dispersed species with properties distinct from those of an isotropic solution containing monomeric surfactant molecules (Myers, 1992).

Micelles are dynamic structures where a frequent exchange of monomers between micelles and the bulk solution occurs. Thermodynamics of the self-assembly of surfactants or aggregates is determined by the free energy of transfer of a surfactant monomer from water to the micelle.

Several models have been developed to interpret micellar behavior (Mukerjee, 1967; Lieberman et al., 1996). Two models, the mass-action and phase-separation models are described here in more detail. In the mass-action model, micelles are in equilibrium with the unassociated surfactant or monomer. For nonionic surfactants with an aggregation number of n, the mass-action model predicts that n molecules of monomeric nonionized surfactants, S, react to form a micelle, M:

$$nS \Leftrightarrow M \tag{12.2}$$

with its equilibrium constant for micelle formation given as

$$K_{\mathrm{m}} = \frac{[\mathrm{M}]}{[\mathrm{S}]^n} \tag{12.3}$$

Values of K_{m} determine the extent of aggregation, in that as K_{m} increases, so does the amount of aggregation. The standard free energy of micellization at the critical micelle concentration (CMC) is

$$\Delta G_{\mathrm{m}}^0 = RT\ \ln[S]_{\mathrm{CMC}} \tag{12.4}$$

The basis for the phase-separation model (Mukerjee, 1967) assumes that the occurrence of the phase change happens at the CMC. This model uses the chemical potentials of the free surfactant in the aqueous phase (μ_{s}) and the associated surfactant in the micellar phase (μ_{m}^0),

$$\mu_{\mathrm{s}} = \mu_{\mathrm{s}}^0 + RT\ \ln[S] \tag{12.5}$$

where μ_{s}^0 refers to the standard state of the surfactant in the aqueous phase. The micellar material is in its standard state, and therefore $\mu_{\mathrm{m}} = \mu_{\mathrm{m}}^0$. The standard free energy of micellization is

$$\Delta G_{\mathrm{m}}^0 = \mu_{\mathrm{m}}^0 - \mu_{\mathrm{s}}^0 = RT\ \ln X_{\mathrm{S}} - \left(\frac{RT}{m}\right)\ln\left(\frac{X_{\mathrm{m}}}{m}\right) \tag{12.6}$$

where X_{m} and X_{s} are the mole fractions of monomer in the micellar and aqueous phase, respectively, and m is the number of monomers. For large micelles, m goes to infinity, and Equation 12.6 reduces to Equation 12.4. Micellization, in general, is exothermic and therefore negative values indicate spontaneous micelle formation. Equation 12.6 corresponds to a true phase separation, and according to the Gibbs Phase Rule, X_{s} is the single monomer concentration that can exist in equilibrium with the micelles (Marsh and King, 1986). However, this model is not very realistic because it predicts the change occurring at the CMC to be infinitely sharp, whereas in reality, the change is shown to be continuous (Mukerjee, 1967).

Critical Parameters

Critical Micellization Concentration

It has been well documented that surfactants self-associate in aqueous solution to minimize the area of contact between their hydrophobic tails and the aqueous solution (Mukerjee, 1979; Tanford, 1980). This phenomenon occurs at a critical concentration of surfactant, the critical