

## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Surfactant

A Surfactant (a contraction of the term surface active agent) is a substance that, when presents at low concentration in a system, has the properties of adsorbing onto the surface or interfaces free energies of those surfaces (or interfaces) (Rosen ,1989). It consists of a hydrophilic end (the charge head group) and the hydrocarbon tail (the hydrocarbon chain) as shown in Figure 2.1. Generally, there are four types of surfactants depending on their structure: nonionic surfactant, cationic surfactant, anionic surfactant and zwitterionic surfactant.

#### 2.2 Micellization

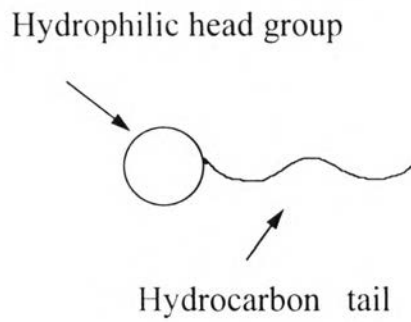
Micellization is the basic phenomenon of the surfactant. When an high enough number of separate surfactant molecules (monomer) present in solution, they can form micelle due to the Van De Walls force or hydrophobic bonding. In aqueous solution, the charge head groups place near the surface of the micelle and the hydrophobicallykyl chain extend toward the center of aggregate (Figure 2.2). The concentration at which micelle first forms is called “The Critical Micelle Concentration (CMC)”. The average number of monomer that incorporates into the micelle called “aggregation number”. This number can be used to justify the structure of the micelle.

Several factors affect the CMC including: (1) the structure of surfactant, (2) the presence of electrolyte, (3) the presence of various organic additives, (4) temperature. The CMC in aqueous media decrease as the hydrophobic character of the surfactant increases. Presence of electrolyte generally decrease the CMC in ionic surfactants. The addition of organic additives will have various effects depending on the organic. Increasing temperature can either cause the CMC to increase or decrease.

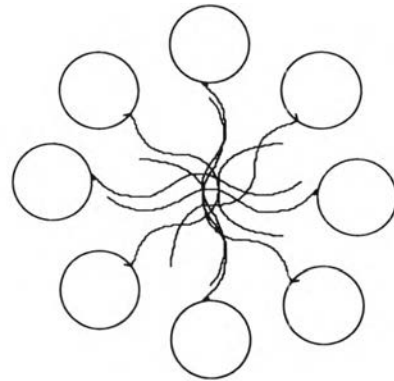
### 2.3 Solubilization

Solubilization is one of the most principle phenomenon of surfactant. Rosen (1989) defined solubilization as the spontaneous dissolving of a substance (solid, liquid or gas) by reversible thermodynamically stable isotropic solution with reduced thermodynamic activity of solubilize material. There are four different sites of micelles to adsolubilize : (1) in the hydrophobic core, (2) in the palisade layer which is the site between the hydrophobic group and the first few carbon atom of the hydrophobic tail, (3) the micelle surface, (4) in nonionic micelle in the polyoxyethylene cell (Dunn et al., 1985) as shown in Figure 2.3.

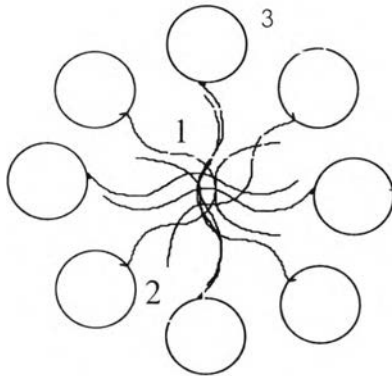
An organic molecule that has the polar head group like  $\text{OH}^-$  and  $\text{COO}^-$  tend to solubilize with the hydrophobic groups oriented towards the micelle surface (Lee et al., 1991). The extent of solubilization will be determined by some factor: structure of the surfactant, structure of the solubilizate, electrolyte, monomeric organic additive, polymeric organic additive, mixed anionic-nonionic micelle, temperature, liquidcrystal formation.



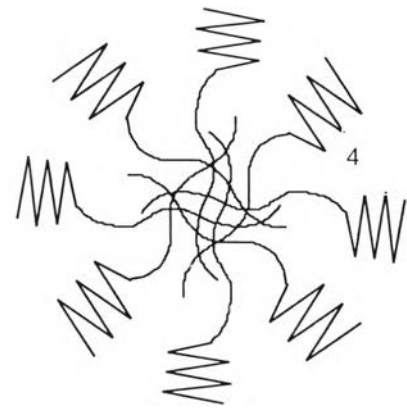
**Figure 2.1** Surfactant structure.



**Figure 2.2** Ionic micelle.



**Figure 2.3** Solubilization in nonionic micelle.



**Figure 2.4** Solubilization in ionic micelle.

Solubilization sites:

- 1) Hydrocarbon core
- 2) Palisade layer
- 3) Micelle structure
- 4) Between the head groups of nonionic surfactants

## 2.4 Surfactant adsorption onto the solid surface

One of the characteristics feature of surfactants is their tendency to adsorb at interfaces in their oriented fashion. The factors affecting the adsorption of surfactants are the nature of the structural group on the solid surface, the molecular structure of surfactant being adsorbed (adsorbate) and the environment of the aqueous solution (pH).

Charge on the solid oxide can be developed in the aqueous solution by the adsorption of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  from the solution onto the surface of the oxide. Those ion are called "Potential determining ion". The pH that makes the charge of the solid surface equal zero is called point of zero charged (PZC). If the pH of the solution is greater than PZC, the solid surface can be developed more negatively charged because the  $\text{OH}^-$  will adsorb on the solid surface and vice versa. As a result of, the cationic surfactant can adsorb on the solid that has the contacting aqueous solution greater than PZC. For example, silica having  $2 \leq \text{PZC} \leq 3$  will be negatively charge when the pH of aqueous solution exceed 3.

The adsorption isotherm for an ionic surfactant onto an oppositely charged substrate, for example, sodium alkanesulfonate (Rosen, 1989) and alkylbenzenesulfonate (Scamehorn, 1982) adsorbed on positively charged  $\text{Al}_2\text{O}_3$  is typically S-shaped. Typically, the shape of the isotherm can be divided into 4 regions (Figure 2.4 ). The relationship of the adsorption isotherm can be represented as log-log plot of adsorbed surfactant and equilibrium concentration of surfactant (Somasundarun and Fuerstenau, 1966: and Scamehorn et al., 1982).

Region 1 corresponds to both very low concentration of surfactants and very low adsorption. The surfactants adsorb mainly by ion-exchange possibly with the hydrophobic more or less prone on the substrate (Scamehorn, 1982),

thus the interaction between molecules of surfactant is negligible. This region is commonly referred to as the Henry's Law region because the adsorbed surfactant is considered to be in infinite dilution in the surface phase.

Region 2 is distinguished by a sharp increase of the adsorption isotherm. There is a marked increase resulting from the interaction between the oncoming surfactant and the adsorbed surfactant. These adsorbed surfactant aggregates are called admicelles (Harwell et al., 1985) or hemimicelles (Somasundarun and Fuerstenau, 1966) depending on whether the aggregate are viewed as bilayer or monolayer. The admicelle is considered as local bilayer structure with a lower layer of head groups adsorbed on the substrate surface and the upper layer of head group in contact with solution. The hemimicelle is a monolayer structure having the head group adsorbed on the surface while the tail group is in contact with aqueous phase. The transition point from region 1 to 2, representing the first formation of adsorbed surfactant aggregates, is called the critical admicelle concentration (CAC) (Harwell et al., 1985) or the hemimicelle concentration (Somasudarun and Fuerstenau, 1966).

Region 3: the slope of the isotherm is reduced because the adsorption must overcome the repulsion between the similar solid charged surface and the oncoming ion.

Region 4 is the plateau region, the adsorption in this region is usually completed when the surface is covered with a monolayer or bilayer of the surfactant (Scamehorn, 1982). Typically, the transition point between region 3 and region 4 is called "Critical Micelle Concentration (CMC)".

## 2.5 Adsolubilization

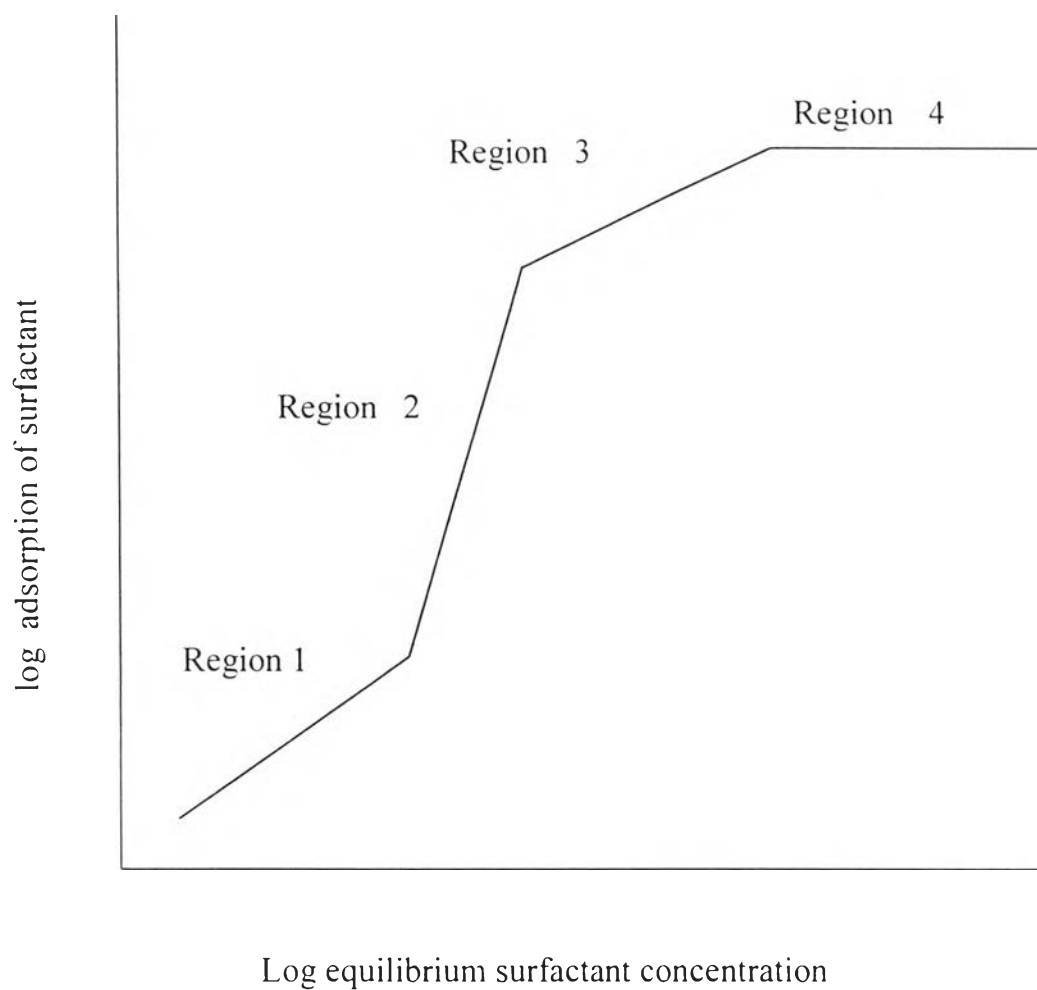
The partitioning of organic solute from the aqueous solution into the interior of the adsorbed surfactant aggregates is termed adsolubilization. This phenomenon is the surface analog of solubilization, with adsorbed surfactant bilayers playing role of micelle as shown in Figure 2.5. Adsolubilization is defined as “the incorporation of compounds would not be in excess in the surface without surfactant” (Scamehorn and Harwell, 1986).

Nunn et al. (1982) presented the visual evidence of pinacyanol chloride, a dye of the cyanide class, adsolubilized into the adsorbed anionic surfactant on alumina surface. The color changes of the dye indicated the partitioning of pinacyanol between the admicelles is similar in nature to the interior of micelle.

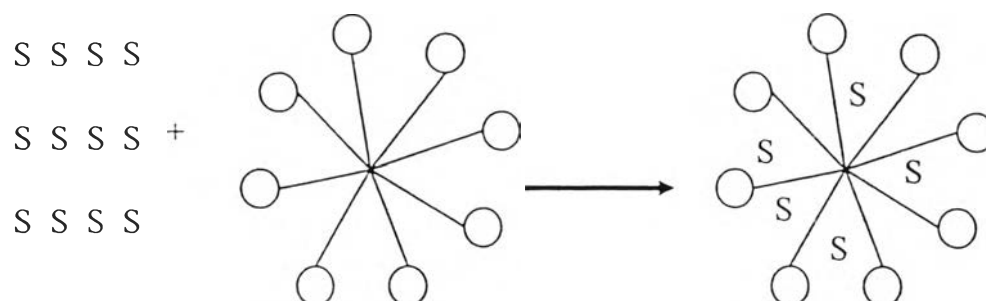
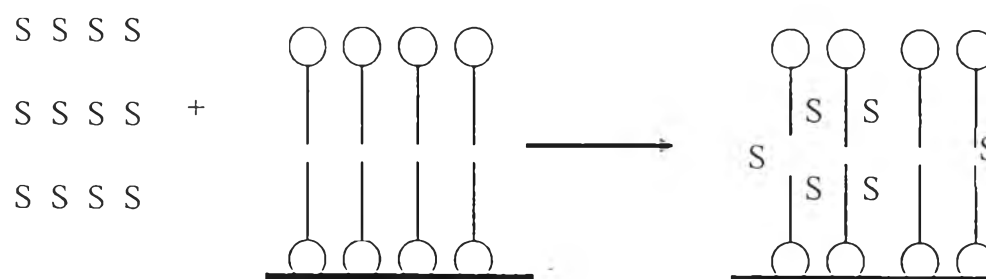
Levitz et al. (1984) and Levitz et al. (1986) studied the structure of the adsorbed bilayer of Triton X-100 (octylphenoxyethanol with an average of 9 to 10 oxyethylene units) by using fluorescence decay spectroscopy and pyrene as as probe. This evidence supported the hydrophobic environment of the core of micelle and confirmed the adsolubilization of the hydrophobic molecules.

Yeskie (1988) studied the adsolubilization of both alcohols and alkanes in the admicelles of sodiumdodecylsulphate on alumina. This research indicated that the admicelles structure may change with the increase in the adsolubilization and also showed that the adsolubilization was thermodynamically similar to solubilization into micelle.

Admicelles have been also used as two-dimensional template for reaction. Yu et al. (1992) studied the process called “Admicellar catalysis” to catalyze the acidic hydrolysis of trimethylorthoobenzoate (TMOB). The results showed that the adsorbed Sodium Dodecyl Sulfate (SDS) aggregates have catalytic activity comparable to that of SDS micelles for the acidic hydrolysis



**Figure 2.5** A typical adsorption isotherm for an ionic surfactant on an oppositely charged substrate.

SOLUBILIZATIONADSOLUBILIZATION

**Figure 2.6** A comparison of solubilization to adsolubilization.



of trimethylorhobenzoate. furthermore, the rate can be increased with the increasing surface coverage.

Furthermore, admicelles can also be applied to the polymerization processes. Orear et al. (1995) studied the formation of poly (tetrafluorethylene) thin films on the adsorbed sodium perfluoroheptanoate onto alumina. Their result indicated the three steps for the formation of thin film: the formation of admicelles, the adsolubilization on the admicelles, the polymerization of the adsolubilized monomer.

## **2.6 Formation of hydrocarbon aggregate chemically bonded to mineral oxide surface**

Generally, the desorption of surfactants produce some problems in the development of separation and admicellar catalysis. For this reason, some research attempted to solve this problem by using the chemical bond of the surfactant like molecule on the mineral oxide surface.

Silane coupling agent is the most widely used surfactant like molecule. There are essentially 4 different bondings between this coupling agent with silica surface: ester type, amino type, carbon type and siloxane type. The siloxane adsorbent are the most popular type. They are synthesized by the reaction of and organohalogenosilane with the silanol group at the surface of the silica (Colin, 1977).

There are numerous research investigated in the siloxane types . Karch et al. (1976) also constructed the series of siloxane type. The result showed that octadecyltrichlorosilane showed the highest percentage coverage of silica surface and there are no loss of ODS within the pH range 1-9 and the temperature below 220 °C.

Henmion et al. (1978) also studied the capacity ratio and selectivity of non polar and polar solute. The result showed that the capacity ratio and selectivity did not increase continuously with increase surface coverage but these increase continuously with the increasing length of bonded bristles.

Furthermore, silane coupling agent can used to construct the monolayer with other solid surface. Ogawa et al. (1994) modified the surface of zeolite by reacting with octadecyltrichlorosilane to catalyze the hydrolysis of water-insoluble esters at the toluene water interface. The result showed that the modified catalyst has 60 times activity of H-ZSM-5 for the hydrolysis of dodecylacetate and this catalyst can still also has the shape-selectivity properties.

Thakulsukanant et al. (1997) chemical bonded the hydrocarbon aggregate on the silica surface and also compared the properties with the physically adsorbed aggregates of cetyltrimethylammoniumacetatebromide (CTAB). The result showed that the adsolubilization of trichloroethylene was similar in CTAB and the bonded ODS, while the phenol adsolubilized to a greater extent in CTAB than in ODS. For stability, the bonded ODS are not affected by the pH, but its stability depended on the ozone concentration.

## 2.7 Ozonation

Ozone,  $O_3$ , is an allotropic form of oxygen first recognized as a unique substance in 1840. It can be produced from oxygen by using the energy source from electron or photon quantum energy. Electron can be used from high voltage sources in the silent corona discharge, from chemonuclear sources, and from electrolytic processes. Suitable photon quantum energy includes UV light

of wavelength lower than 200 nm and  $\gamma$ -rays. (Langlais et al.,1991). Its pungent odor is detectable above 0.01 ppm. In addition to being an excellent disinfectant, ozone is a powerful oxidant not only thermodynamically, but also kinetically, and has many useful synthetic application.

From Table 2.1 (Peterson, 1989) it can be seen that ozone is a powerful oxidant. However, this can be a double-edged sword as ozone is toxic and corrosive.

**Table 2.1** Comparative oxidation potentials

Species	Oxidation Potential (v)
Fluorine	3.06
Hydroxyl Radical	2.80
Oxygen Radicals	2.42
Ozone	2.07
Hydrogen Peroxide	1.77
Chlorine	1.36

### 2.7.1 Ozone decomposition

Ozone in aqueous solution can consume either by reaction or decomposition. The product of this decomposition can be oxygen, oxygen containing molecules and radicals. Factor affecting this decomposition is pH.

Shambaugh and Melnk (1976) found that the change in ozone concentration with time was proportional to the ozone concentration and the proportionality constant in a function of pH.

$$\frac{d[O_3]}{d[t]} = -k_{OH}[OH]^{0.75}[O_3] = -k_1[O_3] \quad \dots\dots(1)$$

where  $k_1$  = pseudo 1<sup>st</sup> order rate constant determined from experiment

$k_{OH}$  = ozone degradation rate constant

Katz (1980) observed that water with pH>6 exhibited ozone half lives that declined linearly with increasing pH

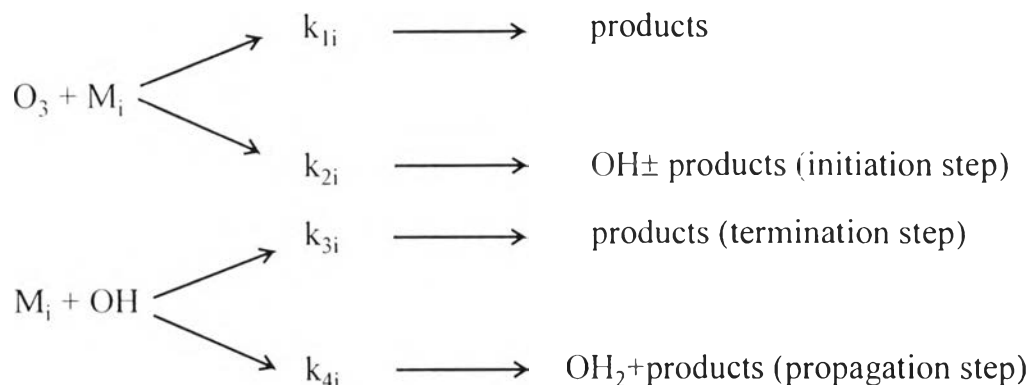
### 2.7.2 Kinetics

Typically, ozone can react with the pollutant by either direct reaction or indirect reaction.

Hoigne and Bader (1976) initiated the research for the fundamental rate equation and reported that ozone (O<sub>3</sub>) may react either directly with substrates, below the critical pH value, or indirectly by OH° with substrate above the critical pH value.

Hoigne and Bader (1978) found that direct reaction, the reaction between the molecular ozone (O<sub>3</sub>) and substrate, is very selective and relatively low reaction. On the other hand, indirect reaction which is the reaction between product species of ozone decomposition (OH°) with substrate, is non-selective and very fast.

The oxidation rate of micropollutant substrate (M<sub>j</sub>) in a solution may be illustrated by the following equation (Langlais, 1991) :



Let

$$-\frac{d[M]}{d[t]} = (k_{1i} + k_{2i})[O_3][M_i] + (k_{3i} + k_{4i})[OH][M_i] \quad \dots\dots\dots(2)$$

where  $O_3$  = concentration of dissolve ozone in solution

$M_i$  = concentration of micropollutant i

According to Yuterri and Gurol (1988)

$$[OH] = \psi [O_3] \quad \dots\dots\dots(3)$$

Where

$$\psi = \frac{\sum k_{2i}[M_i] + 2k_1[OH^-]}{\sum k_{vi}[S_i]} \quad \dots\dots\dots(4)$$

Thus, the total oxidation of the particular substrate is

$$\frac{d[M_i]}{d[t]} = \text{Rate}_i = (k_1^* + k_2^*\Psi)[O_3][M_i] = k_i[O_3][M_i] = k_1[O_3][M_i] \quad \dots\dots\dots(5)$$

Where

$$k_1^* = k_{1r} + k_{2r}$$

$$k_2^{**} = k_{3r} + k_{4r}$$

In the presence of catalyst, the rate equation must take into account of the weight of catalyst then the rate equation can be derived in the form:

$$-\frac{1}{W} * \frac{d[M_i]}{d[t]} = k_1^* [O_3] * [M_i] \quad \dots\dots\dots(6)$$

The integrated form of this equation is

$$\frac{1}{W} * \ln\left(\frac{[M_i]}{[M]_o}\right) = -k_1^* t \quad \dots\dots\dots(7)$$

Where W = weight of catalyst

$M_o$  = TCE concentration at time = 0

$M_i$  = TCE concentration at any time

$k_1$  = overall apparent pseudo first order reaction rate constant

### 2.7.3 Trichloroethylene reaction

Trichloroethylene is a colorless, sweet smelling (chloroformlike odor), volatile liquid. Generally, TCE is used in the vapor degreasing of fabricated metal parts. A variety of miscellaneous applications include use of trichloroethylene as a component in adhesive and paint-stripping formulations, a low temperature heat transfer medium, etc.

The ozonation of trichloroethylene can follow 2 major pathways

- (1) direct reaction of solute with molecular ozone
- (2) oxidation of solute by hydroxyl radicals formed from ozone decomposition

Because of the high resistant of trichloroethylene to the molecular ozone oxidation then the ozonation of aqueous contaminants could be developed to enhance the reaction rate by using “the Advanced Oxidation Process (AOPs)”. This processes generate the highly reactive free radical intermediate ( $\text{OH}^\circ$ ) from the decomposition of ozone or hydrogen peroxide, include  $\text{O}_3/\text{high pH}$ ,  $\text{H}_2\text{O}_2/\text{O}_3$ ,  $\text{O}_3/\text{UV light}$  and  $\text{H}_2\text{O}_2/\text{O}_3$ . Numerous research has been investigated the reaction of ozone and trichloroethylene.

Kusakabe et al.(1991) developed the efficiency of ozonation by combining the use of both ozone and UV radiation. They found that the destruction rate were proportional to the dissolve ozone concentration and the UV intensity in the reactor . The destruction rate of trichloroethylene followed the first order kinetics model and the activation energy was 39 kJ/mol.

Bellamy et al. (1995) studied the advance oxidation process by using both ozone oxidation and hydrogen peroxide. The result showed that the disappearance of TCE consisted of 2 major ways: oxidation effect and stripping effect. The result showed that an  $\text{H}_2\text{O}_2/\text{O}_3$  molar ratio of 0.5 yielded higher TCE oxidation rates and the most efficient use of oxidant compared to other ratios. In the absence of stripping effect, the reaction rate also followed the first order model.

Glaze et al. (1995) discovered the reaction rate both for trichloroethylene with ozone or ozone plus  $\text{H}_2\text{O}_2$  obeyed the first order-kinetic model. In the absence of  $\text{H}_2\text{O}_2$ , the rate constant was  $4.1 \times 10^{-4} \text{s}^{-1}$ , whereas the rate constant was  $8.8 \times 10^{-4} \text{s}^{-1}$  in the  $\text{H}_2\text{O}_2/\text{O}_3$  ratio 0.33.