

CHAPTER II

BACKGROUND

2.1 Surfactant Adsorption

Figure 2-1 is a schematic of a typical surfactant adsorption isotherm. Such isotherms are commonly seen for ionic surfactants adsorbing from aqueous solution onto oppositely charged surfaces. Examples include anionic surfactants such as sodium dodecyl sulfate (SDS) on alumina at low or neutral pH and cationic surfactants such as cetyltrimethylammonium bromide (CTAB) on silica at pH values above 3. Similar isotherms are sometimes observed for nonionic surfactants.

Isotherms like those in figure 1 are commonly divided into four regions. Region 1 is a region of low adsorption densities and is sometimes referred to as the Henry's Law Region. In region 1 the surfactants are adsorbed as monomers and do not interact with one another. For nonionic surfactants and for ionic surfactants with some added electrolyte, the slope of the isotherm is one in this region when the data is plotted on a log-log plot. For ionic surfactants on a surface of moderate charge density with no added electrolyte, the slope of the isotherm may be less than one because the charge on the surface is being reversed by the adsorption of the charged surfactant. In many systems where conditions are favorable to surfactant adsorption, this region may not even be detectable because it occurs at such low surfactant concentrations.

A sharp increase in the slope of the isotherm occurs at the transition

between region 1 and region 2. All investigators of surfactant adsorption have attributed this increase in slope to the formation of micelle-like aggregates of adsorbed surfactants. The transition has been given designations analogous to the critical micelle concentration (CMC) such as critical admicelle concentration (CAC) or critical hemimicelle concentration (CHC). The differences in terminology emphasize different views of the morphology of the aggregates but they also emphasize the consensus that the aggregation phenomenon which occurs at the solid/liquid interface is analogous to micelle formation. This conclusion, which was initially based primarily on the shape of the isotherm, has been reinforced by modern studies using fluorescence and spin probes; these studies indicate that the aggregates that form in region 2 have micelle-like microviscosities and micelle-like internal environments. It is important to note that these micelle-like aggregates are present even though the total adsorption density of the surfactant may be less than 1/100th of a monolayer. Evidence has been found that the reason for the formation of these aggregates locally or patch-wise at the interface is due to the heterogeneity of the surface.

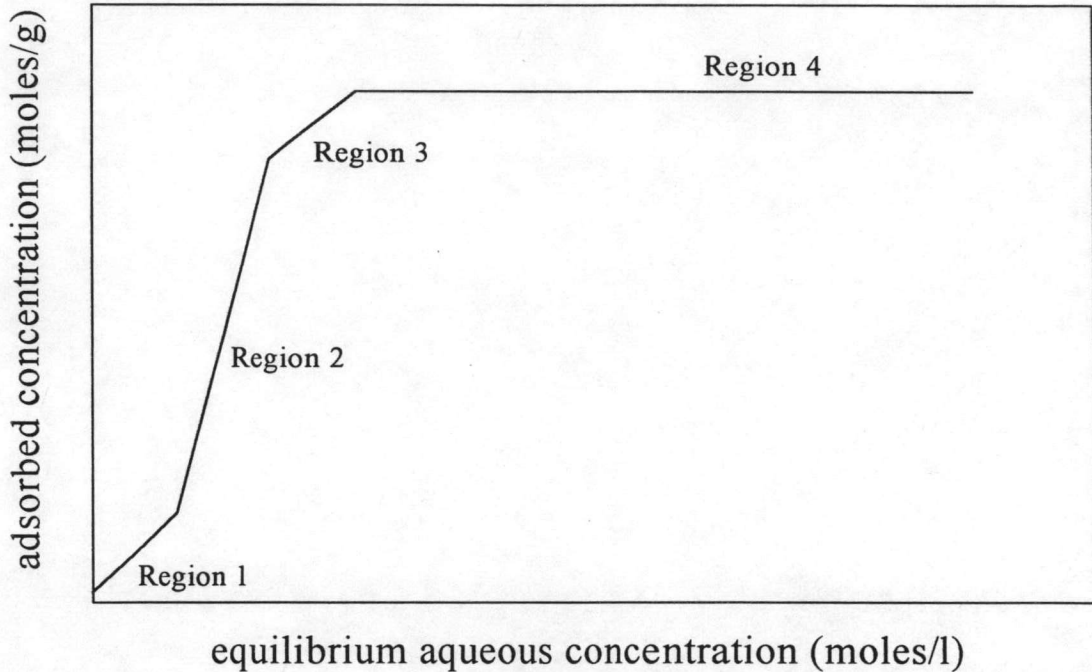


Figure 1-1 A typical adsorption isotherm for an anionic surfactant on alumina.

The region 2/region 3 transition is marked by a decrease in the slope of the isotherm. In some systems, the change in slope can be quite dramatic. While there is widespread agreement about the mechanism for the change in slope from region 1 to region 2, there is little agreement about the reason for the change in slope from region 2 to region 3. The most common explanation is that the aggregates forming in region 2 are monolayers adsorbing head down on an oppositely charged surface and that the change in slope coincides with the cancellation of the charge on the solid surface by the charge on the adsorbed aggregates so that subsequent surfactants are adsorbing onto a like-charged surface. Sometimes it is proposed that a second layer on the aggregates does not begin to form until region 3. Some other data indicate that the second layer forms suddenly at the CMC of the system and that only monolayers are present below the CMC, and have attributed the change in slope to the distribution of patch energies on the surface (Bitting et al 1987). It may be that a critical

component of the change in slope is a Langmuir-like competition between aggregates for the remaining surface area. The region 2/region 3 transition does not always correspond to a change in the charge of the surface, however, and it is also observed in systems of nonionic surfactants adsorbed on silica. Further, it is not clear how a change in the morphology of the aggregates between region 2 and region 3 can be reconciled with the results of fluorescence and spin probe studies which clearly show that both the microviscosity and the polarity of the aggregates is constant from the region 1/region 2 transition through region 3.

A recent study by Kung and Hayes sheds additional light on the morphology of the admicelle which may be important in future applications of adsolubilization. In a comparison of the FTIR spectra of cetyltrimethylammonium bromide micelles, crystals, and adsorbed layers, it was observed that surfactant in the adsorbed layer has a micelle-like spectrum in regions 2 and 3 with no obvious change from region 2 to region 3, which suggests that local bilayers are formed in this system beginning with the region 1/region 2 transition. When, however, the adsorbed layer spectra were compared to the spectra obtained upon drying of the adsorbed samples, it was found that the difference between the adsorbed and the dry samples decreased with increasing surface coverage, this finding was interpreted by the authors to indicate that the structure inside the adsorbed layer was becoming more solid-like at higher coverages. If this interpretation of the FTIR spectra is correct, there may be significant changes in the location of adsolubilizates and the ability of the admicelle to distinguish between adsolubilizates when region 2 adsolubilization is compared to region 3 adsolubilization.

Region 4 is called the plateau adsorption region. In most systems the region 3/region 4 transition occurs near the CMC of the surfactant. When the surfactant is monoisomeric (or nearly so, as in the case of some commercial polyethoxylated alcohols or phenols) the adsorption becomes nearly constant above the CMC. This phenomenon is easily understood in terms of the pseudophase separation model of micelle formation: micelles that form at the CMC have the same chemical potential as the monomer at the CMC. As the concentration of surfactant increases, the surfactant goes into the micellar pseudo-phase at almost the same chemical potential as the surfactant in the first micelles to form and so the chemical potential of the surfactant does not increase as dramatically with surfactant concentration above the CMC as it would in the absence of micelles. Since the admicelles are also in equilibrium with the same monomer phase, the last admicelle to form is also at the same chemical potential as the monomer at the CMC. The only way more admicelles can form is for the chemical potential of the surfactant to increase, but this occurs only slowly because the surfactant added above the CMC forms more micelles at nearly the same chemical potential as that of the micelles that formed near the CMC. The pseudophase separation model is certainly only an approximation, but in general, the better a surfactant is at forming micelles, the more pronounced will be the region 3/region 4 transition, the closer that transition will be to the CMC, and the less the adsorption will increase above the CMC.

2.2 Factors Affecting Admicelle Formation

Though it should be very clear from these observations that admicelles are very much like micelles and so can be expected to exhibit something closely analogous to solubilization, the analogy can be reinforced by the following results: When a surfactant system is modified

in a way that affects the CMC of the system, the CAC and the region 3/region 4 transition vary in the same direction and at about the same rate as the CMC. For example, addition of electrolyte causes a decrease in the CMC of an ionic surfactant; however, the plateau adsorption level of an ionic surfactant will vary little with the addition of electrolyte because the CAC (the region 2/region 3 transition) and the region 3/region 4 transition will vary at about the same rate and in the same direction as the CMC. Similar results have been observed for changes in the length and degree of branching of the hydrophobic moiety of the surfactant.

There is one dramatic difference in the factors which affect micelle formation and the factors influencing admicelle formation: the concentration of potential-determining ions for the solid. This can be illustrated for the case of alumina. In an aqueous suspension of alumina, the charge density on the surface of the alumina will be found to vary dramatically with the pH of the suspension. At pH values below about 9.1 (depending somewhat on the history of surface) the surface of the alumina will be positively charged. Above pH 9.1, the surface will be negatively charged. At pH 9.1, the surface will be uncharged. For this reason, hydrogen and hydroxyl ions are called potential determining ions for alumina. While pH will not greatly affect the CMC of most ionic surfactants, SDS (for example) will hardly adsorb at all on alumina at pH values above 9.1 but will adsorb to the extent of forming a complete bilayer on the surface at a pH of about 4 or below. Lithium ions have been shown to have a similar effect on SDS adsorption on alumina, probably because they are small enough to become incorporated into lattice sites on the surface of the alumina. Potential determining ions are a very powerful tool for manipulating the extent of surfactant adsorption and therefore the concentration of admicelles at a solid/liquid interface.

One final effect should be mentioned. Just as the addition of a small concentration of a low CMC nonionic can dramatically lower the CMC of an anionic surfactant system, so mixed admicelles can be formed; as the use of a mixture lowers the CMC of a system, so the use of mixtures is found to lower CAC values as well. This phenomenon has been studied in some detail for mixtures of anionic and nonionic surfactants adsorbed on alumina by Roberts et. al. and Lopata et.al. The most striking observation is that while the nonionic polyethoxylated nonylphenols will hardly adsorb at all on the alumina by themselves, the addition of only 10 mole percent of anionic surfactant leads to the formation of admicelles which are predominately nonionic in composition.

2.3 Potential Applications of Adsolubilization

As stated before, the possible applications of adsolubilization are only now beginning to be studied. Several promising areas have already begun to develop, however. One is the use of adsolubilization in the formation of thin polymer films on solid surface. Wu et. al. developed a three step process for forming ultrathin (3-4 nm) polymer films on a solid surface. The first step in the process is formation of an adsorbed surfactant layer, the second step is the adsolubilization of a reactive monomer in the admicelle layer, and the third step is the initiation of a polymerization reaction within that layer. This process has now been studied for the formation of new ultrathin solid lubricating layers, for the compatibilization of filler and reinforcer surfaces for polymer composites, and for the formation of reverse phase chromatography packings.

Adsolubilization has also been proposed as the basis of a new surfactant based separation process. One particularly promising variation of

this is the use of chiral surfactants for the resolution of mixtures of optical isomers. More recently Lobban and co-workers have begun to investigate the use of adsolubilization for admicellar catalysis, a surface analogue of micellar catalysis which may give greater stereoselectivity than micellar catalysis and may be more amenable to develop into industrial scale processes because it can be employed in a fixed bed mode. Though the possibilities of use of the phenomenon in drug release applications seem obvious, to our knowledge not a single such study has been reported.

2.4 Micellar Catalysis

In aqueous solutions at concentrations above the critical micelle concentration (CMC), ionic surfactant molecules form roughly spherical aggregates. The hydrophobic alkyl chains are oriented towards the center of the aggregate, and the charged hydrophilic head groups are located at the micelle surface. Organic solutes will tend to solubilize within the hydrophobic core of the micelle causing a high local concentration (compared to the aqueous phase) of the organic solutes. Depending on the chemical moieties involved, the organic solutes may also be specifically oriented within the micelle. For example, a molecule with a polar or charged group (e.g., OH or COO⁻) tends to solubilize with the hydrophilic groups oriented towards the micelle surface (Fendler and Fendler, 1970, 1975; Fendler, 1976). Electrostatic interactions with the charged head groups may also increase the concentration near the micelle of oppositely charged reagents, as well as stabilize reaction transition states within or at the surface of the micelles (Kiefer et al., 1972). The net effects of these multiple interactions can therefore be enhanced rates or selectivities of reactions involving the organic solutes, a phenomenon termed micellar catalysis.

2.5 Surfactant Aggregates

The adsorption of ionic surfactant from aqueous solution on charged mineral oxide surfaces has been studied for quite some time (Rosen, 1989). In an aqueous solution, the solid surface becomes charged by protonation or deprotonation of chemically adsorbed water, depending on the solution pH value (Yopps and Fuerstenau, 1964; Griffiths and Fuerstenau, 1981). Cationic surfactants adsorb on negatively charged surfaces such as silica in mildly basic environments; whereas anionic surfactants adsorb on positively charged surfaces such as alumina in mildly acidic environments.

Surfactant adsorption is generally presented in an adsorption isotherm (a logarithm-logarithm plot of adsorption versus equilibrium bulk phase surfactant concentration), in which four distinct adsorption regions exist and each of these regions corresponds to a different mechanism of surfactant adsorption as shown in Figure 1.

In region 1, surfactant monomers adsorb on the solid surface individually due to the electrostatic attraction. The dependence of adsorption on aqueous concentration follows Henry's Law, i.e.,

$$\Gamma = h \cdot C_m$$

where Γ is the total Gibbs adsorption of the surfactant, h is the Henry's Law coefficient for adsorption at coverages below the onset of aggregation and C_m is the surfactant monomer concentration in the bulk phase.

At the region 1/2 transition, a sharp increase in the slope of isotherm indicates the surfactant aggregate formation by the association of hydrocarbon chains. These aggregates are called hemimicelles (monolayer structure)(Somasundaran and Fuerstenau, 1966) or admicelles (bilayer structure)(Harwell et al., 1985b). The surfactant concentration at this point is labeled the CAC (for critical admicelle concentration) or CHC (for critical hemimicelle concentration), depending on whether one believes that a bilayer or a monolayer morphology exists.

In region 3, the slope starts to decrease. The decrease in slope can be attributed to an increasing electrostatic repulsion of ions from the interface because of interfacial charge reversal. Although there is continuing argument in the literature regarding the structure of surfactant aggregates in regions 2 and 3, studies using fluorescene probe (Chandar et al., 1987a), electron spin resonance and fluorescencce spectra (Esumi et al., 1991a), ^2H NMR spectroscopy (Soderlind and Stilbs, 1993), neutron reflection (Rennie et al., 1990; McDermott et al., 1994) or theoretical predictions (Scamehorn et al., 1982) have shown that at high surface coverage the surfactant aggregates are bilayers. Region 4 is called the plateau region, where either the adsorption achieves completion, or micelles start to form in the bulk phase. For many surfactants the adsorption in this region is nearly constant for all concentrations above the CMC.

2.6 Admicellar Catalysis

Analogous in nature to micelles, adsorbed surfactant aggregates (both hemimicelles and admicelles) incorporate organic solutes into the hydrophobic environment between the hydrocarbon chains (Leveiz et al., 1984; Chandar et al., 1987b; Yeskie and Harwell, 1988). Except for

exploring the nature of the adsorbed surfactant layer, the study of adsolubilization has also been applied to the separation process using admicellar chromatography (Fitzgerald and Harwell, 1986), the polymerization of styrene in admicelles which serve as reaction solvents (Wu et al., 1987; Esumi et al., 1990; 1991b), and the surface modification procelles (O'Haver et al., 1994). Recently, the study of admicellar catalysis in a continuous flow packed bed reactor also presented expected results (Wong, 1994).

Similar to micellar catalysis, admicelles catalyze the reaction by adsolubilizing the organic reactant and/or ionic reactants (e.g., hydrogen ion). Due to the increase of local concentration of hydrogen ions and organics in the admicellar phase, the reaction rate is enhanced.

The mass transport during the adsolubilization and is also very important to the reaction rate, as is often the case in heterogeneous catalysis.