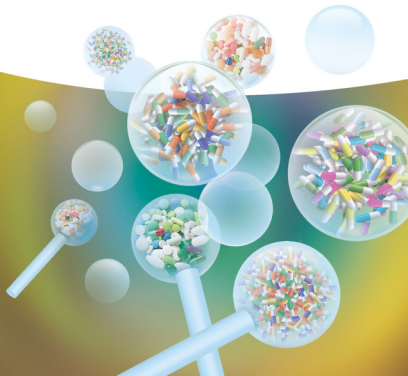


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Emulsion Formation and Stability



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Emulsion Formation and Stability



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Preface

This book is based on selection of some papers from the Fifth World Congress on Emulsions that was held in Lyon, in October 2010. These series of World congresses emphasize the importance of emulsions in industry, including food, cosmetics, pharmaceuticals, agrochemicals, and paints. Following each meeting, a number of topics were selected, the details of which were subsequently published in the journals, *Colloids and Surfaces* and *Advances in Colloid and Interface Science*. The selected papers of the fourth Congress (2006) were published by Wiley-VCH (Germany).

This book contains selected topics from the Fifth World Congress, the title of which “Emulsion Formation and Stability” reflects the importance of emulsification techniques, the production of nanoparticles for biomedical applications as well as the importance of application of rheological techniques for studying the interaction between the emulsion droplets.

Chapter 1 describes the principles of emulsion formation, selection of emulsifiers, and control of emulsion stability. A section is devoted to the rheology of emulsions, including both interfacial rheology as well as the bulk rheology of emulsions. Chapter 2 deals with emulsion formation using membrane and microfluidics devices. In membrane emulsification (ME), the system is produced by injection of a pure disperse phase or a premix of a coarse emulsion into the continuous phase through a microporous membrane. Hydrophobic membranes are used to produce water-in-oil (W/O) emulsions, whereas hydrophilic membranes are used to produce oil-in-water (O/W) emulsions. In microfluidics, the combined two-phase flow is forced through a small orifice that allows one to obtain monodisperse droplets. Chapter 3 deals with adsorption of ionic surfactants at the hexane/water interface using the profile analysis technique (PAT) and the oscillating drop and bubble analyzer (ODBA). Theoretical models were used to analyze the adsorption results. Chapter 4 describes the various techniques that can be applied to investigate emulsion formation during processing. The effect of different emulsion techniques on the droplet size distribution was investigated using various methods such as light diffraction and ultrasound. Particular attention was given to online droplet size measurements. Chapter 5 deals with emulsification using rotor–stator mixers that are commonly used in industry, both in laboratory and large-scale production of emulsions. The various types of rotor–stator mixers are described. The selection

of a rotor–stator mixer for a specific end product depends on the required droplet size distribution and the scale of the process. Chapter 6 describes the formulation, characterization, and property control of paraffin emulsions. The industrial application of paraffin emulsions is described highlighting the property of paraffin and method of preparation. The surfactants used in formation of paraffin emulsions are described in terms of their phase behavior. The control of particle size and its distribution of the resulting emulsion are described at a fundamental level. Chapter 7 describes polymeric O/W nanoemulsions produced by the phase inversion composition (PIC) method with application of the resulting nanoparticles in biomedicine. A description of the PIC method is given with reference to the aspects of choice of the components. The production of ethyl cellulose nanoparticles is described. Chapter 8 gives a detailed analysis of the rheology and stability of sterically stabilized emulsions. A section is devoted to the general classification of polymeric surfactants followed by discussion of the theory of sterically stabilized emulsions. The application of block and graft copolymers for preparation of highly stable emulsions is described. The principles of the various rheological techniques that can be applied to study the interaction between droplets in an emulsion are described. Various types of sterically stabilized emulsions are described: O/W emulsions stabilized with an A-B-A block copolymer of poly(ethylene oxide) (PEO, A) and poly(propylene oxide) (PPO, B); partially hydrolyzed poly(vinyl acetate) (PVAc); and W/O emulsions stabilized with an A-B-A block copolymer of poly(hydroxyl stearic acid) (PHS, A) and PEO (B).

On the basis of the above descriptions and details, it is clear that this book covers a wide range of topics: both fundamental and applied. It also highlights the engineering aspects of emulsion production and their characterization, both in the laboratory and during manufacture. It is hoped that this book will be of great help to emulsion research scientists, in both academia and industry.

I would like to thank the organizers – and in particular Dr Jean-Erik Poirier and Dr Alain Le Coroller – for giving me the opportunity to attend the Fifth World Congress and to edit this book.

October 2012

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1

Emulsion Formation, Stability, and Rheology*Tharwat F. Tadros*

1.1

Introduction

Emulsions are a class of disperse systems consisting of two immiscible liquids [1–3]. The liquid droplets (the disperse phase) are dispersed in a liquid medium (the continuous phase). Several classes may be distinguished: oil-in-water (O/W), water-in-oil (W/O), and oil-in-oil (O/O). The latter class may be exemplified by an emulsion consisting of a polar oil (e.g., propylene glycol) dispersed in a nonpolar oil (paraffinic oil) and vice versa. To disperse two immiscible liquids, one needs a third component, namely, the emulsifier. The choice of the emulsifier is crucial in the formation of the emulsion and its long-term stability [1–3].

Emulsions may be classified according to the nature of the emulsifier or the structure of the system. This is illustrated in Table 1.1.

1.1.1

Nature of the Emulsifier

The simplest type is ions such as OH^- that can be specifically adsorbed on the emulsion droplet thus producing a charge. An electrical double layer can be produced, which provides electrostatic repulsion. This has been demonstrated with very dilute O/W emulsions by removing any acidity. Clearly that process is not practical. The most effective emulsifiers are nonionic surfactants that can be used to emulsify O/W or W/O. In addition, they can stabilize the emulsion against flocculation and coalescence. Ionic surfactants such as sodium dodecyl sulfate (SDS) can also be used as emulsifiers (for O/W), but the system is sensitive to the presence of electrolytes. Surfactant mixtures, for example, ionic and nonionic, or mixtures of nonionic surfactants can be more effective in emulsification and stabilization of the emulsion. Nonionic polymers, sometimes referred to as *polymeric surfactants*, for example, Pluronic, are more effective in stabilization of the emulsion, but they may suffer from the difficulty of emulsification (to produce small droplets) unless high energy is applied for the process. Polyelectrolytes such as poly(methacrylic

Table 1.1 Classification of emulsion types.

Nature of emulsifier	Structure of the system
Simple molecules and ions	Nature of internal and external phase: O/W, W/O
Nonionic surfactants	—
Surfactant mixtures	Micellar emulsions (microemulsions)
Ionic surfactants	Macroemulsions
Nonionic polymers	Bilayer droplets
Polyelectrolytes	Double and multiple emulsions
Mixed polymers and surfactants	Mixed emulsions
Liquid crystalline phases	—
Solid particles	—

acid) can also be applied as emulsifiers. Mixtures of polymers and surfactants are ideal in achieving ease of emulsification and stabilization of the emulsion. Lamellar liquid crystalline phases that can be produced using surfactant mixtures are very effective in emulsion stabilization. Solid particles that can accumulate at the O/W interface can also be used for emulsion stabilization. These are referred to as *Pickering emulsions*, whereby particles are made partially wetted by the oil phase and by the aqueous phase.

1.1.2

Structure of the System

- 1) **O/W and W/O macroemulsions:** These usually have a size range of 0.1–5 μm with an average of 1–2 μm .
- 2) **Nanoemulsions:** these usually have a size range of 20–100 nm. Similar to macroemulsions, they are only kinetically stable.
- 3) **Micellar emulsions or microemulsions:** these usually have the size range of 5–50 nm. They are thermodynamically stable.
- 4) **Double and multiple emulsions:** these are emulsions-of-emulsions, W/O/W, and O/W/O systems.
- 5) **Mixed emulsions:** these are systems consisting of two different disperse droplets that do not mix in a continuous medium. This chapter only deals with macroemulsions.

Several breakdown processes may occur on storage depending on particle size distribution and density difference between the droplets and the medium. Magnitude of the attractive versus repulsive forces determines flocculation. Solubility of the disperse droplets and the particle size distribution determine Ostwald ripening. Stability of the liquid film between the droplets determines coalescence. The other process is phase inversion.

1.1.3

Breakdown Processes in Emulsions

The various breakdown processes are illustrated in Figure 1.1. The physical phenomena involved in each breakdown process are not simple, and it requires analysis of the various surface forces involved. In addition, the above-mentioned processes may take place simultaneously rather than consecutively and this complicates the analysis. Model emulsions, with monodisperse droplets, cannot be easily produced, and hence, any theoretical treatment must take into account the effect of droplet size distribution. Theories that take into account the polydispersity of the system are complex, and in many cases, only numerical solutions are possible. In addition, measurements of surfactant and polymer adsorption in an emulsion are not easy and one has to extract such information from measurement at a planer interface.

In the following sections, a summary of each of the above-mentioned breakdown processes and details of each process and methods of its prevention are given.

1.1.4

Creaming and Sedimentation

This process results from external forces usually gravitational or centrifugal. When such forces exceed the thermal motion of the droplets (Brownian motion), a concentration gradient builds up in the system with the larger droplets moving faster to the top (if their density is lower than that of the medium) or to the bottom (if their density is larger than that of the medium) of the container. In the limiting cases, the droplets may form a close-packed (random or ordered) array at the top or bottom of the system with the remainder of the volume occupied by the continuous liquid phase.

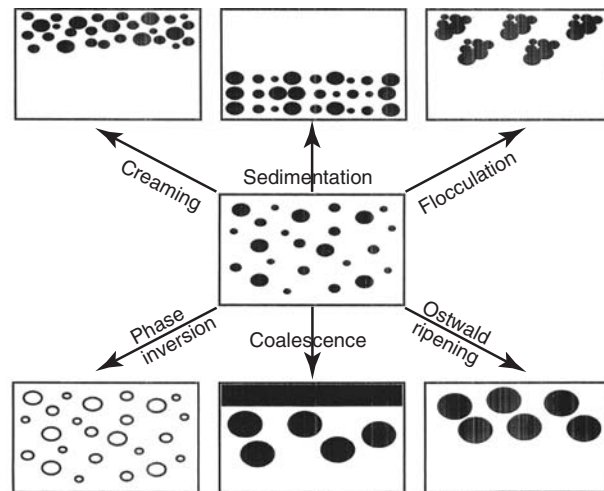


Figure 1.1 Schematic representation of the various breakdown processes in emulsions.

1.1.5

Flocculation

This process refers to aggregation of the droplets (without any change in primary droplet size) into larger units. It is the result of the van der Waals attraction that is universal with all disperse systems. Flocculation occurs when there is not sufficient repulsion to keep the droplets apart to distances where the van der Waals attraction is weak. Flocculation may be “strong” or “weak,” depending on the magnitude of the attractive energy involved.

1.1.6

Ostwald Ripening (Disproportionation)

This results from the finite solubility of the liquid phases. Liquids that are referred to as *being immiscible* often have mutual solubilities that are not negligible. With emulsions, which are usually polydisperse, the smaller droplets will have larger solubility when compared with the larger ones (due to curvature effects). With time, the smaller droplets disappear and their molecules diffuse to the bulk and become deposited on the larger droplets. With time, the droplet size distribution shifts to larger values.

1.1.7

Coalescence

This refers to the process of thinning and disruption of the liquid film between the droplets with the result of fusion of two or more droplets into larger ones. The limiting case for coalescence is the complete separation of the emulsion into two distinct liquid phases. The driving force for coalescence is the surface or film fluctuations which results in close approach of the droplets whereby the van der Waals forces is strong thus preventing their separation.

1.1.8

Phase Inversion

This refers to the process whereby there will be an exchange between the disperse phase and the medium. For example, an O/W emulsion may with time or change of conditions invert to a W/O emulsion. In many cases, phase inversion passes through a transition state whereby multiple emulsions are produced.

1.2

Industrial Applications of Emulsions

Several industrial systems consist of emulsions of which the following is worth mentioning: food emulsion, for example, mayonnaise, salad creams, deserts, and

beverages; personal care and cosmetics, for example, hand creams, lotions, hair sprays, and sunscreens; agrochemicals, for example, self-emulsifiable oils which produce emulsions on dilution with water, emulsion concentrates (EWs), and crop oil sprays; pharmaceuticals, for example, anesthetics of O/W emulsions, lipid emulsions, and double and multiple emulsions; and paints, for example, emulsions of alkyd resins and latex emulsions. Dry cleaning formulations – this may contain water droplets emulsified in the dry cleaning oil which is necessary to remove soils and clays. Bitumen emulsions: these are emulsions prepared stable in the containers, but when applied the road chippings, they must coalesce to form a uniform film of bitumen. Emulsions in the oil industry: many crude oils contain water droplets (for example, the North sea oil) and these must be removed by coalescence followed by separation. Oil slick dispersions: the oil spilled from tankers must be emulsified and then separated. Emulsification of unwanted oil: this is an important process for pollution control.

The above importance of emulsion in industry justifies a great deal of basic research to understand the origin of instability and methods to prevent their break down. Unfortunately, fundamental research on emulsions is not easy because model systems (e.g., with monodisperse droplets) are difficult to produce. In many cases, theories on emulsion stability are not exact and semiempirical approaches are used.

1.3

Physical Chemistry of Emulsion Systems

1.3.1

The Interface (Gibbs Dividing Line)

An interface between two bulk phases, for example, liquid and air (or liquid/vapor), or two immiscible liquids (oil/water) may be defined provided that a dividing line is introduced (Figure 1.2). The interfacial region is not a layer that is one-molecule thick. It is a region with thickness δ with properties different from the two bulk phases α and β .

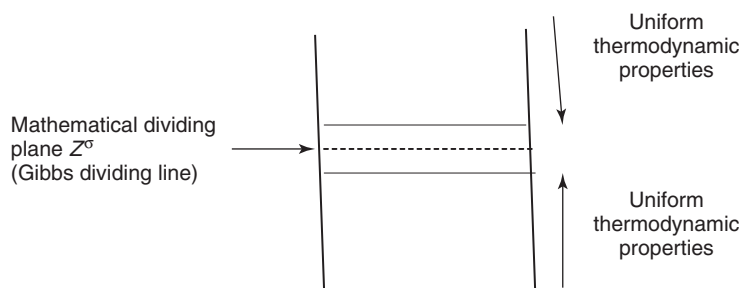


Figure 1.2 The Gibbs dividing line.

Using Gibbs model, it is possible to obtain a definition of the surface or interfacial tension γ .

The surface free energy dG^σ is made of three components: an entropy term $S^\sigma dT$, an interfacial energy term $Ad\gamma$, and a composition term $\sum n_i d\mu_i$ (n_i is the number of moles of component i with chemical potential μ_i). The Gibbs–Deuhem equation is

$$dG^\sigma = -S^\sigma dT + Ad\gamma + \sum n_i d\mu_i \quad (1.1)$$

At constant temperature and composition

$$\begin{aligned} dG^\sigma &= Ad\gamma \\ \gamma &= \left(\frac{\partial G^\sigma}{\partial A} \right)_{T, n_i} \end{aligned} \quad (1.2)$$

For a stable interface, γ is positive, that is, if the interfacial area increases G^σ increases. Note that γ is energy per unit area (mJ m^{-2}), which is dimensionally equivalent to force per unit length (mN m^{-1}), the unit usually used to define surface or interfacial tension.

For a curved interface, one should consider the effect of the radius of curvature. Fortunately, γ for a curved interface is estimated to be very close to that of a planer surface, unless the droplets are very small ($<10 \text{ nm}$). Curved interfaces produce some other important physical phenomena that affect emulsion properties, for example, the Laplace pressure Δp , which is determined by the radii of curvature of the droplets

$$\Delta p = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (1.3)$$

where r_1 and r_2 are the two principal radii of curvature.

For a perfectly spherical droplet, $r_1 = r_2 = r$ and

$$\Delta p = \frac{2\gamma}{r} \quad (1.4)$$

For a hydrocarbon droplet with radius 100 nm , and $\gamma = 50 \text{ mN m}^{-1}$, $\Delta p = 10^6 \text{ Pa}$ (10 atm).

1.4

Thermodynamics of Emulsion Formation and Breakdown

Consider a system in which an oil is represented by a large drop 2 of area A_1 immersed in a liquid 2, which is now subdivided into a large number of smaller droplets with total area A_2 ($A_2 \gg A_1$) as shown in Figure 1.3. The interfacial tension γ_{12} is the same for the large and smaller droplets because the latter are generally in the region of 0.1 to few micrometers.

The change in free energy in going from state I to state II is made from two contributions: A surface energy term (that is positive) that is equal to $\Delta A \gamma_{12}$ (where $\Delta A = A_2 - A_1$). An entropy of dispersions term that is also positive

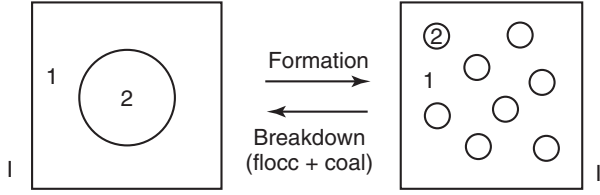


Figure 1.3 Schematic representation of emulsion formation and breakdown.

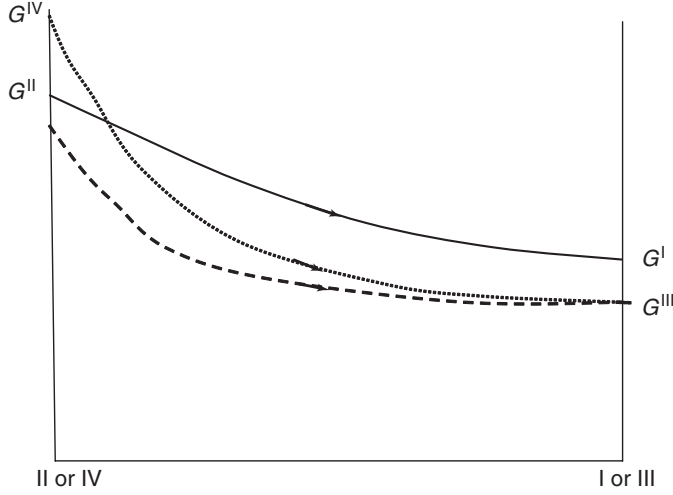


Figure 1.4 Free energy path in emulsion breakdown – (straight line) Flocc. + coal.; (dashed line) Flocc. + coal. + Sed.; and (dotted line) Flocc. + coal. + sed. + Ostwald ripening.

(since producing a large number of droplets is accompanied by an increase in configurational entropy), which is equal to $T\Delta S^{\text{conf}}$.

From the second law of thermodynamics

$$\Delta G^{\text{form}} = \Delta A\gamma_{12} - T\Delta S^{\text{conf}} \quad (1.5)$$

In most cases, $\Delta A\gamma_{12} \gg -T\Delta S^{\text{conf}}$, which means that ΔG^{form} is positive, that is, the formation of emulsions is nonspontaneous and the system is thermodynamically unstable. In the absence of any stabilization mechanism, the emulsion will break by flocculation, coalescence, Ostwald ripening, or combination of all these processes. This is illustrated in Figure 1.4 that shows several paths for emulsion breakdown processes.

In the presence of a stabilizer (surfactant and/or polymer), an energy barrier is created between the droplets, and therefore, the reversal from state II to state I becomes noncontinuous as a result of the presence of these energy barriers. This is illustrated in Figure 1.5. In the presence of the above energy barriers, the system becomes kinetically stable.

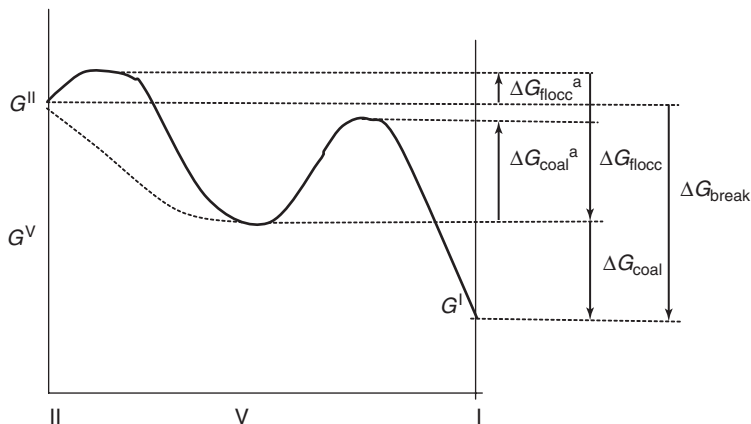


Figure 1.5 Schematic representation of free energy path for breakdown (flocculation and coalescence) for systems containing an energy barrier.

1.5

Interaction Energies (Forces) between Emulsion Droplets and Their Combinations

Generally speaking, there are three main interaction energies (forces) between emulsion droplets and these are discussed in the following sections.

1.5.1

van der Waals Attraction

The van der Waals attraction between atoms or molecules is of three different types: dipole–dipole (Keesom), dipole-induced dipole (Debye), and dispersion (London) interactions. The Keesom and Debye attraction forces are vectors, and although dipole–dipole or dipole-induced dipole attraction is large, they tend to cancel because of the different orientations of the dipoles. Thus, the most important are the London dispersion interactions that arise from charge fluctuations. With atoms or molecules consisting of a nucleus and electrons that are continuously rotating around the nucleus, a temporary dipole is created as a result of charge fluctuations. This temporary dipole induces another dipole in the adjacent atom or molecule. The interaction energy between two atoms or molecules G_a is short range and is inversely proportional to the sixth power of the separation distance r between the atoms or molecules

$$G_a = -\frac{\beta}{r^6} \quad (1.6)$$

where β is the London dispersion constant that is determined by the polarizability of the atom or molecule.

Hamaker [4] suggested that the London dispersion interactions between atoms or molecules in macroscopic bodies (such as emulsion droplets) can be added resulting in strong van der Waals attraction, particularly at close distances of

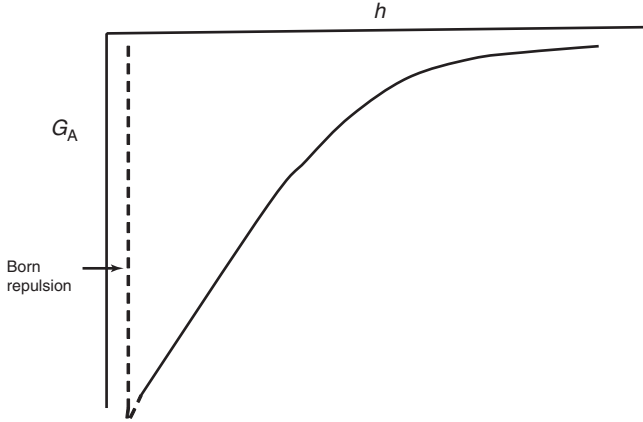


Figure 1.6 Variation of the van der Waals attraction energy with separation distance.

separation between the droplets. For two droplets with equal radii R , at a separation distance h , the van der Waals attraction G_A is given by the following equation (due to Hamaker)

$$G_A = -\frac{AR}{12h} \quad (1.7)$$

where A is the effective Hamaker constant

$$A = \left(A_{11}^{1/2} - A_{22}^{1/2} \right)^2 \quad (1.8)$$

where A_{11} and A_{22} are the Hamaker constants of droplets and dispersion medium, respectively.

The Hamaker constant of any material depends on the number of atoms or molecules per unit volume q and the London dispersion constant β

$$A = \pi^2 q^2 \beta \quad (1.9)$$

G_A increases very rapidly with decrease of h (at close approach). This is illustrated in Figure 1.6 that shows the van der Waals energy–distance curve for two emulsion droplets with separation distance h .

In the absence of any repulsion, flocculation is very fast producing large clusters. To counteract the van der Waals attraction, it is necessary to create a repulsive force. Two main types of repulsion can be distinguished depending on the nature of the emulsifier used: electrostatic (due to the creation of double layers) and steric (due to the presence of adsorbed surfactant or polymer layers).

1.5.2

Electrostatic Repulsion

This can be produced by adsorption of an ionic surfactant as shown in Figure 1.7, which shows a schematic picture of the structure of the double layer according to