the solubilizing power. Thus, Eumulgin C1000 is more efficient than Eumulgin C1500, and Myrj 53 is more efficient than Myrj 59.

Mall et al. (1996) applied a thermodynamic approach to study the solubilization of sulfonamides in a SDS micellar solution via the dissolution behavior of the drugs. From the surface energies of four sulfonamides assessed by contact angle data, the free energy of adhesion between the drugs and SDS head groups and tails was calculated. The most favored interaction was found to be for adhesion to the SDS tails, rather than the head groups. The thermodynamic parameters of activation were calculated from the dissolution rate data. A linear relationship exists between the enthalpy of transfer between water and SDS micelles and the free energy of adhesion between the drugs and both SDS head groups and tails. The interaction between the SDS head group and the drugs dominantly influences the solubilization when comparing the adhesion to the SDS head group and enthalpy of transfer data. The repulsion between the polar sulfanilamide and the SDS head group, as evidenced by the positive free energy of adhesion and positive enthalpy of transfer, may limit solubilization of this drug. The favorable free energy of adhesion and enthalpy of transfer can facilitate solubilization of the other three sulfonamides: sulfamerazine, sulfadiazine, and sulfamethazine. Therefore, the authors concluded that the highly nonpolar drugs had the most favored free energy of adhesion and the most favored enthalpy of transfer. The highly polar drug had a disfavored free energy of adhesion to the SDS head group and a disfavored enthalpy of transfer, thus demonstrating that the most important barrier to the passage from the aqueous media to the hydrophobic core of the micelle is the monopolar repulsion between the polar forces of the drug and head group surface energies. The authors claimed that this provided a new insight into a possible mechanism of solubilization and offered the prospect to better understand the complex partitioning behavior.

LOCATION OF SOLUTES IN MICELLAR SYSTEMS

The location of a solute within a micelle is largely dependent on the overall structure of the solute (Mukerjee, 1979). Thus, nonpolar solutes are primarily dissolved in the hydrocarbon core; whereas amphiphilic compounds containing both polar and nonpolar groups are oriented with the polar group at the surface, and the hydrophobic group is located inside the hydrophobic core of the micelle. Adsorption on the micellar surface has been postulated for some solutes, and suggested that certain solutes such as griseofulvin may be incorporated in the PEO exterior of nonionic surfactant micelles. Solutes that are located within the micelle core increase the size of the micelles and change the number of surfactant molecules per micelle. This means that the aggregation number increases in an effort to fill the swollen micelle core. In contrast, solutes that are located close to the surface of the micelle have little or no effect on the aggregation number, but do increase micelle size by the incorporation of solute molecules (Attwood and Florence, 1983).

Aliphatic hydrocarbon solutes are primarily solubilized within the hydrocarbon core region of the surfactant micelles. Solubilization isotherms (activity coefficient versus mole fraction, X) for these hydrophobic solutes exhibit curves that decrease from relatively large values at infinite dilution to lower values as X increases toward unity (Figure 12.6). The aromatic hydrocarbons are intermediate in behavior between highly polar solutes, which are anchored in the micelle surface region, and aliphatic hydrocarbons, which preferentially solubilize in the hydrocarbon core region (Kondo et al., 1993).

A two-state model of solubilization may be used to describe the location of solutes in micellar systems. This model involves a distribution between a dissolved state, which is associated with the core, and an adsorbed state, associated with the micellar water interface. The molecules in the dissolved state remain in the micelle because of the solvent properties of the core. Molecules in the adsorbed state are due to the surface activity of the dissolved species, similar to a surface excess (Mukerjee, 1979).