CHAPTER II
BACKGROUND

2.1 Surfactant Structure

Surfactants, surface-active agents, have an amphipathic structure consisting of a structural group that has very little attraction for the solvent, known as a lyophobic group, attached to a group that has strong attraction for a solvent, called the lyophilic group (Rosen, 1989). In a highly polar solvent such as water, the hydrophobic group is usually a long-chain hydrocarbon whereas the hydrophilic group is an ionic or highly polar group (Kimchuwanit, 1995). Depending on the nature of the hydrophilic group, surfactants can be classified as anionic, cationic, zwitterionic, and nonionic surfactants.

2.2 Adsorption

When a surfactant is dissolved in the water, the hydrophobic portions of surfactant in the interior of the water cause distortion of the structure of the water molecules around them, increasing the free energy of the system (Rosen, 1989). It means that less work is required to move a surfactant molecule from the bulk solution to the surface to minimize the free energy of the system. At the interface, the hydrophilic portions are in the aqueous phase whereas the hydrophobic portions are oriented away from the solution.

Surfactant molecules at the interface generally cause the reduction of the interfacial tension of the solution, resulting in beneficial processes such as foaming, detergency, and emulsification. In foaming, surfactant promotes the film elasticity and foam persistence, the resulting increase in the stability of foam. Surfactant performs as an emulsifying agent to stabilize the emulsion system. In detergency, the adsorption of surfactant at the bulk solution/soil and bulk solution/substrate interfaces reduce the work necessary to remove the soil from the substrate. Surfactants are also used in enhanced oil recovery processes to increase the efficiency of the recovery by reducing the capillary forces holding oil in the small pores in the ground in order to make it easier to sweep the oil out of the pores.

2.3 Micellization

As previously mentioned, when surfactants are dissolved in water, hydrophobic portions distort the structure of the water and thus increase the free energy of the system. One way to decrease the free energy is adsorption. However, micellization is another way to decrease the distortion of the water structure by the aggregation of the surfactant molecules, or monomers, into cluster, called micelles, with their hydrophobic portions directed toward the interior of the cluster while their hydrophilic portions directed toward the aqueous solution, thereby reducing the free energy of the system (Rosen, 1989). Although micellization results in a decrease in the free energy of the system, the loss of several translational degrees of freedom of monomers in being confined to the micelles, and also the electrostatic repulsion in case of ionic surfactants, between the hydrophilic head groups cause free energy

increases, thus opposing micellization. Therefore micellization depends upon the balance between the factors promoting and opposing it.

The critical micelle concentration, CMC, is the concentration at which micellization occurs. The micellar shape, which may vary from spherical through rod- or disklike to lamellar, produced in aqueous solution is significant in determining the properties of a surfactant solution, such as its capacity to solubilize water-insoluble material. The factors affecting the CMC, aggregation number, and micellar shape in aqueous solution are temperature, concentration of surfactant and additives such as organic compounds.
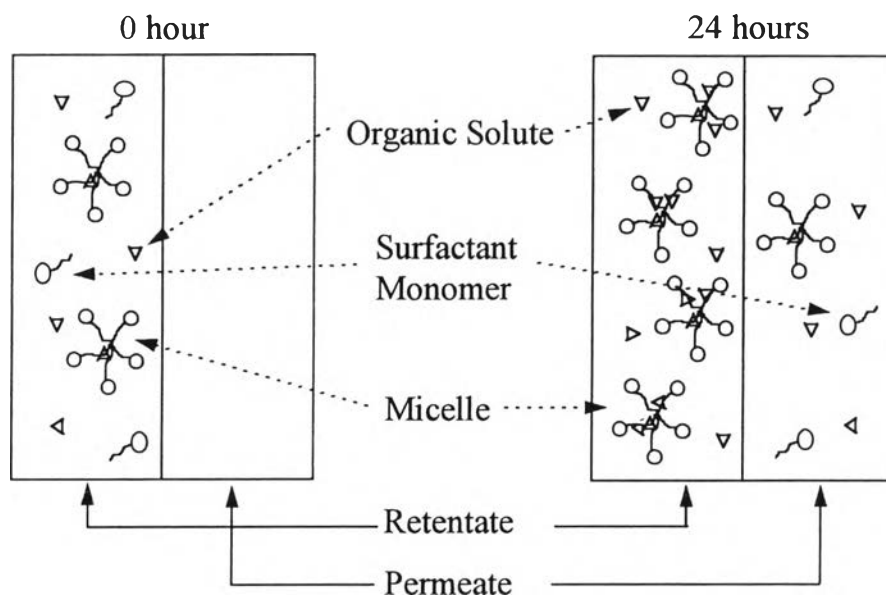
2.4 Solubilization

In aqueous solution, solubilization, that is the ability to dissolve the organic solutes in micelle cores, is an important property of surfactants (Rosen, 1989; Christian and Scamehorn, 1995). An organic compound can be solubilized in five locations of varying polarity within the micelle. The five locations are as follows :

1. the inner hydrocarbon core

2. deep in the palisade layer

3. the palisade layer

4. at the micelle-solvent interface

5. between the nonionic surfactant head groups such as polyoxy-ethylene or polyoxypropylene chains outside the micelle

Organic solutes solubilize into those regions of the micelle which have polar characteristics similar to those of the organic compound. Nonpolarizable organic solutes such as saturated aliphatic hydrocarbons are

solubilized in the interior region of the micelle. Slightly polar organic compounds such as long chain alcohol solubilize with the nonpolar hydrocarbon chain oriented toward the interior of the micelle and the polar hydroxyl group present in the palisade layer near the surfactant head groups (Rosen, 1989). The solubility of organics in surfactant solution is very slight until a critical concentration is reached at which the solubility increases approximately linear with the concentration of the surfactant. Structure of the surfactant and solubilizate, electrolyte, organic additives, mixed micelles, and temperature are factors affecting the solubilization.

Semi-equilibrium dialysis (SED) experiments (Figure 2.1) are performed for measuring the solubilization of organics into micelles. Ordinary equilibrium dialysis cells are used with membranes permeable to small molecules (such as the organic solute and surfactant monomers), but impermeable to the surfactant micelles. The slow migration of surfactant through the membrane (over a period of 16-24 h) occurs simultaneously with the migration of the unsolubilized organic solute, which ordinarily diffuses rapidly enough to reach equilibrium with the solutions on both sides of the membrane.

Figure 2.1 Schematic of semi-equilibrium dialysis.

The ability of micelles to solubilize solutes in the retentate is described by a solubilization equilibrium constant (K) defined by:

$$K = X_m / C_u = [O]_{mic} / (C_u ([Surfactant]_{mic} + [O]_{mic})) \qquad (1)$$

where X_m is the mole fraction of solute in micelles. C_u is the concentration of unsolubilized or monomeric organic solute. $[O]_{mic}$ is the concentration of organic solute associated with surfactant micelles and $[Surfactant]_{mic}$ denotes concentration of surfactant in micellar forms. A small correction needs to be made to account for formation of a few micelles (with solubilization therein) in the permeate (Christian et al., 1985; Smith, Christian, Tucker and Scamehorn, 1986; Bhat, Smith, Tucker and Christian, 1987; Smith et al., 1987; Higazy et al., 1988; Uchiyama, Christian, Tucker and Scamehorn, 1993). It is assumed that C_u is the same in permeate and retentate (activity coefficient of unsolubilized solute is the same). The total concentration of

organic solute [O] and surfactant [Surfactant] in the two compartments can be related to C_u and to the concentration of surfactant monomer, CMC by material balances:

$$[O]_{ret} = C_u + [O]_{mic,ret} \qquad (2)$$

$$[O]_{per} = C_u + [O]_{mic,per} \qquad (3)$$

$$[Surfactant]_{ret} = CMC + [Surfactant]_{mic,ret} \qquad (4)$$

$$[Surfactant]_{per} = CMC + [Surfactant]_{mic,per} \qquad (5)$$

where the subscripts "ret" and "per" refer to the retentate and permeate, respectively. When the only subscript is per or ret, the total concentration of the surfactant or solute in the appropriate compartment is referred to.

While the monomeric surfactant concentration (equals critical micelle concentration or CMC) is mildly dependent on the presence of solubilizate (Rosen, 1989), at the low solute concentrations used here, the CMC is assumed to be that of the pure surfactant.

Combining these equations permits calculation of solubilization constants for SED experiments, K_m , from directly measurable parameters.

$$K_m = ([O]_{ret} - [O]_{per}) / ([O]_{per} [Surfactant]_{mic,ret} - [O]_{ret} [Surfactant]_{mic,per}) \quad (6)$$

2.5 Extraction into Coacervate

Aqueous solutions of most nonionic surfactant micelles become turbid after heating to a temperature known as the cloud point. Above this temperature, the solution separates into two phases: one, generally small in volume, composed of a concentrated surfactant solution (referred to as the

surfactant-rich or coacervate phase) and the other, the bulk aqueous solution (aqueous or dilute phase) in which the surfactant concentration is generally on the order of 3 to 10 times the CMC as shown in Figure 2.2.
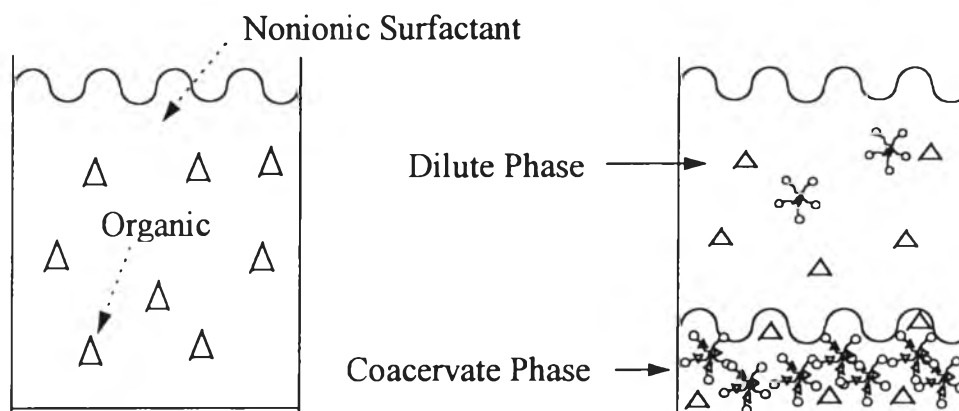
Figure 2.2 Schematic of liquid-coacervate extraction.

The overall distribution coefficient or partition ratio (solute concentration ratio in coacervate to that in dilute phase) is normally reported in studies of coacervate extraction. This only requires straightforward measurement of total concentration in coacervate and dilute phases. In addition in this study, we wish to directly compare the tendency of the solute to "solubilize" into the surfactant aggregate in the coacervate to that tendency in micelles.

This comparison requires definition of a coacervate solubilization equilibrium constant (K_c) exactly analagous to K_m for micelles:

$$K_c = X_c / C_u \qquad (7)$$

where X_c is the mole fraction of solute in the coacervate aggregate and C_u is the concentration of unsolubilized solute. From the definition of X_c and correcting for surfactant and solute not in micelles:

$$K_c = ([O]_c - C_u) / C_u ([Surfactant]_c - CMC + [O]_c - C_u) \qquad (8)$$

where $[O]_c$ and $[Surfactant]_c$ are the total solute and surfactant concentrations in the coacervate phase.

In order to apply eq. 8, the value of C_u is assumed to be the same in dilute and coacervate phases (i.e., unassociated solute activity coefficients are assumed to be similar in the two phases). The surfactant monomer concentration (CMC) is assumed to be the same in dilute and coacervate phases also, so surfactant concentration in aggregated form in the coacervate is equal to total coacervate surfactant concentration minus the CMC (this correction is very small so the validity of this approximation is of little concern). Since micelles are present in the dilute phase, the micellar solubilized solute concentration must be subtracted from the measured total solute concentration in the dilute phase to obtain C_u. The value of K_m obtained from SED experiments for OP(EO)$_9$ is assumed to be the same as that for OP(EO)$_7$ in the dilute phase, both at the same temperature. Applying eqs. 1, 2, and 4 to describe micellization in the dilute phase and combining with eq. 8 permits calculation of K_c from measurable parameters and K_m:

$$K_c = (1 - [O]_c / ([Surfactant]_c + [O]_c)) K_m \qquad (9)$$

For solutes and surfactants of the type used here, K_m can be highly dependent on solute concentration (Uchiyama et al., 1993; Dunaway, Christian and Scamehorn, 1995).

2.6 Phase Separation Extraction

The basis of the phase separation (or cloud point) extraction technique, initially reported by Watanabe (Watanabe, 1982), stems from the well known phase phenomenon exhibited by some micellar surfactant solutions. There are several situations in which surfactant solutions occur in equilibrium with a separate, predominantly aqueous phase (Hall and Tiddy, 1981). The phase separation of zwitterionic micelle solutions and concentrated ionic (anionic or cationic) solutions have been reported (Hall and Tiddy, 1981; Rubingh and Holland, 1991). The best known example, however, of this technique is the separation of a nonionic micellar phase above the cloud point temperature of polyoxyethylene surfactant solutions (Puvvada and Blankschtein, 1990). The specific applications of such systems and their phase behavior for the extractive preconcentration, separation, and/or purification of metal chelates, biomaterials, and organic compounds are summarized and discussed (Hinze and Pramauro, 1993). The cloud point temperature is the lowest temperature at which the nonionic surfactant solutions, once above the CMC, become cloudy upon heating (Clint, 1992). The higher the degree of polymerization in the polyoxyethylene surfactant, the higher the cloud point will be.

Above the cloud point, the nonionic surfactant solutions separate into two isotropic phases. The phases consist of a dilute solution of the nonionic surfactant and a surfactant-rich micellar phase, or coacervate phase. The concentration of surfactant in the dilute phase is above its CMC at that temperature (Corti et al., 1984). The temperature at which the phase separation occurs is a function of the surfactant concentration, so that one can define in the temperature versus surfactant concentration plot a consolution curve which separates the one-phase region from the two-phase region. The

consolution curves exhibit a minimum, referred to as the critical point. The temperature and surfactant concentration at which the minimum occurs are referred to as the critical temperature (T_c) and critical concentration (C_c), respectively.

The exact structure of the surfactant in the coacervate is not known. The aggregate structure, however, probably consists of the surfactant hydrocarbon chains intertwining, removing themselves from the aqueous environment and the hydrophilic groups covering the surface of the hydrophobic region. Structures such as micelles (spherical, rodlike, or lamellar) or vesicles are feasible structures (the coacervate phase does not polarize light, so it is not a liquid crystal).

The origins of such critical phenomena and phase separation behavior of aqueous nonionic surfactant solutions are still the subject of much debate in the literature. Some researchers (Staples and Tiddy, 1978; Hayter and Zulauf, 1982; Triolo, Magid, Johnson and Child, 1982; Zulauf and Rosenbusch, 1983) have concluded that the micelle size at the critical concentration does not change with temperature. They describe that the phase separation occurs because the attractive pair potential between the micelles increases as the temperature is above the consolution curve. This causes the micelles come closer and closer, resulting in less hydration of the micelles. Then the micelles have a possibility to contact with each other and eventually coalesce into bigger micelles. If the density of the bigger micelles, now, is sufficiently different from the bulk solution, then phase separation occurs. Some researchers (Kawaguchi, Hamanaka and Mitsui, 1983; Ravey, 1983; Corti et al., 1984; Kato and Seimiya, 1986; Cummins, Hayter, Panfold and Staples, 1987), however, infer from their data that there is a substantial growth of the micellar aggregation number with temperature because of the dehydration of the micelles, as the temperature is increased, resulting in the

difference between the densities of the micellar phase and the bulk solution causing phases to separate. Nilsson and Lindman (1983) have determined that the micelles remain strongly hydrated near the cloud point. For the sake of argument, it is useful to ascribe the cause of the phase separation to the dehydration of the micelles.

It is important to emphasize that any factor affecting the dehydration of nonionic micelles can alter the cloud point, either increasing it or decreasing it, of a given nonionic surfactant.

Most simple electrolytes typically depress the cloud point of nonionic surfactants due to their salting-out, or dehydrating effect, with the effect of a given salt depending upon the hydrated radii of the ions (Tokiwa and Matsumoto, 1975; Brusdeilins and Zarybnicky, 1984; Aveyard and Lawless, 1986; Marszall, 1987; Rosen, 1989; Zourab, Sabet, Abo-El Dahab, 1991). On the other hand, some ions such as nitrates and thiocyanates raise the cloud point due to a salting-in effect (Tokiwa and Matsumoto, 1975; Aveyard and Lawless, 1986; Marszall, 1987; Zourab et al., 1991).

The addition of nonpolar organic compounds that can be solubilized in the core of the micelle normally raises the cloud point, while polar organic compounds which can be solubilized in the core of the surfactants depress the cloud point remarkably (Maclay, 1956) because the hydrophilic portions are less hydrophilic, resulting in dehydration of the micelles.

The cloud point of aqueous nonionic surfactant solutions above the CMC increases dramatically with the addition of ionic surfactants (Nishikoto, Kisada and Matuura, 1977; Suzuki, Esumi and Meguro, 1983; Valaulikar and Manohar, 1985; Souza, Corti and Degiorgio, 1986; Manohar and Kelkar, 1990; Limbele, Van, Rupert and Zana, 1991). The repulsion between the surfaces of the mixed micelles causes the increment of the cloud point. The addition of another nonionic surfactant changes the cloud point of aqueous

nonionic surfactant solution. The cloud point of the mixed nonionic solution is intermediate between that of the two pure surfactants involved (Maclay, 1956). Thus, the desired cloud point temperature for an application can be obtained by appropriate selection of the mixed nonionic surfactant solution system with or without the proper choice of the additives.