Emulsions, Microemulsions and Foams
(Part I)

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6.1.1 Introduction

- Emulsions, microemulsions and foams constitute a major part of colloidal dispersions. Their applications in industry are quite diverse and have great practical importance. Sometimes their presence creates problems in the processing and manufacturing operations as well.

- The properties of these dispersions can determine both the economic and technical success of the industrial operations. Some of the common occurrences of emulsions and foams are in environment and meteorology (e.g., polluted river foams, foams in oceans, water and sewage treatment emulsions), foods (e.g., champagne, soda and beer heads, whipped cream, ice cream, milk, butter, cheese and sauces), geology, agriculture and soil science (e.g., fumigants, insecticide blankets and sprays), materials science (e.g., foam fractionation, de-inking froth, polishes, paving asphalt, emulsion and latex paints), biology and medicine (e.g., vacuoles, contraceptive foams, gastrointestinal foams, vitamin and hormone products, blood and cells), petroleum production and mineral processing (e.g., refinery foams, mineral flotation froth, fire-extinguishing foam, drilling emulsions, reservoir emulsions and transportation emulsions), and home and personal care products (e.g., shampoos, detergents, hair-styling mousse, skin-care creams and lotions).

- During the past three decades, there have been extensive studies on microemulsions. In some years, more than 1000 research publications have appeared on microemulsion research, which clearly indicates the large emphasis on research on the microemulsions.

- A major impetus behind the commercial use of microemulsions emerged in the 1970s for the enhanced oil recovery (EOR). Since then, there have been many applications in varied areas such as pharmaceuticals, cosmetics, foods, liquid membranes and textiles. Since the microemulsions can co-solubilize high amounts of both water-soluble and water-insoluble materials, they have been used as novel media for chemical synthesis.

- Photographs of emulsion, foam and microemulsion are shown in Fig. 6.1.1.
6.1.2 Emulsions

- The traditional definition of emulsion is the dispersion of one liquid into another liquid in the form of droplets in presence of one or more surfactants, which act as stabilizer. However, with the growth of applications of emulsions in making diverse materials such as lubricating grease, oil-based drilling fluids, foods, pharmaceutical products and cosmetics, more complex structures have emerged, e.g., Pickering emulsions (which are emulsions stabilized by films of fine particles). Emulsions containing solid particles are also known as emulsion-suspensions.

- Depending on the liquid that forms the dispersed phase, emulsions are classified as oil-in-water (O/W) and water-in-oil (W/O) emulsions. These emulsions have relationship with the HLB values of the surfactants which stabilize them (See Lecture 6 of Module 1).

- Emulsions are also classified according to the size of the dispersed droplets. For macroemulsions, the mean droplet diameter of the dispersed phase is between 0.3 and 50 μm. Such emulsions are thermodynamically unstable and tend to break unless stabilized. Energy is required to produce them. On the other hand, microemulsions contain droplets of less than 300 nm average diameter and they are thermodynamically stable.
Generally the term *emulsion* indicates the macroemulsions. With modern mechanical emulsification equipment and a judicious choice of components, it is possible to produce liquid dispersions in which the droplet-size is less than the large droplets of a microemulsion. However, such emulsions are not microemulsions. They are thermodynamically unstable, and hence, emulsions.

The droplet size distribution provides information about the effectiveness of the coalescence and break-up processes occurring within the emulsion system. The total interfacial area in an emulsion is a function of the diameter of the droplets.

Important properties like viscosity, yield strength, flow-ability, pump-ability, color, mouth-feeling, texture and flavor of the product are also influenced by the droplet size distribution.

Typical O/W macroemulsions are milk, water-soluble paint, body lotion and mayonnaise, whereas butter and certain skin creams are W/O macroemulsions.

### 6.1.2.1 Preparation of emulsions

Emulsions can be prepared by several methods. The common emulsification equipment is shown in Fig. 6.1.2.

![Fig. 6.1.2 Commonly used equipment for emulsification.](image)

These machines can be divided into two categories: (i) rotor–stator dispersing machines, and (ii) high pressure homogenizer.

In *stirring vessels*, the average energy input per unit volume is very low. Thus, stirrers are only suitable for the production of coarse emulsions.
In a colloid mill, the droplets are disrupted in a conical gap between the rotor and the stator, each being either smooth or toothed. The design of tooth varies. Gap width, rotor radius, rotational speed and flow rate are very important as far as the disruptive stresses are concerned. Typical gap widths in these machines are 100–3000 µm and the peripheral speed usually varies in the range of 5 to 40 m/s.

Toothed disk dispersing machines consist of one or several pairs of concentrically arranged split disks of various design. The peripheral speed can vary up to 40 m/s. The high-pressure homogenizer operates by pumping the premix through a narrow orifice under high pressure (up to $1 \times 10^8$ Pa). The emulsion flows at a very high speed (up to 200 m/s) inside the homogenizer’s valve. Various designs of the valve are possible. Emulsions are produced continuously in colloid mills, toothed disk dispersing machines and high pressure homogenizers. Stirring vessels are used for batch-wise processing.

For the preparation of emulsions in small-scale (e.g., in laboratory applications), the use of ultrasound is a well-known method. This procedure can be employed to obtain finely-dispersed emulsions in continuous or batch units (see Fig. 6.1.3).

Fig. 6.1.3 Probe sonicator emulsification system (courtesy: PCI Analytics Pvt. Ltd.)
The ultrasonic power is adjustable and can be adapted to the desired products and emulsification requirements. Highly intensive ultrasound supplies the power needed to disperse one liquid into the other in the form of small droplets.

In the dispersing zone, imploding cavitation bubbles cause intensive shock waves in the surrounding liquid, which result in the formation of liquid jets of high velocity. As coalescence of the droplets after disruption influences the final droplet size distribution, efficient emulsifiers are required to maintain the final size distribution of the droplets at a level that is same as the distribution immediately after the droplet disruption in the ultrasonic dispersing zone.

Studies on oil-in-water and water-in-oil emulsions have shown the correlation between the energy density and droplet size. With increasing energy density, droplets with smaller size form. At appropriate levels of energy density, ultrasound can easily achieve a mean droplet size below 1 µm.

Membrane emulsification is a promising method to prepare uniform-sized emulsions. Microporous inorganic and polymeric membranes have been used to prepare emulsions. The advantage of this method is low energy input as compared to the high-pressure homogenizers and rotor-stator equipment.

This method is very useful for the preparation of emulsions containing labile compounds such as bioactive molecules, which are sensitive to shear stress. In membrane emulsification, droplets are formed at the pore-mouth of the membrane by forcing the dispersed phase liquid to permeate through the membrane, and stripping the droplets from the pore into the continuous phase by the action of axial flow.

The size of the droplets depends on the balance between the drag force on the droplets, interfacial tension and the transmembrane pressure. Stability and density of the emulsions prepared by membranes are good, which of course, depend on the emulsion stabilizers. However, the present technology is not suitable for large-scale emulsification due to the low permeation rate.
6.1.2.2 Stability of emulsions

- Emulsions are thermodynamically unstable systems and their free energy of formation \( \Delta G_f \) is greater than zero. Therefore, they show a tendency to destabilize.
- This instability is a result of the energy associated with the large interfacial area of the droplets within the emulsion, given by \( \gamma A \), where \( A \) is the total surface area of the droplets and \( \gamma \) the interfacial tension between the aqueous and non-aqueous phases. This energy term outweighs the entropy of formation, \( \Delta S_f \), associated with the formation of the droplets from the bulk constituents.
- The free energy of formation of the emulsion is given by,
\[
\Delta G_f = \gamma A - T \Delta S_f
\] (6.1.1)
- The interfacial tension in emulsions is generally in the range of 1–10 mN/m. The product of interfacial tension and the large interfacial area produces a large positive interfacial energy term.
- The entropy of formation of emulsions is not very large because the number of droplets formed is rather small in entropic terms. These two factors result in \( \Delta G_f > 0 \), which leads to the thermodynamic instability of the emulsions.
- Emulsions are, however, kinetically stable due to the presence of an adsorbed layer of surfactant molecules at the oil–water interface. This layer may provide electrostatic (in the case of an ionic surfactant) or steric (for a nonionic surfactant) repulsion when the droplets approach each other. These monolayers therefore act as barriers and prevent the emulsion droplets from coming into direct contact. They serve to stabilize the thin film of liquid between two adjacent droplets. Coalescence occurs when this thin film becomes unstable and then ruptures. Therefore, the presence of adsorbed surfactants can reduce the likelihood of rupture.
- As a result of their thermodynamic instability, emulsions tend to reduce their total free energy through an increase in droplet diameter, and hence reduce their total interfacial area. This leads to the degradation of the emulsion.
An emulsion may degrade by various mechanisms such as creaming (with or without aggregation), aggregation (with or without creaming), Ostwald ripening and coalescence. These processes have been shown schematically in Fig. 6.1.4.

![Diagram of emulsion degradation processes](image)

Fig. 6.1.4 Schematic diagram depicting how an emulsion breaks down.

Reversible aggregation of droplets is known as flocculation. Coalescence and Ostwald ripening involve a change in the droplet size distribution and can result in complete phase separation into oil and water, as shown in Fig. 6.1.4.

Coalescence requires the drops to be in close proximity. Ostwald ripening, on the other hand, does not require the droplets to be close, since the process occurs by transport of dissolved matter through the dispersion medium.

In the majority of cases, the predominant degradation mechanism is coalescence, but sometimes, Ostwald ripening is a significant factor. A droplet may be considered to be in equilibrium and show no Ostwald ripening if the following condition is satisfied.

\[ 2 \frac{d\gamma}{d\ln A} > \gamma \]  

(6.1.2)

### 6.1.2.2.1 Ostwald ripening

This phenomenon was first observed by Wilhelm Ostwald in 1896. It has been studied mostly in connection with the preparation of metal alloys, crystallization and artificial blood substitutes.
In emulsion technology, Ostwald ripening refers to mass transfer between drops of different curvature through their surrounding continuous medium. The concentration of the dispersed phase material at the surface of a drop is inversely related to the radius of curvature. Hence, a small drop has a high surface concentration in comparison with a large drop. Therefore, a concentration gradient of the dispersed phase material in the continuous phase is set up.

Mass transfer occurs along the concentration gradient from the small drops to the large drops. Therefore, small drops shrink and ultimately disappear while the large drops grow at their expense, leading to phase separation.

The theory proposed by Lifshitz and Slyozov (1961) deals with Ostwald ripening in infinitely dilute dispersions. This theory has shown that the Ostwald ripening process reaches a stationary state after some time. The cube of the mean drop radius increases linearly with time.

Experimental measurements of Ostwald ripening are relatively few for emulsions. Some of the experimental studies have confirmed the predictions of the Lifshitz–Slyozov theory when the dispersed phase volume fraction is low. However, the measured size distributions for emulsions with high volume fractions of the dispersed phase are usually broader than that predicted by this theory, and the absolute growth rate is observed to be faster.

The effect of the dispersed phase volume fraction can be studied by tracking the location of each drop and determining the local environment through the contribution of source and sink terms for each drop. This approach is suitable for a small number of drops.

Various statistical techniques have been developed to overcome this difficulty. In all cases, the predicted drop size distribution and the variation of cube of mean radius with time is observed to be in better agreement with the experimental observations than the predictions from the Lifshitz–Slyozov theory.

Most of these predictions, however, are valid for dispersed phase volume fractions less than 0.3. However, concentrated emulsions with dispersed phase volume fractions as high as 0.7 can undergo Ostwald ripening (e.g., a creamed emulsion which does not coalesce).
♦ A photograph illustrating Ostwald ripening is shown in Fig. 6.1.5.

Fig. 6.1.5 Photomicrographs reflecting changes with time of a 1,2-dichloroethane emulsion in water in presence of SDS. Double exposure on the same frame; time from the start of experiment: 0 s (image shifted on the left) and 300 s (image shifted on the right) (Kabalnov et al., 1987) (adapted by permission from Elsevier Ltd., © 1987).

♦ Let us consider a big and a small drop as shown in Fig. 6.1.6.

Fig. 6.1.6 Cell model for Ostwald ripening.

♦ The separation between two drops is $2\delta$. The continuous phase is distributed around each drop in the form of a concentric shell of thickness $\delta$. The half-separation (between the drops), $\delta$, is assumed to be identical for all drops regardless of their size.
If \( r_b \) represents the boundary radius for mass transfer and \( a \) is the radius of the drop then, \( \delta = r_b - a \). The mass transfer boundary lies between the drops. The change in radius of a drop by mass transfer can be expressed as,

\[
\frac{da}{dt} = \frac{r_bD}{a(r_b - a)}(\phi_m - \phi_s)
\]  

(6.1.3)

where \( t \) is time, \( D \) is diffusivity, and \( \phi_m \) and \( \phi_s \) are the volume fractions of the dispersed phase liquid in the continuous phase and at the surface of the drop, respectively.

The surface concentration of a drop, in terms of volume fraction, is related to the solubility of the dispersed phase liquid in the continuous phase (expressed as a volume fraction \( \phi_\infty \)) by the Kelvin equation [see Lecture 3 of Module 2] as,

\[
\phi_s = \phi_\infty \exp \left[ \frac{2\gamma \bar{V}}{RTa} \right]
\]  

(6.1.4)

where \( \bar{V} \) is the molar volume of the dispersed phase, \( \gamma \) is the interfacial tension between the two liquids, \( R \) is the gas constant and \( T \) is temperature.

The term \( \left( \frac{2\gamma \bar{V}}{RTa} \right) \) in Eq. (6.1.4) is generally much smaller than unity. Therefore, this equation can be simplified by the first-order approximation of the exponential term to give,

\[
\phi_s = \phi_\infty \left( 1 + \frac{2\gamma \bar{V}}{RTa} \right)
\]  

(6.1.5)

From Eq. (6.1.5), we observe that the concentration of the dispersed phase material at the surface of the drop exceeds the solubility of the dispersed material in the continuous phase. Hence, the continuous phase becomes supersaturated and \( \phi_m \) exceeds \( \phi_\infty \) by some fraction \( \theta \), which we can represent as,

\[
\phi_m = \phi_\infty (1 + \theta)
\]  

(6.1.6)

Substituting \( \phi_s \) and \( \phi_m \) from Eqs. (6.1.5) and (6.1.6) in Eq. (6.1.3) and simplifying we get,
\[ \frac{da}{dt} = \frac{2\eta b D \nu \gamma \phi_e}{RT a^2 (n_a - a)} \left( \frac{a}{a_c} - 1 \right) \]  

(6.1.7)

where \( a_c \) is the critical radius, which is defined as,

\[ a_c = \frac{2\gamma \nu}{RT \theta} \]  

(6.1.8)

The characteristic behavior of Ostwald ripening is evident from Eq. (6.1.7), i.e., for drops with a radius exceeding the critical radius (i.e., \( a/a_c > 1 \)), \( da/dt \) is positive and the drop grows with time. Conversely, drops with a radius below the critical radius (i.e., \( a/a_c < 1 \)) will shrink.

If \( n_b \gg a \), Eq. (6.1.7) becomes,

\[ \frac{da}{dt} = \frac{2D \nu \gamma \phi_e}{RT a^2} \left( \frac{a}{a_c} - 1 \right) \]  

(6.1.9)

This is the ‘infinitely dilute’ form of Eq. (6.1.7). The ‘infinitely concentrated’ form of Eq. (6.1.7) can be derived as follows. Let us substitute \( n_b = a + \delta \) in Eq. (6.1.7), which gives,

\[ \frac{da}{dt} = \frac{2(a + \delta)D \nu \gamma \phi_e}{RT a^2} \left( \frac{a}{a_c} - 1 \right) \]  

(6.1.10)

As \( \delta \) approaches zero (i.e., the “infinitely concentrated” limit), Eq. (6.1.10) becomes,

\[ \frac{da}{dt} = \frac{2D \nu \gamma \phi_e}{RT a} \left( \frac{a}{a_c} - 1 \right) \]  

(6.1.11)

Equation (6.1.10) is a general form of the Ostwald ripening model. It is applicable at any volume fraction of the dispersed phase.

The volumes of the dispersed phase and the emulsion can be expressed in terms of the number of drops as,

\[ V_d = n \frac{4\pi}{3} \sum_i f_i a_i^3 \]  

(6.1.12)

\[ V_t = n \frac{4\pi}{3} \sum_i f_i (a_i + \delta)^3 \]  

(6.1.13)
where $V_d$ and $V_t$ are the volumes of the dispersed phase and the emulsion, respectively, $n$ is the total number of drops, and $f_i$ is the number frequency of the drops with radius $a_i$.

Now, $V_d = \phi_d V_t$, where $\phi_d$ is the volume fraction of the dispersed phase. From Eqs. (6.1.12) and (6.1.13) we obtain,

$$\phi_d = \frac{\sum f_i a_i^3}{\sum f_i (a_i + \delta)^3}. \quad (6.1.14)$$

As $\delta \to 0$, $\phi_d \to 1$, and as $\delta \to \infty$, $\phi_d \to 0$. Thus, Eq. (6.1.14) satisfies the two limiting conditions of dilute and infinitely concentrated cases corresponding to infinite and zero separations, respectively.

Note that $\delta$ has been assumed to be identical for all drops regardless of their size, and represents an average dimension. The effects of different local environments within the emulsion are not accounted in this model.

To solve the ripening problem at a finite dispersed phase volume fraction, the half-separation distance, $\delta$, is found from Eq. (6.1.14) and used to solve Eq. (6.1.10). The differential equations are nonlinear because $a_c$ and $\delta$ are functions of time.

Let us now consider the rate of Ostwald ripening. From the Lifshitz–Slyozov theory, the rate of ripening is given by,

$$\omega = \frac{d a_c^3}{d t} = \frac{8D c_\infty \gamma M}{9 \rho^2 RT} \quad (6.1.15)$$

where $c_\infty$ is the bulk solubility of the dispersed phase liquid in the continuous phase, $M$ is the molecular weight and $\rho$ is the density of the liquid constituting the dispersed phase.

Equation (6.1.15) predicts that a plot of the cube of the critical radius against time will be linear. It is assumed in the Lifshitz–Slyozov theory that the critical radius, $a_c$, is almost equal to the number average radius, $a\overline{a}$, of the emulsion.
This allows us to calculate the rate of ripening from the physical properties of the emulsion, i.e., the interfacial tension, the diffusion coefficient of the dispersed phase liquid in the continuous phase, and its solubility in the continuous phase.

**Example 6.1.1:** Show that the effect of Ostwald ripening in an emulsion of 1 µm (average) drop radius is less than that for an emulsion having 0.5 µm (average) drop radius. Assume that the ripening rate is same in both the cases.

**Solution:** By putting \( \bar{a} = a_e \) in Eq. (6.1.15), we can write,

\[
\frac{d \bar{a}^3}{dt} = \omega
\]

\[\therefore \quad 3\bar{a}^2 \frac{d \bar{a}}{dt} = \omega \]

\[\therefore \quad \frac{d \bar{a}}{dt} = \frac{\omega}{3\bar{a}^2} \]

Thus, for a given rate of ripening, \( \omega \), the rate of change in the average radius is inversely proportional to the square of the average drop radius. Therefore, the rate of increase in the average drop radius in an emulsion of 1 µm average drop radius would be less than that for an emulsion of 0.5 µm average drop radius.
Exercise

Exercise 6.1.1: Calculate the rate of Ostwald ripening for an oil-in-water emulsion at 298 K if the oil has the following properties: density = 850 kg/m³, average molecular weight = 110 kg/mol, diffusivity = $9.15 \times 10^{-9}$ m²/s and solubility in water = 1.2 kg/m³. The interfacial tension is 7 mN/m.

Exercise 6.1.2: 50 cm³ of an oil is to be emulsified in 250 cm³ of water. Initially, the oil is kept in contact with water in a cylindrical glass vessel of 6 cm diameter. After emulsification by a high-speed homogenizer (in the presence of a surfactant), the average diameter of the oil droplets becomes 50 μm. If the interfacial tension is 10 mN/m, calculate the change in interfacial energy upon emulsification.

Exercise 6.1.3: Answer the following questions clearly.

(a) Give three important applications each of emulsions, microemulsions and foams.
(b) Explain how oil-in-water and water-in-oil emulsions are related to the HLB of the surfactants.
(c) Mention three methods of preparation of emulsions. Explain their advantages and disadvantages.
(d) Explain how an emulsion can be prepared by membrane.
(e) Mention the processes by which an emulsion is destabilized.
(f) What is Ostwald ripening? When and why is it important?
(g) Explain the salient features of Lifshitz–Slyozov theory.
Suggested reading

Textbooks

Reference books

Journal articles