Emulsions, Microemulsions and Foams (Part III)

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6.3.1 Stochastic theory of coalescence

- Studies on coalescence of drops (drop–interface coalescence as well as binary coalescence) have indicated that coalescence time does not have a single value, even under identical experimental conditions, but a wide distribution is always observed.

- In the stochastic model of coalescence (see Ghosh and Juvekar, 2002), the variation in coalescence time was attributed to the variation in surface excess at the interfaces. The distribution of surface excess was assumed to be Gaussian. The variation in surface excess is mainly caused by the hydrodynamic fluctuations in the region of contact after the drops strike the interface (or each other in a two drop system) with a high velocity.

- This theory is concerned with the surfactant distribution in the thin liquid film. When a drop approaches the flat interface with a high velocity, the thin liquid film trapped between them drains fast. During the drainage of the film, the surfactant molecules, which were adsorbed on the interfaces, are swept towards the rim of the film, known as ‘barrier ring’, as shown in Fig. 6.3.1.

![Fig. 6.3.1 Illustration of the interfacial diffusion of surfactant molecules when a drop rests at a liquid–liquid interface.](image)

- The stress can be so large that the surfactant molecules are likely to form a liquid-condensed (LC) phase at the barrier ring. The ionic surfactants generate
electrostatic repulsive force whereas the nonionic surfactants generate steric repulsive force that repels the drop from the interface.

- During the approach of the drop, a dimple forms in the film such that the thickness of the film is maximum at the center and minimum at the periphery. The dimple may flatten to some extent with time. Since the thickness of the film is minimum at the barrier ring, the repulsion between the drop and the flat interface is largest at this region.

- After the drop comes to a rest position by the action of the interfacial repulsive force, the surfactant molecules diffuse back towards the center of the film driven by the concentration gradient, as illustrated in Fig. 6.3.1. This reduces the concentration of surfactant at the barrier ring, which leads to the depletion in the repulsive force.

- When the repulsion diminishes, the drop comes closer to the interface. At a certain separation, the thickness of the thin film at the barrier ring becomes very small, and it becomes unstable. At this point, the van der Waals attraction between the two drop surfaces exceeds the repulsive force, resulting in coalescence.

- From the above description, it is apparent that coalescence is likely to occur at the barrier ring, which has been supported experimentally [Charles and Mason (1960); Hodgson and Woods (1969)].

- Based on this physical description of the coalescence process, the following equation for cumulative distribution of coalescence time has been developed.

\[ F(\tau_R) = \frac{1}{2} \left[ \text{erf} \left( \frac{1}{S_{\Gamma} \sqrt{2}} \left( \frac{P_{\Gamma}}{1 + \sum_{i=1}^{\infty} \exp \left( -\lambda_i^2 \tau_R \right)} \right) - 1 \right) \right] + \text{erf} \left( \frac{1}{S_{\Gamma} \sqrt{2}} \right) \]  \hspace{1cm} (6.3.1)

In deriving Eq. (6.3.1), the curvature in the film (due to the presence of the dimple) and the nonuniformity in its thickness were ignored for simplicity.

- In Eq. (6.3.1), \( \text{erf}(y) \) represents the error function and \( \lambda_i \) are the zeros of the Bessel function of first kind and order one \( (J_1) \). \( \tau_R \) is the dimensionless
coalescence time, defined as \( \tau_R = t/\bar{T} \), where \( \bar{T} \) is the characteristic diffusion time given by,

\[
\bar{T} = \frac{R_b^2}{D_\Gamma}
\]

(6.3.2)

- The characteristic diffusion time is usually much longer than the coalescence time because coalescence occurs much before the entire surfactant build-up at the barrier ring is depleted to the initial uniform concentration. \( D_\Gamma \) is the surface diffusivity of the surfactant molecules (see Lecture 3 of Module 5).

- The radius of the barrier ring, \( R_b \), can be estimated from the equation given by Princen (1963),

\[
R_b = 2a^2 \left( \frac{\Delta \rho g}{3\gamma} \right)^{1/2}
\]

(6.3.3)

where \( a \) is the radius of the drop.

- This equation was derived considering the weight-induced deformation of a drop on a flat deformable interface (see Lecture 3 of Module 5). The effects of interfacial tension and the density difference between the two liquid phases were taken into account in Eq. (6.3.3).

- During the period the drops rests on the interface, the barrier ring may expand or shrink. However, the stochastic model does not take into account this possibility. Therefore, \( R_b \) remains constant with time.

- \( P_\Gamma \) is the dimensionless coalescence threshold. It is given by,

\[
P_\Gamma = \frac{\Gamma_m}{\bar{\Gamma}} = \frac{a}{(w_b f_i \nu) \bar{\Gamma}} \left( \frac{\Delta \rho g \gamma}{3} \right)^{1/2}
\]

(6.3.4)

where \( \Gamma_m \) represents the minimum value of surfactant concentration at the barrier ring required to prevent coalescence, and \( \bar{\Gamma} \) is the mean value of surface excess in the film.

- The value of \( \bar{\Gamma} \) is taken to be equal to the surface excess \( \Gamma \), which can be calculated by the procedure presented in Lectures 1–3 of Module 4. In Eq. (6.3.4), \( \nu \) represents the fraction of the total surfactant molecules that remains at the
barrier ring after the second drop strikes the first drop, \( w_b \) is the width of the barrier ring and \( f_r \) is the repulsive force generated by one mole of the adsorbed surfactant molecules. It depends on the type of surfactant used. It can be affected by the presence of salt in the solution if the surfactant is ionic. Equation (6.3.4) can be derived by a simple force balance as explained below.

Let us consider a drop resting on a flat interface as shown in the Fig. 6.3.1. It is evident that during the period of rest, the drop is pressed to the flat interface by the gravity force, \( \left(4\pi a^3 \Delta \rho g / 3\right) \). This force is balanced by the repulsive force exerted by the surfactant molecules, which acts along the barrier ring. Therefore, the minimum repulsive force required at the barrier ring to prevent coalescence is equal to \( \left[ \Gamma_m f_r \left(2\pi R_b\right) w_b \right] \).

Therefore, at the point of coalescence,

\[
\Gamma_m f_r \left(2\pi R_b\right) w_b = \left(\frac{4}{3} \pi a^3\right) \Delta \rho g \tag{6.3.5}
\]

Inserting \( R_b \) from Eq. (6.3.3) and using the definition of \( P_G \left( \equiv \frac{\Gamma_m}{\Gamma V} \right) \), Eq. (6.3.5) can be obtained. In Eq. (6.3.1), \( S_G \) is the normalized standard deviation in surface excess, defined as,

\[
S_G = \frac{\sigma_G}{\Gamma} \tag{6.3.6}
\]

The value of \( S_G \) usually lies between 0.1 and 0.4, depending upon the broadness of the distribution. Therefore, the stochastic model has two unknown parameters, \( P_G \) and \( S_G \), which need to be determined by fitting Eq. (6.3.1) to the experimental coalescence time distributions. Example 6.3.1 illustrates this. The variation of \( P_G \) with the physical properties of the system can be explained from Eq. (6.3.4).

**Example 6.3.1:** Coalescence of 1.5 mm radius carbon tetrachloride drops were studied at water–carbon tetrachloride interface in presence of 1 mol/m³ sodium dodecyl sulfate.
The interfacial tension was 38.5 mN/m. The coalescence time data for 10 observations are given below.

<table>
<thead>
<tr>
<th>Observation no.</th>
<th>$t_c$ (s)</th>
<th>Observation no.</th>
<th>$t_c$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.1</td>
<td>6</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>4.2</td>
<td>7</td>
<td>3.3</td>
</tr>
<tr>
<td>3</td>
<td>6.3</td>
<td>8</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>3.0</td>
<td>9</td>
<td>0.8</td>
</tr>
<tr>
<td>5</td>
<td>1.3</td>
<td>10</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Develop the cumulative distribution of coalescence time. Determine the parameters of the stochastic model. Given: density of carbon tetrachloride = 1600 kg/m$^3$ and surface diffusion coefficient, $D_\Gamma = 1 \times 10^{-10}$ m$^2$/s.

**Solution:** Total number of observations = 10. The minimum coalescence time is 0.8 s and the maximum is 6.3 s. The mean coalescence time is 2.98 s and the standard deviation is 1.54 s. The cumulative distribution is shown in Fig. 6.3.2, where $F$ represents the fraction of drops coalesced on or before $t$ seconds.

![Cumulative distribution of coalescence time](image)

The characteristic diffusion time, $\tau$, is calculated from Eqs. (6.3.2) and (6.3.3). The radius of barrier ring is given by,
\[ R_b = 2 \times \left(1.5 \times 10^{-3}\right)^2 \times \left(\frac{600 \times 9.8}{3 \times 38.5 \times 10^{-3}}\right)^{1/2} = 1.015 \times 10^{-3} \text{ m} = 1.015 \text{ mm} \]

Therefore, the characteristic diffusion time is given by,

\[ \tau = \frac{R_b^2}{D_\Gamma} = \frac{(1.015 \times 10^{-3})^2}{1 \times 10^{-10}} = 10302.25 \text{ s} \]

The parameters of the stochastic model, viz. \( P_\Gamma \) and \( S_\Gamma \), are determined by fitting Eq. (6.3.1) to the cumulative distribution shown in the figure.

The first ten zeros of the Bessel function \( J_1 \) are used for the computation. These are, \( \lambda_1 = 0 \), \( \lambda_2 = 3.8317 \), \( \lambda_3 = 7.0156 \), \( \lambda_4 = 10.1735 \), \( \lambda_5 = 13.3237 \), \( \lambda_6 = 16.4706 \), \( \lambda_7 = 19.6159 \), \( \lambda_8 = 22.7601 \), \( \lambda_9 = 25.9037 \) and \( \lambda_{10} = 29.0468 \).

The optimum fitted values are, \( P_\Gamma = 18.3 \) and \( S_\Gamma = 0.2 \).

- To achieve a finite coalescence time, \( \Gamma \nu \) should be less than \( \Gamma_m \). As \( \Gamma \nu \rightarrow \Gamma_m \), \( \tau_R \rightarrow \infty \). This means that drops for which \( \Gamma \nu \geq \Gamma_m \) will never coalesce. The reason is, if the drop rests at the interface for infinite time, then the quantity of the surfactant, which was initially concentrated at the barrier ring, will spread uniformly over the entire film and the concentration of the surfactant will be \( \Gamma \nu \) everywhere, including the barrier ring.

- Therefore, for all finite times, the concentration at the barrier ring, \( \Gamma(R_b) \), will be greater than \( \Gamma \nu \). Thus, \( \Gamma \nu \geq \Gamma_m \) implies that \( \Gamma(R_b) \) will be greater than \( \Gamma_m \) at all times. Hence, those drops for which this condition is satisfied will never coalesce.

- It can happen in the case of very small drops and also when water soluble polymers are present. For finite coalescence time, the value of \( P_\Gamma \) must be greater than unity. The value of \( P_\Gamma \) increases with decreasing the repulsive force exerted by the surfactant molecules.
For ionic surfactants, addition of salt increases surface excess, and causes decrease in the values of \( f_r \) and \( \gamma \). The relative magnitudes of these quantities determine the value of \( P_\Gamma \). Consequently, the coalescence time changes accordingly. The variation of \( P_\Gamma \) with surfactant concentration, salt concentration and the size of drops has been extensively reported in the literature (Ghosh, 2012).

### 6.3.2 Coalescence equipment

- In many chemical processes, efficient removal of a dispersed aqueous phase from a continuous organic phase (or vice versa) is necessary, e.g., petroleum dewatering. This process is opposite to emulsification, and known as demulsification or emulsion-breaking. It has a great industrial importance.
- At present, there are several available methods, such as chemical demulsification, gravity or centrifugal settling, pH adjustment, filtration, heat treatment, membrane separation and electrostatic demulsification. Each of these methods has its own advantages and disadvantages.
- For example, the use of chemical demulsifiers modifies the interfacial properties of the system, which causes the water droplets to coalesce more easily. However, it is not easy to remove the demulsifier from the aqueous and oil phases. The pH-effect can be utilized to break the oil-in-water emulsions, but it is usually not effective in breaking water-in-oil emulsions.
- Centrifugation is an effective method for some emulsions. However, it has a high operating cost. Heat treatment can reduce the viscosity of the oil, which favors coalescence of water drops present in the oil phase. However, heat treatment and chemical treatment are rather expensive.
- In industrial equipment, coalescence is time dependent. In the dispersions of two immiscible liquids, immediate coalescence seldom occurs when two drops collide. If the drop pair is exposed to turbulent pressure fluctuations, and the kinetic energy of the oscillations induced in the coalescing drop pair is larger than
the energy of adhesion between them, the drops come out of contact before coalescence can take place.

- Experiments with gravity settlers indicate that the time for a drop to grow due to coalescence can be estimated by the following equation.

\[
t = \frac{\pi}{6} \left( \frac{a' - (a_0)^i}{\psi_s K_s} \right)
\]

(6.3.7)

where \( a_0 \) is the initial drop radius, \( a \) is the final drop radius, \( \psi_s \) is the volume fraction of the dispersed phase, \( K_s \) is an empirical parameter, and \( t \) is the time required to grow a droplet of radius \( a \).

- The value of the index, \( i \), is greater than 3. It depends on the probability that the drops will bounce apart before coalescence occurs. When the energy of oscillations is very low so that the drops hardly bounce, the value of \( i \) approaches 3. The time required for growing drops of size much larger than the initial drops (i.e., \( a >> a_0 \)) is given by,

\[
t \approx \frac{a'}{2\psi_s K_s}
\]

(6.3.8)

Therefore, Eq. (6.3.8) predicts that a doubling of residence time increases the radius of drop grown in a gravity settler by \( \sim 19\% \) (for \( i = 4 \)). If \( i > 4 \), the rate of growth in drop size will be slower. For this reason, after an initial short coalescence period, enforcing additional retention time is not very effective. Coalescence occurs more rapidly in concentrated dispersions. The requirement of residence time increases with decreasing concentration of the dispersed phase. In the gunbarrels and treaters in petroleum refineries, oil is washed with water by entering the treating vessel below the oil–water interface. Flocculation and coalescence occurs most effectively at the interface zone between oil and water.

- For finely dispersed water droplets in crude oil, external electric fields have been applied extensively to break the water-in-oil emulsions. Historically, the electrostatic coalescer was invented for the petroleum-related industries in California (USA) in 1911.
The electrostatic coalescence technology is suitable because the oil phase has a significantly lower dielectric constant than that of the dispersed aqueous phase (see Table 3.2.3). Various designs of electrostatic coalescers have been proposed. Most of them use alternating current (a. c.) electric fields. The direct current (d. c.) electric field has been less common in the past as compared to the a. c. In 1980s, the pulsed d. c. electric field was introduced, together with insulated electrodes.

The strength of the a. c. electric field varies according to the water-content of the emulsion and the equipment configuration. The field strength can vary between 60 and 180 kV/m. The magnitude of the applied frequency greatly depends on the type of electric field, as well as on the arrangement of the electrodes. For a. c. electric fields, frequency can vary between 60 and $10^3$ Hz.

However, a much lower frequency is usually used with pulsed d. c. electric fields, usually in the range of 1 to 25 Hz. Bailes and Larkai (1986) applied a d. c. field of 110 kV/m pulsed at a frequency less than 1 Hz. Therefore, there is no fixed value of applied frequency for all the oil systems. The details of various electrostatic coalescers have been presented by Eow and Ghadiri (2002). They have also discussed the advantages and disadvantages of various methods.

Fig. 6.3.2 Electrostatic coalescer: (a) outside view, and (b) internal arrangement.
• Generally, an electrostatic coalescing vessel is made up of a tank equipped with electrodes: at least one of them is earthed and at least one other electrode is suspended by an insulator, to which an electrical potential is applied. However, some specially designed electrical systems using a. c. power have all live grids as electrodes.

• The possible mechanisms of electrostatic coalescence have been identified, based on the attraction of opposite charges due to the polarization effects, and net charges if they are present (Waterman, 1965). In an electric field, the droplets orient in chains along the direction of the field. The droplets become small net dipoles in the oil (which has low dielectric constant) and attract one another. They coalesce at sufficiently high strengths of the electric field. The alignment of water droplets by the application of an electric is illustrated in Fig. 6.3.3.

![Fig. 6.3.3 Effect of electric field on water droplets dispersed in crude oil: (a) no electric field, and (b) at 1 kV/cm voltage gradient.](image)

• The conventional electrocoalescers are huge as large residence times are required for the electrocoalescence regions and settling zones to separate the enlarged water droplets from the crude oil. The maximum coalescence rate depends on the applied potential, the position of the feed inlet, and the separation distance between the insulated electrode and the level of the oil–water interface in the coalescer. The separation distance needs to be optimized to minimize the accumulation of the spongy emulsion.
6.3.3 Phase inversion

- Phase inversion of emulsions refers to an interesting phenomenon in which the dispersed and continuous phases are interchanged, i.e., an oil-in-water emulsion is changed to a water-in-oil emulsion.

- A typical situation where inversion of an O/W occurs is by increasing the volume fraction of the oil in it. At some volume fraction above 0.6–0.7, the emulsion suddenly inverts producing a W/O emulsion.

- A surfactant may stabilize O/W emulsions at low temperature. However, it would stabilize W/O emulsions at some higher temperature. The transition temperature, at which the surfactant changes from stabilizing O/W to W/O emulsions, is known as the phase inversion temperature (PIT).

- The PIT does not only depend on the nature of the surfactant, but also on the type of oil used. At the PIT, the hydrophilic and lipophilic natures of the surfactant are evenly balanced. Emulsifiers are chosen such that their PIT is far from the expected temperatures at which the emulsion will be used and stored.

The effect of increase of temperature on an emulsion system composed of water, hydrocarbon and a nonionic surfactant is illustrated in Fig. 6.3.4.

![Fig. 6.3.4 Schematic of the change of state of dispersion with increase in temperature (Shinoda, 1967) (adapted by permission from Elsevier Ltd., © 1967).](image_url)

- The unadsorbed nonionic surfactant dissolves either in the water or in the hydrocarbon phase, depending upon the temperature of the solution and the
structure of surfactant molecule. Excess surfactant separates as a third phase at higher concentrations over a narrow temperature range.

- The convex or concave curvature of the adsorbed monolayer against water (or oil) is closely related to the dissolution state of the surfactant and to the phase behavior in the three-component system. The hydration forces between the hydrophilic moiety of surfactant and water are stronger at the lower temperature, and the adsorbed monolayer may have convex curvature towards water. This results in an O/W type emulsion.

- A micellar solution containing hydrocarbon within the limit of solubilization is transparent and stable in contrast to an emulsion, but the structure of an oil-swollen micellar solution resembles that of an emulsion. Further addition of hydrocarbon beyond the solubilization limit results in an O/W type emulsion in which the excess oil is dispersed as droplets.

- If the temperature of the solution is raised, the hydration interaction between water and the hydrophilic moiety gradually decreases and the hydrophilic–lipophilic balance (HLB) changes towards more lipophilic character. The convex curvature of the adsorbed monolayer towards water may change gradually to a concave curvature.

- At some temperature at which the curvature of the adsorbed monolayer is nearly zero, the nonionic surfactant aggregates largely and a surfactant phase separates from the solution. This phenomenon is known as clouding and the temperature is known as cloud point (see Section 1.6.8).

- If the solubilizate is completely miscible with the surfactant phase, two phases exist above the cloud point. However, in the case where the solubilizate does not dissolve completely in the surfactant phase, three phases coexist at a higher solubilize concentration.

- The excess oil forms an O/W emulsion up to the PIT. The emulsion is an O/W type below the PIT and a W/O type above the PIT, as shown in Fig. 6.3.4. The existence of a PIT is an evidence that the hydrophobic and lipophilic balance of the nonionic surfactant changes appreciably with temperature.
The change of curvature of the adsorbed monolayer of nonionic surfactant with temperature is the key factor behind phase inversion. The phase inversion is reproducible within a few degrees.

**Haze point** is the temperature near which the nonaqueous surfactant solution becomes hazy rather than cloudy (the haziness and cloudiness of surfactant solutions are quite distinct visually). At haze point, the surfactant separates from the nonaqueous solution. Above the haze point, water-swollen micelles disperse in the oil. The excess water disperses as a W/O type emulsion. The haze point in nonaqueous solution is usually 5–30 degrees higher than the cloud point in aqueous solution.

The phase inversion temperature can be suitably used to prepare uniform and stable emulsions. In this method, an emulsifier with a PIT of about 50 K higher than the use and storage temperature is selected. The emulsion is then prepared at a temperature a few degrees below the PIT, where very small droplets are easily created. Then the emulsion is rapidly cooled to the desired temperature of use, where now the coalescence rate would be slow. Therefore, a stable emulsion results (Shinoda and Saito, 1969).

Very finely divided emulsions can be prepared by increasing the temperature of the system forcing an O/W emulsion to invert to a fine W/O emulsion, passing through a microemulsion phase. Upon cooling the system, re-inversion occurs with the formation of very small droplets of oil, generating a blue colored oil-in-water emulsion. Due to the fine size of the droplets, these emulsions are stable for a long time (Engels et al., 1995).

The mechanism of phase inversion is generally divided into two categories, viz. *translational* and *catastrophic* inversion. Translational inversion is induced by changing parameters which affect the distribution of the emulsifier over the phases, e.g., temperature, HLB of the emulsifier, salinity of the aqueous phase and the polarity of the organic phase. Catastrophic inversion is induced by increasing the fraction of the dispersed phase. It has the characteristics of a catastrophe, i.e., a sudden change in behavior of the emulsion system as a result of gradually changing conditions (Sjöblom, 2006).
6.3.4 Application of emulsions

- Emulsions are used in many industries. Some emulsion-based products are foods, personal care creams and lotions, insecticides and herbicides, polishes, drugs, paving asphalt, biological systems, paints, lacquers, varnishes, and electrical and thermal insulating materials.

- Emulsions are encountered at various stages of petroleum industry such as drilling fluids, injected or in situ emulsions used in enhanced oil recovery, wellhead production emulsions, pipeline transportation emulsions and refinery process emulsions. Many of these emulsions contain not just oil and water, but solid particles and gas as well.

- Emulsions are used for organic chemical synthesis, such as polymerization, oxidation and carbonylation.

- An important application of emulsions is in oil slick, which is formed when crude oil is spilled on the ocean. An oil-in-water emulsion can be formed with expenditure of considerable amount of energy which helps to disperse the oil into the water column and sent away from the sensitive shores. Otherwise, the oil may pick up water and form a water-in-oil emulsion, which is known as chocolate mousse (the name reflects the color and very viscous nature of these emulsions). The mousse emulsions can have a high water content. With weathering, they can become semi-solid and very difficult to handle. These emulsions are hard to break.
Exercise

Exercise 6.3.1: Compute the radius of the barrier ring for a 2.5 mm diameter water drop resting at the interface between an oil and water. Given: density of oil = 860 kg/m$^3$, interfacial tension = 40 mN/m.

Exercise 6.3.2: In a coalescence experiment involving 2 mm diameter air bubbles in an aqueous surfactant solution, the coalescence times obtained in 15 observations are given below.

<table>
<thead>
<tr>
<th>Obs. no.</th>
<th>$t_c$ (s)</th>
<th>Obs. no.</th>
<th>$t_c$ (s)</th>
<th>Obs. no.</th>
<th>$t_c$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.7</td>
<td>6</td>
<td>2.8</td>
<td>11</td>
<td>15.0</td>
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<td>2</td>
<td>8.1</td>
<td>7</td>
<td>12.3</td>
<td>12</td>
<td>0.4</td>
</tr>
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<td>3</td>
<td>17.1</td>
<td>8</td>
<td>4.1</td>
<td>13</td>
<td>7.8</td>
</tr>
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<td>10.5</td>
<td>9</td>
<td>0.6</td>
<td>14</td>
<td>13.5</td>
</tr>
<tr>
<td>5</td>
<td>15.7</td>
<td>10</td>
<td>13.1</td>
<td>15</td>
<td>9.1</td>
</tr>
</tbody>
</table>

Develop the cumulative distribution of coalescence time using these data. Fit the stochastic model to the distribution and obtain the optimum parameters of the model. Show your results graphically. Given: $D_T = 1 \times 10^{-10}$ m$^2$/s and $\gamma = 66$ mN/m.

Exercise 6.3.3: The following results are available for binary coalescence of water drops in xylene in presence of sodium dodecyl benzene sulfonate. The variations of bubble radius and interfacial tension with surfactant concentration are shown below.

<table>
<thead>
<tr>
<th>Surfactant concentration, $c_s$ (mol/m$^3$)</th>
<th>Radius (mm)</th>
<th>$\gamma$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>2.4</td>
<td>20.56</td>
</tr>
<tr>
<td>0.14</td>
<td>2.3</td>
<td>17.22</td>
</tr>
</tbody>
</table>

The increase of the surface excess concentration, $\Gamma$, with the surfactant concentration, $c_s$, is expressed by the equation, $\Gamma = 1.64 \times 10^{-6} \left(\frac{63.2c_s}{1+63.2c_s}\right)$. Calculate the relative
variation of $P_{\Gamma}$ with surfactant concentration from these data. Assume that the quantity, $w_b f_r \nu$, does not vary with surfactant concentration.

**Exercise 6.3.4:** Answer the following questions clearly.

(a) What is barrier ring? Why is it called so?
(b) What is characteristic diffusion time? How can it be calculated?
(c) What is dimensionless coalescence threshold? Explain why at least some drops will never coalesce if the value of this quantity is less than unity.
(d) On what parameters does the dimensionless coalescence threshold depend?
(e) What is the role of surface diffusion on coalescence?
(f) What is normalized standard deviation?
(g) Explain three major methods by which an emulsion is broken.
(h) What is electrostatic coalescence? For what type of emulsions is it used?
(i) Explain the role of the type of electric field and frequency in electrostatic coalescence.
(j) Read the article by Waterman (1965) and explain the mechanism of electrostatic coalescence.
(k) Explain why the conventional electrostatic coalescers are large in size.
(l) What do you understand by phase inversion? How does it occur?
(m) What is phase inversion temperature?
(n) Explain how highly stable emulsions containing very fine droplets can be prepared by the phase inversion method.
(o) Explain the effect of temperature on an emulsion stabilized by a nonionic surfactant.
(p) What is Pickering emulsion?
Suggested reading

Textbooks


Reference books


Journal articles


