

Emulsions, Microemulsions and Foams (Part IV)

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6.4.1 Microemulsions

- ◆ Microemulsions are thermodynamically stable mixtures of oil and water. The stability is due to the presence of fairly large amounts of surfactants. They are often transparent or translucent. Some microemulsions exhibit strong light scattering and the transmitted light is typically reddish while the reflected light is whitish.
- ◆ Oil and water are not molecularly dispersed in a microemulsion, but are coarsely mixed, i.e., oil and water are present in domains spanning over several nanometers. As a consequence, microemulsions contain huge oil-water interfacial areas. The interfacial tension is quite low in microemulsion systems (well below 1 mN/m).
- ◆ Microemulsions were introduced in 1940s by Schulman and co-workers (see Hoar and Schulman, 1943). They observed that isotropic and optically transparent dispersions of oil-in-water or water-in-oil formed spontaneously in the presence of a surfactant and a cosurfactant such as an aliphatic alcohol.
- ◆ In many liquid–liquid systems, the interfacial tension did not reach ultra-low values even though the critical micelle concentration (CMC) was reached. However, addition of the cosurfactant solved this problem. These systems were investigated over a period of two decades by several experimental techniques such as X-ray diffraction, ultracentrifugation, light scattering, electron microscopy, viscometry and nuclear magnetic resonance to characterize the size, shape and dynamics of the dispersed phase (see Kumar and Mittal, 1999).
- ◆ The terms *hydrophilic oleomicelles* and *oleophilic hydromicelles* were originally used by Hoar and Schulman (1943) for the droplets depending on whether the continuous medium was non-aqueous or aqueous, respectively. The term ‘microemulsion’ was coined 16 years later (Schulman *et al.*, 1959). Apart from the classical ternary (i.e., water-oil-surfactant) and quaternary (i.e., water-oil-surfactant-alcohol) microemulsions, many quinary systems (water-oil-surfactant-alcohol-salt) are also well known.
- ◆ Microemulsions can have various textures apart from simply oil droplets in water and water droplets in oil, such as random bicontinuous mixtures, ordered droplets

or lamellar mixtures with a wide range of phase equilibria among them and with excess oil and water phases. The bicontinuous structure in microemulsions was proposed by L. E. Scriven (1976), as shown in Fig. 6.4.1.

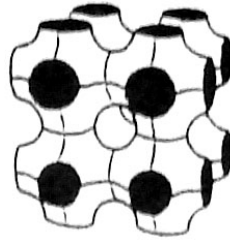


Fig. 6.4.1 Bicontinuous structure.

- ◆ In this structure, the domains are connected in three dimensions. It is an important structure in the microemulsion systems. In addition to the bicontinuous phases, lamellar phases have also been observed.

6.4.2 Winsor's classification of microemulsions

- ◆ P. A. Winsor made detailed studies of the phase behavior of microemulsions. Winsor observed that when water (or an aqueous salt solution) and an organic liquid (either a mixture or a single substance) are mixed with a suitable quantity of a surfactant (which was termed *amphiphile* by Winsor, coined from *amphi* which means 'both sides', and *philos* which means 'liking'), four main types of equilibrium systems may result (Winsor, 1948). These systems are known as Winsor I–IV systems. They are shown in Fig. 6.4.2.

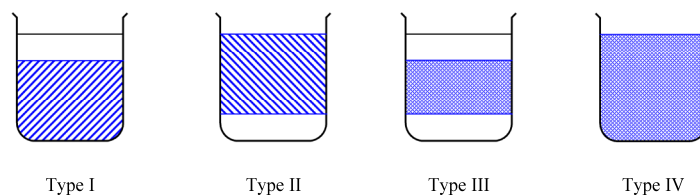


Fig. 6.4.2 Winsor systems of types I–IV.

- ◆ Winsor observed that in majority of cases, the equilibria were rapidly established and there was little tendency to produce metastable conditions. In the Type I system, an organic liquid containing only small proportions of the other

components of the system exists in equilibrium with an aqueous solution of the surfactant containing solubilized organic liquid. In other words, an oil-in-water microemulsion coexists with the excess oil.

- ◆ In the Type II system, water (or an aqueous salt solution) containing only small proportions of the other components of the system exists in equilibrium with a solution of the surfactant in the organic liquid containing solubilized water. Therefore, in this type, a water-in-oil microemulsion coexists with excess water.
- ◆ In the Type III system, free organic and aqueous phases are in equilibrium with a third solubilized phase containing the three components. Therefore, the microemulsion coexists with both the phases. The microemulsion phase in this equilibrium is also known as *middle phase* or *midrange microemulsion*.
- ◆ The Type IV system contains no free organic or aqueous layers and the three components are mutually solubilized.
- ◆ Solubilization of the organic liquid in Type I systems can be increased by: (i) a reduction in the relative proportion of water, (ii) the addition of an oil-soluble component to the organic liquid that is capable of hydrogen bonding and/or that has greater solvent attraction for the surfactant than the organic liquid has (e.g., fatty acids, amines and alcohols), (iii) increasing the lipophilic nature of the surfactant, and (iv) addition of an inorganic salt to the aqueous solution. If sufficient amount of surfactant is present, and if any of the above methods is applied progressively, first a Type IV system is produced, and ultimately in case of the techniques (ii), (iii) and (iv), a Type II system is produced.
- ◆ On the other hand, solubilization of water in the Type II systems can be increased by the methods which, in some respects, are complementary to the four methods described above for the increase of solubilization of organic liquid in Type I systems. These techniques are: (i) a reduction in the relative proportion of the organic liquid, (ii) addition of a water-soluble organic compound which is capable of hydrogen bonding to water (e.g., ethylene glycol and ethanol), (iii) a reduction in the lipophilic nature of the surfactant, and (iv) addition of a less hydrophilic oil-soluble compound to the oil. If sufficient amount of surfactant is present, and if any of the above methods is applied progressively, first a Type IV

system is produced, and ultimately in case of techniques (ii), (iii) and (iv), a Type I system is produced.

- ◆ If the surfactant is an alkali metal salt, a rise of temperature usually diminishes solubilization of the organic liquid in Type I systems and increases the solubilization of water in Type II systems. Winsor (1948) observed that there are exceptions to this behavior, particularly for the Type I systems.
- ◆ In Type IV systems, although no free oil and water phases exist, phase changes can occur in certain cases by the addition of an alcohol and an amine in gradually increasing quantities. According to the observations of Winsor, some of these stages are: a clear sol (which he designated as S_1), a heterogeneous mixture of sol S_1 and gel G , a homogeneous gel G , a heterogeneous mixture of G and a second sol S_2 , and a clear sol S_2 .
- ◆ A schematic representation of the passage from Type I to Type II system via the S_1 , G and S_2 stages of a Type IV system is illustrated in Fig. 6.4.3.

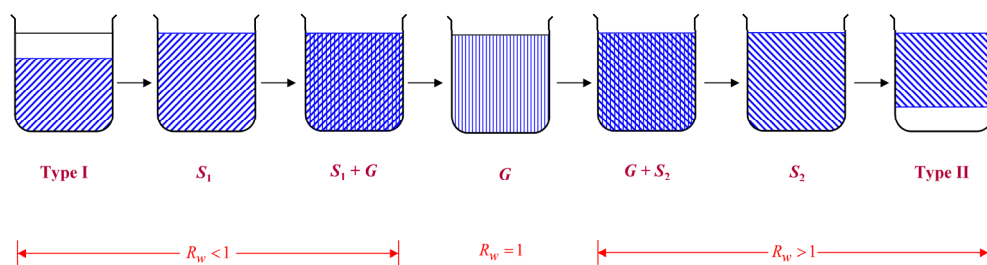


Fig. 6.4.3 Transition from Type I system to the Type II system via the various stages of a Type IV system.

- ◆ In some transitions, the gel state does not appear, and in some cases the sol and gel regions may not be distinguishable.
- ◆ To account for the interactions between oil, water and the surfactant, a ratio, R_w , (termed *Winsor ratio*) is defined as,

$$R_w = \frac{\text{solvent attraction between surfactant and oil in the solubilized phase}}{\text{solvent attraction between surfactant and water in the solubilized phase}} \quad (6.4.1)$$

- ◆ The Winsor ratio can be expressed in terms of the molecular interaction energies per unit area according to the regular solution theory. If we represent the oil,

water and surfactant by O , W and C , respectively, then the interaction between the surfactant and the aqueous phase is given by,

$$\varepsilon_{CW} = \varepsilon_{HCW} + \varepsilon_{LCW} \quad (6.4.2)$$

where ε_{HCW} is the interaction between the hydrophilic group of the surfactant and water, and ε_{LCW} is the interaction between the lipophilic group and water. It is likely that $\varepsilon_{LCW} \ll \varepsilon_{HCW}$.

- ◆ In a similar manner, the interaction between the surfactant and the oil phase is given by,

$$\varepsilon_{CO} = \varepsilon_{HCO} + \varepsilon_{LCO} \quad (6.4.3)$$

where ε_{HCO} is the interaction between the hydrophilic group of the surfactant and oil, and ε_{LCO} is the interaction between the lipophilic group and water. It is likely that $\varepsilon_{HCO} \ll \varepsilon_{LCO}$.

- ◆ The Winsor ratio was originally defined as,

$$R_w = \frac{\varepsilon_{CO}}{\varepsilon_{CW}} \quad (6.4.4)$$

- ◆ This expression has been modified to incorporate the effects of the interactions between the hydrophilic groups of the surfactant molecules (ε_{HH}), lipophilic groups of the surfactant molecules (ε_{LL}), oil molecules (ε_{OO}) and water molecules (ε_{WW}).

- ◆ The modified definition for R_w is,

$$R_w = \frac{\varepsilon_{CO} - \varepsilon_{OO} - \varepsilon_{LL}}{\varepsilon_{CW} - \varepsilon_{WW} - \varepsilon_{HH}} \quad (6.4.5)$$

- ◆ The interface will be convex towards water if $R_w < 1$ and the converse will happen if $R_w > 1$. Therefore, $R_w < 1$ on the extreme left of the diagram and $R_w > 1$ on the extreme right.

- ◆ All the methods, (i)–(iv), discussed earlier for passing from left to right in Fig. 6.4.3 are likely to increase the R_w . Conversely, the methods (i)–(iv) for passing from right to left in Fig. 6.4.3 are expected to decrease R_w .
- ◆ In view of the symmetric character of the figure, $R_w = 1$ corresponds to the center of the diagram, i.e., to the middle of the Type IV region. This region contains liquid crystalline phases. $R_w = 1$ indicates a zero-curvature interface, which is possible with a lamellar liquid crystal structure, a Schwarz-type zero-curvature interface, or a transient and fluctuating combination of the S_1 and S_2 structures.
- ◆ It is now well known that the middle-phase microemulsions exhibit bicontinuous structures, which are not too far from the transient mixture of S_1 and S_2 swollen micelles proposed by Winsor (1948).
- ◆ The Winsor I, II and III phase equilibria are also designated by $\underline{2}$, 3 and $\bar{2}$, where the bar below or above the 2 indicates that the microemulsion is the lower (water-rich) phase and the upper (oil-rich) phase, respectively.
- ◆ The microemulsion composition corresponding to Winsor III is characterized by very low interfacial tension and maximum solubilization of oil and water for a given quantity of surfactant. The system is said to be *optimized* or *balanced*. Thus, there have been intensive investigations on the three-phase region. The transition from Type I and Type II systems to the Type III system can be achieved by varying several parameters such as temperature, salinity, pH, oil/water ratio and molecular geometry (see Kumar and Mittal, 1999).
- ◆ Let us consider the phase behavior in microemulsions in the simplest ternary case involving ionic surfactants. The notations used by Winsor have been followed by many scientists who rediscovered and extended Winsor's work in the 1970s and 1980s. The Type I, Type II and Type III phase behavior are shown in Fig. 6.4.4.
- ◆ In the Type I phase behavior, a S_1 type of aqueous micellar system (and its extension to an oil-in-water microemulsion) is in equilibrium with oil.

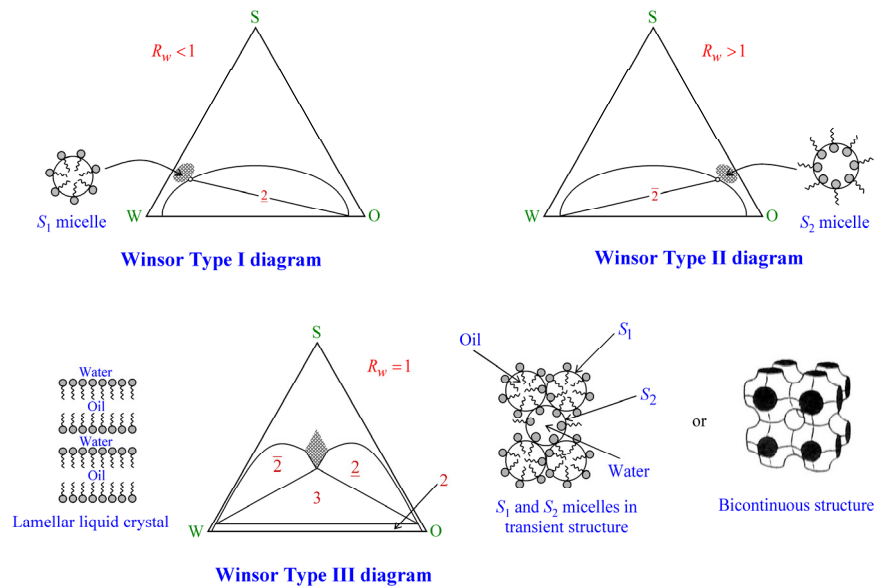


Fig. 6.4.4 Schematic phase diagrams for Winsor systems.

- ◆ A Winsor Type II phase behavior corresponds to the opposite situation in which an inverse micellar organic solution, S_2 (which eventually solubilizes water), is in equilibrium with the aqueous phase. The slope of the tie line in the polyphasic region indicates the partitioning of the surfactant, which is related to physicochemical formulation.
- ◆ Between Types I and II, one could expect a situation in which the tie lines would be horizontal indicating that the surfactant partitions equally in both phases. Such a case may occur with alcohols, but not generally for ionic surfactants, for which the Type III phase behavior is exhibited. In this case, the polyphasic region contains a three phase zone surrounded by three two phase zones.
- ◆ Systems whose compositions lie in the three-phase zone separate into a surfactant-rich phase that is in the middle of the diagram at the boundary of the microemulsion single-phase zone (shaded region), and two excess phases, which are essentially pure aqueous phase and pure oil. This microemulsion phase is called *middle phase* because it appears between the oil and water phases when prepared in a test tube due to its intermediate density. It is in equilibrium with

both excess phases. These three phase systems have been extensively studied due to their importance in enhanced oil recovery.

- ◆ In mixtures of oil, water and surfactant, it is common to have lyotropic liquid crystalline phases (Winsor, 1968). Therefore, isotropic microemulsion phases co-exist with the liquid crystalline phases in the phase diagram for many ternary systems. The phase diagram for the sodium caprylate–decanol–water system is shown in Fig. 6.4.5.

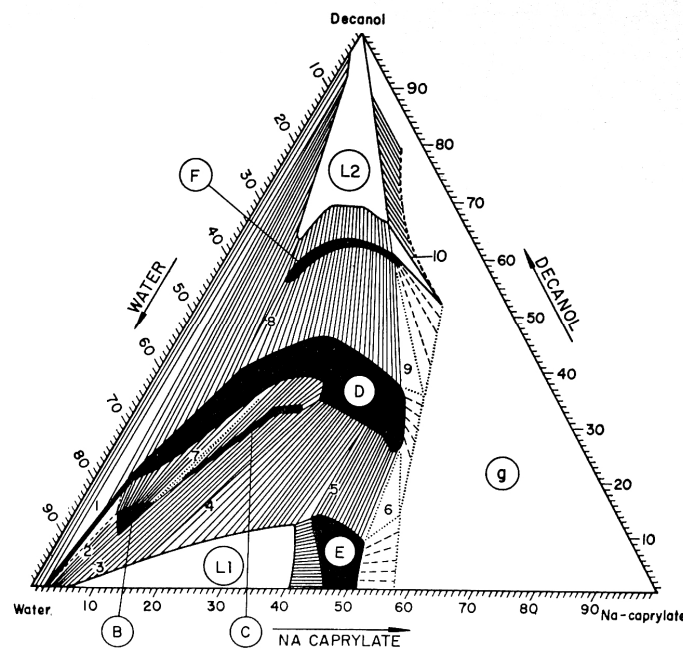


Fig. 6.4.5 Phase diagram for the three-component system: sodium caprylate–decanol–water at 293 K. L1: homogeneous isotropic solutions in water; L2: homogeneous isotropic solutions in decanol; B, C, D, E and F: homogeneous mesomorphic phases; g: solid crystalline sodium caprylate with fiber structure; 1–10: three-phase triangles (Winsor, 1968) (reproduced by permission from The American Chemical Society, © 1968).

- ◆ The X-ray diffraction measurements of the individual phases have revealed that: (i) the phase *E* is the middle phase having hexagonal structure, (ii) the phase *F* is the inverse middle phase having the inverse fibrous hexagonal structure, (iii) the phase *D* is the lamellar phase, and (iv) mobile isotropic micellar phases exist in regions L1 (S_1) and L2 (S_2).

- ◆ It is possible that the region B represents an extension of region D , rather than a new phase. The phase indicated by C represents a viscous dispersion of the orderly phase, D , in the isotropic phase, S_1 . This is in accord with the opacity of C , which contrasts the translucency and lack of any preferred orientation of the liquid crystalline phases. The lack of orientation in the dispersion is a consequence of the averaging effect of Brownian movements over the period of exposure.

6.4.3 Stability of microemulsions

- ◆ Although the name ‘microemulsion’ suggests an emulsion with extremely small droplets, microemulsions possess thermodynamic stability in contrast to the regular emulsions, which are only kinetically stable.
- ◆ The analysis of thermodynamic stability of the microemulsions needs to account for the entropy of dispersion of the droplets in the continuous medium, the free energy of formation of the interface between the two phases, the interaction among the droplets, and the distribution at equilibrium of the species between the two phases and the interface.
- ◆ Let us assume that a large interface has been spontaneously created between the two immiscible phases. The surfactant and cosurfactant are accumulated at the interface. This accumulation has two important effects: (i) it decreases the interfacial tension of the water–oil interface from about 50 mN/m to well-below 1 mN/m, and (ii) because of the large decrease in the concentrations of surfactant and cosurfactant in the two bulk phases, the molecules of surfactant and cosurfactant have a small chemical potential, which decreases the free energy of the system. The latter phenomenon is known as *dilution effect* (Ruckenstein, 1978).
- ◆ In addition to these effects, an ionic surfactant generates a charge on the interface and therefore inter-droplet repulsive double layer forces develop. If the free energy change due to the dilution effect is sufficiently negative to overcome the

positive free energy change due to the surface tension, the overall free energy change is negative and spontaneous dispersion occurs.

- ◆ The formation of droplets occurs at constant temperature and constant volume. Therefore, the main quantity regarding the thermodynamic stability is the Helmholtz free energy of formation (ΔF) per unit volume of microemulsion.
- ◆ This is defined as the difference between the free energy of a microemulsion having droplets of a given radius and the free energy of the same system when the droplets are very large. For a microemulsion, which is stable from a thermodynamic point of view, the free energy of formation has to be negative. The size of the droplets is the radius for which the free energy of formation has a minimum value.
- ◆ Suppose that the surfactant is soluble only in water, which is the continuous phase, and the cosurfactant is soluble only in oil. x_i represents the mole fraction when the radius of the droplets is very large, where the subscripts $i = 1, 2, 3$ and 4 refer to the surfactant, co-surfactant, water and oil, respectively.
- ◆ The bulk chemical potential, μ_i , of one molecule (ion) can be expressed as,

$$\mu_i = \mu_i^0 + kT \ln \phi_i x_i \quad (6.4.6)$$

where μ_i^0 is the standard chemical potential, k is Boltzmann's constant, T is temperature and ϕ_i is the activity coefficient.

- ◆ The free energy of the generated droplet surface is equal to the product of the surface area per unit volume, $3\phi_v/R_d$ (where ϕ_v is the volume fraction of the droplets and R_d is the radius of the droplets, which is assumed to be uniform for the sake of simplicity), and the specific interfacial free energy.
- ◆ The specific interfacial free energy is equal to $(\gamma + \sum \tilde{\Gamma}_i \tilde{\mu}_i)$, where $\tilde{\Gamma}_i$ is the surface excess (the tilde indicates the state of the system after the formation of the droplets of radius, R_d , and adsorption of surfactant and co-surfactant at the surface of the droplets, i.e., the final state). The surface excess quantities for water and oil are assumed zero. Because of thermodynamic equilibrium, the

chemical potentials are the same for the molecules (ions), which are adsorbed, and for those in the bulk solution.

- ◆ If m_i is the total number of molecules (ions) of species i per unit volume of microemulsion, then the number of molecules remaining in bulk solutions after adsorption is, $[m_i - (3\phi_v/R_d)\tilde{\Gamma}_i]$. The corresponding Gibbs free energy is, $[m_i - (3\phi_v/R_d)\tilde{\Gamma}_i]\tilde{\mu}_i$.
- ◆ Now, the change in Helmholtz free energy due to the formation of the interface and dilution from the mole fractions, x_i , before adsorption to the final mole fractions, \tilde{x}_i , is given by,

$$\Delta F_d = \left(\frac{3\phi_v}{R_d}\right)\gamma + \sum_{i=1}^4 m_i (\tilde{\mu}_i - \mu_i) - p_1(1 - \phi_v) - p_2\phi_v + p_\infty \quad (6.4.7)$$

where p_1 is the pressure in the continuous phase, $p_2 (= p_1 + 2\gamma/R_d)$ is the pressure in the dispersed phase and p_∞ is the pressure when the droplets are very large.

- ◆ Since the pressures are different, the standard chemical potentials are not the same in the initial and final states. Neglecting the compressibility, we can write,

$$\tilde{\mu}_i^0 - \mu_i^0 = v_i (p_j - p_\infty) \quad (6.4.8)$$

where v_i is the volume of a molecule of species i . If the component is in the continuous phase then $j=1$, and $j=2$ if the component is in the dispersed phase.

- ◆ Since the surfactant is soluble only in water (which is the continuous phase) and the cosurfactant is soluble only in oil, it can be shown that Eq. (6.4.8) becomes,

$$\Delta F_d = \left(\frac{3\phi_v}{R_d}\right)\gamma + kT \sum_{i=1}^4 m_i \ln \left(\frac{\tilde{\phi}_i \tilde{x}_i}{\phi_i x_i}\right) - p_1(1 - \phi_v) - p_2\phi_v + (v_1 m_1 + v_3 m_3) p_1 + (v_2 m_2 + v_4 m_4) p_2 \quad (6.4.9)$$

- ◆ If $v_2 m_2 + v_4 m_4 \approx \phi_v$, and $v_1 m_1 + v_3 m_3 \approx 1 - \phi_v$, the last four terms of Eq. (6.4.9) cancel and we obtain

$$\Delta F_d = \left(\frac{3\phi_v}{R_d} \right) \gamma + kT \sum_{i=1}^4 m_i \ln \left(\frac{\tilde{\varphi}_i \tilde{x}_i}{\varphi_i x_i} \right) \quad (6.4.10)$$

- ◆ For nonionic surfactants in dilute systems, the ratio of activity coefficients approaches unity. For dilute ionic surfactant systems, however, the ratios $\tilde{\varphi}_i/\varphi_i$ are unity only if the ionic strengths after and before adsorption are sufficiently close.
- ◆ In Eq. (6.4.10), the terms on the right hand side corresponding to $i=1$ and $i=2$ have negative contributions to ΔF_d , and the terms corresponding to $i=3$ and $i=4$ provide positive contributions to ΔF_d . The former is larger in absolute value than the latter. Hence, the dilution effect has a negative contribution to ΔF_d .
- ◆ The equation for the interfacial tension incorporating the effect of electrostatic double layer is given below. Since the interface is charged, the interfacial tension, γ , depends on the surface potential and the surface charge density. These contributions are contained in $\tilde{\mu}_i$.
- ◆ From the Gibbs adsorption equation under isothermal conditions, we have,

$$d\gamma = -\sum \tilde{\Gamma}_i d\tilde{\mu}_i \quad (6.4.11)$$

- ◆ Integrating at constant chemical potentials for all the species with the exception of the surfactant and co-surfactant, we obtain,

$$\gamma = \gamma_0 - \sum \int \tilde{\Gamma}_i d\tilde{\mu}_i \quad (6.4.12)$$

where γ_0 is the surfactant-free interfacial tension for water and oil, and the second term on the right of Eq. (6.4.12) represents the effect of adsorption of the surfactant and co-surfactant on surface tension.

- ◆ Equation (6.4.12) can be expressed in terms of the surface potential (ψ) and surface charge density (σ) as,

$$\gamma = \tilde{\gamma} - \int \sigma d\psi \quad (6.4.13)$$

where the term, $\int \sigma d\psi$, is the free energy of the electrostatic double layer. It can be written as,

$$-\int \sigma d\psi = \gamma_1 + \gamma_2 \quad (6.4.14)$$

where the quantity, γ_1 , is the specific free energy of non-overlapping double layers and γ_2 is the specific free energy of overlapping double layers. The former is negative whereas the latter is positive.

- ◆ Therefore, from Eqs. (6.4.13) and (6.4.14), we can write,

$$\gamma = \tilde{\gamma} - \gamma_1 - \gamma_2 \quad (6.4.15)$$

- ◆ The total free energy of formation per unit volume of microemulsion, ΔF , is given by,

$$\Delta F = \Delta F_d + \Delta F_e \quad (6.4.16)$$

where ΔF_e is the free energy change due to the entropy generated by dispersion of the droplets in the continuous phase. Apparently, $\Delta F_e < 0$. From the minimum of ΔF with respect to R_d , the radius of the stable droplets (\hat{R}_d) can be obtained.

- ◆ The terms, γ and \tilde{x}_i , which appear in the expression for ΔF_d are dependent on the radius. Let us examine the qualitative behavior of various contributions to ΔF_d . The surface tension, $\tilde{\gamma}$, decreases when R_d increases because the bulk concentrations and hence the specific adsorptions become larger with increasing R_d . The free energy term, $(3\phi_v \tilde{\gamma} / R_d) \rightarrow 0$ as $R_d \rightarrow \infty$, and $(3\phi_v \tilde{\gamma} / R_d) \rightarrow \infty$ as $R_d \rightarrow 0$. For sufficiently large values of R_d , $\tilde{\gamma}$ may become negative. Of course, the corresponding radii do not represent equilibrium states but stages of the kinetic process. The free energy of the non-overlapping double layers, $(3\phi_v \gamma_1 / R_d)$, is a negative quantity. This term approaches zero for $R_d \rightarrow \infty$, and tends to $-\infty$ for $R_d \rightarrow 0$. The free energy change due to the double layer interactions has a positive contribution to ΔF_d . Its variation with R_d is similar to that described before.
- ◆ Let us now consider the effect of R_d on the mole fraction terms \tilde{x}_i . As $R_d \rightarrow 0$, *infinite dilution* occurs, and $R_d \rightarrow \infty$ corresponds to *no dilution*. This is apparent, because for low values of R_d , almost the entire amount of surfactant is adsorbed

and $\tilde{x}_1 \propto R_d$. The terms due to dilution approach $\ln(R_d)$ as $R_d \rightarrow 0$, and they approach zero as $R_d \rightarrow \infty$. The free energy change due to the generation of entropy, ΔF_e , tends to $-\infty$ for $R_d \rightarrow 0$, and to zero for $R_d \rightarrow \infty$.

- ◆ From this analysis, it is evident that some of the free energy contributions are positive and decay with increasing R_d , while others are negative and decrease in absolute value when R_d increases. A negative minimum of the free energy of formation of a microemulsion for a particular radius can be obtained if the total negative contribution is sufficiently large in absolute value. This is the radius of the thermodynamically stable microemulsion.
- ◆ Let us consider a system composed of water, oil and a nonionic surfactant. It is assumed, for the sake of simplicity, that the surfactant is soluble only in oil which is also the continuous phase, and that the system is dilute. It is known that microemulsions can sometimes form without a cosurfactant for this kind of systems.
- ◆ For this case,

$$\Delta F = \frac{3\phi_v}{R_d} \gamma + m_s kT \ln\left(\frac{\tilde{x}}{x}\right) + m_o kT \ln\left(\frac{1-\tilde{x}}{1-x}\right) + \Delta F_e \quad (6.4.17)$$

where m_s and m_o are the number of molecules of surfactant and oil, respectively, per unit volume of microemulsion, and \tilde{x} and x are the mole fractions of surfactant after and before adsorption.

- ◆ The equilibrium radius, \hat{R}_d , is obtained by putting the condition, $d\Delta F/dR_d = 0$. Performing this differentiation we obtain,

$$-\frac{3\phi_v \gamma}{\hat{R}_d^2} + \left[\frac{d\Delta F_e}{dR_d} \right]_{\hat{R}_d} = 0 \quad (6.4.18)$$

Because ΔF_e is a small quantity which becomes less negative as R_d increases, the derivative, $d\Delta F_e/dR_d$, is positive. Therefore, the interfacial tension, γ , has to be a small but positive quantity at thermodynamic equilibrium.

- ◆ Assuming further that $\tilde{\Gamma}_s = K_s \tilde{c}_s$ (where K_s is a constant and \tilde{c}_s is surfactant concentration per unit volume of oil), we have,

$$\gamma = \gamma_0 - kK_s T \tilde{c}_s \quad (6.4.19)$$

- ◆ A material balance for surfactant gives,

$$\left(3\phi_v / \hat{R}_d\right) \tilde{\Gamma}_s + \tilde{c}_s (1 - \phi_v) = m_s \quad (6.4.20)$$

- ◆ Substituting the value of $\tilde{\Gamma}_s$ in Eq. (6.4.20) and rearranging we get,

$$\tilde{c}_s = \frac{m_s}{\left(\frac{3\phi_v K_s}{\hat{R}_d}\right) + (1 - \phi_v)} \quad (6.4.21)$$

- ◆ Neglecting the derivative of ΔF_e in Eq. (6.4.18), substituting γ from Eq. (6.4.19) and \tilde{c}_s from Eq. (6.4.21) into Eq. (6.4.18) and simplifying, we obtain,

$$\hat{R}_d = \frac{3\phi_v K_s \gamma_0}{m_s k K_s T - \gamma_0 (1 - \phi_v)} \quad (6.4.22)$$

- ◆ For the case, $m_s k K_s T \gg \gamma_0 (1 - \phi_v)$, Eq. (6.4.22) reduces to,

$$\hat{R}_d = \frac{3\phi_v \gamma_0}{m_s k T} \quad (6.4.23)$$

- ◆ Equation (6.4.23) gives the equilibrium radius of the microemulsion droplets. It has a simple physical interpretation because it can be obtained by writing the proportionality between the translational energy of the surfactant molecules and the product of interfacial tension and the surface area per unit volume.
- ◆ For the high surface concentrations, the gas-like model implied in the equation, $\tilde{\Gamma}_s = K_s \tilde{c}_s$ is not adequate. However, it permits a simple illustration of the main features of the theory.
- ◆ It can be shown that because of the dilution effect, $\Delta F|_{\hat{R}_d} < 0$. Example 6.4.1 illustrates the calculation of \hat{R}_d .

Example 6.4.1: Calculate the equilibrium radius of the microemulsion droplets at 298 K if the interfacial tension between oil and water is 50 mN/m, volume fraction of the droplets is 0.03, and the surfactant concentration in the microemulsion is 100 mol/m³.

Solution: From the given data, we have,

$$\gamma_0 = 0.05 \text{ N/m}, \phi_v = 0.03, m_s = 100 \times 6.023 \times 10^{23} = 6.023 \times 10^{25} \text{ m}^{-3} \text{ and } T = 298 \text{ K}$$

Therefore, from Eq. (6.4.23) we get,

$$\hat{R}_d = \frac{3\phi_v\gamma_0}{m_s kT} = \frac{3 \times 0.03 \times 0.05}{6.023 \times 10^{25} \times 1.38 \times 10^{-23} \times 298} = 1.8 \times 10^{-8} \text{ m} = 18 \text{ nm}$$

- ◆ Another droplet-model of microemulsion is based upon the bending free energy of the interface. As discussed in Section 6.4.2, the surfactants and cosurfactants not only lower the interfacial tension, but their molecular structures affect the curvature of the interface as well. This determines whether a W/O type or an O/W type of microemulsion would be formed.
- ◆ Each composition of the interface has its own curvature at which the interface forms most easily and thus has the lowest interfacial tension. The curvature free energy is expressed by the equation given by Helfrich (1973).

$$E_c = \int_A \left[\frac{\kappa_b}{2} (H_1 + H_2 - H_0)^2 + \kappa_G H_1 H_2 \right] dA \quad (6.4.24)$$

where dA represents the intrinsic area element, κ_b represents the bending modulus, H_0 represents the spontaneous curvature and κ_G represents the Gaussian curvature modulus. H_1 and H_2 are the two principal curvatures. E_c is the free energy contribution due to the bending of a flat interface of area A .

- ◆ For a single droplet of radius R_d , E_c is given by,

$$E_c = 8\pi\kappa_b (1 - H_0 R_d)^2 + 4\pi\kappa_G \quad (6.4.25)$$

where the quantity, $4\pi\kappa_G$, may be viewed as the free energy needed (or furnished if $\kappa_G < 0$) to detach a suitable area of flat interface and close it around the droplet.

- ◆ In Winsor Type I and Type II systems, the tension of the droplet surface, τ , can be related to the interfacial tension, γ , by the relation (see Kumar and Mittal, 1999),

$$\tau(R_d) = \gamma + \int_0^{2/R_d} \frac{\partial^2 E_c}{\partial A \partial (2/R_d)} d\left(\frac{2}{R_d}\right) = \gamma - \frac{4\kappa_b H_0}{R_d} + \frac{2\kappa_b + \kappa_G}{R_d^2} \quad (6.4.26)$$

- ◆ From Eq. (6.4.26), it follows that the minimum of the tension τ of a droplet is found at,

$$\left(\frac{1}{R_d}\right)_{\min} = \frac{2\kappa_b H_0}{2\kappa_b + \kappa_G} \quad (6.4.27)$$

Therefore, Eq. (6.4.27) gives the radius of the droplet that minimizes the curvature free energy.

- ◆ The values of κ_b and κ_G are of the order of kT . The entropy of mixing tends to maximize the number of droplets, and this effect can lead to a smaller average value of R_d than that predicted by Eq. (6.4.27). The system may increase its configurational entropy by exploring a distribution of radius around that given by Eq. (6.4.27).
- ◆ The sign of H_0 determines whether O/W or W/O microemulsion would be formed. The sign and magnitude of H_0 are determined by two competing forces at the droplet interface: (i) the hydrocarbon chains tend to bend the interface around the water-side and has a positive contribution to H_0 , and (ii) the counterions of the ionic head-groups have a negative contribution to H_0 .
- ◆ The origin of these contributions can be explained as follows. The hydrocarbon chains are rather closely packed occupying $\sim 0.25 \text{ nm}^2$ per chain. They repel one another sideways, and as a result tend to bend the interface around the water side. The counterions of the ionic head-groups, on the other hand, repel one another sideways and thus tend to curve the interface around the oil side. The bulky polar groups of nonionic surfactants have a similar effect.

- ◆ At low salt contribution, the contribution of the electrostatic double layer to H_0 is the dominant factor and an oil-in-water microemulsion (i.e., Winsor Type I) is formed. If the salt concentration is increased, H_0 becomes less and less negative and the average droplet radius increases. At a certain salt concentration, the contributions of the electrostatic double layer and the hydrocarbon chains to H_0 balance each other, and a structure with zero mean curvature is expected at this point.
- ◆ Several structures such as flat monolayers and cubic phases can exist here. Since fluctuations around the mean curvature are expected to be present, it is not easy to predict the stable structure. If the salt concentration is increased even further, H_0 becomes positive and a water-in-oil microemulsion (i.e., Winsor Type II system) becomes stable.
- ◆ The average size of the droplets decreases with increasing salt concentration. A similar phase inversion can be observed in systems where a co-surfactant is present. In such a situation, the increase in the concentration of the co-surfactant leads to an increase in adsorption of the co-surfactant molecules at the interface. This results in an increase in surface pressure, which has a positive contribution to H_0 .

Exercise

Exercise 6.4.1: Show that when the radius of the droplet in microemulsion approaches zero (i.e., infinite dilution limit), $\tilde{x}_1 \propto R_d$, where \tilde{x}_1 is the mole fraction of surfactant after the formation of the droplets of radius, R_d , and adsorption of surfactant and cosurfactant at the surface of the droplets.

Exercise 6.4.2: The interaction energy between surfactant and oil, surfactant and water, oil molecules, water molecules, hydrophilic groups of surfactant molecules, and lipophilic groups of surfactant molecules are 142, 42, 15, 27, 5 and 13 J/mol, respectively. Comment on the shape of the oil–water interface.

Exercise 6.4.3: In a microemulsion system, the interfacial bending modulus is 5.35×10^{-21} J, the Gaussian curvature modulus is 4.1×10^{-21} J, and the bending force is 8.23×10^{-13} N. Calculate the radius of microemulsion droplet that minimizes the curvature free energy. Hint: bending force is $\kappa_b H_0$.

Exercise 6.4.4: Answer the following questions clearly.

- 1) What is the main difference between an emulsion and a microemulsion?
- 2) Explain the properties of Winsor Type I – IV microemulsion systems.
- 3) Explain how the solubilization of organic liquid in a Type I microemulsion and solubilization of water in a Type II microemulsion can be increased.
- 4) Define Winsor ratio and explain its significance.
- 5) Draw typical ternary phase diagrams for Winsor Type I, II and III systems and explain the main features of these diagrams.
- 6) Explain briefly the factors which impart thermodynamic stability to microemulsions. What is equilibrium droplet radius? How would you calculate it?
- 7) What is dilution effect? Explain its significance in microemulsion stability.
- 8) Explain the significance of interfacial bending free energy in stabilizing a microemulsion.

Suggested reading

Textbooks

- ◆ A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, John Wiley, New York, 1997, Chapter 14.
- ◆ J. C. Berg, *An Introduction to Interfaces and Colloids: The Bridge to Nanoscience*, World Scientific, Singapore, 2010, Chapter 9.
- ◆ P. Ghosh, *Colloid and Interface Science*, PHI Learning, New Delhi, 2009, Chapter 9.

Reference books

- ◆ P. Kumar and K. L. Mittal (Editors), *Handbook of Microemulsion Science and Technology*, Marcel Dekker, New York, 1999, Chapters 1–3 & 8.

Journal articles

- ◆ E. Ruckenstein, *Chem. Phys. Lett.*, **57**, 517 (1978).
- ◆ J. H. Schulman, W. Stoeckenius, and L. M. Prince, *J. Phys. Chem.*, **63**, 1677 (1959).
- ◆ L. E. Scriven, *Nature*, **263**, 123 (1976).
- ◆ P. A. Winsor, *Chem. Rev.*, **68**, 1 (1968).
- ◆ P. A. Winsor, *Trans. Faraday Soc.*, **44**, 376 (1948).
- ◆ T. P. Hoar and J. H. Schulman, *Nature*, **152**, 102 (1943).
- ◆ W. Helfrich, *Z. Naturforsch.*, **28c**, 693 (1973).