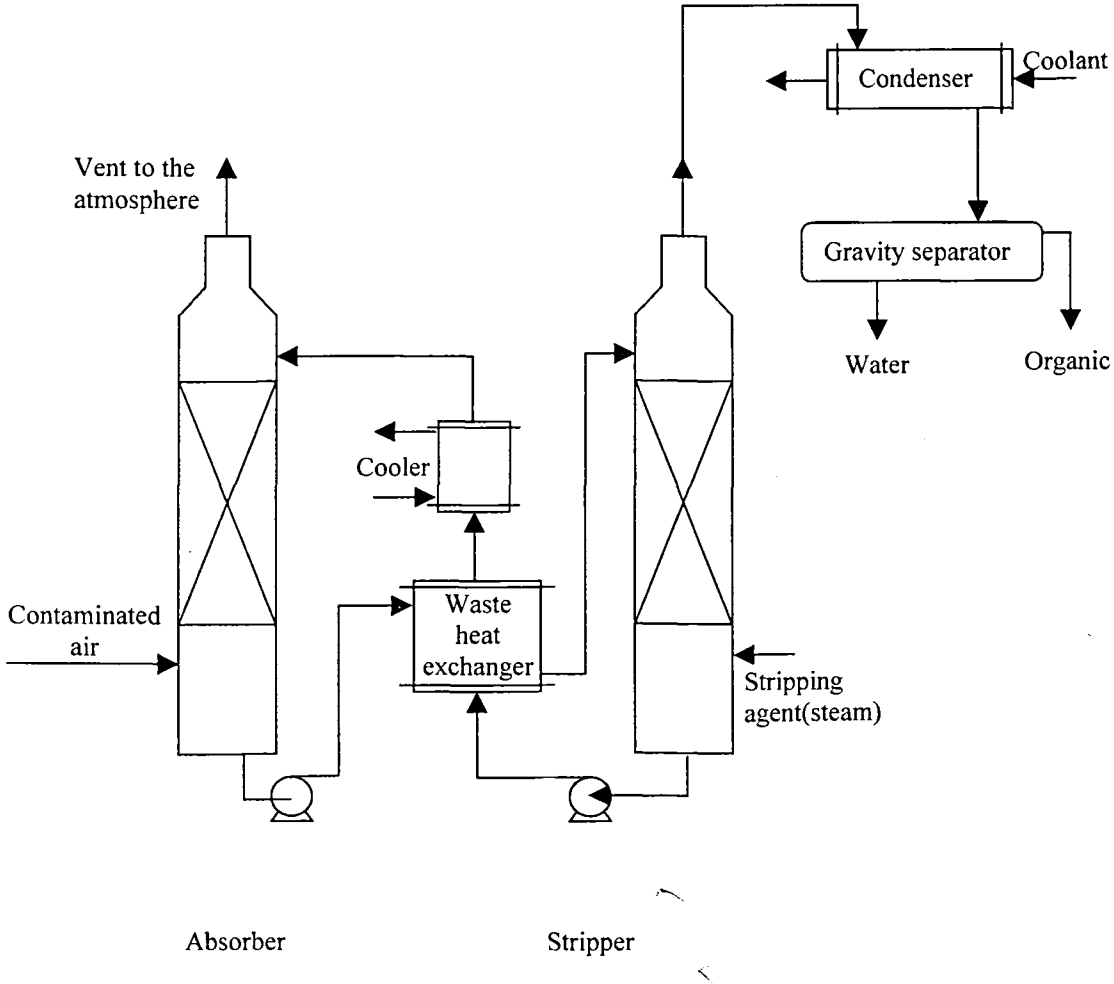


Figure A1: Simple Absorption System

A simple physical absorption system consists of either one or two columns as shown in figure A.1. The contaminated gas streams enter through the base of the absorber and is contacted counter currently with the liquid phase absorbent over a suitable mass transfer media, say packing or plates. In order to maintain efficient operation and effective absorption, the concentration of the absorbed species must be kept low. This can be achieved by bleed and make up streams for single columns while in a two- column system stripping of the compound from solution can be implemented as shown in figure A.1. The contaminated liquid stream leaving the base of the absorber is pumped to the desorption column where the absorbent is recovered. The desorption column strips the contaminant from the liquid absorbent by counter current contact with an inert gas. To improve the efficiency of the system, heating or cooling maybe necessary. Stripped contaminants can be recovered by condensation or they can be passed on to an incinerator. Absorption is controlled by the physical properties of both the contaminant and the absorbent. Generally, the solubility of the contaminant in the liquid phase increases as the temperature is reduced. Therefore it is advisable to cool the adsorbent prior to entering the column.

A.2.1 The QVF Absorption Process

Many organic solutions have limited solubility in aqueous solutions and also even those that are soluble quickly saturate the re-circulating solution. A solution to this problem will be an absorption into an organic solution, followed by stripping and subsequent recovery. The principal components are two packed columns, an absorption column C1 and desorption column C2, with the absorbent circulating between them. Exhaust VOC laden air is passed up through C1 where it is washed counter- currently by the down flowing

liquid. The VOCs are absorbed by the liquid with the aim of making sure that the air leaving the top of the column passes to the atmosphere essentially free of organics. The liquid leaving the base of C1 is now contaminated with the VOCs and must be regenerated before it can be returned to the absorption column. The regeneration is achieved by steam stripping in column C2. The absorbent is heated by first inter-changers (E1) and then by the steam (E3) and fed to the top C2. The VOCs together with the stripping stream are delivered from the top of C2 to the overhead condenser E4, where they are separated into aqueous and organic phases. The stripped absorbent leaving the base of C2 can now be cooled (E1 and E2) and returned to C1. To close the loop, the exhaust from the vacuum pump is vented to the atmosphere through the absorption column.

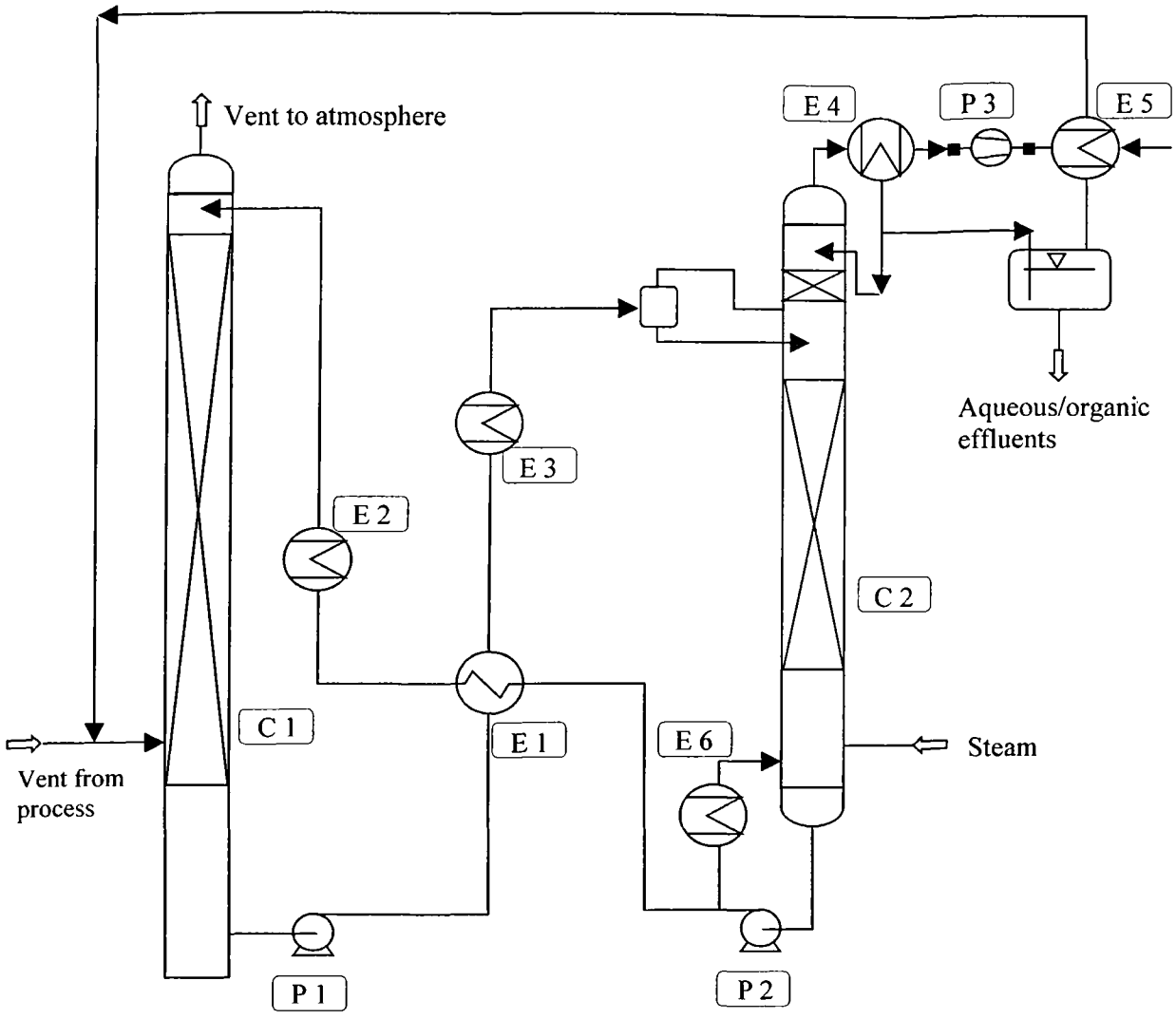


Figure A.2: Absorption of VOCs by the QVF process

The steam used for stripping is delivered as the aqueous effluent although it can be further processed to remove dissolved VOCs and recycled for stripping. Either way, the steam consumption for stripping is usually a major factor in the process economics and should be reduced to a minimum practical level. Correctly designed and operated QVF absorption processes can generally achieve VOC emission levels an order of magnitude better than the current values generally considered as BATNEEC.

A.2.2. Chemical Absorption Systems

In chemical absorption systems the contaminant is removed by reaction with the absorbent. If the reaction is fast compared to the rate of absorption, little or no contaminant is found in the liquid phase. The resulting maintained concentration gradient between the gaseous and liquid phases maintains a strong driving force for mass transfer and hence increased rate of absorption.

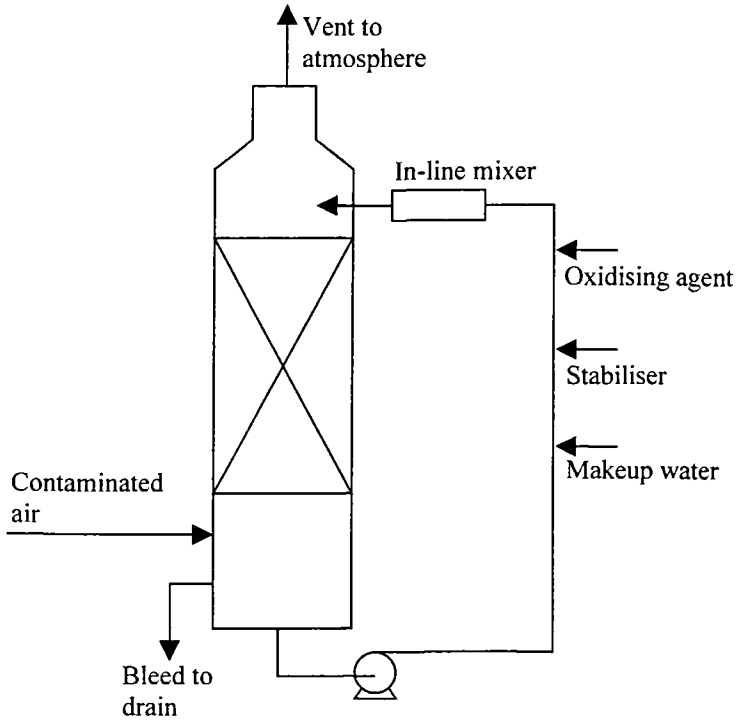


Figure A.3: Single stage chemical absorption system.

The absorbent utilised in chemical absorption systems is chosen for its reactivity with the contaminant to be removed. The following oxidising agents can be used, hydrogen peroxide, nitric acid, potassium permanganate, ozone and sodium hypochlorite. However the most common utilised oxidising agent is alkaline sodium hypochlorite liquor. This is mainly because of its high redox potential, low cost and easy of handling. The drawbacks associated with this system include maintaining a pH of approximately 9 by hydroxide dosing. A pH above 9 will cause excessive hydroxide usage from carbon dioxide

absorption. If the pH is allowed to fall, an increased potential of hypochlorite decomposition producing free chlorine in the off gas exists. Lowering the temperature of the scrubber can decrease free chlorine production.

Figure A.3 shows a simple chemical absorption system. Compared to physical absorption, the absorbent is destroyed by the reaction, therefore there is no need for second regeneration column. Chemical absorption has distinctive features such as the oxidising agent feed (dilute sodium hypochlorite), oxidant stabilizer feed (sodium hydroxide) and top up water feed for evaporative and bleed losses. The importance of including a bleed to drain lies in keeping the concentration of oxidised species in the recycling liquor to acceptable levels.

The autogenous oxidation of absorbed species can be slow requiring substantial liquor reservoir residence times. This results in increased inventory, plant size and eventually cost. Increasing the concentration of sodium hypochlorite to provide scrubbing liquor with increased oxidation potential can overcome the above problem. Increasing hypochlorite concentration introduces other problems, notably the production of chlorinated by-products. Two solutions are available for these problems (i) increasing the oxidation potential of the system without increasing the hypochlorite concentration, this can be done by adding a selective catalyst to increase the rate of reaction (ii) the use of a three stage scrubbing system.

Three-stage chemical scrubbing system.

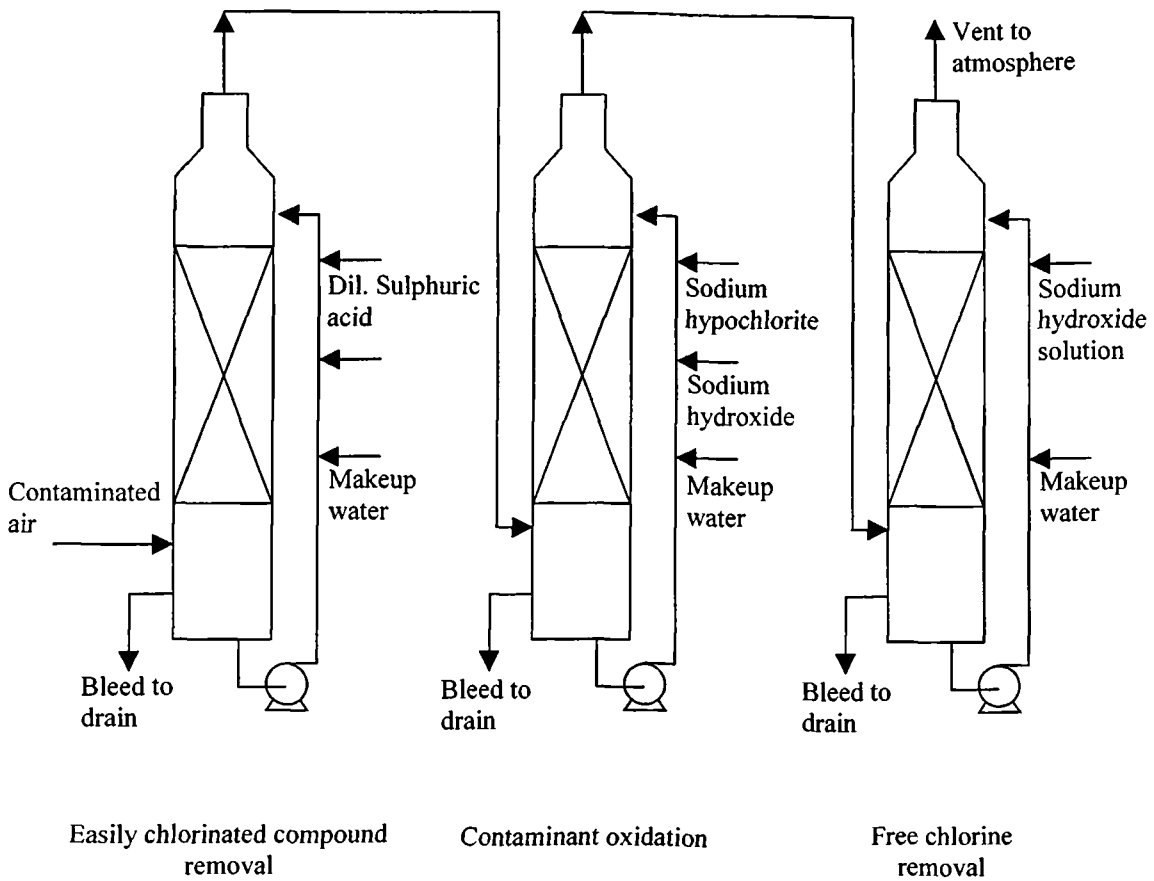


Figure A.4: Three – stage chemical scrubbing system

The three-stage system reduces the chlorination of simple organic compounds such as amines by reaction with sulphuric acid to form soluble salts in the first scrubbing stage. After this, the contaminated stream is passed through a conventional hypochlorite scrubber where VOC removal is by oxidation. In the third absorber, sodium hydroxide is used to absorb any chlorine produced in the second stage from acid decomposition of hypochlorite. In addition to this, the alkaline solution removes acidic components from

the gas stream. Three-stage systems are effective in problematic streams provided that the contaminant or contaminant product concentration in the recycling liquor is kept constant. This is crucial in the second stage and can be achieved by increasing the makeup water and consequently bleed line flow rates.

A.2.3 Summary of physical and chemical absorption systems

Absorption is a frequently used and well-understood VOC abatement technology. Generally physical absorption is controlled by phase equilibrium dynamics while chemical absorption is controlled by liquid phase reaction rate.

Comparison: physical and chemical absorption

1. When the contaminant is valuable, physical absorption is very useful in that the VOC can be collected and recycled.
2. Due to absorbent consumption, running costs of chemical absorption system are most likely to be high.
3. If systems are not designed effectively, there is a risk of producing different and sometimes worse gas phase contaminants.
4. Because of liquid phase contaminant removal by reaction, salt formation or oxidation, gas-liquid mass transfer rates are generally higher in chemical absorption systems.

Advantages

(a) Collection of expensive contaminants for recycle

(b) Relatively low pressure drop

(c) High mass transfer efficiency, thus high VOC removal especially when high efficiency column packings are used.

(d) Low capital cost

(e) Small space requirements

(f) Can be applied to a variety of VOCs

Disadvantages

(a) Particulate laden streams can cause column packing fouling, hence reduction in mass transfer efficiency.

(b) Possibility of different and / or worse gas stream contaminants.

(c) Production of liquid waste.

(d) High running costs for chemical scrubbing

(e) When the inlet gas is at an elevated temperature, cooling in the absorber will reduce the exist gas buoyancy and thus dispersion.

A2.4 Catalytically enhanced chemical absorption systems

A.2.4.1 The Odorgard Process

The odorgard process was pioneered by ICI Katalco and Dr Fred Valentin (1994). The efficient chemical scrubbing is combined with catalytic reaction, pH control and hypochlorite concentration of the re-circulating scrubbing liquor. A simplified process flow diagram of the Odorgard process is shown in figure A.5.

The major components are the (single) scrubbing column, the scrubbing liquor re-circulation loop with the inline catalytic reactor and the controlled addition of the caustic and hypochlorite reagents.

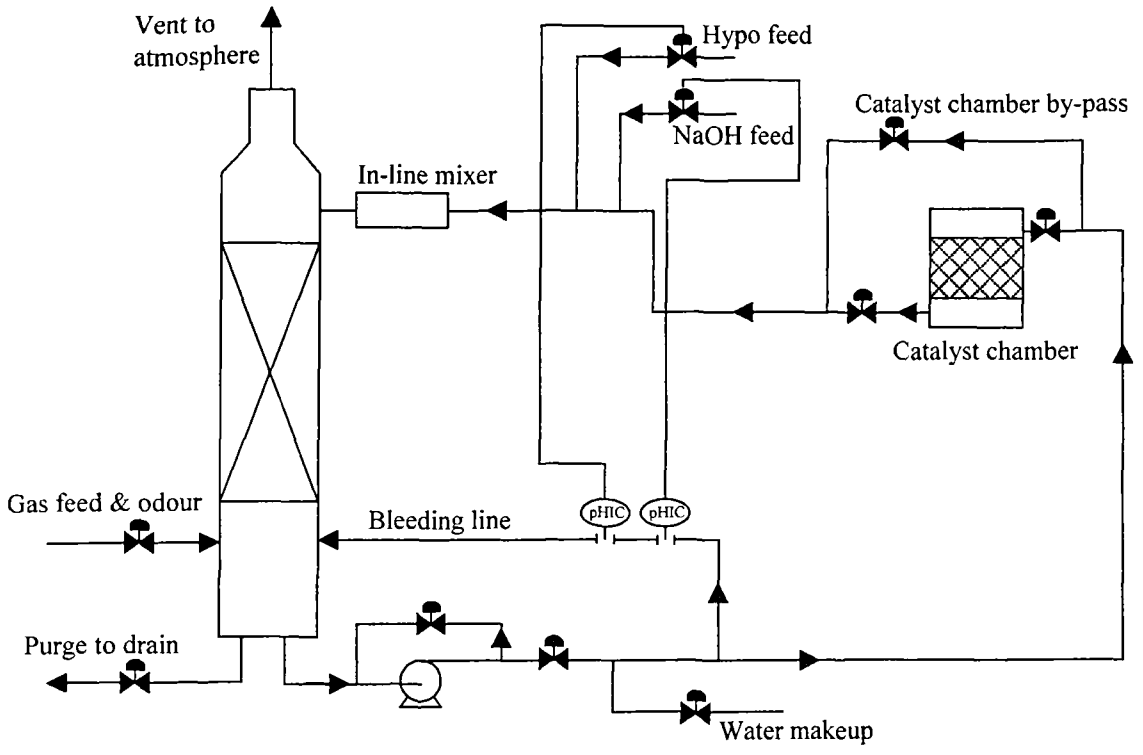


Figure A.5: The Odorgard process

A.2.4.1.1 Systems Components

(a) The Scrubbing Column

In the tower the contaminated gas stream is contacted with the oxidising liquid stream (dilute alkaline hypochlorite liquor) typical gas residence times in the packed section are 1.5 to 2.5 seconds and design superficial velocities 1.6 to 2.2 m/s. However, longer residence times are required at high contaminant loading. The tower must be constructed from U-PVC, polypropylene, stainless steel or equally resistant material.

A liquid purge is taken from the column sump or from downstream of the reactor, to prevent build up of salts and reaction products. The purge rate in normally less than 0.5% of the re-circulation rate. The liquid volume is kept constant through a make up water stream. Losses of chemicals to drain do not generally significantly affect operating costs

or present any effluent disposal problem. In order to protect the catalyst, an anti-scalant should be added unless calcium levels in the water are reliably very low.

(b) Catalytic reactor

The design of the reactor is based on a space velocity in the range 500 to 1500 per hour but design values should be kept flexible and will depend on the type of organic compound present. Large stable organics, particularly aromatics will require longer residence times compared to smaller reactive compounds such as alcohols. The catalyst used is normally 81-1, a nickel oxide based catalyst, produced in spherical pellet form 1 to 3mm in diameter.

(c) Control Systems

In order to maintain a particular operating redox potential and pH to acceptable level, sodium hypocholrite and hydroxide are dosed into the recycle liquor. Control of the dosing is performed by temperature-adjusted rH and pH, together with three term PID controllers, with probes usually located in the sump, recycle line or alternatively the column bleed. Operating pH is usually between 9 and 9.5 which is critical to the system operation. If the pH falls to below 8.5 the catalyst is damaged beyond repair and when it increases to above 9.5 unacceptably high hydroxide use occurs due to CO_2 chemisorption in the column.

A.2.4.1.2 Advantages of the Odorgard process

The following advantages are associated with the Odogdard process

1. Lower hypochlorite concentration can be utilised to achieve same removal rates like similar sized hypochlorite only scrubbers. This lowers the production of chlorinated

by products and the release of chlorine in the off gas. Hence there is a reduction in the use of hypochlorite, which means low running costs.

2. The low liquid residence time can lead to small plant size and low capital costs.
3. The use of catalyst enhancement improves the removal rates.

A.2.5 Absorption in the presence of particulates

Particulate laden gas streams can be treated in a number of ways, usually involving pr-treatment to remove the particulates before VOCs removal commences. However specifically defined absorption systems, such as plate scrubbers or fluidised bed scrubbers can provide both effective VOC and particulate removal in the same unit.

A.2.5.1 Plate scrubbers

One of the major limitations associated with conventional packed column scrubbers is their inability to handle particulate-laden gas streams. The deposition of solids in the packing results in reduced free area and an associated increase in pressure drop. The ability of the unit to extract fumes falls and ultimately the bed can block completely. In plate columns the soluble gases and particulates are removed after passing vertically upwards through a series of holes in a plate across which in layer of liquid is flowing horizontally.

The Impinjet scrubber is a particular example of a plate scrubber, which provides increased removal performance by impinging the gas flow onto a target as it passes through the orifice. Gas scrubbing can take three forms; removal of dust and fume particles, chemical absorption of gases by scrubbing liquid and condensation of gases into the scrubbing liquid.

Scrubbing is accomplished by intimate contact between the gas and the scrubbing liquid on the impingement baffle plate. Two factors contribute to the high scrubbing efficiencies:

(a) Acceleration of dust particles and aspirated droplets through the orifices, with subsequent physical arrestment on the wetted baffle section.

(b) Formation of minute gas bubbles created by the gas impinging on the baffles, causing high turbulence and providing extremely close gas-liquid contact for maximum absorption of contaminants and mass transfer.

While Impinjet scrubbers are installed mainly for air cleaning duties, the basic design enables a number of operations to be combined in an economical process.

Dust Collection

Efficient low – energy collection of particulate material can be achieved using one – or two stage scrubbers so as to control atmospheric pollution. The process may also be utilised to recover valuable products carried over from dryers and cyclones which would otherwise be lost to the atmosphere.

A.2.5.2 Fluidised-bed scrubbing

Under certain demanding circumstances, beds of hollow plastic packing fluidised by an ascending gas stream offer advantages over fixed beds in scrubbers. This applies especially if solids are entrained in both phases, in which case static internals tend to become encrusted and fouled. The solids may be present in the gas stream or in the products of reaction.

An example is the desulphurisation of flue gas by gypsum process. Solids formed in the process would lead to blockage of conventional packing, so that the spray towers without internals represent practically the only means of ensuring reliable operation over long periods. Other cases in which static internals can frequently be ruled out arise if fluvial water is used for scrubbing and algal growth can therefore be expected, or if the scrubbing fluid is recycled through a biological water-treatment plant and micro-organisms are introduced into the scrubber.

The first fluidised scrubbers made use of hollow plastic spheres as contact elements. However, gas velocities and bed depths resulted in ball breakages, forcing designers to experiment with alternative hollow bodies that were stronger and produced increased turbulence between the gas liquid phases. Ellipsoidal fluidised packing elements have proved to be very effective. The ellipsoids also offer lower pressure drop at higher loadings compared with spherical packing.

The main structural difference between columns with fluidised-bed packing and columns with fixed beds is that the former require separate support grids for each bed and a retention grid above the uppermost bed may also be necessary. An efficient gas distributor is also needed to fluidise the packing uniformly; the energy required for fluidisation is then supplied by the stream.

Any extra bonus that can be linked to fluidised beds is their ability to handle particulate-laden gases. The fluidised units also provide effective mass transfer. In fixed beds of packing, the liquid generally flows in the form of a film over the available surface,

whereas in a fluidised bed the liquid is mostly in the form of droplets and rivulets, which results in increased surface area and renewed surfaces. The collisions between the individual elements of packing and the liquid droplets also contribute towards mass transfer because they ensure that the exposed liquid surfaces are constantly renewed. In addition to that the gas phase in the fluidised bed is well mixed by the movement of the solid and liquid particles.

A.3 A brief survey of other abatement techniques

A.3.1 Adsorption systems

Adsorption is considered to be the most widely used recovery method in VOC control. The technique is based on a physical process in which certain molecules from the inlet air collect on the surface of an adsorbent, attracted and held by intermolecular van der Waals forces. As this process is reversible, the 'trapped' molecules can be released and recovered by desorption. Activated carbon, polymeric resins and some molecular sieves are the most common used effective adsorbents for solvent control.

A.3.2 Condensation

Low temperature condensation is in wide spread use throughout the process industries for controlling the emissions of volatile organic compounds from process plant vents to the atmosphere. This is achieved by reducing the temperature of the waste gas stream to a level that vapours condense. For users of nitrogen gas within the fine / speciality chemical and pharmaceutical industries it offers a combination of flexibility, simplicity, high control efficiency and low costs which other techniques can not offer.

A.3.3 Combustion systems

The combustion system as a method of control and removal of organics from waste gas streams, is well documented and practised. The organic contaminant is oxidised in air to form carbon dioxide, water vapour and other products. It is classified into two different technologies, thermal and catalytic oxidation. In thermal oxidation, organic contaminants are heated to combustion temperature and oxidised. Catalytic oxidation relies on a catalyst to convert the contaminants to carbon dioxide and water at a lower temperature than that required in thermal oxidation.

A.3.4 Biological systems

These utilise micro-organisms to break down organic material to harmless by-products. The products formed are dependent on the contaminant, however simple compounds such as carbon dioxide and water are usually produced. The four systems normally used are bio-filtration, bio-scrubbing, bio-trickling and membrane bioreactors.

A.3.5 Membrane technology

Permeation through a membrane is used to separate solvents from a gas stream. The process is best suited to high solvent concentrations.

APPENDIX B: ABSORPTION THEORY

B.1 Introduction

Absorption is a process involving transfer of one or more components from the gas into the liquid phase through physical solubility. It maybe one step in many process applications. Many of these applications may involve subsequent chemical reactions between the absorbed material and some component in the liquid phase. However the material discussed here will apply only to the absorption of some component and any subsequent chemical reactions or transformation are not presented in this treatment. This treatment is presented because after establishing both experimental and theoretical methods for determining phase equilibrium between volatile organic compounds and silicon oils, work on absorption and stripping columns will be done in the future.

Absorption practically never occurs as a single operation in any process or plant. The large volume of solvent required for the absorption process usually dictates that a stripping column be included. Primarily, the purpose of the stripping column is to remove the solvent material absorbed in the absorption column. Therefore, there is a direct interconnected relationship between the efficiency of the absorption column and the efficiency of the stripping column for removing the absorbed components. Although this interconnecting relationship is rarely addressed directly in treatments of absorption, a recognition that it exists is very essential.

All the techniques for mathematically analysing the absorption process assume that the absorber is made up of equilibrium plates or that the equilibrium exists between the vapour and liquid at any point in the absorber. Offcourse, this is not true and could

be one reason as to why it is difficult to analyse the absorber and absorption performance. From a design angle, assuming feed and solvent composition temperatures are fixed, the variables available for specification are the number of theoretical plates to be used in the absorber, the fractional recovery of the solute and the lean solvent rate. Also it is important to note that if a single component is being absorbed increasing the solvent rate will increase the absorption of that component.

B.2 Phase Equilibrium

Estimating the performance of absorbers or strippers requires knowledge of the equilibrium concentrations of the solute and the solvent. These are available in most cases as Henry's constants, vapour pressures or vapour – liquid equilibrium ratios. For a single component absorption, Henry's law constants and vapour pressures are generally more convenient while vapour-liquid equilibrium ratios tend to be used for multi-component hydrocarbon absorption.

B.2.1 Henry's law for a pure physical solvent

Consider a case of an organic component i in contact with a physical solvent in a closed system. Equilibrium is established between the mole fraction of i in the liquid phase x_i and the mole fraction of i in gas phase y_i. At equilibrium assuming ideality

$$Y_i = Hx_i \quad \text{..... (B1)}$$

B.2.2 Effect of temperature on phase equilibrium

Henry's constant depends on temperature, it can vary by a factor of 2 or 3 over a small temperature difference like 10^0C. Henry's law constant for volatile organic compounds can be generally assumed to follow the empirical relationship

$$\log_{10} H = \frac{\Delta H^{l}}{2.3RT} + K$$

..... (B2)

Here H is the Henry's constant at temperature T, R is the universal gas constant, ΔH^{l} is the dissolution enthalpy and K is a constant.

B.3 Physical Absorption

B.3.1 Film Coefficients

Many workers in the field of mass transfer have proposed models to describe the mass transfer that occurs in absorption of a solute from the gas phase to the liquid phase. The proposed models vary in complexity and the mathematical technique used to develop the mass transfer coefficients. Each model was found to be advantageous in certain applications and suffer from drawbacks as far as generality of use in mass transfer is concerned. Of the many proposed models, the most significant in the absorption processes are the two film theory, Whitman (1923), Penetration model Higbie (1935), Surface renewal model of Danckwerts (1951) and the film penetration model of Toor and Marchello (1958).

B.3.1.1 Two film theory

The first serious attempt to model the process of absorption was made by Whitman (1923) in his two film theory. It was the first theory or model proposed for mass transfer across a fluid interface. Although not closely representing the conditions in practical equipment it is still probably the simplest and most widely used and can be applied to the commonly available data.

Figure B.3.1 Two film concentration profile for absorbed component A.

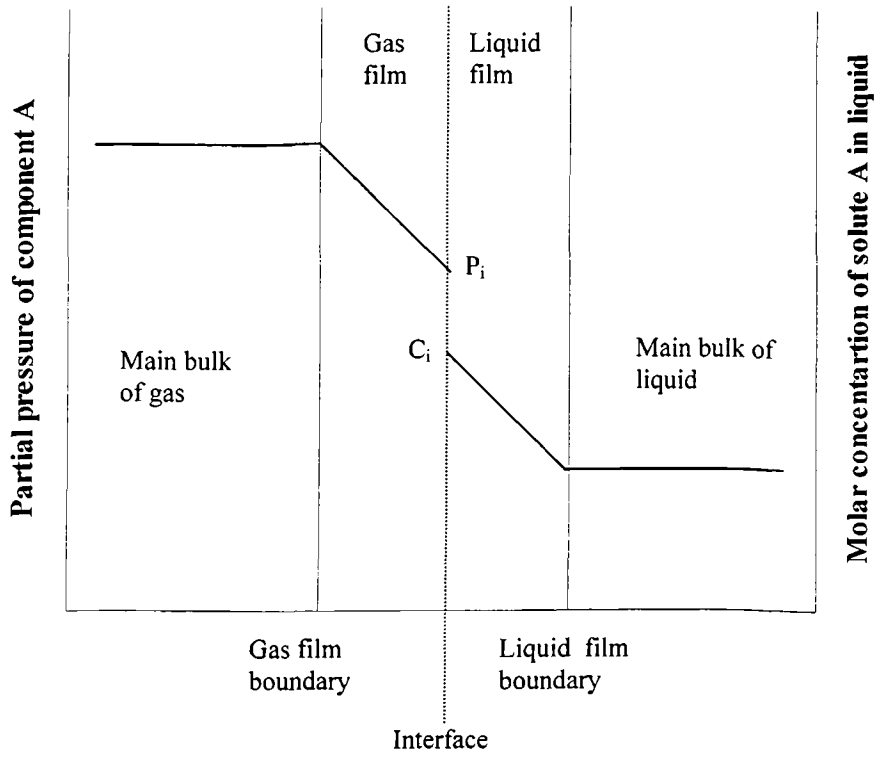


Figure B.1: Two film concentration profile

According to the two-film theory (figure B.1), material is assumed to be well mixed within the bulk of each phase by convection currents. Therefore according to this assumption no mass composition gradients exists in either the gas or liquid phases. Also the composition, temperature and pressure are assumed known in the bulk gas and liquid mixture. On either side of the gas –liquid interface it is assumed that the currents die out and there exists a film, in which the transfer of component A is controlled purely by molecular diffusion. The flow in the film is assumed to be laminar and if the thickness of the films were known, the mass transfer could be calculated through the use of diffusion coefficients. However, measurement of the

film thickness is impractical and hence its inclusion in the mass transfer coefficients developed based on the two – film model.

The rate of mass transfer of component A (r_A) through the liquid film is equal to that through the gas film, so that

$$r_A = k_G a(P_A - P_{Ai}) = k_L a(C_{Ai} - C_A) \quad \text{(B3)}$$

Where k_G and k_L represents the gas and liquid film coefficients respectively, a being the surface area available for mass transfer. As a procedure for obtaining the values of k_G and k_L, the measurements of interface concentrations P_{Ai} and C_{Ai} are required. Such measurements are impossible and therefore equation (B.3) is modified to make use of the overall gas and liquid coefficients K_G and K_L respectively resulting in equation (B.4) below

$$r_A = K_G a(P_A - P_A^*) = K_L a(C_A^* - C_A) \quad \text{(B.4)}$$

Where P_A^* is the partial pressure of A in equilibrium with C_A and C_A^* is the liquid phase concentration of A in equilibrium with P_A. For systems that obey Henry's law, C_A^* and P_A^* can be calculated using equation (B.1). The overall film coefficients $K_G a$ and $K_L a$ can be related to the $k_G a$ and $k_L a$ through equations (B.5) and (B.6) respectively.

$$\frac{1}{K_G a} = \frac{1}{k_G a} + \frac{H}{k_L a} \quad \text{(B.5)}$$

$$\frac{1}{K_L a} = \frac{1}{k_L a} + \frac{1}{HK_G a} \quad \text{(B.6)}$$

From the above two equations it can be deduced that for components with low Henry's law constants the last term in equation (B.5) approaches zero, hence

$K_G a \approx k_G a$. In this situation the process can be considered to be gas film resistance controlled. For components with high Henry's constants, the last term in equation (B.6) approaches zero, thus $K_L a \approx k_L a$. In this case the process is considered to be liquid film controlled.

B.3.1.2 Penetration Model

In developing this model, Higbie (1935) assumed that the liquid surface in contact with the gas consisted of small fluid elements. After each element contacted the gas-phase, it returned to the bulk of the liquid. As it left the interface it was replaced by an element from the bulk liquid phase. Each element was assumed to spend the same time at the surface of the liquid and in contact with gas.

At first, the concentration of dissolved gas in the eddy is uniformly c_{A0}, and the eddy is considered to be stagnant internally. When the eddy is exposed to the gas at the surface, the concentration in the liquid at the gas-liquid surface is $c_{A,I}$. This can be considered to be equal to the equilibrium solubility of the gas in the liquid. During time θ, the liquid particle is subjected to unsteady state diffusion or penetration of solute in a particular direction say z and the following approximation can be applied

$$\frac{\partial c_A}{\partial \theta} = D_{AB} \frac{\partial^2 c_A}{\partial z^2} \quad \text{..... (B.7)}$$

Considering short exposure times and with slow diffusion in the liquid, the solute dissolving molecules are never able to reach the depth z_b corresponding to the eddy, thus from the solute point of view, z_b is essentially infinite.

The following conditions are applied to equation (B.7)

$$c_A = \begin{cases} c_{A0} & at \quad \theta = 0 \quad for \quad all \quad z \\ c_{A,i} & at \quad z = 0 \quad for \quad \theta > 0 \\ c_{A0} & at \quad z = \infty \quad for \quad all \quad \theta \end{cases}$$

Equation (B.7) can be solved to obtain the average flux over the time of exposure as

$$N_{A,av} = 2\left(C_{A,i} - C_{A,o}\right)\sqrt{\frac{D_{AB}}{\pi\theta}} \quad \text{.....(B.8)}$$

and also

$$k_{L,av} = 2\sqrt{\frac{D_{AB}}{\pi\theta}} \quad \text{.....(B.9)}$$

B.3.1.3 Surface renewal model

Danckwerts (1951) suggested a modification of the penetration model by assuming a time distribution for contact of fluid elements with the gas phase. Therefore by using the assumed time distribution, an average exposure time for the element can be determined. The gas-liquid interface is then a mosaic of surface elements of different exposure time histories. Since the rate of solute penetration depends upon the exposure time, the average rate for a unit of surface area must be determined by summing up the individual values. On the assumption that the chance of a surface element's being replaced by another is independent of the time it spend on the surface, taking s as the fractional rate of replacement of elements, Danckwerts (1951) found

$$N_{A,av} = \left(c_{A,i} - c_{A0}\right)\sqrt{D_{AB}s} \quad \text{.....(B.10)}$$

and therefore

$$k_{L,av} = \sqrt{D_{AB}s} \quad \text{.....(B.11)}$$

B.3.1.4 Combination film-surface renewal theory

Dobbins (1956, 1962) dealing with the rate of absorption of oxygen into flowing streams, made two conclusions;

(a) The film theory $(k_L \alpha D_{AB})$ assumes a time of exposure elements sufficiently long enough for the concentration profile within the liquid phase to be characteristic of steady state.

(b) The penetration and surface renewal models $(k_L \alpha D_{AB}^{0.5})$ assume the surface elements to be essentially infinitely deep. Therefore the diffusing solute never reaches the region of constant concentration below.

The observed dependence $(k_L \alpha D_{AB}^{n})$, n being influenced by circumstances, might be explained by allowing for a finite depth of the surface elements or eddies.

Dobbins replaced the third boundary condition on equation (B.7) by $c_A = c_{A0}$ for $z = z_b$, where z_b is finite. Using Danckwerts' rate of renewal of the surface elements, he obtained

$$k_{L,av} = \sqrt{D_{AB^s}} \coth \sqrt{\frac{sz_b^2}{D_{AB}}} \quad \text{..... (B.12)}$$

When there is rapid penetration (D_{AB} large), the rate of surface renewal (s small) or for thin surface elements the rate of mass transfer coefficient is that described by the film theory. For slow penetration or rapid renewal the mass transfer coefficient is that of the surface renewal model, Therefore $(k_L \alpha D_{AB}^{n})$, where n may have any value between the limits 0.5 and 1.0 which could account for many observations. Toor and

Marchello (1958) arrived at the same suggestions by proposing a combination of the film and penetration models.

B.3.2 Estimating gas and Liquid film coefficients

B.3.2.1 Gas – film controlled processes

The simplest way of estimating the gas film coefficients is by relating the Sherwood number (Sh) to the Reynolds (Re) and Schmidt (Sc) numbers. Thus according to Morris and Jackson (1953)

$$Sh = \alpha \operatorname{Re}^{\beta} Sc^{\phi} \qquad \text{(B.13)}$$

Where α, β and ϕ are constants with variation among different authors. By correlating available data on gas absorption in packed columns for a range of packings, Onda *et al* (1968) produced a dimensionless equation (B.14) based on equation (B.13)

$$\frac{k_G RT}{a_t D_g} = \propto \left(\frac{G}{a_t u_g}\right)^{0.7} \left(\frac{u_g}{\rho_g D_g}\right)^{1/3} \left(a_t d_p\right)^{-2} \qquad \text{(B.14)}$$

In the above equation α was found to be 5.23 for ring and saddle packing larger than 12mm. Predictions made with equation (B.14) were found to have an accuracy of $\pm 30\%$. Gilliland et al in Coulson and Richardson (1991) produced another similar equation (A.9) for absorption in wetted wall columns

$$K_G RT \tfrac{d}{D_g} \frac{P_{BM}}{P} = \propto \operatorname{Re}^{0.83} Sc^{0.44} \qquad \text{(B.15)}$$

Values of $\propto$ varied from 0.021 tom 0.027, however it is generally accepted to take a mean value of 0.023. Other correlations for K_G are available in Coulson and Richardson volumes 1 and 2 (1977, 1993).

B.3.2.2 Liquid film controlled processes:

Like gas film controlled process, there are many correlations relating $K_L a$ with system properties. Based on the correlation available absorption and desorption data for a range of packings, Onda et al (1968) presented the empirical equation below.

$$k_L\left(\frac{\rho_L}{u_L g}\right) = 0.0051\left(\frac{L}{a_w u_L}\right)^{2/3}\left(\frac{u_L}{\rho_L D_L}\right)^{-1/2}(a_t d_p)^{0.4} \quad \text{..... (B.16)}$$

It was found that the correlation could represent experimental liquid film coefficients to within accuracy of $\pm 20\%$. Hutchings et al (1949) performed experiments on the absorption of di-methylketone in several packed towers with various sizes of Raschig rings. He found the liquid film mass transfer coefficient to be a function of liquid rates and not a function of gas flow rate and packing size, equation (B.17).

$$K_L a = 0.283 L_m^{0.8} \quad \text{..... (B.18)}$$

L_m represents the liquid molar loading in the column (moles/m^2.sec). Also additional correlations for film controlled processes are available, Coulson and Richardson volume 2 (1991).

B.3.3 Interfacial area estimation

Onda et al (1968) proposed equation (B.19) for predicting wetted surface area in irrigated packed columns. In this equation, the liquid surface tension and the surface energy of the packing are taken into consideration.

$$\frac{a}{a_t} = 1 - \exp\left\{-1.45\left(\frac{\sigma_c}{\sigma_l}\right)^{0.75}\left(\frac{L}{a_t u_l}\right)^{0.1}\left(\frac{L^2 a_t}{\rho_L^2 g}\right)^{-0.05}\left(\frac{L^2}{\rho_L \sigma_L a_t}\right)^{0.2}\right\} \quad \text{..... (B.19)}$$

B.3.4 Packed tower design: NTU and HTU

Consider a packed counter –current absorption tower in figure B2. In this absorption tower, let the gas flow rate be G_m (kg/hr.m^2) and the liquid flow rate down the column be L_m (kg/hr.m^2). X and Y are the mole fractions of the component to be absorbed.

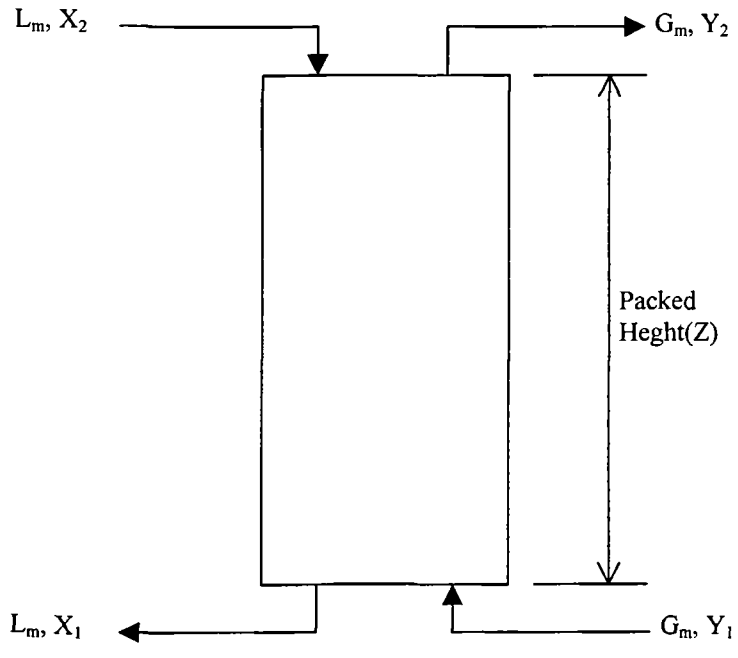


Figure B2: A typical packed counter current absorber

B.3.4.1 Height of column based on the gas film.

Considering the diffusing material over a small height of packing δz, the height of the packing (z) can be related to the gas film coefficient and concentration of solute by equation (B.20)

$$z = \frac{G'_m}{k_G a P} \int_{y_2}^{y_1} \frac{dy}{y - y_i} \quad \text{..... (B.20)}$$

As previously discussed in section B.3.1.1, the measurement of y_i, the mole fraction of solute at the gas/liquid interface is usually impossible. Therefore an overall gas film mass transfer coefficient is employed using an equilibrium value of the phase mole fraction, resulting in equation (B.21) below

$$z = \frac{G'_m}{K_G aP} \int_{y_2}^{y_1} \frac{dy}{y - y^*} \quad \text{..... (B.21)}$$

When the system is dilute, the equilibrium line is taken to be linear over the operating values, then the equation (B.22) below is applicable to the system.

$$\int_{y_2}^{y_1} \frac{dy}{y - y^*} = \frac{y_1 - y_2}{(y - y^*)_{lm}} \quad \text{..... (B.22)}$$

$(y - y^*)_{lm}$ is the log mean concentration difference and is obtained using equation (B.23)

$$(y - y^*)lm = \frac{(\Delta y_1 - \Delta y_2)}{\ln\left(\frac{\Delta y_1}{\Delta y_2}\right)} \quad \text{..... (B.23)}$$

In equation (B.23), y^* represents the equilibrium value of y corresponding to x hence,

$$\Delta y_1 = y_1 - y_1^* = y_1 - Hx_1 \quad \text{..... (B.24)}$$

and

$$\Delta y_2 = y_2 - y_2^* = y_2 - Hx_2 \quad \text{..... (B.25)}$$

B.3.4.2 Height of column based on liquid film

The same procedure as the one used in section B.3.4.1 can be repeated for the liquid film giving equation (B.26) for the overall liquid film coefficient

$$z = \frac{L'_m}{K_L aC_T} \int_{x_2}^{x_1} \frac{dx}{x^* - x} \quad \text{..... (B.26)}$$

Here C_T = (mole of solute + solvent) * (volume of liquid)

B.3.4.3 Height of transfer unit (HTU) and Number of transfer units (NTU)

Considering that the height of packing in absorption tower can be calculated as a product of the height of transfer units, (B.27) and (B.28), then the height and number of transfer units can be calculated.

$$z = HTU_{OG} * NTU_{OG} \quad \text{.....(B.27)}$$

$$z = HTU_{OL} * NTU_{OL} \quad \text{.....(B.28)}$$

HTU_{OG} and HTU_{OL} are the height transfer units based on the overall gas and liquid phase mass transfer coefficients, respectively. These are shown in equations (B.29) and (B.30). Taking the assumption that the systems are dilute and that the operating lines are straight, then NTU_{OG} and NTU_{OL} are the number of transfer units based on the overall gas and liquid mass transfer coefficients, they can be given by equations (B.31) and (B.32).

$$HTU_{OG} = \frac{G_m'}{K_G a P} \quad \text{.....(B.29)}$$

$$HTU_{OL} = \frac{L_m'}{K_L a C_T} \quad \text{.....(B.30)}$$

$$NTU_{OG} = \frac{Y_1 - Y_2}{(Y - Y^*)_{LM}} \quad \text{.....(B.31)}$$

$$NTU_{OL} = \frac{X_1 - X_2}{(X^* - X)_{LM}} \quad \text{.....(B.32)}$$

B.3.5 Choice of absorbent

The points to consider in the selection of a suitable absorbent for any particular application include:

1. Favourable equilibrium and contaminant solubility
2. The air leaving the absorption tower will be saturated with the absorption fluid. Therefore if it is an organic liquid then the vapour pressure must be low enough to be within the legal limits to avoid the absorbent itself becoming a pollutant.
3. Whilst condition (2) above can be satisfied by many organic liquids of low volatility, the majority are oils of relatively high viscosity. Therefore mass transfer between gas and liquid would be so poor that the column height required would not be practical. It is really important that the absorbent have low viscosity.
4. Since the desorption process normally involves distillation or steam stripping at elevated temperature, the absorbent should be thermally stable over the operating range. Thus ease of contaminant desorption in stripper is important because if harsh conditions for example a vacuum are required costs will go up.
5. Low volatility so as to prevent loss of absorbent and / contamination of the off gas stream.
6. In order to achieve the limitation of hazards during operation, the absorbent should be non-toxic, non flammable and if possible non corrosive. Thus it should not present any undue hazards to healthy and safety.
7. For relative performance with more volatile compounds ie those boiling below 80^0C, the activity coefficients should be much greater than unity and be preferably below this value for a broad spectrum of compounds. For higher boiling compounds, the desorption part of the cycle tends to be more difficult and activity coefficients above unity are desirable.

8. Stability, the absorbent should not degrade substantially with time.

In any application, the first absorbent to be considered should always be water. This is because in most cases it is found to satisfy all the above criteria, particularly for organic gases and for some organics for example the absorption of acetone from cellulose manufacture. However the use of water is limited to the water miscible compounds especially those more volatile than water which can be separated fairly readily by distillation to reduce the liquid effluent problems. For organic contaminants which are sparingly soluble in water, the use of high boiling oils is found to be more effective. Oils such as dibutyl phthalate, polyethylene glycol and silicone oils can be utilised. These are more expensive absorbents and therefore column losses should be kept at minimum.

Appendix C: Liquid Phase Activity Coefficients

Appendix C.1 Activity coefficient equations:

The liquid phase activity coefficient is the most important requirement for vapour – liquid equilibrium calculations, which describe the activity coefficient as a function of liquid composition. Important activity coefficient equations appear in the work of Prausnitz (1969), Hala et al (1969), Null (1970), Wilson (1964), NRTL (1968) and UNIQUAC (1975).

C.1.1 The Wilson Equation

It is applicable to homogenous systems and the activity coefficient of component *i* in an N component system is given by

$$\ln\gamma_i = -\ln\left[\sum_{j=1}^{N} x_j \Lambda_{ij}\right] + 1 - \sum_{k=1}^{N}\left[\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{N} x_j \Lambda_{kj}}\right] \quad \text{..... (C1)}$$

where

$$\Lambda_{ij} \equiv \frac{v_j}{v_i}\exp\left[-\frac{(\lambda_{ij}-\lambda_{ii})}{RT}\right] \qquad (\lambda_{ij} = \lambda_{ji}) \quad \text{..... (C2)}$$

where $(\lambda_{ij} - \lambda_{ii})$ and $(\lambda_{ij} - \lambda_{jj})$ are the two Wilson parameters characteristic of components *i* and *j*, obtainable from binary data.

The $(\lambda_{ij} - \lambda_{ii})$ are assumed to be independent of temperature over a narrow temperature range, v_j is the liquid molar volume of pure component *j*.

C.1.2 The Non-Random Two-Liquid Equation (NRTL)

This equation is applicable to both homogeneous and heterogeneous systems. The activity coefficient of component *i* in any component system is given by

$$\ln\gamma_i = \frac{\sum_{j=1}^{N}\tau_{ji}G_{ji}x_j}{\sum_{l=1}^{N}G_{li}x_l} + \sum_{j=1}^{N}\left[\frac{x_jG_{ij}}{\sum_{l=1}^{N}G_{lj}x_l}\left(\tau_{ij} - \frac{\sum_{r=1}^{N}x_{rj}G_{rj}}{\sum_{l=1}^{N}G_{lj}x_l}\right)\right] \quad \text{..... (C3)}$$

where

$$\tau_{ji} \equiv \left(g_{ji} - g_{ii}\right)/RT \qquad \left(g_{ji} = g_{ij}\right)$$

$$G_{ji} \equiv \exp\left(-\alpha_{ji}\tau ji\right) \qquad \left(\alpha_{ji} = \alpha_{ij}\right)$$

where $\left(g_{ji} - g_{ii}\right)$ and $\left(g_{ji} - g_{jj}\right)$ are the two NRTL parameters equivalent to Wilson parameters characteristic of the components *i* and *j*. α_{ji} is a third parameter, a constant varying roughly between 0.2 and 0.47 according to the system concerned.

C.1.3 The UNIQUAC (Universal Quasi Chemical) equation

In this activity coefficient equation, applicable to both homogenous and heterogeneous systems, the activity coefficient of component *i* in an N component system is given by

$$\ln\gamma_i = \ln\frac{\phi_1}{x_1} + \frac{z}{2}q_i\ln\frac{\theta_1}{\phi_i} + l_i - \frac{\phi_i}{x_i}\sum_{j=1}^{N}x_jl_j + q_i\left[1 - \ln\left(\sum_{j=1}^{N}\theta_j\tau_{ji}\right) - \sum_{j=1}^{N}\frac{\theta_j\tau_{ij}}{\sum_{k=1}^{N}\theta_k\tau_{ki}}\right] \quad \text{.... (C4)}$$

where

$$l_i = \frac{z}{2}(r_i - q_1) - (r_i - 1), \qquad z = 10 \quad \text{..... (C5)}$$

$$\theta_i = \frac{q_ix_i}{\sum_{j=1}^{N}q_jx_j}, \qquad \phi = \frac{r_ix_i}{\sum_{j=1}^{N}r_jx_j} \quad \text{..... (C6)}$$

$$\tau_{ji} \equiv \exp\left[-\frac{\left(u_{ji} - u_{ii}\right)}{RT}\right] \qquad \left(u_{ji} - u_{ij}\right) \quad \text{..... (C7)}$$

$(u_{ji} - u_{ii})$ and $(u_{ji} - u_{jj})$ in equation C7 are two parameters characteristic of the components i and j that can be obtained from binary data. θ_i and ϕ_1 are the area fraction and segment fraction respectively. r_i and q_i are measures of respectively, molecular van der Waals volumes and molecular surface area, and are constants for a pure component.

C.2 Analytical Solutions of Groups (ASOG)

The activity coefficient of component i in a solution is commonly represented by γ_i. The excess chemical potential $\ln\gamma_i$ is assumed to be the sum of the contribution $\ln\gamma_i^{FH}$, due to differences in molecular sizes and the group-interaction contribution $\ln\gamma_i^{G}$, due to differences in intermolecular forces.

$$\ln\gamma_i = \ln\gamma_i^{FH} + \ln\gamma_i^{G} \quad \text{..... (C8)}$$

The contribution due to the differences in molecular sizes is calculated by applying an equation similar to the Flory – Huggins equation.

$$\ln\gamma_i^{FH} = \ln\frac{v_i^{FH}}{\sum_j v_j^{FH} x_j} + 1 - \frac{v_i^{FH}}{\sum_j v_j^{FH} x_j} \quad \text{..... (C9)}$$

Here v_j^{FH} and x_j represent the number of atoms (other than hydrogen atoms) in molecule j and the mole fraction of component j in liquid solution respectively. The summations in equation C9 cover all components in liquid solution. From this γ_i^{FH} is calculated, with due attention to the chemical structure of the pure components making up the solution.

The contribution of group interaction is obtained from equation C10, the sum of the contributions of the individual groups making up the solution:

$$\ln\gamma_i^{G} = \sum_k v_{ki}\left(\ln\Gamma_k - \ln\Gamma_k^{(i)}\right) \quad \text{..... (C10)}$$

Where v_{ki} is the number of atoms other hydrogen atoms in group k in molecule i, Γ_k is the group activity coefficient of group k and $\Gamma_k^{(i)}$ represent the group activity coefficient of group k at standard state of pure component i. The summation covers all groups in liquid solution. This method of counting the number of terms v_{ki} in equation C10 is an improvement by Kojima and Tochigi (1979) on Wilson and deal (1962) and Derr and Deal (1969) techniques.

The group activity coefficient Γ_k is a function of temperature and the mole fraction of each group in liquid solution and this was analytically presented by the Wilson equation as follows

$$\ln \Gamma_k = -\ln \sum_l x_l a_{kl} + 1 - \sum_l \frac{X_l a_{lk}}{\sum_m X_m a_{lm}} \quad \text{..... (C11)}$$

In equation C11, a_{kl} is the group interaction parameters characteristic of groups k and l, $(a_{kl} \neq a_{lk})$. X_l is the group fraction of group l in liquid solution and is given by equation C12 below.

$$X_l = \frac{\sum_i x_i v_{li}}{\sum_i x_i \sum_k v_{ki}} \quad \text{..... (C12)}$$

The group activity coefficient $\Gamma_k^{(i)}$ can be calculated using equation C11. The temperature dependence of interaction parameters is expressed as follows

$$\ln a_{kl} = m_{kl} + n_{kl}/T \quad \text{..... (C13)}$$

where m_{kl}, n_{kl} are the group parameters characteristic of groups k and l, independent of temperature and T represents temperature in Kelvins.

Appendix D: Properties of Pure Solutes

Table D1: Properties of Pure Solutes at 303.15K.

Solute	M	$\overline{V}_1^o$ (cm^3mol^{-1})	P (KPa)	$-B_{11}$ (cm^3mol^{-1})
acetone	58.08	74.89	36.78	1771
butylacetate	116.16	124.94	1.92	1536
chloroform	119.39	80.86	32.78	1187
cyclohexane	84.16	101.39	16.23	1702
diethylether	74.12	105.60	86.30	1256
ethylmethylketone	72.11	90.74	18.13	2280
isobutylmethylketone	100.16	126.98	3.56	3988
n-heptane	100.20	148.42	7.79	2721
n –hexane	86.17	132.47	24.95	1810
n- pentane	72.15	117.02	81.97	1147
toluene	92.13	107.42	4.89	2263
triethylamine	101.19	140.74	13.12	2142
xylene	106.16	123.87	1.37	4193

Table D2: Properties of Pure Solutes at 313.15K

Solute	M	$\overline{V}_1^o$ (cm^3mol^{-1})	P (KPa)	$-B_{11}$ (cm^3mol^{-1})
acetone	58.08	75.81	53.33	1595
butylacetate	116.16	126.18	3.32	1356
chloroform	119.39	81.84	48.85	1081
cyclohexane	84.16	110.82	24.63	1642
diethylether	74.12	107.52	122.83	1046
ethylmethylketone	72.11	91.72	25.33	1956
isobutylmethylketone	100.16	128.03	5.80	3619
n-heptane	100.20	150.33	12.33	2590
n –hexane	86.17	134.39	37.25	1702
n- pentane	72.15	119.01	115.62	1073
toluene	92.13	108.25	7.89	2348
triethylamine	101.19	142.32	20.49	1856
xylene	106.16	125.02	2.52	3701

Table D3: Properties of Pure Solutes at 323.15K

Solute	M	$\overline{V}_1^o$ (cm^3mol^{-1})	P (KPa)	$-B_{11}$ (cm^3mol^{-1})
acetone	58.08	76.63	79.99	1331
butylacetate	116.16	127.45	5.52	1178
chloroform	119.39	83.39	70.13	957.7
cyclohexane	84.16	113.09	36.24	1476
diethylether	74.12	109.58	170.25	950
ethylmethylketone	72.11	92.73	37.73	1751
isobutylmethylketone	100.16	130.04	9.17	3059
n-heptane	100.20	152.30	18.88	2355
n –hexane	86.17	136.39	53.33	1481
n- pentane	72.15	121.11	159.15	1003
toluene	92.13	109.48	12.28	2092
triethylamine	101.19	144.58	31.16	1679
xylene	106.16	127.22	4.15	2996

Table D4: Properties of Pure Solutes at 333.15K

Solute	M	$\overline{V}_1^o$ (cm^3mol^{-1})	P (KPa)	$-B_{11}$ (cm^3mol^{-1})
acetone	58.08	78.50	119.72	1231
butylacetate	116.16	128.75	8.89	1024
chloroform	119.39	84.32	101.33	849.9
cyclohexane	84.16	113.63	51.89	1404
diethylether	74.12	111.32	233.05	895
ethylmethylketone	72.11	93.56	53.33	1631
isobutylmethylketone	100.16	131.16	14.11	2812
n-heptane	100.20	154.36	28.02	2016
n –hexane	86.17	138.52	76.35	1394
n- pentane	72.15	123.33	217.85	891.8
toluene	92.13	110.62	18.52	1832
triethylamine	101.19	146.65	46.17	1566
xylene	106.16	128.41	6.59	2708

Table D5: Properties of Pure Solutes at 353.15K

Solute	M	$\bar{V}_1^o$ (cm^3mol^{-1})	P (KPa)	$-B_{11}$ (cm^3mol^{-1})
acetone	58.08	80.52	212.78	1258
butylacetate	116.16	129.32	21.80	924
chloroform	119.39	86.52	182.39	799
cyclohexane	84.16	116.63	92.00	1142
diethylether	74.12	113.65	386.35	714
ethylmethylketone	72.11	94.32	75.22	1346
isobutylmethylketone	100.16	134.587	30.93	2254
n-heptane	100.20	158.77	56.87	1762
n –hexane	86.17	143.09	142.39	1195
n- pentane	72.15	128.29	368.30	801.2
toluene	92.13	113.643	38.82	1512
triethylamine	101.19	155.37	94.86	1304
xylene	106.16	132.246	15.865	2344

Table D6: Properties of Pure Solutes at 373.15K

Solute	M	$\bar{V}_1^o$ (cm^3mol^{-1})	P (KPa)	$-B_{11}$ (cm^3mol^{-1})
acetone	58.08	83.91	358.18	740
butylacetate	116.16	130.87	45.73	788
chloroform	119.39	88.42	354	684
cyclohexane	84.16	120.09	164	840
diethylether	74.12	115.83	633.28	706
ethylmethylketone	72.11	95.89	98.54	1122
isobutylmethylketone	100.16	138.17	62.66	1854
n-heptane	100.20	163.62	106.08	1503
n –hexane	86.17	148.13	244.78	1033
n- pentane	72.15	134.18	592.70	694
toluene	92.13	116.68	74.45	1286
triethylamine	101.19	157.81	180.42	1164
xylene	106.16	133.574	30.26	2214

Table D7: Properties of Pure Solutes at 393.15K

Solute	M	$\bar{V}_1^o$ (cm^3mol^{-1})	P (KPa)	$-B_{11}$ (cm^3mol^{-1})
acetone	58.08	86.94	607.95	662
butylacetate	116.16	132.24	90.89	654
chloroform	119.39	92.31	506.63	576
cyclohexane	84.16	124.16	287.3	750
diethylether	74.12	117.24	972.72	607
ethylmethylketone	72.11	95.89	105.23	984
isobutylmethylketone	100.16	142.8	114.12	1556
n-heptane	100.20	166.25	183.33	1279
n –hexane	86.17	154.21	397.57	912.4
n- pentane	72.15	141.28	903.4	662
toluene	92.13	119.65	131.28	1131
triethylamine	101.19	160.37	332	1002
xylene	106.16	134.52	59.06	1781

Table D8: Properties of Pure Solutes at 423.15K

Solute	M	$\bar{V}_1^o$ (cm^3mol^{-1})	P (KPa)	$-B_{11}$ (cm^3mol^{-1})
acetone	58.08	93.67	1995.80	525
butylacetate	116.16	133.56	151.72	547
chloroform	119.39	98.18	962.59	466
cyclohexane	84.16	131.23	554.19	733
diethylether	74.12	118.89	1780.89	306
ethylmethylketone	72.11	99.21	244.89	742
isobutylmethylketone	100.16	146.9	244.00	1238
n-heptane	100.20	178.99	371.17	1032
n –hexane	86.17	165.49	748.00	739.4
n- pentane	72.15	156.71	1574.00	510.5
toluene	92.13	125.32	266.36	917
triethylamine	101.19	175.56	912.00	814
xylene	106.16	136.12	133.32	1343

Appendix E: Solutes Calibration Data and Curves Using Shaker Flasks

Table E1: Acetone calibration data

Peak Area	Concentration (ppm)	Concentration (kgm^{-3})
8.9888	513	1.33E-03
17.9759	1025	2.66E-03
32.9259	2050	5.32E-03
52.6368	3078	9.98E-03
66.60.98	4100	1.06E-02
96.5817	6156	1.74E-02
109.0025	8200	2.12E-02
163.0111	12312	3.19E-02
210.9821	15390	3.99E-02
278.6996	20520	5.32E-02
347.9466	25650	6.65E-02
406.1936	30780	7.98E-02
484.5854	35910	9.64E-02
536.0004	41040	1.06E-01
598.0092	46170	1.20 E-01
675.5348	51300	1.33E-01

Figure E1: Acetone calibration curve

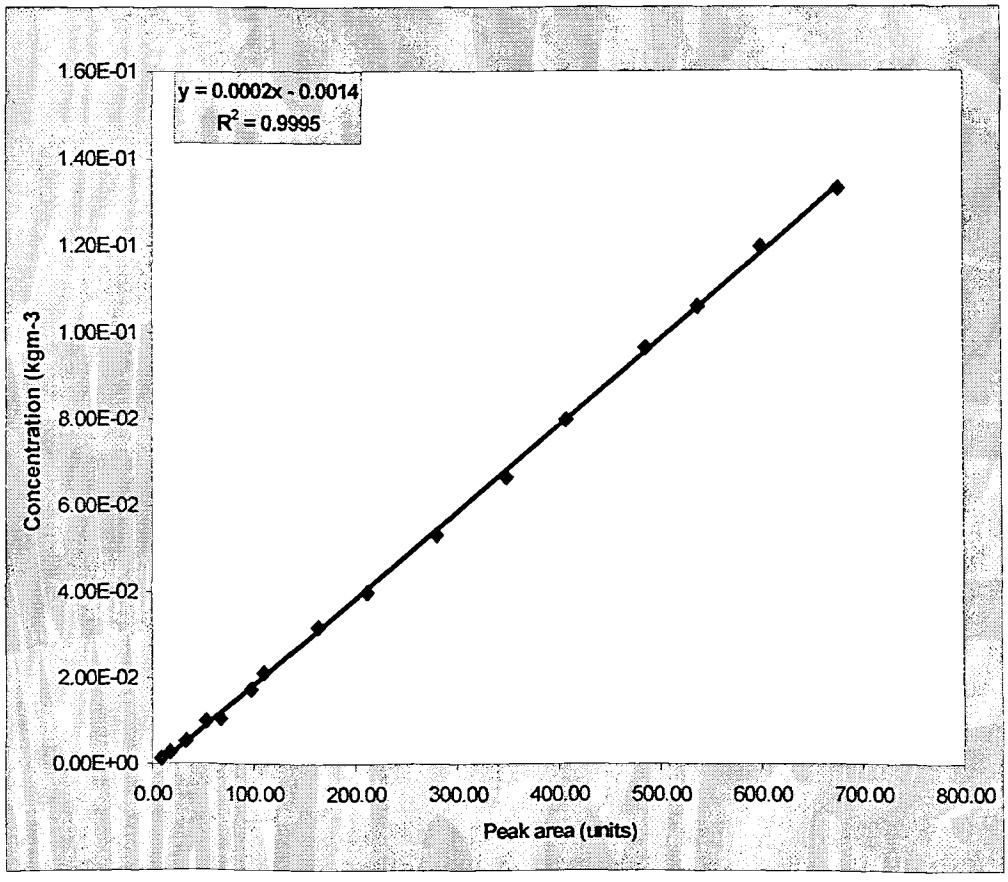


Table E2: Butyl acetate calibration data

Peak area (units)	Concentration (ppm)	Concentration (kgm^{-3})
23.0563	286	1.48E-03
43.3846	571	2.96E-03
109.6781	1428	7.40E-03
215.4376	2857	1.48E-03
430.0135	5714	2.96E-02
650.3672	8571	4.44E-02
860.1677	11428	5.92E-02
1075.7100	14285	7.41E-02
1296.4739	17142	8.89E-02
1503.8776	19990	1.04E-01
1717.2208	22856	1.18E-01
1937.8916	25713	1.33E-01
2149.7826	28570	1.48E-01

Figure E2: Butyl acetate calibration curve

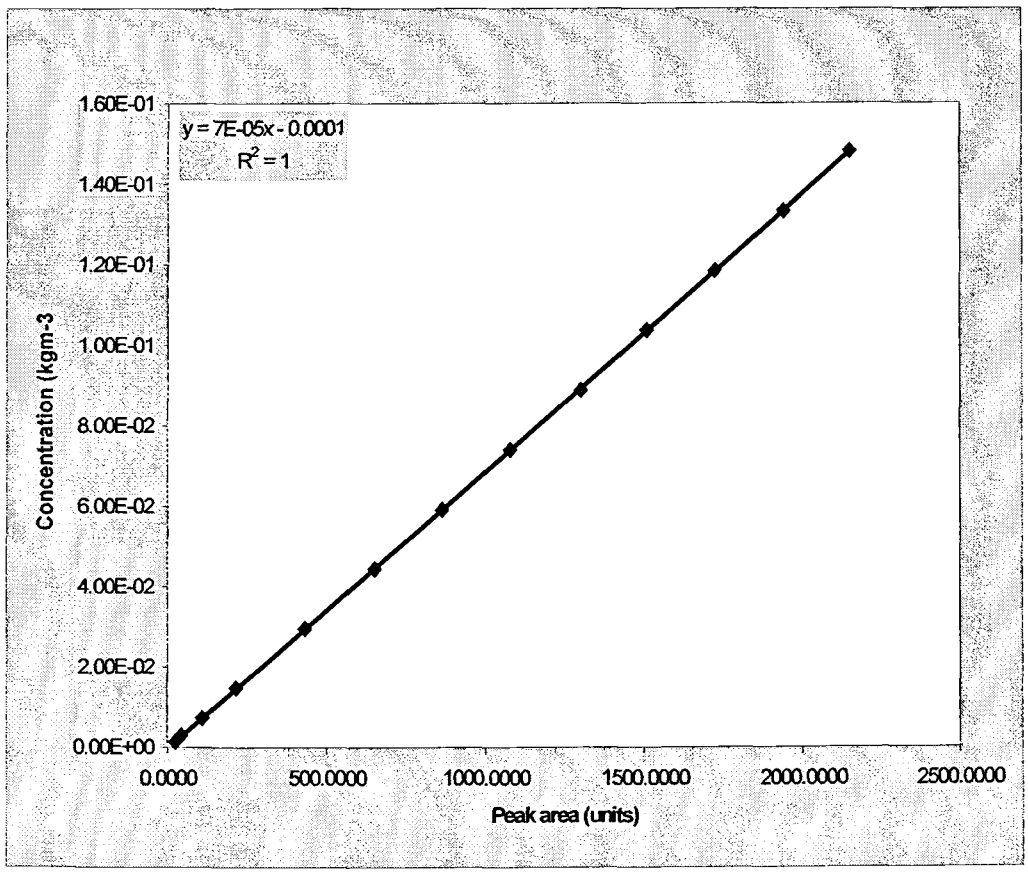


Table E3: Chloroform calibration data

Peak area (units)	Concentration (ppm)	Concentration (kgm^{-3})
14.6160	468	2.49E-03
26.2302	935	4.98E-03
65.7720	2338	1.24E-02
126.6744	4675	2.49E-02
256.8306	9350	4.98E-02
381.7051	14025	7.47E-02
506.3718	18700	9.96E-02
632.5212	23375	1.24E-01
760.4604	28050	1.49E-01
886.6984	32725	1.74E-01
1009.887	37400	1.99E-01
1138.8968	42075	2.24E-01
1265.0772	46750	2.49E-01

Figure E3: Chloroform calibration curve

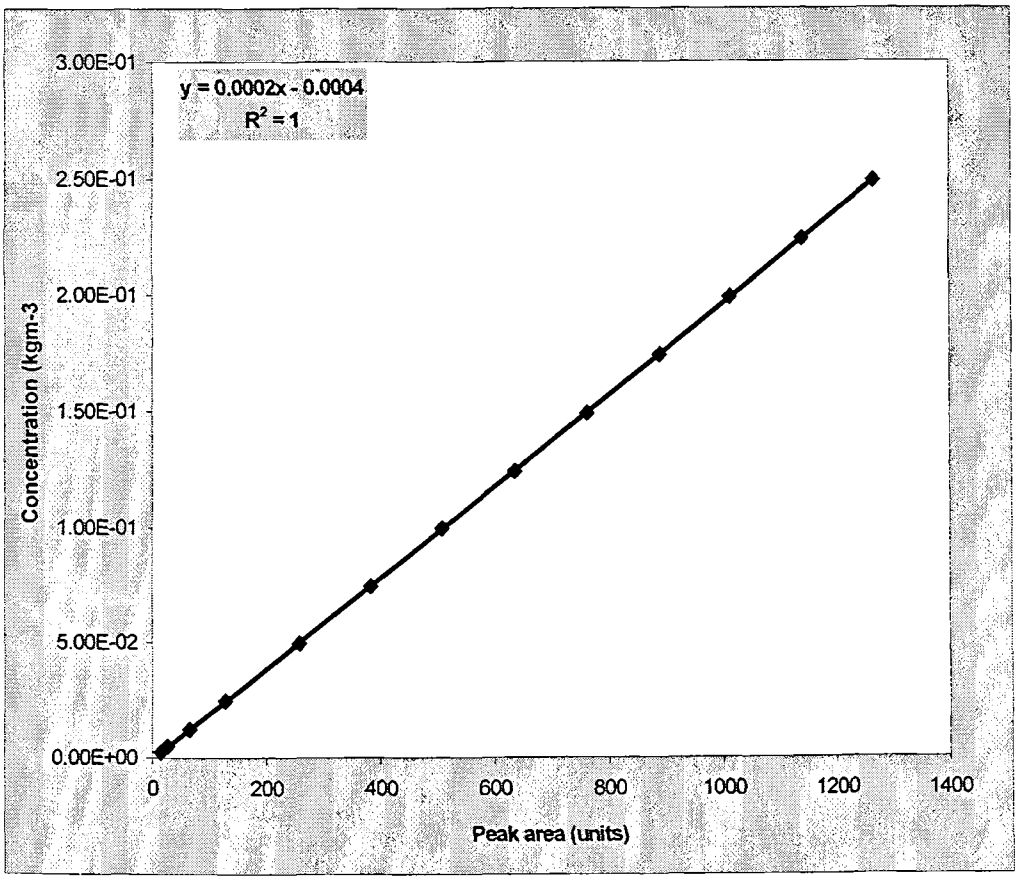


Table E4: Cyclohexane calibration data

Peak area (units)	Concentration (ppm)	Concentration (kgm^{-3})
8.6285	350	1.31E-03
16.7828	700	2.69E-03
42.8518	1750	6.57E-03
85.7114	3500	1.31E-02
171.2505	7000	2.63E-02
255.8257	10500	3.94E-02
338.8576	14000	5.26E-02
426.0159	17500	6.57E-02
499.6785	21000	7.89E-02
589.5619	24500	9.20E-02
676.1386	28000	1.05E-01
756.1386	31500	1.18E-01
822.5125	35000	1.31E-01

Table E4: Cyclohexane calibration curve

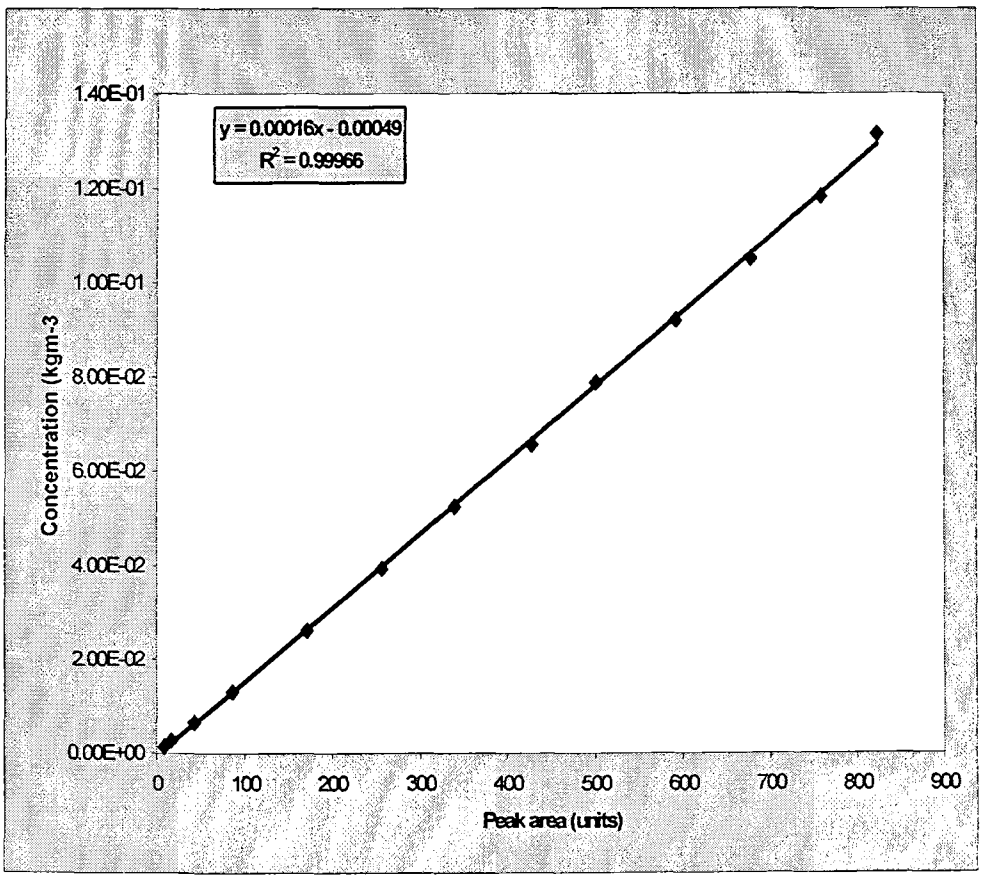


Table E5: Diethyl ether calibration data

Peak area (units)	Concentration (ppm)	Concentration (kgm^{-3})
11.9330	361.3890	1.20E-03
22.8930	722.7780	2.39E-03
46.6594	1445.5560	4.78E-03
69.7706	2168.3340	7.17E-03
94.138	2891.1120	9.56E-03
117.3692	3613.8900	1.20E-02
139.2028	4336.6681	1.43E-02
163.2918	5059.4460	1.67E-02
181.8186	5782.2240	1.91E-02
210.1811	6505.0020	2.15E-02
227.6366	7227.7800	2.39E-02

Figure E5: Diethyl ether calibration curve

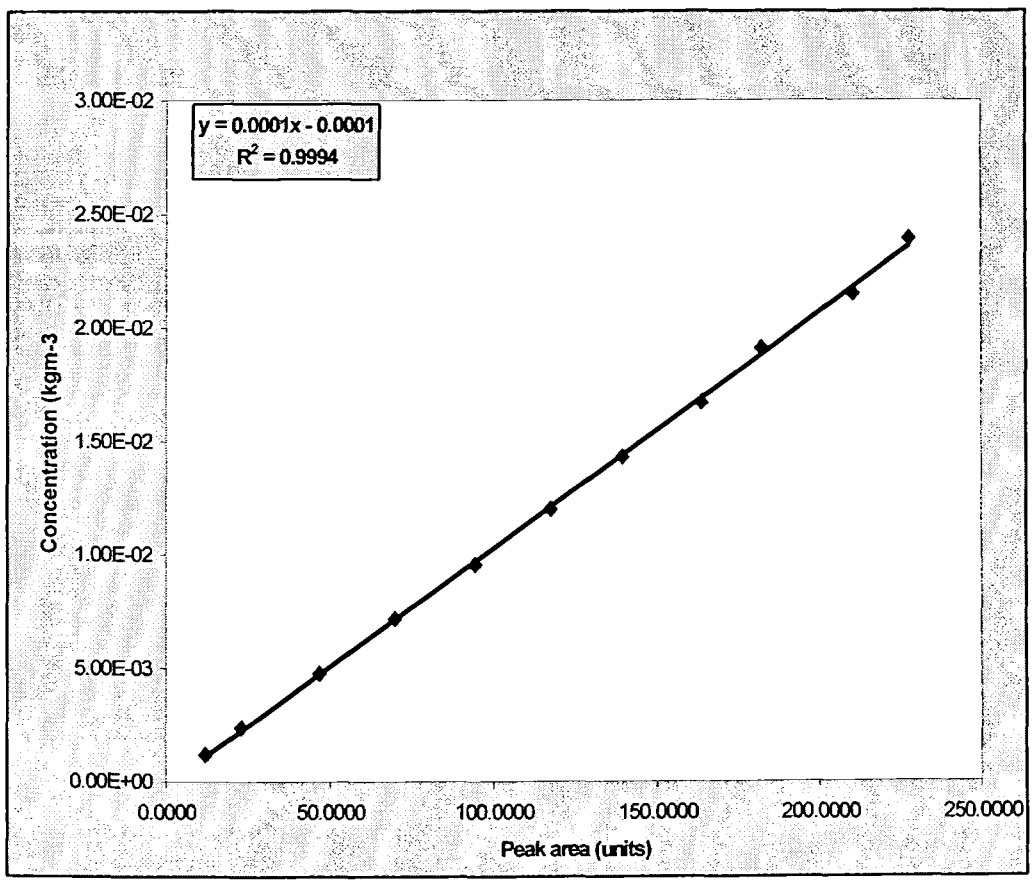


Table E6: Ethyl methyl ketone calibration data

Peak area (units)	Concentration (ppm)	Concentration (kgm^{-3})
13.1688	423	1.36E-03
26.1234	846	2.73E-03
65.3157	2115	6.82E-03
122.3946	4230	1.36E-02
221.5521	8460	2.73E-02
430.0047	16920	5.45E-02
633.0096	25380	8.18E-02
833.3622	33840	1.09E-01
1040.2773	42300	1.36E-01

Figure E6: Ethyl methyl ketone calibration curve

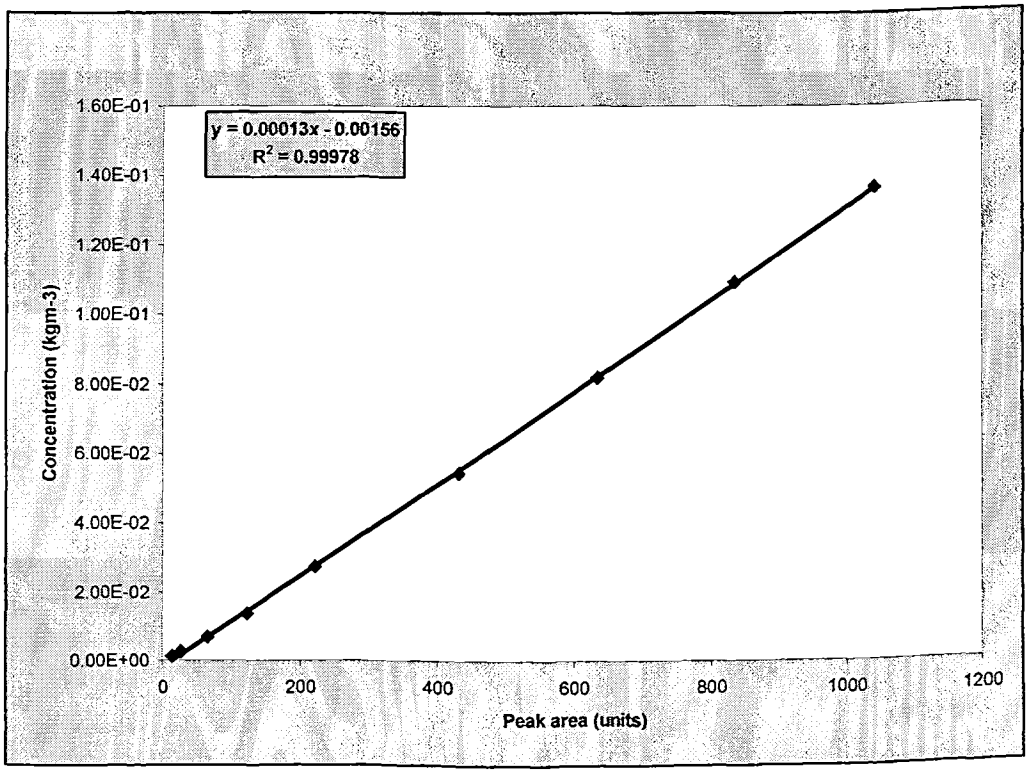


Table E7: Isobutyl methyl ketone calibration data

Peak area (units)	Concentration (ppm)	Concentration (kgm^{-3})
14.0064	301	1.35E-03
26.2688	602	2.69E-03
55.3708	1505	6.73E-03
110.4424	3010	1.35E-02
231.3984	6020	2.70E-02
470.6304	12040	5.39E-02
681.0144	18060	8.08E-02
912.9376	24080	1.08E-01
1133.9696	30100	1.35E-01

Figure E7: Isobutyl methyl ketone calibration curve

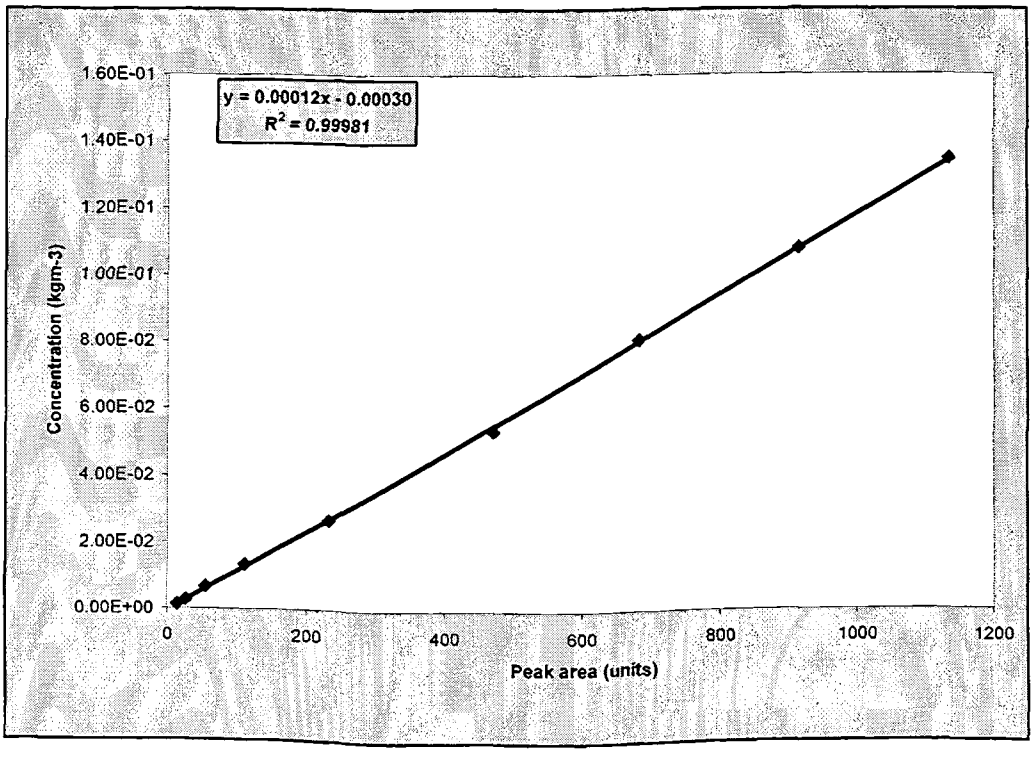


Table E8: n-Heptane calibration data

Peak area (units)	Concentration (ppm)	Concentration (kgm^{-3})
11.1798	256	1.14E-03
24.4013	512	2.29E-03
51.4216	1280	5.72E-03
87.1511	2560	1.14E-02
174.4851	5120	2.29E-02
262.3982	7680	3.43E-02
347.6707	10240	4.58E-02
438.1976	12800	5.72E-02
524.3962	15360	6.87E-02
610.6159	17921	8.01E-02
697.3431	20481	9.16E-02
786.5441	23041	1.03E-01
874.3883	25601	1.14E-01

Figure E8: n-Heptane calibration curve

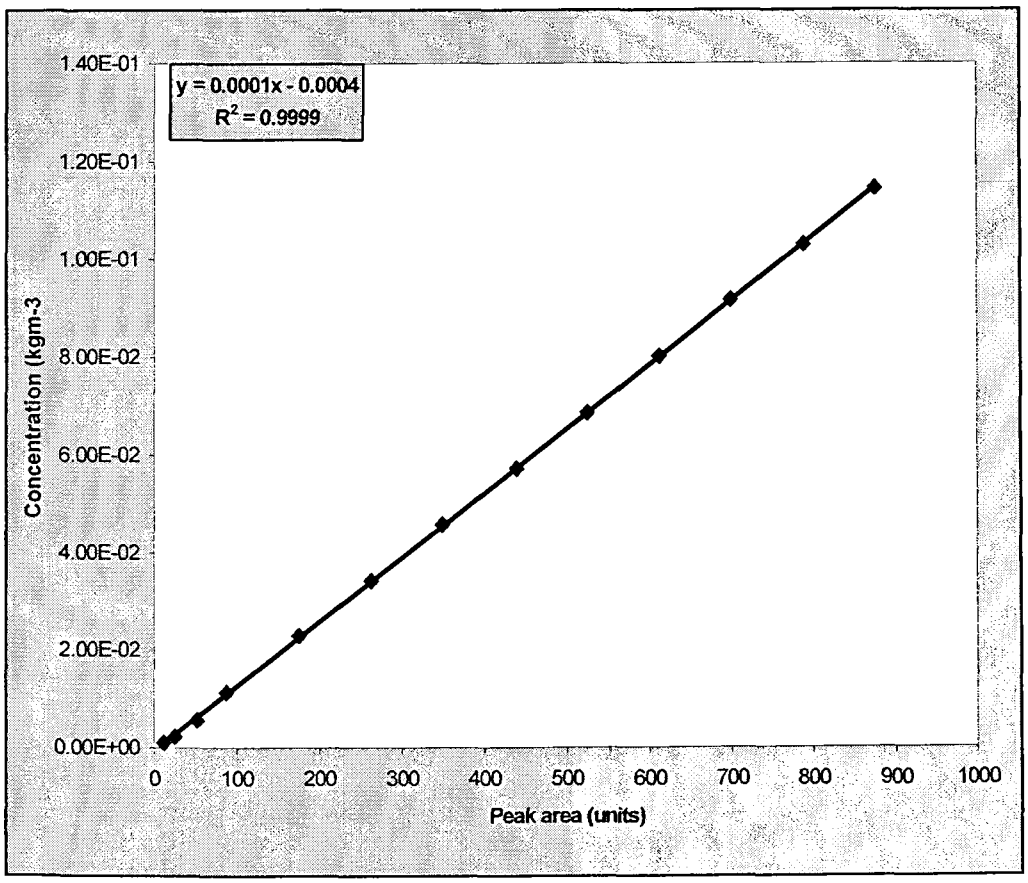


Table E9: n-Hexane calibration data

Peak area (units)	Concentration (ppm)	Concentration (kgm^{-3})
13.5602	390.0560	1.50E-03
26.0147	780.1120	3.00E-03
53.0220	1560.2240	6.00E-03
79.2848	2340.3360	9.00E-03
106.9702	3120.4480	1.20E-02
133.3741	3900.5600	1.50E-02
158.1850	4680.6720	1.80E-02
185.5588	5460.7840	2.10E-02
198.3365	6240.8960	2.28E-02
240.1396	7021.0080	2.70E-02

Figure E9: n-Hexane calibration curve

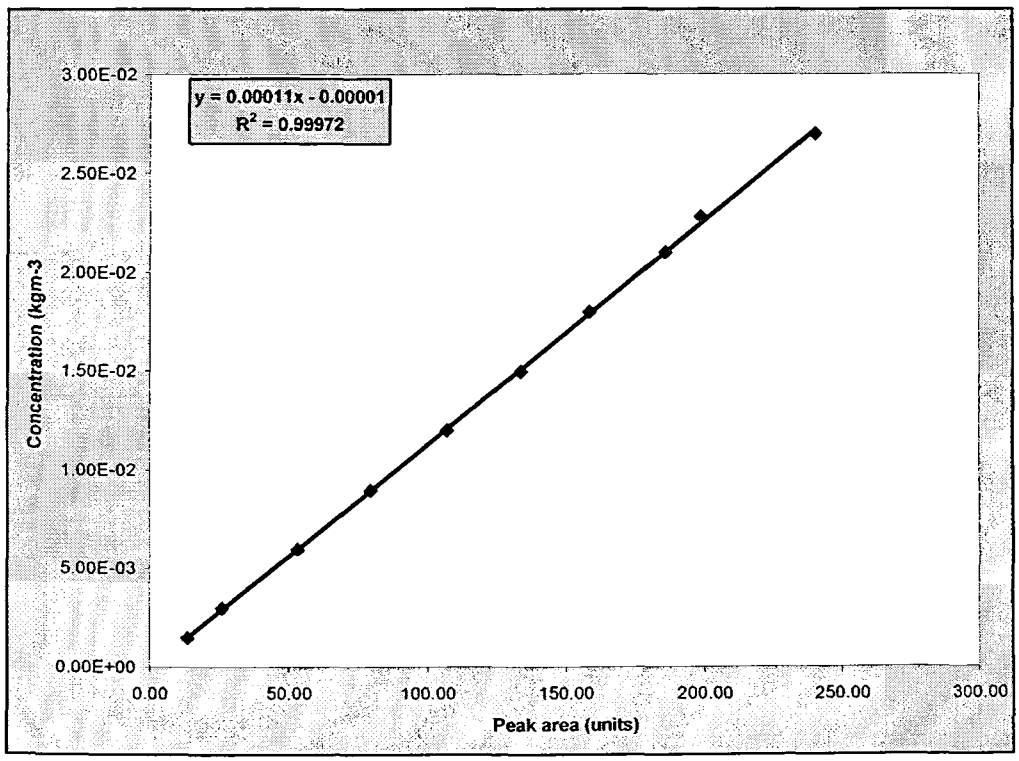


Table E10: n-Pentane calibration data

Peak area (units)	Concentration (ppm)	Concentration (kgm^{-3})
13.5602	494.071	1.59E-03
26.0238	988.142	3.18E-03
53.0220	1976.284	6.36E-03
79.2448	2964.426	9.54E-03
106.9702	3952.568	1.27E-02
133.3338	4940.71	1.59E-02
158.1850	5928.852	1.91E-02
185.5588	6916.994	2.23E-02
212.112	7905.136	2.51E-02

Figure E10: n-Pentane calibration curve

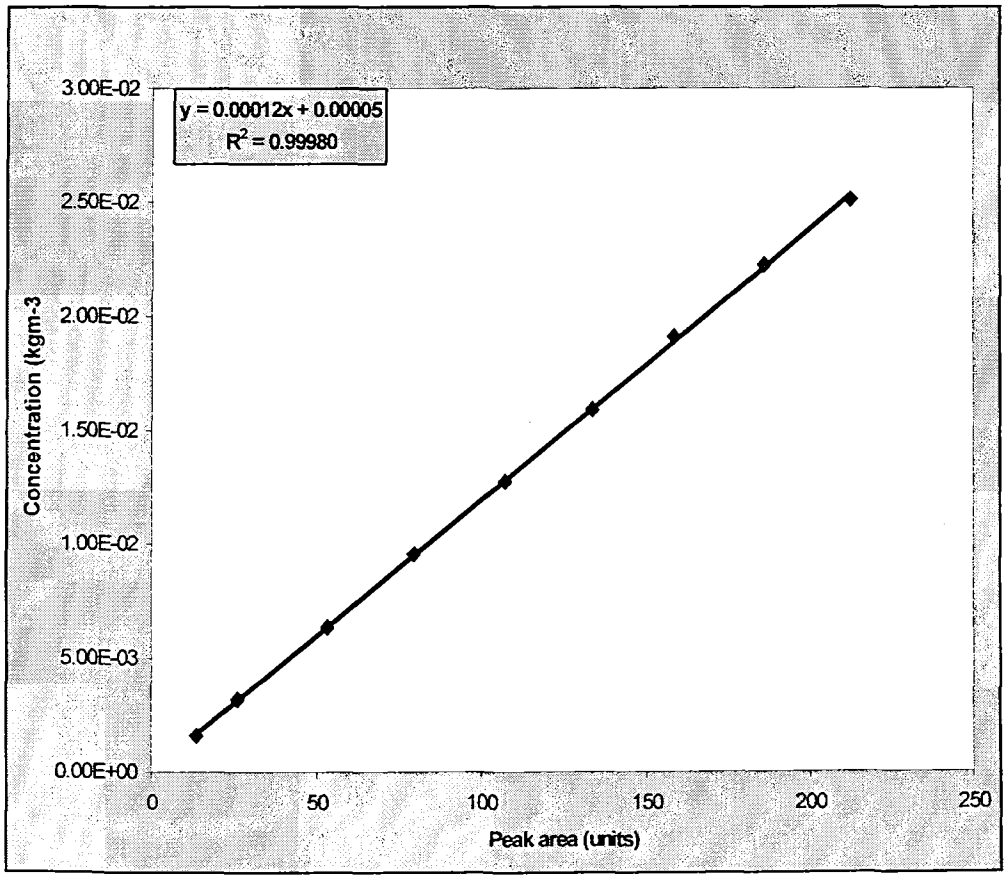


Table E11: Toluene calibration data

Peak area (units)	Concentration (ppm)	Concentration (kgm^{-3})
14.2576	179	7.38E-04
57.0832	1000	4.12E-03
132.2634	4000	1.65E-02
170.2147	5000	2.06E-02
277.3790	9000	3.71E-02
422.2826	13571	5.59E-02
553.8266	18000	7.472E-02
690.0000	22500	9.27E-02
849.7594	27000	1.11E-02
975.4105	31429	1.30E-01
1108.4173	36000	1.48E-01

Figure E11: Toluene calibration curve

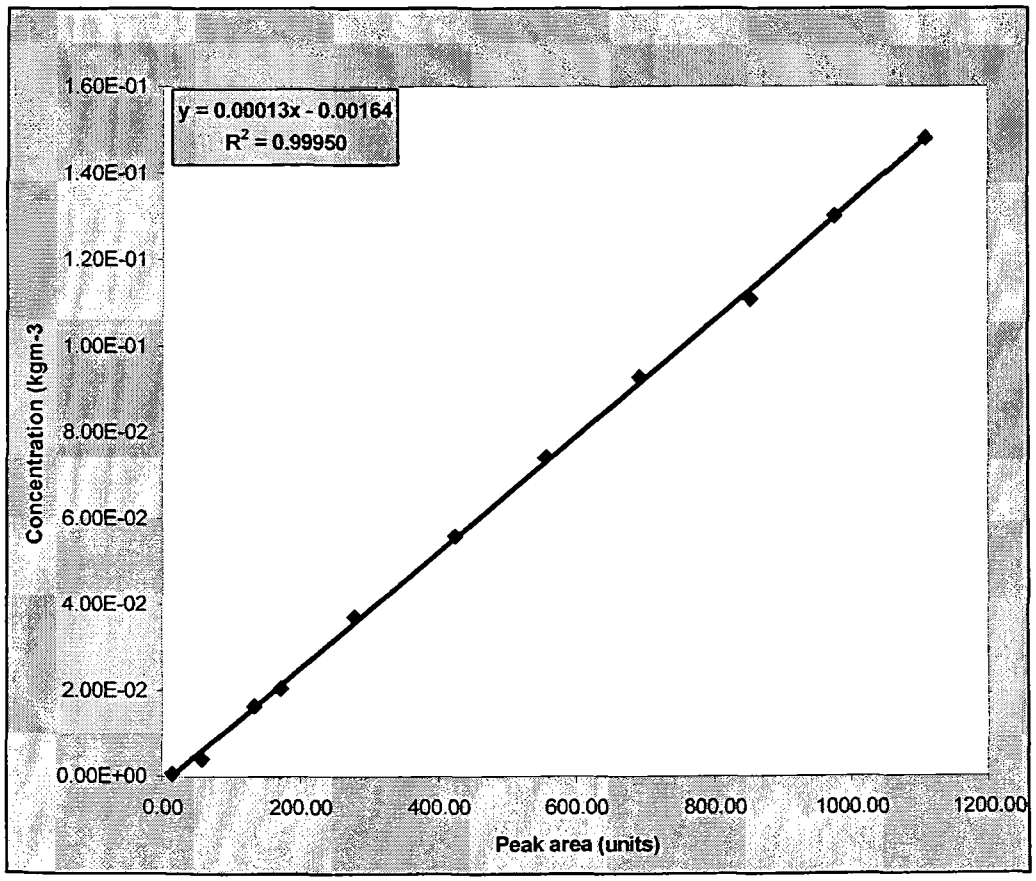


Table E12: Triethylamine calibration data

Peak area (units)	Concentration (ppm)	Concentration (kgm^{-3})
16.4078	272.1680	1.70E-03
31.4778	544.3360	3.30E-03
50.7222	1088.6720	5.30E-03
86.7778	1633.0080	9.70E-03
116.1111	2177.3440	1.34E-02
127.1109	3266.0160	1.47E-02
174.1667	4354.6880	1.97E-02
253.6111	6532.0320	2.95E-02

Figure E12: Triethylamine calibration curve

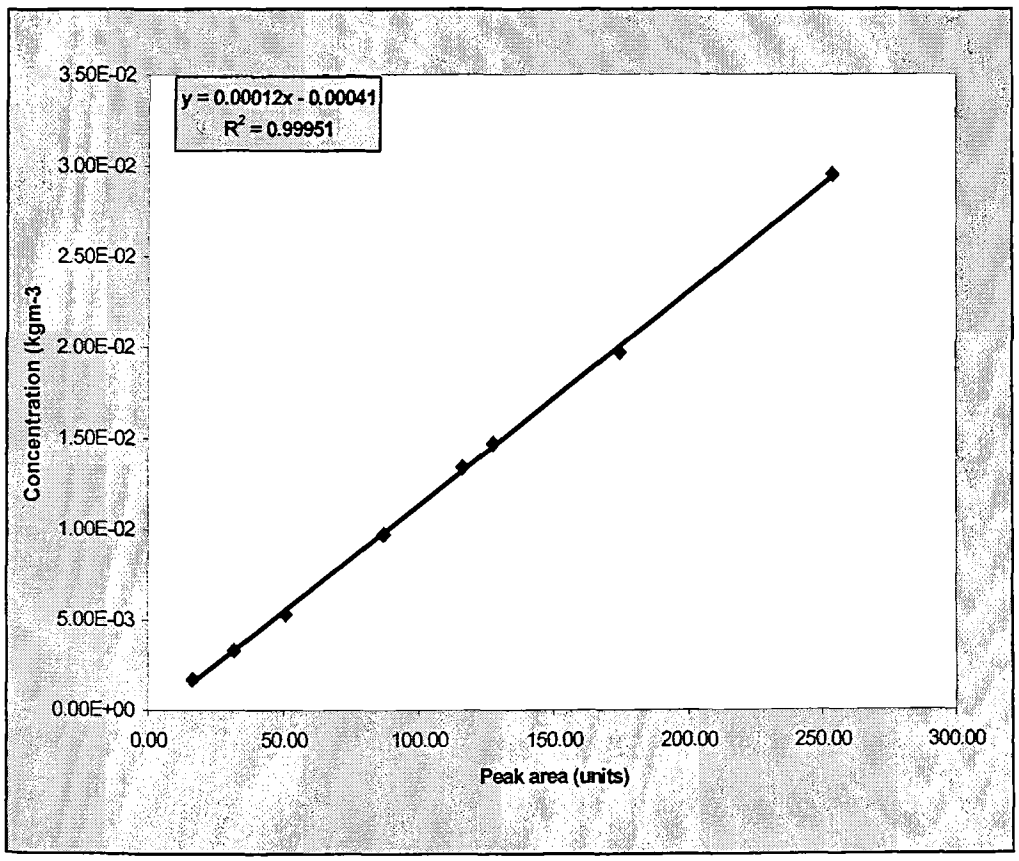
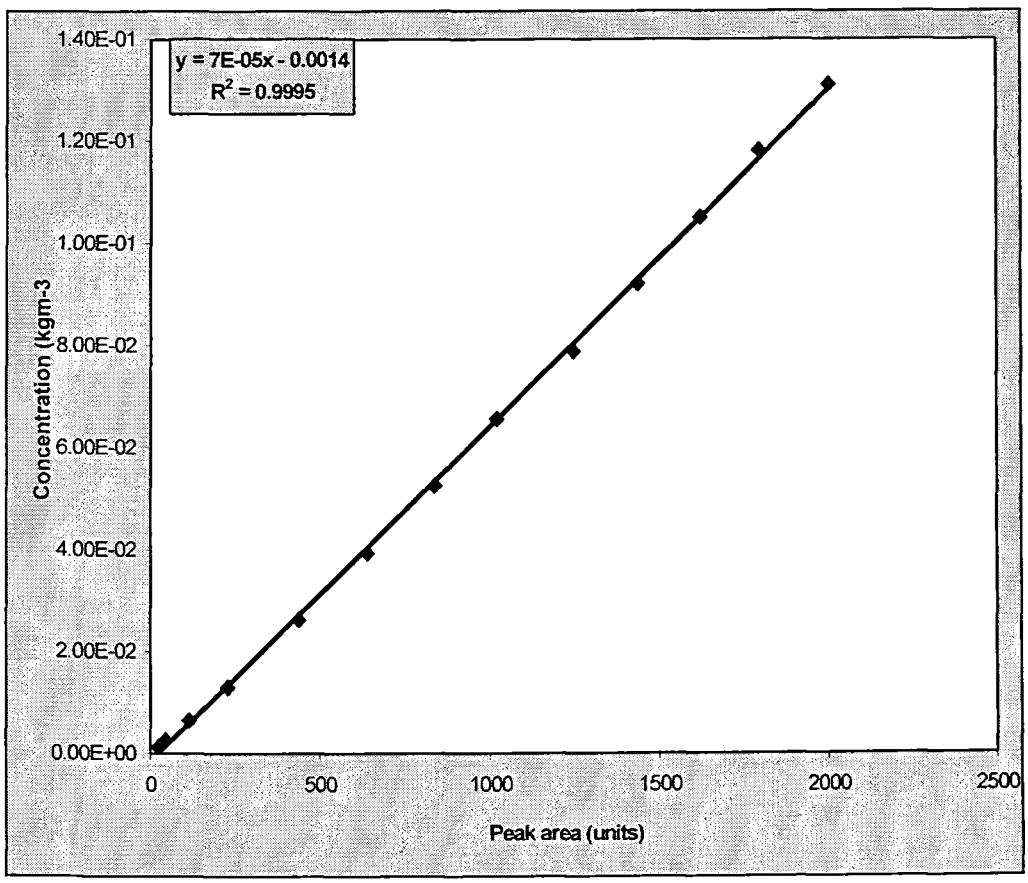


Table E13: Xylene calibration data

Peak area (units)	Concentration (ppm)	Concentration (kgm^{-3})
23.8569	303	1.31E-03
45.3364	606	2.69E-03
113.3655	1515	6.57E-03
225.5421	30330	1.31E-02
436.0568	6060	2.63E-02
636.7081	9090	3.94E-02
834.2516	12120	5.26E-02
1018.3588	15150	6.57E-02
1242.5689	18180	7.89E-02
1432.4196	21210	9.20E-02
1614.8633	24210	1.05E-01
1790.9718	27270	1.18E-01
1999.7856	30300	1.31E-01

Figure E13: Xylene calibration curve



APPENDIX F EXPERIMENTAL RAW DATA

APPENDIX F.1 STATIC HEAD SPACE METHOD

F.1.1 Original Equipment

Table F.1.1.1: Acetone in 50 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.0005	0.4526	0.4520	0.4532	0.4536
0.001	0.7284	0.7286	0.7283	0.7284
0.002	1.4148	1.4149	1.4145	1.4151
0.005	3.2562	3.2561	3.2563	3.2562
0.01	5.8435	5.8425	5.8446	5.8447
0.025	13.0641	13.0651	13.0632	13.0640
0.05	24.1371	24.1372	24.1370	24.1372
0.06	25.8775	25.8785	25.8766	25.8768
0.08	33.6415	33.6430	33.6402	33.6404
0.1	37.3762	37.3761	37.3757	37.3759
0.2	73.8662	73.8652	73.8671	73.8672
0.3	104.6914	104.6907	104.6920	104.6915
0.4	140.6915	140.6910	140.6920	140.6912
0.5	170.2536	170.2526	170.2544	140.2546

Table F.1.1.2: Acetone in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.01	4.5434	4.5430	4.5428	4.5438
0.02	8.5069	8.5079	8.5075	8.5074
0.03	11.7296	11.7286	11.9294	11.9295
0.04	15.3218	15.3228	15.3208	15.3220
0.05	17.8607	17.8614	17.8607	17.8615
0.06	20.3995	20.3994	20.4001	20.4002
0.07	22.8624	22.8625	22.8626	22.8623
0.08	25.3245	25.3246	25.3235	25.3254
0.09	27.6995	27.6985	27.6999	27.6997
0.1	30.0734	30.0738	30.0731	30.0733

Table F.1.1.3: Acetone in 5 cS PDMS

Volume of VOC injected	Peak areas			
0.005	1.4815	1.4820	1.4821	1.4805
0.01	2.8182	2.8181	2.8192	2.8173
0.02	5.4291	5.4292	5.4293	5.4289
0.04	10.2761	10.2762	10.2751	10.2762
0.06	14.4157	14.4156	14.4147	14.4155
0.08	18.3695	18.3694	18.3685	18.3696
0.1	22.1232	22.1222	22.1242	22.1234
0.2	43.3728	43.3738	43.3718	43.3727

Table F.1.1.4: Toluene in 5cS PDMS

Volume of VOC injected	Peak areas			
0.005	0.9464	0.9462	0.9466	0.9465
0.01	1.8828	1.8818	1.8828	1.8827
0.05	8.3142	8.3140	8.3132	8.3152
0.06	10.5971	10.5981	10.5962	10.5973
0.1	17.5966	17.5965	17.5966	17.5976
0.2	23.4616	23.4626	23.4606	23.4615
0.5	59.3357	59.3356	59.3359	59.3355
1	92.6396	92.6393	92.6391	92.6399
2	162.5091	162.5092	162.5081	162.5099
4	324.5625	324.5635	324.5630	324.5620
8	638.5969	638.5979	638.5975	638.5964
10	733.1328	733.1327	733.1338	733.1318

Table F.1.1.5: Toluene in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.01	1.4229	1.4225	1.4233	1.4228
0.02	2.5964	2.5965	2.5963	2.5965
0.03	3.6202	3.6201	3.6198	3.6203
0.04	4.7886	4.7896	4.7886	4.7885
0.05	5.7262	5.7264	5.7260	5.7263
0.06	6.4993	6.4991	6.4995	6.4993
0.07	7.5257	7.5256	7.5255	7.5260
0.08	8.5324	8.5325	8.5326	8.5323
0.09	9.3249	9.3239	9.3259	9.3245
0.1	10.2291	10.2292	10.2294	10.2290

Table F.1.1.6: Toluene in 5 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.025	0.5047	0.5046	0.5048	0.5046
0.05	0.9894	0.9890	0.9898	0.9895
0.075	1.4641	1.4649	1.4633	1.4643
0.1	1.9207	1.9213	1.9201	1.9208
0.2	3.6416	3.6408	3.6423	3.6417
0.5	6.5089	6.5099	6.5085	6.5086
0.75	9.2563	9.2566	6.2560	9.2564
1	11.9818	11.9828	11.9814	11.9812
1.5	16.3865	16.3875	16.3861	16.3859
2	20.6235	20.6245	20.6240	20.6241

F.1.2 Modified Equipment

F.1.2.1: Effect of test volume on H and γ (10 cS PDMS)

PDMS volume (ml)	Peak areas (units)			
200	4.6422	4.6428	4.6416	4.6421
250	3.7254	3.7250	3.7258	3.7255
300	3.1242	3.1244	3.1248	3.1237
350	2.6855	2.6865	2.6860	2.6858
400	2.3608	2.3609	2.3618	2.3601
450	2.0901	2.0908	2.0901	2.0893
500	1.8942	1.8935	1.8944	2.8943

Table F.1.2.2: Effect of shaking time on H and γ (10 cS PDMS)

Shaking time (hrs)	Peak areas			
0.5	4.6423	4.6421	4.6422	4.6424
1	4.6423	4.6422	4.6425	4.6420
2	4.6421	4.6420	4.6423	4.6422
4	4.6418	4.6418	4.6419	4.6417
6	4.6418	4.6420	4.6416	4.6419
8	4.6412	4.6413	4.6412	4.6411
10	4.6406	4.6408	4.6404	4.6405
12	4.6394	4.6392	4.6396	4.6394
14	4.6371	4.6374	4.6368	4.6372
16	4.6341	4.6342	4.6340	4.6341
18	4.6322	4.6323	4.6324	4.6319
20	4.6294	4.6297	4.6291	4.6293
24	4.6243	4.6244	4.6245	4.6242

Table F.1.2.3: Pentane in 10 cS PDMS

Volume of VOC injected	Peak areas			
0.01	3.4324	3.4320	3.4328	3.4323
0.02	5.2379	5.2389	5.2373	5.2375
0.03	6.7349	6.7359	6.7346	6.7342
0.04	8.2043	8.2033	8.2050	8.2046
0.05	9.8929	9.8923	9.8927	9.8938
0.06	11.2129	11.2121	11.2149	21.2118
0.07	12.4583	12.4563	12.4572	12.7571
0.08	13.3561	13.3541	13.3572	13.3552
0.09	14.4066	14.4060	14.4068	14.4070
0.1	15.0496	15.0476	15.0505	15.0507

Table F.1.2.4: Hexane in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.01	1.4586	1.4556	1.4606	1.4596
0.02	2.8446	2.8546	1.8346	1.8445
0.03	4.1121	4.1021	4.1222	4.1118
0.04	5.2231	5.2211	5.2241	5.2242
0.05	6.3254	6.3234	6.3244	6.3245
0.06	7.3425	7.3445	7.7336	7.3395
0.07	8.3879	8.3878	8.3884	8.8372
0.08	9.4561	9.4461	9.4662	9.4559
0.09	10.4166	10.4066	10.4266	10.4167
0.1	11.3386	11.3346	11.3406	11.3407

Table F.1.2.5: Heptane in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.002	0.1229	0.2221	0.1231	0.1237
0.005	0.2632	0.2639	0.2627	0.2629
0.01	0.4386	0.4382	0.4387	0.4389
0.02	0.7632	0.7622	0.7642	0.7633
0.03	1.0629	1.0619	1.0639	1.0630
0.04	1.3399	1.3389	1.3404	1.3405
0.05	1.6438	1.6437	1.6442	1.6435
0.06	1.8775	1.8755	1.8717	1.8483
0.07	2.1134	1.1104	1.1150	1.1147
0.08	2.3426	2.3416	2.3432	2.2431
0.09	2.5411	2.5408	2.5409	2.5416
0.1	2.7420	2.7428	2.7425	2.7407

Table F.1.2.6: Triethyl amine in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.01	0.8784	0.8790	0.8780	0.8778
0.02	1.2387	1.2380	1.2382	1.2399
0.03	1.7653	1.7633	1.7644	1.7642
0.04	2.1032	2.1022	2.1027	2.1028
0.05	2.4833	2.4834	2.4832	2.4834
0.06	2.7644	2.7640	2.7641	2.7651
0.07	3.1105	3.1110	3.1103	3.1102
0.08	3.3351	3.3331	3.3371	3.3372
0.09	3.4556	3.4456	3.4656	3.4554
0.1	3.5689	3.5680	3.5687	3.5686

Table F.1.2.7: Toluene in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.01	0.3541	0.3551	0.3531	0.3542
0.02	0.6012	0.6010	0.6011	0.3015
0.03	0.7842	0.7832	0.7851	0.7243
0.04	1.0222	1.0211	1.0228	1.0227
0.05	1.2104	1.2100	1.2101	1.2110
0.06	1.3257	1.3251	1.3260	1.3261
0.07	1.5259	1.5219	1.5285	1.5264
0.08	1.6819	1.6720	1.6921	1.6816
0.09	1.8698	1.8587	1.8804	1.8802
0.1	2.0148	2.0147	2.0146	1.0152

Table F.1.2.8: Xylene in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.005	0.1457	0.1356	0.1558	0.1456
0.01	0.2394	0.2384	0.2404	0.2393
0.02	0.4054	0.4051	0.4057	0.4055
0.03	0.5415	0.5405	0.5425	0.5426
0.04	0.6542	0.6540	0.6542	0.6541
0.05	0.7999	0.7889	0.8102	0.9988
0.06	0.9037	0.9034	0.9038	0.9035
0.07	0.9643	0.9622	0.9664	0.9644
0.08	1.0596	1.0588	1.0602	1.0597
0.09	1.1812	1.1810	1.1811	1.1816
0.1	1.2945	1.2846	1.3046	1.2943

Table F.1.2.9: Cylohexane in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.005	0.3448	0.3346	0.3551	0.3447
0.01	0.6124	0.6122	0.6120	0.6126
0.02	1.0396	1.0346	1.0436	1.0418
0.03	1.3554	1.3551	1.3557	1.3552
0.04	1.6849	1.6839	1.6859	1.6848
0.05	1.9099	1.9078	1.9102	1.9098
0.06	1.2014	1.2016	1.2018	1.2002
0.07	2.5282	1.5278	1.5284	1.5283
0.08	2.8134	2.8128	2.8140	2.8133
0.09	3.1487	3.1483	3.1491	3.1488
0.1	3.4218	3.4228	3.4225	3.4231

Table F.1.2.10: Butyl acetate in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.01	0.5645	0.5656	0.5634	0.5643
0.02	0.8614	0.8604	0.8624	0.8612
0.03	1.1074	1.1072	1.1062	1.1086
0.04	1.3597	1.3498	1.3699	1.3595
0.05	1.6267	1.6238	1.6298	1.6266
0.06	1.8439	1.8448	1.8451	1.8438
0.07	2.0487	1.8447	1.8443	1.0527
0.08	2.1963	2.1961	2.1964	2.1965
0.09	2.3692	2.3691	2.3695	2.3689
0.1	2.4749	2.4745	2.4751	2.4748

Table F.1.2.11: Diethyl ether in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.01	7.7244	7.7234	7.7255	7.7254
0.02	15.2242	15.2241	15.2251	15.2230
0.03	22.3327	15.3337	15.3346	15.3316
0.04	28.9658	28.9647	28.9657	28.9666
0.05	35.6093	35.6196	35.5994	35.6094
0.06	41.6906	41.6907	41.6911	41.6901
0.07	47.8333	47.8233	47.8354	47.8352
0.08	53.8226	53.8228	53.8226	53.8224
0.09	59.4467	59.4456	59.4478	59.4466
0.1	65.0519	65.0518	65.0521	65.0518

Table F.1.2.12: Chloroform in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.01	2.3586	2.3574	2.3598	2.3585
0.02	4.0161	4.0152	4.0170	4.0164
0.03	4.1578	4.1568	4.1676	4.1478
0.04	6.4565	6.4556	4.4577	4.4568
0.05	7.7984	7.7883	7.8084	7.7985
0.06	8.9772	8.9774	8.9785	8.9762
0.07	10.0761	10.0762	10.0760	10.0759
0.08	11.4420	11.4421	11.4418	11.4422
0.08	12.2482	12.2481	12.2483	12.2485
0.09	13.1535	13.1536	13.1555	13.1516
0.1	21.7245	21.7235	21.7236	21.7266
0.2	31.4726	31.4727	31.4720	31.4734
0.3	39.1817	39.1824	39.1830	39.1818
0.5	47.2329	47.2338	47.2312	47.2328
0.6	55.4559	55.4552	55.4563	55.4558
0.7	63.3907	63.3914	63.3901	63.3906
0.8	70.7369	70.7368	70.7369	70.7370
0.9	77.7575	77.7679	77.7471	77.7574
1	85.1757	85.1758	85.1754	85.1762

Table F.1.2.13: Acetone in 10 cS PDMS

Volume of VOC injected(ml)	Peak areas			
0.01	3.0502	3.0510	3.0494	3.0503
0.02	6.0402	6.0403	6.0408	6.0395
0.03	8.9456	8.9452	8.9460	8.9454
0.04	11.7697	11.7696	11.7695	11.7699
0.05	14.5074	14.5072	14.5076	14.5073
0.06	17.2327	17.2326	17.2325	17.2330
0.07	20.1113	20.1012	12224	20.1106
0.08	22.8534	22.8532	22.8522	20.8542
0.09	25.5345	25.5342	25.5348	25.5346
0.1	28.1872	28.1861	28.1884	28.1871

Table F.1.2.14: Ethyl methyl ketone in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.002	0.2371	0.2374	0.2377	0.2365
0.005	0.5371	0.5372	0.5369	0.5372
0.01	1.0009	1.0008	1.0011	1.0009
0.02	1.9207	1.9208	1.9206	1.9207
0.04	3.5525	3.5527	3.5523	3.5524
0.06	4.7102	4.7100	4.7098	4.7106
0.08	6.0679	6.0678	6.0687	6.0688
0.1	7.3095	7.3096	7.3098	7.3094
0.2	13.3126	13.3125	13.3136	13.3125
0.4	23.8636	23.8633	23.8639	23.8638
0.6	33.8636	33.8635	33.8636	33.8635
0.8	43.2951	43.2943	43.2958	43.2952

Table F.1.2.15: Isobutyl methyl ketone in 10 cS PDMS

Volume of VOC injected (ml)	Peak areas			
0.005	0.2645	0.2642	0.2647	0.2645
0.01	0.5076	0.5075	0.5076	0.5077
0.02	0.9349	0.9348	0.9358	0.9360
0.04	1.3165	1.3174	1.3154	1.3165
0.06	1.7284	1.7283	1.7284	1.7283
0.08	2.1188	2.1189	2.1176	2.1202
0.1	2.3832	2.3840	2.3836	2.3846
0.2	3.8630	2.8636	3.8633	3.8632
0.4	6.5078	6.5080	6.5079	6.5077
0.6	9.2510	9.2512	9.2514	9.2511
0.8	10.5352	10.5350	10.5351	10.5352

Table F.1.2.16: Effect of temperature on H and γ (Acetone)

Temperature(K)	Peak areas			
298	4.0514	4.0518	4.0512	4.0520
303	4.6422	4.6412	4.6434	4.6424
308	5.4133	5.4127	5.4138	5.4128
313	6.0240	6.0248	6.0232	6.0241
318	6.9017	6.9016	6.9018	6.9017
323	7.5262	7.5261	7.5264	7.5263

Table F.1.2.17: Pentane in water

Volume of VOC injected (ml)	Peak areas			
0.01	131.5667	131.5568	131.5467	131.5668
0.02	261.2334	251.2335	272.2444	261.2552
0.03	385.9946	385.8883	386.1102	385.9968
0.04	511.5223	505.5234	516.2354	510.5246
0.05	642.5891	622.6996	642.6891	632.5888
0.06	746.2229	746.2258	746.2201	746.2205
0.07	852.3579	852.2578	852.4684	852.3574
0.08	951.4102	951.5118	951.3141	951.5114
0.09	1028.2448	1028.1338	1028.3557	1028.2418
0.1	1098.4962	1057.5972	1135.6252	1099.3956

Table F.1.2.18: Hexane in water

Volume of VOC injected (ml)	Peak areas			
0.01	150.6245	140.6243	160.5244	150.6239
0.02	300.0056	290.0042	310.1100	300.1102
0.03	448.5624	443.5735	451.6413	449.6325
0.04	596.2493	598.5626	594.2354	595.2364
0.05	743.3254	743.3253	743.6246	743.0254
0.06	888.3425	888.3450	888.3402	888.3411
0.07	1030.8564	1030.8579	1030.4665	1030.8456
0.08	1169.4561	1169.2232	1169.6871	1169.7821
0.09	1305.2388	1300.0566	1310. 2428	1306.2356
0.1	1431.3386	1452.4385	1409.6534	1452.3625

Table F.1.2.19: Heptane in water

Volume of VOC injected (ml)	Peak areas			
0.01	130.8554	135.9552	125.8234	130.8455
0.02	261.2506	261.4508	261.0008	261.2510
0.03	390.9887	390.9899	390.9854	390.9902
0.04	519.6487	519.5477	519.7489	519.6488
0.05	646.3284	646.6483	646.0085	646.3292
0.06	771.2512	771.7530	770.7501	771.2501
0.08	1022.6512	1022.7510	1022.5424	1022.6425
0.1	1262.2512	1262.5010	1262.0025	1262.2532
0.2	2472.5877	2470.4877	2474.6902	2474.5867

Table F.1.2.20: Triethyl amine in water

Volume of VOC injected (ml)	Peak areas			
0.01	1.5688	1.5589	1.5786	1.5689
0.02	2.2173	2.2174	2.2271	2.2174
0.03	3.1599	3.1559	3.1548	3.1588
0.04	3.7647	3.7627	3.7668	3.7645
0.05	4.4451	4.4452	4.4455	4.4448
0.06	4.9482	4.9485	4.9478	4.9481
0.07	5.5679	5.5673	5.5685	5.5678
0.08	5.9698	5.9697	5.9699	5.9697
0.09	6.1676	6.1675	6.1677	6.1675
0.1	6.3883	6.3886	6.3880	6.3882

Table F.1.2.21: Toluene in water

Volume of VOC injected (ml)	Peak areas			
0.005	21.6294	21.6298	21.6290	21.6293
0.01	41.8436	41.8435	41.8415	41.8457
0.02	81.2118	81.2136	81.2102	81.2117
0.04	153.5664	153.6654	153.4562	153.5654
0.06	213.8611	213.8612	213.7526	213.9745
0.08	260.1964	263.2869	264.5362	260.0954
0.1	290.5499	295.5488	285.5488	290.5505
0.2	458.6332	458.6334	456.7334	460.6248
0.4	721.6792	731.5896	712.5786	722.2356
0.6	924.2082	924.4092	924.0072	924.2092
0.8	1127.7840	1127.6950	1127.8960	1127.7846
1	1308.9822	1308.8824	1309.2415	1310.0025

Table F.1.2.22: Xylene in water

Volume of VOC injected (ml)	Peak areas			
0.001	13.0089	13.0058	13.0123	13.0078
0.002	22.8749	22.8769	22.9748	22.9842
0.005	46.9303	46.9404	46.9202	46.9314
0.01	76.7945	76.7866	76.8001	76.7974
0.05	279.6697	279.6698	279.5598	279.5586
0.1	517.5706	517.4705	517.6845	517.5475
0.2	897.7994	898.8955	899.2123	898.2145
0.4	1601.8949	1610.9865	1596.2354	1601.2568
0.6	2174.0202	2176.2586	2174.3625	2172.5689
0.8	2679.9596	2689.3562	2669.5328	2678.2564
1	2998.6221	2996.6232	3002.2513	2999.2543

Table F.1.2.23: Cyclohexane in water

Volume of VOC injected (ml)	Peak areas			
0.001	8.4532	8.4533	8.4562	8.4501
0.002	16.7242	16.7282	16.7213	16.7243
0.005	40.9464	40.9465	40.9468	40.9756
0.01	80.8456	80.8554	80.8335	80.8452
0.05	366.2548	366.1325	366.0125	366.5424
0.1	675.1222	674.256	676.5895	675.2354
0.2	1286.0032	1285.2356	1286.0021	1284.2561
0.4	2384.0233	2375.5624	2396.3548	2388.3364
0.6	3512.4412	3542.2354	3495.3578	3514.2101
0.8	4725.6554	4725.6454	4733.2584	4716.5842
1	5879.1114	5861.3561	5855.5842	5875.6548

Table F.1.2.24: Butyl acetate in water

Volume of VOC injected (ml)	Peak areas			
0.005	0.5276	0.5275	0.5279	0.5275
0.01	0.8305	0.8304	0.8306	0.8305
0.02	1.5264	1.5263	1.5266	1.5264
0.04	2.7701	2.7704	2.7702	2.7704
0.08	4.9452	4.8450	4.9462	4.9443
0.1	8.8364	8.8365	8.8364	8.6332
0.2	9.6408	9.6407	9.6409	9.6406
0.4	16.2307	16.2314	16.2301	23.1215
0.6	19.8969	19.8967	19.8968	19.8967
0.8	23.6511	23.6522	23.6524	23.3542
1	26.2657	26.2564	23.2575	26.2856

Table F.1.2.25: Diethyl ether in water at 303K

Volume of VOC injected (ml)	Peal areas			
0.01	15.4488	15.6524	15.2265	15.3264
0.02	30.5462	30.9954	30.0025	30.4521
0.03	44.6658	44.6352	44.5641	44.3256
0.04	58.9654	58.9256	58.2652	58.2563
0.05	70.6093	70.5326	70.2654	70.2531
0.06	82.1206	82.3561	82.2541	82.1204
0.07	94.8332	94.2356	94.5621	94.2536
0.08	107.4523	107.3658	107.3254	107.2564
0.09	120.6897	121.2562	122.4526	118.2352
0.1	130.6897	128.3652	129.2332	133.3526

Table F.1.2.26: Chloroform in water at 303K

Volume of VOC injected (ml)	Peak areas			
0.001	1.0536	1.0562	1.0256	1.0822
0.002	1.9596	1.9952	1.9325	1.9542
0.005	4.3831	4.3586	4.4215	4.3831
0.01	7.4065	7.4025	7.4121	7.5489
0.02	12.6391	12.6352	12.6421	12.6254
0.05	26.8361	26.3215	26.6523	26.9532
0.1	49.3316	49.6632	49.0201	49.2653
0.2	86.2361	86.3246	86.2331	86.2356
0.3	120.0028	123.2154	120.2214	119.5868
0.4	154.6265	153.6253	154.5623	154.5236
0.5	180.8672	180.8564	180.5423	180.8754
0.6	213.8325	214.14263	214.5324	213.3652

Table F.1.2.27: Acetone in water at 303K

Volume of VOC injected (ml)	Peak areas			
0.01	0.3339	0.4412	0.2952	0.3325
0.02	0.5624	0.5632	0.5648	0.5602
0.04	0.8978	0.8975	0.8956	0.8754
0.06	1.2638	1.2745	1.5421	1.2263
0.08	1.5747	1.4785	1.4253	1.5424
0.1	1.7361	1.5845	1.9357	1.7359
0.2	2.9865	2.9658	2.5624	2.3342
0.5	5.5766	5.5764	5.5768	5.5766
1	8.7589	8.7523	8.7624	8.7566
1.5	12.1589	12.1423	12.1632	12.4521
2	15.7023	15.3256	15.5241	15.3586

Table F.1.2.28: Ethyl methyl ketone in water at 303K

Volume of VOC injected (ml)	Peak areas			
0.005	2.0184	2.0154	2.0251	2.1124
0.01	3.8082	3.8401	3.8021	3.4123
0.02	9.7952	9.6985	9.8854	9.5264
0.04	12.2364	12.4325	12.1224	12.5421
0.06	15.9524	15.9652	15.9659	15.9511
0.08	19.2575	19.2546	19.3352	19.5241
0.1	22.8452	22.8422	22.8425	22.3264
0.2	39.5542	39.5421	39.2543	39.5462
0.4	72.7915	72.6548	72.6514	72.6541
0.6	103.5562	103.5624	105.3255	101.5324
0.8	131.0956	135.5418	128.3256	132.9878
1	153.2657	153.8457	154.2365	155.2341

Table F.1.2.29: Isobutyl methyl ketone in water at 303K

Volume of VOC injected (ml)	Peak areas			
0.02	1.4238	1.4253	1.4222	1.4237
0.04	2.6448	2.6442	2.6452	2.6441
0.06	3.6654	3.6653	3.5525	3.7741
0.08	4.4526	4.4532	4.4562	4.4533
0.1	5.2838	5.2832	5.2842	5.24846
0.2	8.9854	8.9855	8.9841	8.9855
0.4	15.9236	15.9263	15.9253	15.9236
0.6	21.5688	21.5685	21.5687	21.5684
0.8	26.8326	26.8354	26.8325	26.8326
1	30.5218	30.5126	30.5123	30.5201

F.2 Gas – Liquid Chromatographic Technique

Table F.2.1: Flow rate calibrations for 5 cS PDMS column (10% loading)

GC set (ml/min)	Bubble flow time (sec)				
40	34.78	34.90	34.87	34.82	34.83
50	28.49	28.47	28.45	28.50	28.49
60	24.10	24.18	24.19	24.10	24.13
70	21.13	21.07	21.15	21.06	21.09
80	18.74	18.72	18.64	18.73	18.68
90	16.72	16.64	16.74	16.63	16.67

Table F.2.2: Flow rate calibrations for 10 cS PDMS column (10 % loading).

GC set (ml/min)	Bubble flow time (sec)				
40	63.63	63.56	63.70	63.65	63.61
50	50.96	50.90	50.91	50.96	50.95
60	42.46	42.40	42.39	42.48	42.47
70	36.32	36.40	36.33	36.37	36.36
80	31.75	31.87	31.78	31.86	31.84
90	28.26	28.32	28.30	28.26	28.31

Table F 2.3: Flow rate calibrations for 50 cS PDMS column (10 % loading)

GC set (ml/min)	Bubble flow time (sec)				
40	35.98	36.06	36.08	35.96	36.01
50	29.41	29.56	29.44	29.49	29.51
60	24.94	24.90	24.86	24.93	24.97
70	23.53	23.51	23.52	23.50	23.54
80	19.17	19.19	19.15	19.14	19.17
90	17.24	17.27	17.28	17.23	17.28

Table F.2.4: Flow rate calibrations for 50 cS PDMS column (20 % loading)

GC set (ml/min)	Bubble flow time (sec)				
40	36.23	36.24	36.22	36.25	36.21
50	29.80	29.86	29.87	29.86	29.83
60	24.98	25.06	25.08	24.97	25.01
70	21.60	21.66	21.68	21.59	21.62
80	19.25	19.19	19.26	19.21	19.19
90	17.36	17.40	17.32	17.43	17.39

Table F.2.5: Flow rate calibrations for 50 cS PDMS column (30 % loading)

GC flow rate set (ml/min)	Bubble flow time (sec)				
40	36.54	36.56	36.52	36.58	36.51
50	30.34	30.30	30.27	30.28	30.36
60	25.58	25.66	25.59	25.61	25.65
70	22.30	22.33	22.34	22.27	22.35
80	19.32	19.34	19.32	19.28	19.35
90	17.23	17.25	17.20	17.27	17.28

Table F.2.6: Flow rate calibrations for 500 cS PDMS column (10 % Loading)

GC set (ml/min)	Bubble flow time (sec)				
40	29.98	29.94	29.99	29.96	30.03
50	24.02	24.04	23.99	23.98	24.05
60	20.11	20.04	20.10	20.07	20.08
70	17.14	17.10	17.16	17.11	17.12
80	15.04	14.99	14.97	15.03	14.97

Table F.2.7: Effect of liquid loading(30%) on retention volumes (50 cS PDMS columns)

Compound	Solute retention times (min)				
Pentane	3.51	3.52	3.50	3.51	3.52
Hexane	7.82	7.80	7.78	7.86	7.84
Heptane	17.62	17.58	17.64	17.60	17.61
Diethyl ether	3.23	3.24	3.23	3.22	3.23
Acetone	2.62	2.61	2.63	2.61	2.62
Chloroform	7.50	7.51	7.48	7.46	7.45

Table F.2.8: Effect of liquid loading(20%) on retention volumes (50 cS PDMS columns

Compound	Solute retention times(min)				
Pentane	2.33	2.32	2.33	2.34	2.32
Hexane	5.11	5.12	5.11	5.12	5.11
Heptane	11.38	11.39	11.39	11.38	11.39
Diethyl ether	2.21	2.21	2.22	2.21	2.22
Acetone	1.79	1.79	1.79	1.80	1.79
Chloroform	5.12	5.11	5.12	5.11	5.12

Table F.2.9: Effect of liquid loading(10%) on retention volumes (50 cS PDMS columns

Compound	Solute retention times (min)				
Pentane	2.61	2.60	2.63	2.62	2.63
Hexane	6.76	6.77	6.76	6.74	6.79
Heptane	17.98	17.96	18.00	17.98	17.97
Diethyl ether	2.51	2.52	2.51	2.52	2.50
Acetone	2.18	2.21	2.15	2.17	2.18
Chloroform	6.29	6.30	6.28	6.29	6.28

Table F.2.10: Effect of sample size on retention volumes (500 cS PDMS column) – Pentane

Sample size (µl)	Retention times (sec)				
0.10	0.89	0.90	0.88	0.90	0.89
0.50	0.88	0.89	0.87	0.89	0.88
1.00	0.83	0.80	0.82	0.84	0.83
5.00	0.67	0.66	0.68	0.66	0.68
10.00	0.50	0.48	0.51	0.52	0.47

Table F.2.11: Effect of sample size on retention volumes (500cS PDMS column) – Acetone

Solute sample (µl)	Retention times (mins)				
0.10	0.83	0.82	0.80	0.83	0.82
0.50	0.82	0.80	0.83	0.82	0.83
1.00	0.77	0.78	0.76	0.77	0.78
5.00	0.61	0.62	0.60	0.61	0.60
10.00	0.44	0.43	0.44	0.45	0.43

Table F.2.12: Effect of sample size on retention volumes (500 cS PDMS column) – Chloroform

Sample size (µl)	Retention times (mins)				
0.10	1.57	1.59	1.58	1.56	1.57
0.50	1.56	1.55	1.56	1.58	1.54
1.00	1.53	1.55	1.53	1.54	1.50
5.00	1.42	1.43	1.44	1.42	1.43
10.00	1.31	1.32	1.33	1.29	1.31

Table F.2.13: Effect of sample size on retention volumes (500 cS PDMS column) – Diethyl ether.

Sample size (µl)	Retention times (mins)				
0.10	0.92	0.90	0.94	0.92	0.91
0.50	0.90	0.88	0.92	0.89	0.91
1.00	0.86	0.88	0.87	0.85	0.86
5.00	0.71	0.74	0.68	0.71	0.72
10.00	0.58	0.56	0.60	0.58	0.59

Table F.2.14: Effect of sample size on retention volumes (500 cS PDMS column) – Ethyl methyl ketone

Sample size (µl)	Retention times				
0.10	1.46	1.47	1.45	1.48	1.46
0.50	1.45	1.44	1.45	1.46	1.45
1.00	1.42	1.43	1.40	1.44	1.42
5.00	1.27	1.28	1.26	1.30	1.27
10.00	1.11	1.12	1.10	1.13	1.09

Table F.2.15: Effect of carrier gas flow rate on retention data (500 cS PDMS) – Acetone

Flow rate (ml/min)	Retention times (mins)				
20.01	1.37	1.39	1.35	1.37	1.38
24.94	1.17	1.16	1.18	1.17	1.16
29.88	1.02	1.03	1.01	1.02	1.03
35.02	0.93	0.94	0.92	0.95	0.92
40.01	0.95	0.94	0.96	0.95	0.94

Table F.2.16: Effect of carrier gas flow rate on retention data (500 cS PDMS) – Pentane

Flow rate (ml/min)	Retention times (mins)				
20.01	1.42	1.43	1.41	1.42	1.43
24.98	1.21	1.22	1.23	1.19	1.20
29.88	1.06	1.05	1.06	1.07	1.06
35.02	0.96	0.94	0.98	0.96	0.97
40.01	0.88	0.89	0.88	0.87	0.88

Table F.2.17: Effect of carrier gas flow rate on retention data (500 cS PDMS) – Chloroform

Flow rate (ml/min)	Retention times				
20.01	2.71	2.73	2.70	2.72	2.71
24.94	2.24	2.22	2.23	2.24	2.23
29.88	1.93	1.94	1.93	1.94	1.93
35.02	1.69	1.70	1.68	1.70	1.69
40.01	1.52	1.54	1.53	1.50	1.51

Table F.2.18: Effect of carrier gas flow rate on retention data (500 cS PDMS) – Diethyl ether

Flow rate (ml/min)	Retention times (mins)				
20.01	1.42	1.40	1.44	1.41	1.42
24.98	1.21	1.20	1.21	1.22	1.21
29.88	1.06	1.05	1.07	1.06	1.05
35.02	0.96	0.95	0.97	0.96	0.97
40.01	0.88	0.87	0.89	0.88	0.87

Table F.2.19: Effect of carrier gas flow rate on retention data (500 cS PDMS) – Ethyl methyl ketone

Flow rate (ml/min)	Retention times				
20.01	4.43	4.42	4.44	4.43	4.44
24.98	3.61	3.60	3.62	3.61	3.60
29.88	3.07	3.08	3.06	3.07	3.08
35.02	2.67	2.65	2.69	2.68	2.66
40.01	2.38	2.39	2.40	2.36	2.37

Table F.2.20: Packing information data (5 cS PDMS column)

Material	*Mass (g)*
Beaker	*90.160*
Support	*9.000*
Support + beaker	*99.160*
Beaker after removing support	*90.160*
Flask	*113.220*
Stationary phase + flask	*114.226*
Stationary phase	*1.006*
Flask + stationary phase + support before packing	*123.014*
Flask after packing	*116.168*
Support + stationary phase in column	*6.846*
Stationary phase in column	*0.688*

Table F.2.21: Packing information data (10 cS PDMS column)

Material	*Mass (g)*
Beaker	*90.154*
Support	*9.074*
Support + beaker	*99.233*
Beaker after removing support	*90.170*
Flask	*111.212*
Stationary phase + flask	*112.237*
Stationary phase	*1.025*
Flask + stationary phase + support before packing	*121.274*
Flask after packing	*113.158*
Support + stationary phase in column	*8.116*
Stationary phase in column	*0.825*

Table F.2.22: Packing information data (50 cS PDMS column) – 10 % loading

Material	*Mass (g)*
Beaker	*90.174*
Support	*7.200*
Support + beaker	*97.374*
Beaker after removing support	*90.174*
Flask	*111.173*
Stationary phase + flask	*111.978*
Stationary phase	*0.805*
Flask + stationary phase + support before packing	*119.178*
Flask after packing	*118.188*
Support + stationary phase in column	*7.99*
Stationary phase in column	*0.804*

Table F.2.23: Packing information data (50 cS PDMS column) – 20% loading

Material	*Mass (g)*
Beaker	*90.164*
Support	*7.212*
Support + beaker	*97.376*
Beaker after removing support	*90.166*
Flask	*111.174*
Stationary phase + flask	*112.975*
Stationary phase	*1.801*
Flask + stationary phase + support before packing	*120.185*
Flask after packing	*111.184*
Support + stationary phase in column	*9.001*
Stationary phase in column	*1.800*

Table F.2.24: Packing information data (50 cS PDMS column) – 30% loading

Material	*Mass (g)*
Beaker	*91.112*
Support	*7.001*
Support + beaker	*98.113*
Beaker after removing support	*90.174*
Flask	*111.172*
Stationary phase + flask	*114.142*
Stationary phase	*2.97*
Flask + stationary phase + support before packing	*121.0046*
Flask after packing	*111.131*
Support + stationary phase in column	*9.874*
Stationary phase in column	*2.97*

APPENDIX G: CALCULATIONS

G: Simple Static Headspace Method

G1.1: Calculation of the volume of toluene for calibration

ppm = $1/10^6$ = mole toluene / mole water

1 mole air = 22410 ml

No. of moles in 594ml flask = 594/22410 = 2.6506E-02

No. of moles in 1000ppm = (1000/1000000)2.6506E-02
= 2.6506E-05

Mass of toluene in 1000ppm = no. of moles x toluene Mw
= 2.6506E-05 x 92.14
= 2.4423E-03g

Volume of toluene = mass/density
= 2.4423E-03/0.86694
= 2.8171E-03ml
= 2.8171µl

Table G.1.1: Volume of toluene used in the calibration

Concentration (ppm)	Volume of toluene (µl)	Concentration (kg/m^3)
1000	2.8	4.120E-03
2000	5.6	8.250E-03
3000	8.4	1.238E-02
4000	11.2	1.648E-02
5000	14.0	2.064E-02
6000	16.8	2.476E-02
8000	22.4	3.296E-02
9000	25.2	3.708E-02
10000	28.0	4.120E-02

G.1.2: Toluene Calibration Data

Mean Peak Area (units)	Concentration (ppm)	Concentration (kgm^{-3})
14.2576	179	7.38E-04
57.0832	1000	4.12E-03
132.2634	4000	1.65E-02
170.2147	5000	2.06E-02
277.3790	9000	3.71E-02
422.2826	13571	5.59E-02
553.8266	18000	7.47E-02
690.0000	22500	9.27E-02
849.7594	27000	1.11E-01
975.4105	31429	1.30E-01
1108.4173	36000	1.48E-01

G.1.3 Fitting a straight line into calibration data

Taking the peak area as x values and concentration (kgm^{-3}) as the y values, the least squares straight line to fit the data is obtained as follows:

$S_x = \sum_{i=1}^{n}$

= (14.2576+57.0832+132.2634+170.2147+277.3790+422.2836+
553.8266+690.0000+849.7594+975.4105+1108.4173)

= 5250.8943

$S_y = \sum_{i=1}^{n} y_i$

= (7.38E-04+4.12E-03+1.65E-02+2.06E-02+3.71E-02+5.59E-02+
7.47E-02+9.27E-02+1.11E-01+1.30E-01+1.48E-01)

= 0.691358

$S_{xy} = \sum_{i=1}^{n} x_i y_i$

= [(14.2576*7.38E-04)+(57.0832*4.12E-03)+(132.2634*1.65E-02)+
(170.2147*2.06E-02)+(277.3790*3.71E-02)+(422.2826*5.59E-02)+

$$= (553.8266*7.47E\text{-}02) + (690.0000*9.27E\text{-}02) + (849.7594*1.11E\text{-}01) + (975.4105*1.30E\text{-}01) + (1108.4173*1.48E\text{-}01)]$$

$$= \underline{530.3266}$$

$$S_{xx} = \sum_{i=1}^{n} x_i^2$$

$$= [(14.2576)^2+(57.0832)^2+(132.2634)^2+(170.2147)^2+(277.3790)^2+ (422.2826)^2+(553.8266)^2+(690.000)^2+(849.7594)^2+(975.4105)^2+ (1108.4173)^2]$$

$$= \underline{3\ 990\ 119.621}$$

$$m = \frac{(nS_{xy} - S_x S_y)}{(nS_{xx} - S^2{}_x)}$$

$$= \frac{(11*530.3266) - (5250.8943*0.691358)}{(11*3990119.621) - 27571890.95}$$

$$= \underline{0.000135}$$

$$c = \frac{(S_y S_{xx} - S_{xy})}{(nS_{xx} - S^2 x)}$$

$$= \frac{(0.691358*3990119.621) - 530.3266}{(11*3990119.621) - 27571890.95}$$

$$= \underline{0.1690}$$

Therefore the equation of the calibration line is y =0.000135x + 0.1690. The gradient value, 0.000135 agrees very well with the one obtained graphically see appendix E11. In addition to that it also agrees with that obtained by Yoswathana (2000) using the EPICS method.

G.1.4 Calculation of Henry's law constants and activity coefficients

G.1.4.1: Toluene in PDMS (10 cS)

Sample 1: The experimental conditions were as follows:

- Equilibrium temperature at 303.15K
- Flask volume is 594ml (5.94E-04m^3)
- The volume of silicon oil is 0.02ml (2E-04m^3)

- The volume of toluene injected into the flask is 0.01ml (1E-08m^3)
- The volume of gas injected into the the GC is 0.5ml
- Total pressure P is 1 atm.
- Molecular weight of toluene (RMM) is 92.14 kg/kmol
- The density of toluene is 866.94kg/m^3
- The universal gas constant is 0.08207 atm.m^3.$K^{-1}$$mol^{-1}$
- Peak area after 1 hour shaking time is 0.3541
- The gradient of calibration curve is 1.35E-04 (kg/m^3)/peak area

-

Vapour phase calculation

Conc. of tol in vapour phase = gradient x peak area
= 1.35E-04 x 0.3541
= 4.7803E-05kg/m^3

Mass of tol in vapour phase = conc of tol x vol above liq phase
= 4.7803E-05 x (5.94-2)E-04
= 1.8E-08kg

K mol air = (PV/RT)
$$= \frac{1x[95.94-2)E-04}{[0.08207*(30+273.15)]}$$
= 1.5836E-05

Kmol tol in vapour = mass of tol / RMM of tol
= 1.8E-08/92.14
= 1.9535E-10

Mole fraction of tol in vapour (y) = k mol tol in vapour / (kmol tol in vapour +kmol air)
$$= \frac{1.9535E-10}{(1.9535E-10+1.5836E-05)}$$
= 1.2335E-05

Liquid Phase Calculation

Mass of tol injected into flask = density of tol x volume injected
= 866.94 x 1E-08
= 8.6694E-06

Mass of toluene in liquid = total injected – mass in gas phase
= (8.6694E-06 – 1.8E-08)
= 8.651E-06kg

kmol of toluene in liquid = mass of toluene/RMM of toluene
= 8.651E-06/92.14
= 9.3E-08

Mass of PDMS in flask = density x PDMS volume
= $0.94gm^{-1}$x200ml
= 188g

Kmol silicon oil = PDMS mass/ PDMS RMM
= 0.188/1000
= 0.000188

Mole fraction tol in liquid phase (x) = Kmol tol in liq phase / Kmol tol liq + Kmol PDMS
= $\frac{9.3E-08}{(9.3E-08+1.88E-04)}$
= 0.000499189

Henry's law constants (H) calculation

H = Tol Partial pressure in vap phase / Mole frac. of tol in liq phase
= yP/x
= (1.2335E-05x1)/4.9919E-04
= 0.02471
= 0.02471x1000E-06
= $2.471E-05\ atm.m^3mol^{-1}$
= $2.471E-05 \times 101.325KPam^3mol^{-1}$
= $0.002504KPam^3mol^{-1}$

Activity coefficients $({}^x\gamma)$ calculation

$${}^x\gamma = \frac{yP}{xP_i^o} = \frac{(1.2335E-05x101.325)}{(4.9919E-04x4.893)} = 0.512$$

Activity coefficients $({}^w\gamma)$ calculation (weight fraction based)

$({}^w\gamma)$ = $({}^w\gamma)$(Mw polymer/Mw solvent)
= 0.512(1000/92.14)

$$= \quad \underline{5.557}$$

G.2: Gas Chromatographic Technique

The homologous series method was used to calculate gas hold-up volume. A mixture of three members of a homologous series (n-pentane, n-hexane and n-heptane) were injected into the column. The gas hold-up was calculated using the equation below to obtain retention time of the non-absorbed component (t_M).

$$t_M = \frac{t_{R_1} t_{R_3} - t^2_{R_2}}{t_{R_1} + t_{R_3} - 2t_{R_3}}$$

G.2.1. Calculation of gas hold-up in 5 cS PDMS Column.

Conditions

- Column temperature (T_c) at 303.15K
- Sample size of 0.1µl
- Inlet pressure at 140 Kpa
- Outlet pressure at 101 Kpa (atmospheric)
- Carrier gas flow rate at 35.97ml/min
- Retention times of pentane, hexane and n-heptane were as follows 1.75, 4.38 and 11.44 minutes respectively
- Weight of stationary phase in column (W_s) is 0.688g

Then, the gas hold-up is calculated as follows:

Retention time (t_R)

$$t_M = \frac{t_{R_1} t_{R_3} - t^2_{R_2}}{t_{R_1} + t_{R_3} - 2t_{R_3}}$$

$$= \frac{(175x11.44) - (4.38)^2)}{(1.75 + 11.44) - (2x4.38)}$$

$$= \underline{0.19\text{mins}}$$

Gas hold-up volume (V_M)

$$V_M = F \text{ (carrier gas flow rate x } t_M) = 35.97 \text{ml min}^{-1} \times 0.19 \text{ mins} = \underline{6.834\text{ml}}$$

G.2.2 Infinite Dilution Activity Coefficients

Chloroform infinite dilution activity coefficients in 5 cS PDMS column were calculated using the procedure below. The conditions in the column are those stated in section D.2.1.1 and in addition to that, the retention time of chloroform was found to be 4.25mins.

Retention Volume (uncorrected) V_R

$$V_R = Ft_R = 35.97 \times 4.25 = \underline{152.87\text{ml}}$$

Adjusted Retention Volume V'_R

$$V'_R = V_R - V_M = 152.87 - 6.834 = \underline{146.04\text{ml}}$$

Carrier Gas Compressibility Factor (j_3^2)

$$j_3^2 = \frac{3}{2}\left[\frac{(p_i/p_o)-1}{\left(p_i/p_o\right)-1}\right] = \frac{3}{2}\left[\frac{\left(\frac{140}{101}\right)^2-1}{\left(\frac{140}{101}\right)^3-1}\right] = \underline{0.831}$$

Net Retention Volume (V_N)

$$V_N = j_3^2 V'_R$$

$$= \frac{3}{2}\left[\frac{\left(p_i/p_o\right)^2 - 1}{\left(p_i/p_o\right)^3 - 1}\right] V'_R$$

$$= 0.831 \text{ x } 146.04\text{ml}$$

$$= \underline{121.36\text{ ml}}$$

Specific Retention Volume $\left(V_g^o\right)$

$$V_g^o = \frac{273.16 V_N}{W_s T_c}$$

$$= \frac{273.16x121.36}{303.15x0.688}$$

$$= \underline{159\text{ml}}$$

Infinite Dilution Activity Coefficients

Mole fraction based activity coefficients

$$\ln {}^x\gamma_1^\infty = \ln \frac{273.16R}{V_g P_1^o M_s} - \frac{P_1^o\left(B_{11} - \bar{V}_1^o\right)}{RT}$$

$$= \ln \frac{273.16R}{V_g P_1^o M_s} - \frac{32.80(-1187.00 - 80.86)}{8314x303.16}$$

$$= \ln 0.5729 + 0.016499$$

$$= -0.5570 + 0.016499$$

$$= \underline{-0.5405}$$

Therefore ${}^x\gamma_1^\infty = e^{\ln {}^x\gamma_1^\infty}$

$$= e^{-0.5405}$$

$$= \underline{0.5825}$$

Weight fraction based activity coefficients

$${}^w\gamma_1^\infty = \frac{{}^\infty\gamma_1^\infty M_s}{M_1}$$

$$= \frac{0.5825x760}{119.389}$$

$$= \underline{3.708}$$

G.3 SAMPLES OF MANUAL UNIFAC CALCULATIONS

G.3.1 Calculation of heptane activity coefficient in water

The activity coefficient is calculated using UNIFAC for the binary system of heptane (1) / water (2) at x_1 = 8.7645E-08

The combinatorial part calculations

Constituent groups information

Molecule (i)	Group Identification				
	Name	No.	$\nu_k^{(i)}$	R_k	Q_k
Heptane (1)	CH_3	1	2	0.9011	0.8480
	CH_2	2	5	0.6744	0.5400
Water (2)	H_2O	3	1	0.9200	1.400

$$r_1 = \nu_1^{(1)} xR_1 + \nu_2^{(1)} xR_2 = (2)(0.9011) + (5)(0.6744) = 5.1742$$

$$r_2 = \nu_3^{(2)} xR_3 = (1)(0.9200) = 0.9200$$

$$q_1 = \nu_1^{(1)} xQ_1 + \nu_2^{(1)} xQ_2 = (2)(0.8480) + (5)(0.5400) = 4.3960$$

$$q_2 = \nu_3^{(2)} xQ_3 = (1)(1.400) = 1.4000$$

$$l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - 1) = \frac{10}{2}(5.1742 - 4.3960) - (5.1742 - 1) = -0.2832$$

$$l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - 1) = \frac{10}{2}(0.9200 - 1.4000) - (0.9200 - 1) = -2.32$$

$$\phi_1 = \frac{r_1 x_1}{r_1 x_1 + r_2 x_2} = \frac{(5.1742)(8.7645E-08)}{((5.1742)(8.7645E-08) + (0.9200)(0.999999)} = 0.000000492$$

$$\phi_2 = \frac{r_2 x_2}{r_1 x_1 + r_2 x_2} = \frac{(0.9200)(0.999999)}{((5.1742)(8.7645E-08) + (0.9200)(0.999999)} = 0.999999$$

$$\theta_1 = \frac{q_1 x_1}{q_1 x_1 + q_2 x_2} = \frac{(4.3960)(8.7645E-08)}{((4.3960)(8.7645E-08) + (1.4000)(0.999999)} = 0.000000275$$

$$\theta_2 = \frac{q_2 x_2}{q_1 x_1 + q_2 x_2} = \frac{(1.400)(0.999999)}{((4.3960)(8.7645E-08)+(1.4000)(0.999999)} = 0.999999$$

$$\ln \gamma_1^c = \ln \frac{\phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\phi_1} + l_1 - \frac{\phi_1}{x_1}(x_1 l_1 + x_2 l_2)$$

$$= \ln\left(\frac{0.000000492}{8.7645E-08}\right) + \frac{10}{2}(4.3690)\ln\left(\frac{0.000000275}{0.000000492}\right) - 0.2832$$

$$-\frac{0.000000492}{8.7645E-08}((8.7645E-08)(-0.2832)+(0.999999)(-2.32))$$

$$= 1.6797$$

The residual part calculations

The binary group interaction parameters are

$a_{1,2} = a_{1,1} = a_{2,1} = a_{2,2} = a_{3,3} = 0$

$a_{1,3} = 1.452,\ a_{2,3} = 1.452,\ a_{3,1} = a_{3,2} = 657.7$

$\psi_{1,2} = \psi_{1,1} = \psi_{2,1} = \psi_{2,2} = \psi_{3,3} = 1$

$$\psi_{1,3} = \psi_{2,3} = \exp\left(\frac{-1.452}{30+273.15}\right) = 0.99522$$

$$\psi_{3,1} = \psi_{3,2} = \exp\left(\frac{-657.7}{30+273.15}\right) = 0.11423$$

Assigning identification numbers to groups, CH_3 = 1, CH_2 = 2, H_2O = 3. Now one can compute $\Gamma_k^{(1)}$, the residual activity coefficient of group k in a reference solution containing only molecules of type *i*. For n-heptane (1), the mole fraction of group i, $X_1^{(1)}$ is:

$$X_1^{(1)} = \frac{v_1^{(1)}}{v_1^{(1)} + v_2^{(1)}} = \frac{2}{2+5} = 0.2857$$

$$X_2^{(1)} = \frac{v_2^{(1)}}{v_1^{(1)} + v_2^{(1)}} = \frac{5}{2+5} = 0.7143$$

$$X_3^{(2)} = \frac{v_3^{(2)}}{v_3^{(2)}} = 1$$

$$\theta_1^{(1)} = \frac{X_1^{(1)}Q_1}{X_1^{(1)}Q_1 + X_2^{(1)}Q_2} = \frac{(0.2857)(0.8480)}{((0.2857)(0.8480) + (0.7143)(0.5400))} = 0.3858$$

$$\theta_2^{(1)} = \frac{X_2^{(1)}Q_2}{X_1^{(1)}Q_1 + X_2^{(1)}Q_2} = \frac{(0.7143)(0.5400)}{((0.2857)(0.8480) + (0.7143)(0.5400))} = 0.6142$$

$$\theta_3^{(2)} = \frac{X_3^{(2)}Q_3}{X_3^{(2)}Q_3} = 1$$

Since there is one main group in heptane, the following is obtained $\Gamma_1^{(1)}$ and $\Gamma_2^{(1)} = 0$ and since there is one main group in water $\Gamma_3^{(2)} = 0$.

The group residual activity coefficients can now be calculated as follows:

$$X_1^{(1)} = \frac{x_1 v_1^{(1)}}{(x_1(v_1^{(1)} + v_2^{(1)}) + x_2(v_3^{(2)}))} = \frac{(8.7645E-08)(2)}{((8.7645E-08)(7) + (0.9999999)(1))} = 0.000000175$$

$$X_2^{(1)} = \frac{x_1 v_2^{(1)}}{(x_1(v_1^{(1)} + v_2^{(1)}) + x_2(v_3^{(2)}))} = \frac{(8.7645E-08)(5)}{((8.7645E-08)(7) + (0.999999)(1))} = 0.000000438$$

$$X_3^{(2)} = \frac{x_2 v_3^{(2)}}{(x_1(v_1^{(1)} + v_2^{(1)}) + x_2(v_3^{(2)}))} = \frac{(0.999999)(1)}{((8.7645E-08)(7) + (0.9999999)(1))} = 0.9999994$$

$$\theta_1 = \frac{X_1Q_1}{(X_1Q_1 + X_2Q_2 + X_3Q_3)} = \frac{(0.000000175)(0.8480)}{((1.75E-07)(0.8480) + (4.38E-07)(0.5400) + (0.999999)(1.4))}$$

$$= 0.000000106$$

$$\theta_2 = \frac{X_2Q_2}{(X_1Q_1 + X_2Q_2 + X_3Q_3)} = \frac{(0.000000438)(0.5400)}{((1.75E-07)(0.8480) + (4.38E-07)(0.5400) + (0.999999)(1.4))}$$

$$= 0.000000168$$

$$\theta_3 = \frac{X_3Q_3}{(X_1Q_1 + X_2Q_2 + X_3Q_3)} = \frac{(0.999999)(1.4000)}{((1.75E-07)(0.8480) + (4.38E-07)(0.5400) + (0.999999)(1.4))}$$

$= 0.9999997$

$$\ln \Gamma_1 = Q_1[1 - \ln(\theta_1\psi_{1,1} + \theta_2\psi_{2,1} + \theta_3\psi_{3,1}) - (\frac{\theta_1\psi_{1,1}}{(\theta_1\psi_{1,1} + \theta_2\psi_{2,1} + \theta_3\psi_{3,1})}$$

$$+ \frac{\theta_2\psi_{1,2}}{(\theta_1\psi_{1,2} + \theta_2\psi_{2,1} + \theta_3\psi_{3,2})} + \frac{\theta_3\psi_{1,3}}{(\theta_1\psi_{1,3} + \theta_2\psi_{2,3} + \theta_3\psi_{3,3})})]$$

$$= (0.8480)[1 - \ln((0.000000106)(1) + (0.000000168)(1) + (0.999999)(0.11423))$$

$$-(\frac{(0.0000106)(1)}{((0.000000106)(1) + (0.000000168)(1) + (0.999999)(0.11423))}$$

$$+ \frac{(0.000000168)(1)}{((0.000000106)(1) + (0.000000168)(1) + (0.999999)(0.11423))}$$

$$+ \frac{(0.999999)(0.99522)}{((0.000000106)(0.99522) + (0.000000168)(0.99522) + (0.999999)(1))})]$$

$\therefore \ln \Gamma_1 = 1.843821$

$$\ln \Gamma_2 = Q_2[1 - \ln(\theta_1\psi_{1,2} + \theta_2\psi_{2,2} + \theta_3\psi_{3,2}) - (\frac{\theta_1\psi_{2,1}}{(\theta_1\psi_{1,1} + \theta_2\psi_{2,1} + \theta_3\psi_{3,1})}$$

$$+ \frac{\theta_2\psi_{1,2}}{(\theta_1\psi_{1,2} + \theta_2\psi_{2,2} + \theta_3\psi_{3,2})} + \frac{\theta_3\psi_{1,3}}{(\theta_1\psi_{1,3} + \theta_2\psi_{2,3} + \theta_3\psi_{3,3})})]$$

$$= (0.5400)[1 - \ln((0.000000106)(1) + (0.000000168)(1) + (0.9999997)(0.11423))$$

$$-(\frac{(0.0000106)(1)}{((0.000000106)(1) + (0.000000168)(1) + (0.9999997)(0.11423))}$$

$$+ \frac{(0.000000168)(1)}{((0.000000106)(1) + (0.000000168)(1) + (0.9999997)(0.11423))}$$

$$\frac{(0.9999997)(0.99522)}{((0.000000106)(0.99522) + (0.000000168)(0.99522) + (0.9999997)(1))})]$$

$\therefore \ln \Gamma_2 = 1.174133$

$$\ln \gamma_1^R = \nu_1^{(1)}\left(\Gamma_1 - \Gamma_1^{(1)}\right) + \nu_2^{(1)}\left(\Gamma_2 - \Gamma_2^{(1)}\right) = 2(1.84382088 - 0) + 5(1.174132516) = 9.558306$$

$$\ln \gamma_1 = \ln \gamma_1^C + \ln \gamma_1^R = 1.6797 + 9.558306 = 11.238006$$

$$\therefore \gamma_1 = 75963.33$$

G.3.2 Calculation of heptane activity coefficient in silicone oil

The activity coefficient is calculated using UNIFAC for the binary system of heptane (1) / oil (2) at $x_1 = 7.19E\text{-}05$

The combinatorial part calculations

Constituent groups information

Molecule (i)	Group Identification				
	Name	No.	$\nu_k^{(i)}$	R_k	Q_k
Heptane (1)	CH_3	1	2	0.9011	0.8480
	CH_2	2	5	0.6744	0.5400
PDMS (2)	CH_3	1	2	0.9011	0.8480
	SiO	3	1	1.1044	0.4657

$$r_1 = \nu_1^{(1)}R_1 + \nu_2^{(1)}R_2 = (2)(0.9011) + (5)(0.6744) = 5.1742$$

$$r_2 = \nu_1^{(2)}R_1 + \nu_3^{(2)}R_3 = (2)(0.9011) + (1)(1.1044) = 2.9066$$

$$q_1 = \nu_1^{(1)}xQ_1 + \nu_2^{(1)}xQ_2 = (2)(0.8480) + (5)(0.5400) = 4.3960$$

$$q_2 = \nu_1^{(2)}Q_1 + \nu_3^{(2)}Q_3 = (1)(1.400) = 1.4000$$

$$l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - 1) = \frac{10}{2}(5.1742 - 4.3960) - (5.1742 - 1) = -0.2832$$

$$l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - 1) = \frac{10}{2}(2.9066 - 2.1617) - (2.9066 - 1) = 1.8179$$

$$\phi_1 = \frac{r_1 x_1}{r_1 x_1 + r_2 x_2} = \frac{(5.1742)(7.19E-05)}{((5.1742)(7.19E-05)+(2.9066)(0.9999281)} = 0.000127986$$

$$\phi_2 = \frac{r_2 x_2}{r_1 x_1 + r_2 x_2} = \frac{(2.9066)(0.9999281)}{((5.1742)(7.19e-05)+(2.9066)(0.9999281)} = 0.999872$$

$$\theta_1 = \frac{q_1 x_1}{q_1 x_1 + q_2 x_2} = \frac{(4.3960)(7.19E-05)}{((4.3960)(7.19E-05)+(2.1617)(0.9999281)} = 0.999853796$$

$$\theta_2 = \frac{q_2 x_2}{q_1 x_1 + q_2 x_2} = \frac{(2.1617)(0.9999281)}{((4.3960)(7.19E-05)+(2.1617)(0.9999281)} = 0.999853796$$

$$\ln \gamma_1^c = \ln \frac{\phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\phi_1} + l_1 - \frac{\phi_1}{x_1}(x_1 l_1 + x_2 l_2)$$

$$= \ln\left(\frac{0.000127986}{7.19E-05}\right) + \frac{10}{2}(4.3690)\ln\left(\frac{0.000146203}{0.000127986}\right) - 0.2832$$

$$- \frac{0.000127986}{7.19E-05}((7.19E-05)(-0.2832)+(0.9999281)(1.8179))$$

$$= 1.6797$$

The residual part calculations

The binary group interaction parameters are

$a_{1,2} = a_{1,1} = a_{2,1} = a_{2,2} = a_{3,3} = 0$

$a_{1,3} = a_{2,3} = 252.7,\ a_{3,1} = a_{3,2} = 110.2$

$\psi_{1,2} = \psi_{1,1} = \psi_{2,1} = \psi_{2,2} = \psi_{3,3} = 1$

$$\psi_{1,3} = \psi_{2,3} = \exp\left(\frac{-252.7}{30+273.15}\right) = 0.43449$$

$$\psi_{3,1} = \psi_{3.2} = \exp\left(\frac{-110.2}{30+273.15}\right) = 0.6523$$

Assigning identification numbers to groups, CH_3 = 1, CH_2 = 2, SiO = 3. Now one can compute $\Gamma_k^{(1)}$, the residual activity coefficient of group k in a reference solution containing only molecules of type *i*. For n-heptane (1), the mole fraction of group i, $X_1^{(1)}$ is:

$$X_1^{(1)} = \frac{v_1^{(1)}}{v_1^{(1)} + v_2^{(1)}} = \frac{2}{2+5} = 0.2857$$

$$X_2^{(1)} = \frac{v_2^{(1)}}{v_1^{(1)} + v_2^{(1)}} = \frac{5}{2+5} = 0.7143$$

For poly(dimethylsiloxane)

$$X_1^{(2)} = \frac{v_1^{(2)}}{v_1^{(2)} + v_3^{(2)}} = \frac{2}{2+1} = 0.6667$$

$$X_3^{(2)} = \frac{v_3^{(2)}}{v_1^{(2)} + v_3^{(2)}} = \frac{1}{2+1} = 0.3333$$

Since there is one main group in heptane, the following is obtained $\Gamma_1^{(1)}$ and $\Gamma_2^{(1)}=0$

The residual activity coefficients can now be calculated as follows

$$X_1^{(1)} = \frac{x_1 v_1^{(1)} + x_2 v_1^2}{(x_1(v_1^{(1)} + v_2^{(1)}) + x_2(v_1^{(2)} + v_3^{(2)}))} = \frac{(7.19E-05)(5) + (0.999928)(2)}{((7.19E-05)(7) + (0.9999281)(3)} = 0.666603$$

$$X_2^{(1)} = \frac{x_1 v_2^{(1)}}{(x_1(v_1^{(1)} + v_2^{(1)}) + x_2(v_1^{(2)} + v_3^{(2)}))} = \frac{(7.19E-05)(5)}{((7.19E-05)(7) + (0.9999281)(3)} = 0.00011982$$

$$X_3^{(2)} = \frac{x_2 v_3^{(2)}}{(x_1(v_1^{(1)} + v_2^{(1)}) + x_2(v_1^{(2)} + v_3^{(2)}))} = \frac{(0.9999281)(2)}{((7.19E-05)(7) + (0.9999281)(3)} = 0.333277$$

$$\theta_1 = \frac{X_1 Q_1}{X_1 Q_1 + X_2 Q_2 + X_3 Q_3} = \frac{(0.666603)(0.8480)}{((0.666603)(0.8480) + (0.00011982)(0.5400) + (0.333277)(0.4657)))}$$

$$= 0.784510$$

$$\theta_2 = \frac{X_2 Q_2}{X_1 Q_1 + X_2 Q_2 + X_3 Q_3} = \frac{(0.00011982)(0.5400)}{((0.666603)(0.8480) + (0.00011982)(0.5400) + (0.333277)(0.4657)))}$$

$$= 0.000089796$$

$$\theta_3 = \frac{X_3 Q_3}{X_1 Q_1 + X_2 Q_2 + X_3 Q_3} = \frac{(0.333277)(0.4657)}{((0.666603)(0.8480) + (0.00011982)(0.5400) + (0.333277)(0.4657)))}$$

$$= 0.215402$$

$$\ln \Gamma_1 = Q_1[1 - \ln(\theta_1\psi_{1,1} + \theta_2\psi_{2,1} + \theta_3\psi_{3,1}) - (\frac{\theta_1\psi_{1,1}}{(\theta_1\psi_{1,1} + \theta_2\psi_{2,1} + \theta_3\psi_{3,1})}$$

$$+ \frac{\theta_2\psi_{1,2}}{(\theta_1\psi_{1,2} + \theta_2\psi_{2,1} + \theta_3\psi_{3,2})} + \frac{\theta_3\psi_{1,3}}{(\theta_1\psi_{1,3} + \theta_2\psi_{2,3} + \theta_3\psi_{3,3})})]$$

$$= (0.8480)[1 - \ln((0.4510)(1) + (0.000089796)(1) + (0.215402)(0.69523))$$

$$-(\frac{(0.784510)(1)}{((0.784510)(1) + (0.000089796)(1) + (0.215402)(0.69523))}$$

$$+ \frac{(0.000089796)(1)}{((0.784510)(1) + (0.000089796)(1) + (0.215402)(0.69523))}$$

$$+ \frac{(0.215402)(0.43449)}{((0.784510)(0.43449) + (0.000089796)(0.43449) + (0.215402)(0.69523))})]$$

$$\therefore \ln \Gamma_1 = 0.0319527$$

$$\ln \Gamma_2 = Q_2[1 - \ln(\theta_1\psi_{1,2} + \theta_2\psi_{2,2} + \theta_3\psi_{3,2}) - (\frac{\theta_1\psi_{2,1}}{(\theta_1\psi_{1,1} + \theta_2\psi_{2,1} + \theta_3\psi_{3,1})}$$

$$+ \frac{\theta_2\psi_{1,2}}{(\theta_1\psi_{1,2} + \theta_2\psi_{2,2} + \theta_3\psi_{3,2})} + \frac{\theta_3\psi_{1,3}}{(\theta_1\psi_{1,3} + \theta_2\psi_{2,3} + \theta_3\psi_{3,3})})]$$

$$= (0.5400)[1 - \ln((0.78510)(1) + (0.0000897796)(1) + (0.215402)(0.69523))$$

$$-(\frac{(0.784510)(1)}{((0.784510)(1) + (0.000089796)(1) + (0.215402)(0.69523))}$$

$$+ \frac{(0.000089796)(1)}{((0.784510)(1) + (0.0000089796)(1) + (0.25402)(0.69523))}$$

$$+ \frac{(0.215402)(0.43449)}{((0.784510)(0.43449) + (0.000089796)(0.43449) + (0.215402)(1))})]$$

$$\therefore \ln \Gamma_2 = 0.0323674$$

$$\ln \gamma_1^R = v_1^{(1)}\left(\ln \Gamma_1 - \ln \Gamma_1^{(1)}\right) + v_2^{(1)}\left(\ln \Gamma_2 - \ln \Gamma_2^{(1)}\right) = 2(0.0319527 - 0) + 5(0.0323674) = 0.2257424$$

$$\ln \gamma_1 = \ln \gamma_1^C + \ln \gamma_1^R = -0.017256 + 0.225424 = 0.208486$$

$$\therefore \gamma_1 = 1.2318$$

G.4. MODIFIED UNIFAC CALCULATIONS

Kikic et al (1980) developed the modified UNIFAC by proposing a modification to the volume fraction in the Staverman-Guggenheim Combinatorial term while the residual term remained unchanged.

The modified combinatorial term is given by

$$\ln \gamma_i^C = \left\{\ln \frac{\psi_i}{x_i} + 1 - \frac{\psi_i}{x_i}\right\} - \frac{zq_i}{2}\left\{\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}\right\}$$

where ψ_i is calculated from

$$\psi_i = \frac{x_i r_i^{\frac{2}{3}}}{\sum_j x_j r_i^{\frac{2}{3}}}$$

G.4.1. Heptane in water

$$\psi_1 = \frac{(5.1742)^{\frac{2}{3}}(8.7645E-08)}{(5.1742)^{\frac{2}{3}}(8.7645E-08) + (0.9200)^{\frac{2}{3}}(0.999999915)} = 0.000000277$$

$$\ln \gamma_1^c = \ln\left(\frac{0.00000027}{8.7645E-08}\right) + 1 - \frac{0.00000027}{8.7645E-08} - (5)(4.3690)\left[\ln\left(\frac{4.92E-07}{2.75E-07}\right) + 1 - \frac{4.92E-07}{2.75E-07}\right]$$

$$= 3.520528$$

$$\ln \gamma_1 = \ln \gamma_1^c + \ln \gamma_1^R = 3.520528 + 9.558306 = 13.078834$$

$\therefore \gamma_1 = 478702$

G.4.2. Heptane in silicone oil

$$\psi_1 = \frac{(5.1742)^{\frac{2}{3}}(7.19E-05)}{(5.1742)^{\frac{2}{3}}(7.19E-05)+(2.9066)^{\frac{2}{3}}(0.9999281)} = 0.000105605$$

$$\ln \gamma_1^c = \ln\left(\frac{0.000105605}{7.19E-05}\right)+1-\frac{0.000105605}{7.19E-05}-(5)(4.3690)\left[\ln\left(\frac{0.000127986}{0.000146203}\right)+1-\frac{0.000127986}{0.000146203}\right]$$

$$= 0.101912$$

$$\ln \gamma_1 = \ln \gamma_1^c + \ln \gamma_1^R = 0.101912 + 0.2257424 = 0.327654$$

$\therefore \gamma_1 = 1.387709$

G.5. Effective UNIFAC Calculations

Nagata and Koyabi (1981) chose not to change the Stavenman-Guggeheim combinatorial term of the UNIFAC. They modified the residual term and this is expressed in the following manner.

$$\ln \gamma_i^R = \sum_k v_k^{(i)} \left\{ \ln \Gamma_k - \ln \Gamma_k^{(i)} \right\} - \left\{ \ln \frac{\theta_i}{x_i} + 1 - \frac{\theta_i}{x_i} \right\}$$

In the effective UNIFAC, the residual activity coefficients, Γ_k and $\Gamma_k^{(i)}$ are calculated by

$$\ln \Gamma_k = 1 - \left(\ln \sum_m X_m \psi_{mk} \right) - \sum_m \left[\frac{X_m \psi_{km}}{\sum_n X_n \psi_{nm}} \right]$$

The above differs from the corresponding UNIFAC expression in that the group surface area fraction, θ_m, has been replaced by the group mole fraction X_m and the group interaction parameters are modified by the ratio of group surface area parameters as follows

$$\psi_{mn} = \frac{Q_m}{Q_n} \exp\left(- a_{mn} / T \right)$$

G.5.1. Heptane in water

The group binary interaction parameters are

$$\psi_{1,2} = \frac{Q_1}{Q_2} \exp(0) = 1.556$$

$$\psi_{1,1} = 1$$

$$\psi_{2,1} = 0.636792$$

$$\psi_{2,2} = 1$$

$$\psi_{3,3} = 1$$

$$\psi_{1,3} = \frac{0.8480}{1.400} \exp\left(- \frac{1.452}{30 + 273.15} \right) = 0.602819$$

$$\psi_{2,3} = \frac{0.5400}{1.400} \exp\left(- \frac{1.452}{30 + 273.15} \right) = 0.383871$$

$$\psi_{3,1} = \frac{1.400}{0.8400}\exp\left(-\frac{657.7}{30+273.15}\right) = 0.188587$$

$$\psi_{3,2} = \frac{1.400}{0.5400}\exp\left(-\frac{657.7}{30+273.15}\right) = 0.296152$$

The group mole fractions are as follows:

$X_1^{(1)} = 0.000000175$

$X_2^{(1)} = 0.000000438$

$X_3^{(2)} = 0.9999997$

$$\ln \Gamma_1 = Q_1\left[1 - \ln\left(X_1\psi_{1,1} + X_2\psi_{2,1} + X_3\psi_{3,1}\right) - \left(\frac{X_1\psi_{1,1}}{X_1\psi_{1,1} + X_2\psi_{2,1} + X_3\psi_{3,1}}\right.\right.$$

$$\left.\left. + \frac{X_2\psi_{1,2}}{\left(X_1\psi_{1,2} + X_2\psi_{2,1} + X_3\psi_{3,2}\right)} + \frac{X_3\psi_{1,3}}{\left(X_1\psi_{1,3} + X_2\psi_{2,3} + X_3\psi_{3,3}\right)}\right)\right]$$

$$\ln \Gamma_1 = (0.8480)[1 - \ln((0.000000175)(1) + (0.000000438)(0.636792) + (0.999999)(0.188587))$$

$$= \left(\frac{(0.000000175)(1)}{((0.000000175)(1) + (0.000000438)(0.636792) + (0.999999)(0.188587))}\right.$$

$$+ \frac{(0.000000438)(1.556)}{((0.000000175)(1) + (0.000000438)(0.636792) + (0.999999)(0.1888587))}$$

$$\left. + \frac{(0.999999725)(0.602819)}{((0.000000175)(0.602819) + (0.000000438)(0.383871) + (0.999999)(1))}\right)]$$

$\ln \Gamma_1 = 1.414626$

$$\ln \Gamma_2 = Q_2\left[1 - \ln\left(X_1\psi_{1,2} + X_2\psi_{2,2} + X_3\psi_{3,2}\right) - \left(\frac{X_1\psi_{12,1}}{X_1\psi_{1,1} + X_2\psi_{2,1} + X_3\psi_{3,1}}\right.\right.$$

$$\left.\left. + \frac{X_2\psi_{1,2}}{\left(X_1\psi_{1,2} + X_2\psi_{2,2} + X_3\psi_{3,2}\right)} + \frac{X_3\psi_{1,3}}{\left(X_1\psi_{1,3} + X_2\psi_{2,3} + X_3\psi_{3,3}\right)}\right)\right]$$

$$\ln \Gamma_2 = (0.5400)[1 - \ln((0.000000175)(1.556) + (0.000000438)(1) + (0.999999)(0.296152))$$

$$= \left(\frac{(0.000000175)(0.636792)}{((0.000000175)(1) + (0.000000438)(0.636792) + (0.999999)(0.188587))} \right.$$

$$+ \frac{(0.000000438)(1.556)}{((0.000000175)(1.556) + (0.000000438)(1) + (0.999999)(0.296152))}$$

$$\left. + \frac{(0.999999)(0.602819)}{((0.000000175)(0.602819) + (0.000000438)(0.383871) + (0.999999)(1))} \right)]$$

$$\ln \Gamma_2 = 0.871592$$

$$\ln \gamma_1^R = \nu_1^{(1)}\left(\ln \Gamma_1 - \ln \Gamma_1^{(1)}\right) + \nu_2^{(1)}\left(\ln \Gamma_2 - \ln \Gamma_2^{(1)}\right) = (2)(1.414626) + (5)(0.871592) = 7.187212$$

$$\ln \gamma_1 = \ln \gamma_1^C + \ln \gamma_1^R = 1.6797 + 7.187212 = 8.866912$$

$$\therefore \gamma_1 = 7093.34$$

G.5.2. Heptane in silicone oil

The group binary interaction parameters are

$$\psi_{1,1} = \psi_{2,2} = \psi_{3,3} = 1$$

$$\psi_{1,2} = \frac{0.8480}{0.5400}\exp(0) = 1.57037$$

$$\psi_{2,1} = \left(\frac{0.5400}{0.8480}\right)(1) = 0.63679$$

$$\psi_{1,3} = \frac{0.8480}{0.4657}\exp\left(-\frac{252.7}{30 + 273.15}\right) = 0.79117$$

$$\psi_{2,3} = \frac{0.5400}{0.4657}\exp\left(-\frac{252.7}{30 + 273.15}\right) = 0.50381$$

$$\psi_{3,1} = \frac{1.400}{0.8400}\exp\left(-\frac{110.2}{30 + 273.15}\right) = 0.38180$$

$$\psi_{3,2} = \frac{0.4657}{0.5400}\exp\left(-\frac{110.2}{30+273.15}\right) = 0.599572$$

The group mole fractions are as follows:

$X_1 = 0.666603$

$X_2 = 0.00011982$

$X_3 = 0.333277$

$$\ln \Gamma_1 = Q_1\left[1 - \ln\left(X_1\psi_{1,1} + X_2\psi_{2,1} + X_3\psi_{3,1}\right) - \left(\frac{X_1\psi_{1,1}}{X_1\psi_{1,1} + X_2\psi_{2,1} + X_3\psi_{3,1}}\right.\right.$$

$$\left.\left. + \frac{X_2\psi_{1,2}}{\left(X_1\psi_{1,2} + X_2\psi_{2,1} + X_3\psi_{3,2}\right)} + \frac{X_3\psi_{1,3}}{\left(X_1\psi_{1,3} + X_2\psi_{2,3} + X_3\psi_{3,3}\right)}\right)\right]$$

$$\ln \Gamma_1 = (0.8480)\left[1 - \ln((0.666603)(1) + (0.00011982)(0.63679) + (0.333277)(0.38180))\right.$$

$$- \left(\frac{(0.666603)(1)}{((0.666603)(1) + (0.00011982)(0.63679) + (0.333277)(0.38180))}\right.$$

$$+ \frac{(0.00011982)(1.57037)}{((0.666603)(1.57037) + (0.00011982)(0.63679) + (0.333277)(0.599572))}$$

$$\left.\left. + \frac{(0.333277)(0.79117)}{((0.666603)(0.79117) + (0.0001982)(0.50381) + (0.333277)(1))}\right)\right]$$

$$\ln \Gamma_1 = 0.071778$$

$$\ln \Gamma_2 = Q_2\left[1 - \ln\left(X_1\psi_{1,2} + X_2\psi_{2,2} + X_3\psi_{3,2}\right) - \left(\frac{X_1\psi_{12,1}}{X_1\psi_{1,1} + X_2\psi_{2,1} + X_3\psi_{3,1}}\right.\right.$$

$$\left.\left. + \frac{X_2\psi_{1,2}}{\left(X_1\psi_{1,2} + X_2\psi_{2,2} + X_3\psi_{3,2}\right)} + \frac{X_3\psi_{1,3}}{\left(X_1\psi_{1,3} + X_2\psi_{2,3} + X_3\psi_{3,3}\right)}\right)\right]$$

$$\ln \Gamma_2 = (0.5400)\left[1 - \ln((0.666603)(1.57037) + (0.00011982)(1) + (0.333277)(0.59972))\right.$$

$$= \left(\frac{(0.666603)(1)}{((0.666603)(1) + (0.00011982)(0.63679) + (0.333277)(0.38180))} \right.$$

$$+ \frac{(0.00011982)(1.57037)}{((0.666603)(1.57037) + (0.00011982)(1) + (0.333277)(0.59972))}$$

$$\left. + \frac{(0.333277)(0.79117)}{((0.666603)(0.79117) + (0.00011982)(0.50381) + (0.333277)(1))} \right) \Bigg]$$

$$\ln \Gamma_2 = -0.198022$$

$$\ln \gamma_1^R = v_1^{(1)} \left(\ln \Gamma_1 - \ln \Gamma_1^{(1)} \right) + v_2^{(1)} \left(\ln \Gamma_2 - \ln \Gamma_2^{(1)} \right) = (2)(0.071778 - 0) + (5)(-0.198022) = -0.846554$$

$$\ln \gamma_1 = \ln \gamma_1^C + \ln \gamma_1^R = -0.017256 - 0.846554 = -0.86381$$

$$\therefore \gamma_1 = 0.421553$$

H. GROUP CONTRIBUTION PARAMETERS FROM LITERATURE

Table H.1: Group volume and Surface area parameters (Fredenslund et al – 1975)

Main group	Subgroup	R_k	Q_k
CH_2	CH_3	0.9011	0.848
	CH_2	0.6744	0.540
	CH	0.4469	0.228
C=C	C=C	1.3454	1.176
ACH	ACH	0.5313	0.400
$ACCH_2$	$ACCH_2$	1.0396	0.660
	$ACCH_3$	1.2663	0.968
COH	COH	1.2044	1.124
	MCOH	1.4311	1.432
	CHOH	0.9769	0.812
H_2O	H_2O	0.9200	1.400
ACOH	ACOH	0.8952	0.680
CO	CO	0.7713	0.640
O	O	0.2439	0.240
CNH_2	CNH_2	1.3692	1.236
	$MCNH_2$	1.5959	1.544
NH	NH	0.5326	0.396
$ACNH_2$	$ACNH_2$	1.0600	0.816
CCN	MCCN	1.8701	1.724
	CCN	1.6434	1.416
Cl	Cl-1	0.7660	0.720
	Cl-2	0.8069	0.728
$CHCl_2$	$CHCl_2$	2.0672	1.684
ACCl	ACCl	1.1562	0.844

Table H.2: Group Interaction parameters, a_{mn} (Fredenslund et al – 1975)

Group	CH_2	C=C	ACH	$ACCH_2$	COH	H_2O	ACOH	CO	CHO
CH_2	0	-200.0	32.06	26.78	931.2	1.452	1.860	1.565	685.9
C=C	2.520	0	651.6	1.490	943.3	578.3	-	1.400	-
ACH	15.26	-144.3	0	167.0	705.9	860.7	1.310	651.1	-
$ACCH_2$	-15.84	-309.2	-146.8	0	856.2	3.000	740.0	3.000	-
COH	169.7	-254.2	83.50	92.61	0	-320.8	-	462.3	480.0
H_2O	657.7	-485.4	361.5	385.0	287.5	0	462.6	470.8	234.5
ACOH	3.000	-	3.000	3.000	-	-558.2	0	-	-
CO	3.000	3.000	101.8	75.00	106.5	-532.6	-	0	-49.24
CHO	343.2	-	-	-	3.000	-226.4	-	39.47	0
COO	348.0	-	325.5	3.000	167.5	-	-254.1	333.6	-
O	2.160	-	75.5	3.000	-13.44	-	-	-39.81	-
CNH_2	-16.74	90.37	38.64	-	-109.8	-527.7	-	-	-
NH	3.000	8.922	37.94	-	-700.0	-882.7	-	-	-
$ACNH_2$	3.000	-	3.000	3.000	-	236.6	-	-	-
CCN	27.31	43.03	66.44	-150.0	337.9	227.0	-	447.7	-
Cl	-119.6	242.1	90.43	52.69	357.0	618.2	-	62.00	-
$CHCl_2$	31.06	-72.88	-	-	-	467.0	-	37.63	-
ACCl	121.1	-	1.000	-	586.3	1.472	-	-	-

Table H.2. cont

Group	COO	O	CNH_2	NH	$ACNH_2$	CCN	Cl	$CHCl_2$	ACCl
CH_2	687.5	472.6	422.1	800.0	1.330	601.6	523.2	60.45	194.2
C=C	-	-	349.9	515.2	-	691.3	253.8	259.5	-
ACH	159.1	37.24	179.7	487.2	680.0	290.1	124.0	-	-99.9
$ACCH_2$	110.0	680.0	-	-	640.0	3.000	33.84	-	-
COH	174.3	-204.6	-166.8	3.000	-	79.85	194.6	-	69.97
H_2O	-	-	385.3	743.8	-314.6	118.5	158.4	247.2	190.6
ACOH	-470.2	-	-	-	-	-	-	-	-
CO	180.1	475.5	-	-	-	-307.4	6.28	874.5	-
CHO	-	-	-	-	-	-	-	-	-
COO	0	-26.15	-	-	-	-	-	-	-
O	-290.0	0	-	-	-	-	-	-	-
CNH_2	-	-	0	-	-	-	-	-	-10.0
NH	-	-	-	0	-	-	-	-	-60.0
$ACNH_2$	-	-	-	-	0	-	-	-	3.000
CCN	-	-	-	-	-	0	-100.0	-	25.0
Cl	-	-	-	-	-	100.0	0	-308.5	-
$CHCl_2$	-	-	-	-	-	-	790.0	0	-
ACCl	-	-	3.000	3.000	110.0	3.000	-	-	0

Table H.3: Group Contributions for the GCLF-EOS (High and Danner –1990)

Group	$e_{kk,300}$ / kJ.kmol^{-1}	$e_{kk,400}$ / kJ.kmol^{-1}	$R_{k,300}$ / m^3.kmol^{-1}	$R_{k,400}$ / m^3.kmol^{-1}	Q_k
CH_3	640.87	640.79	0.01596	0.01628	0.848
CH_2	943.33	987.68	0.01524	0.01498	0.540
CH	2,209.38	2,708.76	0.01311	0.01175	0.228
C	5,378.38	7,731.24	0.01071	0.08463	0.150
Cy-CH_2	895.44	911.40	0.1260	0.01256	0.540
Cy-CH	1,727.56	2,043.28	0.01255	0.01199	0.228
Cy-C	4.069.49	5,993.67	0.01242	0.01126	0.150
AC-H	975.38	971.62	0.01059	0.01073	0.400
AC-CH_3	994.41	1,022.68	0.02465	0.02456	0.968
AC-CH_2	1,471.59	1,581.80	0.02351	0.02302	0.660
AC-CH	2,780.93	3,281.53	0.02220	0.02060	0.348
AC-C	5,452.73	6,771.48	0.01985	0.01700	0.270
-O-	868.47	679.56	0.00760	0.00798	0.240
H_2O	949.12	1,154.31	0.07611	0.07544	1.400
CH_3C=O-	1,237.10	1,171.50	0.03117	0.03254	1.488
-CH_2C=O-	1,542.00	1,509.50	0.02968	0.03039	1.180
-CHCl-	1,364.40	1,387.30	0.04865	0.05036	0.952

Table H.4: Group Interaction energy, Reference volume and Area parameters (James H Hand – 1994, Byung et al –1996)

Main - group	Sub-group	$e_{0,k}$	$e_{1,k}$	$e_{2,k}$	$R_{0,k}$	$R_{1,k}$	$R_{2,k}$	Q_k
CH_2	CH_3	642.019	10.186	-4.817	25.979	-0.388	0.814	0.848
	CH_2	919.390	-67.757	78.384	14.089	2.039	-0.963	0.540
	CH	1300.351	331.832	391.739	2.522	3.362	-2.943	0.228
C	C	1480.016	1125.680	1967.093	-11.793	7.681	-5.795	0.150
$cyCH_2$	$cyCH_2$	899.910	-41.547	33.970	15.810	0.747	-0.168	0.540
	cyCH	1546.001	-381.152	472.951	3.432	5.248	-2.638	0.228
	cyC	1591.986	11.798	1230.965	-8.931	10.852	-5.362	0.150
ACH	ACH	1132.433	-209.906	78.217	12.189	1.834	-0.389	0.400
	AC	9247.801	-7299.508	2824.623	3.062	0.806	0.000	0.120
$ACCH_2$	$ACCH_3$	959.652	-11.693	33.812	26.370	3.136	-1.092	0.968
	$ACCH_2$	1210.034	49.549	87.374	16.051	3.558	-1.907	0.660
	ACCH	2134.993	-232.701	560.421	2.933	7.462	-4.174	0.348
C=C	CH_2=CH	696.741	74.646	-17.603	35.587	1.550	-0.192	1.176
	CH=CH	982.211	6.384	44.321	20.234	7.337	-2.659	0.867
	CH_2=C	948.063	-33.316	64.267	19.593	7.767	-3.143	0.988
	CH=C	1499.562	-66.818	136.874	9.821	6.231	-3.240	0.676
CCl	CH_2Cl	1289.876	-271.806	80.704	32.244	5.257	-0.599	1.264
	CHCl	1319.789	-156.664	92.332	21.359	8.441	-3.179	0.952
	CCl	1556.418	-176.378	233.935	12.810	9.171	-4.941	0.724
CCl_2	CH_2Cl_2	1354.956	-384.293	103.352	51.888	6.083	1.028	1.988
	$CHCl_2$	1392.832	-349.566	113.018	39.812	14.427	-4.119	1.684
CCl_3	$CHCl_3$	1173.525	-247.029	81.134	64.532	10.792	-1.937	2.410
	CCl_3	1133.307	-174.685	84.569	55.461	11.675	-3.471	2.184
CCl_4	CCl_4	1007.887	-124.396	60.094	79.623	10.807	-2.673	2.910
CCl	ACCl	1190.694	-25.681	34.993	23.688	4.975	-1.822	0.844
CH_2O	CH_3O	1213.041	-440.261	123.117	31.624	1.853	0.721	1.088
	CH_2O	1145.190	-86.586	71.257	17.426	7.991	-3.073	0.780
	CHO	1762.751	-336.174	230.502	4.233	12.855	-6.125	0.468
CH_2CO	CH_3CO	1623.041	-542.555	149.255	33.358	9.281	-1.182	1.488
	CH_2CO	2004.018	-741.998	240.219	22.438	11.103	-3.557	1.180
COO	COO	2182.434	-782.011	226.335	14.091	10.712	-3.344	0.880
COOH	HCOOH	2510.362	-790.266	134.835	31.687	2.967	2.102	1.532
	COOH	3963.163	-2101.752	485.316	19.362	15.684	-3.114	1.224
SiO	SiO	560.883	107.387	260.550	15.570	1.242	-3.836	0.4657

Table H.5: Group Binary Interaction Parameters (James H. Hand – 1994, Byung et al 1996)

Main groups	CH_2	C	cy- CH_2	ACH	$ACCH_2$	C=C	CCl	CCl_2	CCl_3	CCl_4
CH_2	0.0000	0.02300	0.0000	0.0363	-0.0064	0.0000	0.0407	0.0701	0.0290	0.0000
C		0.0000	0.0000	0.0202	-0.3946	N.A**	N.A**	N.A**	N.A**	0.8948
cy- CH_2			0.0000	0.0226	0.0183	0.0000	0.0390	N.A**	0.0285	0.0000
ACH				0.0000	0.0183	-0.0126	0.0138	0.0126	-0.0206	0.0000
$ACCH_2$					0.0116	0.0375	0.0295	N.A**	-0.0415	0.0000
C=C					0.0000	0.0000	0.1365	0.0000	-0.0411	0.0000
CCl							0.0000	0.0000	0.0000	0.0555
CCl_2								0.0000	0.0000	0.0435
CCl_3									0.0000	0.0000
CCl_4										0.0000
ACCl										
CH_2O										
CH_2CO										
COO										
COOH										
S_iO										
CH_3OH										
OH										
H_2O										

Table H.5. cont

Main groups	ACCl	CH_2O	CH_2CO	COO	COOH	S_iO	CH_3OH	OH	H_2O
CH_2	-0.0074	0.0333	0.1490	0.1020	0.1020	0.0349	0.1732	0.3994	0.0000
C	N.A**	N.A.**	-0.4285	N.A**	N.A.**	N.A.**	1.8040	1.2601	N.A.**
cy- CH_2	0.0322	0.1688	0.1272	0.2029	0.1091	0.0349	0.2037	0.3662	N.A.**
ACH	0.0000	-0.2003	-0.1259	-0.1408	0.1294	-0.1178	0.1698	0.1031	N.A.**
$ACCH_2$	-0.0509	0.1632	0.1050	0.0415	0.0656	N.A.**	0.2687	0.3770	N.A.**
C=C	-0.0990	N.A**	-0.1114	0.4554	0.1176	N.A.**	0.0158	-0.0484	N.A.**
CCl	-0.3350	-0.1277	-0.1775	N.A**	0.1094	N.A.**	0.1516	0.0750	N.A.**
CCl_2	N.A**	-0.5183	-0.3259	-0.5160	0.0053	N.A**	0.0928	-0.1656	0.0754
CCl_3	N.A**	-0.5444	-0.2919	-0.4515	0.1218	N.A**	0.0952	-0.1398	N.A.**
CCl_4	0.0000	0.1593	0.0071	0.0302	0.1041	N.A**	0.1616	0.2819	N.A.**
ACCl	0.0000	N.A**	-0.0738	0.1722	-0.4201	N.A**	0.4054	0.0359	N.A.**
CH_2O		0.0000	-0.8271	-0.7928	N.A.**	N.A**	-0.5642	-1.0634	-1.2774
CH_2CO			0.0000	-0.7579	N.A.**	N.A**	-0.2303	-1.3451	-0.3778
COO				0.0000	-0.9330	N.A**	-0.3211	-1.4501	-0.6527
COOH					0.0000	N.A**	-0.2754	-1.9989	-0.1690
S_iO						0.0000	0.0000	0.0000	N.A.**
CH_3OH							0.0000	-1.4001	0.0520
OH								0.0000	-0.7455
H_2O									0.0000

H.5. The group volume and surface area parameters, R and Q, for use with the UNIQUAC and UNIFAC models (Phase equilibria- Raal and Muhlbauer).

Main group	Subgroup	No.	*R*	*Q*	Example assignments
1	CH_3	1	0.9011	0.8480	N-Hexane: $4CH_2$, $2CH_3$
CH_2	CH_2	2	0.6744	0.5400	Isobutane: 1CH, $3CH_3$
	CH	3	0.4469	0.2280	Neopentane: 1C, 4 CH_3
	C	4	0.2195	0.0000	
2	CH_2=CH	5	1.3454	1.1760	1-Hexene: 1 CH_2=CH, 3 CH_2, 1 CH_3
C=C	CH=CH	6	1.1167	0.8670	2-Hexene: 1CH=CH, 2 CH_3, 2 CH_2
	CH_2=C	7	1.1173	0.9880	
	CH=C	8	0.8886	0.6760	
	C=C	9	0.6605	0.4850	
3	ACH	10	0.5313	0.4000	Benzene: 6ACH
ACH	AC	11	0.3652	0.1200	
4	$ACCH_3$	12	1.2663	0.9680	Toluene: 5ACH, $1ACCH_3$
$ACCH_2$	$ACCH_2$	13	1.0396	0.6600	Ethylbenzene: 5ACH, $1ACCH_3$, 1 CH_3
	ACCH	14	0.8121	0.3480	
5 OH	OH	15	1.0000	1.2000	N-Propanol: 1OH, $1CH_3$, 2 CH_2
6 CH_3OH	CH_3OH	16	1.4311	1.4320	Methanol
7 Water	H_2O	17	0.9200	1.400	Water
8 ACOH	ACOH	18	0.8952	0.6800	Phenol 1ACOH, 5ACH
9	CH_3CO	19	0.6724	1.4880	Dimethylketone: 1 CH_3CO, 1 CH_3
CH_2CO	CH_2CO	20	1.4457	1.1880	Diethylketone: 1 CH_2CO, 2 CH_3, 1 CH_2
10 CHO	CHO	21	0.9980	0.9480	Ethanal: CHO, 1 CH_3
11	CH_3COO	22	1.9031	1.7280	Methyl acetate:$1CH_3COO$, $2CH_3$
CCOO		23	1.6764	1.4200	Methyl propionate: $1CH_2COO$, $2CH_3$
12 HCOO	HCOO	24	1.2420	1.1880	Methyl formate: IHCOO, $1CH_3$
13	CH_3O	25	1.1450	1.0880	
CH_2O	CH_2O	26	0.9183	0.7800	Ethyl ether: $1CH_2O$, $1CH_3$, $1CH_2$
	CO-O	27	0.6908	0.4680	
	F CH_2O	28	0.9183	1.1000	Tetrahydrofuran: FCH_2O, $3CH_2$
14	CH_3NH_2	29	1.5959	1.5400	
CNH_2	CH_2NH_2	30	1.3692	1.2360	Propyl amine: 1 CH_2NH_2, $1CH_3$, 1 CH_2
	$CHNH_2$	31	1.1417	0.9240	
15	CH_3NH	32	1.4337	1.2440	Diethyl amine: CH_2NH, $2CH_3$, 1 CH_2
CNH	CH_2NH	33	1.2070	0.9360	
	CNH	34	0.9795	0.6240	
16	CH_3N	35	1.1865	0.9400	Triethyl amine: 1 CH_2N, 2 CH_2, 3 CH_3
$(C)_3N$	CH_2N	36	0.9597	0.6320	
17 $ACNH_2$	$ACNH_2$	37	1.0600	0.8160	Aniline: $1ACNH_2$, 5 ACH
18	C_5H_5N	38	2.9993	2.1130	Methyl pyridine: 1 C_5H_4N, $1CH_3$
Pyridine	C_5H_4N	39	2.8332	1.8330	
	C_5H_3N	40	2.6670	1.5530	
19	CH_3CN	41	1.8701	1.7240	Propionitrile : $1CH_2CN$, $1CH_3$
CCN	CH_2CN	42	1.6434	1.4160	
20	COOH	43	1.3013	1.2240	Acetic acid: 1 COOH, $1CH_3$
COOH	HCOOH	44	1.5280	1.5330	
21	CH_2Cl	45	1.4654	1.2640	Chloroethane: CH_2Cl, $1CH_3$
CCl	CHCl	46	1.2380	0.9520	
	CCl	47	1.0060	0.7240	
22	CH_2Cl_2	48	2.2564	1.9880	1,1-Dichloroethane: 1 $CHCl_2$, $1CH_3$
CCl_2	$CHCl_2$	49	2.0606	1.6840	
	CCl_2	50	1.8016	1.4480	
23	$CHCl_3$	51	2.8700	2.4100	1,1,1-Trichloroethane: 1 CCl_3 ,$1CH_3$
CCl_3	CCl_3	52	2.6401	2.1840	
24 CCl_4	CCl_4	53	3.3900	2.9100	Chloroform
25 ACCl	ACCl	54	1.1562	0.8440	Chlorobenzene: 1 ACCl, 5ACH
26 CNO_2	CH_3NO_2	55	2.0086	1.8680	Nitromethane
	CH_2NO_2	56	1.7818	1.5600	Nitroethane: 1 CH_2NO_2, 1 CH_3
	$CHNO_2$	57	1.5544	1.2480	
27 $ACNO_2$	$ACNO_2$	58	1.4199	1.1040	Nitrobenzene: 1 $ACNO_2$, 5ACH
28 CS_2	CS_2	59	2.0570	1.6500	Carbon disulphide

29 CH_3SH	CH_3SH CH_2SH	60 61	1.8770 1.6510	1.6760 1.3680	Methanethiol Ethanethiol: CH_2SH, 1 CH_3
30 Furfural	Furfural	62	3.1680	2.4810	Furfural
31 DOH	$(CH_2OH)_2$	63	2.4088	2.2480	Ethylene glycol
32 I	I	64	1.2640	0.9920	Iodomethane: 1I, 1 CH_3
33 Br	Br	65	0.9492	0.8320	Bromomethane: 1 Br, 1 CH_3
34 C≡C	CH≡C C≡C	66 67	1.2920 1.0613	1.0880 0.7840	1-Hexyne: 1CH≡C, 1CH_3, 3CH_2 2-Hexyne: 1 C≡C, 2CH_3, 2CH_2
35 Me_2SO	Me_2SO	68	2.8266	2.4720	Dimethyl sulfoxide
36 ACRY	ACRY	69	2.3144	2.0520	Acrylonitrile
37 ClCC	Cl(C≡C)	70	0.7910	0.7240	Trichloroethylene: 3Cl(C≡C), 1 CH≡C
38 ACF	ACF	71	0.6948	0.5240	Hexafluorobenzene; 6ACF
39 DMF	DMF-1 DMF-2	72 73	3.0856 2.6322	2.7360 2.1200	Dimethyl formamide Diethyl formamide: DMF-2, 2 CH_3
40 CF_2	CF_3 CF_2 CF	74 75 76	1.4060 1.0105 0.6150	1.3800 0.9200 0.4600	Perfluorohexane: 4 CF_2, 2 CF_3
41 COO	COO	77	1.3800	1.2000	Butylacetate:1COO, 2CH_3, 3CH_2
42 SiH_2	SiH_3 SiH_2 SiH Si	78 79 80 81	1.6035 1.443 1.2853 1.0470	1.2632 1.0063 0.7494 0.4099	Methylsiloxane: 1 SiH_3, 1 CH_3 Hexamethyldisiloxane: 1 Si, 1SiO, 6CH_3
43 SiO	SiH_2O SiHO SiO	82 83 84	1.4838 1.3030 1.1044	1.0621 0.7639 0.4657	Hexamethyldisiloxane:1 Si, 1 SiO, 6CH_3
44 NMP	NMP	85	3.9810	3.2000	N-methylpyrrolidone
45 CClF	CCl_3F CCl_2F $HCCl_2F$ HCClF $CClF_2$ $HCClF_2$ $CClF_3$ CCl_2F_2	86 87 88 89 90 91 92 93	3.0356 2.2287 2.4060 1.6493 1.8174 1.9670 2.1721 2.6243	2.6440 2.9160 2.1160 1.4160 1.6480 1.8280 2.1000 2.3760	Trichlorofluoromethane: 1Cl_3F Dichlorofluoromethane1$HCCl_2F$ 1-Chloro-12,2,2-tetrafluoroethane: 1CF_3, 1HCClF 1,2-Dichlorotetrafluoroethane: 2$CClF_2$ Chlorodifluoromethane: 1$HCClF_2$ Chlorotrifluoromethane: 1$CClF_3$ Dichlorodifluoromethane: 1CCl_2F_2
46 CON	$CONH_2$ $CONHCH_3$ $CONHCH_2$ $CON(CH_3)_2$ $CONCH_3CH_2$ $CON(CH_2)_2$	94 95 96 97 98 99	1.4515 2.1905 1.9637 2.8589 2.6322 2.4054	1.2480 1.7960 1.4880 2.4280 2.1200 1.8120	Acetamide: 1 CH_3, 1$CONH_2$ N-Methylacetamide: 1 CH_3, 1 $CONHCH_3$ N-Ethylacetamide: 2 CH_3, 1CONH CH_2 N,N-Dimethylacetamide: 1 CH_3, $CONH(CH_3)_2CH_2$ N,N-Methylethylacetamide: 2 CH_3, 1 $CONCH_3CH_2$ N,NDiethylacetamide:3CH_3,1$CON(CH_2)_2$
47 OCCOH	$C_2H_5O_2$ $C_2H_4O_2$	100 101	2.1226 1.8952	1.904 1.592	2-Ethoxyethanol: 1 CH_3, 1CH_2, $C_2H_5O_2$ 2-Ethoxy-1-propanol: 2 CH_3, 1CH_2, 1$C_2H_4O_2$
48 CH_2S	CH_3S CH_2S CHS	102 103 104	1.6130 1.3863 1.1589	1.3680 1.0600 0.7480	Dimethylsulphide: CH_3, CH_3S Diethylsulphide:2 CH_3, 1CH_2, 1 CH_2S Diisopropylsulfide: 4 CH_3, 1CH, 1 CHS
49Morpho-line	MORPH	105	3.4740	2.7960	Morpholine: 1MORPH
50 Thiophene	C_4H_4S C_4H_3S C_4H_2S	106 107 108	2.8569 2.6908 2.5247	2.1400 1.8600 1.5800	Thiophene: C_4H_4S 2-Methylthiophene: CH_3, C_4H_3S 2,3-Dimethylthiophene: 2 CH_3, 1C_4H_2S

Table H.6: Values of a_{mn} for UNIFAC method (Phase equilibria- Raal and Muhlbauer).

Group	1	2	3	4	5	6	7	8	9	10
1. CH2	0.000	86.02	61.13	76.50	986.5	697.2	1318.0	1333.0	476.4	677.0
2. C=C	-35.36	0.0000	38.81	74.15	524.1	787.6	270.6	526.1	182.6	448.8
3.ACH	-11.2	3.4446	0.0000	167.0	636.1	637.4	903.8	1329.0	25.77	347.3
4. ACCH2	-69.70	-113.6	-146.8	0.0000	803.2	603.3	5695.0	884.9	-52.10	586.6
5. OH	156.4	457.0	89.60	25.82	0.000	-137.1	353.5	-259.7	84.00	-203.6
6.CH3OH	16.51	-12.52	-50.00	-44.50	249.1	0.0000	-181.0	-101.7	23.39	306.4
7. H2O	300.0	496.1	362.3	377.6	-229.1	289.6	0.0000	324.5	-195.4	-116.0
8. ACOH	275.8	217.5	25.34	244.2	-451.6	-265.2	-601.8	0.0000	-356.1	-271.1
9. CH2CO	26.76	42.92	140.1	365.8	164.5	108.7	472.5	-133.1	0.0000	-37.36
10.CHO	505.7	56.30	23.39	106.0	529.0	-340.2	480.8	-155.6	128.0	0.0000
11. CCOO	114.8	132.1	85.84	-170.0	245.4	249.6	200.8	-36.72	372.2	185.1
12. HCOO	329.3	110.4	18.12	428.0	139.4	227.8	n.a.	n.a.	385.4	-236.5
13. CH2O	83.36	26.51	52.13	65.69	237.7	238.4	-314.7	n.a.	191.1	-7.838
14. CNH2	-30.48	1.163	-44.85	296.4	-242.8	-481.7	-330.4	n.a.	n.a.	n.a.
15. CNH	65.33	-28.70	-22.31	223.0	-150.0	-370.3	-448.2	n.a.	394.6	n.a.
16. (C)3N	-83.98	-25.38	-223.0	109.9	28.6	-406.8	-598.8	n.a.	1225.3	n.a.
17. ACNH2	1139.0	2000.0	247.5	762.8	-17.40	-118.1	-341.6	-253.1	-450.3	n.a.
18. Pyridine	-101.6	-47.63	31.87	49.80	-132.3	-378.2	-332.9	-341.6	29.10	n.a.
19. CCN	24.82	-40.62	-22.97	-138.4	185.4	162.6	242.8	n.a.	-287.5	n.a.
20. COOH	315.3	1264.0	32.32	89.86	-151.0	339.8	-66.17	-11.00	-297.8	-165.5
21. CCl	91.46	40.25	4.680	122.9	562.2	529.0	698.2	n.a.	286.3	-47.51
22. CCl2	34.01	-23.50	121.3	140.8	527.6	669.9	708.7	n.a.	82.86	190.6
23. CCl3	36.70	51.06	288.5	69.90	742.1	649.1	826.8	n.a.	552.1	242.8
24. CCl4	-78.45	160.9	-4.700	134.7	856.3	709.6	1201.0	10000.0	372.0	n.a
25. ACCl	106.98	70.32	-97.27	402.5	325.7	612.8	-274.5	622.3	518.4	n.a
26. CNO2	-32.69	-1.996	10.38	-97.05	261.6	252.6	417.9	n.a.	-142.6	n.a
27. ACNO2	5541.0	n.a.	1824	-127.8	561.6	n.a.	360.7	n.a.	-101.5	n.a.
28. CS2	-52.65	16.62	21.50	40.68	609.8	914.2	1081.0	1421.0	303.7	n.a.
29. CH3SH	-7.481	n.a.	28.41	19.56	461.6	448.6	n.a.	n.a	160.6	n.a.
30. Furfural	-25.31	82.64	157.3	128.8	521.6	n.a.	23.48	n.a.	317.5	n.a.
31. DOH	140.0	n.a	221.4	150.6	267.6	240.8	-137.4	838.4	135.4	n.a.
32. I	128.0	n.a.	58.68	26.41	501.3	431.3	n.a.	n.a.	138.0	245.9
33. Br	-31.52	174.6	-154.2	1112.0	524.9	494.7	n.a.	n.a.	-142.6	n.a.
34. C---C	-72.88	41.38	n.a	n.a	68.95	n.a.	n.a.	n.a.	443.6	n.a.
35. Me2SO	50.49	64.07	-2.504	-143.2	-25.87	695.0	-240.0	n.a.	110.4	n.a.
36. ACRY	-165.9	573.0	-123.6	397.4	389.3	218.8	386.0	n.a.	n.a.	354.0
37. ClC=C	47.41	124.2	395.8	419.1	738.9	528.0	n.a.	n.a.	-40.90	183.8
38. ACF	-5.132	-131.7	-237.2	-157.3	649.7	645.9	n.a.	n.a.	n.a.	n.a.
39. DMF	-31.95	249.0	-133.9	-240.2	64.16	172.2	-287.1	n.a.	97.04	13.89
40. CF2	147.3	62.40	140.6	n.a	n.a.	n.a	n.a.	n.a.	n.a.	n.a.
41. COO	529.0	1397.0	317.6	615.8	88.63	171.1	284.4	-167.3	123.4	577.5
42. SiH2	-34.36	n.a.	787.9	191.6	1913.0	n.a.	180.2	n.a.	992.4	n.a.
43. SiO	110.2	n.a.	234.4	221.8	84.85	n.a.	n.a.	n.a.	n.a	n.a.
44. NMP	13.89	16.11	-23.88	6.214	769.9	n.a.	832.2	-234.7	n.a.	n.a.
45. CClF	30.74	n.a.	167.9	n.a.	794.4	762.7	n.a.	n.a.	n.a.	n.a.
46. CON	27.97	9.755	n.a.	n.a.	394.8	n.a.	-509.3	n.a.	n.a	n.a.
47. OCCOH	-11.92	132.4	-86.88	-19.45	517.5	n.a.	-205.7	n.a.	156.4	n.a.
48. CH2S	39.93	543.6	n.a.	n.a	n.a.	420.00	n.a.	n.a.	n.a.	n.a.
49Morpholine	-23.61	161.1	142.9	274.1	61.20	-89.24	-384.3	n.a.	n.a.	n.a.
50.Thiophene	-8.479	n.a.	23.93	2.845	682.5	597.8	n.a.	810.5	278.8	n.a.

Table H.6: Values of a_{mn} for UNIFAC method continued

Group	11	12	13	14	15	16	17	18	19	20
1. CH2	232.1	507.0	251.5	391.5	255.7	206.6	920.7	287.8	597.0	663.5
2. C=C	37.85	333.5	214.5	240.9	163.9	61.11	749.3	280.5	336.9	318.9
3.ACH	5.994	287.1	32.14	161.7	122.8	90.49	648.2	-4.449	215.5	537.4
4. ACCH2	5688.0	197.8	213.1	19.02	-49.29	23.50	664.2	52.80	6096.0	872.3
5. OH	101.1	267.8	28.06	8.6420	42.70	-323.0	-52.39	170.0	6.712	199.0
6.CH3OH	-10.72	179.7	-128.6	359.3	-20.98	53.90	489.7	580.5	53.28	-202.2
7. H2O	72.87	n.a.	540.4	48.89	168.0	304.0	243.2	459.0	112.6	-14.09
8. ACOH	-449.4	n.a.	n.a.	n.a.	n.a.	n.a.	119.9	-305.5	n.a.	408.9
9. CH2CO	-213.7	-190.4	-103.6	n.a.	-174.2	-169.0	6201.0	7.341	481.7	669.4
10.CHO	-110.3	766.0	304.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	497.5
11. CCOO	0.0000	-241.8	-235.7	n.a.	-73.50	-196.7	475.5	n.a.	494.6	660.2
12. HCOO	1167.0	0.0000	n.a	n.a.	n.a.	n.a.	n.a.	-233.4	-47.25	-268.1
13. CH2O	461.3	n.a.	0.0000	-78.36	251.5	5422.3	n.a.	213.2	-18.51	664.6
14. CNH2	n.a	n.a.	222.1	0.0000	-107.2	-41.11	-200.7	n.a.	358.9	n.a.
15. CNH	136.0	n.a.	-56.08	127.4	0.0000	-189.2	n.a	n.a.	147.1	n.a.
16. (C)3N	2889.0	n.a.	-194.1	38.89	865.9	0.0000	n.a.	n.a.	n.a.	n.a.
17. ACNH2	-294.8	n.a.	n.a.	-15.07	n.a.	n.a.	0.0000	89.70	-281.6	-396.0
18. Pyridine	n.a.	554.4	-156.1	n.a	n.a.	n.a.	117.4	0.0000	-169.7	-153.7
19. CCN	-266.6	99.37	38.81	-157.3	-108.5	n.a.	777.4	134.3	0.0000	n.a.
20. COOH	-256.3	193.9	-338.5	n.a.	n.a.	n.a.	493.8	-313.5	n.a.	0.0000
21. CCl	35.38	n.a.	225.4	131.2	n.a.	n.a.	429.7	n.a.	54.32	519.1
22. CCl2	-132.9	n.a.	-197.7	n.a.	n.a.	-141.4	n.a.	587.3	258.6	543.3
23. CCl3	176.5	235.6	-20.93	n.a.	n.a.	-293.7	n.a.	18.98	74.04	504.2
24. CCl4	129.5	351.9	113.9	261.1	91.13	316.9	898.2	368.5	492.0	631.0
25. ACCl	-171.1	383.3	-25.15	108.5	102.2	2951.0	334.9	n.a.	363.5	993.4
26. CNO2	129.3	n.a.	-94.49	n.a.	n.a.	n.a.	n.a.	n.a.	0.2827	n.a.
27. ACNO2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a	134.9	2475.0	n.a.	n.a.
28. CS2	243.8	n.a.	112.4	n.a.	n.a.	n.a.	n.a.	n.a.	335.7	n.a.
29. CH3SH	n.a.	201.5	63.71	106.7	n.a.	n.a.	n.a.	n.a.	161.0	n.a.
30. Furfural	-25.31	n.a.	-87.31	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	570.6
31. DOH	146.3	n.a.	9.207	n.a.	n.a.	n.a.	193.3	n.a.	169.6	n.a.
32. I	21.92	n.a.	476.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	616.6
33. Br	24.37	n.a.	736.4	n.a.	n.a.	n.a.	n.a	-42.71	136.9	5256.0
34. C---C	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	329.1	n.a.
35. Me2SO	41.57	n.a.	-93.51	n.a.	n.a.	-257.2	n.a.	n.a.	n.a.	-180.2
36. ACRY	175.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-42.31	n.a.
37. ClC=C	611.3	134.5	-217.9	n.a.	n.a.	n.a.	n.a.	281.6	335.2.	898.8
38. ACF	n.a.	n.a.	167.1	n.a.	-198.8	116.5	n.a.	159.8	n.a.	n.a.
39. DMF	-82.12	-116.7	-158.2	49.70	n.a.	-185.2	343.7	n.a.	150.6	-97.77
40. CF2	n.a.	n.a	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
41. COO	-234.9	65.37	-247.8	n.a.	284.5	n.a.	-22.10	n.a.	-61.60	1179.0
42. SiH2	n.a	n.a.	448.5	961.8	14.64.0	n.a.	n.a.	n.a.	n.a.	2450.0
43. SiO	n.a.	n.a.	n.a.	-125.2	16.04.0	n.a.	n.a.	n.a.	n.a.	2496.0
44. NMP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
45. CClF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
46. CON	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-70.25
47. OCCOH	-3.444	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	119.2	n.a.
48. CH2S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
49Morpholine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
50.Thiophene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	221.4	n.a.	n.a.

Table H.6: Values of a_{mn} for UNIFAC method (continued)

Group	21	22	23	24	25	26	27	28	29	30
1. CH2	35.93	53.76	24.90	104.3	11.44	661.5	153.6	543.0	184.4	354.6
2. C=C	-36.87	58.55	-13.99	-109.7	100.1	357.5	76.30	n.a.	n.a.	262.9
3.ACH	-18.81	-144.4	-231.9	3.000	187.0	168.0	52.07	194.9	-10.43	-64.29
4. ACCH2	-114.1	-110.0	-80.25	-141.3	-211.0	3629.0	-9.451	4448.0	393.6	48.49
5. OH	-75.62	65.28	-98.12	143.1	123.5	256.5	488.9	157.1	147.5	-120.5
6.CH3OH	-38.32	-102.5	-139.4	-44.76	-28.25	75.14	-31.09	n.a.	17.50	n.a.
7. H2O	325.4	370.4	353..7	497.5	133.9	220.6	8877.1	399.5	n.a.	188.0
8. ACOH	n.a.	n.a.	n.a.	1827.0	6915.0	n.a	8484.0	n.a.	n.a.	n.a.
9. CH2CO	-191.7	-130.3	-354.6	-39.20	-119.8	137.5	216.1	548.5	-46.28	-163.7
10.CHO	751.9	67.52	-483.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
11. CCOO	-34.74	108.9	-209.7	54.57	442.4	-81.13	183.0	n.a.	n.a.	202.3
12. HCOO	n.a	n.a.	-126.2	179.7	25.18	n.a.	n.a.	n.a.	103.9	n.a.
13. CH2O	301.1	137.8	-154.3	47.67	134.8	95.18	140.9	n.a.	-8.538	170.1
14. CNH2	-82.92	n.a.	n.a	-99.81	30.05	n.a.	n.a.	n.a.	-70.14	n.a.
15. CNH	n.a.	n.a.	n.a	71.23	-18.93	n.a.	n.a.	n.a.	n.a.	n.a.
16. (C)3N	n.a.	-73.85	-352.9	-262.0	-181.9	n.a.	n.a.	n.a.	n.a.	n.a.
17. ACNH2	287.0	n.a.	n.a	882.0	617.5	n.a.	n.a.	-139.3	n.a.	n.a.
18. Pyridine	n.a.	-351.6	-114.7	-205.3	n.a.	n.a.	n.a.	2845.0	n.a.	n.a.
19. CCN	4.933	-152.7	-15.62	-54.86	-4.6240	-0.5150	230.9	n.a.	0.4604	n.a.
20. COOH	13.41	-44.70	39.63	183.4	-79.08	n.a.	n.a.	n.a.	n.a.	-208.9
21. CCl	0.0000	108.3	249.2	62.42	153.0	32.73	450.1	86.20	59.02	n.a.
22. CCl2	-84.53	0.0000	0.0000	56.33	223.1	108.9	n.a.	n.a.	n.a.	n.a.
23. CCl3	-157.1	0.0000	0.0000	-30.10	192.1	n.a.	116.6	n.a.	n.a.	-64.38
24. CCl4	11.80	-17.97	51.90	0.0000	-75.97	490.9	132.2	534.7	n.a.	546.7
25. ACCl	-129.7	8.309	-0.2266	248.4	0.0000	132.7	n.a.	2213.0	n.a.	n.a.
26. CNO2	113.0	-9.639	n.a.	-34.68	132.9	0.0000	320.2	533.2	n.a.	n.a.
27. ACNO2	1971.0	n.a.	n.a.	514.6	-123.1	-85.12	n.a.	0.0000	n.a.	n.a.
28. CS2	-73.09	n.a.	-26.06	-60.71	n.a.	277.8	0.0000	n.a.	n.a.	n.a.
29. CH3SH	-27.94	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.0000	n.a.
30. Furfural	n.a.	n.a.	48.48	-132.2	n.a.	n.a.	n.a.	n.a.	n.a.	0.0000
31. DOH	n.a.	n.a.	n.a.	n.a.	n.a.	481.3	n.a.	n.a.	n.a.	n.a.
32. I	n.a	-40.82	21.76	48.49	n.a.	64.28	-27.45	2448.0	n.a.	n.a.
33. Br	-262.3	-174.5	n.a.	77.55	-185.3	125.3	n.a.	4288.0	n.a.	n.a.
34. C---C	n.a.	n.a.	n.a.	n.a.	n.a.	174.4	n.a.	n.a.	n.a.	n.a.
35. Me2SO	n.a.	-215.0	-343.6	-58.43	n.a.	n.a.	n.a.	n.a.	85.70	n.a.
36. ACRY	n.a.	n.a.	n.a.	-85.15	n.a.	n.a.	167.9	n.a.	n.a.	n.a.
37. ClC=C	383.2	301.9	-149.8	-134.2	n.a.	379.4	n.a.	n.a.	n.a.	82.64
38. ACF	n.a.	n.a.	n.a.	-124.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
39. DMF	n.a	n.a.	n.a.	-186.7	n.a.	223.6	n.a.	n.a.	-71.00	n.a.
40. CF2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	885.5	n.a.	n.a.	n.a.
41. COO	182.2	305.4	-193.0	335.7	335.7	-124.7	n.a.	n.a.	n.a.	-64.28
42. SiH2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
43. SiO	n.a.	n.a.	n.a.	70.81	70.81	n.a.	n.a.	n.a.	n.a.	n.a.
44. NMP	n.a.	n.a.	-196.2	n.a.	n.a.	n.a.	n.a.	n.a.	-274.1	n.a.
45. CClF	n.a.	n.a.	n.a.	n.a.	n.a.	844.0	n.a.	n.a.	n.a.	n.a.
46. CON	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
47. OCCOH	n.a.	-194.7	n.a.	3.163	3.163	n.a.	n.a.	n.a.	n.a.	n.a.
48. CH2S	n.a.	n.a.	-363.1	-11.30	-11.30	n.a.	n.a.	n.a.	6.971	n.a.
49Morpholine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
50.Thiophene	n.a.	n.a.	n.a.	-79.34	-79.34	176.3	n.a.	n.a.	n.a.	n.a.

Table H.6: Values of a_{mn} for UNIFAC method (continued)

Group	31	32	33	34	35	36	37	38	39	40
1. CH2	3025.0	335.8	479.5	298.9	526.5	689.0	-4.189	125.8	485.3	-2.859
2. C=C	n.a.	n.a.	183.8	31.14	179.0	-52.87	-66.46	359.3	-70.45	449.4
3.ACH	210.4	113.3	261.3	n.a.	169.9	383.9	-259.1	389.3	245.6	22.67
4. ACCH2	4975.0	259.0	210.0	n.a.	4284.0	-119.2	-282.5	101.4	5629.0	n.a.
5. OH	-318.9	313.5	202.1	727.8	-202.1	74.27	225.5	44.78	-143.9	n.a.
6.CH3OH	-119.2	212.1	106.3	n.a.	-399.3	-5.224	33.47	-48.25	-172.4	n.a.
7. H2O	12.72	n.a.	n.a.	n.a.	-139.3	160.8	n.a.	n.a.	319.0	n.a.
8. ACOH	-687.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
9. CH2CO	71.46	53.59	245.2	-246.6	-44.58	n.a.	-34.57	n.a.	-61.70	n.a.
10.CHO	n.a.	117.0	n.a.	n.a.	n.a.	-339.2	172.4	n.a.	-268.8	n.a.
11. CCOO	-101.7	148.3	18.88	n.a.	52.08	-28.6	-275.2	n.a.	85.33	n.a.
12. HCOO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-11.40	n.a.	308.9	n.a.
13. CH2O	-20.11	-149.5	-202.3	n.a.	128.8	n.a.	240.2	-273.9	254.8	n.a.
14. CNH2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-164.0	n.a.
15. CNH	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	570.9	n.a.	n.a.
16. (C)3N	n.a.	n.a.	n.a.	n.a.	243.1	n.a.	n.a	-196.3	22.05	n.a.
17. ACNH2	0.1104	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-334.4	n.a.
18. Pyridine	n.a.	n.a.	-60.78	n.a.	n.a.	n.a.	-160.77	-158.8	n.a.	n.a.
19. CCN	117.5	n.a	-62.17	-203.0	n.a.	81.57	-55.77	n.a.	-151.5	n.a.
20. COOH	n.a.	228.4	-95.00	n.a.	-463.6	n.a.	-11.16	n.a.	-228.0	n.a.
21. CCl	n.a.	n.a.	344.4	n.a.	n.a.	n.a.	-168.2	n.a.	n.a.	n.a.
22. CCl2	n.a.	177.6	315.9	n.a.	215.0	n.a.	-91.80	n.a.	n.a.	n.a.
23. CCl3	n.a.	86.40	n.a.	n.a.	363.7	n.a.	111.2	n.a.	n.a.	n.a.
24. CCl4	n.a.	247.8	146.6	n.a.	337.7	369.5	187.1	n.a.	498.6	n.a.
25. ACCl	n.a.	n.a.	593.4	n.a.	n.a.	n.a.	n.a.	215.2	n.a.	n.a.
26. CNO2	139.8	304.3	10.17	-27.70	n.a.	n.a.	10.76	n.a.	-223.1	n.a.
27. ACNO2	n.a.	2990.0	-124.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28. CS2	n.a.	292.7	n.a.	n.a.	n.a.	n.a.	-47.37	n.a.	n.a.	n.a.
29. CH3SH	n.a.	n.a.	n.a.	n.a.	31.66	n.a.	n.a.	n.a.	78.92	n.a.
30. Furfural	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	262.9	n.a.	n.a.	n.a.
31. DOH	0.000	n.a.	n.a.	n.a.	-417.2	n.a.	n.a.	n.a.	302.2	n.a.
32. I	n.a.	0.0000	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
33. Br	n.a.	n.a.	0.0000	n.a.	32.90	n.a.	n.a.	n.a.	n.a.	n.a.
34. C--C	n.a.	n.a.	n.a.	0.0000	n.a.	n.a.	2073.0	n.a.	-119.8	n.a.
35. Me2SO	535.8	n.a.	n.a.	n.a.	0.0000	n.a.	n.a.	n.a.	-97.71	n.a.
36. ACRY	n.a.	n.a.	-111.2	n.a.	n.a.	0.0000	-208.8	n.a.	-8.804	n.a.
37. ClC=C	n.a.	n.a.	n.a.	631.5	n.a.	837.2	0.0000	n.a.	255.0	n.a.
38. ACF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.0000	n.a.	-117.2
39. DMF	-191.7	n.a.	n.a.	6.699	136.6	5.150	-137.7	n.a.	0.0000	-5.579
40. CF2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	185.6	55.80	0.0000
41. COO	-264.3	288.1	n.a.	n.a.	-29.34	-53.91	-198.0	n.a.	-28.65	n.a.
42. SiH2	n.a.	n.a.	627.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
43. SiO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
44. NMP	262.0	n.a.	n.a.	n.a.	n.a.	n.a.	-66.31	n.a.	n.a.	n.a.
45. CClF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-32.17
46. CON	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
47. OCCOH	515.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
48. CH2S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	148.9	n.a.	n.a.	n.a.
49Morpholine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
50.Thiophene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table H.6: Values of a_{mn} for UNIFAC method (continued)

Group	41	42	43	44	45	46	47	48	49	50
1. CH2	387.1	-450.4	252.7	220.3	-5.869	390.9	553.3	187.0	216.1	92.99
2. C=C	48.33	n.a.	n.a.	86.46	n.a.	200.2	268.1	-617.0	62.56	n.a.
3.ACH	103.5	-432.3	238.9	30.04	-88.11	n.a.	333.3	n.a.	-59.58	-39.16
4. ACCH2	69.26	683.3	355.5	46.38	n.a.	n.a.	421.9	n.a.	-203.6	184.9
5. OH	190.3	-817.7	202.7	-504.2	72.96	-382.7	-248.3	n.a.	104.7	57.65
6.CH3OH	165.7	n.a.	n.a.	n.a.	-52.10	n.a.	n.a.	37.63	-59.40	-46.01
7. H2O	-197.5	-363.8	n.a.	452.2	n.a.	835.6	139.6	n.a.	407.9	n.a.
8. ACOH	-494.2	n.a.	n.a.	-659.0	n.a.	n.a.	n.a.	n.a.	n.a.	1005.0
9. CH2CO	-18.80	-588.9	n.a.	n.a.	n.a.	n.a.	37.54	n.a.	n.a.	-162.6
10.CHO	--275.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
11. CCOO	560.2	n.a.	n.a.	n.a.	n.a.	n.a.	151.8	n.a.	n.a.	n.a.
12. HCOO	-70.24	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
13. CH2O	417.0	1338.0	1338.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
14. CNH2	n.a	-664.4	-664.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
15. CNH	-38.77	448.1	448.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
16. (C)3N	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
17. ACNH2	-89.42	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
18. Pyridine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
19. CCN	120.3	n.a.	n.a.	n.a.	n.a.	n.a.	16.23	n.a.	n.a.	-136.6
20. COOH	-337.0	169.3	169.3	n.a.	n.a.	-322.3	n.a.	n.a.	n.a.	n.a.
21. CCl	63.67	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
22. CCl2	-96.87	n.a.	n.a.	n.a.	n.a.	n.a.	361.1	n.a.	n.a.	n.a.
23. CCl3	255.8	n.a.	n.a.	-35.68	n.a.	n.a.	n.a.	565.9	n.a.	n.a.
24. CCl4	-256.5	n.a.	n.a.	n.a.	n.a.	n.a.	423.1	63.95	n.a.	n.a.
25. ACCl	-145.1	n.a.	n.a.	n.a.	n.a.	n.a.	434.1	n.a.	n.a.	108.5
26. CNO2	248.4	n.a.	n.a.	n.a.	-218.9	n.a.	n.a.	n.a.	n.a.	n.a.
27. ACNO2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	-4.565
28. CS2	469.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
29. CH3SH	n.a.	n.a.	n.a.	1004.0	n.a.	n.a.	n.a.	-18.27	n.a.	n.a.
30. Furfural	43.37	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
31. DOH	347.8	n.a.	n.a.	-262.0	n.a.	n.a.	-353.5	n.a.	n.a.	n.a.
32. I	68.55	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
33. Br	-195.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
34. C---C	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
35. Me2SO	153.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
36. ACRY	423.4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
37. ClC=C	730.8	n.a.	n.a.	26.35	n.a.	n.a.	n.a.	2429.0	n.a.	n.a.
38. ACF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
39. DMF	72.31	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
40. CF2	n.a.	n.a.	n.a.	n.a.	111.8	n.a.	n.a.	n.a.	n.a.	n.a.
41. COO	0.0000	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
42. SiH2	n.a.	0.0000	-21.660	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
43. SiO	n.a.	745.3	0.0000	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
44. NMP	n.a.	n.a.	n.a.	0.0000	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
45. CCIF	n.a.	n.a.	n.a.	n.a.	0.0000	n.a.	n.a.	n.a.	n.a.	n.a.
46. CON	n.a.	n.a.	n.a.	n.a.	n.a.	0.0000	n.a.	n.a.	n.a.	n.a.
47. OCCOH	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.000	n.a.	n.a.	n.a.
48. CH2S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.0000	n.a.	n.a.
49Morpholine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.0000	0.0000
50.Thiophene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.