

# OZONATION RATE OF WATER-SOLUBLE CHELATES AND RELATED COMPOUNDS

SHIGEHARU MOROOKA, KIYOSHI IKEMIZU, HIDEYUKI KAMANO  
AND YASUO KATO

*Department of Applied Chemistry, Kyushu University, Fukuoka 812*

**Key Words:** Environment, Chemical Reaction, Degradation Rate, Waste Water, Ozone, Ozonation, Heavy Metal, Chelate, Stability Constant

Metal-EDTA complexes and related compounds were oxidized by ozone, and the destruction rates of chelates were obtained over a wide range of pH values.

The degradation of EDTA was initiated by the electrophilic attack of ozone on the nitrogen lone pair. Therefore, the reactivity of EDTA chelates was strongly affected by the conditional stability constant,  $K$ , which was related to the availability of the nitrogen lone pair.

In the range of  $K < \text{about } 1 \times 10^4$ , the formation of the coordinate bond was not sufficiently strong, and the degradation rate of the EDTA chelates was nearly equal to that of free EDTA. In the range of  $K > 10^5$ , however, the degradation rate of the EDTA chelates decreased with an increase in the stability constant.

The removal rate of metals from EDTA, NTA and IDA complexes decreased with an increase in the number of coordination sites per ligand. Approximately two molecules of ozone were needed to destruct one coordination site of each ligand.

## Introduction

Hazards of heavy metals are of general concern, and their discharge in waste water is strictly controlled by legal measures. The precipitation method is conventionally applied for waste-water treatment, but is not effective when metal ions form water-soluble complexes with chelating agents. These metal complexes can be destroyed by microbial degradation<sup>1,15)</sup> or electrochemical oxidation processes.<sup>8)</sup>

Ozonation is also very promising for the degradation of water-soluble chelates because of its powerful oxidizing ability<sup>3,5,10)</sup> and less harmful products. Although many works have been published on the ozonation of metal ions, very little attention has been paid to the degradation rate of chelates in water.

Shawbaugh and Melnyk<sup>13)</sup> ozonized Mn, Cd, Ni and Pb complexes of ethylenediaminetetraacetic acid (EDTA). They claimed that the ozonation rate of the metal-EDTA complexes was an order of magnitude faster than that of EDTA alone, but no experimental data for the ozonation of EDTA were reported.

Games and Staubach<sup>2)</sup> studied the ozonation of nitrilotriacetate acid (NTA) dissolved in water. The initial degradation rate of free NTA calculated from the ozone consumption was increased by about three times when NTA formed complexes with metals. However, the degradation rate of free NTA calcu-

lated from the unreacted NTA concentration was much faster than that of NTA chelates. These discrepancies must be clarified by more quantitative experiments.

In this study, water-soluble chelates were oxidized by ozone over a wide range of pH values, and the degradation rate of chelating agents and the removal rate of metals were determined. The ozonation of free EDTA and EDTA chelates was mainly dealt with in the present experiments because EDTA is widely used as a water-soluble chelating agent. The ozonation of other chelates and the ozone consumption efficiency were also studied.

## 1. Experimental

**Apparatus and procedure** A bubble column of 0.032 m i.d. and 1 m height was used as the gas-liquid contactor for the ozonation. The column was encased with a water jacket and was maintained at a constant temperature of  $296 \text{ K} \pm 0.5 \text{ K}$  unless otherwise mentioned.

Dry oxygen containing ozone was bubbled into the column through a glass-filter gas distributor, while the solution was charged batchwise. Most experiments were carried out at a gas flow rate of  $10 \text{ cm}^3 \cdot \text{s}^{-1}$ . The shape of gas bubbles was determined photographically, and the mean volume-surface diameter of the gas bubbles was obtained.

The ozone concentration in the inlet and outlet gas flow was measured by iodometry. The inlet ozone

Received January 9, 1986. Correspondence concerning this article should be addressed to S. Morooka. H. Kamano is now with Kawasaki Steel Corp., Chiba 260.

concentration was kept at about  $0.5\text{--}0.8\text{ mol}\cdot\text{m}^{-3}$ . No dissolved ozone was detected in the liquid bulk during ozonation. The pH value of the solution was automatically kept at a constant value by using a pH controller equipped with feeding systems for dilute  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  aqueous solutions.

**Determination of ligands and chelates** In the ozonation of chelates, liquid samples were periodically withdrawn from the column. Then, the pH value of each sample was raised to 9 for the Cu-EDTA and Zn-EDTA systems or to 11 for the Mg-EDTA system by adding a  $\text{NaOH}$  aqueous solution, and the total concentration of complexed metal in the clarified solution was determined by atomic absorption spectroscopy. These pH values were chosen to keep the solubility of metal hydroxides lower than  $10^{-3}\text{ mol}\cdot\text{m}^{-3}$ , where metal ions free from chelation were almost completely precipitated. When the ozonation was carried out at a pH value higher than 9 for the Cu-EDTA and Zn-EDTA systems or 11 for the Mg-EDTA system, the total concentration of complexed metal in sampled solutions was determined without further adjustment of pH value.

In the course of ozonation, unreacted EDTA as well as reaction products were able to form chelates with metal ions. After each sample was processed by the precipitation method described above, the concentrations of chelating agents other than EDTA were determined by titration with EDTA using 1-(2-pyridylazo)-2-naphthol (PAN) as indicator. The concentration of remaining EDTA chelate was calculated by subtracting the concentration of the newly produced chelating agents from that of total complexed Cu. Typical chelating agents were also determined by gel permeation chromatography. The total organic carbon in the solution was measured by a TOC meter (GCT125, Sumitomo Chemical Co.). The initial concentration of free ligands or chelates was about  $10\text{ mol}\cdot\text{m}^{-3}$ .

## 2. Calculation of Apparent Degradation Rate

When the degradation rate of chelating agents is much faster than the decomposition rate of dissolved ozone, the local concentration of ozone in the liquid diffusion film is given by

$$D_{\text{O}_3} \frac{d^2[\text{O}_3]}{dx^2} - bk_0 \bar{C}_E [\text{O}_3] = 0 \quad (1)$$

where  $b$  moles of dissolved ozone react with one mole of chelating agent  $E$ .

Under the condition of  $D_E \bar{C}_E \gg D_{\text{O}_3} [\text{O}_3]_i$ , the concentration of chelating agent in the liquid film is considered to be the same as that in the bulk liquid. In the case of  $\delta \sqrt{bk_0 \bar{C}_E / D_{\text{O}_3}} \gg 3$ , the absorption flux of ozone at the gas-liquid interface is given by<sup>11)</sup>

$$J_{\text{O}_3} = -D_{\text{O}_3} \left. \frac{d[\text{O}_3]}{dx} \right|_{x=0} = \sqrt{bk_0 \bar{C}_E D_{\text{O}_3}} [\text{O}_3]_i \quad (2)$$

The degradation rate of chelates in the bulk liquid is expressed as follows:

$$-V_L \frac{\Delta \bar{C}_E}{\Delta t} = S_b J_{\text{O}_3} / b \quad (3)$$

From Eqs. (2) and (3),

$$\frac{\Delta \bar{C}_E}{\Delta t} = a [\text{O}_3]_i \sqrt{k D_{\text{O}_3} \bar{C}_E} \quad (4)$$

where  $k = k_0/b$ . The degradation rate constant is obtained by integrating Eq. (4) with respect to time.

$$k = \frac{1}{D_{\text{O}_3}} \frac{2(\sqrt{\bar{C}_{E0}} - \sqrt{\bar{C}_E})}{a [\text{O}_3]_i t} \quad (5)$$

The degradation rate constant was calculated from the initial slope of the degradation curve.

**Evaluation of variables** Figure 1 shows the Henry constant of ozone as a function of temperature. The Henry constant is defined as the ratio of mole fraction of ozone in the gas phase to that in the liquid phase. The value at 296 K was determined as 4850 and was in good agreement with that given in the reference.<sup>7)</sup>

Figure 2 shows the volume-surface mean diameter of gas bubbles and the mean gas holdup in the column. When  $1\text{ kmol}\cdot\text{m}^{-3}$  of  $\text{NaCl}$  was added,  $d_{vs}$  was as small as 1.0 mm at a gas flow rate of  $10\text{ cm}^{-3}\cdot\text{s}^{-1}$ . The gas-liquid interfacial area per unit volume of the liquid phase is calculated from

$$a = 6\{\varepsilon_g / (1 - \varepsilon_g)\} / d_{vs} \quad (6)$$

The diffusivity of ozone in water,  $D_{\text{O}_3}$ , was estimated to be  $2.0 \times 10^{-9}\text{ m}^2\cdot\text{s}^{-1}$  at 296 K from the Wilke-Chang equation.<sup>16)</sup>

In the case of ozonation, the concentration of dissolved ozone at the gas-liquid interface is considered to be in equilibrium with the logarithmic mean value of inlet and outlet ozone concentrations in the gas phase.

## 3. Ozonation of Chelates

**Ozonation of EDTA** Figure 3 shows the changes in concentrations of EDTA and its reaction products with elapsed time. Nitrilotriacetic acid (NTA), iminodiacetic acid (IDA) and glycine were dominant reaction products. The total carbon of EDTA, NTA, IDA and glycine comprised about 67% of the total organic carbon dissolved in the solution. The product pattern suggests that dissolved ozone first attacks the nitrogen lone pair and then cleaves the nitrogen-methylene bond. As described later, the reactivity of the nitrogen atom is strongly decreased by the formation of a coordinate bond with metal. Main re-

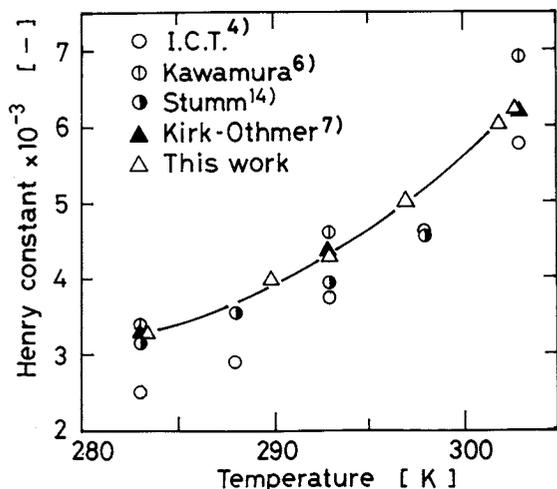


Fig. 1. Henry constant of ozone.

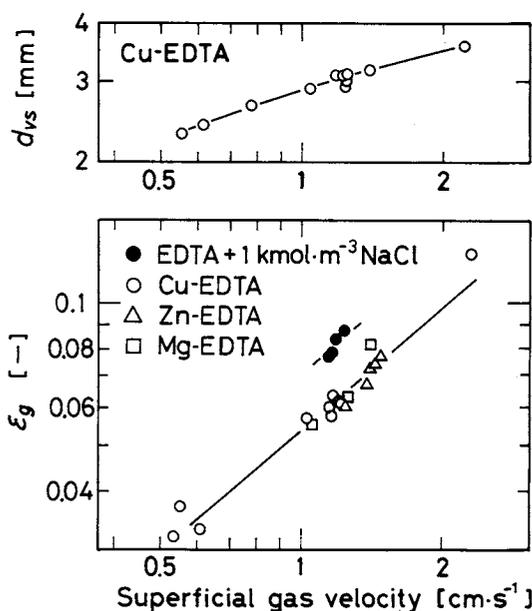


Fig. 2. Volume-surface mean diameter of gas bubbles and mean gas holdup.

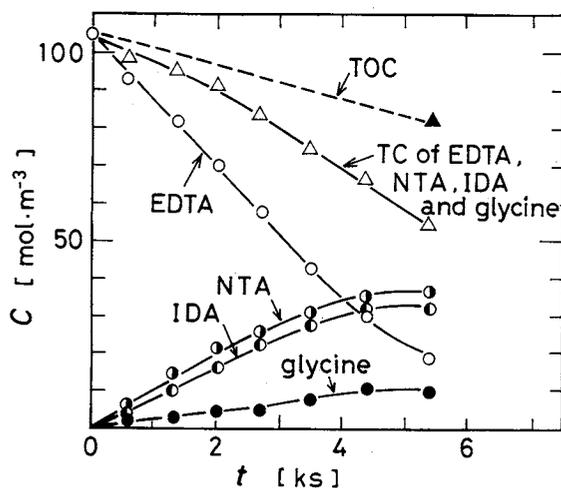


Fig. 3. Changes in concentrations of EDTA and reaction products with elapsed time.

action pathways are illustrated in Fig. 4.

**Ozonation of EDTA complex** Figure 5 shows the changes in concentrations of total complexes Cu, remaining EDTA chelate and newly produced Cu complexes for the ozonation of Cu-EDTA chelate at pH=4 and 10, respectively. In the ozonation at pH=4, Cu ions released by the decomposition of EDTA chelate successively form water-soluble complexes with produced chelating agents. Then the nitrogen lone pair of the produced chelating agents is still engaged in coordination bonding and is rather refractive to the electrophilic attack of ozone.

In the ozonation at pH=10, however, the stability constant of the produced chelating agents is not sufficiently large to mask Cu ion from precipitation as  $\text{Cu}(\text{OH})_2$ . Therefore, nitrogen of the produced chelating agents is mostly free from metal ions and is subject to further ozonation. The oxidation ability of ozone itself also increases with an increase in pH value.

Figure 6 shows the effect of metal species on the changes in concentrations of the total chelates and the newly produced chelates for the ozonation of EDTA chelates at pH=7. The ozonation rate of EDTA chelates is strongly influenced by the metal species and decreases in the order of  $\text{Mg} > \text{Zn} > \text{Cu}$ .

The solubility product of  $\text{Zn}(\text{OH})_2$  is about 300 times larger than that of  $\text{Cu}(\text{OH})_2$ , and the stability constant of Zn chelates is a few orders of magnitude larger than that of Mg chelates. Therefore, the chelating agents produced by the ozonation of Zn-EDTA still form a strong coordinate bond with Zn. This is the reason why the reactivity of the produced chelates is lowest in the case of Zn.

Figure 7 indicates that the degradation rate of free EDTA is well expressed by Eq. (5). The degradation rate of EDTA chelates is also in agreement with Eq. (5). Figure 8 shows the degradation rate constant of EDTA for the ozonation of free EDTA and EDTA chelates in the range of pH=2-12. The magnitude of the degradation rate constant is dependent on the metal species and the value of pH. The uncomplexed EDTA is oxidized more easily than EDTA complexes.

The effect of metal species and pH value on the degradation rate can be explained by the stability constant of EDTA chelates. Figure 9 shows the relationship between the ratio of the degradation rate constant of EDTA chelates to that of free EDTA, and the conditional stability constant<sup>12)</sup> of EDTA chelates. The conditional stability constant increases in the order of  $\text{Mg} < \text{Zn} < \text{Cu}$ , and the degradation rate constant decreases in the same order. In the range of  $K < \text{ca. } 10^4$ , the formation of coordinate bond is not strong enough to suppress the ozonation of the ligand. Thus the value of  $k_{EM}/k_E$  is eventually unity. In the range of  $K > 10^5$ , however, the degradation rate of the ligand decreases with an increase in  $K$ . The

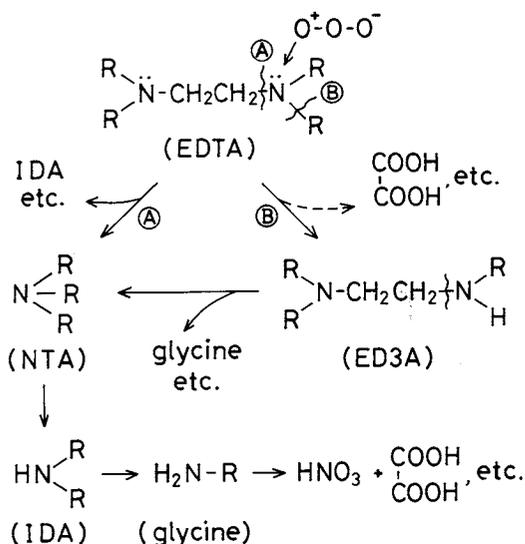


Fig. 4. Main pathways for ozonation of EDTA: R = CH<sub>2</sub>COOH; ED3A means ethylenediaminetriacetic acid.

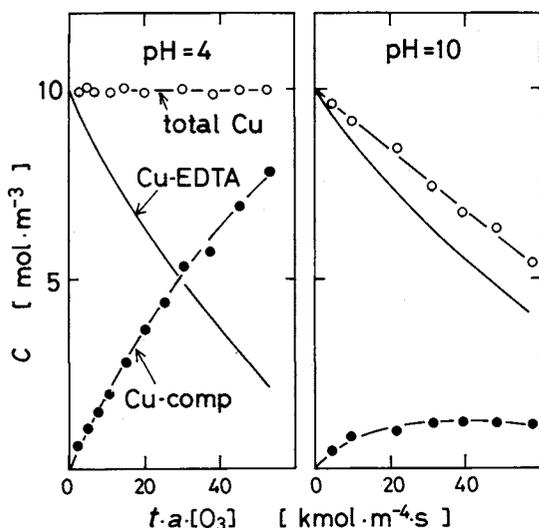


Fig. 5. Effect of pH value on changes in complex concentrations for the ozonation of Cu-EDTA chelate: Total Cu = concentration of total Cu complexes; Cu-EDTA = concentration of unreacted Cu-EDTA complex; Cu-comp = concentration of newly produced Cu complexes.

effect of  $K$  on the degradation rate of EDTA chelates can be expressed by the solid lines in Fig. 7, though the degradation rate in strong alkaline solutions is not clear.

Figure 8 also shows the degradation rate constant of EDTA when 1000 mol·m<sup>-3</sup> of NaCl is added in the solution. The rate constant is decreased by the addition of a large excess of NaCl.

Ozonation of NTA and IDA chelates As shown in Fig. 3, NTA and IDA are major products of the ozonation of EDTA and are still capable of chelation. Therefore, NTA and IDA chelates should be further destroyed by ozone so that metal ions may be removed by alkaline precipitation. Experiments were carried out in the range of pH=4-12 using Cu-NTA

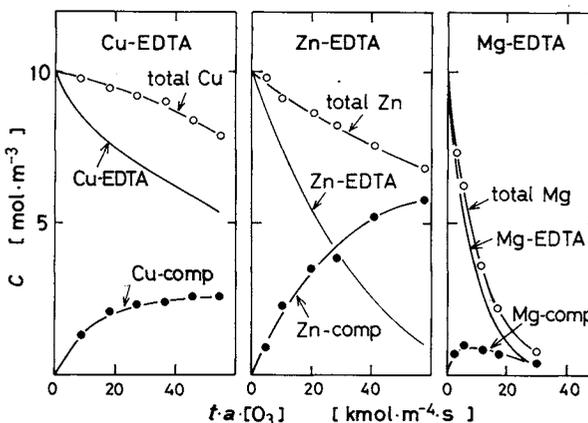


Fig. 6. Effect of metal species on changes in complex concentrations for ozonation of metal-EDTA complexes at pH=7: Notations for complex concentrations are the same as in Fig. 5.

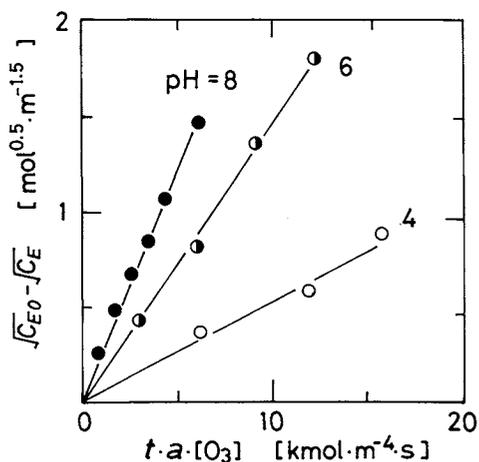


Fig. 7. Experimental evidence of applicability of Eq. (5).

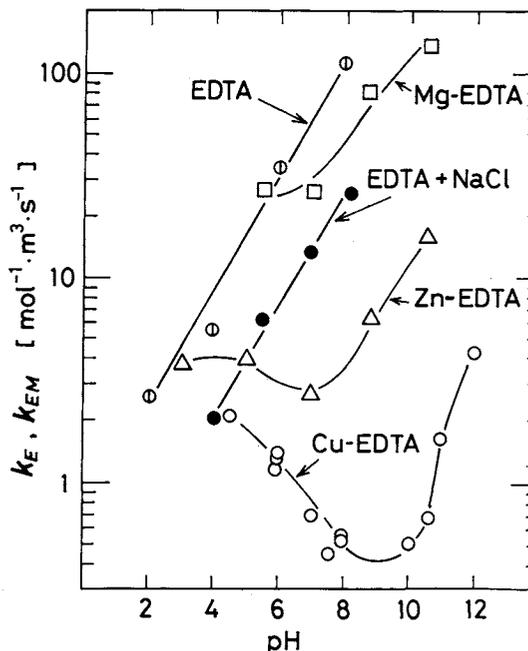


Fig. 8. Effects of metal species and pH value on apparent degradation rate constant of EDTA.

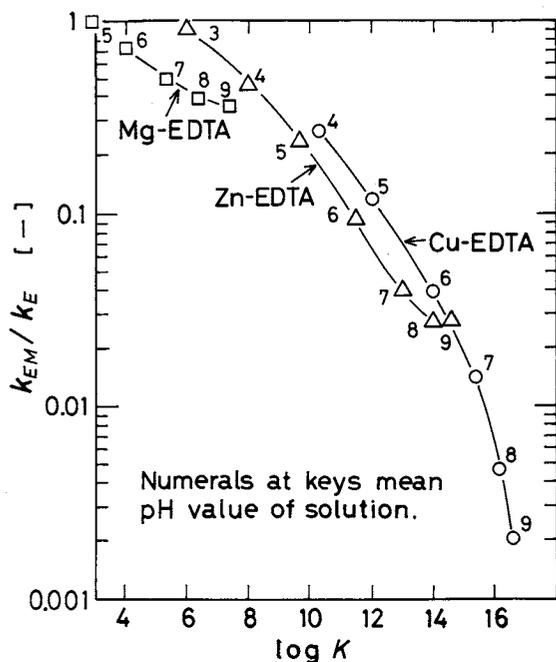


Fig. 9. Relationship between  $k_{EM}/k_E$  and conditional stability constant: The conditional stability constant is expressed in the unit of  $\text{mol}\cdot\text{l}^{-1}$ .

and Cu-IDA chelates, and the concentration of total complexed Cu dissolved in the liquid phase was obtained. The procedure of pH adjustment and precipitation was the same as in the ozonation of Cu-EDTA chelate. The ordinate of Fig. 10 is the reciprocal of the ozonation period when the concentration of total chelates decreases to half the initial chelate concentration. The value of  $t_{1/2}$  is corrected with the gas-liquid interfacial area and the ozone concentration. Figure 10 indicates that the removal rate of complexed metal decreases with an increase in the number of coordination sites in each ligand,  $N$ .

**Consumption of ozone** Figure 11 shows the amount of ozone consumed to release 1 mole of precipitable metal ions. The data are best correlated when the amount of consumed ozone is divided by  $(N-2)$ . This means that ligands with two coordination sites such as glycine cannot mask metal ions from the formation of hydroxides in the range of  $\text{pH} \geq 9$ . The stoichiometric constant,  $b$ , in Eq. (1) was smaller than 2 for EDTA, NTA and IDA chelates. The self-decomposition rate of ozone<sup>9</sup> was at least one order of magnitude smaller than the reaction rate of ligands under the present experimental conditions.

### Conclusion

The ozonation of water-soluble chelates was carried out over a wide range of pH values, and the degradation rate of ligands and the removal rate of metal ions were evaluated.

The degradation of EDTA was initiated by the

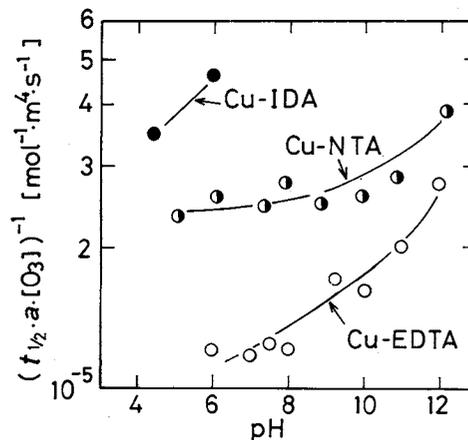


Fig. 10. Reciprocal of ozonation period necessary to remove half the initial amount of metal complexes.

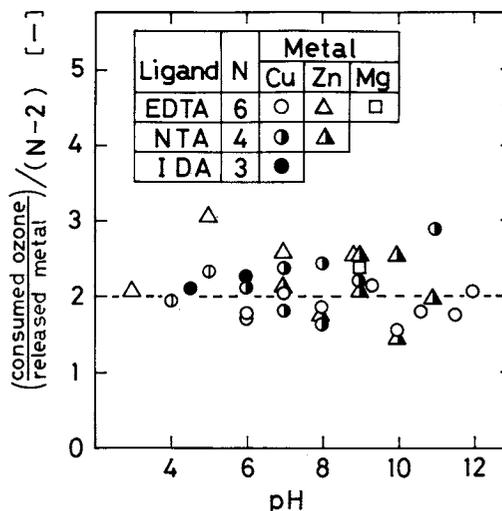


Fig. 11. Amount of ozone consumed to release 1 mol of precipitable metal ions.

electrophilic attack of ozone on the nitrogen lone pair. Thus, the reactivity of the ligand was strongly affected by formation of the coordinate bond with metal. In the range of  $K < \text{about } 1 \times 10^4$ , the coordinate bond was not strong enough to suppress the ozonation rate of the ligand, and the degradation rate of ligand was nearly equal to that of the chelates. In the range of  $K > 10^5$ , however, the degradation rate of the ligand decreases with an increase in  $K$  although the degradation rate in strong alkaline solutions was not clear.

The degradation rates of EDTA, NTA, and IDA chelates decreased with an increase in the number of coordination sites per ligand. The amount of ozone consumed to release a mole of precipitable metal ions was approximately equal to  $2(N-2)$ .

### Acknowledgment

The authors are grateful to Dr. Junichi Hojo (Dept. of Applied Chemistry, Kyushu Univ.), Dr. Makoto Takagi and Dr. Hiroshi

Nakamura (Dept. of Organic Synthesis, Kyushu Univ.), and Dr. Kazuaki Isomura (Laboratory for Waste Water Treatment, Kyushu Univ.) for useful discussion.

#### Nomenclature

$a$	= gas-liquid interfacial area per unit volume of liquid	$[m^{-1}]$
$b$	= stoichiometric coefficient	$[-]$
$C_E$	= concentration of EDTA or metal-EDTA complex	$[mol \cdot m^{-3}]$
$D_E$	= diffusivity of EDTA or metal-EDTA complex	$[m^2 \cdot s^{-1}]$
$D_{O_3}$	= diffusivity of ozone	$[m^2 \cdot s^{-1}]$
$d_{vs}$	= volume-surface mean diameter	$[m]$
$J_{O_3}$	= absorption flux of ozone at the gas-liquid interface	$[mol \cdot m^{-2} \cdot s^{-1}]$
$K$	= conditional stability constant of EDTA complex	$[mol \cdot l^{-1}]$
$k_0$	= degradation rate constant of ligand	$[mol^{-1} \cdot m^3 \cdot s^{-1}]$
$k$	= apparent degradation rate constant of ligand ( $=k_0/b$ )	$[mol^{-1} \cdot m^3 \cdot s^{-1}]$
$k_E, k_{ME}$	= $k$ for uncomplexed EDTA and EDTA complex, respectively	$[mol^{-1} \cdot m^3 \cdot s^{-1}]$
$N$	= number of coordination sites	$[-]$
$[O_3]_i$	= concentration of dissolved ozone at gas-liquid interface	$[mol \cdot m^{-3}]$
$R$	= gas constant	$[J \cdot mol^{-1} \cdot K^{-1}]$
$S_b$	= gas-liquid interfacial area per unit volume of liquid	$[m^2]$
$T$	= temperature	$[K]$
$t$	= time	$[s]$
$t_{1/2}$	= ozonation period when concentration of total chelates decreases to the half	$[s]$

$V_L$	= volume of liquid	$[m^3]$
$x$	= distance in liquid measured perpendicularly from gas-liquid surface	$[m]$
$\varepsilon_g$	= mean gas holdup	$[-]$
$\delta$	= film thickness	$[m]$

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