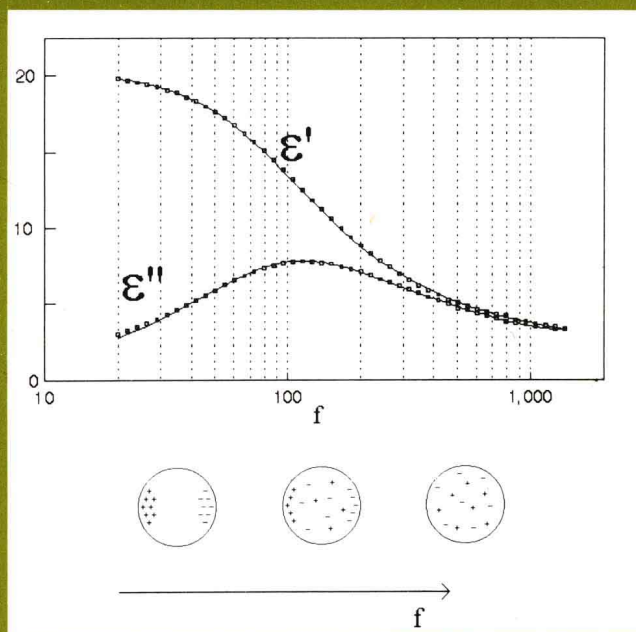


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EMULSIONS AND EMULSION STABILITY



edited by
Johan Sjöblom

EMULSIONS AND EMULSION STABILITY

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Preface

Emulsions are among the most important colloids in everyday life. In food emulsions such as margarine, butter, milk, dressings, and so forth, it is beneficial for the customer that the emulsified system retain high stability. On the other hand, in the process industry a stable emulsion can often cause a problem. Good examples are crude-oil-based emulsions, wash emulsions, and wastewater emulsions. The multiplicity of technical applications has naturally inspired in-depth studies that are needed in order to understand stabilization and destabilization processes in emulsified systems.

In this book, our intention is to give a fundamental presentation of emulsion science. The book gives a basic discussion of such topics as sedimentation, creaming, flocculation, and coalescence whereas the technical part describes crude-oil-based emulsions, food emulsions, and alkyd emulsions. The last mentioned topic is essential for the paint industry. In addition, the book also focuses on experimental techniques that can be conveniently applied to characterize emulsified systems.

In the first chapter, Friberg and Yang analyze emulsion stability in terms of third-phase stabilization (liquid crystal or solid) and necessary wetting/spreading conditions at equilibrium. The authors also describe processes in thin liquid films and surfactant association structures of immediate relevance for emulsion stabilization. Other topics covered are flocculation/coalescence kinetics, polymeric stabilizers and their surfactant complexes, and evaporation processes in emulsions and resulting equilibria.

Dukhin and Sjöblom give an analysis of flocculation/coagulation processes in dilute emulsions in the following chapter. A central topic in this analysis is to mathematically characterize the flocculation kinetics in dilute emulsions, both oil/water (o/w) and water/oil (w/o). In doing so, parallels are drawn between pure coagulation in solid particle systems and the flocculation process in emulsified systems.

In Chapter 3 on flexible surfactant films, Bellocq gives an extensive overview of the most recent achievements in the field of microemulsions. This chapter expresses the fundamental differences between microemulsions and macroemulsions. The author presents recent detailed phase diagram studies and theories for transition between droplet and bicontinuous structures together with experimental verifications from light-scattering experiments. Bellocq also applies the theories about flexible surfactant films to explain the differences in stability between bicontinuous microemulsions, lamellar liquid-crystalline phases, and sponge phases. At the end of the chapter, a summary of pertinent technical applications of microemulsions is presented.

Breen et al. give, in Chapter 4, a detailed discussion of destabilization processes in emulsions in general and in crude-oil-based emulsions in particular. The authors analyze thin-film rheology, Marangoni–Gibbs effects, and the occurrence of microstructures in ultrathin films. The authors also report on the effect of solid particles located at the w/o interface on the stability of w/o emulsions and especially crude-oil emulsions. In addition to this, pH effects and the influence of cosurfactants on crude-oil emulsion stability are also discussed.

Dalgleish gives an extensive analysis of fundamental mechanisms occurring in food emulsions. The author discusses in detail processes taking place at the w/o interface of different food preparations. These processes involve absorption of small surfactant molecules and proteins, competitive adsorption, interaction forms, and conformations at the interface. Dalgleish presents formation mechanisms in these kinds of emulsions together with the importance of accurate droplet size and droplet size distribution measurements. At the end of Chapter 5, the author correlates microscopic interfacial properties and macroscopic stability of food emulsions.

Bergenståhl and Östberg give a review of alkyd-based emulsions in the following chapter. As the authors point out, there is an ever-increasing interest in these kind of formulations rather than in organic solvent-based ones mainly due to health and environmental aspects. Alkyd emulsions are difficult to stabilize because of the presence of their many components. Besides the alkyd phase, the system contains solid pigments, dispersing agents, thickeners, wetting agents, biocides, and so forth. The authors discuss these components, their interaction forms, and their influence on

alkyd emulsion stability. The efficiency of different emulsifiers is also compared from a mechanistic point of view.

Perfluorocarbon-based emulsions as red cell substitutes is the subject of the chapter by Kaufman. The author reviews the use of PFCs in medicine, including such topics as temporary oxygen transport, elimination of gaseous microemboli during cardiopulmonary bypass surgery, percutaneous transluminal coronary angioplasty, myocardial infarction, and cancer therapy. The chapter gives results from recent promising tests in these fields, together with prospects and challenges.

The last three chapters deal with NMR, dielectric spectroscopy, and ultrasound measurements as techniques to characterize emulsified systems. Söderman and Balinov update the reader on the use of NMR self-diffusion measurements on emulsions. The technique gives valuable insight into structures occurring in the continuous phase of the emulsion and how this association affects stability. The authors also present NMR as a nonintrusive method for studies of droplet sizes and size distributions. The technique has been successfully applied to both food and crude-oil emulsions. The NMR technique can also be used to analyze very concentrated emulsions, the so-called aphrons.

Dielectric spectroscopy is presented by Sjöblom et al. It is shown that the time-domain dielectric spectroscopy (TDS) method is very sensitive for monitoring flocculation processes in emulsions. It is shown that this process attains different levels, depending on the type of stabilizer used. The technique is very convenient for on-line analysis of emulsions. When equipped with an external high-voltage unit, the TDS method can be utilized to follow the coalescence in different emulsified systems. Results from model emulsions, food emulsions, and crude-oil emulsions are discussed.

In the last chapter, Frøysa and Nesse present ultrasonic techniques to characterize emulsions. These nonintrusive acoustical methods are used to determine the droplet sizes and the concentration of both the dispersed and continuous phases. An obvious advantage of the technique is its applicability to optically opaque media. The authors discuss different theoretical models for sound propagation in emulsified systems and multiple scattering models, together with the pros and cons of a variety of ultrasound-based experimental techniques. Finally, the authors report on studies of both o/w and w/o emulsions containing disperse phases in the range 30–80% by volume.

When editing a volume such as *Emulsions and Emulsion Stability* it is necessary to ask your colleagues to give priority to completing their contribution to the book. This volume has been very fortunate in that the contributors gave it that priority. Therefore, I would like to express my

deepest gratitude to all the renowned contributors for their time and effort. I hope that our efforts will be well received. Finally, I hope that we have been able to contribute to a deeper understanding of the different kinds of complex emulsified systems.

Johan Sjöblom

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Emulsion Stability

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The stable state of an emulsion is in the form of its phases in layers separated by interfaces, which are as small as allowed by the form and size of the container. However, in an emulsion, several phases are dispersed in the continuous medium in the form of droplets. In the early approaches of emulsion science, only one dispersed phase, a liquid, was considered, and emulsions were defined as macrodispersions of one liquid in another. Such a state is common in commercial emulsions and its properties are

attractive from the fundamental point of view because of the simplicity. In the destabilization, such a two-phase emulsion (Fig. 1) goes through several consecutive and parallel steps before the final stage of separated layers is reached. As a first step, the droplets move due to diffusion or stirring, and if the repulsion potential is too weak, they become aggregated to each other; flocculation has taken place. The single droplets are now replaced by twins (or multiplets) separated by a thin film. This step is important because the destabilization process now passes from the realm of particles in random motion in a medium to describe the phenomena in a thin liquid film of colloidal dimensions. The thickness of the thin film is reduced due to the van der Waals attraction, and when a critical value of its dimension is reached, the film bursts and the two droplets unite to a single droplet. Coalescence has occurred.

In parallel with these phenomena, the droplets rise through the medium (creaming) or sink to the bottom (sedimentation) due to differences in density of the dispersed and continuous phase. This process is enhanced by the fact that larger droplets or aggregates move faster through the medium; in dilute suspensions, the velocity is proportional to the square

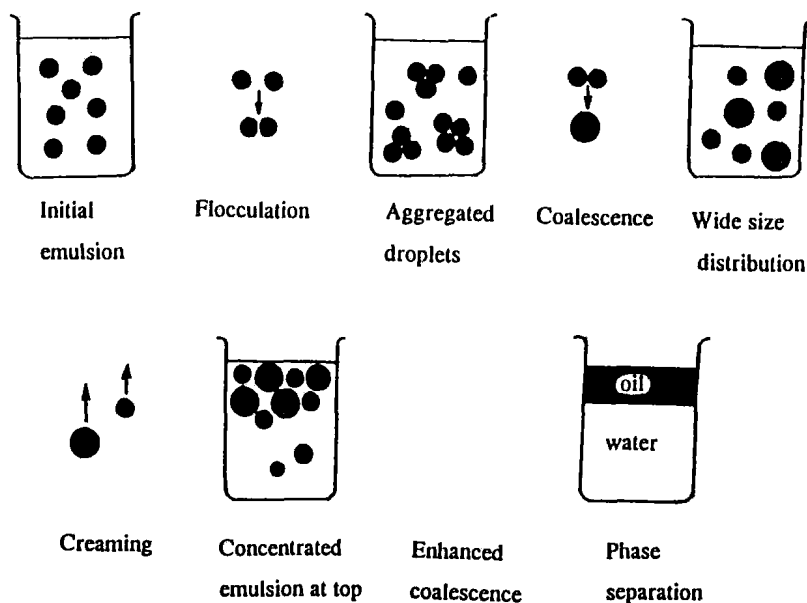


FIG. 1 The destabilization of an emulsion passes through several stages; flocculation, coalescence, and creaming before the final phase separation occurs.

of the radius. As a consequence, larger droplets pass the smaller ones, causing sedimentation-induced flocculation. The final result is a highly concentrated emulsion at the top or bottom of the container, and the increased number of droplets per volume increases the flocculation rate in a most decisive manner. The flocculation and coalescence processes lead to larger and larger droplets until, finally, a phase separation has occurred.

The understanding of flocculation rates using the well-known basis of colloidal behavior for solid particles has, by now, been well developed and reached a mature state as exemplified by the second chapter in this book. With this in mind this chapter will concentrate on two remaining phenomena. Of these, the first is obvious; the events leading to coalescence of the flocculated droplets needs a description. Second, and more important, a large number of commercial emulsions do not consist of two liquid phases only. In addition to these two phases, other phases of liquid, liquid crystalline, or solid state may also be present, as reflected in the International Union of Pure and Applied Chemistry (IUPAC) definition of an emulsions [1].

With this fact in mind, one essential phenomenon of emulsion stability is the question of to what extent the presence of a third phase will influence the different stages of the destabilization process. The influence of the third phase depends on its location and it will be briefly discussed before the general destabilization processes are examined.

One important factor for the location of the third phase at a local equilibrium is the ratio between the surface tensions (Fig. 2). The droplets may exist as individual droplets or they may be flocculated with each other. In the latter case, one droplet (Fig. 3a) may engulf the other (Fig. 3b) if the total surface free energy is reduced during that process.

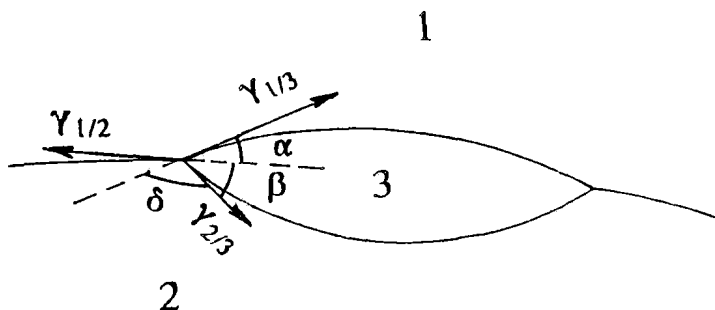


FIG. 2 With two different liquids, 2 and 3, dispersed in a third liquid, 1, the interfacial tension decides the shape of the droplets.