CHAPTER II

BACKGROUND

2.1 Solubilization

In aqueous solutions above the Critical Micelle Concentrations (CMC), ionic surfactant molecules form roughly spherical aggregates (Figure 2.1). The charged hydrophilic head groups are placed near the surface of the micelle, and the hydrophobic alkyl chains are extended towards the center of the aggregate. The organic solutes will tend to solubilize within the interior region (hydrophobic core) of the micelle causing a high local concentration (compared to the bulk phase) of the organic solutes (Figure 2.2). The organic substrates can also be specifically aligned within the micelle. For example, an organic molecule that has the polar or charged group like OH or COO^- tends to solubilize with the hydrophilic groups oriented towards the micelle surface (Fendler and Fendler, 1970; and Lee et al., 1991). The increase of concentration near the micelle surface of oppositely charged reagents may be the effect of electrostatic interactions with the charged head groups which may also stabilize reaction transition states within or at the surface of the micelle (Rosen, 1989). Such factor can therefore enhance rates or selectivities of reactions involving the organic substrates.

According to the pseudophase ion exchange (PIE) model (Romsted, 1977;1984), micelles can be treated as a separate phase. The hydrophobic reactants are assumed to partition preferentially into the micelle, thus enhancing the local (micellar) concentration. Ionic species in the aqueous

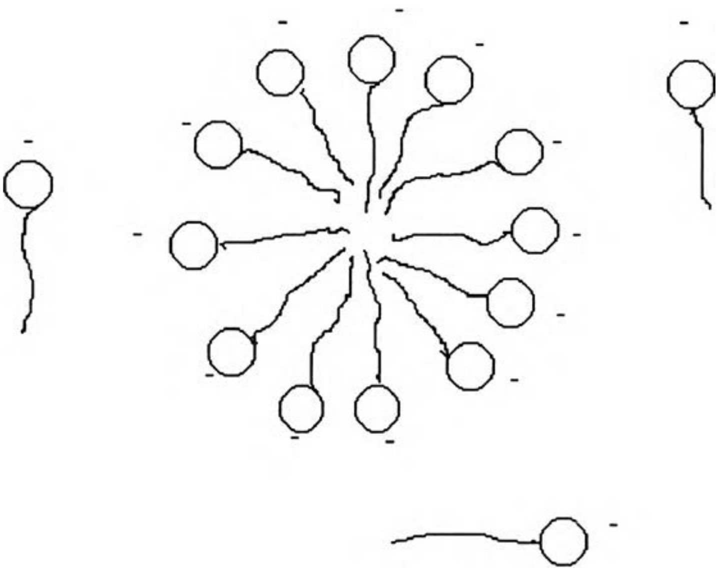


Figure 2.1 Anionic surfactant molecule.

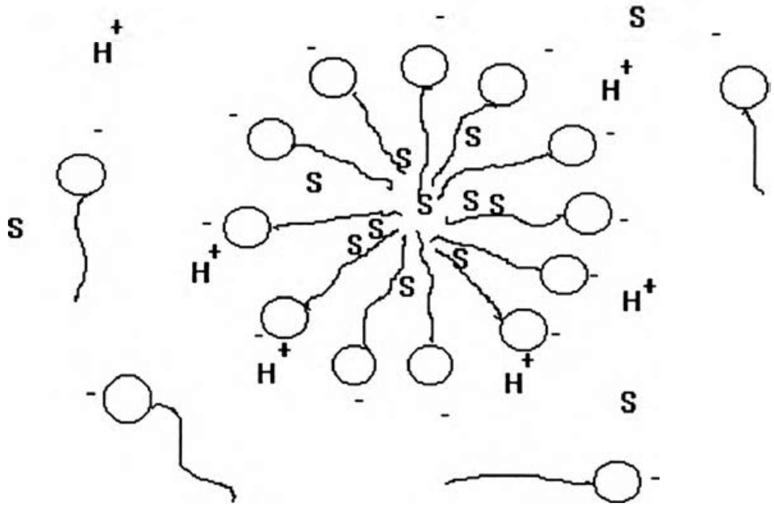


Figure 2.2 Solubilization of organic substrate S and binding of H^+.

phase exchange with counterions bound by electrostatic interaction to the micelle. The ionic species are located primarily in the Stern layer of the micelle. Consequently, the local concentration of positive ions are enhanced in systems with anionic surfactant micelles, while the local concentration of anionic species is enhanced by cationic surfactant micelle systems.

Studies of solubilization of organic solutes by surfactant micelles have been presented in the literature. The solubilization of mono- and dichlorophenols by hexadecylpyridinium chloride (CPC) micelles (Lee et al., 1990) showed that the effect of additional of chloride groups is to increase the value of solubilization equilibrium constant at any value of mole fraction of the phenol present in the micelles, although positional effect are also significant.

The effect of pH was studied in the solubilization of 2-phenylethanol (PEA) by dodecyldimethylamine oxide (DDAO) (Uchiyama et al., 1991). The DDAO in micellar form is all cationic at low pH, all nonionic at high pH and both cationic and nonionic at intermediate pH. The solubilization equilibrium constant decreased with increasing mole fraction of PEA in the micelles for all pH values and was less in the mixed micelles than in either cationic or nonionic micelles, which could be due to the more compact hydrophilic region of the mixed micelle.

Smith et al. (1987) have been able to develop a group contribution method to estimate free energies of transfer of solutes between the ideal gaseous state and the interior of aqueous surfactant micelles. The structure formula of the solute and the value of its Henry's law constant in water are only required to predict the limiting equilibrium constant for transferring the solute from the infinitely dilute solution in water into the micelle.

2.2 Surfactant Adsorption on Solid Surface

The adsorption of ionic surfactant from aqueous solution on the oppositely charged substrates has been studied for quite sometime (Rosen, 1989). In aqueous solution, the protonation or deprotonation of chemically adsorbed water will change the solid surfaces to be charged, depending on the pH value of solution. Numerous studies have indicated the adsorption of surfactant on high surface area solids such as alumina or silica (Scamehorn et al., 1982; and Wu et al., 1988). In mildly basic environments, cationic surfactants readily adsorb on silica; in mildly acidic environments, anionic surfactants adsorb on alumina.

The adsorption isotherm of ionic surfactants on oxide surfaces is generally an 'S'-shaped graph when the adsorbed surfactant is plotted with equilibrium concentration of surfactant in logarithmic system (Somasundarun and Fuerstenau, 1966; and Scamehorn et al., 1982). Normally, there are three or four distinguishable regions of quantitatively different behavior (Figure 2.3). Region I corresponds to both very low concentration and low adsorption of surfactant that governed by Henry's law, i.e.,

$$\Gamma = h^*[C]_w \qquad \text{-----(1)}$$

Here Γ is the total Gibbs adsorption of the surfactant, h is the Henry's law coefficient for adsorption at coverage below the onset of aggregation and $[C]_w$ is the surfactant monomer concentration.

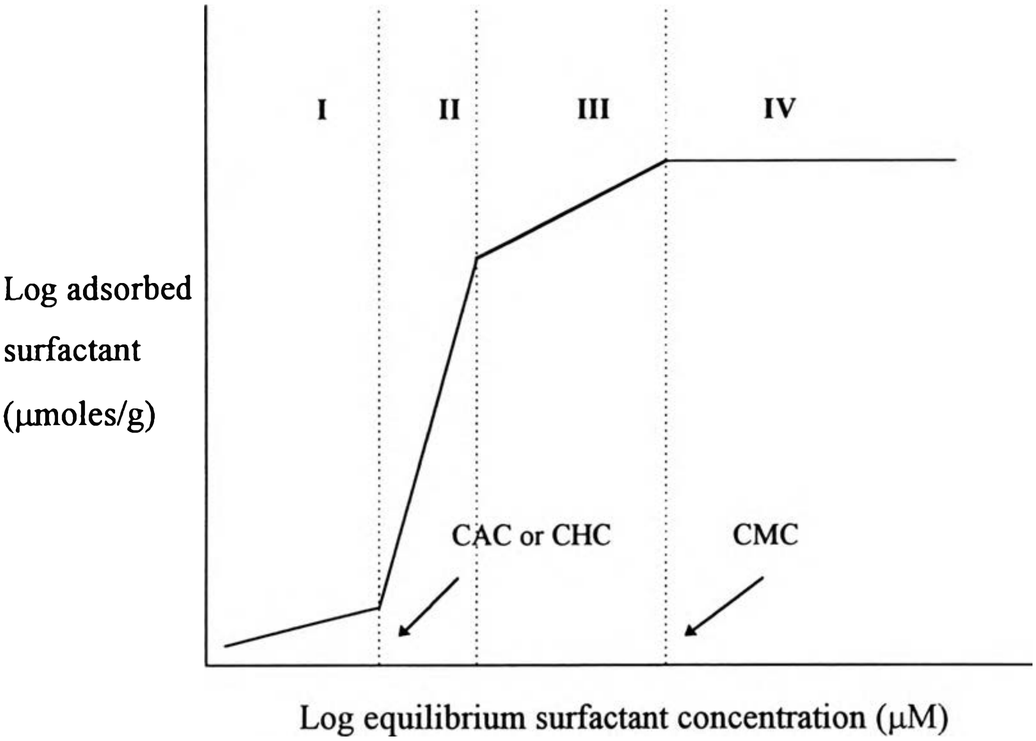


Figure 2.3 A typical surfactant adsorption isotherm.

Region II is distinguished by a sharp increase in the slope of isotherm that indicates the initiating of lateral interactions between neighboring molecules, which results in the formation of surfactant aggregates on the most energetic surface sites (Scamehorn et al., 1982). The surfactant aggregates at the region I/II transition are called hemimicelles (Somasundarun and Fuerstenau, 1966) or admicelles (Harwell et al., 1985). The hemimicelle is a monolayer structure that has the head group adsorbed on the solid surface while the tail group is in contact with the aqueous phase. The admicelle is viewed as a local bilayer structure with head group of lower layer adsorbed on solid surface and the head group of upper layer extended into the solution. The surfactant concentration at this point is labeled the CAC (critical admicelle concentration) or CHC (critical hemimicelle concentration), depending on one's believing which morphology of the aggregates exist.

In region III, the decrease in slope is found and can be ascribed by increasing electrostatic repulsion of ions from the interface because of interfacial charge reversal. The studies of surfactant aggregates in region II and region III by using fluorescence spectra (Esumi et al., 1990), neutrons reflection (Lee et al., 1990) or the theoretical predictions (Scamehorn et al., 1982) have shown that at high surface coverage the surfactant aggregates are bilayers.

Region IV is the plateau region, where the completion of surfactant adsorption is reached and micelles are instantaneously occurred in the aqueous phase. Typically, the equilibrium surfactant concentration at the region III/IV transition point is approximately at the critical micelle concentration (CMC).

There are many parameters affect the adsorption of surfactants such as the electrochemical nature of the substrate, the pH value of solution and the type of surfactant of molecule. The adjust of pH of the contacting aqueous solution can manipulate the charge on mineral oxide surface to be either positive or negative because both H^+ and OH^- are potential determining ions of mineral oxides. The point of zero charge (PZC), the charge on the solid surface will be changed to zero by pH adjusting. When the pH of the contacting aqueous solution is below the PZC of the solid oxide surface, the surface will be protonated and positively charged. On the other hand, the surface will be negatively charged at pH above the PZC.

2.3 Adsolubilization

Analogous in nature to micelles, the organic substrates can be partitioned into the hydrophobic environment between the hydrocarbon chains of the adsorbed surfactant aggregates (both hemimicelles and micelles), as shown in Figure 2.4. The suggest definition of adsolubilization is 'the incorporation of compound into surfactant surface aggregates, which compound would not be in excess at the interface without surfactant" (Scamehorn and Harwell, 1988).

Nun et al., (1982) showed that the organic substrate can be solubilized into the organic environment of adsorbed surfactants by using visual evidence of pinacyanol chloride which is a dye of cyanide class. The dissolved pinacyanol chloride in aqueous solution in which the surfactant was below the CMC gave a red color, indicating that the dye was in an aqueous environment. The blue color appears when the dye was dissolved in aqueous solution of surfactants above the CMC or organic solvents, indicating that the dye is in organic environment. In aqueous surfactant solution below the CMC, the blue color also occurred on an alumina surface on which anionic surfactants had been adsorbed. The blue color was observed both on the surface of alumina and in aqueous phase when the bulk concentration of surfactant was above the CMC. This result indicated that pinacyanol can be partitioned between micelles and admicelles, and showed the similar nature between the interior of admicelles and of micelles.

Livitz and co-workers (Livitz et al., 1984; and Levitz and Van Damme, 1986) used fluorescence decay spectroscopy and pyrene as a probe to determine the structure of the adsorbed bilayer of Triton X-100 (octylphenoxyethanol with an average of 9 to 10 oxyethylene units). This research also supported the hydrophobic environment of the core of micelles and confirmed the adsolubilization of hydrophobic molecules.

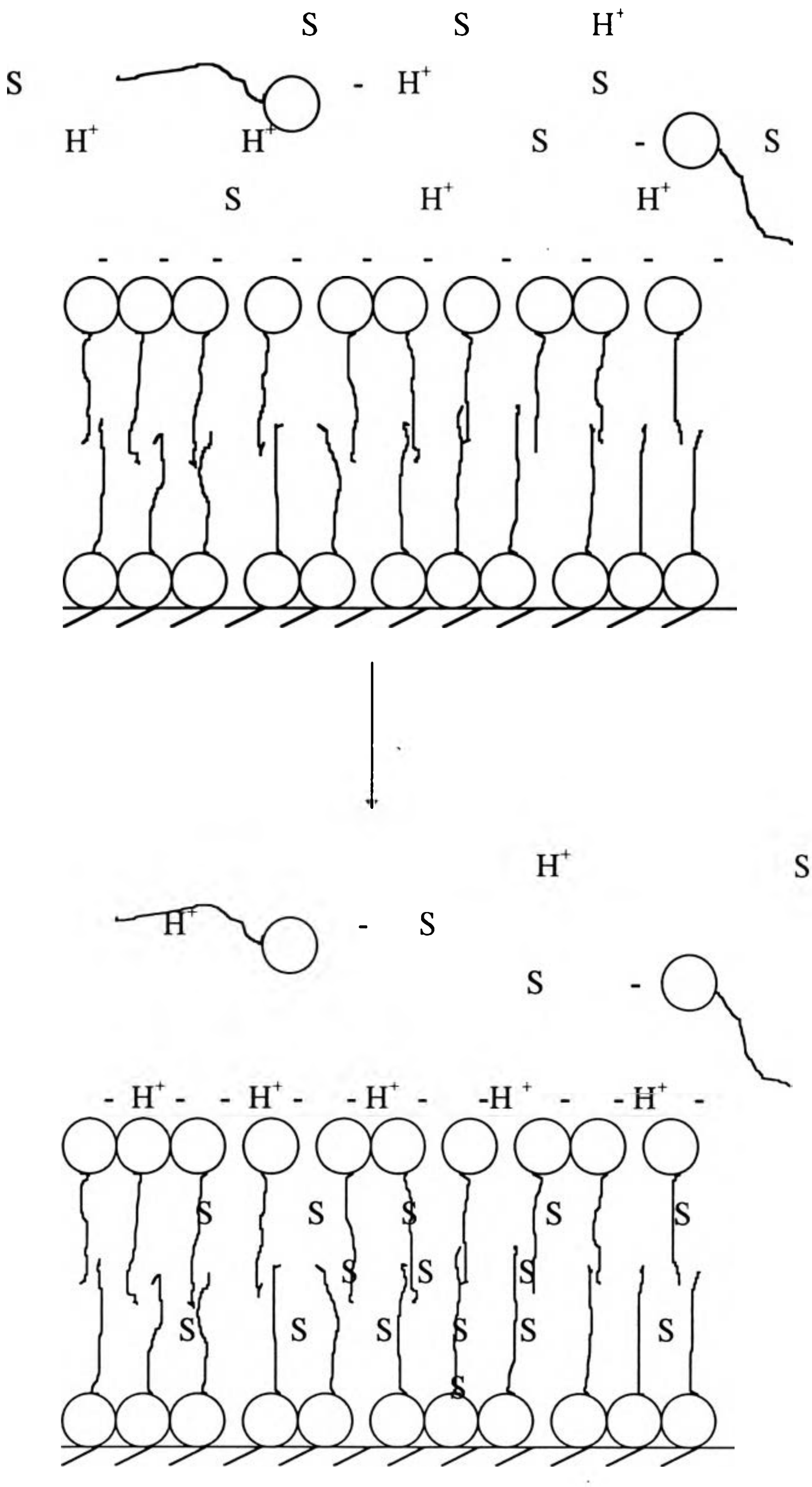


Figure 2.4 Adsolubilization of organic solute S and binding of H$^+$ to admicelle.

In 1988, Yeskie systematically studied the adsolubilization of both series of alcohols and alkanes into admicelles on alumina. For the adsolubilization of alcohols, the ratios of alcohol to SDS molecules in the admicelles were very high at low levels of surfactant adsorption. The increase of surfactant adsorption will be reduced the ratios to a value similar to the ratios of alcohol to surfactant molecules in SDS micelles. Below the CMC (in region I, II and III), the amount of surfactant adsorption was not considerably increased in the presence of alcohol but also increased with increasing alcohol molecular weight. The surfactant adsorptions were increased below the plateau region, eventhough adsorptions in the plateau region were slightly decreased.

The high amount of adsolubilized alkane into SDS admicelles was also observed. Otherwise, adsolubilization of alkane will be increased with increasing surfactant adsorption. It was observed, as predicted, that the standard-state free energy of adsolubilized alkanes into the SDS admicelles is approximately the same as for the alkanes solubilized into micelles. This further showed that the interior of admicelles is similar to the interior of micelles.

Lee et al. (1990) proposed a "patchy bilayer" of adsorbed surfactant to explain the results of adsolubilization of alcohol. They further proposed that the adsorbed surfactant in region II and III of the adsorption isotherm are presented as disk-shaped aggregates. Because of the polar end-group of alcohol, the disk-like admicelles model explained how alcohol could be adsolubilized into two sites of these admicelles. One site is between the head groups of surfactant, and it is also presented in micelles. The other one, which is not appeared in micelles, is the hydrophobic perimeter occurring from the formation of the patchy, disk-like admicelles. The fraction of alcohols adsolubilized at the perimeter will be meaningful when the patchy aggregates are small, thus the very high ratios of adsolubilized alcohols to adsorbed surfactant are obtained at low surfactant adsorption. In addition, the hydrophobicity of the surface phase is increased by the adsolubilized alcohols at the perimeter causing the higher adsorption of surfactant. The increase of chain length of alcohol resulted in the enhancing of surfactant adsorption because of the greater hydrophobic contribution.

Admicellar polymerization is the successful application of admicelles. Wu et al. (1987) investigated the polymerization of adsolubilized styrene monomer in SDS admicelles on the surface of alumina. The processes of thin film polymer consist of 4 steps. First is the formation of admicelles. Step two is the adsolubilization of monomer into the admicelles. Step three is the polymerization of the adsolubilized monomer. The final one is removal of excess surfactant in order to expose the polymer film.

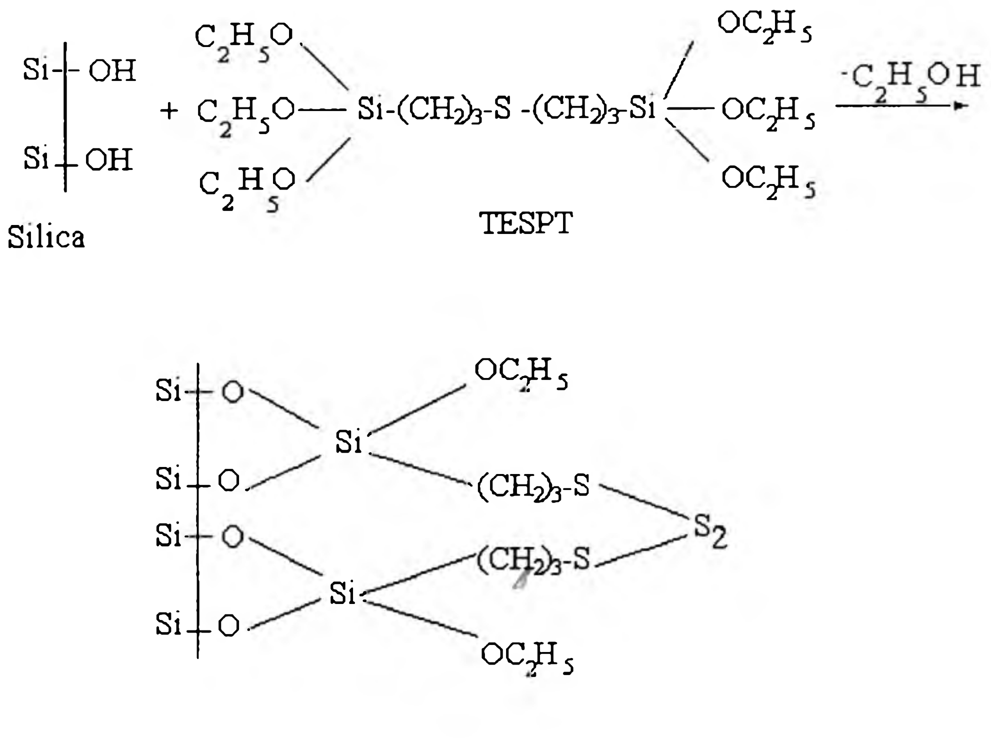
Barton et al. (1988) presented the application of admicelles in separation technology known in admicellar chromatography. Immobilized surfactant aggregates at a solid /liquid interface can act as two dimensional solvents to increase the interfacial concentration of organic compounds' selectivity. The results presented that n-heptanol could be separated from 3-heptanol or 2-methyl-2-hexanol at the low end of the isotherm. At the upper end of the isotherm, 2-methyl-2-hexanol can be separated from either of the two isomer. Each of the alcohols in a ternary mixture might be isolated in a two-stage process operated at opposing ends of the isotherm.

Subsequently, admicelles have been occupied for the reactions as two dimensional templates. Yu et al. (1992) presented a process called admicellar catalysis to catalyze the hydrolysis reaction of trimetylorthobenzoate (TMOB) by use of sodium dodecyl sulfate (SDS) adsorbed on high surface area alumina. The results indicated that the highest specific activity of admicelles is less than that the maximum specific activity of the corresponding micelles, however the admicelles activity is increased with increasing surface coverage above a specific value.

2.4 Formation of Hydrocarbon Aggregates Chemically Bonded to Mineral Oxide Surfaces

Although the admicelles techniques can be applied in many beneficial applications, the desorption of surfactant may be problematic in the development of the admicellar techniques. The method to construct the chemical bond of the surfactant or surfactant-like molecules on the mineral oxide surfaces may solve this problem.

The chemicals that are extensively used to form chemically bonded layer on mineral oxide surfaces are silane coupling agents. Silane coupling agents have been widely used in the rubber industry for the last several years to improve the performance of silica and other mineral fillers in rubber compounds and vulcanizates. Silane coupling agents $R'Si(OR)_3$ are characterized by dual functionality. R' represents an organo-functional group (such as aminoalkyl, mecaptoalkyl, vinyl, etc.) and the other site, OR, represents a readily hydrolyzable alkoxy group (such as OCH_3, or OC_2H_5) bonded to the silicon. In use, the alkoxy group readily hydrolyzes in the presence of moisture normally found on the mineral oxide surfaces to form silanols that can react with or otherwise condense in the presence of silica, clay or metal oxide surfaces.



Modified Silica

Figure 2.5 Modification reaction of silica with bis-(3-triethoxisilylpropyl)-tetrasulfide.

For the application in rubber, Wolff (1982) presented the in-situ modification of a silica with bis-(3-triethoxisilylpropyl)-tetrasulfide (TESPT) as described by the general reaction scheme in Figure 2.5. The equation implies a direct interaction of the silanol groups of the silica surface with the ethoxy groups.

It has been presented the organic compounds containing sulfur adsorb strongly onto gold and other metals to form monolayer (Throughton et al., 1988). The studies of dialkyl sulfide on gold by a variety of physical techniques indicate a rather more disordered structure than that for simple alkyl thiols. (self-assembly monolayer).

More interesting self-assembly systems are those that allow multilayers to be built by adsorption one layer at a time (Netzer and Sagiv, 1983) . A supported chemical is based on 15-hexadecenyl trichlorosilane. The $SiCl_3$ function enables the covalent attachment of the molecules to rich hydroxyl groups' surfaces, while the terminal ethylenic double bond provides a convenient path for the activation of the monolayer.

Ogawa et al. (1994) studied catalysis at the toluene/water interface by using octadecyl immobilized H-ZSM-5 catalyst promoted hydrolysis of water insoluble esters. Octadecyltrichlorosilane-treated HZSM-5 resulted in an effective catalyst for the hydrolysis of water-insoluble esters in a toluene-water solvent system. The catalyst floated at the interface of the two liquids. This modified catalyst had 60 times the activity of H-ZSM-5 for the hydrolysis dodecyl acetate.

2.5 Ozone Oxidation

The utilization of ozone as an oxidizing agent in both drinking and wastewater treatment and in several processes for organic synthesis has been growing. Ozone has been shown to be capable of destroying several organic compounds effectively. However, applications of ozonation processes in order to diminish specified pollutants in wastewater are known to be some what limited because of the low efficiency by which many of these pollutants are oxidized when present only as minor compounds, and because of the high price of oxidants.

Hoigne and Bader (1976) initiated the research for the fundamental rate equations and reported that ozone (O_3) may react directly with substrates or, above the critical pH value, decompose prior to reaction with substrates.

Beyond this critical pH value, hydroxyl radicals ($OH^{\cdot}$), decomposition products of O_3, become the significant oxidants. The critical pH value above which the second type of reaction prevails depends on both the rate with which O_3 reacts directly with the substrates and on the solutes, including reaction products, that enhance or retard O_3 decomposition .

Eisenhauer (1971) presented the effects resulted in increasing and decreasing of the rate of phenol degradation. The rate of phenol degradation may be increased by increasing the ozone dose rate and gas-liquid contact time, reduce gas bubble size and operating at pH 11. The rate is unaffected by pH between 3 and 9, temperature between 20 °C and 50 °C and oxygen concentration in the gas.

Gurol and Vastistas (1987) designed to investigate the reaction mechanisms of oxidation of various phenolic compounds by ozone and ozone + U.V. radiation at pH 2.5, 7.0 and 9.0. Experimental results showed that the molecular ozone is the prevalent oxidant only at acidic pH; at neutral and basic pH, in the absence or presence of U.V. radiation, free radical is the major pathway in the phenolic compounds oxidation. The increase of pH during ozonation with or without U.V. light increases the overall removal of phenols and the removal of TOC.