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Stability and Characterisation of Emulsions in the presence of Colloidal Particles and Surfactants

by

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Abstract

The stability against coalescence of vegetable oil-in-water “food grade” emulsions in the presence of both surfactant and colloidal particles (hydrophilic silica) has been studied and compared to the stability of systems where only the surfactant or the colloidal particles act as the emulsifier. No attempt was made to stop the emulsions from creaming. Two types of surfactants were selected; those that have the ability to stabilise O/W emulsions on their own (O/W surfactants) and those that cannot (W/O surfactants). Tween 60 and Sodium Caseinate were selected as the O/W surfactants, monoolein and lecithin as the W/O surfactants.

These mixed emulsifier systems were shown to induce long-term emulsion stability against coalescence, regardless of the surfactant type, via a synergistic “two-part” mechanism in which both the surfactant and colloidal particles components have specific functions. Nonetheless, the emulsion microstructure was proved to depend on the surfactant’s type and concentration: the use of O/W emulsifiers above a certain concentration induced a displacement of particles from the interface, while such a displacement was not observed using W/O emulsifiers. Further measurements of interfacial tension and contact angle showed that the level of adsorption of solid particles at the interface depended on the surfactant type and concentration.

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Abbreviations

2-D	Two dimensions
3-D	Three dimensions
A200	Aerosil 200, hydrophilic silica particles from Evonik
CA	Contact Angle
fps	frame per second
EG	Ethylene Glycol
HLB	Hydrophilic-Lipophilic Balance
IFT	Interfacial tension
NaCAS	Sodium Caseinate
O/W	oil-in-water
SEM	Scanning electron microscopy
SFT	Surface tension
USB	Ultrasonic bath
UVP	Ultrasonic Vibracell Processor
W/O	water-in-oil

Nomenclature

a	Surface area (m^2)
A_m	Interfacial area occupied per molecule of surfactant (\AA^2)
d_H	Hydrodynamic diameter (m)
D	Translational diffusion coefficient
$D(4,3)$	Weighted mean diameter (m)
g	Acceleration due to gravity (m/s^2)
k	Boltzmann constant ($=1.38 \times 10^{-23} \text{ J/K}$)
L	Length of Wilhelmy plate (m)
m	Mass (g)
M	Molecular weight (g/mol)
n	Number of moles (mol)
N_A	Avogadro number ($=6.02 \times 10^{23} \text{ mol}^{-1}$)
N_{droplet}	Number of emulsion droplets
r	Emulsion droplet radius (m)
R	Radius of curvature (m)
S	Surface (m^2)
$S_{L/S}$	Spreading coefficient (mN/m)

S_m	Mass of surfactant “head” per interfacial area (mg/m ²)
T	Temperature (K or °C)
v	Velocity (m/s)
V	Volume (m ³)
W_a	Work of adhesion (J/m ²)
W_c	Work of cohesion (J/m ²)
We	Weber number

Greek Symbols

ΔP_L	Laplace pressure (Ps)
γ	Interfacial tension (mN/m)
ρ	Density (kg/m ³)
η	Newtonian viscosity (Pa.s)
θ	Contact angle (degree)
τ	Characteristic time/duration (s)

Chapter 1:

Introduction

1.1 Background

A romantic dinner, a piece of cake savoured selfishly in a park on a beautiful summer's day, a Sunday roast shared with family and friends on a cold Sunday of winter... Food is an essential part of our life, providing us with the nutrients we need for healthy bodies and the calories we need for energy, and contributes to our well-being. However, for the last few decades, people in the Western Countries have changed their way of eating, allowing themselves only a short lunch or a dinner break. Fast-food restaurants, serving food with usually very high calorie content are also more and more popular. Combined

with low physical activity, this results in a serious increase of the number of people affected by overweight troubles and even obesity.

In the United Kingdom, for example, according to the OECD (Organisation for Economic Co-operation and Development)¹, the number of obese people has increased more than three times over the last thirty years, to affect about 24% of the population in 2009. Over the same period of time, the number of overweight or obese children has quintupled; 25% of the boys and 33% of the girls would know overweight troubles. Obesity can cause chronic diseases such as, diabetes, hypertension and strokes, and is considered as a public health and policy problem because of its prevalence, costs, and health effects. In addition to its health impacts, obesity leads to many problems including disadvantages in employment and increased business costs. These effects are felt by all levels of society from individuals, to corporations, to governments.

There is a need to develop healthy, nutritionally balanced foods with all of the taste, convenience and enjoyment of current manufactured foods. Healthy food products can be characterised by various attributes, such as low to moderate salt, sugar and fat content. Developing healthy food requires science to find ways to get the maximum perception from the minimum of energy dense ingredients. This can be achieved through the microstructuring of a product matrix², i.e. it is possible to compensate sensorial impacts of reduced sugar or fat contents by replacing these ingredients by low energy dense compounds and by re-structuring the food products.

Emulsions, mixture of two immiscible liquids (typically oil and water) with one of the liquids is dispersed as small droplets in the other, play an important part in the

production of different foods. Salad dressing, mayonnaise, cream puffs, margarine, gravies, ice cream are examples of food emulsions. Emulsions are commonly classified into two types: (1) oil-in-water (O/W) emulsions, in which oil droplets are dispersed in an aqueous medium; (2) water-in-oil (W/O) emulsions, in which water droplets are dispersed in an oil medium. These emulsions can also be divided into two categories, depending on their uses³. Some emulsions are end products in themselves, like coffee creamers or mayonnaise. They are relatively simple as the only requirement is to remain stable during their preparation and shelf-life. Other emulsions are used as ingredients to form more complex structures. Emulsions droplets must interact with other ingredients. In some cases (yoghourts or gelled structures) emulsions must remain stable in the process; in other cases (ice cream) emulsions are required to be destabilised to create new structure.

Emulsion stabilisation is therefore a major issue in the food industry. Mixing oil and water results in very unstable products; the two phases, oil and water, separate very quickly after mixing. It is then necessary to add another compound to stabilise the emulsion. Such an ingredient is called *emulsifier*. For example, egg yolk is used as emulsifier in the recipe of mayonnaise (mixture of oil, mustard and egg yolk). The emulsifying agent in the egg yolk was identified a long time ago and is called *lecithin*. In some cases, emulsifiers are mixed together to provide better stability, which renders the emulsion formulation complicated.

Nowadays, a lot of emulsifiers are available in order to meet the demand of diversified types of emulsion⁴⁻⁷. Some of these are natural and have been used for centuries (egg yolk is considered as the oldest natural emulsifier); synthetic emulsifiers have only

come into wide commercial use in the second half of the twentieth century. Their development was driven by the processed food industry, which needed shelf-stable products for market distribution.

Approximately 500,000 tons of emulsifiers are produced and sold worldwide⁷. However, food emulsifiers' regulation is not global and depends on the country where the food is consumed. In the United States, they are regulated by the Food and Drug Administration. Two sections of the regulations govern their use: substances affirmed as GRAS, i.e., Generally Recognized As Safe, and Direct Food Additives. GRAS substances have usually less stringent regulations attached to their use. The European Union regulates food emulsifiers in an analogous fashion to the United States. They are usually referred to E-numbers on packaging. Other countries, which have not formed trading communities, may have regulations which are unique.

In spite of the fact that emulsion formulation may be very complicated, emulsion compounds can be simplified as: oil, water and emulsifier(s). Fat content reduction in food products requires the reduction of the oil concentration, or emulsifier concentration or type. In 1869, the French chemist Hippolyte Mège-Mouriés invented margarine to offer an alternative to butter to the Emperor of France, Louis Napoleon III. Even though margarine was created as a low-cost substitute for butter for use by the army and the lower classes, it is nowadays often used by many people because it is lower in fat. Many investigations have been done since this time, and particularly since the second half of the twentieth century⁸⁻¹². Recently, emulsions in which air bubbles were encapsulated in the oil droplets were developed in order to reduce the content of fat¹³.

Lowering the oil concentration in food products is not the only way to reduce the fat content. Emulsifiers, such as monoglycerides or diglycerides, are energy dense ingredients and the possibility to stabilise emulsions by using different materials rather than these “classic” emulsifiers is of growing interest in the development of healthy food. Fine divided solid particles, for example, have been shown to provide long term stable emulsions^{14,15}.

1.2 Aims of this research

The overall aim of this project was to develop a mechanistic understanding of the emulsification processes and emulsion stabilisation mechanisms of solid particle stabilised systems for use in future manufactured foods which are nutritionally balanced. The aims and objectives set at the beginning of this investigation can be summarised as:

- All the components used in this study are “food-grade”, i.e. available for use in food;
- Development of solid particle stabilised emulsions and investigation of particle properties on emulsion stability;
- Investigation of the effect of mixtures of both colloidal particles and other types of emulsifier such as surfactant and protein on emulsion stability, and more particularly the effect of emulsifier concentration on emulsion stability;
- Characterisation of the oil-water interface (interfacial tension and contact angle) in the presence of various emulsifiers such as particles, surfactant and protein.

1.3 Thesis layout

This manuscript is composed of eight chapters: an introduction, a literature review, an experiment chapter, four results chapters and a conclusion and outlook.

- Chapter 1 is an introduction underlining the interest and the aims of this work;
- Chapter 2 is a literature review that defines the main notions used throughout this study and summarises the scientific knowledge related to the subjects mentioned in this thesis;
- Chapter 3 gives all the details necessary to understand the experiments performed during this PhD, and eventually to reproduce them;
- Chapter 4 is the first result chapter, regarding the properties of aqueous dispersions containing various kinds of colloidal particles, and the stabilisation of O/W emulsions with colloidal particles only;
- Chapter 5 is the second result chapter in which the stabilisation of O/W emulsions with both colloids and monoolein is investigated;
- Chapter 6 is the third result chapter that emphasises the stabilisation of emulsions with colloidal particles and different kinds of emulsifier: Tween 60, Sodium Caseinate and lecithin;
- Chapter 7 is the fourth and final result chapter in which the oil-water interface is characterised by measuring interfacial tension and contact angle;
- Chapter 8 summarises the conclusions made throughout this study and suggests the fulfilment of future works.

1.4 Publications and conferences

Publications

- R. Pichot, F. Spyropoulos, I.T. Norton, *Mixed-emulsifier stabilised emulsions: Investigation of the effect of monoolein and hydrophilic silica particle mixtures on the stability against coalescence* (2009), Journal of Colloid and Interface Science, Vol. 329, Issue 2, pp. 284-291, doi:10.1016/j.jcis.2008.09.083.
- R. Pichot, F. Spyropoulos, I.T. Norton, *O/W emulsions stabilised by both low molecular weight surfactants and colloidal particles: The effect of surfactant type and concentration* (2010), Journal of Colloid and Interface Science, Vol. 352, Issue 1, pp. 128-135, doi:10.1016/j.jcis.2010.08.021.
- R. Pichot, F. Spyropoulos, I.T. Norton, *Role of surfactant on the displacement of hydrophilic silica particles from the oil/water interface*, Journal of Colloid and Interface Science, under submission.

Conferences

- R. Pichot, F. Spyropoulos, I.T. Norton, *Emulsions stabilised by Hydrophilic Silica particles & Surfactants*, ICEF 10 (International Congress of Engineering and Food) – April 2008, Viñar del Mar, Chile.
- R. Pichot, F. Spyropoulos, I.T. Norton, *Investigation of the effect of hydrophilic silica particles and monoolein on the stability against coalescence of mixed-emulsifier emulsions*, ISFRS (International Symposium on Food Rheology and Structure) – June 2009, Zurich, Switzerland.

Chapter 2:

Literature survey

2.1 Definitions

This sub-section is dedicated to the definitions of the main notions and concepts used throughout this chapter, and more generally throughout this study.

A *colloidal dispersion* is defined as a two-phase system, where one phase (called dispersed phase) is dispersed in the second phase (called continuous phase). More specifically, it consists of a dispersion of *colloidal particles* in a medium that has no or little affinity with them, i.e. in which particles cannot either combine or dissolve. In

case the continuous phase is a liquid, three main kinds of dispersions can be distinguished, according to the type of particles:

- Solid particles as particles, the dispersion is called *Suspension*;
- Gas molecules as particles, the dispersion is called *Foam*;
- Liquid as particles, the dispersion is called *Emulsion*.

As defined in previous chapter, an ***emulsion*** is a mixture of two immiscible liquids, typically oil and water, homogenous at macroscopic scale, but heterogeneous at microscopic scale. The process of mixing two liquids together in order to prepare emulsions is called ***emulsification***. Mixtures of oil and water are not stable, as oil or water droplets tend to merge with each other (phenomenon known as ***coalescence***) and the introduction of a third agent, called ***emulsifier***, to stabilise the emulsions is necessary. According the size of their droplets, one can distinguish three types of emulsions¹⁶: (1) *macroemulsions*, the most well-known type, with droplets > 400 nm; (2) *miniemulsions*, with droplets between 100 and 400 nm; (3) *microemulsions*, with droplets < 100 nm.

An ***interface*** is a surface forming a common boundary between two phases (liquid/liquid, gas/liquid or solid/liquid). Because interfaces are very thin, they are considered as two-dimensional surfaces and their thicknesses are neglected. However, the third dimension is also of great significance, because of the interactions of the molecules of each phase at the interface. The work required to change the shape of a given interface is known as ***interfacial tension***. It is worth to note that a distinction is made according to the nature of the two phases; the expression *interfacial tension* is used when the two phases are liquid, while *surface tension* is used when one of the

phases is gaseous. In order to simplify further explanations, the term *interfacial tension* will be used, regardless of the nature of the two phases.

Two interpretation can be given to interfacial tension¹⁷⁻¹⁹: the *mechanical interpretation* and the *thermodynamic interpretation*. The first one is illustrated Figure 2-1, where the paper clip remains at the water. The reason for this is that the force applied by the paperclip on the water surface is not high enough to modify the shape of the interface. Interfacial tension is defined as a *force per unit length parallel to the interface*. Indeed, at a given point, this force is the same in all lateral directions along the interface. It is usually expressed in mN/m.



Figure 2-1: Mechanical point of view of interfacial tension – Paperclip at the surface of water – photograph provided by Kruss (*personal communication*).

Interfacial tension of a fluid interface also has a *thermodynamic interpretation*²⁰. Let's consider a binary system where the bulk phases are pure (phase A and phase B). It is clear that in the interfacial region, a molecule of A will have more B molecules and fewer A molecules as nearest neighbours than in bulk liquid A. A similar statement can

be made about a molecule of B. Thermodynamics teaches that for phase separation to occur, the attraction between an A and a B molecule must be less than the average of that between two A molecules and two B molecules²¹. Hence, the total attractive interaction per molecule is less in the interfacial area than in the bulk phases. Thus, the amount of work that can be extracted, called *free energy*, per molecule must be higher in the interfacial area than in the bulk liquids. The interfacial tension is then defined as an *additional free energy per unit area*, caused by the presence of the interface, expressed in J/m².

It is worth to note that the concepts of interfacial tension obtained from the thermodynamic and mechanical approaches – energy per unit area and force per unit length – are dimensionally equivalent.

2.2 Emulsion formation

When oil and water are placed together in a container, a layer of oil is formed over a layer of water (given that the density of oil is lower than the one of water), because this represents their thermodynamically most stable state. Such a “layer position” minimises the contact area between the two phases, minimising their free energy. In order to form an emulsion, it is required to change this layer position by bringing energy into the system. When droplets (of oil or water) are formed under agitation, they are constantly moving, thus collide and may coalesce. Larger droplets are formed and due to gravity, these droplets merge together to re-form the oil and water layers. The use of emulsifier is then necessary to avoid the droplets to merge.

2.2.1 Homogenisation

The process to make an emulsion by mixing two immiscible liquids is known as *emulsification* or *homogenisation*^{22,23}. By extension, mechanical devices used during emulsification are called *homogeniser*. As food emulsions differ from each other in nature, ingredients, structure, etc., many homogenisers have been developed. The aim of this section is not to give an exhaustive description of these devices in the food industry, with their advantages and disadvantages, but to give an overview of some types of homogenisers.

High-speed mixers are probably the most used homogenisers in the food industry^{23,24}. All the ingredients are placed in a vessel and emulsified together directly with a mixing head rotating at high speed. Nonetheless, in order to improve the process efficiency, ingredients may also be added sequentially. The mixer efficiency depends on its ability to re-circulate the mixture throughout the vessel, and thus on the mixing head shape. The size of emulsion droplets is function of the rotating speed and/or the emulsification time.

Ultrasonic homogenisers have also been largely used in the food industry^{25,26}. This method differs from the high-speed mixer method in terms of breaking and dispersing a bulk phase. High-power ultrasound (low-intensity acoustic waves leave the medium unchanged) are used to generate (1) ultrasonic waves that create instability in the bulk phase, inducing the formation of large droplets; (2) acoustic cavitation that breaks the large droplets into smaller ones^{27,28}. There are three main parameters that determine the

efficiency of ultrasonic homogenisers: intensity, duration and frequency of the ultrasonic waves^{29,30}.

A relatively new homogenisation method is the *membrane emulsification*³¹. This method involves using a low pressure to force the dispersed phase to go through a membrane that contains small pores into the continuous phase. Many parameters can affect the size of emulsion droplets, such as the pores of the membranes, the dynamic interfacial tension between the two liquids, the flow rate of the continuous phase, and the transmembrane pressure³²⁻³⁵. Membranes can be made with many different pore diameters and materials, according to required droplet size and emulsion type. The main advantages of these membranes are the high energy efficiency and the potential industrial applications.

In order to get a better understanding of the processes occurring during emulsification, homogenisation is usually divided in two steps: the primary homogenisation, during which the oil and water are converted to an emulsion that contains large droplets; the secondary homogenisation, during which the “primary droplet” size is reduced. Even though some homogeniser can produce very small droplets directly from the separate oil and water phases (e.g. high intensity ultrasound homogeniser), it may be advantageous to use a two step process, using then two types of homogeniser. The choice of the process is driven by the physico-chemical properties of the initial ingredients (oil, water and emulsifier). Nonetheless, in practice, it may be difficult to make a clear distinction between these two steps as many physical phenomena taking place during these two steps are similar and may occur at the same time.

2.2.2 *Parameters affecting emulsion droplet size*

In this study, the stability of oil-in-water emulsions only was investigated. In order to simplify the description of the mechanisms involved in the formation and stabilisation of emulsions, it is assumed from now that oil is the dispersed phase and water the continuous one. Thus, unless mentioned, the term “droplets” refers to oil droplets.

2.2.2.1 *Flow regimes*

The dispersion of an oil phase into small droplets is induced by energy input through homogenisers. Hydrodynamic conditions, i.e. the movement of fluids (oil and water) in the vessel during homogenisation, play an important role in the droplet size^{17,23}. Different *flow regimes*, responsible for the droplet break-up, can be distinguished since they depend on the type of homogeniser and the properties of the fluids. The main factors determining what the regime is, are the type of force and the flow type.

The forces involved in the break-up process are the *viscous forces*, also called *frictional forces*, due to the flow of fluid parallel to the surface of the droplets, and the *inertial forces*, due to local pressure fluctuations in the fluid and that tend to act perpendicular to the surface of the droplets. Flow regimes can be defined and classified as follow:

- *Laminar-viscous regime*: the flow type is laminar (slow flow rate) and the droplet break-up is mainly due to viscous forces;
- *Turbulent-viscous regime*: the flow type is turbulent (high flow rate) and the droplet break-up is mainly due to viscous forces;
- *Turbulent-inertial regime*: the flow type is turbulent and the droplet break-up is mainly due to inertial forces.

Equations are associated with each flow regime and can be derived to predict parameters like drop size, local forces, and time scales of various events. These equations will not be developed here but more details can be found in the literature¹⁷.

2.2.2.2 *Droplet break-up*

During emulsification, oil bulk is broken up into small droplets. In order to control the homogenisation process, it is necessary to understand the nature of the forces responsible for the droplet break-up, also called *droplet disruption*. As mentioned above, oil droplets try to minimise their free energy by minimising interfacial area by holding together into one big droplet, due to *interfacial forces*. These are opposing forces to *disruptive forces*, generated by homogenisers. The balance between these two forces is of great importance to predict whether oil droplets will be formed and the size of disrupted droplets.

The interfacial forces, that keep oil droplets spherical, are characterised by the Laplace pressure (ΔP_L), which is the pressure difference between the inside and the outside of the droplet, across the oil-water interface. It can be expressed by the following equation³⁶⁻³⁸:

$$\Delta P_L = \frac{2\gamma}{r} \quad (2.1)$$

where γ is the interfacial tension between oil and water, and r the droplet radius. Equation 2.1 clearly shows that the pressure gradient increases by increasing the interfacial tension. This equation can also be written:

$$r = \frac{2\gamma}{\Delta P_L} \quad (2.2)$$

which clearly indicates that the droplet diameter depends on the interfacial tension; droplets tend to be bigger if the interfacial tension is higher. Moreover, a significant pressure must be generated by the homogeniser in order to compensate or overcome the interfacial tension. In the case that the Laplace pressure and the interfacial tension are similar, oil droplets may only be deformed.

2.2.2.3 *Disruptive forces*

The disruptive forces responsible for the oil droplet break-up during emulsification depend on the hydrodynamic conditions, i.e. the flow regime that takes place during the mixing process^{17,23}. In order to break up the oil bulk and the big oil droplets initially formed, the disruptive forces must overcome the interfacial forces. The Weber number, $We = \text{Disruptive forces} / \text{Interfacial forces}$, is used to quantify the feasibility of droplet break-up³⁶. Typically, droplets tend to be disrupted only if $We > 1$. Moreover, the time that disruptive forces are applied on the droplet must be longer than the droplet deformation time^{23,39,40}. It is usually convenient to calculate the ratio $\tau_{DIS} / \tau_{DEF} = \text{disruptive forces duration} / \text{droplet deformation duration}$ to determine whether droplets will be disrupted. Typically, droplets tend to be disrupted only if $\tau_{DIS} / \tau_{DEF} > 1$. Weber number and duration ratio can be calculated, according to the different flow regimes. More details to calculate these numbers can be found in the literature^{17,23,36}.

2.2.2.4 *Droplet coalescence*

After the droplet disruption during homogenisation, the droplets are constantly moving and the frequency of collision is very high due to agitation^{17,23,41,42}. These collisions may lead to coalescence, increasing then the droplet size. Thus, the presence of emulsifier in the system is necessary to prevent droplets coalescence. By adsorbing at the oil-water interface, emulsifier molecules form a layer around the droplets that prevents merging. Nonetheless, the concentration of emulsifier must be high enough to cover the droplet surface; in case the concentration is too low, droplets are likely to coalesce with their neighbours⁴³. Another factor that affects the droplet size is the time required by the emulsifier to adsorb at the interface (τ_{ADS}), compared to the time between droplet collision (τ_{COL}). In order to minimise the coalescence during the emulsification process, it is necessary to insure that $\tau_{ADS}/\tau_{COL} \ll 1$.

2.2.2.5 *Role of the emulsifier*

As mentioned in sub-section 2.2.2.2, the disruption of the oil droplets depends on the oil-water interfacial tension; droplet break-up is facilitated when the interfacial tension is low. The presence of emulsifier in the system may help to decrease the interfacial tension and then to minimise the effects of interfacial forces. The time taken by the emulsifier to adsorb at the interface is also important; emulsifier must adsorb quickly at the droplets in order to give time to the interfacial tension to be modified which facilitates the droplet disruption.

The two main functions of an emulsifier during homogenisation are:

- To decrease the oil-water interfacial tension to facilitate droplet disruption;
- To form a protective layer around the oil droplets to prevent coalescence (as mentioned in section 2.2.2.4).

2.3 *Emulsion stability*

The term “emulsion stability” refers to the ability of an emulsion to keep its properties unchanged over a certain period of time. However, as emulsions are thermodynamically unstable, changes of emulsion properties will occur; the more slowly the properties change, the more stable the emulsion is. There are many phenomena that can alter emulsion properties: coalescence, flocculation, creaming, Ostwald ripening, etc. Two or more of these instability phenomena may occur at the same time. It is then important to understand the cause(s) of instability to select suitable components to form stable emulsions.

2.3.1 *Thermodynamic and kinetic stability*

Thermodynamics gives information about processes taking place during emulsification or at quiescent conditions (after homogenisation). Kinetics gives information about the rate at which these processes occur. Mixing pure oil and pure water results in the formation of opaque emulsions. After a certain time, distinct layers of oil and water are visible. Phenomena (coalescence of oil or water droplets) taking place in this example are due to thermodynamic instability. The time taken by the droplets to merge is related to kinetics. In order to understand emulsion stabilisation mechanisms, it is important to distinguish *thermodynamic stability* and *kinetic stability*.

It was shown that emulsions, and particularly food emulsions, are thermodynamically unstable systems^{23,44}. This was demonstrated by considering the free energy of the oil-water system before and after emulsification. During emulsification, the overall free energy is positive, due to the increase of interfacial area, i.e. the food emulsion formation is thermodynamically unfavourable.

Since emulsions are thermodynamically unstable, kinetic stability is of great importance in many fields, including food; as emulsions are almost certain to break down, a crucial issue is to know how long emulsion properties remain the same. Despite the fact that emulsions exist in a thermodynamically unstable state, some remain kinetically stable for months or years. This metastable state (thermodynamically unstable and kinetically stable), is due to the fact that phenomena responsible for thermodynamically instability take place over a long period a time. The changes in emulsion properties occur then very slowly.

2.3.2 Phase separation

Emulsion droplets and continuous media have in most of the cases different densities. Due to gravity, droplets tend to move up or down through the continuous phase^{23,45-47}. If the droplets have a lower density, they tend move up to form a layer of emulsion droplets at the top of the emulsion. This phenomenon is known as **creaming**. On the contrary, if the droplets have a higher density, they tend to move down to form a layer at the bottom of the emulsion. This phenomenon is known as **sedimentation**. Generally, the density of oil is lower than the density of water, thus droplets of O/W emulsions tend to cream, while those of W/O emulsions tend to sediment.

As in this study the stability of O/W emulsions was investigated, the causes of creaming and the methods to reduce creaming will be discussed. The creaming velocity v of a single droplet that is not subject to deformation is given by the Stokes' law²³:

$$v = \frac{2gr^2(\rho_{cont} - \rho_{drop})}{9\eta_{cont}} \quad (2.3)$$

where g is the acceleration due to gravity, r and ρ_{drop} respectively the radius and the density of the droplet, ρ_{cont} and η_{cont} respectively the density and Newtonian viscosity of the continuous phase. It is worth to note that this equation is applicable only to dilute emulsions. The creaming velocity depends on the density difference between the two liquids, the viscosity of the continuous phase and the droplet size. There are many ways to reduce creaming^{23,45,48,49}.

- *Minimisation of the density difference between the two phases*: matching the densities between oil and water phase would slow creaming. This can be achieved by adding a weighting agent to the oil phase, increasing the oil density before emulsification. It is also possible to use highly dense emulsifiers; by adsorbing around the oil droplet, the emulsifier will increase the density of the droplet, reducing the density difference between water and emulsion droplets.
- *Reduction of the droplet size*: the formation of small droplets is due to the high energy input in the system, to the reduction of interfacial tension between oil and water and to the prevention of coalescence. The use of efficient homogenisers is one of the solutions to reduce droplet size. The use of emulsifiers at adequate concentration allows both more efficient oil disruption and resistance against droplet coalescence.

- *Increase of the continuous phase viscosity*: Increasing the viscosity of the liquid surrounding a droplet decreases the velocity at which the droplet moves up. This can be achieved by introducing a thickener or a gelling agent in the continuous phase (biopolymer for example).
- *Increase of the droplet concentration*: at very high concentration, droplets will be closely packed, which tends to prevent their movement. However, it may be very difficult to increase the droplet concentration, due to physico-chemical limits of the system.

2.3.3 Droplet Aggregation

Because they are constantly moving, due to Brownian motion, gravity or mechanical agitation, emulsion droplets frequently collide with each other. Then, they can either move apart or aggregate. There are two main types of aggregation: ***flocculation*** and ***coalescence***. Flocculation is the aggregation of droplets that keep their physical properties; coalescence is the aggregation of droplets that merge together. Flocculation may be reversible (weak flocculation) or irreversible (strong flocculation) while coalescence is irreversible^{23,45}.

Emulsion droplets are surrounded by the continuous phase in which the droplets are formed and dispersed. As droplets move close to each other, a thin layer, usually called ***thin film***, of the continuous phase is formed between the droplets. As long as this film exists, there is no droplets contact, due to hydrodynamic resistance induced by the presence of the thin film^{44,50,51}. Droplet aggregation can only occur when the liquid is squeezed out of the thin layer.

The thickness of the thin film depends on the nature of the colloidal and hydrodynamic interactions in the system^{17,23,44,45,52,53}. The thicker the film is, the weaker the collisions are. The thin film forms a *barrier* between the droplets. The rupture of the film requires a certain level of energy, which determines the nature of the collisions. At high energy barrier, there is no aggregation and the droplets will move apart; at slightly lower energy barrier, droplets are weakly flocculated, as the thin layer still exists; at low energy barrier, droplets are strongly flocculated with a very thin film existing between the droplets. In last instance, the energy barrier is so low that the film is broken, which results in droplets coalescence.

2.3.3.1 *Flocculation*

Droplet flocculation has antagonistic effects in terms of emulsion stability. It is usually considered as an instability phenomenon. The formation of droplets flocs in the emulsion has an influence of the creaming rate^{47,54,55}. In dilute emulsions (Figure 2-2a), flocs, which do not or only little interact with each other, tend to increase the creaming velocity, since bigger particles are more subject to gravitational effect. Moreover, the presence of flocs tends to increase the emulsion viscosity which may not be wanted for some food products. In other hand, the possibility to create a network of flocs in the emulsion (Figure 2-2b) may be an advantage to modify or control the texture of some products. Understanding of flocculation is of great importance in order to control the texture and structure of emulsions. Mathematical models that take into account the phenomena occurring during droplet flocculation (collision frequency and collision efficiency) in order to predict the effect of flocculation on emulsion stability have been developed^{44,51,53,55,56} but they will not be described here.

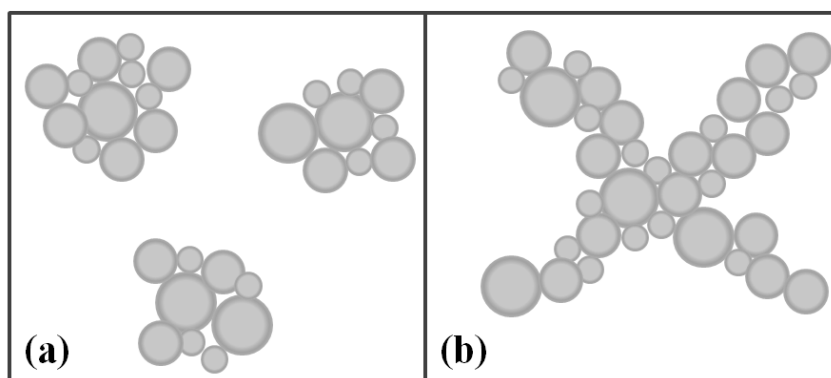


Figure 2-2: Structure of flocculated droplets in (a) dilute emulsion and (b) concentrated emulsion.

There are several methods to control flocculation, depending on the final products. The choice of one of these methods is dictated by the components of the emulsion, and the nature of the emulsion to develop (texture, structure, appearance, etc.)²³. The most efficient way to control the rate and extent of flocculation is to regulate the colloidal interactions between droplets (steric, electrostatic, hydrophobic, etc.).

2.3.3.2 *Coalescence*

Coalescence is the merging of two or more droplets to form a larger single droplet and results in the formation of a layer of oil at the top of emulsion (in the case of O/W emulsions)⁵⁷. This can only occur when the thin film separating two droplets is ruptured. When droplets move close to each other, they may be deformed and the surface of the droplets may be flattened^{17,50,58}. Because the surface area between droplets in contact increases due to the deformation, droplets are more likely to coalesce. The rate at which the thin film ruptures is also of great importance to predict coalescence^{56,59}. Emulsion droplets are moving constantly and so collision time may be very short. However, if this time is long compared to the time required for the film to

break, coalescence is likely to occur. The film rupture mechanisms are largely dependent on the continuous phase properties and on the properties of emulsifiers adsorbed at the droplets. Indeed, emulsifier molecules form a layer, usually called *interfacial membrane*, around the droplets that protects them from rupture. These mechanisms are very complicated and almost unique for each emulsion as they strongly depend on the system properties²³.

Preventing droplet coalescence is a major issue in emulsion stabilisation. A few methods have been developed to control or even prevent coalescence. As coalescence depends both on the colloidal and hydrodynamic interactions between the droplets, and the physic-chemical properties of the components used in the emulsion (particularly the continuous phase and the emulsifier), reducing or preventing droplets contact and interfacial membrane rupture are the two points on which efforts have to be made to prevent coalescence⁶⁰.

Droplet coalescence is mostly prevented by the presence of emulsifiers adsorbed at the oil-water interface. Surfactants' ability to prevent coalescence depends on their physic-chemical properties. For example, the presence of charged (positive or negative) emulsifiers at the droplet interface induces electrostatic repulsion between the droplets, which tends to prevent droplet contact. There are many different emulsifiers. Surface active agents (Surfactants) are the most common emulsifiers. They are very efficient to reduce interfacial tension and prevent droplet contact. Proteins have been shown to provide long term stability against coalescence^{61,62}. Even though the presence of proteins in the emulsion decreases the interfacial tension, it tends to be higher than in case of other surfactants. They form a thick protective interfacial film at the droplets

interface and may provide strong electrostatic repulsive forces between droplets. Fine divided solid particles also provide very good stability against coalescence^{14,63,64}. Solid particles adsorb at the interface and form a solid layer that prevents coalescence. Due to the nature of this emulsifier, the stabilisation mechanisms are quite different from those of emulsions containing surfactant or protein (this will be discussed section 2.5).

2.3.4 *Ostwald ripening*

Ostwald ripening in emulsion is a process of gradual growth of the larger droplets at the expense of smaller ones due to mass transport of soluble dispersed phase (oil) through the continuous phase (water)^{45,65,66}. The solubility of the oil phase increases with decreasing droplet radius. Even though droplet flocculation and coalescence are the most common factors of emulsion instability, Ostwald ripening is an important cause of instability in some food emulsion application, like soft drink emulsions. There are a few methods to control Ostwald ripening²³. As the solubility of the dispersed phase increases with decreasing droplet size, Ostwald ripening will be slowed down if the emulsion droplets are bigger. However, coalescence and flocculation are more likely to occur. In emulsions with a narrow droplet size distribution, i.e. the difference between the smallest and the biggest droplets is small, Ostwald ripening will also be retarded. The solubility of oil in water is due to the presence and the properties of emulsifier. By using emulsifiers that do not increase the oil solubility, Ostwald ripening will be reduced.

2.3.5 Characterisation of emulsion instability phenomena

2.3.5.1 Droplet size measurement

The evolution of droplet size with time is the main parameter to characterise the stability of emulsions because instability phenomena either affect or are affected by the droplet size. Coalescence and Ostwald ripening tend to increase the average droplet size. Flocculation does not affect the droplet size because droplets do not merge. Nonetheless, the presence of flocs may induce a wrong characterisation. Creaming, and more specifically the creaming rate, is directly affected by the size of droplets. Thus, the droplet size measurement is of great importance as it provides a lot of information about the emulsion properties. Many techniques have been developed to measure droplet size distribution; the most used techniques are microscopy⁶⁷, light scattering⁶⁸⁻⁷⁰, ultrasonic methods⁷¹⁻⁷³ and more recently NMR^{69,74,75}.

2.3.5.2 Creaming/Sedimentation characterisation

Creaming or sedimentation process occurring in emulsion can be easily assessed by optical observations. Indeed, in most cases, creaming is characterised by a whitish/yellowish layer at the top of emulsion, while a layer appears at the bottom of an emulsion if sedimentation occurs. Creaming/sedimentation rate can be determined by measuring the volume of cream/sediment in the emulsion with time. This may be done by placing the emulsion in a calibrated beaker or tube and measuring the height of the cream/sediment every second, minute ... (as chosen by user).

In some cases, visual observations are not accurate enough to measure the creaming/sedimentation rate; creaming or sedimentation can occur very quickly or the distinction between continuous phase and cream/sediment layer is difficult to visualise. More sophisticated techniques are then used to measure the creaming rate, using light scattering⁴⁹ or ultrasonic imaging⁷⁶.

2.3.5.3 *Flocculation characterisation*

The easiest method to observe the flocculation of droplets is probably the use of a microscope, even though special care has to be taken not to break the flocs when preparing microscope slides. Image analysis techniques can be used to determine the size of droplets or flocs⁷⁷. Particle sizing instruments can also be used to measure the size of the flocs. The flocculation rate can be determined by measuring the floc size as a function of time.

2.3.5.4 *Coalescence and Ostwald ripening characterisation*

A lot of methods exist to characterise coalescence and Ostwald ripening, even though it may be a challenge to distinguish the two phenomena as they both involve an increase of the average droplet size. The use of optical microscope is the most direct method. Few millilitres of emulsion are placed between microscope slides and changes in droplet shape and size are monitored with time, using eventually image analysis techniques. More sophisticated microscopy techniques to measure coalescence also exist⁷⁸. Coalescence and Ostwald ripening can also be characterised by measuring the evolution of the droplet size distribution with time by using particle sizing techniques.

2.3.5.5 *How to distinguish flocculation, coalescence and Ostwald ripening?*

It is important to determine whether the increase in droplet size is due to coalescence, Ostwald ripening or flocculation. Microscopy techniques can be used to make the distinction between these phenomena. However, most of the microscopes provide 2-D images which may be confusing; two droplets may seem to merge when they are actually only weakly aggregated one over the other which can only be seen in three dimensions. Analysing the time dependence of the droplet size distribution with particle sizing instruments provides information about the increase of the average droplet size. Nonetheless, it is very difficult, from these methods, to know which phenomenon is responsible for the increase.

The simplest method to determine which phenomenon is responsible for the increase of size is to alter the emulsion in order to break the flocs. This can be done for example by modifying the solvent conditions or by applying mechanical agitation. Then droplet size measurement will tell whether flocs are present in the emulsion or not; if there are no flocs, droplets size will not change whereas if there are flocs, droplet size will decrease after emulsion alteration.

It is also possible to use a dye to distinguish the droplets. Two emulsions are prepared with exactly the same components and the same protocol, except that one bulk dispersed phase is dyed, blue for example, and the other bulk phase is dyed, yellow for example. Then the two emulsions are poured together in a vessel. If coalescence occurs, many green droplets should be visible, whereas if there is no coalesced droplet, only

blue and yellow droplets will be seen. In the former case increase of the droplet size is assumed to be due to droplet flocculation.

2.4 *Surfactant-stabilised emulsion*

2.4.1 *Surfactant definition*

A **surfactant**, contraction of the term *surface-active agent*, is a substance that has the property of adsorbing onto the interfaces and of altering significantly the interfacial free energy of those interfaces. Note that the term interface is used here to describe fluid/fluid or fluid/gas interfaces. When one of the fluids is gas (most commonly air) the term *surface* tends to be used instead of *interface*. Surfactants usually act to reduce the interfacial free energy rather than to increase it. Surface-active agents have a characteristic molecular structure, known as **amphipathic** structure. This consists of a group that has no or little attraction for the solvent, called **lyophobic group**, and a group that has strong attraction for the solvent, called **lyophilic group**. In aqueous media, the terms **hydrophobic** or **hydrophilic** groups are used as lyophobic or lyophilic groups respectively. The surfactant structure is then called **amphiphilic**. Hydrophilic and hydrophobic moieties of the surfactant are commonly called **head** and **tails** respectively. Since the solvent used in this study was water, the terms hydrophilic, hydrophobic and amphiphilic will be used to describe the nature of the surfactants.

The nature of head and tail groups of surfactants can be very different which offers numerous variations of the surfactant structure⁷⁹. The hydrophilic group can be charged or neutral, small and compact in size or a polymeric chain; the hydrophobic group is

usually a single or double, straight or branched hydrocarbon chain, but may also be a fluorocarbon or a siloxane, or contain aromatic group(s). The surfactant's solubility in aqueous media is determined by the affinity of the surfactant hydrophilic part with the media. Surfactant classification is based on the hydrophilic group type as follow:

- *Anionic*: the head moiety bears a negative charge;
- *Cationic*: the head moiety bears a positive charge;
- *Nonionic*: the head moiety bears no apparent charge;
- *Zwitterionic*: the head moiety bears both positive and negative charges.

It is worth to note that anionic and cationic surfactants are generally not compatible, while nonionic and zwitterionic ones are compatible with all other types.

A surfactant dissolved in liquid can either adsorb at the interface or self-assemble to form *micelles* (Figure 2-3). Both phenomena result from the hydrophobic effect^{80,81}. The lyophobic group of the surfactant tends to be expelled from the liquid in which the surfactant is dissolved. The adsorption of surfactants at the interface induces a structural change of the interfacial area, and in many cases, a decrease of the interfacial tension, but this will be discussed further in this Chapter.

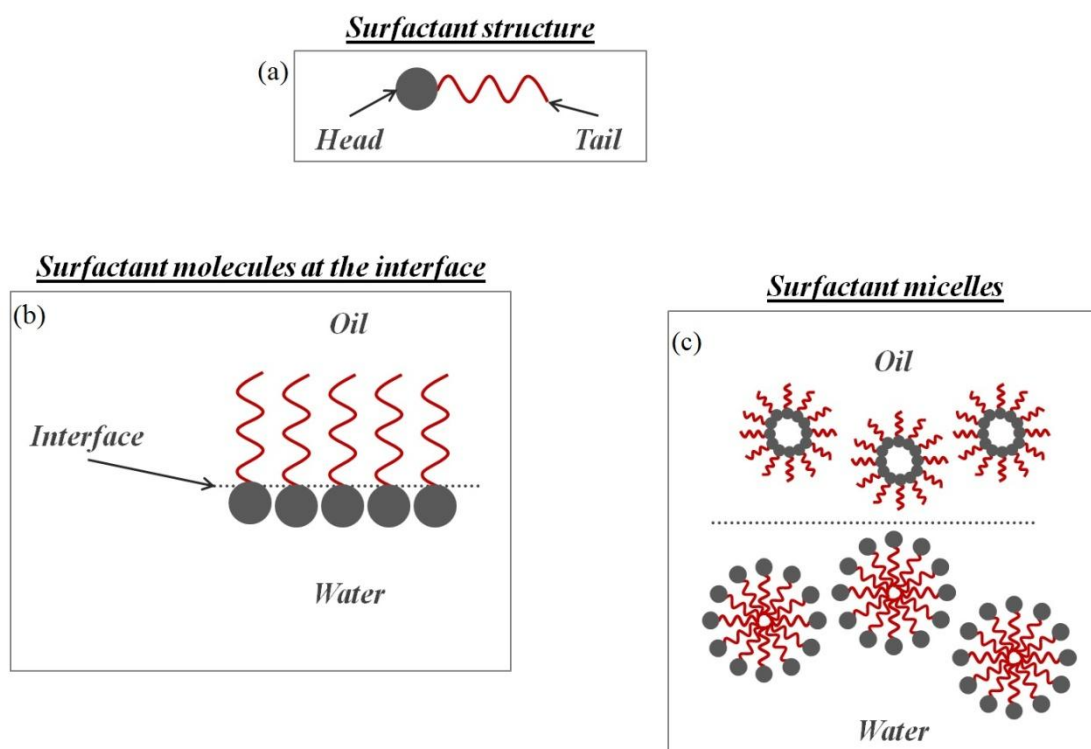


Figure 2-3: Schematic representation of (a) structure of surfactant, (b) surfactant molecules at the interface, and (c) spherical surfactant micelles.

The formation of micelles depends on the surfactant concentration. At sufficiently high concentration micelles form clusters of typically 50 – 200 surfactant molecules. Micelle formation occurs over a fairly sharply defined region called the **critical micelle concentration (CMC)**. Above the CMC, additional surfactant forms the aggregates, whereas the concentration of the unassociated molecules remains almost constant. The size and shape of micelles are governed by the geometry of both lyophobic and lyophilic groups as well as the interactions between surfactant molecules²⁰.

2.4.2 Surfactant as emulsifying agent

Due to the numerous types of surfactants available, from either natural or synthetic sources, they can be used in many fields: detergents, wetting agents, foaming agents, and dispersants. They have also been extensively used as emulsifiers, in many fields: foods, cosmetics, painting, pharmaceuticals, etc. This topic has been long investigated and a very significant amount of studies can be found in the literature, either as theoretical work^{20,22,82-89} or applications in specific fields^{2,3,23,90-95}.

As mentioned earlier in this chapter, three main processes occur simultaneously during emulsification; dispersed bulk phase is broken up and droplets are formed, emulsifier molecules are adsorbed onto the newly formed droplets and droplets encounter each other. These processes also occur numerous times during emulsion formation. The surfactant has two main roles to play: it lowers interfacial tension, facilitating droplet break-up and it prevents re-coalescence^{22,86,89}.

Due to its amphiphilic character, surfactant has its hydrophilic moiety in water and its hydrophobic moiety in oil. The molecules of surfactant adsorbed at the interface replaces the water and oil molecules of the original interface, and thus, the interaction across the interface is now between the hydrophilic group of the surfactant and water on one side and between the hydrophobic group and the oil on the other side of the interface²⁰. The presence of surfactant at the interface increases the interactions between oil and water molecules, which tends to reduce the tension across the interface. It seems obvious that by increasing the concentration of surfactant, the interfacial tension

decreases. Different surfactants also lower the interfacial tension to a different degree which affects the final droplet size.

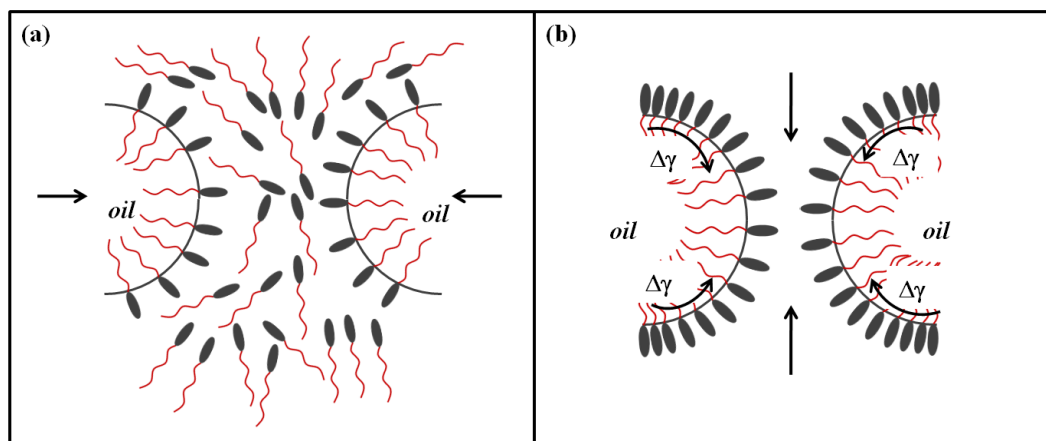


Figure 2-4: Schematic representation of the Gibbs-Marangoni effect acting on two approaching droplets during emulsification. (a) Droplets insufficiently covered approaching; surfactants dispersed in the water phase are less numerous where the film is thinner. (b) Droplets are not covered uniformly by the surfactants, inducing an interfacial tension gradient (bent arrows) responsible for the thin film.

Re-coalescence also depends on the surfactant concentration in the system. If the surfactant concentration is too low to form a protective layer around the droplets, droplets tend to coalesce as they collide. Prevention of coalescence of formed droplets is due to the Gibbs-Marangoni effect⁹⁶ (see Figure 2-4). Consider two droplets insufficiently covered by surfactant, moving towards each other. During their approach, more surfactants get adsorbed at the interface of the two droplets. However, the amount of surfactant available for adsorption is the lowest where the film between the droplets is the thinnest. The coverage of the droplets is then not uniform; less surfactant molecules are present at the region of the interface where the droplets are the closest. This leads to an interfacial tension gradient, which is the highest where the film is the thinnest. The gradient causes surfactant to move at the interface towards the site of

lowest surfactant coverage. This causes water to move in the direction of the highest interfacial tension, which thus drives the droplets away from each other. Moreover, due to specific properties of the surfactant (anionic, cationic, etc.), repulsive interactions exist at the droplet surface which also enhance the prevention of coalescence, during emulsification or at quiescent conditions.

When no emulsifiers are added to pure oil and water system, the type of emulsion depends on the volume fraction of each phase. The phase with the lowest volume fraction will be the dispersed phase. In the presence of surfactant, the type of emulsion is due only to the surfactant properties. For example, mayonnaise is an O/W emulsion even though there is about 80% of oil, due to the presence of lecithin. Surfactant can be dissolved in oil or water, depending on the size of the head group and tail group. Bancroft linked the surfactant ability to stabilise W/O or O/W emulsions to its solubility in oil or water. This is known as Bancroft rule⁸³: oil soluble surfactant tends to stabilise W/O emulsion, while water soluble surfactant tends to stabilise O/W emulsion.

The theoretical choice of surfactant is complicated as both oil and water phases are of variable composition. Experiments are then necessary in many cases to determine which surfactant is suitable for a given system. However, some methods exist to select surfactant as emulsifying agents^{20,79}. The most frequently used method is the **Hydrophilic-Lipophilic Balance (HLB)** method. First described by Griffin^{97,98}, this method assigned a number to the surfactant, between 0 and 20, related to the balance between the hydrophilic and lipophilic parts of the surfactant. In some cases, HLB is calculated from the surfactant molecule structure and in other cases, HLB is based on experimental data. It is worth to note that HLB can also be assigned to agents which are

not considered as surfactant, but are frequently used as emulsifiers, such as protein. In that case, HLB is based on emulsification experiments. The Table 2-1 shows the classification of surfactants according to their HLB values and ability to stabilise emulsions^{38,97}. In some cases, in order to obtain the right HLB for a given system, surfactants can be mixed; typically, as suggested by the Bancroft rule, W/O surfactant is dissolved in the oil phase and O/W surfactant in the aqueous phase.

Table 2-1: Surfactant characterisation as a function of HLB value.

Application	HLB range
<i>W/O emulsifier</i>	3 – 6
Wetting Agent	7 – 9
<i>O/W emulsifier</i>	8 – 18+
Detergent	13 – 16
Solubiliser	15 – 18

2.4.3 Examples of W/O surfactant-stabilised emulsion

The word ***lecithin*** was originally used in 1847 by French chemist and pharmacist Theodore Gobley to designate pure phosphatidylcholine. Lecithin is nowadays a generic term to designate any group of yellow-brownish fatty substances occurring in animal and plant tissues, and in egg yolk. Lecithin can easily be extracted chemically or mechanically from readily available sources such as soy beans. Lecithin has been used for many years as emulsifier, particularly to stabilise mayonnaise, and also in many different fields⁹⁹. One the characteristic of lecithin is that it can be used as O/W or W/O emulsifier¹⁰⁰⁻¹⁰², depending on the source from which it is extracted or the composition of the emulsion.

Pan *et al.*¹⁰² investigated the effect of various types of sunflower lecithin on the stability of W/O (30/70) emulsions. They showed that the emulsion droplet size depended on the surfactant concentration; at 0.1% lecithin, the droplet size was similar to the size of an emulsion with no emulsifier, while at 1.0% the droplets significantly decreased in size. Sedimentation at high lecithin concentration was slower than at 0.1% and could even be stopped by increasing the level of phospholipids in the lecithin. However, they showed that W/O emulsions with 0.1% sunflower lecithin were more stable against coalescence. A mechanism explaining the ability of lecithin to stabilise emulsion was given by Shchipunov and Schmiedel¹⁰³, based on two observations of the oil-water interface in the presence of lecithin. The first observation was the formation of a thick film at the interface. The second was the formation of a liquid phase at the interface, less dense than oil and water, which separates from the interface. They suggested a mechanism in which water is transferred from aqueous solution into the oil phase through hydration of the adsorbed lecithin. This promotes a sequence of phase at the interface; spherical surfactant micelle shape changes to precipitated compact gel. This gel-like structure, as well as the thick layer, would give these good stabilising agent properties to the lecithin.

Monoolein is another example of a W/O surfactant. It is a generic term to designate any monoglyceride of oleic acid. *Glycerol monooleate* (*GMO*) is a very common form of monoolein. GMO is a clear amber liquid, insoluble in water¹⁰⁴⁻¹⁰⁶. This is a synthetic surface-active chemical, widely used as a nonionic surfactant which has numerous food applications¹⁰⁴, despite its complicated structure when mixed with oil and water. Mele *et al.*¹⁰⁷ investigated the formation of long-term stable W/O emulsions based on monoolein. Glycerol monooleate was mixed with diglycerol monooleate (DGMO) or

lecithin (LET), at various concentrations. These mixtures were added to triolein, used as “continuous phase”. Water was added to this system in order to determine the phase diagrams of the three phases emulsion (water/monoolein/triolein) at 25°C. Regardless of the system (containing DGMO/LET or not), long-term stable W/O emulsions were formed. However, the emulsion structure depended on the concentration of monoolein and triolein in the system. A microemulsion was formed at very low water content and relatively high triolein content (> 35%). A W/O emulsion was formed at triolein content between 10 and 20%, water content above 20% and monoolein content below 70%. A two-phases region exists at low water content (< 20%) and triolein content between 5 and 35%, where a dominant reverse hexagonal phases coexists with very small amount of lamellar phase. Depending on the content of each phase (water/monoolein/triolein), emulsion structure was shown to differ from “classic” emulsion to microemulsion and crystal lattice.

2.4.4 Examples of O/W surfactant-stabilised emulsion

Tween surfactants, also known as *polysorbates*, are *polyoxyethylene* (POE) type nonionic surfactants commonly used as emulsifier in a wide variety of food, cosmetic and pharmaceutical products¹⁰⁸⁻¹¹¹. The most common types of Tween are listed below:

- Tween 20 or polyoxyethylene (20) sorbitan monolaurate;
- Tween 40 or polyoxyethylene (20) sorbitan monopalmitate;
- Tween 60 or polyoxyethylene (20) sorbitan monostearate;
- Tween 80 or polyoxyethylene (20) sorbitan monooleate.

The number 20 in brackets refers to the total number of oxyethylene groups - (CH₂CH₂O)- found in the molecule (head group). The number following Tween (20, 40, 60 or 80) is related to the type of fatty acid associated with the polyoxyethylene sorbitan part of the molecule (tail group).

Hsu and Nacu¹¹² investigated the stability of soybean oil-in-water emulsions with a series of Tween (20, 60, 80 and 85). Regardless of the type of surfactant, O/W emulsions were found to be stable for at least a few days. Nonetheless, the surfactant concentration required to stabilise emulsions depended on the type of Tween. Tween 20 stabilised emulsion at a relatively low concentration, but it was necessary to increase the concentration of other Tween surfactants to provide stable emulsions. Moreover, it was shown that Tween 20 yields the smallest droplets, while Tween 80 has the lowest efficiency in terms of droplet size reduction. The evolution of droplet size with surfactant concentration also showed that in case of Tween 60, increasing the concentration above the minimum concentration to stabilise emulsion had no effect on the droplet size, while in case of Tween 85, droplet size keeps on decreasing by increasing the surfactant concentration (in the range of concentrations studied).

Protein is not considered as a surfactant due to its physicochemical properties. However, proteins are the most commonly used emulsifier in the food industry. They are natural, non-toxic, cheap and widely available, thus making them ideal ingredients^{61,96,113}. They stabilise emulsions by forming a viscoelastic adsorbed layer around the droplets. Stabilisation of the interface is achieved in three stages: adsorption, denaturation and coagulation¹¹⁴. There are many different proteins used to stabilise emulsions, e.g. milk protein¹¹⁵, egg protein¹¹⁶ or vegetable protein¹¹⁷.

Casein is the predominant phosphoprotein, that accounts for nearly 20% of the proteins in cow milk and cheese. Casein is often referred as Sodium Caseinate, Calcium Caseinate or milk protein. Many studies have been published about the stabilisation of O/W emulsions by Sodium Caseinate^{111,118-121}.

2.5 Pickering emulsion

The fact that emulsions can be stabilised by finely divided solid particles was first reported over a century ago. Ramsden first mentioned in 1903 that “*solid matter has the power of forming persistent emulsions*”¹²². Nonetheless, the discovery of this type of emulsions is usually ascribed to Pickering (hence the term “Pickering emulsions”) who published the first extensive experimental study on particle-stabilised emulsions for plant spray applications⁶⁴.

A few studies on the ability of solid particles to stabilise emulsion was published during the few decades following the discovery by Pickering^{89,123-126}, but interest in this type of emulsions has only seriously increased in the last three decades, mainly due to their potential for enhanced stability, over the more common surfactant stabilised emulsions, and also as a result of the recent achievements in material sciences and nanoparticle technology¹²⁷⁻¹³⁰. Consequently, some reviews describing the stabilisation mechanisms of Pickering emulsions and comparing particles and surfactants, in terms of their ability to stabilise emulsions and foams, have recently been published^{14,131-133}. The ability of many different kinds of solid particles to stabilise emulsions has been investigated, such as silica, clays, calcium carbonate, polystyrene, hydroxides, etc. Theoretical understanding on the behaviour of these systems can be gained from the food science

area, since it has been known for some time that in many food emulsions, stabilised primarily by phospholipids or proteins, particles are necessary for the required stabilisation, e.g. fat particles in margarine¹³⁴. Other industrial applications can be encountered in areas including cosmetics, pharmaceuticals, oil-recovery and wastewater treatment¹³³.

2.5.1 Pickering stabilisation mechanisms

Due to the growing interest in emulsions stabilised by fine divided solid particles, a significant amount of work has been published for the last few decades. Thus, the stabilisation mechanisms are well understood. Emulsion stabilisation by colloidal particles occurs as a result of their strong adsorption at the water-oil interface, which was first quantified by Levine *et al.*¹³⁵. Assuming that the particle is small enough that the effect of gravity can be neglected, the energy E required to remove a spherical particle from the oil-water interface is given by:

$$E = \pi r^2 \gamma_{ow} (1 \pm \cos \theta)^2 \quad (2.4)$$

where r is the radius of the particle, γ_{ow} the interfacial tension between oil and water and θ the **contact angle** that the particle has at the interface (see Figure 2-5). The sign inside the bracket is negative if the particle is removed into the water phase and positive if removed into the oil phase.

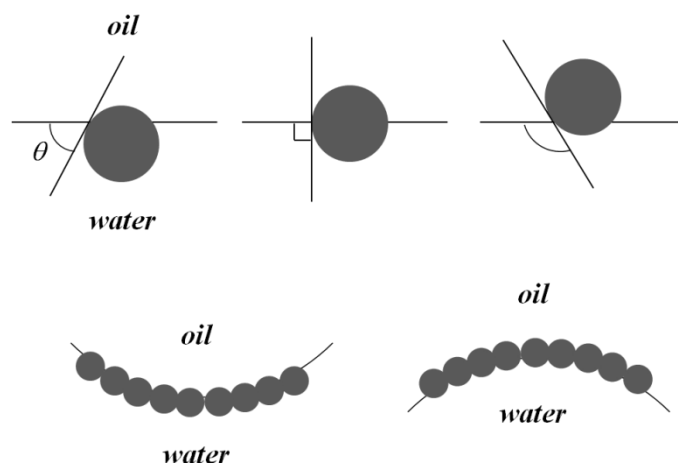


Figure 2-5: (Upper) Various contact angles of a small particle at a planar oil-water interface; (Lower) Position of solid particles at a curved interface – for $\theta < 90^\circ$ (left) O/W emulsion can be formed, for $\theta > 90^\circ$ (right) W/O emulsion can be formed.

The adsorption of a particle at the oil-water interface is driven by its degree of hydrophobicity. The positioning of a spherical particle at the interface can be best quantified by the contact angle θ . Equation 2-4 shows that the maximum energy required to remove the particle from the interface is reached for $\theta = 90^\circ$. In many ways like the surfactant's HLB, the contact angle determines the type of emulsion that the particle can stabilise¹³¹. Particles of contact angles (measured through the water phase) $\theta < 90^\circ$ tend to stabilise O/W emulsions and particles of $\theta > 90^\circ$ tend to stabilise W/O emulsions. However, pure hydrophilic particles (very small contact angle) or too hydrophobic (very high contact angle) particles are more likely to stay dispersed in the water or the oil phase respectively.

In other words, the ability of particles to stabilise an emulsion depends on its wettability by the oil and water phases of the emulsion^{64,89,125,136}. Particles that cannot be wetted by one of the two liquids do not act as emulsifiers as they remain in the liquid in which they are dispersed. Emulsion stability by solid particles requires then that these particles

are wetted by both liquids. Nonetheless, particles must be wetted more by one liquid than the other, which determines the type of emulsion; water-wetted particles should stabilise O/W emulsions, while oil-wetted particles should stabilise W/O emulsions.

Like surfactants, solid particles acting as emulsifier are adsorbed at the oil-water interface. However, despite the fact that particles sit at the interface, their effects on the interfacial tension remain not well-understood. Only a few studies have been published and the results presented in these works seem to be contradictory, since some authors mentioned that the particles do not modify the interfacial tension, while some demonstrated that interfacial tension was affected by the presence of particles. Vignati *et al.*¹³⁷ investigated the effect of silica particle concentration and hydrophobicity on isooctane/water and octanol/water systems respectively. They first showed that hydrophilic particles adsorbed at the interface do not modify the interfacial tension, at any colloids concentration. Then the demonstration was made that by increasing the hydrophobicity of the particles, interfacial tension did also not change. The presence of particles, regardless of their concentration and hydrophobicity, was shown not to affect the interfacial tension. This was confirmed by Drelich *et al.*¹³⁸ who proved experimentally that interfacial tension of paraffin oil-water was not modified by the presence of hydrophobic silica particles.

However, these experimental data are in contradiction with the conclusions made by Levine *et al.*¹³⁹. They developed a theoretical model to calculate the interfacial tension of oil-water-particles system in which particles are closely packed at a planar interface. According to this model, the interfacial tension depends on the particles' hydrophobicity; the interfacial tension decreases as contact angle increases from 0° to

90° or decreases from 180° to 90°. This was supported by recent experiments. Kim *et al.*¹⁴⁰ investigated the amphiphilic character of graphite oxide. They measured the interfacial tension of toluene-water system in the presence of particles at various pHs. It was shown that, regardless of the pH, the adsorption of graphite oxide at the interface lowered the interfacial tension. Moreover, the decrease of interfacial tension was greater as the pH decreased. Glaser *et al.*¹⁴¹ published a study about the effect of Janus particles (amphiphilic particles with a hydrophilic hemisphere and a hydrophobic hemisphere) at the liquid-liquid interface. Janus particles were made of iron oxide (Fe₃O₄, hydrophilic particles) and gold (hydrophobic particles). The *n*-hexane/water interfacial was measured in the presence of iron oxide or gold, and it was shown that the presence of these metals at the interface lowers the interfacial tension in a very similar way. Compared to these homogenous particles, Janus particles have higher interfacial activities; interfacial tension measured in the presence of Janus particles was significantly lower than the one measured with either iron oxide or gold.

The examples given above show the contradictory effect of particles adsorbed at the oil-water interface. However, these particles (hydrophilic or hydrophobic silica, graphite oxide, Janus particles) were proved to provide, under certain conditions, long-term stable emulsions (O/W or W/O). As this stability cannot be directly linked to the lowering of the interfacial tension, it is worth wondering how solid particles stabilise emulsions.

Pickering⁶⁴ was the first to mention that emulsion stabilisation should not depend on a decrease of the interfacial tension but on the size of the colloidal particles. Tambe and Sharma investigated the mechanism of coalescence of droplets covered by solid

particles¹⁴². When they are adsorbed at the interface, solid particles form a solid layer around the droplets which prevents the droplets to coalesce. Thus, the ability of particles to stabilise emulsion depends on the magnitude of the steric hindrance to droplet coalescence. Tambe and Sharma considered that a spherical particle could be displaced from the interface by three different mechanisms. The particle can be:

- pushed into the dispersed phase (due to droplet collision);
- pulled into the continuous phase by gravity;
- displaced laterally at the interface.

The latter is due to the movement of the continuous phase liquid that flows during the formation of the thin film between droplets. As shown Figure 2-6a, the force required to push particles into the dispersed phase is extremely large compared to the others. Coalescence is unlikely to be due to the displacement of the particles into the droplet. The authors suggested that coalescence is only possible when particles are laterally displaced at the interface, making the uncovered droplet surface large enough for the droplets to merge. Droplets insufficiently covered tend to coalesce due to particle displacement along the interface (Figure 2-6b). Thus, the effectiveness of solid particles in stabilising emulsions seems to be due to the formation closely packed layer of particles at the oil-water interface. Nonetheless, some recent studies have shown that emulsions could be stabilised by solid particles despite of low droplet surface coverage^{137,143}. Vignati et al. investigated systems where the silica concentration was only 15% of a packed monolayer, and showed that emulsions were stable in this range. They proved that individual particles adsorbed at the interface exhibited Brownian

motion, which suggests that, below concentrations causing packed networking, individual particles can easily move laterally around the droplet surface.

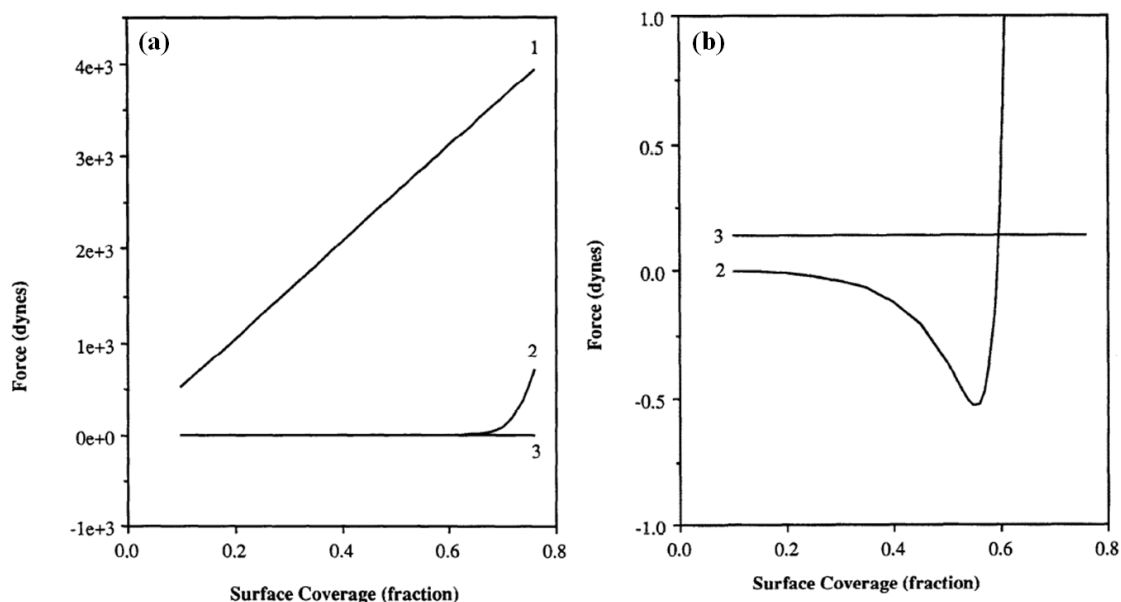


Figure 2-6: Extracted from Tambe and Sharma publication¹⁴². (a) comparison between the force required to push particles into the dispersed phase (curve 1), the force required to displace particles laterally along the interface (curve 2) and the force due to gravity for two droplets to coalesce (curve 3). (b) Zoom on the curves 2 and 3 of the figure (a).

2.5.2 Parameters influencing the stability of Pickering emulsions

2.5.2.1 Hydrophobicity

As mentioned earlier, the strength at which a particle is adsorbed at the oil-water interface depends on its hydrophobicity, which is directly related to the contact angle that this particle assumes at the oil-water interfaces. Particles must be wetted by both liquids to be adsorbed at the interface; too hydrophilic or hydrophobic particles remain

in the liquid in which they are dispersed. The effect of particle hydrophobicity on emulsion stability has received a lot of interest^{89,125,136,144-147}. Binks and co-workers have shown that predictions based on considerations of the energy of attachment of a spherical particle at the oil-water interface (Equation 2.4) were directly related to emulsion stability^{136,144}. It is generally accepted nowadays that particles with a contact angle between 60° and 80° stabilise O/W emulsions while those with a contact angle between 100° and 130° stabilise W/O emulsions.

2.5.2.2 *Oil type and volume fraction*

The type of emulsions stabilised by particles with a contact angle around 90° depends on the volume fraction of water^{148,149}. For emulsions prepared with toluene-water, it was shown that when the volume fraction of water is lower than 0.6, a W/O emulsion was formed while an O/W emulsion was formed for higher volume fractions of water. The ability to make O/W or W/O emulsions with the same particles, for a given oil-water system, represents a significant advantage compared to surfactant systems.

Particles at intermediate hydrophobicity (contact angle around 90°) can be dispersed in both water and oil. Binks and Lumsdon¹⁵⁰ showed that, for the same toluene-water system in the presence of particles at intermediate hydrophobicity, the type of emulsion was also dictated by the phase in which the particles were initially dispersed; W/O emulsions were preferentially formed if particles were dispersed in oil, while O/W emulsions were preferentially formed if particles were dispersed in water.

The effect of oil type was also investigated in the same study. The authors showed that O/W emulsions were preferentially formed when polar oils (hydrocarbons) were used whereas W/O emulsions were preferentially formed when non-polar oils (esters, alcohols) were used. This was confirmed by Frelichowska *et al.*¹⁵¹ who investigated the effect of oil type on the stability of O/W emulsions in the presence of purely hydrophilic silica particles. They proved that O/W emulsions could only be stabilised by bare silica particles, i.e. silica particles which received no surface treatment and remain hydrophilic, if polar oils were used. Interfacial tension was used to provide a criterion for the selection of favourable oils; oils for which oil-water interfacial tension was lower than about 15 mN/m provide stable O/W emulsions, provided the particles were dispersed in aqueous phase.

2.5.2.3 *Solid particles concentration*

Tambe and Sharma showed that droplets must be covered by closely packed layer of particles in order to prevent coalescence¹⁴². This was confirmed by Frelichowska *et al.*¹⁵² who investigated the effect of hydrophobic silica particles on the stability of O/W emulsions. They proved that at low silica concentration, emulsions were not stable, while by increasing the silica content, emulsion stability was enhanced. Moreover, they showed that droplet size could be controlled by adjusting particle concentration, even though beyond a certain silica concentration, there was no change in the droplet size. They also showed that the oil-to-silica ratio was the relevant parameter to control the droplet size.

Many authors have investigated the effect of solid particle content on droplet size^{14,153-155}; they all showed that droplet size decreases by increasing the particles concentration. This is due to limited re-coalescence during emulsification at higher particle content. Disrupted small droplets have a higher surface area that is necessary to cover in order to prevent coalescence of these droplets. By increasing particle concentration, more colloids are available in the system to adsorb at the newly formed droplet surface. The re-coalescence is then stopped at higher particles content. This results in the formation of smaller droplets at high particle content than at low particle content.

2.5.2.4 *Flocculated particles*

Briggs was the first scientist to mention that *“if the finely divided solid forms a stable suspension in one of the liquids, it may be necessary to add a weak flocculating agent before a satisfactory emulsion can be produced; but a powerful flocculating agent will usually prevent emulsification”*¹⁵⁶. Since, many studies have been published regarding the effect of flocculated particles on the emulsion stability^{63,157-163}.

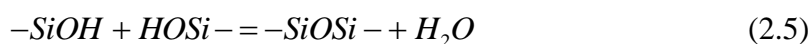
The two main methods to achieve particle flocculation are the addition of electrolytes in the system and the adjustment of the pH of the aqueous phase. Yan et al. investigated the effect of both addition of salt¹⁶² and pH modification¹⁶³ on the stability of an emulsion containing the same compounds (oil, water and particles). They concluded that the zeta potential decreased by either adding salt (from ~43 to 35 mV) or increasing the dispersion pH (from ~40 to 20 mV), which causes the flocculation of particles. The formation of flocs was shown to promote the adsorption of particles at the interface (by

modifying the contact angle) and the formation of a network between particles adsorbed at the interface. Both phenomena are known to enhance emulsion stability^{158,164}.

2.5.3 Silica particles

Among all the solid particles used for the stabilisation of emulsions, silica particles are those which have been the most extensively used in many investigations. This is mainly due to the fact that silica particles are used in many different fields, such as painting, coating, pharmaceuticals, food, etc. and then the surface chemistry of these particles is well known.

The first complete description of silica formation and surface properties was given by Iler¹²⁷. He suggested that particles were formed by polymerisation of monosilicic acid ($\text{Si}(\text{OH})_4$), the soluble form of silica in water. There is general agreement that silica polymerisation, i.e. the reactions that result in an increase in molecular weight of the silica, involves the condensation of silanol groups to form siloxane bounds:



The typical structure of a hydrophilic silica particle is schematically shown in Figure 2-7. The core of the particle is composed of siloxane bounds. The silica surface is composed of silanol groups, which are of different types. Surface SiOH groups are subdivided:

- isolated free (single silanols), $\equiv \text{SiOH}$;
- geminal free (geminal silanols or silanediols), $=\text{Si}(\text{OH})_2$;
- vicinal, or bridged, where OH groups bound through the hydrogen bond (H-bonded single silanols, H-bonded geminals, and their H-bonded combinations).

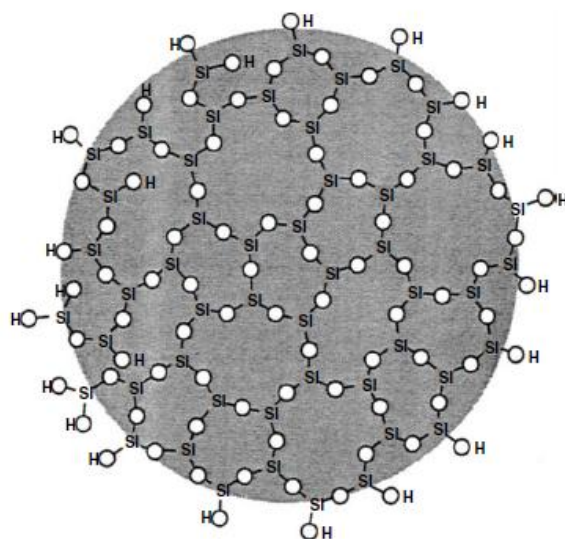


Figure 2-7: Schematic representation in two dimensions of a dehydrated but fully hydroxylated colloidal silica particle. (Taken from “Colloidal Silica: Fundamentals and Applications”¹⁶⁵, Chap. 3.)

Modification of the surface of hydrophilic silica particles is then necessary in order to prepare silica particles at various hydrophobicity levels. There are many ways to modify the silica surface¹⁶⁶⁻¹⁷¹. Zhuravlev developed a physico-chemical model of modification of amorphous silica surface as a function of temperature¹³⁰. He described the different stages of the dehydroxylation of initial raw hydrophilic silica particles by increasing the temperature.

2.6 Mixed-emulsifier stabilised emulsion

Although the properties of emulsifiers, surfactant HLB or particle contact angle, can be used to predict the type of emulsions (O/W or W/O) they will stabilise, the mechanisms of the stabilisation process are different. In recent studies¹³¹⁻¹³³ comparing both emulsifiers (particles and surfactants), the similarities and differences between them

were pointed out. There is the opportunity to make use of the advantages of both surfactant and particle-stabilised emulsions in order to eliminate the disadvantages associated with their individual use as sole emulsifiers. There are few reports of emulsions stabilised by both particles and surfactant^{15,138,142,158,172-189}. In some cases, it was shown that emulsion stability was enhanced by mixing surfactant and solid particles^{158,182}. However, the stabilisation mechanisms, and more particularly the stability enhancement in the presence both surfactant and particles compared to surfactant-stabilised or Pickering systems, remain poorly understood. Note that in this study, the term “mixed-emulsifier” is used to describe systems that contain both solid particles and surfactant. Emulsions stabilised by two different surfactants for example will not be mentioned as mixed-emulsifier stabilised emulsions.

Lucassen-Reynolds and Van Den Temple¹⁵ showed that crystals of glycerol tristearate could stabilise water-in-paraffin oil emulsions if small quantities of surfactants were added. The authors explained this stability by considering the effect of surfactants on the interactions between the crystals. They argued that the addition of surfactant in the system rendered the crystals less flocculated so they can be adsorbed around the water droplets. Further studies^{63,159} reinforced their argument. Midmore¹⁸⁴ investigated the effect of a combination of silica particles (Ludox) and nonionic surfactants containing polyoxyethylene (POE) chains on the stability of O/W emulsions. Particles were found to form single or multiple layers around the oil droplets. The author pointed out that the particles do not have to be necessarily flocculated before emulsification to stabilise emulsions. It was also shown that emulsion stability depended on the POE chain length, with the longest chain surfactants providing the most stable emulsions.

Nonetheless, some studies mentioned that the use of surfactant enhances emulsion stability by slightly flocculating particles^{174,183}. Binks and Rodrigues¹⁷⁴ showed that stabilisation of O/W emulsions occurs when positively charged alumina-coated silica nanoparticles are mixed with the anionic surfactant SDS in water. The condition of stability was the flocculation of particles, at which they have no charge at their surface.

The ability of surfactants to modify the wettability of solid particles has been studied to some extent^{142,172,174,175,180-183,185,189}. The presence of surfactants in the system can modify the surface properties of the particles and thus their hydrophobicities. Tambe and Sharma¹⁴² showed that small concentrations of stearic acid improved the stability of water-in-decane emulsions stabilised by either hydrophilic or hydrophobic particles. Binks *et al.* investigated the effect of a mixture of cationic surfactant (CTAB) and negatively charged silica particles (Ludox HS-30)¹⁷⁵ and a mixture of anionic surfactant (SDS) and positively charged silica particles (Ludox CL)¹⁷⁴ on the stability of O/W emulsions. In both cases, the authors showed that emulsion stability was improved by using both emulsifiers, in comparison to that achieved by using each of them alone. The change in wetting behaviour of solid particles in the presence of surfactant depends on the interactions between surfactant and particles. Wang *et al.*¹⁸⁷ studied the effect of Span 80 (W/O surfactant) on the hydrophobicity of two types of particles, layered double hydroxide (LDH) and Laponite, both prone to stabilise O/W emulsions. They showed that water-in-paraffin oil (W/O) emulsions were stabilised by the mixture of Span 80 and LDH, due to hydrophobisation of the particles by the surfactant. Mixtures of Laponite and Span 80, however, were shown to stabilise O/W emulsions only, regardless of the surfactant concentration.

In a series of publications¹⁷⁶⁻¹⁷⁸, Binks and co-workers have investigated the effect of double-chain cationic surfactant on the stability of emulsions in the presence of hydrophilic silica particles. They showed that double inversion, from O/W to W/O to O/W, was achieved by increasing the surfactant concentration. The first inversion (O/W to W/O) was due to the hydrophobisation of silica particles by the surfactant adsorbed at the oil-water interface. The second inversion (W/O to O/W) occurred by increasing the surfactant concentration as particles are deflocculated and become highly charged again (thus hydrophilic again) through formation of a surfactant bilayer.

In a few recent studies, it was mentioned that the presence of both solid particles and surfactant could lead to the displacement of particles from the interface^{138,183,186}. Vashisth *et al.*¹⁸⁶ investigated the effect of anionic surfactant (SDS) on the stability of O/W emulsion stabilised by slightly hydrophobic silica particles ($\theta \sim 60^\circ$). The authors showed that silica particles were displaced from the interface with increasing SDS concentration. They suggested that at surfactant concentrations insufficient to stabilise emulsions alone, the droplets obtained were stabilised by both particles and surfactant. By increasing the SDS concentration above the critical micelle concentration, particles were fully displaced. Drelich *et al.*¹³⁸ investigated the effect of Span 80 and hydrophobic silica particles on the stability of water-in-paraffin oil emulsion. Particles provided long-term stable emulsions, while emulsions stabilised by Span 80 showed destabilisation processes. A solid particle stabilised emulsion was diluted by a solution containing Span 80. Initially stable, this mixed-emulsifier stabilised emulsion showed the same instabilities as the Span 80 stabilised emulsion after a certain time. The authors

concluded this was due to displacement of silica particles from the interface by surfactant molecules.

The protocol of preparing emulsions stabilised by both surfactant and colloidal particles was found to be very important^{173,179,188}, with Eskandar *et al.*¹⁷⁹ reporting that the phase in which the particles were initially added determined the emulsion stability. O/W emulsions were found to be stable for long periods when the particles were added to the oil phase, but of poor stability when these particles were added in the water phase. The unfavourable adsorption of the particles at the interface is explained by the forces involved when the particles are initially dispersed in water. Repulsive hydration forces and electrostatic forces may prevent silica particle adsorption at the interface. In another study, Whitby *et al.*¹⁸⁸ also reported that the phase in which the surfactant is present plays a significant role in emulsion stability; when the surfactant and the particles were in different phases (surfactant –octadecylamine– in oil and particles –laponite– in water), O/W emulsions were stable against coalescence and the droplet size decreased (in comparison to droplets of O/W emulsions stabilised only with laponite). It was argued that this was due to a better adsorption of the particles at the interface caused by synergistic interactions between surfactant and particles. Emulsions where particles and surfactant were initially included in the water phase were unstable.

2.7 Interfacial Tension

2.7.1 A few examples of surface and interfacial tensions

Surface and interfacial tensions have been measured for many systems. Table 2.2 gives some values of common systems or similar systems to those used in the present work.

Table 2-2: (a) Liquid/Air Surface Tension, (b) Water/Liquid Interfacial Tension and density of common materials at 20°C. All values from Walstra¹⁷, except (1) from Saïen and Akbari¹⁹⁰ and (2) from Gaonkar¹⁹¹.

Material	SFT ^(a) (mN/m)	IFT ^(b) (mN/m)	Density (g/cm ³)
Water	72	-	0.998
Ethanol	22	0	0.789
Paraffin Oil	30	50	0.8
Toluene ⁽¹⁾	29	38	0.866
Benzene	28	35	0.877
Vegetable Oil ⁽²⁾			
Olive oil	/	19	/
Corn oil	/	24	/

Note that no data are presented for vegetable oils surface tension and density. In the study by Gaonkar¹⁹¹ where the interfacial tension values were taken from, no surface tension values were given by the author. These vegetable oils are not pure, they contain impurities that may affect their properties. Any data taken from other studies would probably not agree with these data. For this reason, density and surface tension of vegetable oils are not given here.

Interfacial tension between water and ethanol is 0, which is easily explained by the fact that the two liquids are perfectly miscible at 20°C, and then no interface is formed.

Water/ethanol is a homogeneous mixture for which interfacial tension cannot be measured.

Regarding pure liquids (paraffin oil, toluene and benzene), it is interesting to note that the interfacial tension decreases by increasing the density of oil. This can be explained by the density profile at the interface, as discussed below.

2.7.2 Density profile at the interface

Let us consider two pure immiscible liquids A and B. The interface between these liquids is three-dimensional, with a finite thickness (typically a few molecule diameters) where density changes continuously. As the A/B system strives to minimise its free energy, it seems quite obvious that the density profile in the interface is dictated by the minimisation of the free energy into the interface. There are two factors which influence the shape and profile of the interface¹⁸.

If the interface is considered as a layer of finite thickness (Figure 2-8a), materials in the interface will have densities of intermediate values between the density of liquid A and the density of liquid B. These materials have very high free energy, compared to bulk liquids (Figure 2-8c). As a result, the system will try to minimise the amount of these materials, i.e. minimise the thickness of the interface.

At the interface, each material has a specific density and can only interact with material of the same density. But the density varies sharply in the interface. The sharper the interface is, the greater the density gradient is (Figure 2-8b). Thus, interactions between

materials having the same density are less probable at sharp interface than at broad interface. This results in an increase of the free energy of a specific material. Hence, the minimisation of the free energy at the interface is favoured by a broad interface.

The difference of density of the liquids A and B has two antagonistic effects on the thickness of the interface; one minimises the free energy by reducing the thickness of the interface, the other one minimises the free energy by enlarging the interface¹⁹².

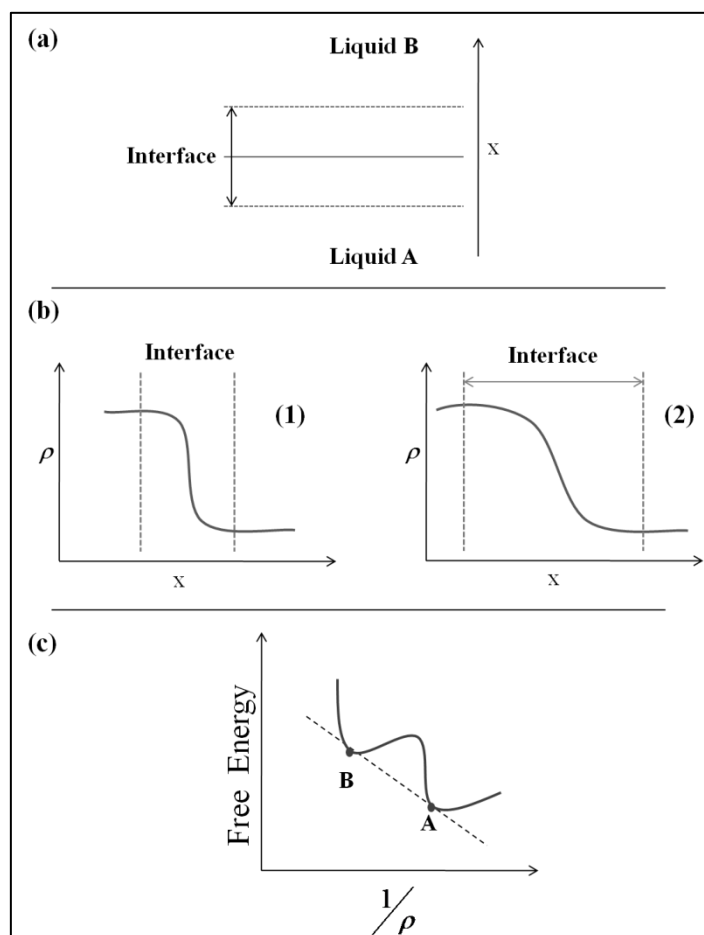


Figure 2-8: (a) Schematisation of "thick" interface; (b) density profile at the interface, (1) sharp profile, (2) broad profile; (c) Free energy at the interface as a function of the inverse of density.

2.7.3 *Parameters influencing interfacial tension*

The two main parameters affecting the interfacial tension are the temperature and the presence of a solute (sugar, salt, surfactant, etc.) in the bulk phases.

When interfacial tension is given, the temperature is usually mentioned. This is because interfacial tension is strongly dependent on the temperature¹⁹³⁻¹⁹⁸. Lutton *et al.*¹⁹⁸ showed that triglyceride oil-water interfacial tension increased by increasing the temperature. They also noticed a “break” in the slope of interfacial tension versus temperature curves for a system containing a small quantity of a surface active agent. They suggested that this break was due to melting of a crystalline monolayer of surface active component at the oil-water interface. Gaonkar¹⁹⁷ also noticed that the interfacial tension of commercially vegetable oil-water systems increased by increasing the temperature. He suggested that the adsorption of the impurities contained in the oil (mono- or diglyceride) decreased with the temperature. In the contrary, Jennings¹⁹⁶ showed that the interfacial tension of pure oil/pure water (benzene and n-decane/water) systems decreased with increasing the temperature. The author linked this decrease to the decrease of density with the temperature. Cabrerizo-Vilchez *et al.*¹⁹⁴ showed the same kind of behaviour; interfacial tension decreasing with temperature. There is no theoretical model to describe the evolution of interfacial tension as a function of temperature, only empirical equations were developed, such as Eötvös’ or Guggenheim-Katayama’s law¹⁹⁹.

The presence of solute is the other main factor that influences interfacial tension. Solute types can be very different, such as sugar, salt, surfactant, etc. Sugar is considered for

having no or extremely little effect on interfacial tension. Salt is known to usually to slightly increase the interfacial tension^{17,197,200-202}. The effect of surfactant on the interfacial tension has been long investigated^{17,18,20,202-209}. As already mentioned, surfactants replace molecules of water and oil at the interface. The interaction across the interface is then between the hydrophilic moiety of the surfactant and water molecules on one side of the interface and between the hydrophobic moiety of the surfactant and the oil molecules on the other side of the interface. These interactions are much stronger than the original oil-water interactions, which reduces significantly the interfacial tension.

2.7.4 Measurement techniques for interfacial tension

A few different techniques have been used for measuring interfacial tension among which *pendant drop*, *spinning drop*, *Wilhelmy plate* or *Du Nouÿ ring* are the most commonly used. They all present advantages and disadvantages and their uses are dictated by the phases' properties and the range of interfacial tension to measure.

Spinning drop is a method where measurements are carried out in a rotating horizontal tube²¹⁰⁻²¹². The tube contains the denser liquid of the two liquids between which interfacial tension is to be measured. One drop of a less dense liquid is placed inside the fluid. Since the rotation of the horizontal tube creates a centrifugal force towards the tube walls, the liquid drop elongates until interfacial tension forces and centrifugal forces are balanced (Figure 2-9). Values obtained at this equilibrium point are used to estimate interfacial tension by using appropriate correlations. This method is usually

preferred for measuring very low interfacial tensions (typically below 10^{-2} mN/m), which are not accessible with the other methods mentioned above.

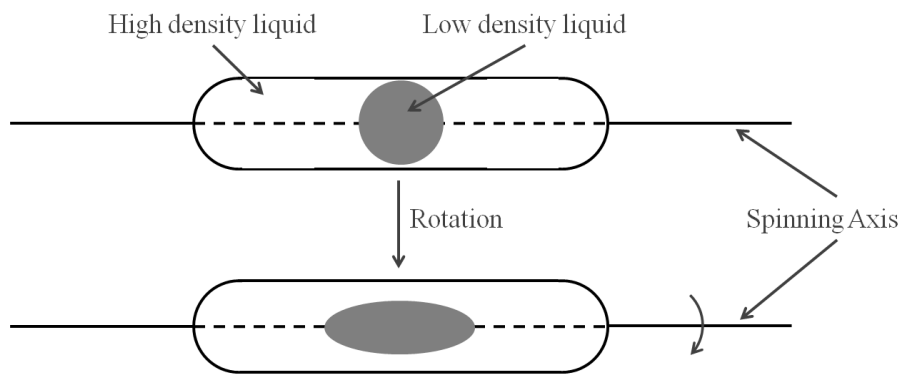


Figure 2-9: Scheme of interfacial tension measurement with Spinning Drop method.

Wilhelmy plate and Du Nouÿ ring are methods of measuring the vertical force acting on a solid body when the former is withdrawn from the interface. The nature of the solid is different for the Wilhelmy plate and for the Du Nouÿ ring (Figure 2-10). A Wilhelmy plate is a vertical thin plate, usually made of Platinum, and a Du Nouÿ ring is a horizontal circular ring, usually made of a mixture of Platinum and Iridium.

In case of the Wilhelmy plate method²¹³⁻²¹⁵, the force F is measured when the lower edge of the plate, oriented perpendicular to the interface, is at the same level as the flat interface (far from the plate). The contact angle between the interface and the surface is extremely small and assumed to be 0. The force pulling up the plate is then given by:

$$F = mg + 2\gamma L \quad (2.6)$$

where m is the mass of the plate, g the acceleration due to gravity, γ the interfacial tension and L the length of the plate. As all the parameters of the Equation 2.6 are known or measured except γ , the interfacial tension is easily calculated.

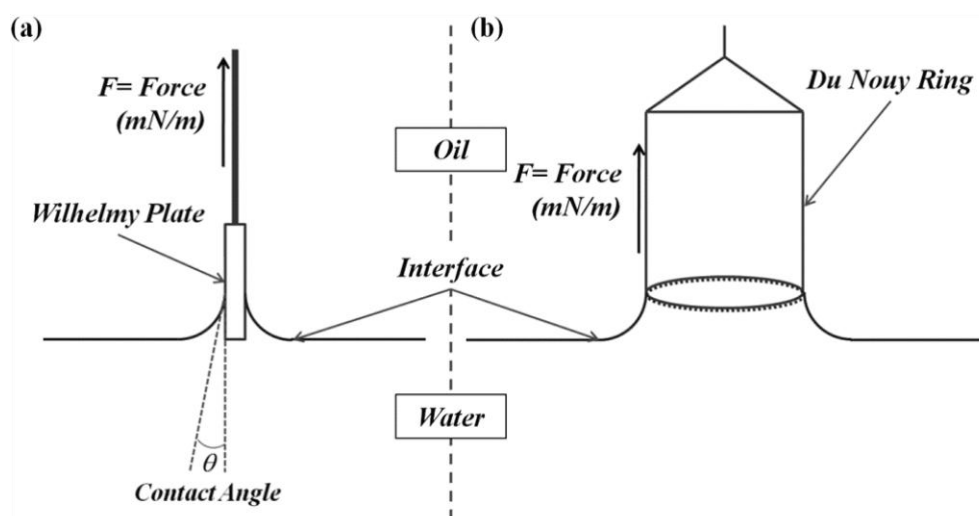


Figure 2-10: Interfacial tension measurement by (a) Wilhelmy plate and (b) Du Nouy ring methods.

The calculation of interfacial tension by the Du Nouy ring method is based on the same principle; the measurement of the “pulling-up” force to determine the interfacial tension²¹⁵⁻²¹⁷. However, due the different geometry, the calculation mathematical model is much more complicated and will not be discussed here. The main advantages of the Wilhelmy plate method are that it does not require the density values of the liquids to be known and it can be used to measure the time dependence of interfacial tension. However, both methods have been used in many studies to measure interfacial tension.

The pendant drop method is another often used method to measure interfacial tension²¹⁸. This method will be described in detail in Chapter 3 as it is the method that was used in this study to measure interfacial tension.

2.8 Wettability and Contact Angle

2.8.1 Introduction

Wetting is a phenomenon easily observable in everyday life. For example, a drop of water on a horizontal glass surface tends to spread to form a thin film layer, while the same drop on a waxed surface tends to remain as a drop, eventually slightly deformed. The ability of a liquid drop to spread on a solid or to keep its original shape depends on the liquid's affinity for the solid; strong affinity will lead the drop to spread, while weak affinity will lead the drop to remain as a drop or to form smaller beads when a shear force is applied on the drop. This affinity is referred to as *wettability*. In other words, wettability is the ease with which an air/solid interface can be converted to a liquid/solid interface when a liquid is dropped onto the solid^{20,219-221}.

Wetting involves three phases: a solid and two immiscible liquids, or a gas, a liquid and a solid, or a gas and two immiscible liquids, or at some extent, three immiscible liquids. As the last two examples of a wetting phenomenon are relatively rare, only the first two examples will be discussed here. The most relevant parameter to characterise the wettability of a solid surface by a liquid is the contact angle θ that a liquid drop makes with the surface (Figure 2-11). As wettability is the ability of a liquid to spread on a solid, the interfacial energies must also be taken into consideration.

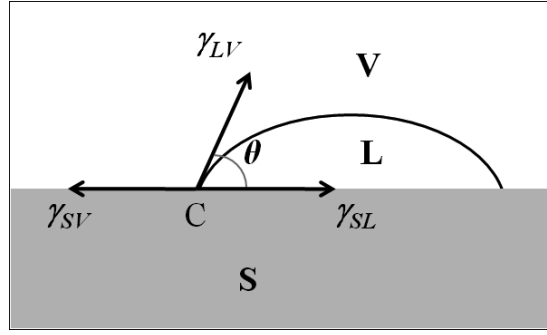


Figure 2-11: Interfacial forces acting on a liquid drop (L) placed on a solid (S) surrounded by vapour (V). γ_{SV} is the interfacial tension between the solid and the vapour; γ_{SL} is the interfacial tension between the solid and the liquid; γ_{LV} is the interfacial tension between the liquid and the vapour.

Note that in Figure 2-11, the two fluids phases are liquid and vapour but the scheme would be the same if the vapour was replaced by a liquid, under the conditions that this liquid is immiscible with the liquid that forms the drop on the solid. In this figure, there are three interfaces: solid-liquid (SL), solid-vapour (SV) and liquid-vapour (LV). The line common to the three phases is called the contact line. If it is assumed that the interfacial tensions γ_{SV} , γ_{SL} and γ_{LV} can be taken as forces even for solid/fluid interfaces, the force balance at point C on the contact line can be written as²¹⁹:

$$\gamma_{SL} + \gamma_{LV} \cos \theta - \gamma_{SV} = 0 \quad (2.7)$$

This equation is known as the Young's equation (also called Young-Dupre equation sometimes) and is essential in the understanding of wetting phenomena. This equation is valid only when there is no adsorption at the interfaces and the interfacial tensions are taken far from the contact point.

The contact angle is very convenient to discuss the wettability of a solid by a liquid, as it can be seen in Figure 2-12:

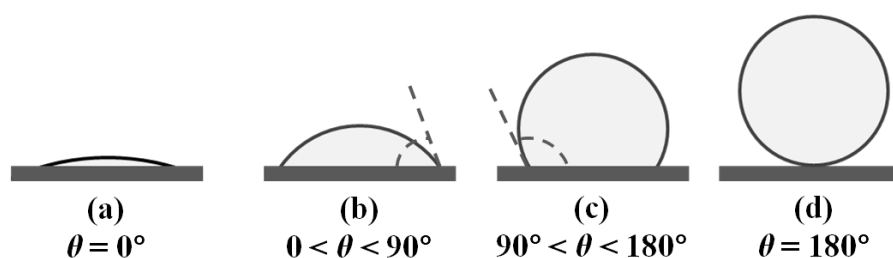


Figure 2-12: Wetting described by various values of the contact angle; (a) Perfect Wetting, (b) Partial Wetting, (c) Non Wetting, and (d) Perfect non-wetting.

When the contact angle is zero (or very close to zero), the solid is perfectly wetted by the liquid. When the contact angle is between 0° and 90° , the solid is partially wetted. Between 90° and 180° , the solid is considered as non-wetted, and at 180° the liquid does not wet at all the solid. It is also common to characterise the wettability of a solid by its surface energy. For example, the wettability of a solid of high surface energy (e.g. magnesium oxide or mercury) by water is excellent, while the wettability of solid of low surface energy (e.g. polyethylene) by water is very poor.

2.8.2 Different types of wetting

Osterhof and Bartell²²² identified three different types of wetting: *spreading*, *adhesional wetting* and *immersional wetting*. A brief overview of these various types of wetting is given here.

2.8.2.1 Spreading

Spreading occurs when a liquid in contact with a solid spreads on the solid and displaces another fluid (air or immiscible liquid) also in contact with the solid (Figure 2-13).

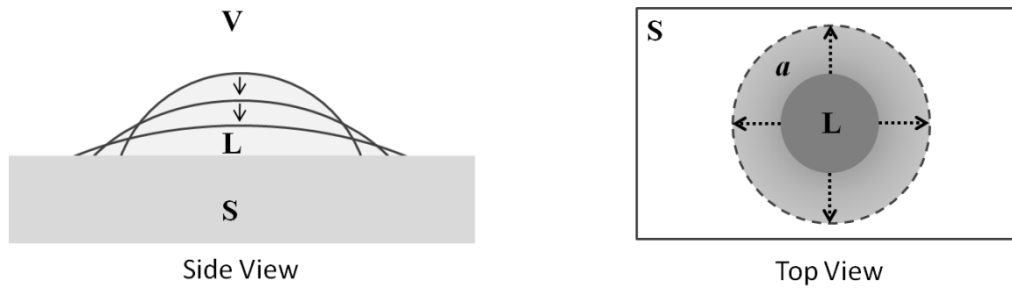


Figure 2-13: Evolution of a liquid drop (L) spreading on the solid (S) surrounded by vapour (V); a is the area covered by the spreading liquid.

During spreading, liquid L completely spreads out on the solid surface which results in a decrease of the surface free energy of the system. If a is the surface covered by the spreading liquid, the decrease in surface energy due to the decrease in area of the solid/vapour interface will be $a \times \gamma_{SV}$. Similarly, the increase in surface energy due to the increase in area of the solid/liquid interface is $a \times \gamma_{SL}$. Since the liquid/vapour interfacial area increases as the liquid spreads over the solid, the increase in surface energy due to the increase in area of the liquid/vapour interface is $a \times \gamma_{LV}$. The total decrease in surface free energy is then given by:

$$-\Delta G = a \times (\gamma_{SV} - \gamma_{SL} - \gamma_{LV}) \quad (2.8)$$

The force that drives the spreading is quantified by $\gamma_{SV} - \gamma_{SL} - \gamma_{LV}$. This quantity is called the *spreading coefficient* S_{LS} :

$$S_{L/S} = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \quad (2.9)$$

Note that the spreading coefficient was defined for vapour/liquid/solid systems. In the same way it can be defined for liquid/liquid/solid systems, gas/liquid/liquid systems or liquid/liquid/liquid systems:

- liquid (L₁)/liquid (L₂)/solid: $S_{L_1/S} = \gamma_{SL_2} - \gamma_{SL_1} - \gamma_{L_1L_2}$, with L₁ the liquid drop spreading over the solid, and L₂ the liquid surrounding the L₁ drop;
- gas/liquid (L₁)/liquid (L₂): $S_{L_1/L_2} = \gamma_{L_2V} - \gamma_{L_1L_2} - \gamma_{L_1V}$, where the liquid L₁ is more dense than the liquid L₂;
- liquid (L₁)/liquid (L₂)/liquid (L₃): $S_{L_1/L_2} = \gamma_{L_2L_3} - \gamma_{L_1L_2} - \gamma_{L_1L_3}$, where density ρ of the liquids is as follow: $\rho_{L_1} > \rho_{L_2} > \rho_{L_3}$.

In case the substrate is a solid (Liquid or gas/liquid/solid systems), the spreading coefficient must be calculated by indirect methods, because the surface and interfacial tensions of solid cannot be measured. Measurement of the contact angle θ between the spreading liquid and the solid is necessary. When the system is at equilibrium, i.e. the liquid has completely spread out or has stopped spreading, Equation 2.9 can be combined with the Young's equation (Equation 2.7), which gives:

$$S_{L/S} = \gamma_{LV} (\cos \theta - 1) \quad (2.10)$$

If θ is 0°, the spreading coefficient will be zero and complete spreading occurs. If θ is 180°, $S_{L/S} = -2\gamma_{LV}$ and the solid is not wet at all by the liquid.

2.8.2.2 Adhesional wetting

Adhesional wetting occurs when a liquid, which is initially not in contact with a solid, makes contact with the solid and adheres to it (Figure 2.14). Contrary to spreading, the vapour/liquid interfacial area decreased as the liquid adheres to the solid. The change in surface free energy is in this case:

$$-\Delta G = a \times (\gamma_{SV} + \gamma_{LV} - \gamma_{SL}) \quad (2.11)$$

where a is the surface of the solid that the liquid covers. The force that drives the adhesion of a liquid to a solid is quantified by $\gamma_{SV} + \gamma_{LV} - \gamma_{SL}$. This quantity is known as the **work of adhesion** W_a , which is the force necessary to separate the liquid from the solid.

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (2.12)$$

Combining Equation 2.12 with Equation 2.7, the work of adhesion can be expressed by:

$$W_a = \gamma_{LV} (\cos \theta + 1) \quad (2.13)$$

In case that θ is 180° , the work of adhesion is zero, which means that the liquid cannot wet the solid.

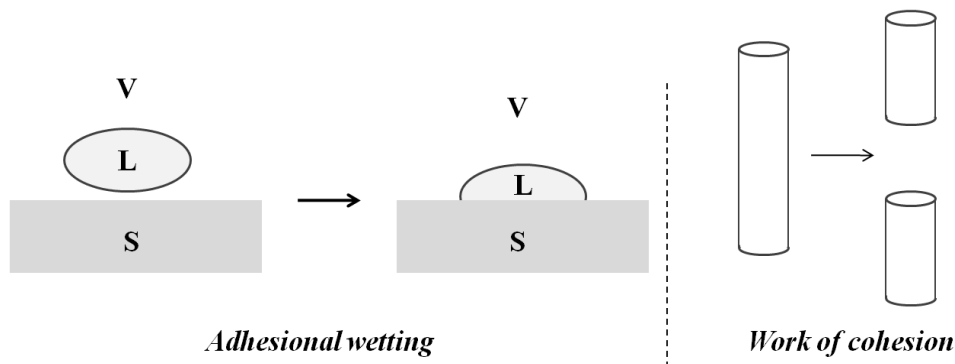


Figure 2-14: Adhesional wetting of liquid (L) on solid (S) surrounded by vapour (V), and schematic representation of the work of cohesion.

The **work of cohesion** W_c is defined as the work required to produce two units area of interface from an original unbroken column of liquid (Figure 2-14) and quantified by: $W_c = 2\gamma_{LV}$. The difference between the work of adhesion and the work of cohesion is the spreading coefficient:

$$S_{L/S} = W_a - W_c \quad (2.14)$$

If $W_a > W_c$ the spreading coefficient will be positive, the contact angle will be zero and the liquid will spread spontaneously over the liquid. If $W_a < W_c$ the spreading coefficient will be negative, the contact angle will be greater than zero and the liquid will not spread over the liquid but will form droplets of a finite contact angle.

2.8.2.3 Immersional wetting

Immersional wetting occurs when a solid is immersed into a liquid through a fluid-fluid interface. The surface free energy in case of complete immersional wetting (Figure 2.15a) is given by:

$$-\Delta G = a \times (\gamma_{SV} - \gamma_{SL}) \quad (2.15)$$

where a is the solid/liquid interface. Note that Equation 2.15 does not take into account the interfacial tension between the liquid and the vapour because at equilibrium the solid is immersed into the liquid, thus there is no three phase contact point.

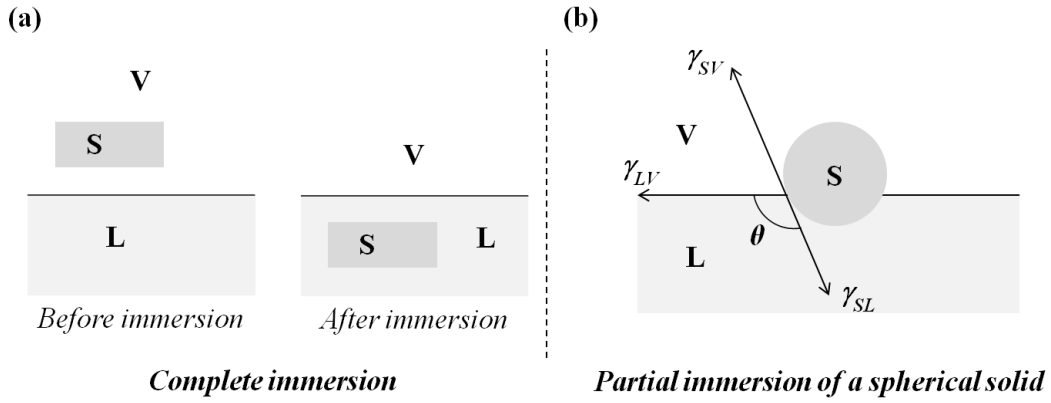


Figure 2-15: Position of a solid for immersional wetting type; (a) complete immersion, (b) partial immersion.

Nonetheless, during immersion, the solid goes through the interface (Figure 2.15b). The spreading coefficient $S_{L/S}$ defined in sub-section 2.8.2.1 is used to quantify the ability of the solid to completely immerse into the liquid. If

- $S_{L/S} \geq 0$, the contact angle θ will be zero and complete immersion will be spontaneous;
- $S_{L/S} < 0$, $\theta > 0$ which means that the solid will only be partially immersed into the liquid. Thus, work must be done to “push” the solid into the liquid and achieve complete immersion. Modification of the interfacial tension, by using surfactant for example, is required to facilitate the immersion.

2.8.3 Contact Angle Measurement

The contact angle that a liquid assumes on a solid surface is of great importance to predict and understand the wetting process between the three phases (gas or liquid/liquid/solid). Two types of contact angle are distinguished: **static contact angle** and **dynamic contact angle**. The static contact angle represents the angle that a liquid

drop of given volume assumes on a solid surface; the dynamic contact angle refers to the situation when the three phase (vapour or liquid/liquid/solid) boundary is in motion. When the drop has expanded on a dry surface, the angle is said to represent the ‘advanced’ contact angle and is called *advancing contact angle*. When the drop has contracted on a wet surface, the angle is said to represent the ‘receded’ contact angle and is called *receding contact angle*²²⁰.

Measurement of the static contact angle gives an idea of the wettability of a solid by a liquid. However, this static contact angle varies with many parameters, among which are the volatility of the liquid and the time required by the liquid to spread on the solid (in case that the spreading wetting is not spontaneous). It is frequent that the static contact angle decreases with time. Measuring static contact angle with time may give information regarding the spreading velocity. Solid wettability is usually best characterised by measuring advancing and receding contact angles. These angles fall within a range with advancing angles approaching a maximum value and receding angles approaching a minimum value. The difference between the maximum and minimum contact angle values is called the *contact angle hysteresis*. It has been used to characterise surface heterogeneity, roughness and mobility.

There are two different approaches that are commonly used to measure contact angles of non-porous solids, goniometry and tensiometry. Goniometry involves the observation of a sessile drop of liquid on a solid substrate. More details about goniometry will be given in the next Chapter, as this technique was used in this study. Force tensiometry involves measuring the forces of interaction as a solid is in contact with a liquid. The force tensiometric method measures the forces that are present when a solid is brought

into contact with a liquid. If the interaction forces, the geometry of the solid and the surface tension of the liquid are known, the contact angle may be calculated. It is common to use the Wilhelmy plate or the Du Nouÿ ring to measure this force. The advancing contact angle is measured when the plate or the ring is pushed into the solid; the receding contact angle is measured when the plate or the ring is pulled up out of the liquid.

For porous solid, the most commonly used method is the Washburn method²²³. Briefly, the solid is placed in a vertical tube that ends with a porous filter at the bottom, and is brought into contact with the liquid. The mass of liquid absorbed into the solid is measured as a function of time. If the viscosity, density and surface tension of the liquid are known, the contact angle can be calculated.

Chapter 3:

Materials and Methods

3.1 Materials

3.1.1 Silica Particles

All particles used in this study were hydrophilic silica particles and were kindly provided by two companies: Evonik (formerly Degussa) and Nyacol.

Aerosil 200 (provided by Evonik), also called A200 in this study, are hydrophilic fumed silica particles, with a primary particle diameter of 12 nm and a specific surface area (BET) of 200 m²/g. They are provided as a fine white powder. The content of silicon dioxide, based on ignited material, is higher than 99.8%, which guarantees a high purity

of the sample. These particles are largely used in many fields: paints and coatings, adhesives and sealants, printing inks, but also in cosmetics and foods (anti-caking, flow aid, anti-settling, etc.).

Three different amorphous hydrophilic silica particles DP5820, DP5480 and DP5540, were provided by Nyacol as a stable dispersion of the colloids (30 wt%) in a solution of ethylene glycol (EG). These particles present very similar properties, except for their sizes. For each particle, two diameters were given by the provider. The first diameter (e.g. 20 nm for DP5820) was measured by TEM microscopy and the second diameter is the Z-average measured by light scattering (HPPS from Malvern Instrument, UK):

- DP5820 = 20 – 50 nm;
- DP5480 = 50 – 85 nm;
- DP5540 = 100 – 120 nm.

Nyacol's ethylene glycol silica sols were developed mainly to provide anti-block and abrasion resistance properties to polyester film and tape. This material allows the processor to maintain transparency in products.

3.1.2 Chemicals

The oil used in this study was commercially available vegetable oil (“pure vegetable oil” from Sainsbury’s). The water used in all experiments was first passed through a reverse osmosis unit and then a Milli-Q water system (18.2mΩ.cm at 25°C). All materials were used with no further purification or modification of their properties.

Three surfactants (lecithin, monoolein and Tween 60) and one protein (Sodium Caseinate) were used in this study. Lecithin (L- α -Phosphatidylcholine from soybean, Type II-s, 14-23% choline basis, HLB \sim 4) was purchased from Sigma Aldrich. Monoolein (monooleate-1-glycerin) was purchased from Fluka AG Buchs SG (Switzerland). The HLB value was given to be 3.8. Because of their low HLB values, these two surfactants are expected to stabilise W/O emulsions. Tween 60 was obtained from Fluka AG Buchs SG (Switzerland). The HLB value was given to be 14.9. Sodium Caseinate (EM 7, milk protein type) was provided by DMV International. Since Sodium Caseinate is not considered as a surfactant, there is no HLB value for this component. Nonetheless, due to its amphiphilic characters and to its high solubility in water, the HLB of Sodium Caseinate is assigned a value of about 14 (*personal conversation with DMV representative*). Tween 60 and Sodium Caseinate, due to their high HLB values, are supposed to stabilise O/W emulsions.

3.1.3 Concentration units

The mass of all components, used in each of the sample preparation stages described in next sections, were carefully selected in order to produce the required “final” concentrations of components in the dispersions or emulsions. The concentrations of all material used in this study were calculated as the percentage of weight of a component per weight of the final product –dispersion or emulsion– (wt/wt %), but they are given only as % to simplify the script.

3.2 *Liquid density measurement*

The density of the liquids was measured using the density kit of the tensiometer K100 from Kruss, Germany. The measurement uses of the fact that, as a result of the buoyancy of a solid in a liquid, the measured weight in a liquid is less than that measured in air. The mass of the volume of liquid displaced by the measuring rod corresponds to the difference in weight. As the density of the measuring rod is known, the density of the liquid can be obtained by differential weighing, by using Equation 3.1:

$$\rho_L = \rho_p \frac{M_{pA}}{M_{pL}} \quad (3.1)$$

where ρ_L is the density of the liquid, ρ_p is the density of the probe (rod + hook), M_{pA} is the weight of the probe in the air, and M_{pL} is the weight of the probe in the liquid.

The Table 3-1 shows the results for different liquids containing various concentrations of surfactant or particles. As can be seen, the addition of emulsifier in the liquid (water or oil) does not modify the density of these liquids when measured pure.

Table 3-1: Density of water and vegetable oil, measured pure or in the presence of emulsifier, with the Tensiometer K100 from Kruss, equipped with a density kit. The concentrations for each emulsifier are the lowest and the highest concentration used in this study.

		Water	Vegetable Oil
No Surfactant		0.998 ± 0.0001	0.915 ± 0.0005
Tween 60	0.02%	0.998 ± 0.0003	0.914 ± 0.0004
	2%	0.998 ± 0.0005	0.915 ± 0.0002
Aerosil 200	0.02%	0.998 ± 0.0003	N/A
	2%	0.999 ± 0.0007	N/A
NaCAS	0.004%	0.997 ± 0.0005	N/A
	0.2%	0.998 ± 0.0003	N/A
Lecithin	0.1%	N/A	0.915 ± 0.0003
	1%	N/A	0.916 ± 0.0006

3.3 Preparation and characterisation of colloidal dispersions

3.3.1 Aerosil 200-in-water dispersion

A known amount (by weight) of hydrophilic silica particles Aerosil 200, provided as powder, was placed in a tall form glass beaker (150 mL). Milli-Q water was then carefully added to the beaker until it reached approximately 90% of the final weight of the dispersion (for a preparation of 100 g of dispersion, 90 g of water was added). Then the pH of the solution was adjusted by using hydrochloric acid (HCl, 1M) or sodium hydroxide (NaOH, 1M). The solution was finally completed by adding water adjusted at the required pH. The concentration of silica particles was varied from 0.2 to 2% (in 0.2% increment). The pH was varied from 2 to 10 (in 2 increment).

Three methods to disperse the Aerosil 200 particles in water were investigated. For each method, a quantity of hydrophilic silica particles Aerosil 200 was added to water in a tall form glass beaker (150 mL) to form a 1% A200-in-water dispersion. The pH of the solution, called “natural pH”, was measured to be around 4.5 and no attempt was made to adjust it.

The first method consisted in dispersing the particles using a high shear mixer (Silverson L4RT, equipped with a fine emulsor screen, 19mm of diameter), at 8000 rpm for 30 minutes. Due to the heat given off by the mixing with the Silverson, it was necessary to cool the solution down. A large (1L) beaker containing tap water at room temperature ($\sim 25^{\circ}\text{C}$) was placed around the beaker containing the dispersion and the tap water was replaced after 15 minutes.

The second method consisted in using an ultrasonic bath (BRANSONIC B2210E, Ultrasonic Cleaner, Frequency 47kHz). A tall form glass beaker (150 mL) containing the dispersion was placed in the bath containing distilled water for 4 hours. Due to the heat given off by the ultrasonic vibrations, ice was used to maintain the temperature around $25 - 30^{\circ}\text{C}$ and replaced every hour.

The final method consisted in using a high intensity ultrasonic vibracell processor (Jencons-PLS) operating at 20kHz and 700W. The probe was placed in the centre of a tall form glass beaker (150 mL) containing the dispersion and used for 3 minutes. Due to the heat given off by the ultrasonic vibrations, ice was used to cool the dispersion down during the dispersion.

3.3.2 *Particles from Nyacol*

The particles from Nyacol were provided as a dispersion (30 wt%) in ethylene glycol solution. In order to adjust the particle concentration, the EG solution was diluted with water. The protocol to adjust the pH, when required, was the same as for Aerosil 200-in-water dispersion.

3.3.3 *Characterisation of the dispersion*

3.3.3.1 *Particle charge measurement*

According to the medium in which the particles are dispersed, they may contain charges at the surface. A Zetamaster from Malvern Instruments was used to determine the zeta potential of the colloidal dispersions²²⁴, i.e. the potential difference between the dispersion medium and the stationary layer of liquid attached to the dispersed particle. Briefly, the Zetamaster works backwards on the theory of electrophoresis measurement. Laser doppler electrophoresis (LDE) is the measurement of the movement of colloidal particles when they are placed in an electric field. The measurement can be used to determine the sign of the charges on the particles and also their electrophoretic mobility, which is related to the surface charge and zeta potential.

In order to measure the zeta potential of the particles used in this study, a dispersion of 0.1% A200-in-water was prepared and adjusted at required pH (from 2 to 10), as described in section 3.1.1. The solution was placed in an optical glass cell, situated in the Zetamaster, and the zeta potential was measured.

3.3.3.2 Particle size measurements

Particle size was measured using the HPPS (High Performance Particle Sizer) from Malvern Instrument. The HPPS is a particle sizer based on Dynamic Light Scattering (DLS) technique which allows the measurement of particles size typically in the sub micron region²²⁵. DLS measures Brownian motion and relates this to the size of the particles. Brownian motion is the random movement of particles due to the interactions with the solvent molecules that surround them²²⁶.

The velocity of the Brownian motion is defined by a property known as the translational diffusion coefficient (usually given the symbol D). The size of a particle is calculated from the translational diffusion coefficient by using the Stokes-Einstein equation:

$$d_H = \frac{kT}{3\pi\eta D} \quad (3.2)$$

Where d_H is the hydrodynamic diameter, k is the Boltzmann constant, T the absolute temperature and η the viscosity. The diameter measured by DLS is a value that refers to how a particle diffuses within a fluid. Thus, it is referred to as the hydrodynamic diameter. The velocity of the particles diffusing through the medium due to Brownian motion is quantified by measuring the rate at which the intensity of the scattered light fluctuates when detected using a suitable optical arrangement (Figure 3-1). The laser is scattered in all directions by the particles and captured by many detectors. This scattered light forms a speckle pattern of bright (constructive lights) and dark (destructive lights) areas. Between instants t and $t+\delta t$ ($\delta t \ll t$), the pattern will change due to Brownian motion. The rate at which these intensity fluctuations occur will depend on the size of the particles.

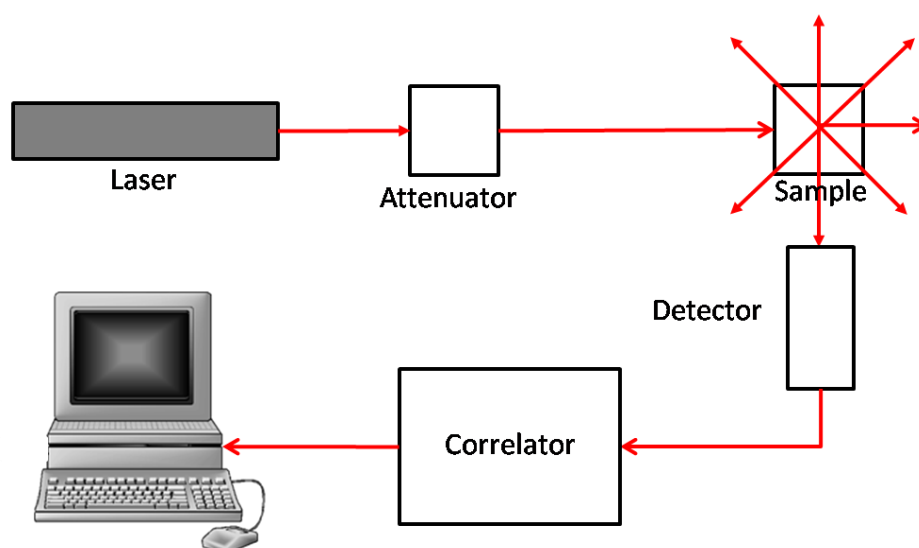


Figure 3-1: Scheme of a Dynamic Light Scattering device, as the HPPS from Malvern Instruments.

Large particles tend to move slowly, which will result in the slow fluctuation of the intensity of the speckle pattern. Similarly, as small particles tend to move quickly, the intensity of the speckle pattern will also fluctuate quickly. A correlator, which measures the degree of similarity between a signal and the same signal over a short period of time, is then used to measure the fluctuations of the intensity of the scattered light. By using a correlation function and various algorithms, the particle size is calculated. The diameter provided by the software linked to the HPPS is the *Z-average diameter* which is the mean diameter based on the intensity of scattered light.

Dispersion of 1% of silica particles was firstly prepared at the required pH and then diluted 10 times with water at the same pH. A small volume of the diluted dispersion was placed in a disposable standard optical polystyrene cuvette 10×10×45 (mm) and the cuvette was placed in the HPPS for analysis.

The HPPS software requires the refractive index of the dispersant (water) and its viscosity, and the refractive index of the sample (silica particles) and its absorption. Malvern Instruments provides a list of properties of the most common materials used as dispersant and sample. As the companies which provided the particles (Evonik and Nyacol) were unable to give accurate values of the refractive index and absorption of the silica particles, it was chosen to use the Malvern list for these measurements. The refractive index of water is 1.33 and the one of silica particles is 1.46. The viscosity of water depends on the temperature, but as measurement was conducted at 25°C, the water viscosity was given to be 0.8872 mPa.s. The absorption of silica particles was given to be 0.001.

3.4 Preparation and characterisation of O/W emulsions

3.4.1 Emulsion preparation

All O/W emulsions in this study were prepared using a Silverson L4RT high shear mixer equipped with a fine emulsor screen of 19 mm diameter at 8000 rpm for 5 minutes. No effort was made to control the temperature during emulsification.

✓ Pure Pickering emulsions

Initially silica-in-water dispersions were prepared at the required pH and concentration, as previously described (sections 3.3.1 and 3.3.2). A carefully weighted quantity of pure vegetable oil was then added to the silica-in-water dispersion and the mixture was emulsified with the high shear mixer.

✓ Surfactant-stabilised emulsions

Monoolein and Tween 60 (used separately) were added to the vegetable oil and gently agitated at 40-45°C until dissolved. Similarly, lecithin was dissolved in the oil phase at 60-65°C. The oil solution, kept at a constant temperature of 45°C, was then added to pure water (of adjusted pH) and the mixture was emulsified with the high shear mixer. It should be stressed that monoolein hydrolysis was not considered as it takes place to the same extent for all systems (all adjusted at pH 2) and therefore does not affect any of the observed trends in this study.

Sodium Caseinate was initially dissolved in pure water (of adjusted pH) at 50°C and the solution was cooled down at room temperature. Vegetable oil, heated up at 40-45°C, was then added the solution and the mixture was emulsified using the high shear mixer.

✓ Mixed-emulsifier emulsions

Mixed-emulsifier emulsions were initially prepared in the presence of monoolein and hydrophilic silica particles (Aerosil 200). Two methods were investigated to prepare these emulsions. In both method, monoolein was added to the vegetable oil and gently agitated at 40 – 45°C until dissolved. The oil solution was kept constant to 40 – 45°C until emulsification. Aerosil 200 particles were dispersed in water at pH 2. This particular pH was chosen in order to compare mixed-emulsifier stabilised emulsions and pure Pickering emulsions, which was found to be stable only at pH 2 (this will be shown in more details further in Chapter 4).

The first method (*Method 1*) to prepare O/W mixed-emulsifier emulsions consisted in emulsifying, using the high shear mixer, the oil mixture, kept constant at 40 – 45°C, directly with the dispersion (A200-in-water at pH 2).

The second method (*Method 2*) consisted in mixing, firstly, the oil solution (kept constant at 40 – 45°C) with pure water at pH 2 for a few seconds with the high shear mixer at 8000 rpm, to produce an O/W pre-emulsion. Finally, the dispersion adjusted to pH 2 was added to the pre-emulsion and the system was further emulsified for an additional 5 minutes with the high shear mixer to produce the final emulsion. The mass of all components, used in each of the stages described here, were carefully selected in order to produce the required “final” concentrations of components in the mixed-emulsifier stabilised emulsions.

It will be proved in Chapter 5 that only emulsions prepared using the *Method 2* are stable. In order to compare mixed-emulsifier emulsions prepared with monoolein to mixed-emulsifier emulsions prepared with other surfactants (lecithin, Tween 60 and Sodium Caseinate), all mixed-emulsifier stabilised emulsions were prepared using the Method 2. Lecithin and Tween 60 were dissolved in oil, as detailed for surfactant-stabilised emulsions. As Sodium Caseinate cannot be dissolved in oil, it was dissolved in water, as detailed for surfactant-stabilised emulsions. The aqueous solution was then mixed with vegetable oil, heated at ~45°C, for a few second to form a pre-emulsion. The final emulsion is obtained as described above.

3.4.2 Emulsion characterisation

The stability against coalescence of the oil-in-water (Pickering, surfactant-stabilised or mixed-emulsifier stabilised) emulsions as a function of time was assessed by optical observation and emulsion droplet size measurements. The emulsion microstructure was visualised by microscopy.

Following their preparation, a small quantity of the oil-in-water emulsions was sampled and collected in a small glass vial (~25 mL of emulsion) where the rate of creaming was assessed. The volume of the formed cream layer, expressed as volume fraction ($V_{f_{cr}}$), was measured, as a function of time, using the following relation:

$$V_{f_{cr}} = (V_{cr} / V_{em}),$$

where V_{cr} is the volume of the cream phase and V_{em} the total volume of the emulsion (see Figure 3-2). Furthermore by observing the occurrence (or not) of an oil film at the top of the cream phase, emulsion stability against coalescence was assessed.

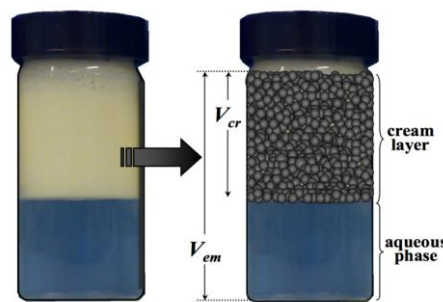


Figure 3-2: Scheme of emulsion structure; creaming and droplets in the cream layer.

Information about instability phenomena like coalescence, Ostwald ripening or flocculation was obtained by monitoring the evolution of the emulsion droplet size

distribution with time. Emulsion droplet size distribution was obtained using a Mastersizer HYDRO 2000 SM from Malvern Instruments. The Mastersizer is a particle sizer based on Static Light Scattering (SLS) techniques²²⁷. For SLS experiments, a high intensity monochromatic light, usually a laser, is passed through a solution containing the particles. The laser beam is scattered by the particles in many directions and detectors are used to measure the scattering intensity at one or many angles as shown in Figure 3-3.

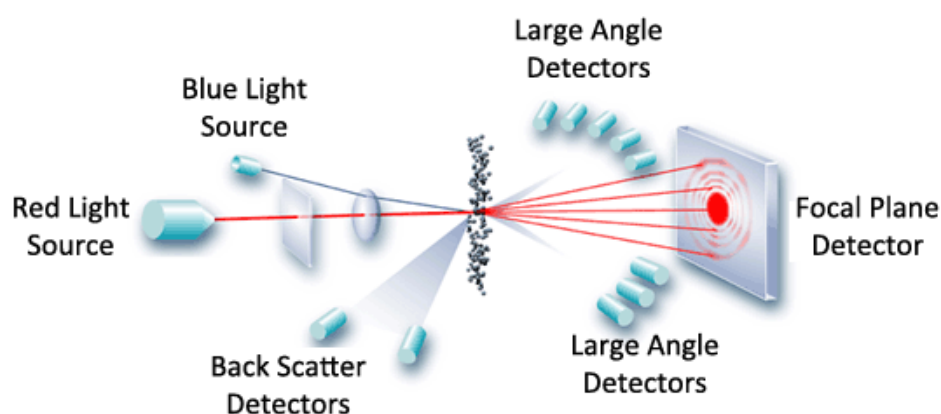


Figure 3-3: Scheme of Static Light Scattering as applied in the Mastersizer HYDRO 2000 SM.

Typically, the Focal Plane Detector is used to detect small scattered angles ($< 10^\circ$), the Large Angle Detectors to measure higher angles ($10^\circ - 90^\circ$) and the Back Scatter Detectors to measure very high angles ($100^\circ - 135^\circ$). The Mastersizer is composed of three parts: the dispersion unit, the optical bench and the analysis unit. The dispersion unit is composed of a dispersion unit (stirrer and pump), a controller unit and a flow cell, situated in the optical bench and through which the laser beam passes. The optical bench is composed of the transmitter (where the laser beam is created), the sample area

(where the flow cell is located and where the laser beam is scattered) and the receiver (where the scattered light is collected and stored). The optical bench is connected to the analysis unit which converts raw information to data related to the particle size (distribution, diameters, etc.). Mastersizer software provides a few diameters such as $D(4,3)$ (volume weighted mean diameter), $D(3,2)$ (surface weighted mean diameter), $D(0.5)$ (volume median diameter, for which 50% of the distribution is above and 50% is below), $D(0.1)$ or $D(0.9)$ (for which 10% or 90% of the volume distribution is below this value, respectively). In this study, the weighted mean diameter $D(4,3)$ was chosen as emulsion droplet diameter. Unless stated, droplet diameter always refers to $D(4,3)$.

The Mastersizer software requires certain information about the physical properties of the emulsion. Specifically these are the refractive index of the continuous phase (water), and the refractive index of the emulsions droplet and its absorption. Malvern Instruments provides a list of properties of the most common materials. The refractive index of water and silica particles is to be 1.33 and 1.46 respectively. The refractive index of vegetable oil is ~ 1.47 . The absorption of silica particles and vegetable oil is to be 0.001 and 0 respectively.

In order to measure the droplet size distribution of Pickering emulsions, oil droplets were assumed to be covered by silica particles (this will be shown next chapter), which form a solid layer around the droplets. The laser beam is assumed to be scattered by the particles. The properties of the emulsion droplets were chosen to be these of silica particles (refractive index of 1.46 and absorption of 0.001).

In order to measure surfactant stabilised emulsions droplet size, the emulsion droplet properties were assumed to be the properties of vegetable oil (refractive index of 1.47 and no absorption).

As will be shown further, the surface properties of mixed-emulsifier emulsion droplets depend on the type and the concentration of the surfactant. When droplets were covered by particles, the droplet size calculation was based on the properties of silica particles; when droplets were not covered by silica particles, the calculation was based on the properties of vegetable oil. As the refractive index and the absorption of silica particles and vegetable oil are very close, the direction of the laser scattered by particles or vegetable oil should be very similar. Thus, the difference on the final emulsion droplet size measured with the Mastersizer is minor.

The emulsion microstructure was assessed by scanning electron microscopy (SEM). The SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample²²⁸⁻²³⁰. More specifically, accelerated electrons in SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-

rays), visible light (cathodoluminescence-CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 5 μm to 1 cm in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm).

The microstructure of the emulsions prepared in this study was analysed by using a Philips XL30 FEG Cryo Scanning Electron Microscopy, which has a Gatan low temperature preparation system fitted. The experimental procedure is the following one. A drop of emulsion was frozen at -198°C in a nitrogen slush. Then, the sample was placed in the preparation chamber to be fractured at -180°C and etched for 2 minutes at

-90°C. The sample was cooled down to -130°C and the exposed surface area of the emulsion was coated by gold. Finally, the prepared sample was transferred onto the cold stage and imaged at -130°C. This protocol was set up by Mr Paul Stanley, manager of the Centre for Electron Microscopy, School of Metallurgy and Materials, University of Birmingham, who performed the measurements with me.

3.5 Interfacial tension and contact angle measurement

3.5.1 Goniometer

The instrument used in this study to measure interfacial tension and contact angle was a goniometer EasyDrop from Kruss, Germany. It is composed of monochrome interline CCD camera (25 fps), a light source (halogen lamp), a syringe control unit and moveable sample table (Figure 3-4). A needle is attached to the syringe. The instrument is connected to a PC for data analysis with the Drop Shape Analysis (DSA) software provided by Kruss. The range of contact angle measured by the EasyDrop is 1 – 180°, with an accuracy of $\pm 0.1^\circ$.

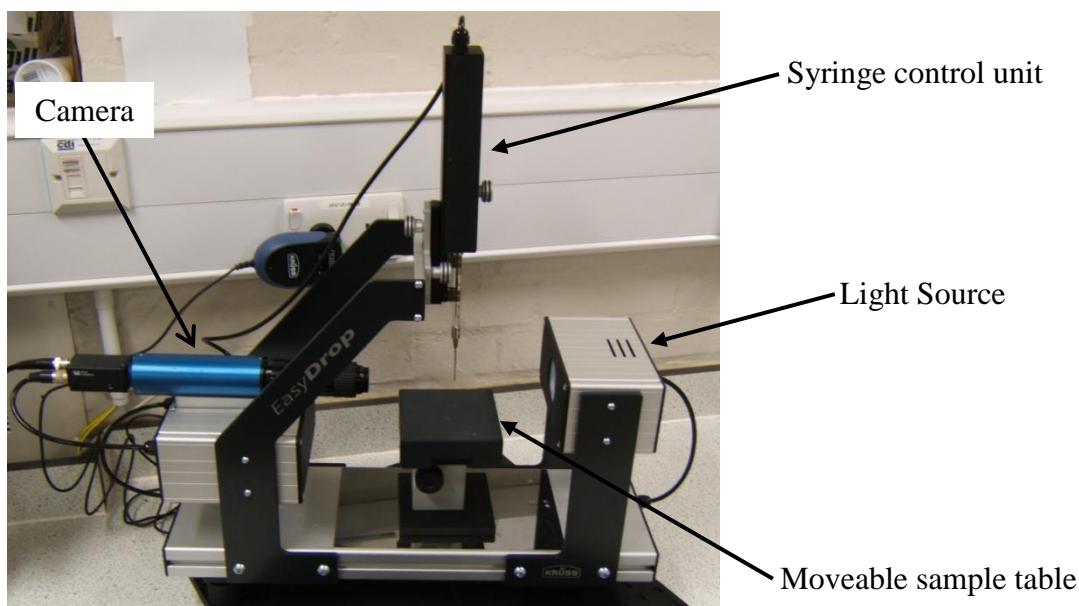


Figure 3-4: Goniometer EasyDrop from Kruss.

3.5.2 *Contact Angle*

To measure the contact angle (typically called θ) with EasyDrop, a drop is placed on a solid sample located on the moveable sample table (Figure 3-5). The drop is illuminated from one side and the camera at the opposite side records an image of the drop. This image is then analysed by the DSA software to calculate the contact angle. The calculation is based on the sessile drop method, i.e. drops of liquid are deposited on a solid surface (as smooth and horizontal as possible)²³¹⁻²³⁴. The protocol to deposit the drop on the sample surface has an influence on the final result and a differentiation has to be made between the various methods of measuring the drop.

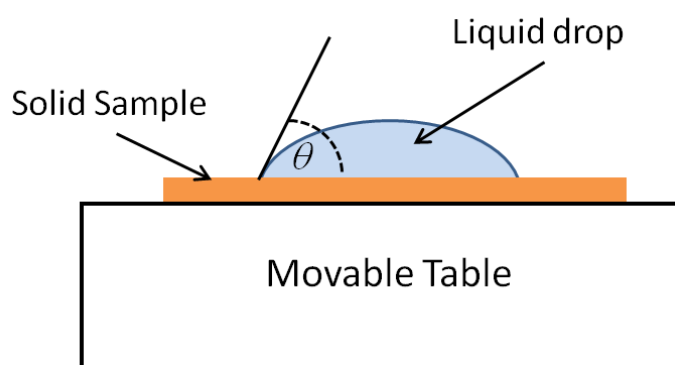


Figure 3-5: Definition of contact angle θ measured with the goniometer.

3.5.2.1 *Static contact angle*

The drop is produced before measuring the static contact angle and the drop size does not alter during the measurement. However, the contact angle does not always remain constant: the interactions at the drop surface (liquid evaporation, migration of surfactants from the solid surface to the liquid surface, substances dissolved in the drop migrating to the surface or in the opposite direction, chemical reaction, etc.) can considerably alter the contact angle with time. Measuring static contact angle can be chosen to study its variation as a function of time. Another advantage of static contact angle measurement is that the needle does not remain in the drop during the measurement which facilitates the calculation.

3.5.2.2 *Dynamic contact angle*

The dynamic contact angle is measured while the drop volume is being increased or reduced. Contact angles measured on increasing drop volume are known as advancing angles, those measured on reducing drop volume as receding (or retreating) angles.

Dynamic contact angles describe the processes at the liquid/solid boundary during the increase or decrease in volume of the drop, i.e. during wetting and dewetting.

During the measurement of the advancing contact angle, the syringe needle remains in the drop throughout the whole measurement. In practice a drop with a volume of about 3-5 μL is formed through the needle on the solid surface and then slowly increased in volume. At the beginning, the contact angle measured depends on the volume of liquid added into the drop. At a certain drop volume the contact angle stays constant; in this area the advancing contact angle can be measured as shown Figure 3-6. As a result of the wetting process, advancing angles always simulate a fresh surface for the contact angle; this is formed immediately after the creation of the contact between the liquid and the surface. This type of measurement is therefore the most reproducible way of measuring contact angles.

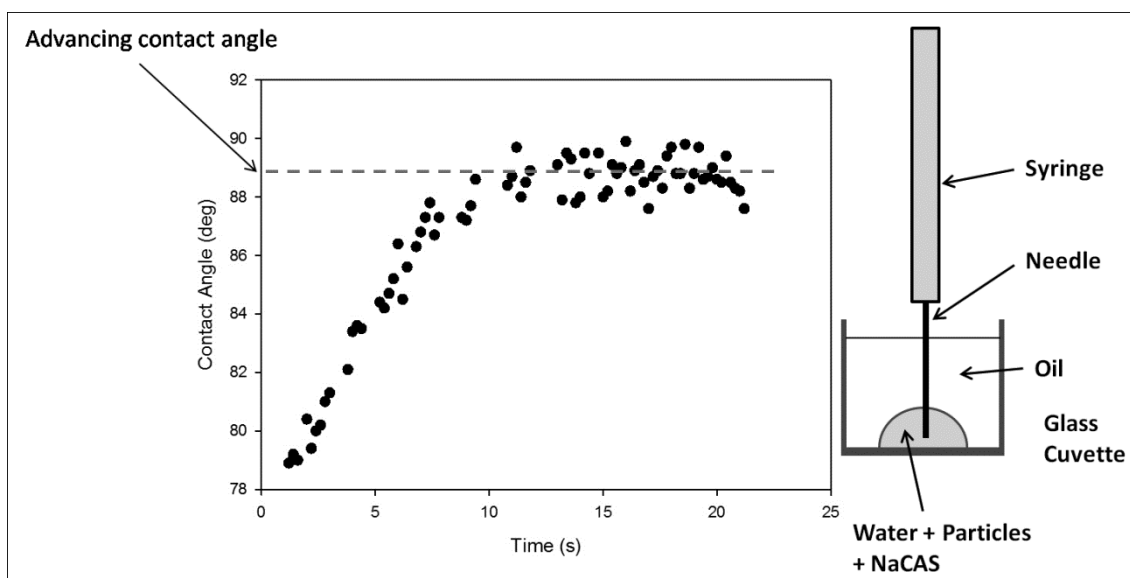


Figure 3-6: Evolution of contact angle vs. time for a system Water (pH2) + Silica Particles (1wt/wt%) + NaCAS (0.04wt/wt%) – Vegetable Oil.

In practice it may be very difficult to keep the needle in the drop throughout the whole measurement due to many factors (moveable table not perfectly horizontal, needle not perfectly straight ...). Another way to measure advancing contact angle is to firstly form a droplet on the surface. The needle is then placed in the middle of the drop and the liquid is added at a slow rate (typically 5-15 $\mu\text{L}/\text{min}$).

During the measurement of the receding angle, the contact angle is measured as the size of the drop is being reduced, i.e. as the surface is being de-wetted. In practice a relatively large drop with a diameter of $\sim 6\text{mm}$ is deposited on the solid and then slowly reduced in size with a constant flow rate. By using the difference between the advancing and the receding angles it is possible to make statements about the roughness of the solid or chemical inhomogeneties.

3.5.2.3 *Methods for evaluating the drop shape*

The basis for the determination of the contact angle is the image of the drop on the surface. In the DSA program the actual drop shape and the contact line (baseline) with the solid are first determined by the analysis of the grey level values of the image pixels. The found drop shape is adapted to fit a mathematical model which is then used to calculate the contact angle. The various methods of calculating the contact angle therefore differ in the mathematical model used for analyzing the drop shape. Either the complete drop shape, part of the drop shape or only the area of phase contact are evaluated. All methods calculate the contact angle as $\tan(\theta)$ at the intersection of the drop contour line with the solid surface line (baseline).

- Tangent method 1

The complete profile of a sessile drop is adapted to fit a general conic section equation. The derivative of this equation at the intersection point of the contour line with the baseline gives the slope at the 3-phase contact point and therefore the contact angle. If dynamic contact angles are to be measured, this method should only be used when the drop shape is not distorted too much by the needle.

- Tangent method 2

The part of the profile of a sessile drop which lies near the baseline is adapted to fit a polynomial function of the type $(y = a + bx + cx^{0.5} + d/\ln x + e/x^2)$. The slope at the 3-phase contact point at the baseline and from it the contact angle are determined using the iteratively adapted parameters. This function is the result of numerous theoretical simulations. The method is mathematically accurate, but is sensitive to distortions in the phase contact area caused by contaminants or surface irregularities at the sample surface. As only the contact area is evaluated, this method is also suitable for dynamic contact angles. Nevertheless, this method requires an excellent image quality, especially in the region of the phase contact point.

- Height-width method

In this method the height and width of the drop shape are determined. If the contour line enclosed by a rectangle is regarded as being a segment of a circle, then the contact angle can be calculated from the height-width relationship of the enclosing rectangle. As the drop height cannot be determined accurately when the needle is still in the drop, this method is not suitable for dynamic drops. This method also has the disadvantage that

the drops are regarded as being symmetrical, so that the same contact angle is obtained for both sides, even when differences between the two sides can be seen in the actual drop image.

- Circle fitting method

As in the height-width method, in this method the drop contour is also fitted to a segment of a circle. However, the contact angle is not calculated by using the enclosing rectangle, but by fitting the contour to a circular segment function. The same conditions apply to the use of this method as to the height-width method with the difference that a needle remaining in the drop disturbs the result far less.

- Young-Laplace (sessile drop fitting)

The most complicated, but also the theoretically most accurate method for calculating contact angle is the Young-Laplace fitting method. In this method the complete drop contour is evaluated; the contour fitting includes a correction which takes into account the fact that it is not just interfacial effects which produce the drop shape, but that the drop is also distorted by the weight of the liquid it contains. After the successful fitting of the Young-Laplace equation the contact angle is determined as the slope of the contour line at the 3-phase contact point. This model assumes a symmetric drop shape. Therefore, it cannot be used for dynamic contact angles where the needle remains in the drop.

3.5.2.4 *Measurements*

Ideally, the contact angle that a hydrophilic silica particle makes at the oil – water interface would have been measured. However, due to the very small size of the

particles, it was impossible to use the goniometer or any other instruments available in the lab. In order to work only with the compounds used in this study (oil, water, surfactant and particles), some attempts were made to measure the contact angle between oil, water and a layer of particles.

A layer of particles was first created on a glass surface by drying a high concentrated dispersion (of silica) on the surface. However, the layer of particles was cracked on the glass and was too heterogeneous. Then, some tablets of particles were prepared using a compaction machine. However, the particle compaction was not tight enough and the water droplet spread and adsorbed on the “tablet surface” immediately after pouring. Finally, the decision was made to introduce a new parameter, a glass surface, to measure the contact angle and to disperse the silica particle into the aqueous phase.

The contact angle between the oil phase, the water phase and a substrate of glass was measured at various concentrations of silica particles, various types and concentrations of surfactant. The substrate was the bottom of a cuvette (cell) made of optical glass 40×40×30 (mm). The cell was initially cleaned and soaked by a solution of high concentrated sodium hydroxide (NaOH, 2M) for 30 minutes. It was then rinsed with distilled water and dried. The oil phase was then poured into the optical cuvette and left for 1 hour in the cell to reach the equilibrium between the glass bottom and the oil phase. The aqueous phase was placed in a syringe (Hamilton 1750 TLLX with stop, 500 μ L) equipped with a needle (diameter \sim 0.5 mm).

When static contact angle was measured, a drop of aqueous phase $\sim 5 \mu\text{L}$, was dropped off at the bottom of the glass cell and the evolution of the contact angle with time was assessed by using the Drop Shape Analysis software from Kruss. When advancing contact angle was measured, a drop of aqueous phase ($\sim 5 \mu\text{L}$) was initially dropped off at the bottom of the glass cell. The needle was then carefully placed in the middle of the drop, and the aqueous phase was injected in the drop through the needle at low flow rate ($\sim 10 \mu\text{L}/\text{min}$). The evolution of the contact angle with time was assessed by using the Drop Shape Analysis software from Kruss. Table 3-2 shows the type of contact angle measured for each surfactant, as well as the surfactant concentration and the phase in which the surfactant was dissolved. When hydrophilic silica particles (Aerosil 200, 1%) were present, they were dispersed in the aqueous phase.

Table 3-2: Type of contact angle measured for various surfactants – Surfactant concentration and phase in which each surfactant was dissolved.

		Concentration (%)	Phase		Contact Angle	
			Water	Oil	Static	Advancing
Tween 60	No Part.	0.01 – 1.4	✓	-	-	✓
	A 200		✓	-	✓	✓
NaCAS	No Part.	0.01 – 0.2	✓	-	-	✓
	A 200		✓	-	-	✓
Lecithin	No Part.	0.1 – 1.0	-	✓	✓	N/A
	A 200		-	✓	✓	N/A

In case lecithin was used, the advancing contact angle could not be measured because it was impossible to place the needle into the water droplet previously formed at the bottom of the glass cuvette. Figure 3-7 illustrates the problem. This is a sequence representing a small droplet of dispersion (1% silica particles dispersed in water at pH

2) attached at the needle coming down (Figure 3-7.1 to 3- 7.3) and up (Figure 3-7.4) to the aqueous droplets sat on the glass substrate and surrounded by a mixture of pure vegetable oil and lecithin (0.1%). It appears clearly that the small droplet cannot merge with the bigger one. It seems that the lecithin forms a layer at the interface which prevents any penetration of the needle into the droplet. This is likely to be due to the elastic properties of the lecithin which renders the interface more elastic²³⁵.

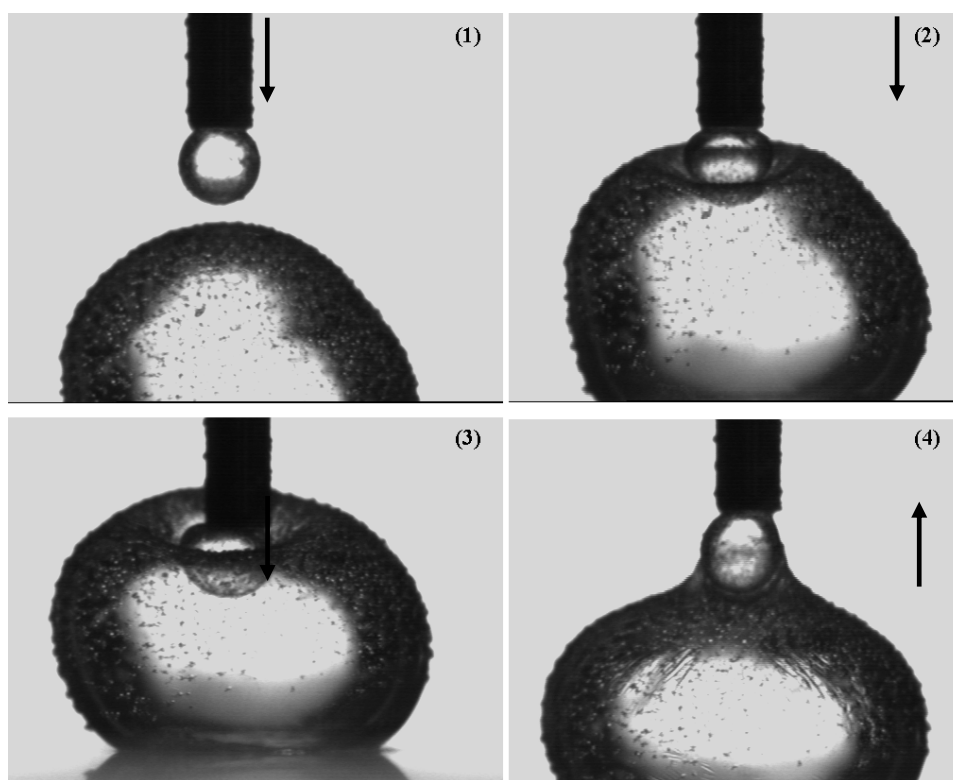


Figure 3-7: Effect of lecithin (0.1%) and silica particles (1%) on the interface of a water droplet in oil. From pictures (1) to (3), the needle is pushed down into the water droplet; picture (4), the needle is pulled up out of the water droplet.

3.5.3 Interfacial tension

3.5.3.1 Pendant drop method

The measurement of interfacial tension with the EasyDrop is based on the pendant drop method^{231,236-238}. The pendant drop method involves the determination of the profile of a drop of one liquid suspended in another liquid at hydromechanical equilibrium. The profile of a drop of liquid suspended in another is determined by the balance between gravity and surface forces.

When in hydromechanical equilibrium, the force of gravity acting on the drop and, depending on its particular height, corresponds to the Laplace pressure, which is given by the curvature of the drop contour at this point. The Laplace pressure ΔP_L results from the radii of curvature (R_1 and R_2) standing vertically upon one another in the following way:

$$\Delta P_L = \gamma \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (3.3)$$

This equation describes the difference in pressure between the outside of the drop and its inside. Mathematical models have been developed to calculate interfacial tension from a drop shape, but this will not be detailed here. More information can be found in the literature^{231,236,238}.

3.5.3.2 *Interfacial Tension measurements*

In this study, interfacial tension of oil-water systems was measured by using the pendant drop method. As described above, the pendant drop method requires the formation of a drop of one liquid in another liquid.

A cuvette made of optical glass 40×40×30 (mm) was used to contain the oil phase. The cell was initially cleaned and soaked by a solution of high concentrated sodium hydroxide (NaOH, 2M) for 30 minutes. It was then rinsed with distilled water and dried. The oil phase was then poured in the optical cuvette. The needle (diameter ~ 1.8 mm) attached to the syringe containing the water phase and attached to the goniometer was placed in the oil. The water drop was then formed at the end of the needle in the oil phase. The drop shape was then monitored by the Drop Shape Analysis (DSA) software provided by Kruss and the interfacial tension was given as a function of time. The only information required by the software is the density of both liquids (oil and water). As shown Table 3-1, the density of the water phase and oil phase in the presence or not of surfactant or silica particles does not change. It was chosen to perform the IFT measurements with a constant water phase density and oil phase density at 0.998 kg/L and 0.915 kg/L respectively.

The interfacial tension of systems with no particles (water at required pH, oil and surfactant) was first measured. Surfactants were dissolved in water or oil according to their solubility, as shown Table 3-3, at the required concentration. Initially, for each surfactant, a water drop is formed in the oil at the highest surfactant concentration and grown up until the drop is detached from the needle. Thus the maximum water drop size

(before the drop is detached from the needle) is determined and then used for the interfacial tension measurements, for each surfactant, at any concentration. Table 3-3 shows the drop size for each surfactant and the rate at which the drop is formed.

Interfacial tension in the presence of particles was also measured. Particles were dispersed in the water phase at the concentration of 1%. In order to compare both systems (with and without particles), the measurements were made with the same water drop size and the same dispersing rate as systems containing no particles.

Table 3-3: Dispersion phase of the surfactant, water drop size, dispersing rate of the water phase in the oil phase and surfactant concentration.

Surfactant	Concentration (%)	Dispersed in	Drop size (μL)	Dispersing rate (μL/min)
No Surfactant		-	50	50
Tween 60	0.01 – 1.4	Water	10	50
NaCAS	0.01 – 0.2	Water	45	50
Lecithin	0.1 – 1.0	Oil	3	50

It was not possible to control temperature during the measurement of interfacial tension (or contact angle) using the goniometer. The ambient temperature in the lab varied from 21°C to 27°C. This change in temperature was due to the heat given off by the different equipments in the lab (water bath, hot plates, etc.). In this range of temperature, the interfacial tension measurement between water and vegetable oil is not expected to be affected by the change of temperature^{197,239}. Each measurement was repeated three times at different moments of the day or at different days, when the temperature was different. As it will be shown in Chapter 7, interfacial tension measurements exhibited a very good reproducibility.

3.6 Conclusion

Methods to prepare and analyse various kinds of samples were described in this chapter. Three different methods are proposed to prepare silica-in-water dispersions and their effects on the dispersion properties will be studied in next chapter. Similarly, emulsions were prepared following different protocols that may affect emulsion stability and properties. This will be analysed next chapters. Goniometer, EasyDop from Kruss, is used to measure interfacial tension and contact angle. Despite the fact that efforts were made to match the experimental conditions of contact angle and interfacial tension with the ones of emulsion preparation, this was only possible until a certain extent as a result of limitations of the goniometer. Physico-chemical properties of the components used in this study may be affected by modifying the temperature at which they are used. This may have an effect on experimental results, particularly on interfacial tension, contact angle and density measurement. Variations of room temperature, between 21°C and 27°C, were noted during the experiments. Nonetheless, in this range of temperature, experimental results, that showed good reproducibility, seem not be affected.

Chapter 4:

Silica Particle Dispersions

and

Stability of O/W Pickering Emulsions

The level of interest in Pickering emulsions, i.e. emulsions stabilised by fine divided solid particles, has increased in the last three decades. The mechanisms involved in emulsion stabilisation have been long investigated and are now well understood. However, the ability of solid particles to stabilise emulsions depends strongly on the oil and water properties, as well as the particles properties themselves. In this chapter, the properties of various kinds of particles are described, as well as the dispersion of these particles in aqueous media.

The ability of these particles to stabilise O/W emulsions is also investigated and discussed, as a function of various parameters, such as pH, particle concentration, oil-water ratio and particles size. It is worth to note that no attempt was made to stabilise the emulsions against creaming; this work is only assigned to the investigation of the stability of O/W emulsions against coalescence.

4.1 Dispersion of hydrophilic silica particles Aerosil 200 in water

4.1.1 Characterisation of Aerosil 200 particles

In order to understand the surface forces taking place at the interface of the particles, and particularly the electrostatic forces, the zeta potential of a suspension of dry powder of silica particles (from Evonik, Aerosil 200) in water adjusted to various pHs (from 2 to 10) was measured as described in section 3.3.3.1. As can be seen Figure 4-1, at pHs below 3, the zeta potential is nearly zero. By increasing the pH up to 8, zeta potential drops down to -45 mV, and then stays constant at higher pHs.

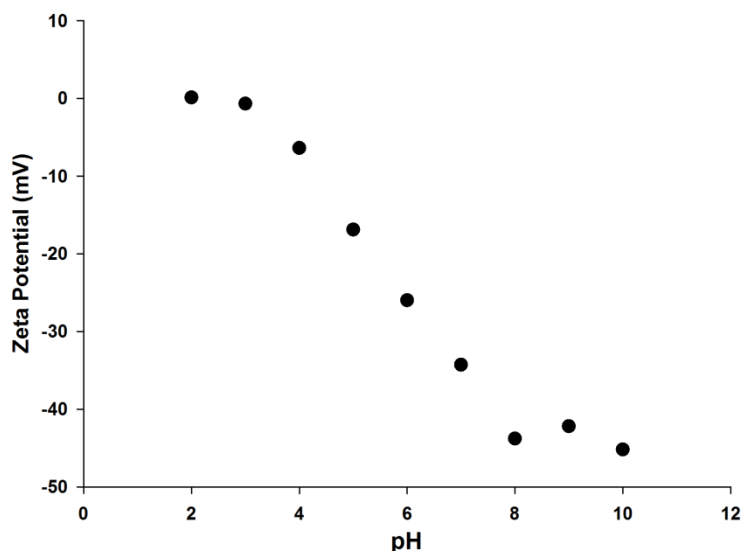


Figure 4-1 Effect of pH on the zeta potential of hydrophilic silica particles (Aerosil 200, 0.1%) in water.

Electrostatic repulsion between hydrophilic silica particles depends on the pH of the solution as the zeta potential changes with pH. At low pH (< 4), particles tend to flocculate rapidly as there is little to no colloidal repulsion and particles dispersion is likely to be unstable. Dispersion stability increases with increasing the pH as the electrostatic repulsion between particles becomes stronger which prevents any colloids flocculation. At high pHs (≥ 8), the dispersion is supposed to be stable as it is commonly admitted that the electrostatic repulsion of solution with zeta-potential higher than ± 40 mV is strong enough to completely prevent particle flocculation²⁴⁰.

4.1.2 Method of dispersion

The three methods described in section 3.3.1 (ultrasonic vibracell processor, ultrasonic bath and high shear mixer) were used to disperse the silica particles in water. As can be seen Figure 4-2, the particle size distribution of a dispersion produced by using a high

shear mixer (Silverson) presents two peaks: a main peak around 0.150 μm and a secondary peak around 8 μm . When placed in water, silica particles tend to aggregate to form big flocs. Big particles ($>1 \mu\text{m}$) present in the dispersion are particles aggregates that were not broken the high shear mixer, due to a lack of energy input in the system. The results produced by using UVP and USB were very similar. After dispersion, the particle size distributions were monomodal and the average size was measured to be around 150 μm . Moreover, the size distribution is narrower using ultrasonic methods than using a high shear mixer.

The difference between the diameter of the primary hydrophilic silica particles ($\sim 12 \text{ nm}$), as provided by the manufacturer, and their measured average diameter after dispersion in aqueous solutions ($\sim 150 \text{ nm}$) has been ascribed to the aggregation of the particles inherently taking place in dry nano-powders²⁴¹. Equipments available in the lab and tested in this study do not allow the breakage of particle aggregates under the size of 150 nm.

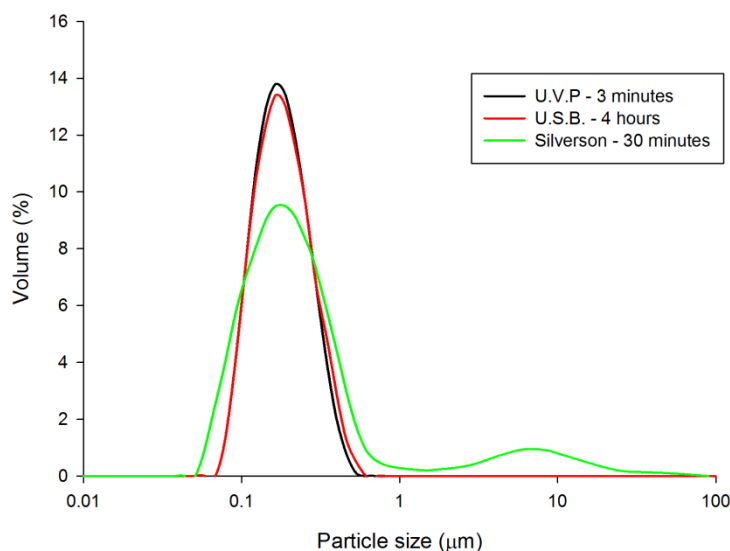


Figure 4-2: Particle size distributions – 1 wt/wt% Aerosil 200 in water at natural pH – 3 methods: UVP (Ultrasonic Vibracell Processor); USB (Ultrasonic Bath) and Silverson L4RT equipped with a fine emulsor screen (19 mm) at 8000 rpm.

Ultrasonic methods (ultrasonic vibracell processor or ultrasonic bath) were shown to be more efficient to disperse hydrophilic silica particles in water than high shear mixer one. However, the time required to disperse the colloids in water with an ultrasonic bath is very long (4 hours) compared to the time required by an ultrasonic vibracell processor (3 minutes) for a very similar result. In order to optimise the lab work during this study, it was decided to disperse the particles by using an ultrasonic vibracell processor. Any dispersion of silica particles in water mentioned further in this study will have been prepared by using this method.

4.1.3 Effect of pH on the colloidal dispersion

In order to investigate the effect of pH, dispersions of 1% of Aerosil 200 in water at various pHs (2, 4, 6, 8 and 10) were prepared. As can be seen Figure 4-3, the particle size distribution of the dispersions prepared at the five different pHs is very similar,

monodispersed with an average size around 150 μm . As mentioned in section 4.1.1, the surface of the particles at pH 2 is not (or only slightly) charged while the presence of negative charges at the surface increases by increasing the pH. The electrostatic force, induced by the presence of charges at the surface, tends to promote the stability of the silica particles-in-water dispersion as the particles (all negatively charged) repulse each other, but it is shown here that the presence of charges has no effect on the break-up of silica particles aggregates during the dispersion. It is also worth noting that optical observation revealed that after two weeks, no sedimentation of particles was found whatever the pH of the colloidal dispersion.

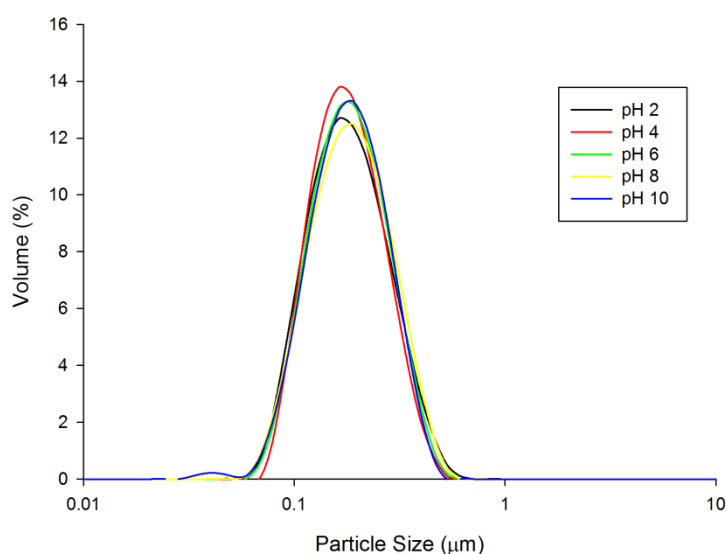


Figure 4-3: Particle size distributions – 1% Aerosil 200 in water at various pHs – Dispersion prepared with an ultrasonic vibracell processor for 3 minutes.

4.2 Dispersion of hydrophilic silica particles from Nyacol

Nyacol particles were provided as a dispersion of hydrophilic silica particles in a solution of Ethylene Glycol (30%). The size (measured by light scattering) of these three particles is given to be:

- DP5820: 50 nm
- DP5420: 85 nm
- DP5540: 120 nm

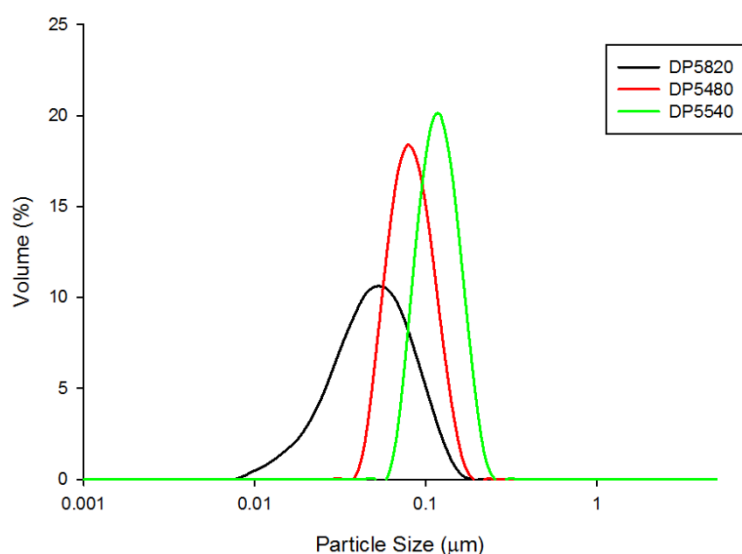


Figure 4-4: Particle size distributions – 1% silica particles-in-water, natural pH – 3 different particles from Nyacol.

The aim of the experiments reported in this section was to check that the particles size of the Nyacol dispersion is not modified by the dilution with water. After dilution, the diameter of the Nyacol particles was measured to be (Figure 4-4):

- DP5820: 44 ± 2 nm
- DP5420: 78 ± 1 nm
- DP5540: 118 ± 2 nm

The size of the three kinds of particles is not changed by diluting the dispersion, as the size measured after dilution is very similar to the size given by Nyacol.

Remark:

Some attempts were made to remove the ethylene glycol from the dispersion by successively centrifuging the solution to sediment the particles, removing the liquid and replacing it by water, and dispersing the particles by ultrasonication. However, as the centrifugation leads to the formation of particle aggregates, the particle size after ethylene glycol “cleaning” was found to be around 150 μ m, regardless of the type of the particles (DP5820, DP5420 or DP5540). The interest of using Nyacol particles was to work with particles with the same surface properties, but with various sizes. As it was impossible to remove the ethylene glycol without affecting the particles size, it was decided to work with the dispersion provided by Nyacol, adjusting only the particle concentration (and eventually the pH) by diluting the solution with water.

4.3 Stabilisation of O/W Pickering emulsions with hydrophilic silica particles

The stability against coalescence of O/W Pickering emulsions as a function of the system's pH value, the concentration of silica particles, the concentration of oil and the particle size in the system has been investigated. Even though creaming was found to

occur for all investigated emulsions, this work was only dedicated to the investigation of the stability of these systems against coalescence. Therefore, for the purposes of the work presented in this section and from this point onwards, when there is mention of “emulsion stability” what is implied is “emulsion stability against coalescence”, unless stated otherwise.

4.3.1 Effect of pH

The effect of pH on the stability of O/W emulsions (prepared as described in section 3.4.1) containing 1% silica particles was initially investigated. O/W emulsions stabilised by 1% silica particles were adjusted to pH values of 2, 4, 6, 8 and 10 (before emulsification) and their stability was monitored over time. Optical observation for systems of pH 4 and over revealed that with time an oil layer develops directly above the cream layer, which clearly indicates that coalescence phenomena are taking place for these systems. Long-term stability against coalescence was only achieved for systems of low pH values ($\text{pH} < 4$). This is in agreement with Binks and Lumsdon who investigated the stabilisation of O/W emulsions with silica particles⁶³. Furthermore, the size distribution of the oil droplets in the cream layer of systems of varied adjusted pH values was measured shortly after emulsification (see Table 4-1). It was observed that the size of the emulsion droplets is reduced as the pH of the system is increased.

Table 4-1: Effect of pH on the droplet size $D(4,3)$ of O/W Pickering emulsions containing 1% silica particles (Aerosil 200).

pH	2	4	6	8	10
$D(4,3)$ (μm)	33.57	33.52	33.74	21.90	16.45

Both these observations seem to relate to the effect of pH on the physical properties of the silica particles in the system. As mentioned in section 4.1.1, the zeta potential of silica particles depends strongly on the pH of the system. For low pH values ($\text{pH} < 4$) the zeta potential of the silica particles was practically zero, which suggests that the silica particles are not charged. Increasing the pH value of the system ($\text{pH} \geq 4$), was found to introduce increasing amounts of charge onto the silica surface, thus increasing inter-particle repulsion. This pH-induced introduction of charge appears to affect the stability against coalescence in the investigated systems. As can be seen in Figure 4-5a, silica particles in O/W emulsions adjusted to $\text{pH} < 4$ are closely packed on the oil-water interface which would be due to the absence of charge under these conditions. The possible arrangement of the uncharged silica particles in these systems could extend to the formation of multiple layers around the oil-water interfaces. Freeze fracture image of an emulsion droplet cross section could not be obtained in order to confirm the presence of a multiple layer around the droplets. As shown in Figure 4-5b, uncharged silica particles are not only located around the oil droplets, but also in the cream layer where they form silica flocs inter-connecting the oil droplets. Any of these events is expected to enhance the stability of O/W Pickering emulsions against coalescence, as indeed it was found for all investigated systems under this pH regime.

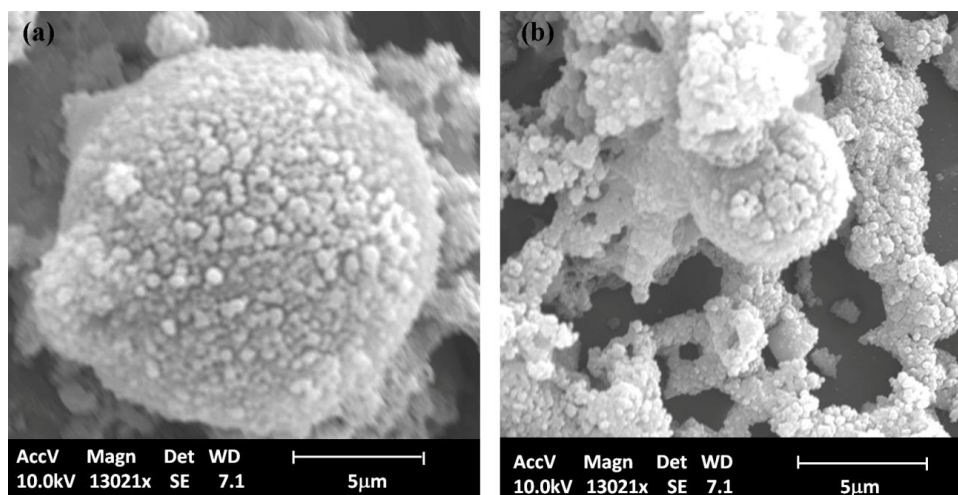


Figure 4-5: Freeze fracture images (cryo-SEM) of O/W (20/80) emulsions stabilised with 1% Aerosil 200 at pH 2.

Silica particles in O/W emulsions adjusted to $\text{pH} \geq 4$ are likely to be more “spread out” on the oil-water interface, due to the existence of charge under these conditions. Furthermore, the occurrence of double layers at the oil-water interface or silica flocs inter-connecting the oil droplets would appear to be a less probable event. Therefore, as the pH in these systems was increased, it was expected that the amount of silica particles residing at the oil-water interface decreased. The latter was confirmed by optical observation of the aqueous layers of the investigated systems (Figure 4-6). More specifically it was revealed that, although the aqueous layers of systems at pH 2 were clear, as the pH is increased ($\text{pH} \geq 4$) these aqueous layers became increasingly “cloudy”, due to the presence of silica particles. Therefore, it seems that the amount of silica particles residing at the oil-water interface is indeed decreasing with increasing pH and as a result the remaining silica particles are “forced” to stay dispersed in the water phase, thus becoming increasingly visible in the aqueous layer, which does not contain any oil droplets. The former would then indicate that, with increasing pH, packing of the silica particles at the oil-water interface becomes increasingly sparse.

Even though emulsion droplets are, to a small extent, electrostatically stabilised, this is achieved by what is a charged but “patchy” silica layer, which consequently results in large sections at the droplet interface to be “exposed” to coalesce with other droplets. After emulsification (quiescent conditions) these droplets are all in the cream layer of the systems where, due to close packing, contact time between them is infinite. It is proposed that, due to this close packing, it is the increasingly “sparse” surface packing of the droplets that dominates (over their increasing surface charge), causing the increased coalescence events observed under these pH conditions.

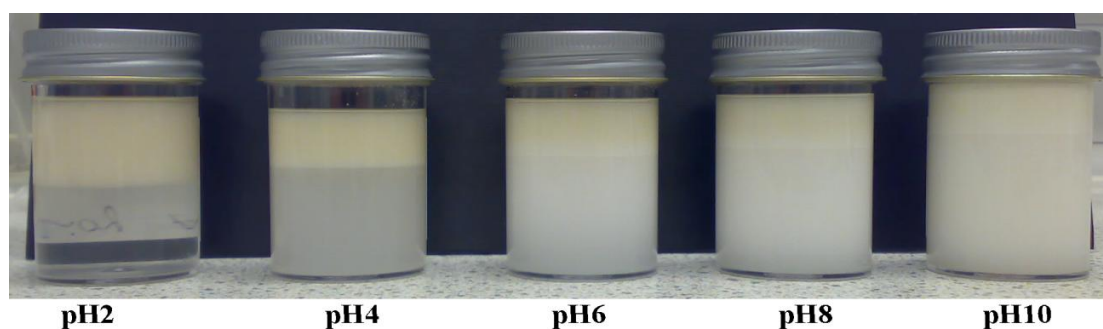


Figure 4-6: Effect of increasing the pH on the cream layer and aqueous phase of O/W (20/80) emulsions for 1 wt/wt% Aerosil 200, after 1 week.

The observation that the size of the emulsion droplets immediately after emulsification is lower, as the pH is increased, is again related to the existence of charged ($\text{pH} \geq 4$) or not charged ($\text{pH} < 4$) particles in the system. The size of emulsion droplets produced at the end of emulsification is determined by the balance between the break-up and re-coalescence events taking place during the process. As opposed to the infinite contact times involved for droplets at the cream layer (quiescent conditions), contact times between droplets during emulsification are extremely small. In this case it is the increasing surface charge of the droplets that dominates (over their increasingly

“sparse” surface packing) and therefore, for systems of $\text{pH} \geq 4$, what was earlier described as a “patchy” but charged silica layer on the droplet interface, should be expected to reduce re-coalescence (reduced back reaction during emulsification), due to electrostatic repulsion of the coated oil droplets. This would explain the size reduction of the emulsion droplets, produced via the emulsification process, as the system’s pH is increased.

4.3.2 Effect of silica particle concentration

The effect of the concentration of silica particles on the stability of O/W emulsions adjusted to pH 2 was also investigated. The concentration of colloidal particles in the system was varied from 0.2 to 2% (in 0.2% increments) and emulsion stability was assessed by measuring the size distribution of the emulsion droplets in the cream layer as a function of time (Table 4- 2 and Figure 4-7).

Table 4-2: Mean droplet sizes $D(4,3)$ and standard deviations (calculated from at least three light scattering measurements) of O/W (20/80) Pickering emulsions (adjusted to pH 2) and the volume fractions $V_{f_{cr}}$ of their cream layers as a function of silica concentration. $D(4,3)$ and $V_{f_{cr}}$ values are given as measured immediately after emulsification and also one month after emulsification (values in brackets).

	Silica Concentration (wt/wt%)					
	0.2	0.4	0.8	1	1.4	2
$D(4,3)$ (μm)	51.53 ± 0.36 (56.64)	36.94 ± 2.69 (34.95)	24.22 ± 0.06 (23.97)	23.61 ± 0.45 (22.86)	21.84 ± 0.42 (21.01)	18.90 ± 0.35 (18.79)
$V_{f_{cr}}$	0.38 (0.37)	0.48 (0.37)	0.74 (0.44)	0.82 (0.47)	0.97 (0.56)	1.00 (0.72)

Stability against coalescence for O/W Pickering emulsions was achieved for all investigated silica concentrations, with the size of the oil droplets, contained in the cream layers of the systems, changing only marginally within a period of a month.

Silica particles were therefore found to provide long-term stability, even at concentrations as low as 0.2%, for these food-grade emulsions at pH 2.

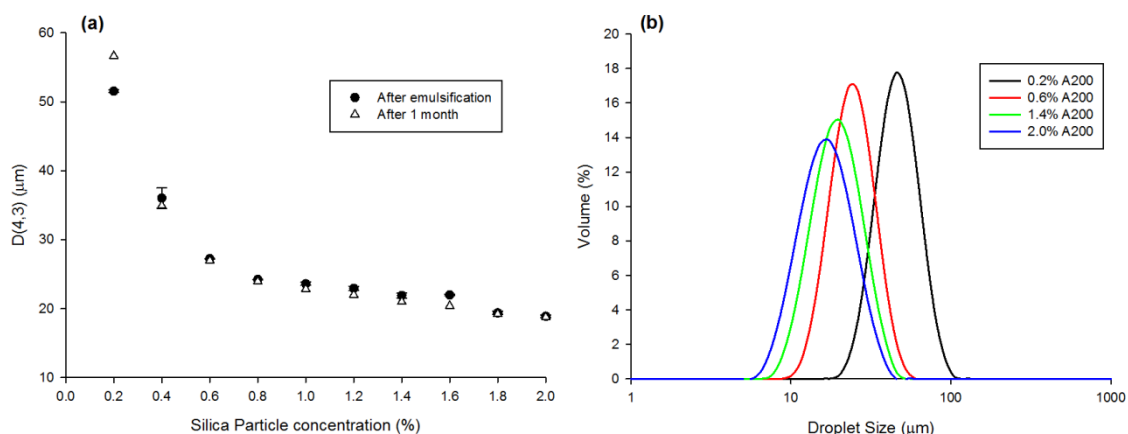


Figure 4-7: Effect of silica particle concentration on the droplet size of O/W (20/80) emulsion prepared at pH 2. (a) Average size $D(4,3)$ of emulsion droplets as a function of silica particle concentration after emulsification and after 1 month; (b) Emulsion droplet size distributions as a function of silica particle concentration; where not visible, error bars are smaller than the symbols.

However, the concentration of silica particles was found to affect the size of the produced emulsion droplets, which eventually reside in the cream layer of the system. In particular, increasing concentrations of silica particles in the system resulted in the reduction of the emulsion droplet size (Figure 4-7). As discussed earlier, emulsion droplet size depends on the emulsification process, but what seems to be of equal importance is also the rate by which the silica particles deposit onto the oil-water interface in the emulsification process and subsequently provide stability. By increasing the concentration of silica particles in the system, the transport of colloidal particles to the oil-water interface would become an increasingly faster process and therefore, emulsion droplets would be stabilised in increasingly smaller sizes as the re-coalescence during the emulsification process is slowed or even stopped.

Finally, the concentration of silica particles was also found to affect the volume fraction of the cream layer in the investigated systems. Increasing the concentration of colloidal particles in the system (with the oil phase volume fraction kept constant at 20%) resulted in increasing volume fractions of cream layer; a month after producing the emulsion, the cream layer volume fraction of the system containing 0.2% silica particles was 0.37 while the one containing 2% silica particles was 0.72. This has been ascribed to changes in the arrangement of the emulsion droplets in the cream layer induced by the increasing concentration of silica particles. As discussed earlier, silica particles in these systems (uncharged at pH 2) are expected to form multiple layers around the oil-water interfaces or even form flocs inter-connecting the oil droplets in the cream layer. In either case emulsion droplets would be forced further apart thus increasing the volume of the cream layer containing them.

4.3.3 Effect of the oil phase volume

The effect of the oil phase volume (i.e. the percentage of oil in the emulsion) on the stability of O/W emulsions adjusted to pH 2 was investigated. Emulsions were prepared at three various oil/water ratios: 10/90, 20/80 and 30/70 with a silica particles concentration constant at 2%. The emulsion stability was assessed by measuring the droplet size after emulsification and after 1 month, and also by visual observation.

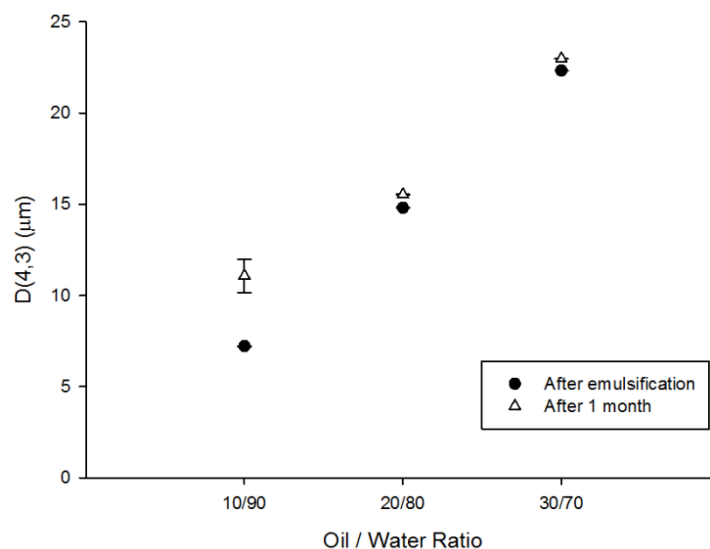


Figure 4-8: Effect of oil phase volume on the stability of O/W emulsion adjusted to pH 2 prepared with 2% Aerosil 200 – Average size D(4,3) as a function of O/W ratio and time.

As can be seen in Figure 4-8, for an oil/water ratio of 20/80 and above, the average emulsion droplet size does not change after a month. For a ratio of 10/90, droplet size was around 6.5 μm after emulsification and around 11 μm after 1 month, which represents a significant change. In first instance, emulsion stability seems to depend on the O/W ratio. However, no oil released was observed at the top of emulsion after a month. The change in the droplet size at low oil ratio may be explained by considering the packing of oil droplets in the cream layer.

By decreasing the oil phase volume, the number of oil droplets formed during emulsification is likely to decrease, which results in lowering the “naked” oil surface. As a consequence, all the particles are not adsorbed at the interface, and some remain “free” in the system. These particles are likely to form a network with the silica particles adsorbed at the O/W interface at quiescent conditions, as discussed in section 4.3.1.

Over a month, uncharged silica particles (“free” and adsorbed) would aggregate. These silica flocs may affect the measurement of emulsion droplet size by light scattering, which can explain the difference between the emulsion droplet size measured after emulsification and after a month.

The O/W ratio also has an effect on the emulsion droplet size. As can be seen in Figure 4-8, the droplet size increases by increasing the concentration of oil in the system. As mentioned earlier, the droplet size is determined by the balance between the break-up and re-coalescence events taking place during the process. During emulsification, oil droplets are formed and dispersed into the bulk phase. Increasing the O/W ratio results in reducing the distance between oil droplets in the bulk phase. This induces higher re-coalescence of oil droplets at higher O/W ratio. As the re-coalescence during emulsification increases by increasing the oil concentration, the final emulsion droplets size also tends to increase.

Optical observations revealed that the O/W ratio has an effect on the emulsion creaming (see Figure 4-9). For ratios of 20/80 and 30/70, creaming occurs quickly after emulsification and the aqueous phase is perfectly clear. The cream volume fraction (after 1 month) of 30/70 emulsion (77%) is slightly higher than the cream volume fraction of 20/80 emulsion (71%).



Figure 4-9: Effect of the oil concentration on the O/W emulsions prepared at pH 2 with 2 wt/wt% Aerosil 200 – after 1 month.

At 10/90 ratio, phase separation between cream and aqueous phase also occurs, but instead of creaming, the emulsion droplets tend to sediment, as can be seen in Figure 4-9. The fact that emulsion droplets sediment at low ratio (10/90) can be explained by considering the emulsion droplet density. The calculation of the droplet density (Table 4-3) is based on the hypothesis that silica particles form a uniform monolayer at the droplet interface and all the particles have the same diameter. The volume weighted diameter $D(4,3)$ is taken as the average diameter of emulsion droplets. As can be seen in Table 4-3, the average density of emulsion droplets prepared at an O/W ratio of 10/90 is slightly higher than the water density ($1057 \text{ kg/m}^3 > 998 \text{ kg/m}^3$), while the average density of emulsion droplets prepared at higher ratio (20/80 or 30/70) is higher than the water density. This explains why emulsion droplets tend to sediment when made at an O/W ratio of 10/90, while they tend to cream at higher ratios.

Table 4-3: Calculation of the emulsion droplet average density at 3 ratios, assuming that the silica particles form a uniform monolayer at the droplet interface.

Oil and Particles Properties	$\rho_{A200} = 2000 \text{ kg / m}^3$ $D_{A200} = 0.15 \text{ }\mu\text{m}$		
	$\rho_{oil} = 915 \text{ kg / m}^3$		
O/W Ratio	10/90	20/80	30/70
Emulsion droplet diameter ($D_{droplet}$) (μm)	6.5	14.8	22.3
Oil diameter (D_{oil}) (μm) $D_{oil} = D_{droplet} - D_{A200}$	6.2	14.5	22.0
Mass of silica particle layer (m_{A200}) (kg) $m_{A200} = \rho_{A200} \times \frac{4}{3} \times \pi \times (D_{droplet}^3 - D_{oil}^3)$	3.041×10^{-13}	1.618×10^{-12}	3.699×10^{-12}
Mass of oil in the droplet (m_{oil}) (kg) $m_{oil} = \rho_{oil} \times \frac{4}{3} \times \pi \times D_{oil}^3$	9.115×10^{-13}	1.166×10^{-11}	4.072×10^{-11}
Volume of droplet ($V_{droplet}$) (m^3) $V_{droplet} = \frac{4}{3} \times \pi \times D_{droplet}^3$	1.150×10^{-15}	1.358×10^{-14}	4.645×10^{-14}
Droplet density ($\rho_{droplet}$) (kg/m^3) $\rho_{droplet} = \frac{m_{droplet}}{V_{droplet}} = \frac{m_{A200} + m_{oil}}{V_{droplet}}$	1057	<u>978</u>	<u>956</u>

4.3.4 Effect of particle size

The aim of the work presented in this section was to investigate the effect of particle size on the stability of O/W emulsions. In order to minimise the number of variables in the system the volume fraction of the oil-phase and the concentration of silica particles were kept constant (20% oil phase; 1% silica particles). The emulsion stability was assessed by optical observations only.

As can be seen in Figure 4-10, emulsions prepared with the smallest particles DP5820 (~50 nm) was unstable to coalescence as a layer of oil appeared at the top of the

emulsion after a few days. The use of bigger particles, DP5480 particles (~85nm) and DP5540 (~120 nm), allowed the preparation of stable emulsions. No oil release was observed at the top of the emulsions even after a month (not shown here). After creaming, the aqueous phase was cloudy regardless of the particle size. This is likely to be due to the presence of ethylene glycol in the system which renders the water cloudy. Thus the particle size was shown to have an important effect on the emulsion stability as small particles do not provide long-term stability. This may be explained by considering the adsorption energy of a single particle at the O/W interface. The energy E required to remove a single particle from the interface (assuming that the gravity can be neglected) is given by the Equation 4.1:

$$E = \pi r^2 \gamma (1 \pm \cos \theta)^2 \quad (4.1)$$

where r is the radius of the particle, γ is the interfacial tension between oil and water and θ is the contact angle that the particle assumes at the interface. As oil and water are the same for all the emulsions, γ remains the same and so cannot be responsible for the instability of the emulsions prepared with very small droplets. Moreover, all the particles, regardless of their size, are supposed to have the same surface properties. Thus, the contact angle θ can be assumed to remain constant for the three particles used here. The equation above clearly indicates that reducing the particles size considerably lowers the energy required to remove the particles from the interface. It seems that the adsorption energy of DP5820 particles is too low to keep these particles adsorbed at the interface. After emulsification, the energy induced by the movement of droplets during creaming and then by the contact between emulsion droplets at quiescent conditions, seems to be higher than the adsorption energy. This induces desorption of the particles from the interface and so the coalescence of emulsion droplets.

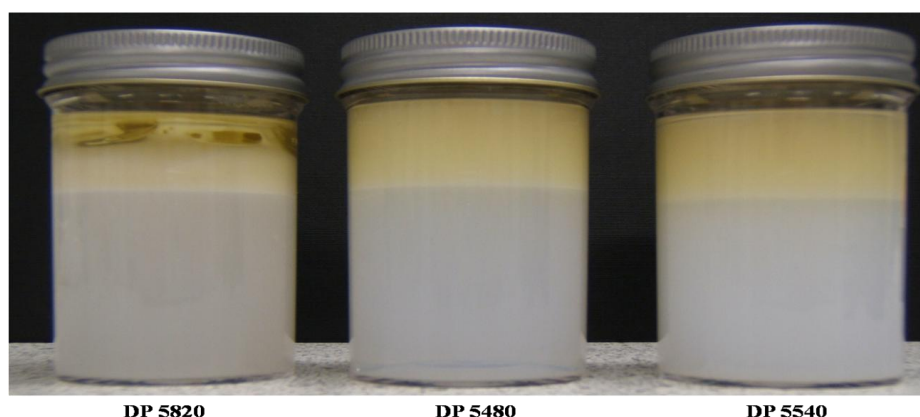


Figure 4-10: Effect of the particle size on the O/W emulsion stability prepared at natural pH with 1% hydrophilic silica particles – after 1 week.

This study of the effect of the particle size on the emulsion stability would require some further work, particularly in terms of measuring emulsion droplet size by light scattering. However, due to the presence of ethylene glycol in the system and the impossibility to remove it without affecting the particle size, and also the aim to work with food-grade components in this PhD, it was decided that the use of Nyacol particles was not suitable for this project. Nonetheless, it was interesting to note that the size of particles presenting the same characteristics has an effect on emulsion stability. Further work could be the determination of the adsorption energy barrier above which emulsions are not affected by the particle size. In other words, what is the minimum particle size which can provide stable emulsions? This would require to work in close collaboration with a company which can provide particles at various sizes (Evonik, Nyacol, Wacker, etc.) or eventually to synthesise one's own particles.

4.4 Conclusion

In this chapter, the dispersion of hydrophilic silica particles in water and the stability of O/W emulsions in the presence of colloidal particles only were investigated. Aerosil 200-in-water dispersions were stable at any investigated pH and the size of particles in water was around 150 nm. Emulsion stability depended on the pH of the dispersion; at low pH (≤ 2), emulsions were stable against coalescence for at least a month, while at higher pH, coalescence occurred. Silica particles at low pH are not charged which allows them to be closely packed at the interface, enhancing then the emulsion stability. Increasing the particle charge (by increasing the pH) results in a less efficient oil droplet coverage as particles repulse each other. Emulsion droplet size decreased by increasing silica particle concentration, as a result of faster adsorption of particles at the interface at high concentration. Emulsion stability also depended on particle size; very small particles were not able to stabilise emulsion because of very low energy of adsorption at the interface.

Chapter 5:

Effect of monoolein and hydrophilic silica particle mixtures on the stability of O/W emulsions

Emulsions stabilised by both colloidal particles and low molecular weight surfactants have so far received little interest. A few studies have been published, but the stabilisation mechanisms are not well-understood. However, the use of both emulsifiers may be of great interest in order to develop new materials with new properties. In this chapter, the effect of monoolein and hydrophilic silica particles mixtures on O/W emulsion stability against coalescence has been reported. The emulsion stability is discussed as a function of various parameters, such as the protocol, the monoolein and

silica particles concentration. The effect of emulsifier concentration on the emulsion droplet size is also described.

5.1 Surfactant-stabilised emulsions

The stability of O/W emulsions, adjusted to pH 2, against coalescence in the presence of monoolein, acting as the sole emulsifier, was initially investigated at various monoolein concentrations, from 0 to 10% (in 1% increments). Although the presence of oil droplets in the investigated systems was detected by light microscopy, shortly after emulsification, these O/W emulsions were found to be very unstable against coalescence. More specifically complete phase separation into the oil and aqueous phases was found to occur within 2-3 hours after emulsification and regardless of the monoolein concentration in the system. Therefore monoolein, even though it does indeed initially stabilise the oil droplets of the O/W emulsions, does not offer long-term stability against coalescence. This is not surprising since emulsifiers of low HLB values (such as monoolein, HLB = 3.8) will tend to stabilise W/O emulsions. However, having shown in this section the failure of monoolein to stabilise O/W emulsions, the advantages of using this surfactant in the mixed emulsifier systems will be demonstrated next section.

5.2 Mixed-emulsifier stabilised emulsions

The stability of O/W emulsions in the presence of a mixed-emulsifier system consisting of both surfactant (monoolein) and colloidal particles (hydrophilic silica particles) was investigated. The concentrations of surfactant and colloidal particles in the mixed-

emulsifier system were varied from 0 to 10% (in 1% increments) and from 0 to 2% (in 0.2% increments) respectively. The stability of the prepared mixed-emulsifier stabilised O/W emulsions was assessed by measuring the droplet size distribution in the cream layer, together with the volume change of the layer, over time.

5.2.1 Conditions of stability

Mixed-emulsifier emulsions were prepared according to the two protocols (*Method 1* and *Method 2*) described in section 3.4.1. The stability of O/W emulsions depended on the method to prepare them. By using *Method 1*, emulsions were unstable against coalescence, regardless of the concentration of silica particles or monoolein in the system. Phase separation occurred after a few hours, with a cloudy aqueous phase due to the presence of silica particles. *Method 2* showed interesting results in emulsion stability. Creaming occurred at all particles and monoolein concentrations but emulsions were found to be stable against coalescence under certain conditions of surfactant and particle concentrations.

Mixed-emulsifier systems containing small concentrations of monoolein ($\leq 1\%$) and concentrations of silica particles less than 1.6% proved to be poor in terms of stabilising O/W emulsions against coalescence. Analysis of these systems revealed that emulsion droplet size increased as a function of time, with some systems exhibiting up to 40% increase in their droplet size within the space of a month. In order to achieve stability by using a mixed-emulsifier system of such low monoolein concentration it was necessary to increase the concentration of colloidal particles to at least the 1.6% “threshold”. Mixed-emulsifier systems in these concentration regimes were indeed able to stabilise

O/W emulsions, with minimal to no coalescence occurring for the emulsion droplets in the cream layer for at least a month (Table 5-1). These findings come into contrast to what was previously observed for O/W emulsions stabilised solely by colloidal particles, where stability was achieved for silica concentrations as low as 0.2%.

Table 5-1: Mean droplet sizes D(4,3) and standard deviations (calculated from at least three Light Scattering measurements) of O/W (20/80) mixed-emulsifier stabilised emulsions (adjusted to pH 2) and the volume fractions $V_{f_{cr}}$ of their cream layers as a function of silica and monoolein concentrations. D(4,3) and $V_{f_{cr}}$ values are given as measured immediately after emulsification and also one month after emulsification (values in brackets).

		Silica Particle Concentration (%)							
		0.2	0.4	0.8	1.0	1.4	1.6	2.0	
Monoolein Concentration (%)	1	V _{f_{cr}}	0.35 (0.32)	0.37 (0.30)	0.36 (0.31)	0.42 (0.35)	0.40 (0.33)	0.42 (0.37)	0.38 (0.35)
		D(4,3)	87.58 ± 7.51 (92.98)	38.59 ± 0.61 (53.29)	48.46 ± 0.16 (55.11)	34.92 ± 0.17 (46.02)	36.00 ± 0.16 (51.42)	34.57 ± 0.10 (36.98)	30.81 ± 0.01 (34.42)
	2	V _{f_{cr}}	0.42 (0.32)	0.46 (0.32)	0.66 (0.38)	0.61 (0.38)	0.75 (0.47)	0.94 (0.51)	0.70 (0.49)
		D(4,3)	35.71 ± 0.11 (35.31)	42.98 ± 0.11 (42.85)	22.12 ± 0.02 (23.21)	21.89 ± 0.02 (22.68)	13.08 ± 0.02 (16.43)	12.86 ± 0.02 (16.22)	14.85 ± 0.02 (17.32)
	3	V _{f_{cr}}	0.56 (0.34)	0.62 (0.36)	0.80 (0.43)	0.83 (0.46)	0.92 (0.50)	0.98 (0.57)	0.93 (0.64)
		D(4,3)	31.11 ± 0.08 (31.00)	24.20 ± 0.03 (23.47)	15.18 ± 0.01 (15.30)	13.96 ± 0.02 (14.06)	11.60 ± 0.00 (11.70)	9.81 ± 0.03 (14.74)	9.75 ± 0.01 (13.15)
	4	V _{f_{cr}}	0.48 (0.36)	0.66 (0.41)	0.82 (0.45)	0.89 (0.47)	0.92 (0.56)	0.98 (0.62)	0.94 (0.62)
		D(4,3)	29.26 ± 0.06 (29.65)	17.97 ± 0.01 (19.06)	13.08 ± 0.01 (13.85)	12.72 ± 0.01 (12.77)	10.10 ± 0.01 (10.19)	9.44 ± 0.14 (12.90)	9.25 ± 0.02 (11.89)
	6	V _{f_{cr}}	0.52 (0.38)	0.67 (0.43)	0.82 (0.51)	0.91 (0.54)	0.94 (0.62)	0.95 (0.67)	0.95 (0.73)
		D(4,3)	28.11 ± 0.03 (29.83)	16.29 ± 0.01 (16.80)	12.39 ± 0.01 (12.51)	11.17 ± 0.01 (11.25)	9.019 ± 0.01 (9.16)	8.97 ± 0.04 (13.05)	9.10 ± 0.01 (11.72)
	8	V _{f_{cr}}	0.56 (0.42)	0.78 (0.45)	0.81 (0.57)	0.93 (0.59)	0.95 (0.66)	0.98 (0.62)	0.98 (0.77)
		D(4,3)	34.09 ± 0.08 (35.20)	16.35 ± 0.01 (16.70)	11.68 ± 0.01 (11.97)	11.01 ± 0.02 (11.06)	8.96 ± 0.01 (9.05)	9.51 ± 0.03 (16.08)	8.96 ± 0.03 (16.46)
	10	V _{f_{cr}}	0.58 (0.44)	0.79 (0.53)	0.87 (0.62)	0.90 (0.62)	0.96 (0.69)	0.94 (0.74)	0.99 (0.77)
		D(4,3)	36.20 ± 0.07 (38.76)	16.36 ± 0.01 (17.10)	12.32 ± 0.01 (12.38)	10.96 ± 0.01 (11.04)	9.91 ± 0.02 (10.31)	9.41 ± 0.04 (17.00)	9.03 ± 0.03 (16.36)

By increasing the concentration of monoolein over 1%, and having silica particles present, regardless of their concentration, mixed-emulsifier systems proved capable of stabilising O/W emulsions (Table 5-1). Mixed-emulsifier systems containing silica concentrations as low as 0.2% (monoolein concentration > 1%) were found to render

O/W emulsions stable for over a month, since analysis of these systems revealed that emulsion droplets did not (or only slightly) change in size. Stability seems to be enhanced at higher concentrations of both monoolein and silica particles in the mixed-emulsifier systems.

It then appears that the level of stability introduced to O/W emulsions by mixed-emulsifier systems, of such low monoolein concentrations, is dictated and therefore limited by the concentration of silica in the system. What has become clear, from the discussion in section 5.1, is that monoolein can only “temporarily” stabilise the O/W droplets produced by the emulsification process used in this study, and therefore merely delays or prolongs the coalescence phenomena, taking place in the system and resulting in complete phase separation. Furthermore, and from findings reported in Chapter 4, it is suggested that it is the colloidal particles, in the mixed-emulsifier systems investigated here, which eventually render the O/W emulsion droplets stable. However, due to their size the process by which the colloidal particles assemble at the interface takes longer than the time required to get the monomeric surfactant such as monoolein to the interface. The role of monoolein in the mixed-emulsifier systems is therefore of great importance since it is the aforementioned delay of the coalescence phenomena, induced in the presence of monoolein, which allows time for the silica particles to assemble at the oil-water interface and stabilise the emulsion.

Therefore, it is quite understandable for this series of events, leading to the stabilisation of the O/W emulsion droplets, to be affected by both the monoolein and silica concentrations in the mixed-emulsifier systems. Thus, as it was experimentally observed, mixed-emulsifier systems with monoolein concentrations below 1%, cannot

substantially delay coalescence and hence render stable emulsions unless the concentration of silica particles, also contained in these systems, is increased over a certain “threshold” value (1.6%). By increasing the monoolein concentration (over 1%) the mixed-emulsifier systems are now capable of delaying the coalescence events in the emulsion for long enough to allow for even the smallest concentrations of silica to provide long-term stability.

What also should be addressed is the earlier observation that the silica concentration needed in mixed-emulsifier systems (of low monoolein concentrations) to achieve emulsion stability is much higher than that previously observed for emulsions stabilised only by colloidal particles, where stability was achieved for silica concentrations as low as 0.2% (section 4.3.2). This difference should only be due to the presence of monoolein in the former systems. More specifically it seems to be caused by the “additional step”, in the stabilisation process of O/W emulsion droplets by the mixed-emulsifier systems, which involves the displacement of monoolein from the oil-water interface by the silica particles. Such an additional step, which does not take place in the O/W emulsion stabilisation process by colloidal particles alone, delays the silica particles getting from the bulk into and then assembling at the oil-water interfaces. Emulsion stability is therefore jeopardised and can only be restored by reducing the effect of this “step”, either by increasing silica concentration (i.e. to at least 1.6%) or by increasing the monoolein concentration (i.e. to 1%) in the mixed-emulsifier systems.

5.2.2 Effect of monoolein and colloid concentrations on emulsion droplet size

The concentrations of monoolein and silica particles in the mixed-emulsifier systems were also found to affect the droplet size of the prepared O/W emulsions. The effect of each of the components' concentration (e.g. monoolein) in these mixed-emulsifier systems is discussed in isolation by considering those systems where the concentration of the other component (e.g. silica particles) is kept constant.

Mixed-emulsifier systems where the concentration of monoolein was varied, but the concentration of silica particles was kept constant are firstly discussed. The droplet sizes of O/W emulsions stabilised by such mixed-emulsifier systems were found to initially decrease with increasing monoolein concentrations of up to 3% (Figure 5-1). Further increases of the monoolein concentration seem to have little effect on the emulsion droplet size, which remain more or less constant. What was additionally observed is that the effect of monoolein concentration on the emulsion droplet size follows the same pattern regardless of the silica concentration in the mixed-emulsifier systems. Similar findings can be reported for mixed-emulsifier systems where the concentration of silica particles is varied but the concentration of monoolein is now kept constant (Figure 5-2). The droplet size of O/W emulsions, stabilised by such mixed-emulsifier systems, initially decreases with increasing concentrations (of up to 1.2%) of silica particles, but further increases of the particles' concentration (up to 2%) seem to have little effect on the emulsion droplet size. What can be similarly concluded is that the effect of silica concentration on the emulsion droplet size follows the same pattern regardless of the monoolein concentration in the mixed-emulsifier systems. Overall, it seems that the

concentrations of both monoolein and silica particles in the mixed-emulsifier systems affect the droplet size of the resulting emulsion up to a set of respective “threshold” concentrations, above which the droplet size is then limited by the emulsification process.

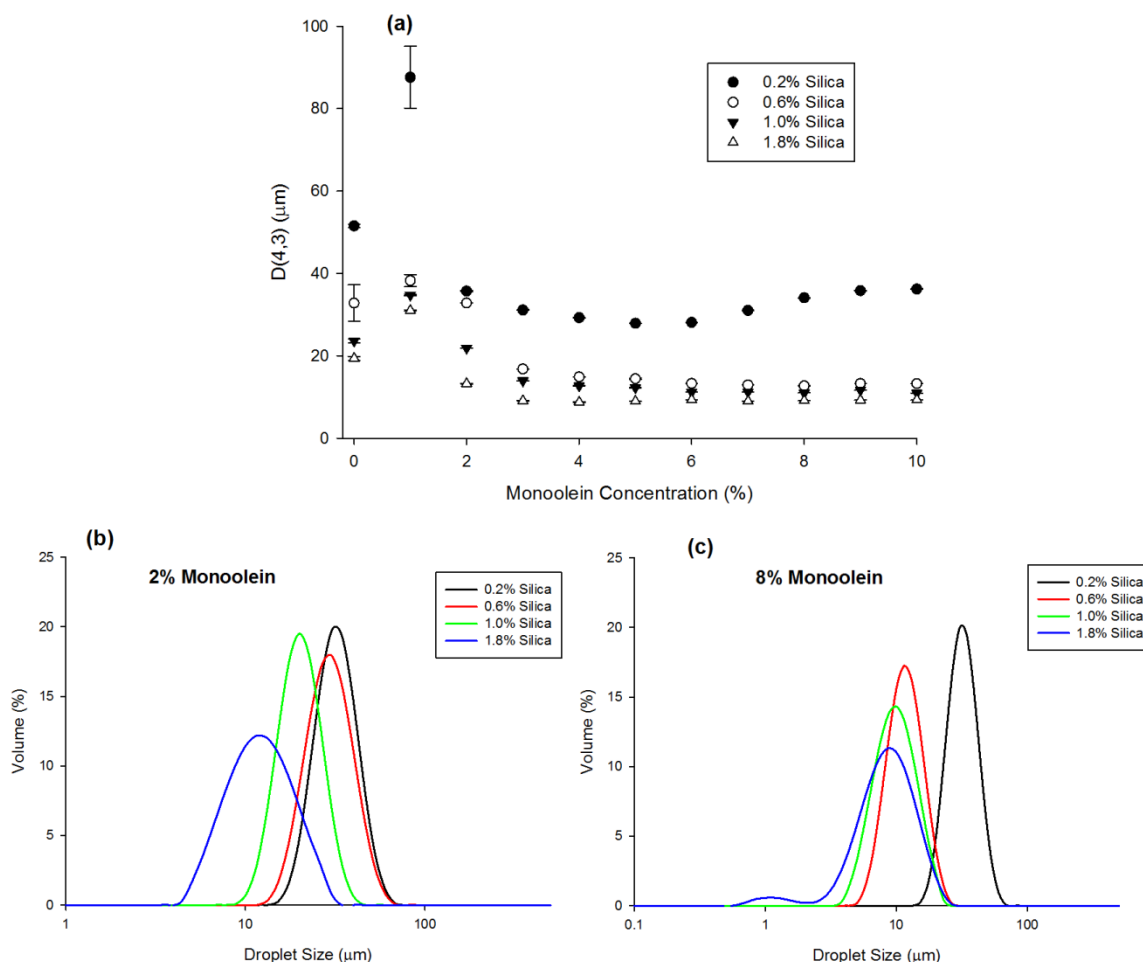


Figure 5-1: (a) Average size $D(4,3)$ of emulsion droplets (after emulsification) as a function of monoolein concentration and for various concentrations of colloidal particle; where not visible, error bars are smaller than the symbols. (b/c) Droplet size distributions of emulsions prepared at pH2, for 2%/8% of monoolein for various silica particle concentrations.

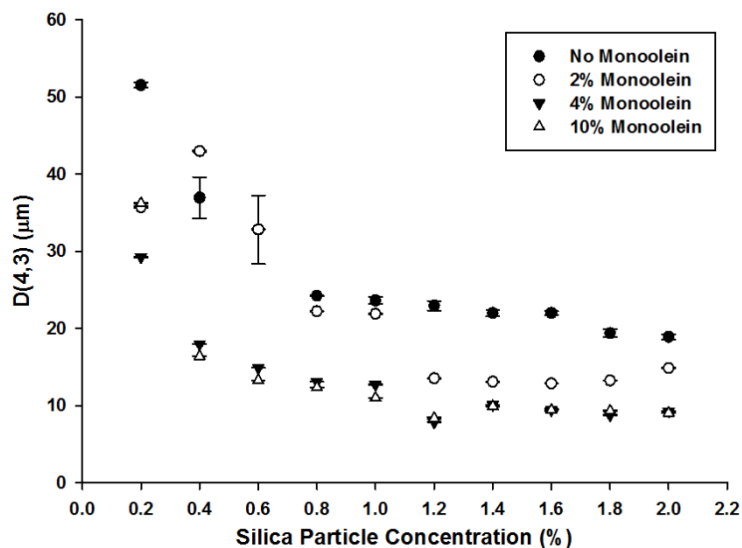


Figure 5-2: Average size D(4,3) of emulsion droplets (after emulsification) as a function of silica concentration and for various concentrations of surfactant in the system; where not visible, error bars are smaller than the symbols.

The effect of the monoolein and silica particle concentrations, in the mixed-emulsifier systems, on the droplet size of the prepared O/W emulsions can be explained by considering the mechanism by which these systems induce stability. As previously discussed, the final droplet size of the formed emulsion is determined by both the break-up and re-coalescence phenomena taking place during the emulsification process. Both phenomena can be affected by variation in the concentration of monoolein and/or silica particles in the mixed-emulsifier systems. For instance, re-coalescence events in the system should be further delayed by increasing the concentration of monoolein in the mixed-emulsifier systems due to more efficient surface coverage. Furthermore, this could facilitate/promote the droplet break-up phenomena during emulsification due to a more rapid interfacial tension reduction induced by the increasing monoolein concentration. On the other hand, by increasing the concentration of silica particles in the system, the transport of colloidal particles to the oil-water interface should become

an increasingly faster process. Therefore, in both cases, emulsion microstructure is stabilised at increasingly earlier stages, after its formation, and thus the final emulsion droplet size decreases. Eventually, after a certain set of threshold concentrations for the monoolein and silica particles in the mixed-emulsifier systems is reached, the emulsion droplet size becomes limited by the process and remains constant (Figures 5-1 and 5-2).

Another noteworthy observation lays with the difference in size between emulsion droplets stabilised solely by colloidal particles and those stabilised by mixed-emulsifier systems containing monoolein in concentrations below 1%. It was observed that emulsion droplets stabilised by the mixed-emulsifier systems (in these concentration regimes) were larger than those stabilised solely by colloidal particles, with both containing the same concentration of colloidal particles. This difference is suggested to be a result of what was previously described as an “additional step”, in the stabilisation process of O/W emulsion droplets by the mixed-emulsifier systems, which is the displacement of monoolein from the oil-water interface and its replacement by silica particles. Earlier in this section it was argued that such an additional step, which does not take place for the stabilisation process of O/W emulsions by colloidal particles, should delay the assembly of silica particles from the mixed-emulsifier systems, onto the oil-water interfaces. Following the same line of reasoning it can be concluded that this “delay” should also account for the difference in size between emulsion droplets stabilised solely by colloidal particles and those stabilised by mixed-emulsifier systems of low monoolein concentrations ($\leq 1\%$).

Optical observation of O/W emulsions stabilised by the mixed-emulsifier systems revealed that in some instances their aqueous phases (see Figure 5-3) became “cloudy”

by a small quantity of “free” silica particles, which eventually sediments. Preliminary experiments showed that the aqueous phases of these systems, regardless of whether they appear cloudy or not, do not contain oil droplets or monoolein. This clearly indicates that it is indeed the silica (aggregated) particles that cause the observed cloudiness and not a “secondary emulsion” formed in the aqueous phase. What can also be concluded is that the observed phenomenon does not arise as a result of any interactions between the silica particles and monoolein, which would affect the aggregation of the former thus causing the observed “cloudiness”. The occurrence of a cloudy aqueous phase seems to be determined only by the concentration of monoolein in the mixed-emulsifier systems; regardless of the silica concentration, systems of monoolein concentrations below 3% develop cloudy aqueous phases while in those containing higher monoolein concentrations the aqueous phases are clear. An explanation for this phenomenon is that the surface area (at the cream layer) becomes large enough, due to the increasing monoolein concentration. This leads to smaller emulsion droplets, so as to hold all the available silica particles, which otherwise would collect in the aqueous phase where they would become visible (cloudiness).

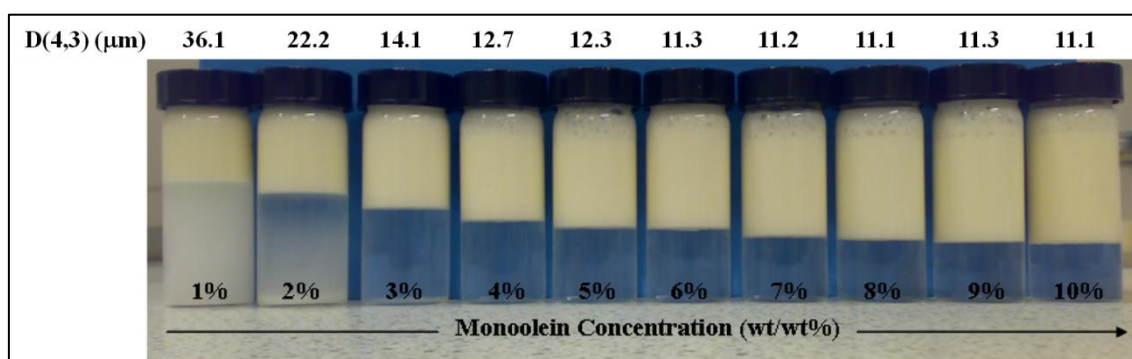


Figure 5-3: Effect of increasing monoolein concentrations on the cream layer of 20% oil-in-80% water emulsions at pH 2 and for a constant concentration of silica particles (1%).

In terms of the volume (fraction) of the cream layer of O/W droplets, developed shortly after emulsification, it was observed that it increases with increasing concentrations of monoolein (evident in Figure 5-3) and silica particles in the mixed-emulsifier systems (see Table 5-1). The increase in cream layer volume can be partly attributed to the reduction in emulsion droplet size associated with increasing monoolein and/or silica concentrations (see Table 5-1). However, this effect seems to persist even for those concentrations of mixed-emulsifier systems for which the size of the emulsion droplets remains unchanged; that is mixed-emulsifier systems of monoolein concentrations over 3% and silica particles concentrations over 1.2%. This change in phase volume (especially at high concentrations of monoolein and silica particles) is most likely due to the way that the droplets interact/pack for the cream layer. One explanation for this would be that the droplets are aggregating and starting to form a three dimensional network thus changing the inter-droplet arrangement in the cream layer. This aggregation would seem to be a consequence of having uncharged silica particles positioned in the interface by the monoolein in such a way as to stick together on contact. This is probably due to capillary forces between particles as they approach each other.

5.3 Conclusion

The stability of O/W emulsions prepared at pH 2 in the presence of both hydrophilic silica particles and monoolein was investigated in this chapter. The hypothesis proposed here is that emulsion stability is induced via a mechanism in which both components in these mixed-emulsifier systems have specific functions. More specifically, the role of

monoolein is to initially “delay” the re-coalescence phenomena and induce further droplet break-up, during emulsification, by rapidly covering the newly created interface and reducing interfacial tension, in order to allow for the silica particles to assemble at the oil-water interface and provide long-term stability after the end of the emulsification process. This dual manner by which mixed-emulsifier systems induced stability was found to depend on the concentrations of both monoolein and silica particles.

In order to promote such a stabilisation mechanism, oil, water, particles and monoolein have to be emulsified following a specific protocol. In addition to the long-term emulsion stability provided by the mixture of particles and monoolein, emulsion droplet size also decreased compared to droplet size of emulsions stabilised only by silica particles. This is also due to the 2-step mechanism and particularly the fact that droplet break-up is enhanced and re-coalescence is prevented by the presence of monoolein.

Chapter 6:

Effect of Surfactant HLB on the stability of O/W Pickering Emulsions

As discussed in Chapter 5, the stability of O/W emulsions prepared with monoolein and hydrophilic silica particles was enhanced, compared the stability of solid particles stabilised emulsion and surfactant stabilised emulsion. Moreover, the emulsion droplet size was shown to decrease in the presence of both monoolein and silica particles. The aim of this chapter is to extend the study started Chapter 5, by investigating the effect of various kinds of surfactant, chosen according to their HLB value (W/O or O/W stabiliser), on the stability of O/W Pickering emulsions. The effect of Tween 60, Sodium Caseinate and lecithin, acting as sole emulsifier, on the stability of O/W

emulsion will be described first. Then, the feasibility of combining these surfactants with hydrophilic silica particles to stabilise O/W emulsion will be discussed.

6.1 Surfactant – stabilised emulsions

The stability of O/W emulsions, adjusted to pH 2, in the presence of surfactant (prepared as described in section 3.4.1) was initially investigated. The effect of the Tween 60 and Sodium Caseinate concentration on the emulsion droplet size and emulsion stability is shown in Figure 6-1. Tween 60 concentration was varied from 0.05% to 2.0% (0.05%, 0.1%, 0.2% to 1.0% in 0.2% increment, 1.5% and 2.0%) and NaCAS concentration was varied from 0.004% to 0.2% (0.004%, 0.008%, 0.01%, 0.02% to 0.1% in 0.2% increment, and 0.2%) The droplet size was measured immediately after emulsification and after 1 month in order to assess the systems stability. Emulsions prepared with Tween 60 concentrations of 0.4% and above were stable against coalescence, but systems containing less surfactant ($< 0.4\%$) did exhibit some level of coalescence after a month. In all cases, no oil layer was observed at the top of the emulsions for at least a month. In agreement to previous studies^{242,243}, the droplet size decreased with increasing Tween 60 concentrations up to 1.5%. In a similar way the emulsions prepared with Sodium Caseinate were stable at concentrations above 0.08% and there was no change in emulsion droplet size with time (Figure 6-1b). Droplet sizes decreased with increasing protein concentrations, with a constant droplet size achieved for Sodium Caseinate concentrations $\geq 0.02\%$; again this is in agreement to what has been reported elsewhere^{120,244}. At concentrations of 0.01% and below, bulk phase separation occurred, while at concentrations between 0.01 and 0.06% coalescence is occurring with time as shown by the increase in the measured droplet size.

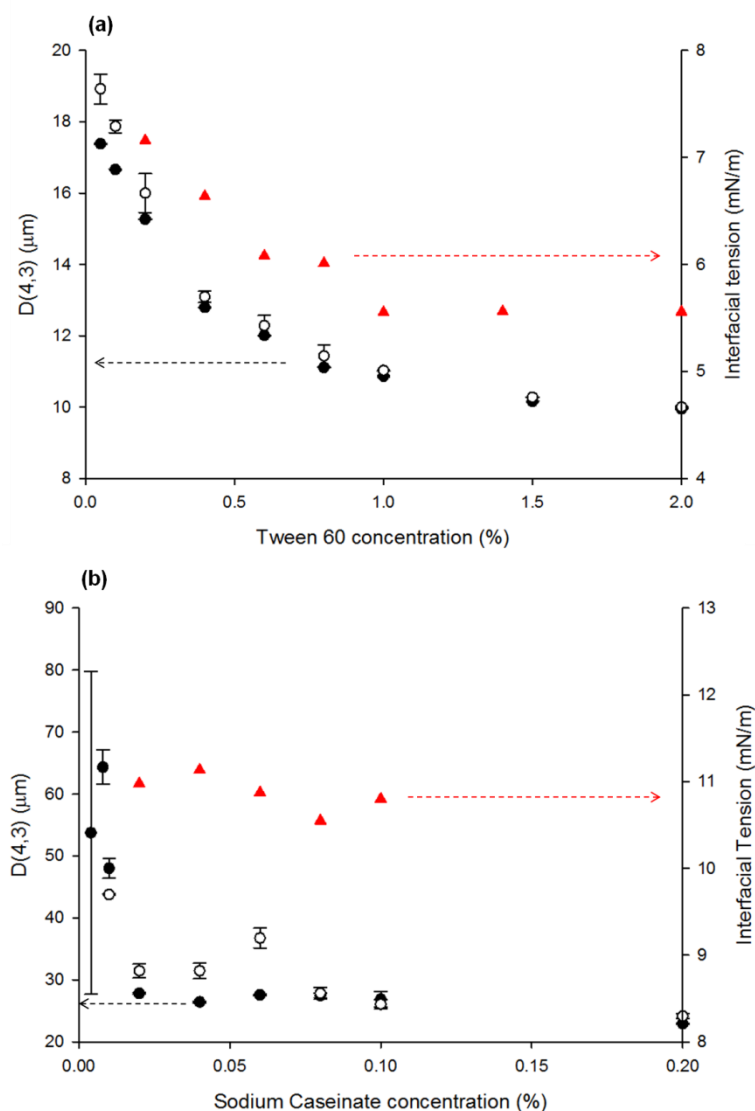


Figure 6-1: Effect of Tween 60 concentration (Figure a) and Sodium Caseinate concentration (Figure b) on the average size $D(4,3)$ of emulsion (prepared at pH 2) droplets measured after emulsification (black circle) and after a month (white circle) and on the O/W interfacial (measured after 30 minutes, at ambient temperature, $24^{\circ}\text{C} \pm 3^{\circ}\text{C}$, red triangle). Where not visible, error bars are smaller than the symbols.

The droplet sizes and their dependency on surfactant concentration can be explained by considering the interfacial tension. The interfacial tension measured after 30 minutes is reported in Figure 6-1, right Y-axis. Note that the effect of surfactant type and concentration on the interfacial tension will be developed in more details in Chapter 7. As can be seen Figure 6-1a, the IFT decreases with increasing Tween 60 concentration,

allowing more efficient oil droplet break-up during emulsification. Moreover, the interfacial tension measured for systems with Tween 60 concentrations of 1.0 and 2.0% was constant, and the droplet size showed no dependency on surfactant concentration. As shown in Figure 6-1b, by increasing the Sodium Caseinate concentration, the droplet sizes of the O/W emulsions decreased with increasing protein concentration reaching a minimum of 30 μm at 0.02%. Again this fits well with interfacial tension measurements. Above 0.02%, there was only a slight change in the interfacial tension, which remains more or less the same. This indicates that the oil droplet break-up efficiency during emulsification is not improved by adding Sodium Caseinate at concentrations above 0.02% or Tween 60 above 1%.

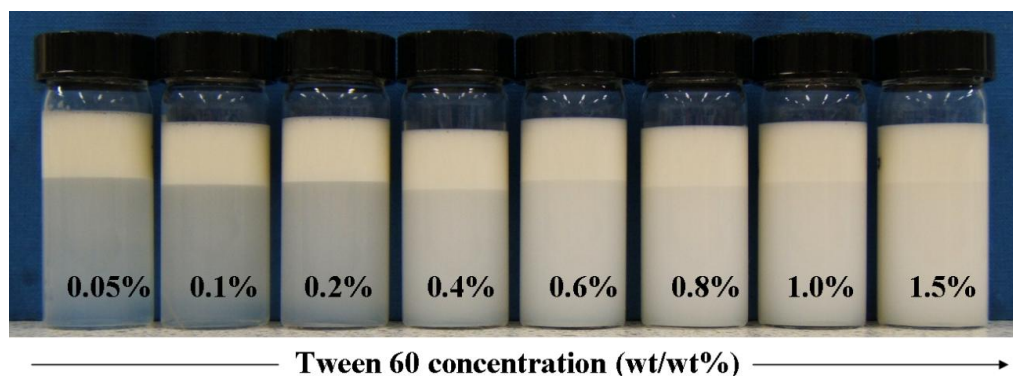


Figure 6-2: Effect of Tween 60 concentration on the stability of O/W (20/80) emulsions prepared at pH 2, after 1 week.

Optical observation of O/W emulsions stabilised by Tween 60 revealed that increasing the concentration had no effect on the cream layer volume, which was constant at ~30% of the total volume of the emulsion (Figure 6-2). However, the continuous phase became cloudier, either as a consequence of “free” Tween 60 (Tween 60 concentration is above the CMC) or due to the presence of small oil droplets. The results are quite

different with the protein (Figure 6-3): optical observation revealed that the cream layer volume increases with increasing Sodium Caseinate concentration and the turbidity of the aqueous phase was slightly increased probably as a consequence of increasing “free” Sodium Caseinate molecules. As the droplet size is constant for NaCAS concentrations above 0.02%, the coverage of emulsion droplets by Sodium Caseinate also remains constant. NaCAS molecules, added in excess, are likely to stay in the aqueous phase as they do not adsorb at the oil-water interface.

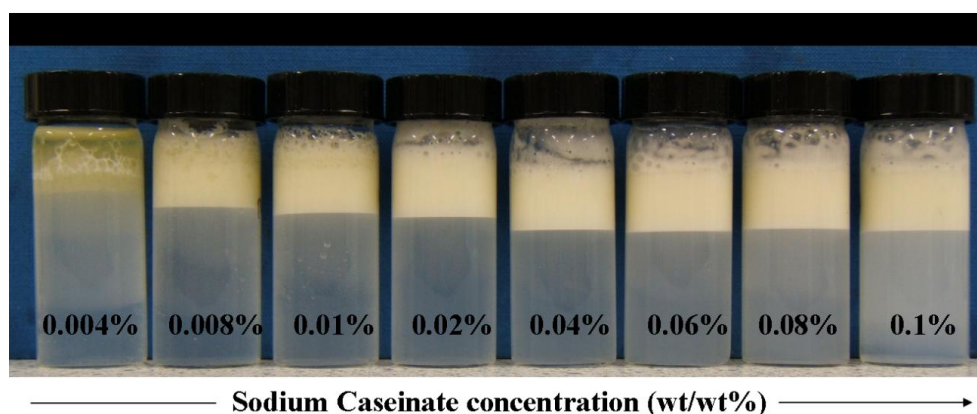


Figure 6-3: Effect of NaCAS concentration on the stability of O/W (20/80) emulsions prepared at pH 2, after 1 week.

The efficiency of lecithin to stabilise O/W emulsions, adjusted to pH 2, was also investigated, for lecithin concentrations between 0.05 and 1% (0.05%, 0.1%, 0.3%, 0.6% and 1.0%). Although emulsions droplets were formed in the presence of lecithin during the process, complete separation into an oil and aqueous phase occurred after a few minutes, at low surfactant concentrations, and after few hours, at high concentrations (Figure 6-4). The fact that, in Figure 6-4, the oil content seems to be different at different lecithin concentrations is only due to experimental approximations; as creaming occurs very quickly after emulsification, the volume of cream (containing

oil droplets) poured from the emulsification beaker to glass vial may not have been the same for all the emulsions. Nonetheless, this does not affect what is aforementioned, i.e. emulsions prepared were not stable at any lecithin concentration.

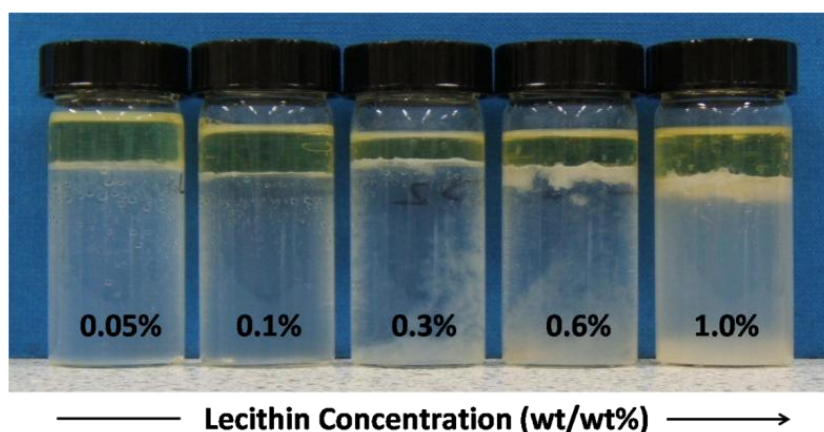


Figure 6-4: Effect of lecithin concentration on the stability of O/W (20/80) emulsions prepared at pH 2, after a few hours.

6.2 Mixed-emulsifier stabilised emulsions

The stability of O/W emulsions in the presence of the mixed emulsifier systems, thus both silica particles and surfactant (Tween 60, Sodium Caseinate or lecithin), was investigated. The *Method 2*, described section 3.4.1, was used to prepare these emulsions. The droplet sizes of the formed emulsions were measured both immediately after emulsification and after 1 month. The surfactant type and concentration in the mixed emulsifier systems were both varied as shown Table 6-1, while the concentration of colloidal particles was kept constant at 1% regardless of the surfactant type and concentration. The obtained droplet size data, as a function of surfactant concentration, are shown in Figure 6-5.

Table 6-1: W/O and O/W surfactant concentrations used in the mixed-emulsifier systems.

W/O surfactant concentrations	
Lecithin	0.05%, 0.07%, 0.1% to 1.0% in 0.1% increment
O/W surfactant concentrations	
Tween 60	0.02% to 0.1% in 0.02% increment, 0.2%, 0.4%, 0.6% to 1.5% in 0.1% increment
NaCAS	0.002% to 0.01% in 0.002% increment, 0.02% to 0.1% in 0.02% increment, 0.2%

The data in Figure 6-5 show that the use of mixed emulsifier systems has resulted in the production of stable emulsions for all tested types and concentrations of surfactant. The droplet sizes of the emulsions prepared using Tween 60 or NaCAS in the emulsifier mixture do not change even after a month. In case of lecithin, droplet size slightly decreases with time, even though they do not exhibit coalescence; no oil layer was detected at the top of emulsion at any lecithin concentration. These differences are thought to be within experimental error and could be associated with the fact that lecithin is not the “natural choice” to stabilise oil-in-water emulsions. In terms of the droplet size dependency to the surfactant concentration, the behaviour of the systems containing Tween 60 and NaCAS was complex. In contrast to the behaviour displayed by systems stabilised solely by the two surfactants, the reduction in droplet size here is not monotonic. Rather, the droplet sizes of the mixed-emulsifier stabilised emulsions initially decrease sharply (up to a concentration of 0.6% for Tween 60 and 0.04% for Sodium Caseinate) and then show an increase for intermediate concentrations (between 0.6 and 1% for Tween 60, and 0.04 and 0.06% for NaCAS). In the case of Tween 60 this is then followed by a secondary decrease of droplet size ($> 1\%$), and in the case of NaCAS, a stable droplet size as the surfactant concentration is further increased ($> 0.6\%$). When lecithin is used as the surfactant in the mixed emulsifier system, droplet

sizes do not display the same complex behaviour, as they initially decrease, for surfactant concentrations up to ~0.6%, and eventually reach a constant size (> 0.6%).

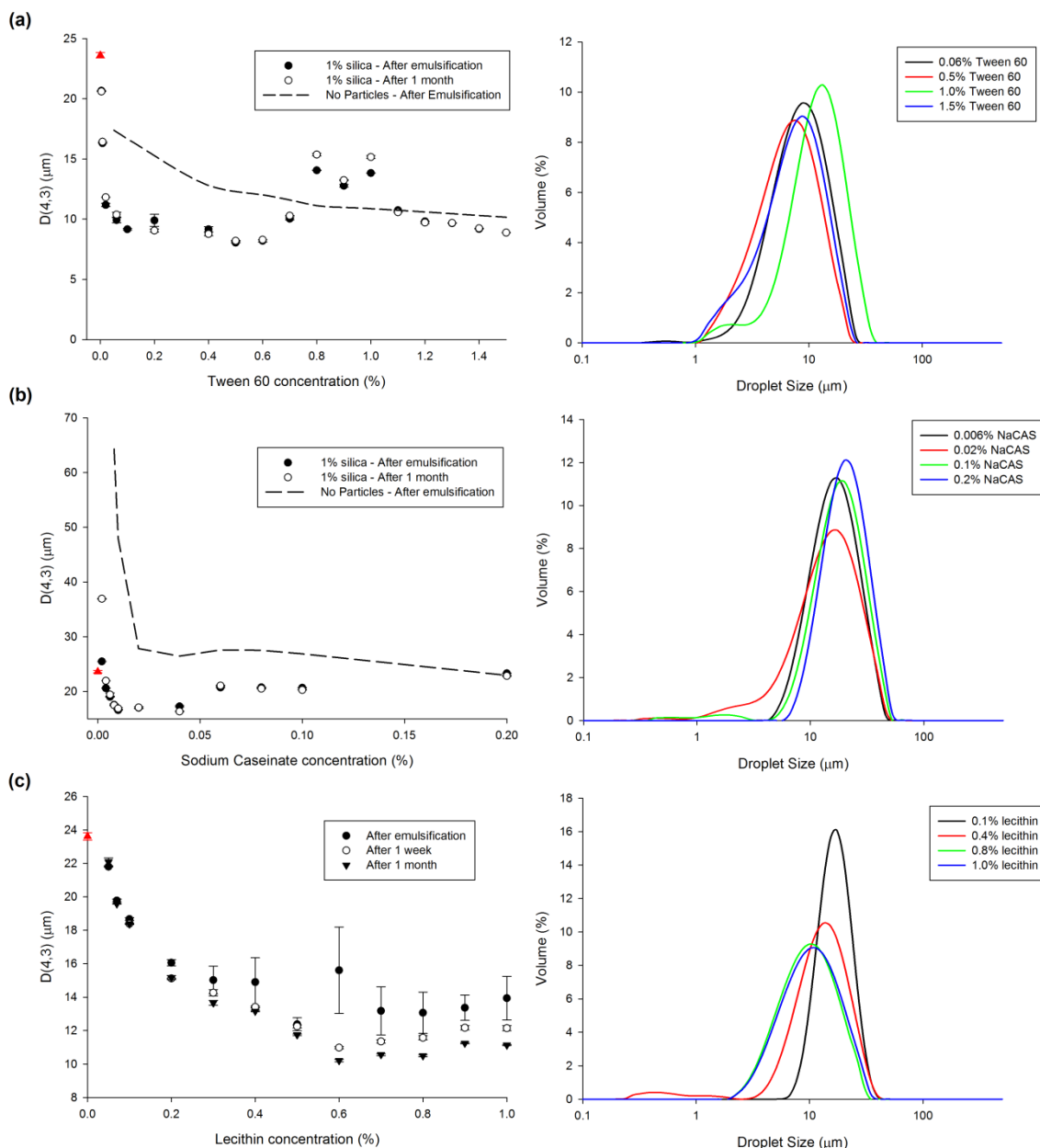


Figure 6-5: Effect of Tween 60 concentration (Figure a), Sodium Caseinate concentration (Figure b) and lecithin concentration (Figure c) on the average size $D(4,3)$ of emulsion droplets (left figures) and droplet size distribution (right figures). ▲ is the average size of emulsions prepared with 1% Aerosil 200 and no surfactant. Where not visible, error bars are smaller than the symbols.

The complex behaviour displayed by the systems containing Tween 60 and NaCAS can be explained by considering the mechanism by which surfactants and particles get to the interface formed during the emulsification process. As the droplet size is drastically reduced at the initial stages of the process, the “naked” interfacial area in the system increases at a fast rate. The role of the low molecular weight surfactant is to assemble quickly at the formed interfaces, and thus promote further break-up, by reducing the interfacial tension but also stabilise (at least temporarily) the emulsion droplets. This gives valuable time for the less mobile colloidal particles to eventually coat all of the available oil-water interfaces and significantly reduce the occurrence of coalescence events. It is this stabilisation mechanism of these mixed emulsifier systems that results in emulsion droplets of smaller sizes than those in the presence of surfactants or particles alone. In fact, the benefit from using mixed emulsifiers arises even when the surfactant used is unable to provide stable emulsions by itself; this is clearly demonstrated in this study in the case of lecithin (Figure 6-5c).

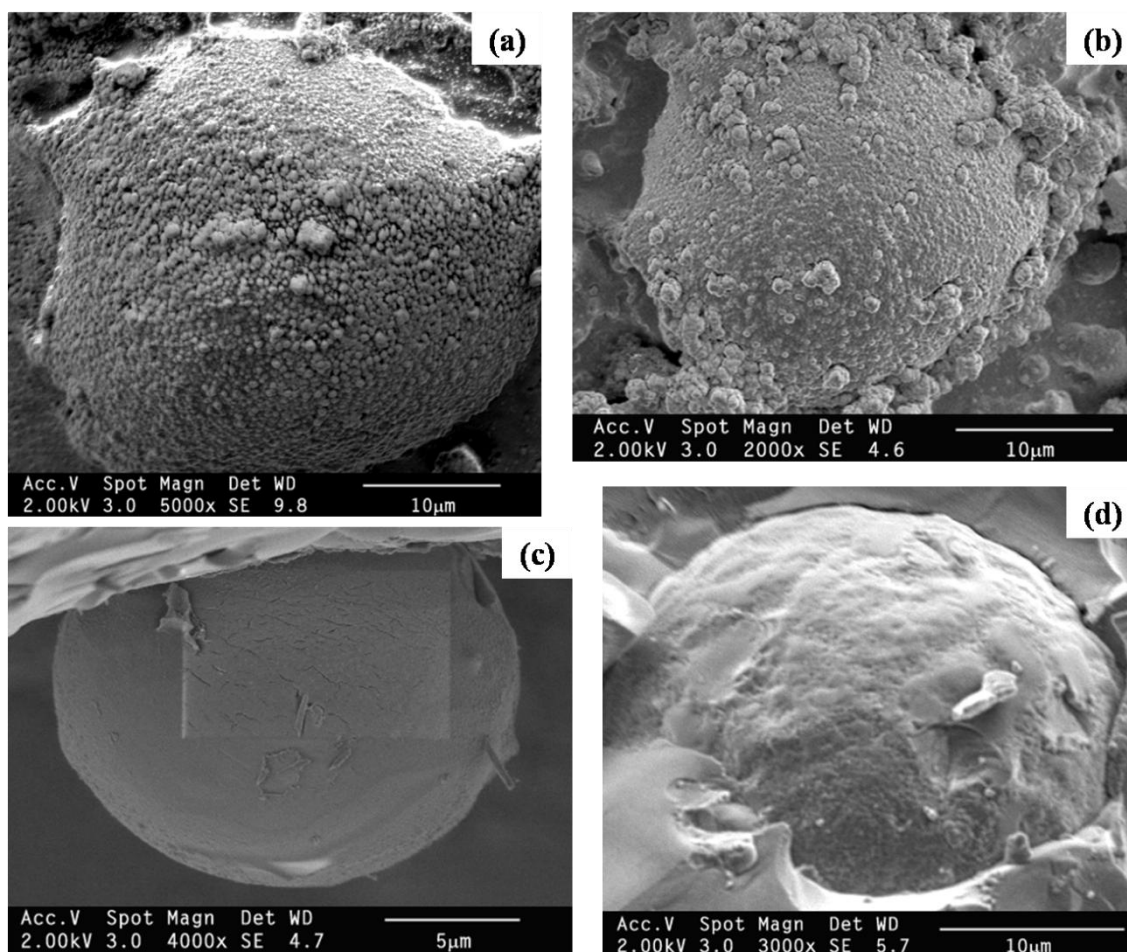


Figure 6-6: Freeze fracture images of emulsions formed in the presence of silica particles (1%) and various Tween 60 concentrations: (a) 0.4%; (b) & (c) 1.0%; (d) 1.5%.

What becomes evident from Figure 6-5 is that the suggested mechanism by which these mixed-emulsifier systems provide stability depends on the surfactant concentration. At relatively low surfactant concentrations (Tween 60 and NaCAS), mixed emulsifiers do provide a droplet size reduction when compared to emulsions stabilised solely by surfactants or silica particles. Nonetheless, for intermediate concentrations the emulsion droplet size now increases, eventually reaching the size of the surfactant-stabilised emulsions droplets (dashed curve in the Figure 6-5a and b). The reason for the observed behaviour is suggested to relate to changes in the positioning of the particles at the emulsion interface induced by the changes in the concentration of surfactant in the

system. This hypothesis was tested by obtaining a series of SEM micrographs of droplets stabilised by mixed emulsifier systems with a constant concentration of particles (1%) but of varying surfactant (Tween 60) content (Figure 6-6). Oil droplets at low Tween 60 concentrations (0.4%) appear to be fully covered by closely packed silica particles (Figure 6-6a), which explains the size reduction also observed for these systems. Increasing the Tween 60 concentration further, between 0.6 and 1%, actually results in a reduced number of particles at the interface (Figure 6-6b and c), which is the reason for the observed increase in droplet size. The increase of the emulsion droplet size induced by increasing the Tween 60 concentrations between 0.6 and 1% is accompanied by a reduced number of particles at the interface (Figure 6-6b and c). At these concentrations of surfactant two different types of droplets were observed; some droplets were completely covered by silica particles and are similar to droplets of emulsions at lower concentration ($< 0.6\%$) while some droplets had no particles. The enhanced stability associated with the previously densely packed interfaces is no longer provided and these systems are more prone to coalescence events. At even higher Tween 60 concentrations (Figure 6-6d), all particles have now been removed from the interface and stability is only provided by the surfactant component. As a result the droplet sizes measured in this case are more or less the same as those in systems stabilised only by Tween 60 (dashed line in Figure 6-3a). This argument is further supported by visual inspection of the bulk emulsions (Figure 6-7). Notice that as the particles are slowly removed from the surface of the droplets, they reside at the serum phase of the bulk emulsions, which progressively becomes cloudy.

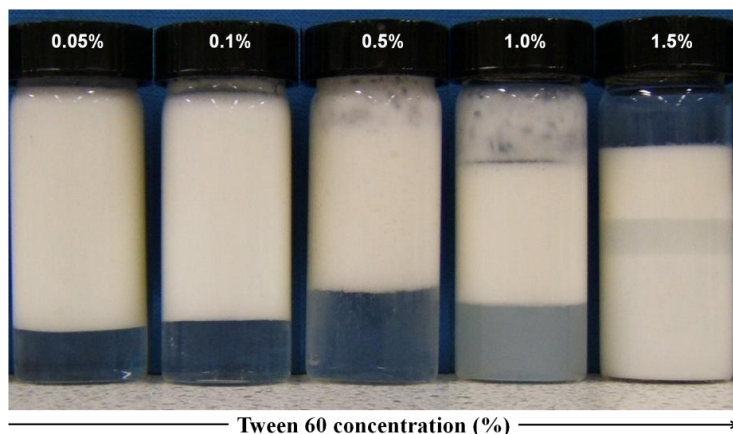


Figure 6-7: Effect of Tween 60 concentration on the stability of O/W (20/80) emulsions prepared with 1% Aerosil 200 at pH 2, after 1 week.

SEM micrographs of emulsion droplets stabilised by mixed emulsifier systems containing Sodium Caseinate revealed a very similar behaviour (Figure 6-8). Micrographs show that at low NaCAS concentration (0.02%) emulsion droplets are fully covered by silica particles and at high concentration (0.2%), there are no particles around the droplets. Again, optical observations revealed that the aqueous phase of the emulsions becomes cloudier as the concentration of Sodium Caseinate increases.

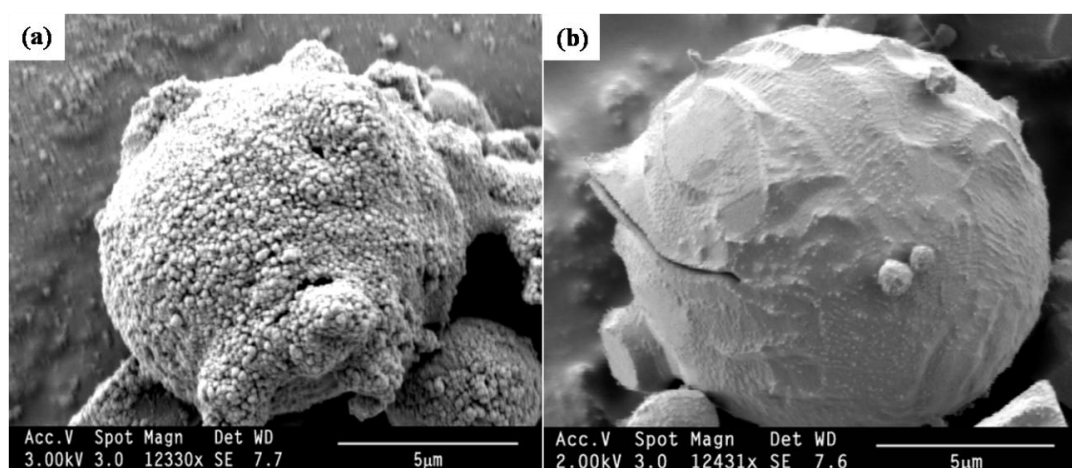


Figure 6-8: Freeze fracture images of O/W (20/80) emulsions formed at pH 2 in the presence of silica particles (1%) and two NaCAS concentrations: (a) 0.02%; (b) 0.2 %.

Overall, it does indeed appear that particles' positioning at the interface is controlled by the surfactant concentration in the system, which, if increased above a certain "critical" value, can even lead to displacement of the particles. Nonetheless, analysis of SEM micrographs of emulsions droplets stabilised by mixed emulsifier systems containing lecithin (Figure 6-9) also revealed that the behaviour of these mixtures does not just depend on the surfactant concentration, but also on the type of surfactant used. In contrast to mixed emulsifiers containing Tween 60 or NaCAS, those with lecithin did not display the same droplet size dependency as a function of surfactant concentration (Figure 6-5c). The SEM micrographs obtained for the mixed emulsifier systems containing lecithin show that droplets are stabilised by particles regardless of the surfactant concentration used (Figure 6-9). At low lecithin concentrations ($\leq 0.1\%$) the serum phase of the bulk emulsions appears to have at its bottom a small deposit of particles, which is no longer observed at higher ($> 0.1\%$) surfactant concentrations, as can be seen Figure 6-10. It therefore appears that increasing the surfactant concentration in the case of lecithin promotes further adsorption of the particles at the interface.

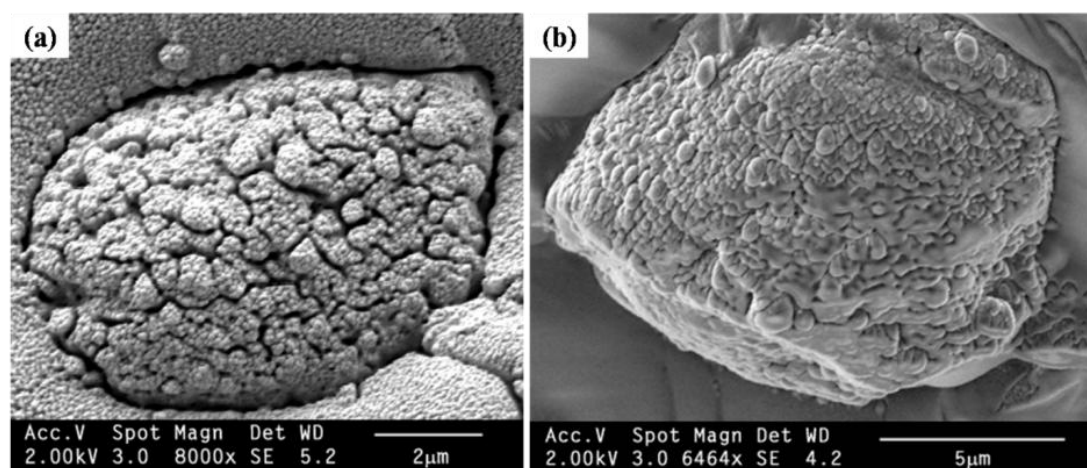


Figure 6-9: Freeze fracture images of O/W (20/80) emulsions formed at pH 2 in the presence of silica particles (1%) and two lecithin concentrations: (a) 0.05 %; (b) 0.8 %.

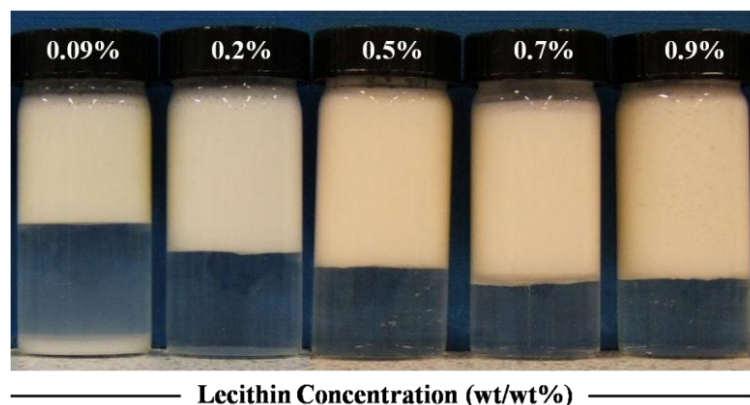


Figure 6-10: Effect of the lecithin concentration on the stability of O/W (20/80) emulsions prepared at pH 2 with 1% Aerosil 200, after 1 week.

The mass m_{th} of Tween 60 (Table 6-2) and lecithin (Table 6-3) theoretically required for the surfactant's head to fully cover the water-side of droplet interface was calculated, and compared to the mass m_{exp} of Tween 60 or lecithin used to make O/W emulsions. The calculation of m_{th} does not provide an exact value, but an estimation of the amount of surfactant necessary to fully cover emulsion droplets. It is based on the hypothesis that emulsion droplets at a given surfactant concentration have all the same diameter $D(4,3)$ and that the interface covered by the head of Tween 60 is $A_m \sim 50 \text{ \AA}^2$, reported elsewhere^{245,246}. In case of lecithin, as the molecular weight was unknown, the amount of lecithin per interfacial area $S_m \sim 2.04 \text{ mg/m}^2$ was reported²⁴⁷.

When Tween 60 is used as surfactant (Table 6-2), it appears that at low concentration (0.02%), emulsion droplets are not fully covered by the surfactant as the amount of Tween 60 introduced in the emulsion is lower than the theoretical amount required to cover the droplets ($m_{exp} < m_{th}$). By increasing the surfactant concentration, the amount of Tween 60 in the emulsion becomes in excess ($m_{exp} > m_{th}$); emulsion droplets are

assumed to be fully covered by the surfactant. At high surfactant concentration, a large amount of Tween 60 molecules cannot adsorb at the interface. As Tween 60 affinity for water is higher than the one for oil, it is assumed that most of the Tween 60 molecules that do not adsorb at the interface remain in the aqueous phase as single molecules or more likely as micelles. When lecithin is used as surfactant (Table 6-3), the mass of surfactant introduced during emulsification is higher than the amount of lecithin required to cover the droplet interface, regardless of the lecithin concentration. Likewise Tween 60, a large number of lecithin molecules do not adsorb at the interface, but, on the contrary to Tween 60, these molecules tend to remain in the oil phase, i.e. inside emulsion droplets, as lecithin preferentially dissolves in oil.

In spite of the fact that m_{th} calculation is an estimation, it appears clearly that, in the range of Tween 60 concentration investigated, there is a transition in the surface coverage of emulsion droplets, from partially covered to fully covered. This induces, as aforementioned, that a large number of Tween 60 molecules, likely as micelles, remains in the aqueous phase. It is suggested here that these micelles react with the silica particles also present in the aqueous phase to form flocs of particles/micelles that will not adsorb at the interface and sediment at quiescent conditions. This is confirmed by visual observations of O/W emulsions stabilised by both Tween 60 and silica particles (Figure 6-7), at high surfactant concentration (1.5%). The turbidity of the aqueous phase is high compared to the turbidity of aqueous phase containing dispersed particles only or Tween 60 molecules only (after dissolution).

As aforementioned, in the range of lecithin concentrations investigated, the quantity of lecithin used to prepare emulsions is higher than the minimum quantity to cover the

surface. However, contrary to emulsions stabilised with particles and O/W surfactant, no displacement of the particles was observed from the interface when W/O surfactants are used. It is suggested that this is due to the fact that lecithin molecules in excess remain in the oil phase and, thus, are not likely to interact with silica particles to form flocs. The presence of lecithin in the emulsion does not affect the diffusion of particles through the aqueous phase, which can adsorb at the interface to provide long term stable emulsions.

Table 6-2: Surface coverage calculation for O/W (20/80) emulsions prepared with Tween 60 at various concentrations and hydrophilic silica particles (1% Aerosil 200) – comparison between the mass of Tween 60 introduced during emulsification and the mass of Tween 60 theoretically required to fully cover emulsion droplets.

Tween 60								
Concentration (%)	0.02	0.06	0.2	0.5	0.6	0.7	0.8	1.0
D(4,3) (μm)	11.2	9.9	9.6	8.0	8.2	10.0	14.1	13.8
m_{exp} (g)	0.009	0.029	0.096	0.24	0.29	0.34	0.38	0.48
m_{th} (g)	0.015	0.017	0.018	0.021	0.021	0.017	0.012	0.013

Notation:

A_m = interfacial area occupied per molecule of surfactant ($\sim 50 \text{ \AA}^2$);

m_{exp} = mass of Tween 60 measured;

$N_{droplet}$ = number of emulsion droplets;

$V_{droplet}$ = volume of one emulsion droplet;

$S_{droplet}$ = surface of one emulsion droplet;

V_{tot} = Total volume of oil;

m_{th} = mass of Tween 60 calculated;

NA = Avogadro number ($= 6.02 \times 10^{23} \text{ mol}^{-1}$);

n_{th} = number of moles of Tween 60 calculated;

$n_{th/droplet}$ = number of moles of Tween 60 calculated per droplet;

$n_{molecules/droplet}$ = number of Tween 60 molecules calculated per droplet;

$M_{Tween\ 60}$ = Tween 60 molecular weight ($= 1309 \text{ g/mol}$).

Calculation:

$$m_{th} = n_{th} \times M_{\text{Tween 60}}$$

$$n_{th} = n_{th/droplet} \times N_{droplet}$$

$$n_{th/droplet} = n_{\text{molecules/droplet}} \times N_A$$

$$n_{\text{molecules/droplet}} = S_{droplet} \times A_m$$

$$N_{droplet} = \frac{V_{tot}}{V_{droplet}}$$

Table 6-3: Surface coverage calculation for O/W (20/80) emulsions prepared with lecithin at various concentrations and hydrophilic silica particles (1% Aerosil 200) – comparison between the mass of lecithin introduced during emulsification and the mass of lecithin theoretically required to fully covered emulsion droplets.

Lecithin				
Concentration (%)	0.05	0.1	0.4	0.8
D(4,3) (mm)	21.8	18.7	14.9	13.1
m_{exp} (g)	0.024	0.048	0.192	0.384
m_{th} (g)	0.003	0.004	0.005	0.006

Notation:

S_m = mass of surfactant “head” per interfacial area (~2 mg/m²);

m_{exp} = mass of Lecithin measured;

$N_{droplet}$ = number of emulsion droplets;

$V_{droplet}$ = volume of one emulsion droplet;

$S_{droplet}$ = surface of one emulsion droplet;

V_{tot} = Total volume of oil;

m_{th} = mass of lecithin calculated;

$m_{th/droplet}$ = mass of lecithin calculated per droplet.

Calculation:

$$m_{th} = m_{th/droplet} \times n_{droplet}$$

$$m_{th/droplet} = S_m \times S_{droplet}$$

$$N_{droplet} = \frac{V_{tot}}{V_{droplet}}$$

6.3 Conclusion

In this chapter, it was proved that the 2-step mechanism suggested in Chapter 5 for the stabilisation of emulsions in the presence of hydrophilic silica particles and monoolein could be extended to various kinds of surfactant. Emulsion microstructure depended on the type and concentration of surfactant:

- In case of W/O surfactant (lecithin), the component responsible for the long-term emulsion stability was the colloidal particles, strongly attached at the interface. Regardless of the surfactant concentration, emulsion microstructure was Pickering emulsion-like, i.e. emulsion droplets are covered by solid particles;
- In case of O/W surfactant (Tween 60 or Sodium Caseinate), emulsion microstructure depended on the surfactant concentration as a displacement of silica particles from the interface was observed by increasing the surfactant concentration. At low concentration, microstructure was Pickering emulsion-like. At high concentration, emulsions exhibited a surfactant stabilised emulsion-like. At intermediate concentration, two kinds of droplets were found in the emulsions; some covered by silica particles and some only stabilised by surfactant molecules.

The effect of surfactant type on the behaviour of O/W emulsions stabilised by mixed emulsifiers relates to the ability of the surfactant to solely stabilise these systems. Increasing the concentration of those surfactants that can provide stable O/W emulsions

when used on their own (i.e. Tween 60 and NaCAS in this case) eventually results in the displacement of particles due to the stronger competition for adsorption at the interface and interactions between surfactant and particles. On the other hand, increasing the concentration of surfactants that cannot provide stable O/W emulsions (i.e. lecithin in this case) does not disrupt particle adsorption at the interface and the achieved Pickering stabilisation is maintained.

Droplet size of mixed-emulsifier emulsions that exhibit a Pickering emulsion-like structure is significantly decreased compared to emulsion only stabilised with surfactant or silica particles. This is a consequence of the 2-step mechanism aforementioned.

Chapter 7:

Effect of surfactant type and concentration and hydrophilic silica particles on the Interfacial Tension and Contact Angle

Interfacial tension is of great importance to understand the stabilisation mechanism taking place during emulsification. Concerning Pickering emulsions, the contact angle that a particle makes at the oil-water interface, is linked to the strength of the particle adsorption at the interface, and so to the emulsion stability. As mentioned in previous chapters, the presence of surfactant in silica particles stabilised emulsion is likely to modify the interfacial properties during emulsification, but also the contact angle between the colloids and the modified interface (oil – water – surfactant).

In this chapter, interfacial tension and contact angle were measured to characterise the oil-water interface and understand the role of both particles and surfactant in modifying the interface. In order to get a better understanding of the stabilisation mechanism of mixed-emulsifier emulsions, some efforts were made to measure interfacial tension and contact angle within the same experimental conditions as emulsions were prepared. However, due to experimental issues with the goniometer, some modifications have to be made in order to measure contact angle and interfacial tension (see sections 3.5.2.4 for CA measurement and 3.5.3.2 for IFT measurement).

7.1 Interfacial Tension of Oil – Water systems

7.1.1 Effect of hydrophilic silica particles

The effect of hydrophilic silica particles on the oil-water interfacial tension was investigated. Interfacial tension of a pure system, i.e. IFT between vegetable oil and water (adjusted at pH 2), was first measured over 500 seconds as described section 3.5.3.2. IFT between vegetable oil and a silica-in-water dispersion (1% Aerosil 200, pH 2) was then measured over the same period (Table 7-1). It can be seen from this table that interfacial tension, regardless of the presence of silica particles in the system, slightly decreases with time and the presence of the silica particles has no effect.

Table 7-1: Interfacial tension (IFT) measured at ambient temperature ($24^{\circ}\text{C} \pm 3^{\circ}\text{C}$) of pure vegetable oil and water (adjusted to pH 2) system as a function of time in the presence (or not) of hydrophilic silica particles.

		Time (s)					
		0	100	200	300	400	500
IFT (mN/m)	No Particles	25.40 ± 0.44	24.69 ± 0.25	24.39 ± 0.21	24.10 ± 0.36	23.86 ± 0.11	23.77 ± 0.09
	1% Aerosil 200	25.15 ± 0.98	24.31 ± 0.29	24.25 ± 0.49	23.62 ± 0.21	23.49 ± 0.17	23.32 ± 0.17

This can be explained by considering the interfacial properties of the particles. As mentioned Chapter 4, Aerosil 200 particles, dispersed in water at pH 2, adsorb at the interface during emulsification to stabilise O/W emulsions. Nonetheless, on the contrary to surfactant, particles do not replace molecules of water and oil at the interface, as these molecules adsorb into the porous structure of the particles. It is argued here that the interactions between oil and water are not modified by the presence of particles at the interface which results in the fact that interfacial tension is not reduced in the presence of the particles. In addition, there is evidence in the literature, Vignati *et al.*¹³⁷, and Drelich and co-workers¹³⁸ that even when hydrophobic particles are strongly adsorbed at the interface, there is no reduction of the interfacial tension and in all cases (hydrophilic and hydrophobic particles), no modification of the O/W interfacial tension was observed.

7.1.2 Effect of O/W surfactant

The effect of Tween 60 and Sodium Caseinate (O/W surfactant) on interfacial tension between pure vegetable oil and water, adjusted to pH 2 was investigated. Details regarding interfacial tension measurements and the surfactant concentrations investigated in this section were given Table 3-3 (section 3.5.3.2). The effect of

colloidal particles in the presence of each O/W surfactant was also studied by adding hydrophilic silica particles (Aerosil 200, 1%) into the water phase.

7.1.2.1 Effect of Tween 60

As reported before^{242,243,248}, interfacial tension decreases as Tween 60 concentration is increased. As can be seen in Figure 7-1 the same behaviour is observed in the presence of colloidal particles. However, the difference is that the interfacial tension of systems containing no particles (Figure 7-1a) does not strongly depend on the surfactant concentrations, the IFT decreasing from ~8 mN/m at a concentration of 0.2% to ~6 mN/m at 1.4% (values after 30 minutes). In the presence of silica particles (Figure 7-1b), the interfacial tension decreases significantly by increasing the Tween 60 concentration; from ~11 mN/m at 0.2% to ~6 mN/m at 1.0% (values after 30 minutes). Any further increase of the surfactant concentration does not affect the interfacial tension.

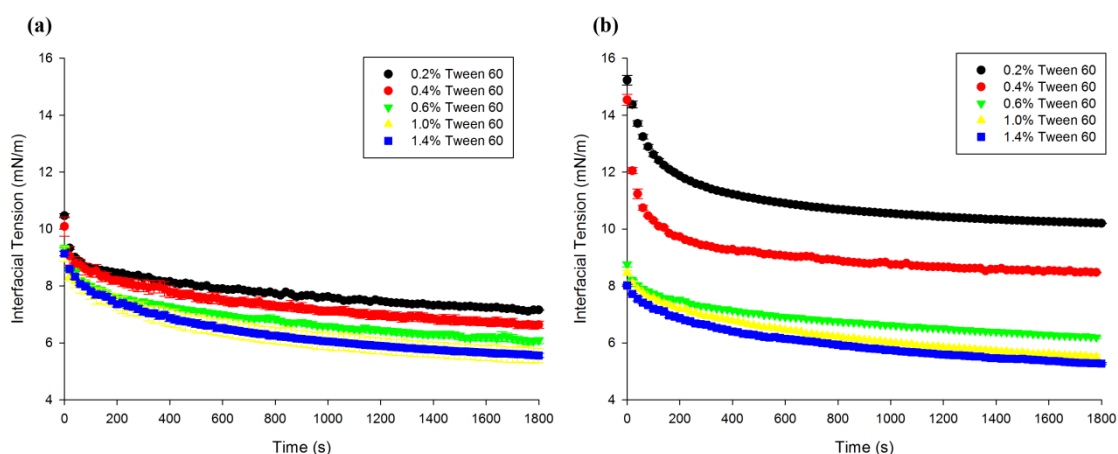


Figure 7-1: O/W interfacial tension versus time of systems containing water (pH 2) + Tween 60 – oil in the absence (a) or presence (b) of hydrophilic silica particles (Aerosil 200, 1% dispersed in the water phase), for various Tween 60 concentrations, measured at ambient temperature (24°C ± 3°C). Where not visible, error bars are smaller than the symbols.

These data show that the presence of particles in the system affects the Tween 60 efficiency in reducing interfacial tension at low surfactant concentrations ($< 0.4\%$ Tween 60). At high concentration ($\geq 0.6\%$ Tween 60), IFT is very similar for both systems; the differences are given in Table 7-2. The data shown Table 7-2 suggest that, at low Tween 60 concentration, both silica particles and Tween 60 molecules are adsorbed at the interface. By adsorbing at the oil-water interface, colloidal particles reduce the interfacial area covered by the surfactant molecules, lowering the effective surface coverage and giving a higher interfacial tension. At Tween 60 concentration higher than 0.6%, the interfacial tension is not affected by the presence of particles. This could either be due to displacement of particles from the interface or, as a consequence of the higher Tween concentrations, the surfactant molecules cover the interface faster during emulsification, thus preventing the particles entering the interface in the first place.

Table 7-2: Difference between interfacial tension, measured at ambient temperature ($24^{\circ}\text{C} \pm 3^{\circ}\text{C}$), of systems containing particles (Aerosil 200, 1%) and the systems without particles, versus time, at various Tween 60 concentrations.

Time (s)	Interfacial Tension Difference (mN/m)				
	Tween 60 concentration (%)				
	0.2	0.4	0.6	1.0	1.4
0	4.76	4.45	-0.59	-0.76	-0.67
200	3.41	1.54	-0.05	-0.69	-0.25
600	3.00	1.56	-0.10	-0.54	-0.09
1000	2.92	1.63	0.04	-0.35	-0.05
1400	3.02	1.74	0.08	-0.32	-0.04
1800	3.04	1.85	0.13	-0.26	-0.06

Regardless of the concentration of Tween 60 or the presence of particles in the system, the interfacial tension does not reach the thermodynamic equilibrium even after 30

minutes, i.e. that the IFT continuously decreases with time (Figure 7-1). The slopes of the curves IFT vs. Time at all Tween 60 concentrations and in the presence or absence of particles were measured to be the same (~ -0.03 mN/m/min, after 30 minutes). Thus, the decrease of interfacial tension with time does not depend on the presence of surfactant or particles, but is more likely to be due to the nature of oil. As mentioned by Gaonkar¹⁹¹, the interfacial tension of commercial vegetable oils against water decreases with time due to surface active impurities. After purification of vegetable oils, the interfacial tension time dependency no longer exists. However, due to oxidative damage, diglycerides and monoglycerides are produced with time on storage of the triglyceride oil, so this time dependent IFT will reoccur.

By closer inspection of Table 7-2, it can be seen that silica particles do not only affect Tween 60 efficiency in reducing the interfacial tension, but also play a role in the kinetics of Tween 60 molecules adsorption at the oil-water interface. At low Tween 60 concentrations ($\leq 0.4\%$), the IFT difference decreases over the first 400 seconds, i.e. the surfactant adsorbs at the interface slower when the silica particles are present in the aqueous phase. The diffusion of surfactant molecules through the water phase to reach the interface is delayed by the particles, probably to the competition between the two components to adsorb at the interface. After 400s, the IFT difference remains constant, i.e. the profile of the interfacial tension versus time, at a given Tween 60 concentration, does not depend on the presence of particles. At higher Tween 60 concentration ($\geq 0.6\%$), there is almost no evolution of the IFT difference with time.

7.1.2.2 Effect of Sodium Caseinate

The effect of Sodium Caseinate on the interfacial tension between water (adjusted to pH 2) and vegetable oil, in the absence or presence of hydrophilic silica particles are shown in Figure 7-2. As can be seen, in the absence of particles all the IFTs are the same and have the same time course (after 30 minutes, the IFT ~ 11 mN/m).

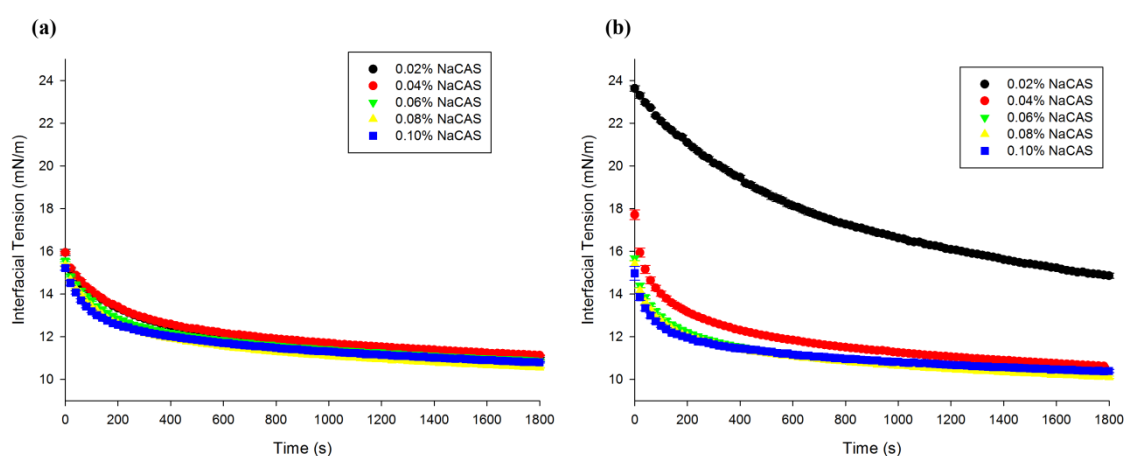


Figure 7-2: O/W interfacial tension versus time of systems containing water (pH 2) + NaCAS – oil in the absence (a) or presence (b) of hydrophilic silica particles (Aerosil 200, 1% dispersed in the water phase), for various NaCAS concentrations, measured at ambient temperature ($24^{\circ}\text{C} \pm 3^{\circ}\text{C}$).

In the presence of silica particles (Figure 7-2b), the interfacial tension is much higher at 0.02% NaCAS than when no particles are present. There is a slight indication that this behaviour is still maintained at shorter times in the presence of 0.04% NaCAS, however, above this concentration, particles have no effect at any time. This shows that, at 0.04% NaCAS, the interfacial tension at the thermodynamic equilibrium is dictated by the protein, but the presence of particles delays the adsorption of Sodium Caseinate molecules at the interface. As can be seen in Figure 7-2, interfacial tension decreases with time, regardless of the presence of silica particles and the concentration of Sodium

Caseinate. Except for the interfacial tension of system containing 1% silica particles and 0.02% NaCAS, the slope of the curve “IFT vs. time” was measured about -0.03 mN/m/min. This rate is the same as that measured for Tween 60, reinforcing the hypothesis that this is due to impurities present in the vegetable oil. The slope of the curve “IFT vs. time” for the system containing 1% silica particles and 0.02% NaCAS was measured, after 30 minutes, about -0.03mM/m/min, i.e. 4 times the slope of other systems. In this case, the decrease of the interfacial tension with time is the slow adsorption of the NaCAS molecules as the particles are displaced from the interface as discussed for Tween 60 above.

7.1.3 Effect of W/O surfactant

The effect of Lecithin in the absence and presence of silica particles on the interfacial tension between pure vegetable oil and water, adjusted to pH 2 are shown in figure 7-3. Measurements with no particles exhibited a poor reproducibility, regardless of the Lecithin concentration, for approximately the first 600 seconds (Figure 5a). Then, measurements appeared to be very reproducible. Even though a particular attention was paid during the experiments, this is probably due to lecithin remaining on the needle containing the water phase affecting the results. At lecithin concentrations of 0.3% and above in the presence of silica particles (Figure 7-3b), the reproducibility is good over the whole experimental timescale.

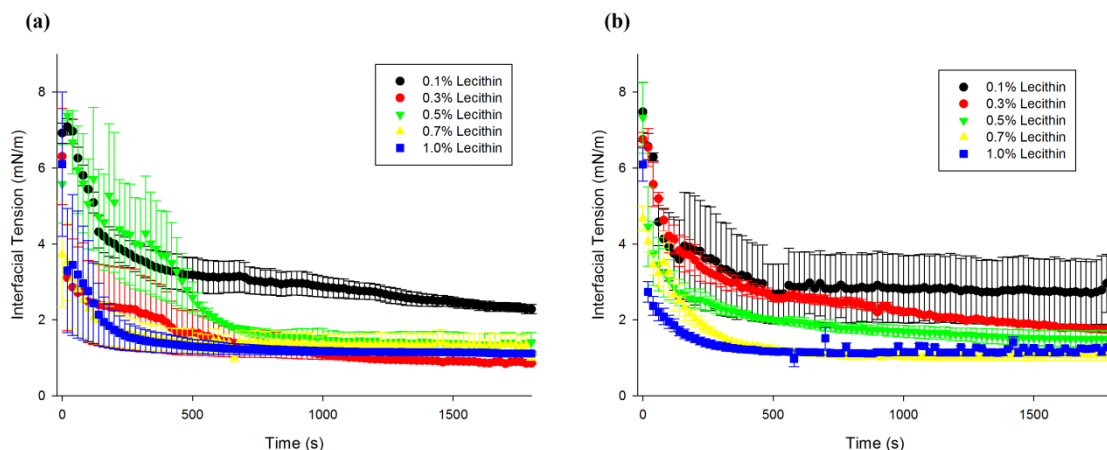


Figure 7-3: O/W Interfacial tension versus time of systems containing water (pH 2) – oil – lecithin in the absence (a) or presence (b) of hydrophilic silica particles (Aerosil 200, 1%), for various lecithin concentrations, measured at ambient temperature ($24^{\circ}\text{C} \pm 3^{\circ}\text{C}$).

The evolution of the IFT with time is very similar for each concentration of Lecithin with and without particles with the time required to reach the equilibrium depending on the lecithin concentration and the presence of silica particles. For example, for systems containing no particles, equilibrium is reached after ~ 700 s at 0.5% lecithin, while reached after 300 s at 1.0%. Thus, systems reach the equilibrium faster at high lecithin concentration than at low concentration. This is due to a faster adsorption of these molecules at the interface; surfactant molecules at higher concentration are closer to the interface and so have less distance to diffuse through the interface. As can be seen from the Figure 7-3, for concentrations up to 0.3%, interfacial tension decreases for both cases and then remains constant at higher concentrations. The comparison between the two systems (with or without particles) shows that the particles have no effect on the interfacial tension.

A major difference between lecithin and NaCAS or Tween 60 is that after 700s the interfacial tension does not change with time. This means that in the presence of

lecithin, the system has reached the thermodynamic equilibrium after adsorption of the surfactant at the interface. For Tween 60 and NaCAS, interfacial tension was shown to decrease with time whatever the concentration of surfactant. This was attributed to impurities in the oil, which modify the oil properties with time. As the same oil has been used throughout this study, the same impurities are present in all the experiments. The difference in time course of the interfacial tension may be explained by considering the steric effect of surfactant at the interface (Figure 7-4). O/W surfactant' heads (hydrophilic part) are closely packed at the “water side” of the interface due to their sizes while the tails (lipophilic part), smaller than the heads, do not fully cover the “oil side” of the interface. Thus, the interface can be affected by the impurities contained in the vegetable oil, resulting in the decrease of the interfacial tension with time. On the contrary, with lecithin the tails are closely packed at the “oil side” of the interface due to their sizes so the impurities are stopped from entering the interface.

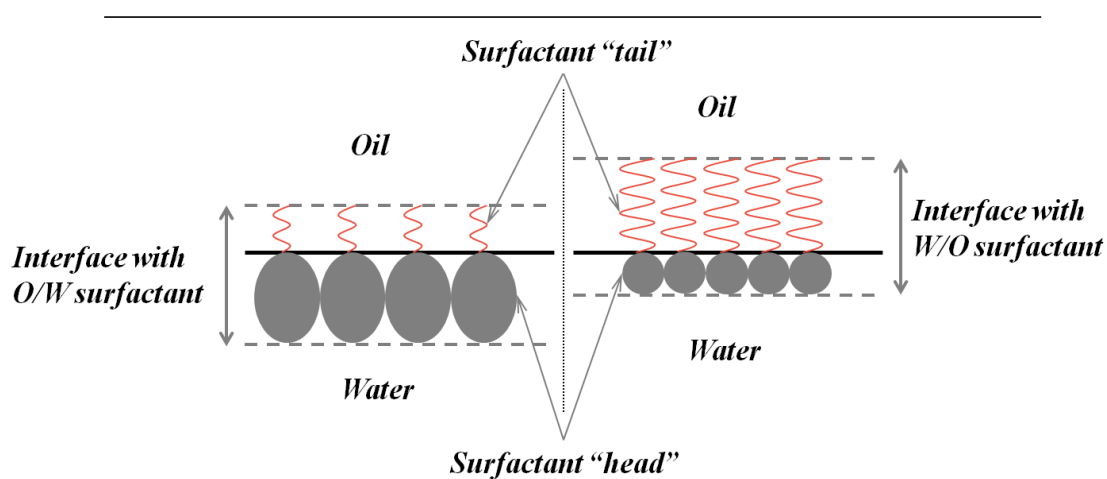


Figure 7-4: Scheme of oil-water interface in the presence of two kinds of surfactant: W/O (right part) and O/W (left part).

7.2 Contact Angle of three-phase systems Oil-Water-Glass substrate

7.2.1 Effect of colloid concentration on the contact angle

The effect of hydrophilic silica particles (Aerosil 200) on the contact angle of a system water (adjusted to pH 2) – oil – glass substrate was first investigated. The colloids concentration was varied from 0.2% to 2.0% (0.4% increment) and advancing contact angle was measured as described section 3.5.2.4. As can be seen Figure 7-5, the contact angles measured on the right side and on the left side of the droplet are very similar. This represents a validation of the measurement method and shows that the glass surface was thoroughly cleaned. Results regarding contact angle presented later on in this chapter will be the mean value of the CA measured on the right of the drop and the CA measured on the left. The error bars will represent the standard deviation of the right and left CA, measured three times.

As can be seen, the silica particles concentration has no effect on the contact angle; the CA remains constant around 90° and is the same as measured for the pure system (no particles, no surfactant). The balance of forces of a wet droplet on a solid surface is given, as defined section 2.8.1, by the Young equation (Equation 2.7), which can be written as follow for the systems considered in this Chapter (water – oil – glass):

$$\gamma_{ws} + \gamma_{ow} \cos \theta - \gamma_{os} = 0 \quad (7.1)$$

where γ_{ws} is the water-solid (W/S) interfacial tension, γ_{os} is the oil-solid (O/S) interfacial tension and γ_{ow} is the oil-water interfacial tension. As aforementioned, the

contact angle is approximately 90° , meaning that $\gamma_{ow} \cos \theta = 0$ in the Young equation, which can simply be written as $\gamma_{os} = \gamma_{ws}$. The W/S and O/S interfacial tensions are then similar, regardless of the concentration of silica particles. Moreover, as the oil phase is identical for all the measurements, as well as the glass surface, the O/S interfacial tension is assumed to remain the same, regardless of the colloid concentration. This shows that the W/S interfacial tension, in the three phase system is not affected by the presence of hydrophilic silica particles, at any concentrations.

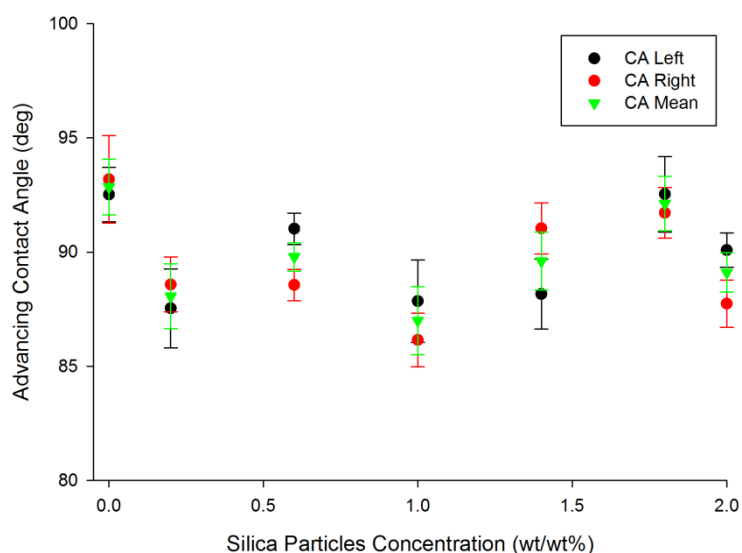


Figure 7-5: Effect of silica particle concentration on the advancing contact angle of a system Water (pH 2) + silica particles – Oil – Glass substrate, measured at ambient temperature ($24^\circ\text{C} \pm 3^\circ\text{C}$).

7.2.2 Effect of Tween 60 concentration on the contact angle

The effect of Tween 60 concentration on the contact angle of a system water (adjusted to pH 2) + Tween 60 – Oil – glass substrate in the presence or absence of hydrophilic silica particles (dispersed in the aqueous phase) was investigated by measuring advancing contact angle (as described section 3.5.2.4) as a function of Tween 60 concentration (Figure 7-6).

The contact angle of particles-free systems initially increases from about 90° to 120°, by increasing the Tween 60 concentration up to 0.2% (Figure 7-6, red circles). Then, further increases of the surfactant concentration do not modify the CA, which remains constant around 120°. In other words, the wettability of the glass surface by the aqueous phase is initially reduced by increasing the Tween 60 concentration, and is then not affected by any further concentration increase. This change of contact angle is due to modifications of the interfacial properties of the liquids (solid/liquid or liquid/liquid interactions) in the presence of surfactant. The Equation 7-2 can also be written:

$$\theta = \arccos\left(\frac{\gamma_{OS} - \gamma_{WS}}{\gamma_{OW}}\right) \quad (7.2)$$

As mentioned, the interfacial tension γ_{OW} slightly decreases by increasing the Tween 60 concentration from 0.2% Tween 60 to 1.4%. Nonetheless, this difference of interfacial tension is very small and can be neglected. Given that the contact angle is higher than 90° (and the interfacial tension is positive), it is clear from the previous equation that the difference $\gamma_{OS} - \gamma_{WS}$ is negative. Due to the high HLB value of the Tween 60, the modifications, induced by the presence of surfactant at the three-phase

contact point C (as defined Figure 2-11), in terms of interfacial tension gradient are such as $\Delta\gamma_{WS} > \Delta\gamma_{OS}$; at point C , the difference of W/S interfacial tension induced by an increase of the surfactant concentration is higher than the difference of O/S interfacial tension. This results in the following equation

$$(\gamma_{OS} - \gamma_{WS})_{\text{low concentration}} > (\gamma_{OS} - \gamma_{WS})_{\text{high concentration}} \quad (7.3)$$

By taking into account the Equations 7-2 and 7-3, it becomes clear that $\theta_{LC} < \theta_{HC}$ (LC: low concentration; HC: high concentration). Thus, theoretically, the contact angle tends to increase by increasing the Tween 60 concentration, which is confirmed here by experiments.

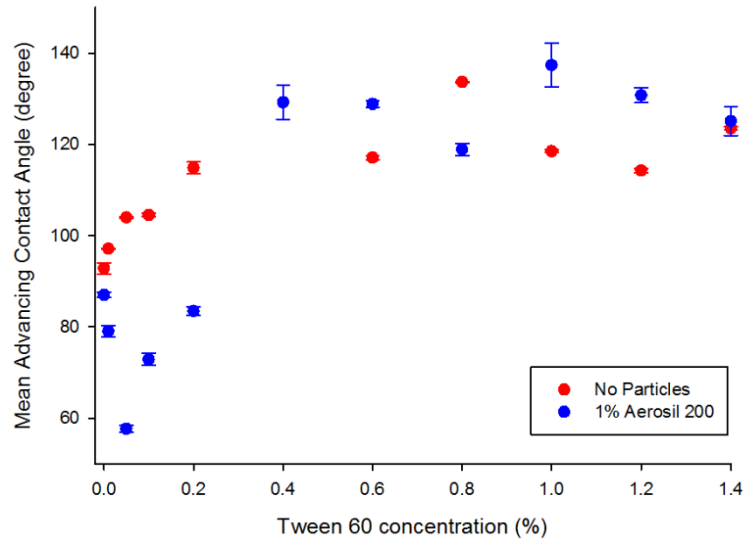


Figure 7-6: Effect of Tween 60 concentration on the advancing contact angle of a system Oil – Water (pH 2) + Tween 60 – Glass Substrate in the absence (red circles) or presence (blue circles) of hydrophilic silica particles in the aqueous phase (Aerosil 200, 1%), measured at ambient temperature ($24^{\circ}\text{C} \pm 3^{\circ}\text{C}$). Where not visible, error bars are smaller than the symbols.

Systems containing hydrophilic silica particles exhibited very different contact angle behaviour as a function of Tween 60 concentration (Figure 7-6, blue circles). For Tween

60 concentrations up to 0.05%, the CA initially decreases from $\sim 90^\circ$ to a minimum of $\sim 60^\circ$. As Tween 60 concentration increases, the CA increases to the same value as observed without particles. These results show that on addition of silica particles, the spreadability is initially increased suggesting that the particles have replaced surfactant at the interface. Further increase of the Tween 60 concentration shows that the wettability of the glass by the water droplet is lowered. Due to the significant difference between systems containing particles and free-particles systems and in order to ensure that the evolution of the advancing contact angle with Tween 60 concentration is a real response of the system, static contact angle of the same system was measured with time at various Tween 60 concentrations.

Figure 7-7 shows the effect of Tween 60 on the static contact angle, measured after 200s. This time was chosen because the thermodynamic equilibrium was reached as shown Figure 8a. Static contact angle initially decreases from $\sim 65^\circ$ to $\sim 50^\circ$ by increasing the Tween 60 concentration up to 0.05%. Then, up to 0.4% Tween 60, the static CA increases to reach a maximum value ($\sim 100^\circ$). Further increase of surfactant concentration does not affect the contact angle which remains stable $\sim 100^\circ$. Static CA is lower than advancing CA (which was expected) but, by comparing Figures 7-6 and 7-7, it is clear that the response of the system to an increase of the Tween 60 concentration in the presence of silica particles is a real response and is not due to experimental errors.

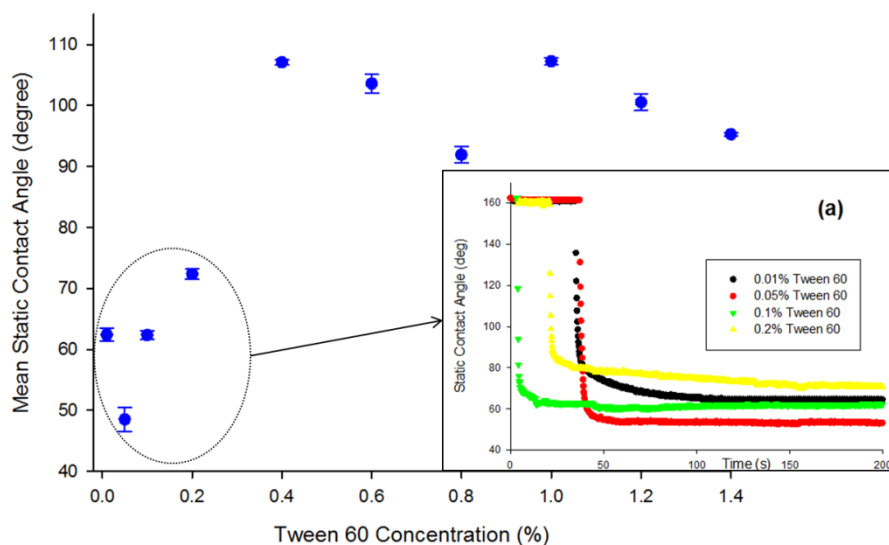


Figure 7-7: Effect of Tween 60 concentration on the static contact angle of a system Oil – Water (pH 2) + Tween 60 + 1% Aerosil 200 – Glass Substrate, measured at ambient temperature ($24^{\circ}\text{C} \pm 3^{\circ}\text{C}$). The mean static contact angle was measured after 200s. Figure 7-7a: Evolution of static contact angle with time at various Tween 60 concentrations.

In order to explain this behaviour, the interactions between the Tween 60 molecules and the hydrophilic silica particles have to be taken into consideration. It was noted during the experiments that when the particles and the Tween 60 were mixed in the same medium (water), this resulted in the formation of flocs made of particles and surfactant molecules. This is due to interactions between the surfactant's heads (hydrophilic part) and the particles (fully hydrophilic). Such interactions would result in modifying the structure of the surfactant adsorbed at the interface. As the particles have no interfacial properties (no change of IFT or CA), their interactions with the surfactant's head would affect the surfactant's ability to modify the wettability of the glass surface. In term of forces involved at the three-phase contact point *C*, these interactions induce that the W/S interfacial tension (γ_{ws}) in the presence of both particles and Tween 60 is lower than the one in the presence of Tween 60 only. Meanwhile, as the silica particles do not

interact with the surfactant's tail (hydrophobic), the O/S interfacial tension is very similar in the presence or absence of silica particles. This results in the following equation:

$$(\gamma_{OS} - \gamma_{WS})_{\text{Tween 60}} < (\gamma_{OS} - \gamma_{WS})_{\text{Tween 60 + Silica Particles}} \quad (7.4)$$

Thus, the contact angle decreases in the presence of hydrophilic silica particles at low Tween 60 concentration.

At higher Tween 60 concentration (>0.05%), the contact angle increases and then reaches a threshold. Moreover, at high concentration (>0.4% Tween 60), the contact angle, measured in the presence of silica particles, is very similar than the one measured without particles. By increasing the Tween 60 concentration, surfactant molecules are introduced in excess, compared to the silica particles. Numerous molecules of Tween 60 are likely not to interact with the silica particles. These molecules, smaller than the particles or the particles/Tween 60 flocs, diffuse faster through and are likely to reach the interface before the particles and/or flocs. The contact angle is then dictated only by the presence of the surfactant.

7.2.3 Effect of Sodium Caseinate concentration on the contact angle

The effect of Sodium Caseinate on the advancing contact angle of Water (adjusted to pH 2) + NaCAS – Oil – Glass substrate in the presence or not of hydrophilic silica particles (1% dispersed in the aqueous phase) was investigated (Figure 7-8).

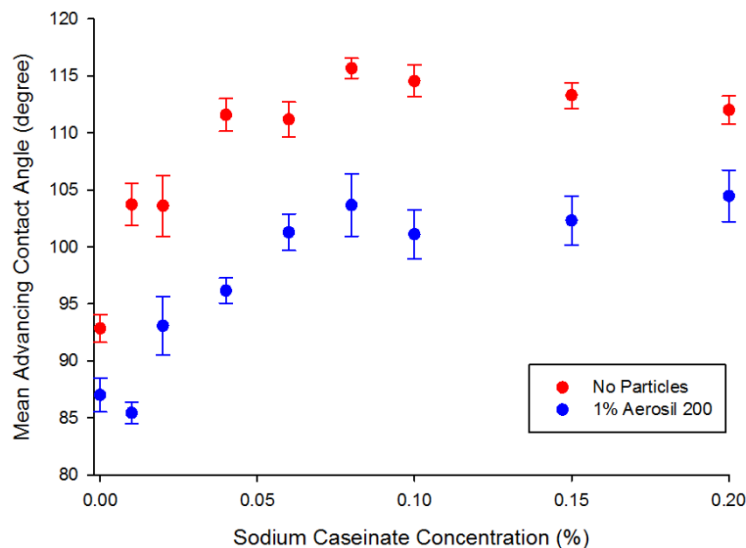


Figure 7-8: Effect of NaCAS concentration on the advancing contact angle of a system Oil – Water (pH 2) + NaCAS – Glass Substrate in the absence (red circles) or presence (blue circles) of hydrophilic silica particles in the aqueous phase (Aerosil 200, 1%), measured at ambient temperature (24°C ±3°C).

The contact angle of particle-free systems initially increases from ~90° to ~115° by increasing the NaCAS concentration up to 0.04% (Figure 7-8, red circles). Further increase of the concentration does not change the contact angle, which stays constant around 115°. The wettability of glass surface by the aqueous droplet is initially reduced by increasing the NaCAS concentration which then, reaches the thermodynamic equilibrium, where increasing the NaCAS concentration does not modify the wettability. As mentioned in section 7.1.2.2, the O/W interfacial tension is not effected by increasing the NaCAS concentration (from 0.02% to 0.2%) so the increase of the contact angle is caused by modification of the L/S interfacial tension (γ_{OS} or γ_{WS}). Sodium Caseinate, like Tween 60, is an O/W surfactant (high HLB value), which induces that $\Delta\gamma_{WS} = \gamma_{WS}^{HC} - \gamma_{WS}^{LC} > \Delta\gamma_{OS} = \gamma_{OS}^{HC} - \gamma_{OS}^{LC}$. Hence, the contact angle in the presence of NaCAS only increases by increasing the surfactant concentration.

Regarding systems containing silica particles (Figure 7-8, blue circles), the contact angle is constant (or even slightly decreases) around 85° for concentrations up to 0.01%. Then, by increasing the NaCAS concentration up to 0.08%, the contact angle increases up to $\sim 105^\circ$. At higher concentration, the contact angle remains constant around 105° . These results show that increasing the NaCAS concentration reduces the glass wettability by the aqueous phase. The comparison between the two systems (in the presence and absence of silica particles) shows that (1) at low NaCAS concentration, solid particles prevent the protein from modifying the glass wettability; (2) the glass wettability in the presence of solid particles is lower than in the absence of particles, regardless of the NaCAS concentration. As it was shown that colloidal particles do not affect the contact angle on their own, it is suggested that the particles have resulted in reducing the efficiency of Sodium Caseinate to occupy the interface.

7.2.4 Effect of lecithin on the contact angle

The effect of lecithin on the contact angle of Water (adjusted to pH 2) – Oil + lecithin – Glass substrate systems in the presence or absence of hydrophilic silica particles was investigated by measuring static contact angle over 1 hour as a function of lecithin concentration (Figure 7-9). This period of time was chosen in order to ensure the system had reached the thermodynamic equilibrium. As can be seen from Figure 7-9, contact angle decreases by increasing the lecithin concentration; particle-free system CA

reduces from $\sim 160^\circ$ at 0.1% to $\sim 135^\circ$ at 1.0% lecithin, while in the presence of particles the change is from $\sim 145^\circ$ to $\sim 130^\circ$. This seems to be in contradiction with the observations made for systems containing Tween 60 or Sodium Caseinate; in these cases the contact angle was found to increase by increasing the concentration of surfactant. Nonetheless, this can be explained by considering the opposite nature of the surfactants: lecithin is a W/O emulsifier while Tween 60 and Sodium Caseinate are O/W emulsifiers. As mentioned earlier, the difference $\gamma_{OS} - \gamma_{WS}$ is of major importance to predict the contact angle evolution. The L/S interfacial tension increases by increasing the surfactant concentration. Due to the low HLB value of the Lecithin, the increase of the W/S interfacial energy is likely to be lower than the increase of the O/S interfacial energy, i.e. $\Delta\gamma_{WS} = \gamma_{WS}^{HC} - \gamma_{WS}^{LC} > \Delta\gamma_{OS} = \gamma_{OS}^{HC} - \gamma_{OS}^{LC}$. This leads to:

$$(\gamma_{OS} - \gamma_{WS})_{low\ concentration} < (\gamma_{OS} - \gamma_{WS})_{high\ concentration} \quad (7.5)$$

Comparing Equation 7-5 and Equation 7-3 shows they are the opposite of each other; meaning that W/O surfactants and O/W surfactants have opposite effect on the contact angle. The presence of W/O emulsifiers tends to decrease the contact angle, i.e. the wettability of the glass substrate by the aqueous phase is promoted by increasing the surfactant concentration; the presence of O/W emulsifiers tends to increase the contact angle, i.e. the wettability of the glass substrate by the oil is promoted by increasing the surfactant concentration.

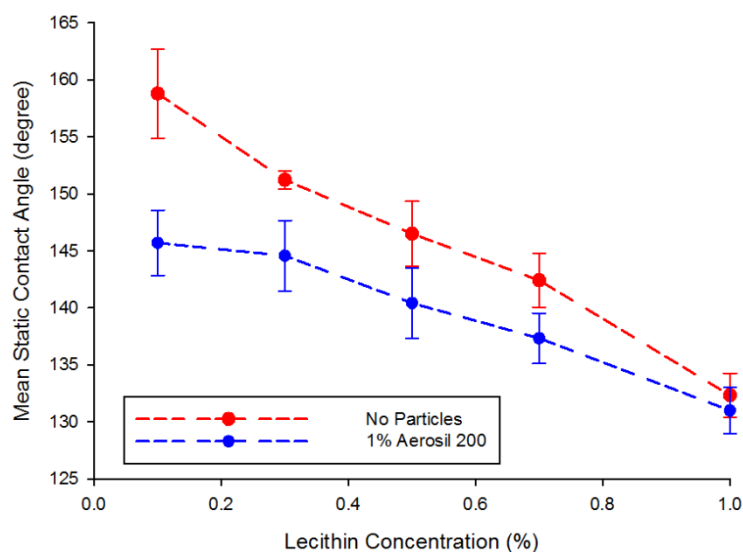


Figure 7-9: Effect of lecithin concentration on the static contact angle (measured after 1 hour) of system Water (pH 2) – Oil + lecithin – Glass substrate, in the absence (red points) or presence (blue points) of hydrophilic silica particles (1% Aerosil 200). Where not visible, error bars are smaller than the symbols.

As can be seen Figure 7-9, the contact angle of systems containing silica particles is lower than the CA of particle-free systems. Nonetheless, the difference between these two systems becomes lower by increasing the lecithin concentration; at 0.1% lecithin, the contact angle difference is $\sim 15^\circ$, while at 1.0% Lecithin, there is almost no difference. More specifically, up to 0.3% Lecithin, the difference between the two systems is significant, while at higher concentration, both systems are very similar. Indeed, by taking into accounts the experimental approximations (error bars on the Figure 7-9), the addition of silica particles can be considered as having no effect on the contact angle. At low lecithin concentration, the adsorption of silica particles at the interface tends to prevent the adsorption of Lecithin, which affects the wettability of the glass substrate by the aqueous phase. However, at higher concentration, the contact angle is only dictated by the Lecithin concentration.

7.3 Conclusion

In this chapter, the effect of both silica particles and various types of surfactant on interfacial tension and contact angle was investigated in order to characterise their effect on the oil-water interface.

Interfacial tension decreased by increasing the surfactant concentration, regardless of the presence of particles. Nonetheless, major differences were noted between system containing particles or not, in the presence of O/W surfactant. Interfacial tension measured in the presence of lecithin (W/O surfactant) was not affected by the presence of silica particles. At low O/W surfactant concentration, both particles and surfactant molecules were adsorbed at the interface, which increased the interfacial tension compared to the interfacial tension measured only with surfactant. At high concentration, no difference was observed between systems containing or not silica particles.

The use of W/O and O/W surfactants showed an antagonistic response of the contact angle to these different surfactant; by increasing the surfactant concentration, the contact angle decreases or increases as the surfactant is of W/O or O/W type, respectively. This is due to the modification of the wettability of the glass by the oil or water induced by the use of one of the surfactants. Regardless of the surfactant's type, the contact angle profile was proved to be dictated by both particles and surfactant at low surfactant concentration, whereas it is dictated by the surfactant only at high concentration. More specifically, the wettability of the glass surface by the aqueous phase was strongly affected by the Tween 60 concentration; initially enhanced at very

low Tween 60 concentration, the wettability is then reduced by increasing the surfactant concentration. Interactions between hydrophilic silica particles and Tween 60 molecules seem to be the reason on such changes of the glass wettability.

In spite of the differences in terms of experimental conditions between emulsion preparation and contact angle measurement, due to the introduction of a new parameter (glass substrate), contact angle results shown in this chapter confirmed the hypothesis made in Chapter 6, i.e. Tween 60 molecules when introduced in excess tend to interact with silica particles and prevent the adsorption of the colloids at the interface.

Chapter 8:

Conclusions and Outlook

This thesis described the effect of mixtures of both hydrophilic silica particles and surfactants on the stability of “food-grade” O/W (20/80) emulsions. This work was focused on the following objectives:

- Working with components that are used in the food industry;
- Optimisation of the dispersion of hydrophilic silica particles in water and stabilisation of O/W emulsion by colloidal particles only;
- Development of O/W emulsions stabilised by both surfactant and silica particles;
- Investigation of the effect of surfactants type and concentration, as well as colloids concentration, on the emulsion stability;

- Investigation of the effect of surfactants type and concentration, as well as colloids concentration, on the oil-water interfacial tension and three-phase contact angle – water-oil-glass.

8.1 *Solid particles stabilised emulsions*

The stability of O/W emulsion in the presence of hydrophilic silica particles, acting as sole emulsifier, was shown to depend on the pH of silica-in-water dispersion. At very acidic conditions, emulsions were stable against coalescence, while by increasing the pH (from slightly acid to basic conditions), coalescence of the oil droplets occurred. It was suggested that, at low pH, the particles are closely packed onto the oil-water interface due to the absence of charge under these conditions. Moreover, the presence of aggregated “free” particles in the system induces the formation of silica flocs inter-connecting the oil droplets, resulting in the creation of a network between the emulsion droplets in the cream layer. Any of these events is expected to enhance the stability of O/W Pickering emulsions against coalescence. At high pH, silica particles are likely to be more “spread out” on the oil-water interface, due to the existence of charge, resulting in probable oil droplets coalescence.

The silica particles and oil concentrations were shown to have no effect on the emulsion stability. Nonetheless, either increasing the colloids concentration or decreasing the oil concentration resulted in decreasing the emulsion droplet size. By decreasing the ratio $[oil]/[silica\ particles]$, the time that particles adsorb at the oil-water interface decreases which prevents re-coalescence occurring during emulsification.

8.2 *Mixed-emulsifier stabilised emulsions*

Monoolein and lecithin were unable to provide stable emulsions under acidic conditions. Emulsion droplets formed during emulsification coalesce after a few hours under quiescent conditions, resulting in separation between water and oil phases. Nonetheless, when used with silica particles, these emulsifiers provided long term stable emulsions, under a few conditions:

- At low surfactant concentration, high silica particle content is required;
- Above a certain surfactant concentration, emulsions were stable regardless of the colloids concentration.

Mixture of W/O surfactant and hydrophilic silica particles also allowed a significant reduction of emulsion droplet size, compared to emulsions stabilised by particles only. A “two-step” mechanism, in which both components (surfactant and silica particles) in these mixed-emulsifier systems have specific functions, was suggested to explain the emulsion stability and the response of the system to the increase of surfactant concentration. More specifically, the role of surfactant is to initially “delay” the re-coalescence phenomena during emulsification by rapidly covering the newly formed interface caused by droplet break-up and then by reducing interfacial tension, in order to allow for the silica particles to assemble at the oil-water interface and provide long-term stability. Cryo-SEM micrographs of droplet of emulsion stabilised by lecithin and silica particles confirmed that emulsion droplets were fully covered by silica particles.

Tween 60 and Sodium Caseinate, acting as sole emulsifier, were able to stabilise O/W emulsions above a certain surfactant concentration. Emulsions prepared in the presence of both hydrophilic silica particles and surfactant (Tween 60 and Sodium Caseinate)

were proved to be long term stable, regardless of the surfactant and at any surfactant concentration. This is an enhancement compared to emulsion stabilised by Sodium Caseinate only. The same mechanism proposed for emulsions stabilised by both W/O surfactants and silica particles was suggested. Emulsion microstructure was shown to depend on the surfactant concentration; from a Pickering emulsion-like microstructure at low concentration, it turned to a surfactant stabilised emulsion-like microstructure at high surfactant concentration. This was suggested to be due to a displacement of the silica particles from the interface into the aqueous phase by increasing the surfactant concentration.

Emulsions stabilised by both hydrophilic silica particles and W/O surfactant did not exhibit such a change in the emulsion microstructure; droplets were fully covered by silica particles at any concentration. This difference between systems containing W/O or O/W emulsifier is ascribed to the eventual interactions between surfactant molecules introduced in excess and the silica particles; when W/O surfactant is used, there is no interaction between particles and surfactant as the surfactant molecules in excess remain in the oil phase, while, when O/W surfactant is used, interactions between both emulsifiers are likely to occur as surfactant molecules in excess tend to remain in the aqueous phase.

8.3 Interfacial tension and Contact Angle

Interfacial tension was shown to depend on both the presence of silica particles in the aqueous phase and the surfactant type and concentration. When W/O surfactants were used (like lecithin), interfacial tension profile was only dictated by the lecithin

concentration, i.e. the silica particles had no effect on interfacial tension. When O/W surfactants were used (e.g. Tween 60 or Sodium Caseinate), interfacial tension was affected by the presence of silica particles; the presence of silica particles at the interface was found to be restrained to the surfactant concentration. By increasing the surfactant concentration, the competition between the particles and the surfactant molecules to adsorb at the interface becomes harder. As the surfactant tends to move faster than the particles, they fully cover the interface, giving no space to the particles to adsorb.

The use of W/O and O/W surfactants showed an antagonistic response of the contact angle to these different surfactant; by increasing the surfactant concentration, the contact angle decreased or increased as the surfactant is of W/O or O/W type, respectively. This is due to the modification of the wettability of the glass by the oil or water induced by the use of one of the surfactants. Regardless of the surfactant type, the contact angle profile was proved to be dictated by both particles and surfactant at low surfactant concentration, whereas it is dictated by the surfactant only at high concentration. More specifically, the wettability of the glass surface by the aqueous phase was strongly affected by the Tween 60 concentration; initially enhanced at very low Tween 60 concentration, the wettability is then reduced by increasing the surfactant concentration. Interactions between hydrophilic silica particles and Tween 60 molecules were suggested to be the reason on such changes of the glass wettability.

8.4 Further work

Based on the findings from this work, some further work could be undertaken in the following areas:

- In this work, an attempt was made to investigate the effect of particle size on the stability of Pickering emulsion. However, due to the presence of ethylene glycol in the aqueous phase, the decision was taken not to study this in more details. It would be interesting to get a better understanding of stabilisation mechanisms as a function of particle size. As the preparation of silica particles at various sizes that keep the same properties (hydrophilicity, surface area, etc.) is a difficult task, this would require to work in collaboration with company (Evonik, Wacker, Nyacol, etc.) that would supply the particles.

Such a work could be followed by a study of the feasibility to stabilise emulsions by using particles of various diameters. It would be interesting to determine whether the mixture of particles of different diameters would provide a better oil droplet surface covering, and then a better stability. In the hypothesis that the level of adsorption of these particles is different, it is possible to imagine new food products in which some particles would detach from the interface to release new taste in the mouth, under acidic conditions or mechanical actions.

- Four surfactants were used in this study to investigate the effect of surfactant HLB on the emulsion stability. In order to extend the conclusions made regarding the emulsion microstructure, it would be interesting to work with more surfactants, covering a wider HLB values scale. This could result in better

understanding of the displacement of the particles from the interface. Calculating accurately the oil droplet surface covered by the “head” or the “tail” of the surfactant, either at the oil-side or water-side of the interface, would also help in understanding the displacement phenomenon.

- Hydrophilic silica particles were used in this work. Even though these particles are used as additive in the food industry, it is difficult to imagine food products prepared with a high level of “sand”. A natural extend of this study would be to replace these particles by proper colloids for use in food, e.g. fat crystals. This could result in finding direct application for these “new” emulsions.
- Food emulsions are usually stable against creaming. No attempt was made here to stabilise emulsions against creaming. In order to use the conclusions of this work in the food industry, the next stage seems to introduce another agent in the emulsion composition (e.g. gelling agent) to prevent the creaming phenomenon.
- As mentioned already, it was impossible to measure the contact angle that a particle makes with the oil-water interface. In order to understand how the presence of surfactant modifies the adsorption of particles at the interface, it is necessary to know this parameter. It may be possible to compress/compact the particles to form tablets. However, due to the very small size of the particles, the compression/compaction force must be very high. Interfacial tension and contact angle are closely linked. Then it may possible to measure the interfacial tension by using the Wilhelmy method, covering the plate with the particles or replacing

the usual platinum plate by a plate made of particles, and then to determine the contact angle.

- Rheological measurements seem to be essential to understand the properties of mixed-emulsifier stabilised emulsions. It would also be interesting to compare their rheological behaviour with the behaviour of Pickering and surfactant-stabilised emulsions. Rheological behaviour of Pickering emulsions is sometimes associated with the one of dispersions. It would be worth to know if mixed-emulsifier stabilised emulsions behave like dispersions, “classic” emulsions or something in between.

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