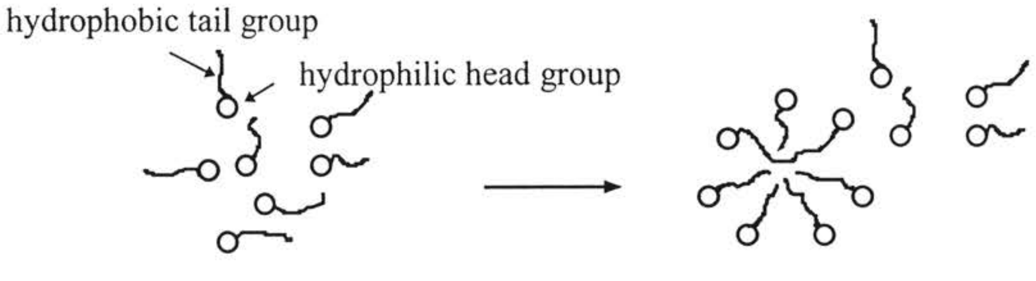
CHAPTER II

LITERATURE SURVEY

2.1 Formation of surfactant aggregates

2.1.1 Micellization

In aqueous media above the critical micelle concentration (CMC), surfactant molecules are oriented with their polar heads toward the aqueous phase and their hydrophobic groups away from it. The interior region of the micelle, containing the hydrophobic groups, is of radius approximately equal to the length of the fully extended hydrophobic chain (see Figure 2.1). It may be a spherical, rod-like, disk-like, or lamellar structure.



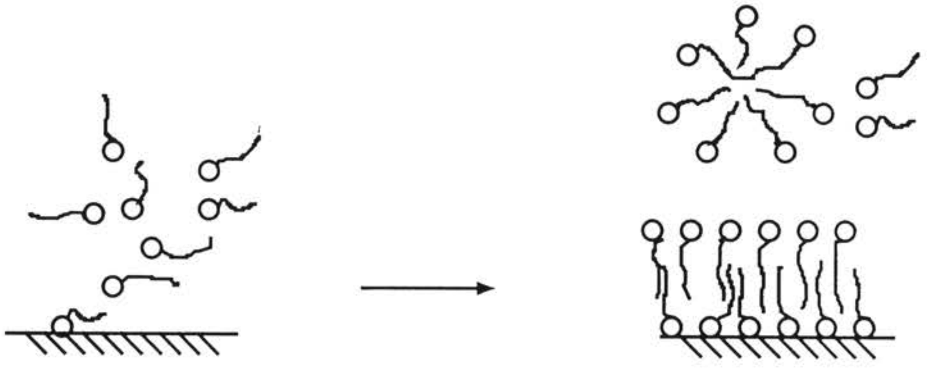
Below CMC
(surfactant monomers)

Above CMC
(monomers and micelles)

Figure 2.1 Formation of micelle (West et al., 1992).

2.1.2 Admicellization

The adsorption of ionic surfactants from aqueous solutions onto oppositely charged substrates has been studied for quite some time (Rosen, 1989). The formation of admicelles is shown in Figure 2.2. 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 examined 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.



Below CMC
(monomers and solid)

Above CMC
(admicelle, micelles, and monomers)

Figure 2.2 Formation of admicelles (West et al., 1992).

The adsorption isotherm of ionic surfactants on oxide surfaces is generally an "S" shaped graph when the adsorbed surfactant is plotted versus the equilibrium concentration of surfactant in logarithmic system (Somasundarun et al., 1966; and Scamehorn et al., 1982). Normally, there are three or four distinguishable regions of quantitatively different behavior as shown in Figure 2.3.

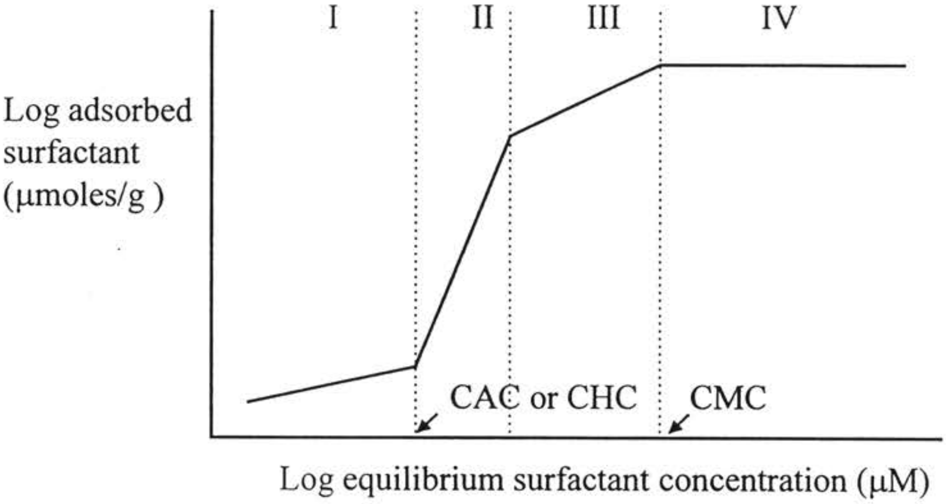


Figure 2.3 Schematic of a typical surfactant adsorption isotherm from aqueous solution onto a mineral oxide (Bitting et al., 1987).

From Figure 2.3 it can be described as follows:

Region I corresponds to both very low concentration and low adsorption of surfactant governed by Henry's law, that is.

$$\Gamma = h * [C]_w$$

Where 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;

$[C]_W$ is the surfactant monomer concentration.

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 et al., 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), neutron 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 form in the aqueous phase. Typically, the equilibrium surfactant concentration at the region III/IV transition point is approximately at the critical micelle concentration (CMC).

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 adjustment for pH of the contacting aqueous solution can manipulate the charge on the mineral oxide surface to be either positive or negative because both H^+ and OH^- are potential determining ions of mineral oxides. There exists the point of zero charge (PZC) at which the charge on the solid surface will be changed to be zero by adjusting the pH of aqueous solution. 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.

2.2 Solubilization and adsolubilization

Since the cores of both micelle and admicelle are hydrophobic, the nonpolar organic solutes will tend to solubilize within the interior region or hydrophobic core. The phenomena can be illustrated in Figure 2.4.

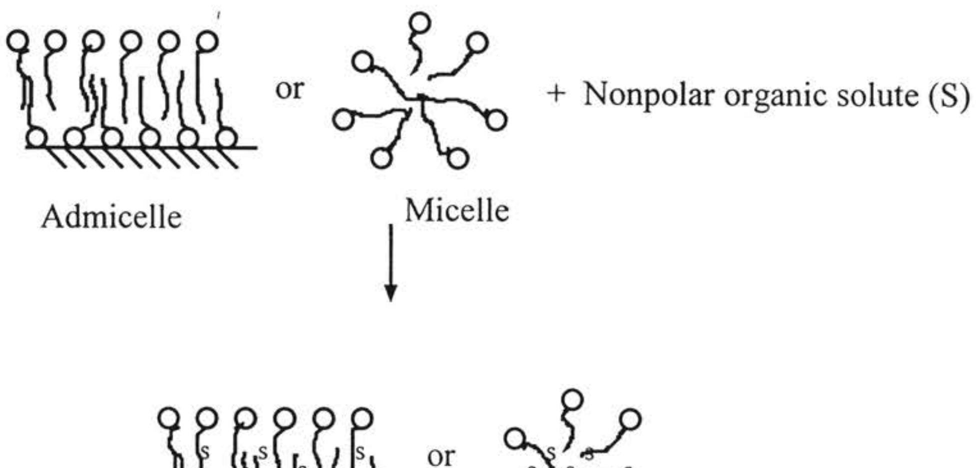


Figure 2.4 Solubilization and adsolubilization of nonpolar organic solute into micelle and admicelle (O'Haver et al., 1997).

Nunn et al. (1982) showed that the organic solutes could be adsolubilized into the organic environment of adsorbed surfactants by using visual evidence of pinacyanol chloride which is a dye of the 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. A blue color appeared when the dye was dissolved in aqueous solution of surfactants above the CMC or organic solvents, indicating that the dye was in an 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 the alumina and in the aqueous phase when the bulk concentration of surfactant was above the CMC. This result indicated that pinacyanol chloride could be partitioned between micelles and admicelles, and demonstrated the similar nature of the interiors of admicelles and of micelles.

Livitz and colleagues (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.

2.2.1 Solubilization

Solubilization has been defined as the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material (Rosen, 1989). Studies of solubilization of organic solutes by surfactant micelles have been presented in much literature.

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. Only the structure formula of the solute and the value of its Henry's law constant in water are required to predict the limiting equilibrium constant for transferring the solute from the infinitely dilute solution in water into the micelles.

The solubilization of mono- and dichlorophenols by hexadecylpyridinium chloride (CPC) micelles (Lee et al., 1990) showed that the effect of addition of chloride groups was to increase the value of the solubilization equilibrium constant at any value of mole fraction of the phenol present in the micelles although positional effects were 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 was 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 either cationic or nonionic micelles, which could be due to the more compact hydrophilic region of the mixed micelle.

2.2.2 Adsolubilization

Adsolubilization is the surface analog of solubilization, with adsorbed surfactant playing the role of micelles. The suggested 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).

Admicellar polymerization is the successful application of admicelles. Wu et al. (1987) investigated the polymerization of adsolubilized styrene monomer in sodium dodecylsulfate (SDS) admicelles on the surface of alumina. They proposed that the process of thin film formation consisted of the 4 following steps. The first step was the formation of admicelles. Step two was the adsolubilization of monomer into the admicelles. Step three was the polymerization of the adsolubilized monomer. The last one was the removal of excess surfactant in order to expose the polymer film.

Yeskie (1988) systematically studied the adsolubilization of both a series of alcohols and a series of 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 reduced the ratios to a value similar to the ratios of alcohol to surfactant molecules in SDS micelles. Below the CMC (regions I, II, and III) the amount of surfactant adsorption was not only considerably increased in the presence of alcohol but also increased with increasing alcohol molecular weight. The surfactant adsorptions were increased below the plateau region even though adsorptions in the plateau region were slightly decreased. The high amount of adsolubilized alkane into SDS admicelles was also observed. Otherwise, adsolubilization of alkane would be increased with increasing surfactant adsorption. It was observed, as predicted, that the standard-state free energy of adsolubilized alkanes into the SDS admicelles was approximately the same as for the alkanes solubilized into micelles. This was evidence that the interior of admicelles was similar to the interior of micelles.

Barton et al. (1988) presented an application of admicelles in separation technology known as admicellar chromatography. Immobilized surfactant aggregates at the solid/liquid interface can act as two dimensional solvents to increase the interfacial concentration of an organic compound. The results showed that n-heptanol could be separated from 3-heptanol or 2-methy-2-hexanol at the low end of the isotherm. At the upper end of the isotherm, 2-methyl-2-hexanol could be separated from either of the other two components.

Each of the alcohols in a ternary mixture might be isolated in a two-stage process operated at opposing ends of the isotherm.

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 regions II and III of the adsorption isotherm were 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 was the same as micelles, at the region between the headgroups of surfactants. The other was a site not present in micelles, the hydrophobic perimeter arising from patchwise adsorption of the "disk-shaped" admicelles. The fraction of alcohols adsolubilized at the perimeter would be meaningful when the patchy aggregates were small, thus the very high ratios of adsolubilized alcohols to adsorbed surfactant were obtained at low surfactant adsorption. In addition, the hydrophobicity of the surface phase was increased by the adsolubilized alcohols at the perimeter causing the higher adsorption of surfactant because of the greater hydrophobic contribution.

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 trimethylorthobenzoate (TMOB) by the use of sodium dodecyl sulfate (SDS) adsorbed on high surface area alumina. The results indicated that the highest specific activity of admicelles was less than a maximum specific activity of the corresponding micelles. However the admicelle activity was increased with increasing surface coverage above a specific value.

Nayyar et al. (1994) studied the adsolubilization of contaminants by media-sorbed surfactants. The medium and surfactant investigated were alumina and sodium dodecyl sulfate, respectively. Naphthalene, naphthol, and

4-amino, 1- naphthalene sulfonic acid (ANSA) were respectively investigated as nonpolar, polar, and ionizable organic compounds. In addition, adsolubilization by modified admicelles was studied under operating below the surfactant's Krafft temperature. They found that the adsolubilization capability of naphthalene was higher than that of naphthol, and ANSA consecutively. For modified admicelles, the results showed that they were still effective in removing the contaminants from solution.

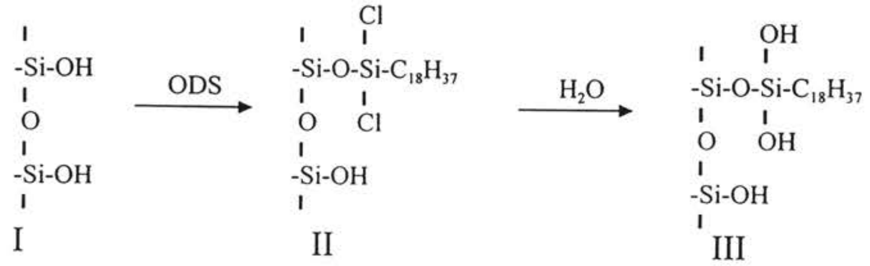
2.3 Preparation of chemically bonded phases on mineral oxide surfaces

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

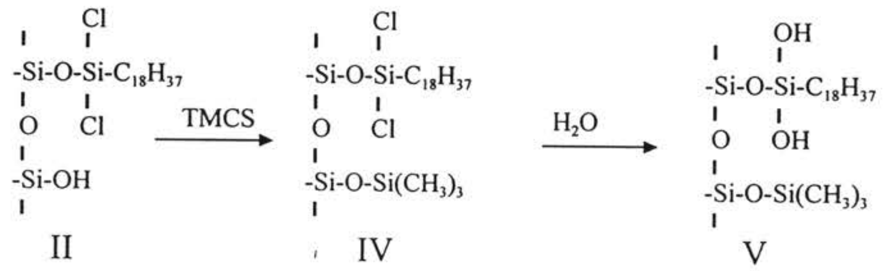
In 1969, the monolayer with organic groups permanently bonded to the surface of mineral oxides were introduced in chromatography. The organic molecules can be bonded to the surface of silica in three different ways (Karch et al., 1976). First, the reaction of silanol groups on the surface with alcohols results in an ester bond (Si-O-C). The alcoholic reactant can contain different functional groups. These chemically bonded phases have excellent properties in gas chromatography, but their use in liquid chromatography is restricted owing to their insufficient stability against hydrolysis. Second, the reaction of the silanol groups, especially their chloride derivatives, with primary or secondary amines, yields aminosilanes (Si-N-C) with a reasonable stability even in aqueous systems. The last one is the reaction of the silanol groups with chlorosilane, resulting in chemically bonded phases that are stable over the pH range of 1-8.5 whereas at higher pH values the silica carrier starts dissolving.

The problem of the generation of silanol groups is the hydrolysis of unreacted chlorosilane moieties. This significantly reduces the hydrophobicity of the support and is of particular importance when trichlorosilanes are used for bonding, as a certain percentage of these chlorosilane groups do not react with the silica surface. Little et al. (1979) studied the optimization of reaction conditions for the preparation of chemically bonded supports to eliminate the unreacted silanol sites by the use of monochlorosilanes and the "capping" of unreacted sites with trimethylchlorosilane, the smallest monochlorosilane available. Other silanes were also used such as dimethyldichlorosilane. Three main categories of bonding can be defined in Figure 2.5.

(a) Conventional bonding with a trichlorosilane



(b) Unreacted silanol groups "CAPPED"



(c) Untreated & hydrolyzed groups "CAPPED"

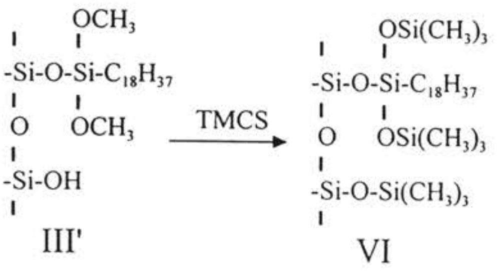


Figure 2.5 Schemes for chemical bonding (Little et al., 1979).

a) Conventional bonding with a trichlorosilane. This process involves the reaction of a trichlorosilane with the silica surface. After washing the excess of reagent from the silica by multiple decantations with the bonding solvent, the structure designated II is obtained. When used in an aqueous reversed-phase mode, residual chlorosilane groups are hydrolysed to III.

b) "Capping" the unreacted silanol groups. This process is an extension of the conventional bonding procedure. After the primary silanization with, for example, octadecyltrichlorosilane (ODS), trimethylchlorosilane (TMCS) is added to the reaction mixture. Being a more compact, smaller molecule than ODS, TMCS can react with the residual surface silanol groups, particularly those deep within the support particle, which were previously unavailable to the ODS owing the steric factors. After reaction has taken place, all excess of reagent was washed from the support. When used in an aqueous reversed-phase mode, residual chlorosilane groups are hydrolysed to V.

c) "Capping" of unreacted and hydrolysed silanol groups. Both processed described so far do not account for the hydrolysis of the unreacted chlorosilane groups. This procedure is unnecessary for monochlorosilane. In practice, this procedure is straight forward. After the primary silanization, unreacted ODS is washed from the support using the bonding solvent. Methanol is then added in order to convert the chlorosilane II into the methoxy derivative (III'). The support is washed free of methanol using the bonding solvent and TCMS is added. After washing the residual silane from the support, the final product VI is obtained.

Berendsen et al. (1980) studied the preparation of various bonded phase by using monochlorosilane. They concluded that the chemically bonded phase could be easily and reproducibly synthesized with relatively high surface coverage independent of the type of bond phase that was with or without a functional end-group. With monochlorosilanes higher surface coverages were reached than with monoalkoxysilanes under equivalent condition. Chemically bonded phases prepared at room temperature showed a slightly lower surface coverage than those prepared at a higher temperature (~100 °C). Provided that the bonding reaction was run to completion, post-silanization (e. g., with trimethylchlorosilane) did not enhance the carbon percentage and left the chromatographic properties unaffected, at least under reversed phase conditions.

For the application in rubber, 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. Wolff (1982) presented the in situ modification of a silica with bis-(3-triethoxisilylpropyl)-tetrasulfide (TESPT).

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 based on 15-hexadecenyl trichlorosilane was used. It was found that the $SiCl_3$ function enabled the covalent attachment of the molecules to hydroxyl-rich surfaces, while the terminal ethylenic double bond provided a convenient path for the activation of the monolayer.

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

Ogawa et al. (1994) studied catalysis at the toluene/water interface 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 of dodecyl acetate.

In 1996, the chemical bond of octadecyltrichlorosilane (ODS) was constructed to study the adsolubilization of phenol and trichloroethylene compared to adsolubilization in physically adsorbed CTAB (Thakulsukanant et al., 1997). Both bonded ODS and CTAB admicelles on silica showed almost the same trend in adsolubilization of TCE due to the nonpolar property of TCE, but the adsolubilization of polar phenol was significantly different. Although there was a small loss with increasing agitation speed, temperature, and pH values, the loss of bonded ODS under ozone conditions has yet been a problem.

2.4 Ozone oxidation

The utilization of ozone as an oxidizing agent in both drinking and wastewater treatments 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 process in order to diminish specified pollutants in wastewater are known to be somewhat 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.

Eisenhauer (1971) studied the conditions which affect the rate of phenol degradation. The rate of phenol degradation may be increased by increasing the ozone dose rate and gas-liquid contact time, reducing gas bubble size and operating at pH 11. The rate was unaffected by pH ranged from 3 to 9, temperature of 20-50°C and oxygen concentration in the gas.

Hoigne and Bader (1976) initiated research to determine 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), decomposition products of O_3, became the significant oxidants. They also found that the critical pH value above which the second type of reaction prevails depended on both the rate with which O_3 reacted directly with the substrates and the solutes, including reaction products, that enhanced or retarded O_3 decomposition.

Gural and Vastistas (1987) investigated the reaction mechanism of oxidation of various phenolic compounds by ozone and ozone in the presence of UV radiation at pH of 2.5, 7.0, and 9.0. Experimental results showed that the molecular ozone was the prevalent oxidant only at acidic pH; at neutral and basic pH, in the absence or presence of UV radiation, free radicals were the major pathway in the phenolic compound oxidation. The increase of pH during ozonation with or without UV light increased the overall removal of phenols and the removal of total organic compound (TOC).