CHAPTER II
LITERATURE SURVEY

2.1 Cationic Surfactant Adsorption on Mica

In the studies of surfactant adsorption on solid surface, a full understanding of the results is often hampered by unknown factors such as surface heterogeneities, roughness and porosity. Molecularly smooth surfaces, such as mica, may be used to overcome these uncertainties. Mica is a layered silicate or phyllosilicate with a structure containing two-dimensional parallel sheets that control most of its physical properties. It is easily cleaved along a basal plane forming an atomically smooth surface with well defined structure of known ion-exchange property. The mica surface carries 2.1×10^{14} negative charges, which may be neutralized by an equivalent amount of potassium and sodium ions (~95%). Its point of zero charge (PZC) is 2.7-3.0. These features make it close to ideal for many fundamental studies (Chen *et al.*, 1992).

Because of the low PZC, cationic surfactants, many times a quaternary ammonium salt, are used as adsorbates. These are useful because of their versatile nature in controlling the stability of hydrocolloids (Meguro and Kondo, 1955) and modifying the surface properties of the solid. Kekicheff *et al.* (1989) studied adsorption of cetyltrimethylammonium bromide on mica at concentrations below the CMC using a surface force apparatus (SFA). They suggested that the adsorption of cetyltrimetylammonium cation ($C_{16}TA^+$) leads to the formation of a hydrophobic, near-neutral surface at a concentration about 1/200 of the CMC. At higher bulk concentrations a positive charge builds up as further $C_{16}TA^+$ ions adsorb, probably oriented with the polar group towards the water phase. A highly charged stable bilayer is formed at a concentration approximately ½ CMC. The adsorption process is governed by electrostatics as well as hydrophobic interaction. The molecular mechanisms and kinetics of adsorption of $C_{16}TA^+$ were studied by Chen *et al.* (1992). It was found that when the cationic surfactant (along with its counterion)

adsorbs onto mica, most of the surfactant molecules initially adsorb as dipoles onto the mica surface. After that, the oppositely charged counterions unite with the surface charges on the mica to form an ion pair that proceeds to slowly diffuse out of the head group region through the hydrophobic layer into the bulk solution, leaving behind heads that are now bound to the surface much more strongly via Coulombic (ionic) bonds. The ratio of adsorbed cationic surfactant molecules with single alkyl chains to the maximum potassium ions on mica surface is twice as large as that of surfactants having two alkyl chains (Bangyin et al., 1999; Fujii et al., 2001). The occupied area of quaternary ammonium surfactants on mica strongly depends on number of alkyl chain but is independent of alkyl chain length (Fujii et al., 2001). Exact surfactant structure at bulk concentrations above the CMC was first directly imaged by Manne and Gaub (1994) using atomic force microscopy. They found that tetradecyltrimethylammonium surfactant ($C_{14}TA^+$), at approximately twice its CMC, adsorbed primarily in structures consisting of meandering stripes of full cylinders separated by 5.3± 03 nm, and that these cylinders showed no consistent orientation with respect to the underlying lattice, in agreement with Sakai et al. (2001). In addition, Sakai et al. (2001) showed that the hexagonal lattice-like structure of surfactant aggregates was different from mica lattice in a wide range of surfactant covering both above and below the CMC. The thickness of adsorbed surfactant aggregates above the CMC was roughly twice the molecular length, in agreement with Kekicheff et al. (1989). However, cetyltrimethylammonium bromide ($C_{16}TAB$) behaves differently to other cationic surfactants in that it may form multilayered aggregates on mica at concentrations above the CMC (Grosse and Estel, 2000). The structure of CTA^+ on mica was parallel to those observed in bulk for both micellar and concentrated phases. Although shifted toward lower curvature aggregates, systematic structural changes within the molecules lead to changes in the adsorbed layer structure on mica. Even subtle effects such as chain length variation produce similar effects in bulk as at this interface (Patrick et al., 1999). For CTA^+ up to the CMC, AFM studies found that CTA^+ aggregates form patches with the thickness of about 4.2 nm (Ceotto et al., 2001). With the addition of salt, the sequence of adsorbed surfactant structure transformation is opposite to that of surfactant aggregates in solution, that is, transition from bilayer to long ordered cylinders,

disordered cylinders, short cylinders, and spheres occur as salt concentration is increased (Reuben *et al.*, 1998). The sharp Kraft transition in bulk is not accompanied by a similar change in morphology at the interface. Above Kraft temperature, where micelles are present in solution, adsorption proceeds via micelle-like structures, whereas below Kraft temperature, adsorption occurs via growth of flat islands, which gradually coalesce. (Liu, and Ducker, 1999) Heterogeneous growth and self-repairing processes of adsorbed CTA^+, below CMC, on mica directly involve two-dimensional Laplace pressure, linear tension, and two-dimensional isothermal distillation, as depicted by the simple analogy of Laplace-Kevin equation (Fujii *et al.*, 1999).

2.2 Ultra Thin Film Formation through Admicellar Polymerization

Surfactants adsorbed at the solid-liquid interface can form aggregates that are much like micelles. These micelles can be used to solubilize organic molecules in the same manner that micelles are used (O'Haver *et al.*, 1995). This phenomenon has been explored as a way to deposit ultra-thin films on solid surfaces. The process may be described as occurring in 4 major steps, (1) adsorption of surfactant to form two-dimensional aggregates on solid surface acting as reactant storage, (2) incorporation or adsolubilization of reactant monomer or initiator into the aggregates, (3) polymerization of monomer and/or initiator within the aggregates, and (4) removal of surfactant. The overall process, called admicellar polymerization, occurs below the CMC to minimize partitioning of monomer/initiator into micelles. Adsolubilization of monomer extensively depends on electrostatic contributions, monomer molecular volumes, the hydrophobic effect, and dipole interactions. The monomer can be liquid or gas and, to maximize adsolubilization, should be insoluble or only slightly soluble in water so that only a very small fraction is present in the bulk phase. Potential monomers are such as styrene, pyrrole, acrylonitrile, and tetrafluoroethylene. These monomers were used to modify solid surfaces such as alumina, silica, mica, and glass fibers in order to obtain specific surface functionality, surface morphology, mechanical properties, electrical properties and other specific properties depending on the applications.

Wu *et al.* (1987) reported polystyrene polymerized in sodium dodecylsulphate admicelles on alumina showing 75% and higher conversions of adsolubilized monomer to polymer after 25 minutes and uniform film with thickness of 13.0 nm. Styrene was also polymerized in quaternary ammonium surfactant on glass fiber by Sakhalkar and Hirt (1995) where nonuniform films were reported.

Ochiai *et al.* (2001) adsolubized acrylonitrile in sodium dodecylsulphate admicelles on mica in aqueous solution. Acrylonitrile was polymerized to polyacrylonitrile as a precursor to carbonization to form a carbon thin film. The acrylonitrile film shrank to form a granular structure on the mica after stabilization and granules aggregated after carbonization.

Funkhouser *et al.* (1995) studied pyrrole admicellar polymerization using sodium dodecylsulphate as surfactant on alumina powder. Pyrrole was found to decrease surfactant adsorption in contrast to alcohols, alkanes, and aromatic hydrocarbons. A particular pyrrole adsolubilization value can be attained with lower surfactant concentrations by the addition of salt. The interfacial concentration of pyrrole is increased by the addition of salt, enabling the use of admicellar polymerization with ammonium persulphate to produce thin, well-connected films on alumina plate. No film formation was observed using solutions of sodium dodecylsulphate without salt. In the same manner, Yuan *et al.* (2001) synthesized polypyrrole film with and without surfactant. Films grown in the absence of surfactant were thicker than 150 nm with wrinkles present, suggesting that internal film cohesion forces are stronger than the film-substrate interactions. Improved adhesion and suppressed formation of wrinkles were achieved by oxidative polymerization with surfactant, giving 50 nm thick films.

The admicellar polymerization of gaseous monomer was achieved by Lia *et al.* (1995). They accomplished to partition tetrafluoroethylene gas into admicelles of sodium perfluoroheptanoate on alumina in a high-pressure reactor.

2.3 Sol-Gel Reaction of Metal Alkoxide

Sol-gel is a method for preparing specialty metal oxide glasses and ceramics by hydrolyzing a chemical precursor or mixture of chemical precursors that pass sequentially through a solution state and a gel state before being dehydrated to glass or ceramic. Preparation of metal oxides by the sol-gel route proceeds through three basic steps: (1) partial hydrolysis of metal alkoxides to form reactive monomers (2) the polycondensation of these monomers to form colloid-like oligomers (sol formation) (3) additional hydrolysis to promote polymerization and cross-linking leading to a 3-dimensional matrix (gel formation). As polymerization and cross-linking progress, the viscosity of the sol gradually increases until the sol-gel transition point is reached. At this point the viscosity abruptly increases and gelation occurs. Further increases in the cross-linking are promoted by drying and other dehydration methods. Maximum density is achieved in a process called densification in which the isolated gel is heated above its glass transition temperature. The densification rate and transition (sintering) temperature are influenced primarily by the morphology and composition of gel. Although presented sequentially, these reactions occur simultaneously after the initial processing stage (Klein, 1988).

2.4 Hydrolysable Alkoxysilane Emulsion and Possibility of Adsolubilization of Tetra-N-Alkoxysilane

As well as emulsion polymerization, admicellar polymerization prefers highly hydrophobic monomer to minimize the lost of monomer in bulk solution. Thus, monomers which are commonly used for emulsion polymerization can be also used in admicellar polymerization because of the similarities between polymerization sites. Yet, admicellar polymerization has not to date been accomplished with inorganic monomers. Some inorganic compounds have been used to encapsulate components of surfactant solutions, specifically, the encapsulation of components in an oil-in water emulsion. Here, alkoxysilanes have been the primary compounds of focus.

Oil-in-water alkoxysilane emulsion polymerization has not been extensively studied yet. Most research works involving alkoxysilane emulsion focus on encapsulation of polymerisable alkoxysilane without its releasing and controlling the size of emulsion droplets. The surfactant can be nonionic, amphoteric, ionic, or combinations thereof. Typical pH and HLB values of the studied surfactants are 6-9 and 1.5-20, respectively. Without special encapsulation methods the low molecular weight emulsified silane compound has sufficient solubility in water to diffuse from smaller particles through the aqueous phase into larger particles via the Ostwald Ripening process. This results in a net increase in the average particle size of the emulsion with time. This can lead to consistent behavior or performance of the emulsion in commercial use due to changing properties of the emulsion with age.

To achieve good emulsion stability, Maeda (2001) prepared emulsions of hydrolysable silanes, such as alkoxysilanes, using an oil concentrate. The emulsifiers were initially stirred with water. An oil concentrate was then prepared by adding a hydrolysable silane to the stirring mixture of emulsifiers and water. Additional water was then dispersed in the oil concentrate to form the desired emulsion. Emulsions prepared by this process have shelf stabilities exceeding 6 months.

Fisher (2000) disclosed an aqueous emulsion of nonpolar silanes. The emulsion contains an emulsifier system that prevents particle size increase with time. The emulsifier system contains a primary surfactant that prevents coalescence of the particles by ionic repulsion between particles and a cosurfactant. The amounts of each surfactant in the emulsifier system are sufficient to provide an outer mixed monolayer that contacts the water phase and a second inner monolayer of essentially water insoluble cosurfactant. The mixed monolayer is a combination of both surfactants. The surfactant bilayer provides a barrier that prevents diffusion of the silane into the water phase, thereby minimizing diffusion of the silane out of the particle.

These applications with emulsification of polymerisable alkoxysilane raises the possibility of highly hydrophobic monomer, such as tetra-n-butoxysilane with moderately long alkyl chain and very low solubility in water being used in adsorbed surfactant systems. Electrostatic contribution, monomer molecular volume,

hydrophobic effect, and dipole interaction are still considered for adsolubilization of such monomer. Tetra-n-butoxysilane can be hydrolyzed in water very slowly (less than 1µmol/day at 15-100 °C, and pH 5-9) at TBOS concentration of 10-100 mg/L (Vancheeswaran *et al.*, 1999). Its solubility in water is less than 0.5 mg/L (less than styrene) indicating that it is highly hydrophobic. Because of high hydrophobicity, if TBOS is encapsulated by surfactant, it is gradually released to aqueous bulk. This aspect should be good for its encapsulation within admicelles.