

**Macro- and
Microemulsions**
Theory and Applications

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Theory and Applications

Dinesh O. Shah, EDITOR
University of Florida

Based on a symposium sponsored by
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FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

PREFACE

THE CURRENT STATE OF THE ART of various aspects of macro- and microemulsions is reflected in this volume. The symposium upon which this volume is based was organized in six sessions emphasizing major areas of research. Major topics discussed include a review of macro- and microemulsions, enhanced oil recovery, reactions in microemulsions, multiple emulsions, viscoelastic properties of surfactant solutions, liquid crystalline phases in emulsions and thin films, photochemical reactions, and kinetics of microemulsions.

This volume includes discussions of various processes occurring at molecular, microscopic, and macroscopic levels in macro- and microemulsions. I earnestly hope that this book will serve its intended objective of reflecting our current understanding of macro- and microemulsions, both in theory and practice, and that it will be useful to researchers, both novices as well as experts, as a valuable reference source.

I wish to convey my sincere thanks and appreciation to the chairmen of the sessions, namely, Professor K. S. Birdi, Professor S. E. Friberg, Dr. E. D. Goddard, Dr. K. L. Mittal, and Professor S. N. Srivastava. I also wish to convey my thanks to the Division of Industrial and Engineering Chemistry as well as various corporations: Alcon Laboratories Inc., Atlantic Richfield Company, GAF Corporation, Gulf Research and Development Company, Hercules Inc., Johnson & Johnson Inc., Phillips Petroleum Company, Procter & Gamble Company, SOHIO Corporation, Velsicol Chemical Corporation, Westvaco, and Syntex, U.S.A., Inc., for their generous support that allowed me to invite many researchers from overseas to participate in this symposium. I also wish to convey my sincere thanks to the Editorial Staff of the American Chemical Society's Books Department.

I am grateful to reviewers of the manuscript, as well as to my colleagues, postdoctoral associates, and students for their assistance throughout this project. Specifically, I wish to thank Dr. M. K. Sharma for his administrative and editorial assistance, as well as Ms. Melissa Maher, Mrs. Jeanne Ojeda, and Mrs. Derbra Owete for the typing of correspondence and manuscripts. I also convey my sincere thanks and appreciation to all the authors and coauthors of the papers without whose assistance this symposium proceedings would not have been completed.

I wish to convey my sincere thanks and appreciation to my colleagues and chairpersons, Dr. J. P. O'Connell in the Department of Chemical

Engineering, and Dr. J. H. Modell in the Department of Anesthesiology at the University of Florida for their assistance. Finally, I wish to convey my sincere thanks and appreciation to my wife and children for allowing me to spend many evenings and weekends working on this volume.

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Introduction to Macro- and Microemulsions

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This paper reviews various aspects of macro- and micro-emulsions. The role of interfacial film of surfactants in the formation of these systems has been high-lighted. The formation of a surfactant film around droplets facilitates the emulsification process and also tends to minimize the coalescence of droplets. Macroemulsion stability in terms of short and long range interactions has been discussed. For surfactant stabilized macro-emulsions, the energy barrier obtained experimentally is very high, which prevents the occurrence of flocculation in primary minimum. Several mechanisms of microemulsion formation have been described. Based on thermodynamic approach to these systems, it has been shown that interfacial tension between oil and water of the order of 10^{-3} dynes/cm is needed for spontaneous formation of microemulsions. The distinction between the cosolubilized and microemulsion systems has been emphasized.

Macroemulsions have been known for thousands of years. The survey of ancient literature reveals that the emulsification of beeswax was first recorded in the second century by the Greek physician, Galen (1). Macroemulsions are mixtures of two immiscible liquids, one of them being dispersed in the form of fine droplets with diameter greater than $0.1\ \mu\text{m}$ in the other liquid. Such systems are turbid, milky in color and thermodynamically unstable (i.e. the macroemulsion will ultimately separate into two original immiscible liquids with time). Since the early 1890s, extensive and careful studies have been carried out on macroemulsions and several excellent books have been written on various aspects of formation and stability of these systems (2,10). In addition, several theories and methods of macro-emulsion formation have been discussed in the recent articles (11-17). In spite of this progress, we still do not have good predictive methods for the formation or breaking macroemulsions. For the formation of a stable macroemulsion from two immiscible liquids, there is no reliable predictive method for selecting the emulsifier or

technique of emulsification for obtaining the optimum results. One can use the concept of hydrophilic-lipophilic balance (HLB) for initial screening (1,6) and most of the new macroemulsions are ultimately perfected by trial and error approach.

Macroemulsions are utilized in many applications and are very important from the technical point of view. Many technologies and processes involve production of stable emulsions, such as skin creams (cosmetics), metal cutting fluids, fiber cleaning or removal of oil deposits (detergency), mayonnaise (food industry), bitumen emulsions (road construction), fuel (energy), herbicides and pesticides (agricultural sprays) and drug solubilization in emulsions (pharmacy). In addition, it has been observed that some processes require emulsions of long-term stability, whereas other require limited stability of emulsions. There are processes such as formation of emulsions in oil storage tanks and petroleum reservoirs where naturally occurring, unwanted stable emulsions have to be broken down. In view of the wide range of applications and technical importance of macroemulsions, it is worth discussing various aspects of these systems.

Classification of Macroemulsions

In this section, we will briefly describe the classification of macroemulsions. Based on the dispersion of water or oil in continuous phase and on the number of phases present in the system, macroemulsions can be subdivided into two categories.

Single Emulsions. These emulsions are formed by two immiscible phases (e.g. oil and water), which are separated by a surfactant film. The addition of a surfactant (or emulsifier) is necessary to stabilize the drops. The emulsion containing oil as dispersed phase in the form of fine droplets in aqueous phase is termed as oil-in-water (O/W) emulsion, whereas the emulsion formed by the dispersion of water droplets in the oil phase is termed as water-in-oil (W/O) emulsion. Figure 1 schematically illustrates the O/W and W/O type emulsions. Milk is an example of naturally occurring O/W emulsion in which fat is dispersed in the form of fine droplets in water.

Double or Multiple Macroemulsions. These macroemulsions are formed by two or more than two immiscible phases which are separated by at least two emulsifier films. Multiple emulsions can also be subdivided as single emulsions in two categories (O/W/O) and (W/O/W) emulsions (14). For a O/W/O system, the immiscible water phase separates the two oil phases, whereas for a W/O/W system, the immiscible oil phase separates the two aqueous phases. These emulsions are schematically shown in Figure 2.

The phase contained in the subdrops is often referred to as the encapsulated phase. These systems are very relevant to transport phenomena and separation processes (14), such as controlled release of drugs in which the encapsulated phase can serve as a reservoir of the active ingredient.

Mechanism of Macroemulsion Formation

Macroemulsions can be produced in different ways starting with two immiscible liquids and by applying mechanical energy, which deforms

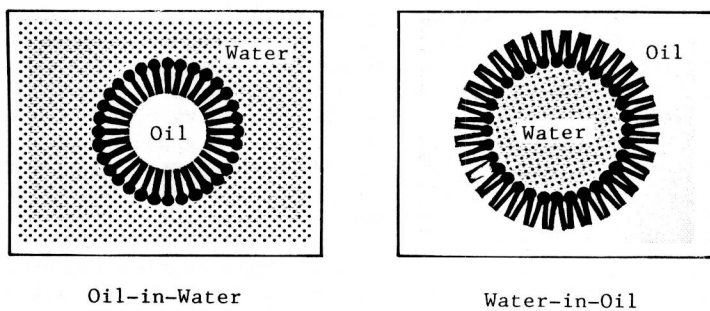


Figure 1. Schematic illustration of oil-in-water (O/W) and water-in-oil (W/O) macroemulsions

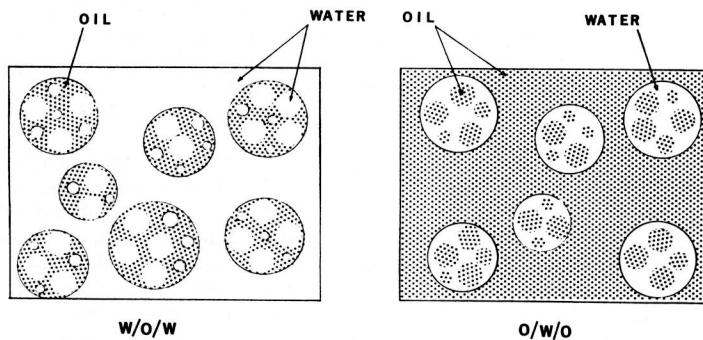


Figure 2. Schematic illustration of multiple W/O/W and O/W/O macroemulsions

the interface to such an extent that it generates droplets. The formation of final emulsion droplets can be viewed as the stepwise process. Therefore, the disruption of droplets is a critical step in the process of emulsification. During emulsion formation, the deformation is opposed by the Laplace pressure. For spherical droplet of radius (r), the difference in pressure (Δp) at the concave side of a curved interface with interfacial tension (γ) is $\frac{2\gamma}{r}$. Further division of droplets leads to an increase in Δp as r decreases. In order to disrupt such a small droplet, the pressure gradient of the magnitude of $\frac{2\gamma}{r^2}$ must be applied externally. The viscous forces exerted by the continuous phase can also deform the emulsion droplets. The viscous stress ($G\eta$) should be of the same magnitude as the Laplace pressure to deform the droplets (9), where G is the velocity gradient and η is the viscosity of continuous phase. In any case, the pressure gradient or velocity gradient required for emulsion formation are mostly supplied to the system by agitation. The various methods of agitation to produce emulsions have been described recently (18). In addition, the emulsions of smaller droplets can be produced by applying more intense agitation to disrupt the larger droplets. Therefore, the liquid motion during the process of emulsification is generally turbulent (9) except for high viscosity liquids.

Energy Needed for Emulsion Formation. The total interfacial area (A) generated due to emulsification process is much larger because of the formation of the smaller droplets. Therefore, the increase in surface free energy of the system is given by $\gamma\Delta A$. It can easily be calculated that the energy needed to produce the emulsion of average droplet diameter ($2\mu\text{m}$) from the two immiscible liquids (1 ml of each) with interfacial tension $\gamma = 10$ dyne/cm would be about 3000 times higher than that of the surface free energy of the system. For the formation of some emulsions, the pressure gradient of 2×10^9 dynes/cm³ and velocity gradient of 2×10^7 /sec (assuming $\eta = 1.0$ cp) are needed (9).

The large excess of energy required to produce emulsions can only be supplied by very intense agitation, which needs much energy. In order to reduce the agitation energy needed to produce a certain droplet size, a suitable surfactant can be added to the system. The addition of surfactant reduces interfacial tension, which in turn decreases the surface free energy of the system. The formation of a surfactant film around the droplets facilitates the process of emulsification, and a reduction in agitation energy by a factor of 10 or more can be achieved (9). The nature and concentration of surfactant also affects the droplet size and energy requirement to form the emulsion. Besides lowering the interfacial tension, the surfactant film also tends to prevent the coalescence of droplets.

Interfacial Film of Surfactants. The droplets are surrounded by an interfacial film of surfactant in emulsion systems. The stability of such films can be increased by adding appropriate surfactants. The rate of change in interfacial tension with surface area from its equilibrium value is termed as the Gibbs elasticity $E = 2d\gamma/d(\ln A)$ (9). The factors which control E are the rate of transport toward or from the interface and the structure of surfactant as well as the

rate of compression and expansion of the interface. The film elasticity also plays an important role to stabilize emulsion droplets. As the film is stretched, the local concentration of surfactant in the film decreases. This causes a transient increase in interfacial tension. The highest elasticity in the presence of sufficient amount of surfactant, provides the greatest resistance against stretching (9). Moreover, Prins (19) has shown that a stretched thin film can also break if the interfacial tension exceeds a critical value which depends on the system. For low surfactant concentration and rapid stretching, the critical value of interfacial tension is attained rapidly. Based on the above mentioned factors, it can be suggested that the surfactant is of primary importance for the stability, or flocculation of the emulsions. In conclusion, the interfacial tension gradients are essential in emulsion formation as suggested previously by Tadros and Vincent (20).

Stability of Macroemulsions

The emulsions are complex systems which present major challenges to the scientists working in this field. Previous investigators applied various theoretical approaches at the droplet level and also at the molecular level to explain the behavior of these systems. The forces such as electrical double layer, forces between emulsion droplets, hydrodynamic inertial forces, entropic (Diffusional) forces and the dispersion forces which act on the droplets or between the droplets separated at tens or hundreds of nanometers. Sedimentation and flocculation processes involve the forces such as the centrifugal force, applied electrostatic force and gravitational force. Before discussing the emulsion stability in terms of these forces, we would like to explain the thermodynamics of emulsion stabilization.

Thermodynamic Approach to Emulsion Stability. In this section, we would like to discuss thermodynamic approach to emulsion stability. Let us assume that the total free energy of the emulsion can be separated into several independent contributions. Considering hypothetically the formation or coalescence of emulsion of two immiscible liquids (e.g. oil and water), such that external field forces are absent. The total free energy (G_B) of the system just before emulsification process can be expressed in the form (10)

$$G_B = G_I + G_E + G_{IE} + G_S \quad (1)$$

where G_I , the free energy of the internal phase; G_E , the free energy of the external phase; G_{IE} , the free energy of the interface between two liquids and G_S , the free energy of the interface between the liquids and the surface of the container. In general, the solid/liquid interfacial area will be small and therefore, G_S can be neglected. The free energies, G_I and G_E , will remain almost the same before and after emulsification, whereas, G_{IE} will be at a minimum before emulsification. The interfacial free energy, G_{IE} , can be expressed in the form

$$G_{IE} = \gamma_{IE} A \quad (2)$$

where γ_{IE} , the interfacial tension and A , the interfacial area. After emulsification, the interfacial area greatly increases, therefore, G_{IE} is larger than that before emulsification. The free energy of emulsion formation can be written in the form (10)

$$\Delta G_{Emul.} = \gamma_{IE} \Delta A - T \Delta S \quad (3)$$

where ΔS is the change in entropy due to the process of emulsification. In general, the free energy of interface ($\gamma_{IE} \Delta A$) term is much larger than the $T \Delta S$ term. Therefore, the change in free energy of emulsion formation ($\Delta G_{Emul.}$) will be positive. This indicates that most of the macroemulsions are thermodynamically unstable or metastable. Moreover, the free energy of emulsification is positive; this means that the free energy of demulsification ($\Delta G_{Demul.}$) is negative. This implies that an external supply of free energy is needed for the formation of macroemulsions, and once formed, they are unstable. Tadros and Vincent (20) have shown that the variation in free energy change as a function of the demulsification processes (e.g. flocculation, coalescence) is continuous, and there is no free energy barriers to the processes until the drops are close enough for short range repulsive and attractive forces.

Short Range Interactions and Emulsion Stability. The stability of macroemulsions in terms of short range (e.g. inter-droplet) interactions will be discussed in this section. The dispersion (London) forces arise from charge fluctuations within a molecule associated with the electronic motion (21). Therefore, these forces can operate even between nonpolar molecules. London (21) reported an equation for mutual attractive energy between two molecules in vacuum in the form

$$V_A = \frac{3}{4} h \nu_o \frac{\alpha}{d^6} = \frac{\beta_{11}}{d^6} \quad (4)$$

where h is the Planck's constant; ν_o , the characteristic frequency of the molecule; α , the polarizability of the molecule and d , the distance between the molecules. The London forces between two molecules are short range as the V_A is inversely proportional to the sixth power of their separation. Assuming these forces between molecules could be summed for all the molecules in a particle of radius (r), the Equation (4) can be expressed (22) in the form

$$V_A \approx - \frac{Ar}{\pi} \left[\frac{2.45\lambda}{120H^2} - \frac{\lambda^2}{1045H^3} + \frac{\lambda^3}{5.62 \times 10^4 H^4} \right] \quad (5)$$

valid for $H > 150 \text{ \AA}^0$, and

$$V_A \approx - \frac{Ar}{12H} \left[\frac{\lambda}{\lambda + 3.5\pi H} \right] \quad (6)$$

valid for $H < 150 \text{ \AA}^0$

where A is the Van der Waals constant; λ , the wavelength of the intrinsic electronic oscillations of the atoms ($\sim 10^{-5} \text{ cm}$); H , the interparticle distance between droplets and r is the average radius of droplets.

The so called Hamaker/Van der Waals constant, A , required to evaluate energy of attraction between two droplets (Equations 5 and 6) in vacuum is defined by

$$A = \pi^2 B_i^2 L_i \quad (7)$$

where L_i is the London constant, B_i , the number of atoms (molecules with i th kind contained in cm^3 of the substance). If the droplets are suspended in a continuous medium, then the net interaction is reduced and the Equation 7 can be rewritten in the form

$$A \approx (A_{o-o}^{1/2} - A_{w-w}^{1/2})^2 \quad (8)$$

and generally lies in the range of 10^{-13} to 10^{-14} ergs (15, 17).

The repulsive (e.g. electrical double layer) forces have been discussed in detail in literature (23,25). The repulsive energy derived by Derjaguin and Kassakov (26) is given by

$$V_R = \frac{\epsilon \epsilon_0 \psi_o^2}{2} \ln(1 + e^{-\kappa H}) \quad (9)$$

where ϵ is the dielectric constant of the medium; ψ_o , the surface potential and κ is the reciprocal "thickness" of the electrical double layer, given by

$$\kappa = \left(\frac{8\pi n z^2 e^2}{\epsilon kT} \right)^{1/2} \quad (10)$$

where z is the valency of counter ions; e , the electronic charge; n , the number of ions per cm^3 in the solution; k , the Boltzmann's constant and T , the absolute temperature.

The total interaction energy is obtained by summing the V_A and V_R contributions. A schematic representation of these energies (3) is given in Figure 3. This curve shows a primary minimum at very short distances between the droplets (e.g. close contact), a maximum at intermediate interdroplet distances and a secondary minimum at large interdroplet distances. For irreversible flocculation into the primary minimum to occur, the energy barrier has to be surmounted. The height of the barrier is primarily controlled by the electrolyte concentration (15, 17). The reversible flocculation may occur in the secondary minimum as reported previously by several investigators (15,17,27). For surfactant stabilized emulsions, it has been reported that the energy barriers obtained experimentally are very high, which prevents the occurrence of flocculation in primary minimum (15,27).

Long Range Interactions and Emulsion Stability. The processes such as sedimentation, creaming and flocculation can be controlled by external forces, e.g. centrifugal, gravitational or applied electrostatic forces. These forces are considered to be essentially long range. In this section we would like to discuss processes controlled by long range forces.

Sedimentation and Creaming. The creaming and sedimentation processes occur in emulsion systems mainly due to the density difference between the dispersed and continuous phases. Assuming a steady state,

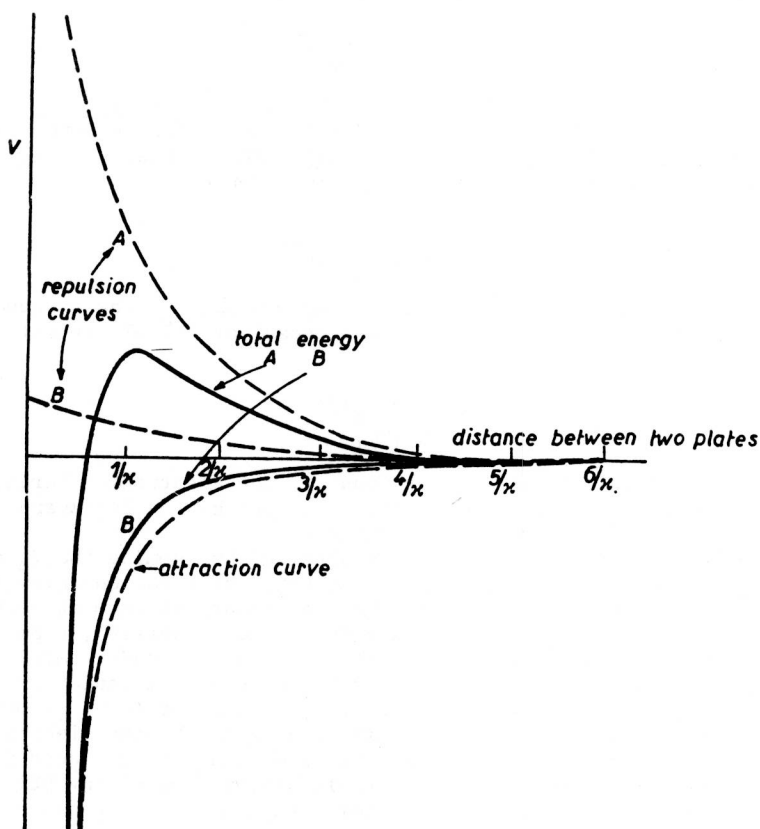


Figure 3. Schematic illustration of interaction energies as a function of interparticle distance between two droplets.