CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Surfactant

2.1.1 General Features and Behavior

A surfactant is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surfaces or interfacial free energies of those surfaces (or interfaces). Surfactants have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a lyophobic group, together with a group that has strong attraction for the solvent, called the lyophilic group. This is known as an amphipathic structure. . If the solvent is water, the terms hydrophobic and hydrophilic are commonly used for the two portions of the molecule. The amphipathic structure of the surfactant therefore causes not only concentration of the surfactant at the surface and reduction of the surface tension of the water, but also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it. The hydrophobic group is usually a long chain hydrocarbon residue, and less often a halogenated or oxygenated hydrocarbon or siloxane chain; the hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are classified as:

1. Anionic. The surface-active portion of -the molecule bears a negative charge, for example, $RCOO^-Na^+$ (soap), $RCH_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate).

2. Cationic. The surface-active portion bears a positive charge, for example, $RNH3^+Cl^-$ (salt for a long-chain amine), $RN(CH_3)_3^+Cl^-$ (quarternary ammonium chloride).

3. Zwitterionic. Both positive and negative charges may be present in the surface-active portion, for example, $RN^+H_2CH_2COO^-$ (long-chain amino acid), $RN^+(CH_3)_2CH_2CH_2SO_3^-$ (sulfobetaine).

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4. Nonionic. The surface-active portion bears no apparent ionic charge, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid), $RC_6H_4 (OC_2H_4)_xOH$ (polyoxyethylenated alkylphenol).

Differences in the nature of the hydrophobic groups are usually less pronounced than in the nature of the hydrophilic group. Generally, they are long-chain hydrocarbon residues. However, they include such different structures as:

1. Straight-chain, long alkyl groups (C_8-C_{20})
2. Branched-chain, long alkyl groups (C_8-C_{20})
3. Long-chain (C_8-C_{15}) alkyl benzene residues
4. Alkylnaphthalene redues (C_3 and greater-length alkyl groups)
5. Rosin derivatives
6. High-molecular-weight propylene oxide polymers (polyoxypropylene glycol derivatives)
7. Long-chain perfluoroalkyl groups
8. Polysiloxane groups
9. Lignin derivatives

2.1.2 General Effects of the Nature of the Hydrophobic Group

a. Length of the hydrophobic group

Increase in the length of the hydrophobic group results in: (1) decreases the solubility of the surfactant in water and increases its solubility in organic solvents, (2) causes closer packing of the surfactant molecules at the interface (provided that the area occupied by the hydrophilic group at the interface permits it), and (3) increases the tendency of the surfactant to adsorb at an interface or to form micelles.

b. Branching, Unsaturation

The introduction of branching or unsaturation into the hydrophobic group leads to the followings: (1) increases the solubility of the surfactant in water or in organic solvents (compared to the straight-chain, saturated isomer), (2) causes looser packing of the surfactant molecules at the interface (the cis isomer is particularly loosely packed; the trans isomer is packed almost as closely as the

saturated isomer) and inhibits liquid-crystal formation in solution, (3) may decrease biodegradability in branched-chain compound.

c. Aromatic nucleus

The presence of an aromatic nucleus in the hydrophobic group may cause effects such as: increase the adsorption of the surfactant onto polar surfaces, (2) decrease its biodegradability, and (3) cause looser packing of the surfactant molecules at the interface. Cycloaliphatic nuclei, such as those in rosin derivatives, are even more loosely packed.

d. Polyoxypropylene chain

The presence of this in the hydrophobic group is found to: (1) increases adsorption of the surfactant onto polar surfaces via the hydrophobic group, and (2) increases the solubility of the surfactant in organic solvents.

e. Perfluoroalkyl or polysiloxane group

The presence of either of these groups as the hydrophobic group in the surfactant permits reduction of the surface tension of water to lower values that those attainable with a hydrocarbon-based hydrophobic group. Perfluoroalkyl surface are both water- and hydrocarbon-repellent.

2.2 Surfactant Adsorption and Adsolubilization

2.2.1 Adsorption of Surfactant

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors: (1) the nature of the structural groups on the solid surface-whether the surface contains highly charged sites or essentially nonpolar groupings, and the nature of the atoms of which these sites or groupings are constituted; (2) the molecular structure of the surfactant being adsorbed (the adsorbate)-whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic or aromatic; and (3) the environment of the aqueous phase-its pH, its electrolyte content, the presence of any additives such as short-chain polar solutes (alcohol, urea, etc.), and its temperature. Together these factors determine the mechanism by which adsorption occurs, and the efficiency and effectiveness of adsorption (Rosen, 1989).

The adsorption isotherm of an ionic surfactant onto an oppositely charged substrate, for example, sodium alkanesulfonates and alkylbenzenesulfonates onto oppositely charged Al_2O_3 is typically an "S"- shaped curve when one plots the log of the adsorbed surfactant density versus the log of the equilibrium concentration of surfactant. Normally, this "S"- shaped isotherm can be separated into four regions, as shown in Figure 2.1. Region I is a low adsorption density region in which the surfactant adsorption shows a linear dependence on surfactant concentration. This is indicative of an absence of lateral interactions between the adsorbed surfactant molecules. Region II is indicated by an increase in the slope of the adsorption isotherm; this increase in slope is indicative of the onset of attractive lateral interaction between the surfactants that results in the formation of micelle-like surfactant aggregates at the solid/liquid interface. The transition has been given designations analogous to the critical micelle concentration (CMC), that is, the critical admicelle concentration (CAC) or hemimicelle concentration (HMC), depending upon which theory one subscribes to. All of the factors that result in the lowering of the CMC of a surfactant can be expected to increase the formation of admicelles, also.
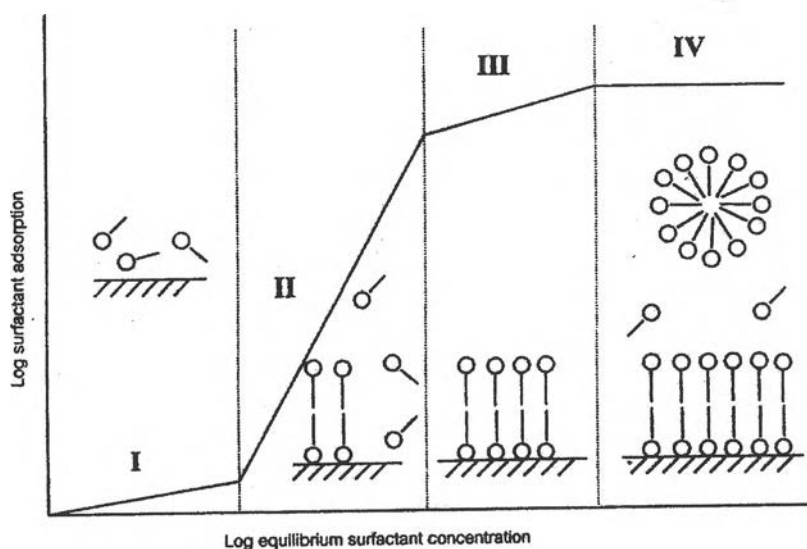
Figure 2.1 Typical adsorption isotherm of surfactant on solid oxide surface.

Region III is a region where the slope of the isotherm decreases because of the onset of repulsive lateral interactions between admicelles. Region IV is a region where the adsorption reaches a plateau either because the surface has become saturated with admicelles or because the surfactant concentration in the solution has reached the CMC of the surfactant. At the CMC, the first micelle forms at the same chemical potential as the last admicelle to form; if the surfactant concentration is increased further, this only results in the formation of more micelles at the same chemical potential as that of the first micelle to form, without an increase in the adsorption of more surfactant.

Yeskie and Harwell (1988) studied the structure of the adsorbed surfactant aggregates, focusing on the surface charge density at the hemimicelle/admicelle transition. They found that surfactants adsorbed from aqueous solution onto mineral oxide surface formed micelle-like aggregates at the interface. It has long been viewed that at low coverage these surfactant aggregates are principally in the form of monolayers, formed on patches of the surface. Individual surfactant molecules or monomers in these aggregates are viewed as being oriented such that the hydrophilic groups of the surfactants are next to the surface, with the surfactant tail groups forming a hydrophilic film in contact with the aqueous solution. Aggregates of this structure are commonly referred to as hemimicelles while it has been proposed that a bilayered aggregate, termed an admicelles, is formed (Scamehorn *et al.,* 1981).

Atkin *et al.* (2000) studied the adsorption of cetyltrimethylammonium bromide (CTAB) to the silica-aqueous interface by using optical reflectometry. They also studied the effect of pH, salt, and surface preparation on the surface excess and adsorption kinetics. The results have been shown that, above the critical micelle concentration (CMC), micelles adsorb directly to the silica surface, and this is reflected in the structure of the surface layer. At the critical surface aggregation concentration (CSAC), the equilibrium surface structure is analogous to adsorbed micelles, but as only monomers are present in solution, the adsorption proceeds to equilibrium slowly.

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2.2.2 Solubilization and Adsolubilization

Solubilization is defined as the spontaneous dissolving of a substance (solid, liquid or gas) by reversible interaction with the micelle of the surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material. The partitioning of organic solutes from aqueous solution into the interior of adsorbed surfactant aggregate is termed adsolubilization. This phenomenon is the surface analog of solubilization, with adsorbed surfactant bilayer playing the role of micelle, as shown in Figure 2.2.
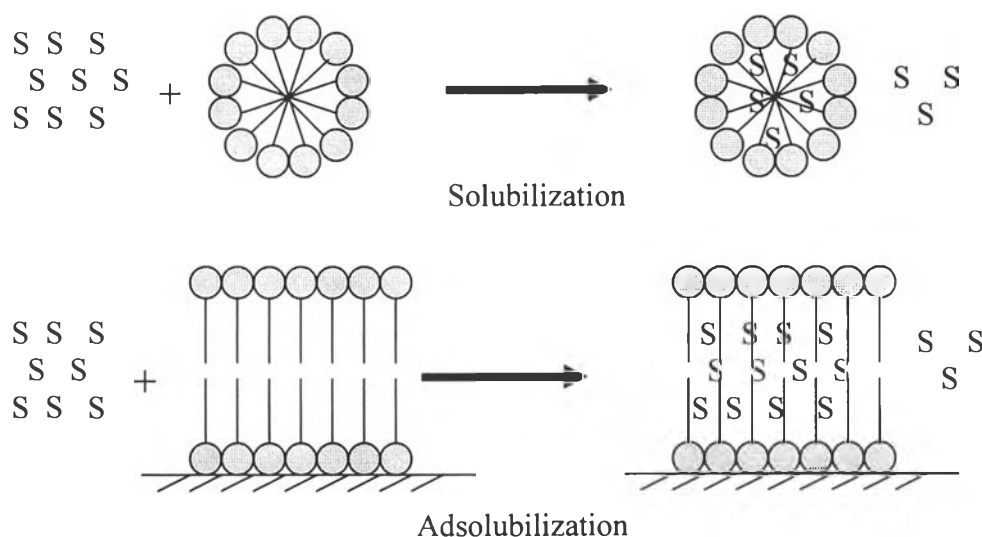

Figure 2.2 The phenomena of solubilization and adsolubilization (Dickson and O'Haver, 2002).

Kitiyanan *et al.* (1996) studied adsolubilization of styrene and isoprene into cetyltrimethylammonium bromide (CTAB) admicelle on precipitated silica. The results from single adsolubilizate systems showed that styrene adsolubilization increase with increasing styrene equilibrium concentration in aqueous phase, and isoprene adsolubilization increases with increasing isoprene partial pressure. The adsolubilization equilibrium constants of both adsolubilizates were calculated, and suggested that styrene is adsolubilized into both the palisade

layer and the core of admicelle, while isoprene is adsolubilized only into the palisade layer.

Thakulsukanant *et al.* (1997) studied adsolubilization characteristics and stability characteristics of hydrocarbon aggregates chemically bonded to porous silica. In this study, octadecyltrichlorosilane (ODS) was chemically bonded with silanol groups of silica surface. The adsolubilization capabilities and stability of the bonded ODS were evaluated and compared to those of physically adsorbed aggregates of cetyltrimethylammonium bromide (CTAB). The adsorption of ODS increased with increasing ODS concentration in the bulk phase and reached a constant value when the equilibrium ODS concentration was higher than 1700 μM.

Dickson and O'Haver (2002) investigated the adsolubilization of Naphthalene and α-Naphthol with have the similar structures but different in polarities, both individually and in pairs, in C_nTAB (n=12, 14, 16) admicelles. They investigated the adsolubilization capacities of the core and palisade regions within the admicelle and their interactions within the admicelle. They also examined the effects of tail length and admicelle packing on the adsolubilization process. The results indicate that there is not a clear relationship between surfactant tail length and the maximum solute adsolubilization. Through an examination of the plateau adsorption and the area per molecule for each surfactant, suggestions concerning the packing of the admicelles have been proposed to explain the observed trend.

2.2.3 Factors Affecting Adsorption and Adsolubilization

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors:

- The nature of the structural groups on the solid surface-whether the surface contains highly charged sites or essentially nonpolar groups, and the nature of the atoms of which these sites or groupings are constituted.

Chorro *et al.* (1999) studied the effect of the state of the silica surface and of the surfactant molecular structure on the adsorption of cationic surface onto silica. The adsorption of sosecyltrimethyl ammonium bromide (DTAB) and the demeric surfactant 12-2-12 (ethanediyl-1, 2-bis (dodecyldimethyl ammonium

bromide)) on raw silica (SiNa) and on HCl washed silica (SiH) were investigated under "free" system conditions. The results showed that the amount of surfactant adsorbed at the point of zero charge and at saturation of the silica particles, the sodium ions released by the surface and the decrease in critical micelle concentration (CMC) of the supernatant with respect to pure water are all larger for the raw silica than for the treated silica.

- The molecular structure of the surfactant being adsorbed-whether it is ionic or nonionic, and whether the hydrophobic group is long or short, straight-chain or branched, aliphatic or aromatic.

The adsorbed amount of quaternary ammonium cationic surfactants on silica at saturation decreased with increasing chain number of the surfactant (one, two, and three alkyl chains). Under a constant feed concentration of 2-naphthol, the adsolubilized amount of 2-naphthol increased, reached a maximum, and then decreased with single-chain or double chain surfactant concentration. The ratio of amount of 2-naphthol adsolubilized to the adsorbed amount of surfactant on silica for the double-chain and triple-chain surfactants were not so different and were quite large compared to that for the single-chain surfactant. In addition, from the two-step adsorption-adsolubilization procedure, it was found that the double-chain or triple-chain surfactant adsorbs strongly on the silica surface (Esumi *et al.*, 1996).

- The environment of the aqueous phase (pH and ionic strength). Properties of the aqueous phase such as pH that usually causes marked changes in the adsorption of ionic surfactants onto charged solid substrate. As the pH of the aqueous phase is lowered, a solid surface will usually become more positive, or less negative, because of adsorption onto charged sites of protons from the solution, with consequent increase in the adsorption of cationic. The reverse is true when the pH of the aqueous phase is raised. These effects are shown markedly for mineral oxide, such as silica and alumina, and by wool and other polyamide. Change in the pH also may affects surfactant molecules, notably those containing carboxylate group (soap) or nonquaternary ammonium group. In these cases, change in the pH may convert the surfactant from one containing an ionic group capable of strong adsorption onto oppositely charged sites on the adsorbent to a neutral molecule capable of adsorption only through hydrogen bonding or dispersion forces. Change in pH also may affect

nonionic surfactants, notably those having polyoxyethylene chain, because the ether linkage in these chains can be protonated at low pH, yielding positively charged grouping that may adsorb onto negatively charged substrate. Moreover, the effect of the ionic strength on the adsorption is also very important to study because it can change the CMC, counterions stabilize ionic surfactant micelles by binding to the micelle surface and screening the electrostatic repulsions between the ionic headgroups, the effect being more pronounced for anionic and cationic than for zwitterionic surfactant and more pronounced for zwitterionic than for nonionic.

Monticone and Treiner (1995) studied effect of pH and ionic strength on the adsorption of cetylpyridinium chloride and the coadsorption of phenoxypropanol at a silica/water interface. The effects of pH and ionic strength on both of these phenomena were investigated. It was shown that the solute partition coefficient between the adsorbed aggregates and the solution was independent of pH and of ionic strength and was equal to the partition coefficient of the classical micellar solubilization effect for the same solute/surfactant system.

Behrends and Herrmann (2000) studied the adsolubilization of anthracene on surfactant covered silica in dependence of pH: indications for different adsolubilization in admicelle and hemimicelle. They studied the distribution of anthracene between aqueous solution and silica gel covered with the cationic surfactant hexadecyltrimethylammonium bromide (HDTMA) in batch experiments as a function of the adsorption density of HDTMA and in dependence on pH. It was observed that the partitioning constant (K) normalized on the content of organic carbon in the surfactant coverage was not only a function of the surface concentration but also depended on pH. At low concentrations of adsorbed HDTMA, no adsolubilization of anthracene was measured.

Pradubmook (2003) studied the effect of pH on adsolubilization of a cationic surfactant, cetyltrimethylammonium bromide (CTAB), on precipitated silica and adsolubilization of toluene and acetophenone in CTAB at two pH values. Both single-solute and mixed-solute systems were investigated using batch liquid adsorption at pH 5 and pH 8. The results from the adsorption of CTAB revealed that increasing pH led to high amounts of surfactant adsorbed on the precipitated silica. In the single solute system, the adsolubilization of both solutes increased with

increasing equilibrium concentration of the solute in the aqueous phase. For toluene, pH appeared to have little effect on the adsolubilization. In contrast, the pH effect was more pronounced in the case of acetophenone as indicated by significant increase in the acetophenone adsolubilization when pH was increased from 5 to 8. In the mixed solute system, the presence of acetophenone had very little effect on toluene adsolubilization whereas the presence of toluene had synergistic effect on acetophenone adsolubilization. Moreover, the analyses through the use of the adsolubilization equilibrium constant (K) suggested that toluene adsolubilized into both the palisade layer and core of admicelle while acetophenone adsolubilized into palisade layer only.

Kanjanakhunthakul (2002) studied the effects of ionic strength on the adsolubilization of toluene and acetophenone into CTAB admicelles on precipitated silica. The adsolubilization of the model organic compounds, toluene and acetophenone, was investigated both in single-solute and mixed-solute systems. For both adsorption and adsolubilization, batch experiments were carried out at two different pH values (5 and 8) under various ionic strengths (1, 10 and 100 mM). The results showed that the adsorption of CTAB on the silica surface increased with increasing ionic strength. In the single-solute system, increasing ionic strength had little effect on the adsolubilization of toluene. However, the adsolubilization of acetophenone significantly increased with increasing ionic strength, especially at 100 mM. In the mixed-solute system, the synergetic effect was observed in the adsolubilization of acetophenone in the presence of toluene and the effect was more pronounced with increasing ionic strength. In contrast, the presence of acetophenone had little effect on the adsolubilization of toluene.

2.2.4 Mixed-Surfactant System

Penfold et $al.$ (2000) studied the adsorption of the mixed cationic and nonionic surfactants of hexadecyltrimethylammonium bromide ($C_{16}TAB$) and hexaethylene monododecyl ether ($C_{12}EO_6$) at the hydrophilic silicon-solution interface by using specular neutron reflection. The effect of solution composition and concentration on the adsorbed amount, surface structure, and composition has been investigated at pH 2.4. The results obtained are compared with those reported

elsewhere for the adsorption of the same surfactant mixture at the air-water interface and for surfactant mixing in micelles. Consistent with other studies, the structure of the adsorbed layer is described as a "defective" bilayer or "flattened" micelles. The variation in the adsorbed amount with solution composition is a maximum at an equimolar solution composition. For solutions richer in $C_{16}TAB$, the surface and solution compositions are identical. Whereas for solutions richer in $C_{12}EO_6$ there is a departure from ideality, and the surface is richer in the cationic surfactant.

Esumi *et al.* (2001) investigated the adsolubilization of 2-naphthol by binary mixtures of cationic and nonionic surfactants on silica. Two cationic surfactants were hexadecyltrimethyl ammonium bromide (HTAB) and 1,2-bis(dodecyldimethyl ammonio) ethane dibromides (2RenQ), and a nonionic surfactant was hexaoxyethylenedecyl ether ($C_{10}E_6$). In the single surfactant systems, adsolubilization of 2-naphthol for HTAB and 2RenQ was very similar and was greater than that for $C_{10}E_6$. In the HTAB/ $C_{10}E_6$ system the adsolubilization of 2-naphthol was enhanced by surfactant mixtures of HTAB and $C_{10}E_6$ compared to those of single systems. However, in the 2RenQ/$C_{10}E_6$ system the adsolubilization of 2-naphthol by surfactant mixtures of 2RenQ and $C_{10}E_6$ was rather smaller than that of 2RenQ alone but still larger than that of $C_{10}E_6$. It is found that the adsorbed layers of surfactant mixtures formed from different surfactant structures exhibit different adsolubilization behaviors of 2-naphthol, and the alkyl chain length of the surfactants is an important factor to correlate with the adsolubilization of 2-naphthol.

Penfold *et al.* (2002) investigated the structure and composition of the mixed anionic and nonionic surfactants adsorbed at the hydrophilic silica solid-solution interface by using specular neutron reflectivity. Measurements show that the anionic surfactant sodium dodecyl sulfate (SDS) is adsorbed at the hydrophilic silica surface in the presence of the nonionic surfactant hexaethylene monododecyl ether but has no affinity for the surface in the absence of the nonionic surfactant. The variations of adsorbed amount, composition, and structure of the adsorbed layer are shown to reflect the different affinities of the two surfactants for the hydrophilic surface. At a solution concentration grater than the critical micellar concentration, the adsorbed amount decreases for solutions increasingly rich in SDS, and the surface composition is not consistent with the pseudo phase approximation.

2.3 The Effect of Surfactant Structure on Adsorption and Adsolubilization

The chemical structure of surfactant hydrophobic group influences on the adsorption and adsolubilization. The surface-active properties of a surfactant are therefore determined by its numerous structural characteristics, which include the following (a) the length and number of hydrocarbon chains in the structure, (b) the configuration of the chain or chains including branching and the number and location of double bonds in the chains, (c) the position of the ionic group(s) in the structure, and (d) the number and nature of nonionic hydrophillic group(s) in the structure.

Abdel-Khalek *et al.* (1999) studied the surface and thermodynamic properties of some synthetic surfactants, as well as their efficiency as collectors (surfactants) in the flotation of petroleum coke, are studied. These surfactants are monoisomeric alkylbenzenesulfonate of different alkyl chains (C12 to C14). The results show that the length of the hydrocarbon chain of these surfactants plays a major role in determining their surface and thermodynamic properties. The values of surface excess concentration (Γ_{max}) and Gibbs energy of micellization (ΔG^0_{mic}) are found to increase with increasing number of carbon atoms in the chain while the values of critical micelle concentration (CMC) are decreased. The results also indicate that there is a good relationship between effectiveness of adsorption of a surfactant and its efficiency as a collector.

Downer *et al.* (1999) investigated the adsorption at the air/water interface of four fluorinated surfactants by using tensiometry and neutron reflection (NR). These compounds were two single-chain carboxylates-sodium perfluorononanoate (NaPFN) and sodium 9H-perfluorononanoate (HNaPFN)-and two double-chain sulfosuccinates-sodium bis (1H, 1H-perfluoropentyl)-2-sulfosuccinate (DCF4) and sodium bis (1H, 1H, 5H-octafluoropentyl)-2-sulfosuccinate (DHCF4). The replacement of a terminal fluorine for hydrogen creates a permanent dipole in the hydrophobic chain tip which significantly affects the surfactant behavior. This change in structure leads to an increase in the critical micelle concentration (CMC). Partial structure factors of the adsorbed layers were determined for all four surfactants. The widths of the surfactant distributions were found to be significantly broadened by roughness at the interface. The widths of the solvent distribution were

about 5 A° for the carboxylates and essentially 6 A° for the sulfosuccinates. In all cases the measured separations of the water and surfactant distributions were 5 A°, indicating a greater penetration of water into the sulfosuccinate layers. The contribution of capillary waves to the surface roughness was examined in order to assess the static disorder of molecules in the adsorption layer. The presence of the chain dipole does not appear to cause any significant structural differences normal to the interface.

Factor *et al.* (2001) studied the effects of nonionic surfactant chain length on the properties of tris(2,2'-bipyridyl)ruthenium(II)(Ru(bpy)$_3{}^{2+}$) ,where bpy=2,2'-bipyridine, electrochemiluminescence (ECL) have been investigested. The electrochemistry, photophysics, and ECL of Ru(bpy)$_3{}^{2+}$ in the presence of a series of nonionic surfactants are reported (Triton x-100, 114, 165, 405, 305, and 705-70). These surfactants differ in the number of poly(ethylene oxide) units incorporated into the surfactant molecule. The anodic oxidation of Ru(bpy)$_3{}^{2+}$ produces ECL in the presence of tri-*n*-propylamine (TprA) in aqueous surfactant solution. Increases in ECL efficiency ($\geq$5-fold) and TPrA oxidation current ($\geq$2-fold) have been observed in surfactant media. Slight decreases in ECL intensity are observed as the chain length of the nonionic surfactant increases. The data supports adsorption of surfactant on the electrode surface, thus facilitating TprA and Ru(bpy)$_3{}^{2+}$ oxidation and leading to higher ECL efficiencies.

Jodar-Reyes *et al.* (2002) studied the effect of structural details of nonionic surfactants on micellization in solution and the adsorption on solid-liquid interfaces by applying the classical one-gradient self-consistent-field (SCF) theory for adsorption and/or association. This is illustrated by using two models for the molecule with the same overall structure, one with a linear and one with a more realistic branched hydrocarbon tail. The critical micelle concentration is computed for several lengths of the poly(oxyethylene) headgroup. They also studied the adsorption isotherms of these small surfactants on hydrophobic surfaces. Theoretical results are critically compared to the experimental results for critical micelle concentrations and adsorption isotherms of Triton X-100 and Triton X-405 onto a polystyrene latex dispersion. From this comparison, it was concluded that a SCF

model in which homogeneous adsorbed layers are preassumed fails to reproduce experimetal findings. It is speculated that lateral inhomogeneties must be included in the SCF model to improve its performance.