

CHAPTER II

LITERATURE SURVEY

2.1 Surfactant Adsorption

Many studies have examined the surfactant adsorption isotherms of all types. *Barton et al.* (1988) studied the adsorption isotherm of sodium dodecyl sulfate (SDS) on the alumina for admicellar chromatography in order to separate isomers of heptanol. The results showed that increasing the concentration of SDS in the supernatant causes additional adsorption of surfactant until the plateau adsorption occurs and that surfactant adsorption is enhanced in the presence of alcohol. The increased adsorption in the presence of alcohol provides indirect evidence for the interaction of alcohols with the surfactant at the interface. The isotherms also showed that *n*-heptanol adsorbilizes preferentially over 2-methyl-2-hexanol in SDS admicelles.

Lee et al. (1990) examined the behavior of adsorbed surfactant aggregates (admicelles) which are similar in nature to micelles. In studying the solubilization of solutes into admicelles, a process called adsolubilization, it was observed that while alkanes are adsolubilized only in the hydrocarbon core, there appears to be two sites at which alcohols are adsolubilized, at the core and at the hydrophobic perimeter of the admicelle.

O'Haver et al. (1994) investigated the adsorption isotherm of cetyltrimethylammonium bromide ($C_{16}TAB$), octylphenoxypoly(ethoxy)ethanol (MACOL OP10SP), and methyltri (C8-C10) ammonium chloride bilayer on Hi-Sil 233 surface. The results showed that, at 22°C, the adsorption of $C_{16}TAB$ at a feed pH of 8 and MACOL at a feed pH of 7 on silica yielded isotherm shapes similar to those previously reported. The maximum adsorption of $C_{16}TAB$ on Hi-Sil 233 was found to be approximately 270 $\mu\text{mol/g}$ of silica while the maximum adsorption of the nonionic surfactant on the Hi-Sil 233 was found to be approximately 170 $\mu\text{mol/g}$ of silica.

Kitiyanan et al. (1996) studied cetyltrimethylammonium bromide ($C_{16}TAB$) adsorption isotherm on Hi-Sil 255. The isotherm illustrates the characteristics of

region II, III, and IV. The slope of the isotherm is greater than 1 from a concentration of C₁₆TAB in the aqueous solution of 70 μM. to a concentration of 120 μM. This very high slope indicates the onset of C₁₆TAB aggregation on the surface of the silica, which occurs either at or below 70 μM. The maximum adsorption of C₁₆TAB on Hi-Sil 255 is approximately 550 μmol/g. The comparison of C₁₆TAB adsorption (molecules per nm²) on Hi-Sil 255 and Hi-Sil 233, having specific surface areas of 170 and 145 m²/g, respectively showed that the increase in adsorption of C₁₆TAB is not linear with respect to specific surface area. The adsorption density of C₁₆TAB is 51 A^{0 2}/molecule on Hi-Sil 255 and 89 A^{0 2}/ molecule on Hi-Sil 233.

Arayawongkul et al. (2001) investigated the adsorption of C₁₆TAB on non porous silica (Aerosil OX50), a fumed silica with a N₂ BET surface area of 53.5 m²/g. The isotherm showed only three of the typical regions (II, III, IV) of the standard adsorption isotherm. Plateau adsorption of C₁₆TAB was 130 μmol/g. The results suggest that the bilayer does not completely cover the silica surface. If one assumes that C₁₆TAB formed a perfect bilayer and completely covers the silica surface, the C₁₆TAB will average 1.37 nm²/ molecule. From previous work, C₁₆TAB has consistently had a head group area of 0.5 nm². So it is possible that there was electrostatic repulsion between adjacent C₁₆TAB head groups.

Dickson and O'Haver (2002), investigated adsorption isotherms of surfactants with similar structures but varying tail lengths, C_nTABs with (n=12,14,16) on Hi-Sil 233. As they expected, the CMC increased as the tail length decreased and the values were close to those published in the literature. However, the plateau adsorption and area per molecule did not increase with decreasing hydrophobic tail length, which is in disagreement with results in the literature. They proposed that the impact of the pore size distribution may have caused this. The data from the adsorption isotherm indicated that the tightest and loosest packed admicelles were C₁₄TAB and C₁₂TAB, respectively.

2.2 Adsolubilization Isotherm

In 1994, *O'Haver et al.* studied the adsolubilization isotherm of styrene in cetyltrimethylammonium bromide ($C_{16}TAB$) system. The maximum measured adsolubilization of styrene is approximately $155 \mu\text{mol/g}$ of silica. This measurement was determined for the experimental runs in which surfactant adsorption was $267 \mu\text{mol/g}$ of silica, similar to that reported obtained by the previous work (*Wu et al.* 1987). The higher value of K_{AS} (An equilibrium constant defined to be analogous to the partition coefficients used in solubilization) is possibly due to a lower bulk styrene concentration, since the ratio of adsorbed surfactant molecules to adsolubilized monomer molecules of approximately 2, was similar to reported values. They also found that cationic surfactants tend to have a greater solubilizing power than anionics.

The adsolubilization of styrene, isoprene, and mixtures of styrene and isoprene into cetyltrimethylammonium bromide ($C_{16}TAB$) bilayers (admicelles) on precipitated silica is investigated by *Kitiyanan et al.* (1996). The results showed that the styrene adsolubilization constant is nearly unchanged with the increasing styrene equilibrium concentration in the aqueous phase, while the isoprene adsolubilization constant increases with increasing isoprene partial pressure. The adsolubilization constant suggest that styrene adsolubilizes into both the palisade layer and the core of the admicelle, while isoprene adsolubilizes into the palisade layer. In the comonomer system styrene adsolubilization slightly increased in the presence of isoprene but isoprene adsolubilization is enhanced in the presence of styrene. The adsolubilization isotherms of both monomers have increasing slopes in the comonomer system and show that there is a synergistic effect, possibly due to swelling of the admicelle due to the addition of adsolubilize.

Arayawongkul et al. (2001) studied the adsolubilization isotherm of styrene in $C_{16}TAB$ at two levels of $C_{16}TAB$ adsorption. The result showed that the adsolubilization of styrene increased with increasing styrene equilibration concentration at both adsorption levels. When comparing the two, styrene adsolubilization at the higher $C_{16}TAB$ level is higher than at the low $C_{16}TAB$ adsorption.

Dickson and O'Haver (2002) investigated the adsolubilization isotherm of α -naphthol and naphthalene on C₁₂TAB, C₁₄TAB, C₁₆TAB bilayer. The result showed that as the equilibrium concentration of α -naphthol increased, the amount of adsolubilized per gram of silica increased for all three surfactant systems. The adsorption for α -naphthol onto silica from a water solution was measured, and the results showed no significant adsorption in the absence of surfactant. And the results indicated that there is no clear correlation between the adsolubilization of α -naphthol and the surfactant tail length. The adsolubilization of α -naphthol is almost identical in C₁₆TAB and C₁₂TAB, while that in C₁₄TAB is much lower. They also reported that as the equilibrium naphthalene concentration increased the amount of adsolubilized naphthalene increased for all three surfactants.

2.3 Admicellar Polymerization

Admicellar polymerization, polymerization of monomers solubilized in adsorbed surfactant aggregates, has been examined since 1987 and improved over the years. *Wu et al. (1987)* manipulated the formation of admicelles on the solid surface, and the adsolubilization of organic monomer of interest into admicelles, and developed a novel method of ultra-thin film formation using the organized structure of admicelles as a chemical reaction solvent. They demonstrated the feasibility of this concept by forming a polystyrene film on γ -alumina using admicelles of the anionic surfactant sodium dodecyl sulphate (SDS) and sodium persulfate as the initiator. The results show 75% conversion of monomer to polymer after 25 minutes. There was no attempt to optimize the character of the film in the study but only to confirm the feasibility of forming polymeric films this method.

In 1991, *Esumi et al.* studied polymerization of styrene in surfactant bilayer on alumina. Styrene was adsolubilized into a bilayer of sodium 10-undecenoate on alumina. This resulted in a decrease of micropolarity of styrene as measured by UV and confirmed by IR. The molecular weights of extracted polymer by THF were below 1000 for the sample with and without polystyrene. Further, the dispersion

stability of alumina having a polystyrene layer was increased with UV irradiation time.

Lai et. al (1992) successfully demonstrated the polymerization of tetrafluoroethylene gas in perfluorosurfactant admicelles by using a high-pressure reactor. The effects of surfactant concentration and of initiator concentration were studied. It was found that TFE adsolubilization can be controlled by the partial pressure of monomer above the system and that the initiator concentration was in the range from 0.25-2.5 wt%. Modified powders were characterized by fourier transform infrared spectroscopy (FTIR), wavelength-dispersive spectroscopy, atomic force microscopy (AFM) and wettability testing.

In 1993, *O'Haver et al.* formed ultra-thin polystyrene film on silica. Polystyrene was successfully polymerized into CTAB bilayers using the water-insoluble initiator 2,2'-azobis-2-methylpropionitrile (AIBN). The formed polymer was extracted and characterized by techniques including FTIR and GPC. The molecular weight of formed polymer was investigated with respect to polymerization time. Polymeric film on porous silica causing increases in particle size and decreases in silica surface area.

Applications of the modified silicas have been studied since 1995. *Waddell* and co-worker modified silica with polymerized styrene, isoprene, butadiene and copolymers in order to improve the physical properties in a silica-filled tire compound. Polystyrene-modified silica caused reduction in overall physical properties while polybutadiene-modified silica showed an increasing in tear strength and cut growth resistant. The result showed that copolymers with styrene and butadiene are the most promising system, showing decreasing cure times and hysteresis and increases in tear modulus and good cut growth resistance.

In 1995, *Sakhalkar and Hirt*, examined admicellar polymerization of styrene on glass fibers. Modified fibers were evaluated using scanning electron microscopy (SEM). The micrographs showed a nonuniform coating on the fiber surface. The result appears that polymer formation was not restricted to the surface aggregates but also occurred in the aqueous supernatant.

Kudisi (1997) formed polystyrene-isoprene copolymer on clay using admicellar polymerization. The research studied the effect of the amount of

surfactant and monomer on the physical properties of a rubber compound compared with using unmodified clay. The results show that this process increases the compound cure rate, decreased cure times, and improved tensile properties, tear strength, hardness, flex cracking resistance, and compression set.

In 1998, *Grady* studied admicellar polymerization modified glass cloth used in composite manufacturing. The formation of thin polymeric films of polystyrene-isoprene on glass cloth were accomplished using SDS as the surfactant. The treated glass cloths were combined with epoxy and polyester resins to form a composite. The composite showed improvements in flexural strength and physical properties when compared to the untreated glass cloth composite.

The application of admicellar polymerization was expanded by *Jung* (2000) who improved the admicellar polymerization techniques of polystyrene on clay by using ionic substances to support the surfactant bilayer. The intercalation of twin-tailed amphiphilic dioctadecyldimethyl ammonium (DDA) ion in smectite clay minerals provides a well-defined supported bilayer system. Polymerization of styrene in these aggregates allowed the effect of the restricted medium on the process and polymer to be studied. The result showed that polymerization of styrene in DODA-montmorillonite leads to phase separation between polystyrene and the surfactant matrix.

In 2000, *Bunsomsit* employed admicellar polymerization to produce a thin film of conducting polypyrrole (PPy) coating on natural rubber (NR) latex. Electrically conductive latexes were produced.

A continuous reactor system for admicellar polymerization was developed by *Chaisirimahamorakot* (2001). CTAB, styrene, isoprene, and precipitated silica were used. FTIR proved the existence of styrene and isoprene polymer on the modified silica. Effects of reaction time and monomer loading on amount of silica were studied showing that a loading of 5 g co-monomer per kilogram silica and 60 minutes polymerization time provided the largest amount of polymer on silica surface.

In a recent study of admicellar polymerization, *Yuan et al.* (2002) created thin films of poly(pyrrole) from on the surface of hydrophobic pyrolytic graphite and freshly cleaved mica with SDS and CTAB used as the surfactants. Separate

adsorbing and reacting solutions were used to eliminate diffusion of monomer from the bulk solution to the reacting surface, as well as to reduce or prevent solution polymerization. The result shows that for the hydrophobic substrate, the differences between films formed with and without surfactant were minor, but for hydrophilic substrates the differences were much more pronounced. Without surfactant only very discrete islands of poly(pyrrole) were seen. These differences are not understood at present with the most likely cause being poor reproducibility of transfer between the adsorbing and reacting solutions.

In 2002, *Masataka Hiraide and Atsushi Ishikawa* separated copper (II) ions and humic complexes in water by using alumina particles and admicellar sorbents consisting of anionic surfactants, describing the potential and utility of alumina and admicellar sorbents in chemical speciation. Copper-humic complexes were separated from copper (II) ions with the alumina sorbent, where as total dissolved copper was preconcentrated by the APDC (Ammonium Pyrrolidinedithio Carbamate)-method. Analytical results showed that 60-70 % of the total dissolved copper was present as negatively charged species (mainly humic complexes) in river water.