

# EQUILIBRIUM CONCENTRATION AND OVERALL HENRY'S LAW CONSTANT OF THE DISSOLVED OZONE

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**Abstract** : The purpose of this study were to evaluate Henry's law constants during ozonation in aqueous solution. The influence of the operating variables : pH, temperature, ionic strength, alkalinity and total organic carbon, on the overall Henry's law constant has been investigated. The overall Henry's law constant( $H_0$ ) calculated from the multiple regression analysis for the operating variables can be expressed as follows.

$$\ln H_0 = 0.23 \ln[pH] + 0.57 \ln[Temp] + 1.40 [I.S.] + 0.024 [Alk] + 0.053 [TOC] + 10.71$$

The most relevant was ionic strength. The effect of parameters on  $H_0$  was in proportion to  $[pH]^{0.23}$ ,  $[Temp]^{0.57}$ ,  $e^{1.4[I.S.]}$ ,  $e^{0.024[Alk]}$ ,  $e^{0.053[TOC]}$  for pH, temperature, ionic strength, alkalinity and total organic carbon, respectively. The ranges of  $H_0$ (kPa/mol<sub>l</sub>) were  $0.4 \times 10^6 \sim 20 \times 10^6$ . If the  $H_0$  value in aqueous solution is large enough, the equilibrium ozone concentration will not be increased by the large amount of the gaseous ozone dose. This occurs due to a drop in the liquid phase ozone mass transfer and to a higher ozone discharge in the air. The value of  $H_0$  was used to protect unnecessary gaseous ozone dose and determine the optimum ozone dose.

**Key Words** : equilibrium ozone concentration, overall Henry's law constant, ionic strength, alkalinity, total organic carbon

## INTRODUCTION

Rivers have lost their self-purification ability due to the growing problem of pollution with synthetic organic matter, micropollutants and trace heavy metals caused by the rising tendency of various chemicals and consumer products. A study on the elimination of inorganic matter, non-biodegradable organic matter and carcinogenic substance has been studied in advanced water treatment technique using ozone and granular activated carbon.<sup>1-4)</sup> Especially, the discovery of a blue-green algae that arouses the liver hemorrhage from the eutrophication lakes, a study on the decomposition of the toxins of

blue-green algae has been accomplished. It is very important to remove blue-green algae from water, in order to reduce the cells and dissolved toxins. It was found that ozonation was effective process to remove them, because its high oxidizing and disinfectant character and capacity to reduce the organohalogen formation potential of the water. Thus, the ozonation process has also been extensively studied.<sup>5-9)</sup> In the cases of dosing gaseous ozone to the ozonized contactor, the gaseous ozone and dissolved ozone approaches an equilibrium state by transferring liquid phase through Henry's law. The solubility of a gaseous ozone, that is the concentration of dissolved gas [ $C_{equi.}$ ], in a equilibrium with its partial pressure

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$$p = H [ C_{equi.} ] \quad (1)$$

where  $H$  is the Henry's law constant (kPa/mol<sub>f</sub>),  $[C_{equi.}]$  is the molar fraction (mol<sub>f</sub>) of equilibrium ozone for the water, and  $p$  is the partial pressure (kPa) for the dissolved ozone. The molar fraction in distilled water is in proportion to the concentration of dissolved ozone, but the equilibrium of the dissolved ozone shows a lower level in case of increasing Henry's law constant due to the fact that Henry's law constant is inversely proportional to the equilibrium dissolved ozone. The reason for the increasing of Henry's law constant is that the residual ozone is decreased because the consumption of dissolved ozone will be increased by the conditions of pH, water temperature, ionic strength, alkalinity and water quality.<sup>10-14)</sup> The Henry's law constant is an increasing function of temperature :

$$d \ln H = -\frac{H_a}{R} d\left(-\frac{1}{T}\right) \quad (2)$$

being  $R$  the gas constant and  $H_a$  is heat of absorption of the gas at the water temperature considered. In the case of electrolytic solution, the salt effect can be expressed by

$$\ln \frac{H}{H_w} = h [I.S] \quad (3)$$

where  $H_w$  is the Henry's law constant in water,  $[I.S]$  is the ionic strength of the solution and  $h$  the sum of contributions referring to the species of positive and negative ions present and to the species of gas.<sup>15)</sup> A general Henry's law constant

equation that considers the factors on the various solutions of salts is presented in Table 1.<sup>16)</sup>

The purpose of this study were to evaluate overall Henry's law constant ( $H_0$ ) and the concentrations in the water-gas interface in equilibrium with the gas. The empirical equation of  $H_0$  was estimated by the multiple regression analysis FORTRAN program where the overall operating conditions of factors and measured  $H_0$  value are to be inputted after decision of the reaction order with  $H_0$ . The equations  $H_0$  allow us to know the residual ozone concentration involving the influence of the factors. If the residual ozone concentration is not enough to decompose the objective substances, we would like to preserve the residual ozone by controlling the concentration of factors on  $H_0$ . That is, the residual ozone concentration is to be increased by the factors that make low  $H_0$ . Furthermore, the value of  $H_0$  calculated by this predictive equation was used to protect unnecessary gaseous ozone dose and decide the optimum ozone dosage.

## MATERIALS AND METHODS

The schematic diagram of the laboratory set-up is shown in Figure 1. The ozone generator is KD-800W used as a type of silent electrical discharge, frequently described as a corona discharge, and the ozone concentration was adjusted by the voltage control. The ozone production efficiency was increased by the water cooling system at the external side of the discharge tube. The ozone contactor is a

Table 1. General equations for Henry's law constant on the various solutions of salts

Type of salt	Parameters	pH	Temp. (°C)	I. S. (mol/L)	$H_0$ (kPa/mol <sub>f</sub> )
$\text{Na}_3\text{PO}_4$		2~8	0~20	0.001~0.5	$1.03 \times 10^9 [OH^-]^{0.012} e^{-\frac{2118}{T}} e^{0.96[I.S]}$
$\text{Na}_3\text{PO}_4$ , $\text{Na}_2\text{CO}_3$		7	0~20	0.01~0.1	$4.67 \times 10^7 e^{-\frac{1365}{T}} e^{2.98[I.S]}$
$\text{Na}_2\text{SO}_4$		2~7	20	0.05~0.5	$1.76 \times 10^6 [OH^-]^{0.062} e^{0.033[I.S]}$
NaCl		6	20	0.05~0.5	$4.87 \times 10^5 e^{0.48[I.S]}$
NaCl, $\text{Na}_3\text{PO}_4$		7	20	0.05~0.5	$5.82 \times 10^5 e^{0.42[I.S]}$

cylindrical column with a height of 2 m and a diameter of 0.08 m. The experiment was carried out in the semi-batch ozonation consisted of bubbling ozone gas through the water sample, and the process is termed semi-batch because it is batch in water and continuous in ozone. The off-gas of the ozone contactor was drained under 0.01 mg/L through the inlet hood.

The experiment was to measure the gaseous and dissolved ozone.<sup>17)</sup> In case of gaseous ozone, it will be titrated by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 0.1N with H<sub>2</sub>SO<sub>4</sub> 1N 10 ml after contacting the ozone of 2% KI 400 ml. The concentration of liquid ozone was analyzed by the Indigo colorimetric method, which is based on the principle that the ozone makes a decoloration of blue color for the indigo. The analysis was done after mixing 10 ml of the indigo reagent with 90 ml of the sample, and the measurement was done by the UV absorption at 600 nm. The conditions in the semi-batch reactor for the experiments of the dissolved ozone equilibrium concentration was presented in Table 2. The concentration of gaseous ozone was 2.3 mg/L, the ozone contact time was 30 minutes, and the partial pressure of ozone was 0.11 kPa. The ozone gas flow rate was 0.2 L/min. The test water is a kind of prepared water, and the methods for dispensing of each factor are as follows. The level of pH was controlled by the addition of HCl or NaOH to the pure water, and the buffer was not used to consider the individual effect on pH. The water temperature was controlled by the heater and cooler. The ionic strength was settled by 0.05M~0.25M using MgCl<sub>2</sub>. The alkalinity was controlled by Na<sub>2</sub>CO<sub>3</sub>, and the total organic carbon was regulated by the humic acid that is

a natural organic matter(NOM) in natural water.<sup>1,9)</sup> The ionic strength was measured by the conductometer, and the alkalinity was measured by the Standard Method. The alkalinity was measured by the titration of the solution of 0.02N H<sub>2</sub>SO<sub>4</sub> after placing 100 ml of the sample with two or three drops of methyl red indicator in the flask. The total organic carbon was analyzed by the TOC Analyzer (Dohrmann DC-180, USA) after filtering with 0.45 μm nitrate membrane filter, and the control of concentration was done by humic acid(Aldrich, USA).<sup>1,8,9)</sup>

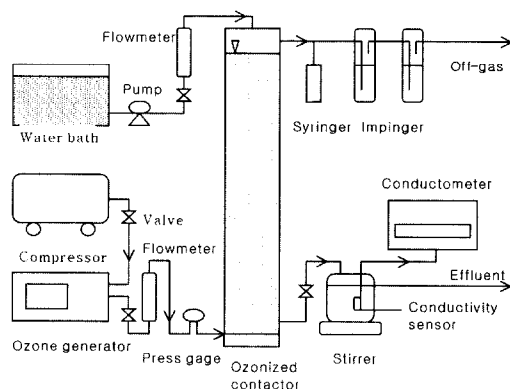


Fig. 1. The schematic diagram of the experimental apparatus.

## RESULTS AND DISCUSSIONS

### Effect of pH and Water Temperature on Equilibrium Ozone Concentration and Henry's Law Constant

In order to examine the equilibrium ozone concentration according to the pH and water temperature, the contact time with the aqueous solution by dosing the gaseous ozone was

Table 2. Conditions for the experiments of the equilibrium concentration of dissolved ozone

No of Run	Parameters	pH	Ionic strength (M)	Alkalinity (mg CaCO <sub>3</sub> /L)	TOC (mgC/L)	Temp. (°C)
Run I		5.0~9.0	0.0	0.0	0.05	20.0
Run II		5.0	0.05~0.25	0.0	0.04	20.0
Run III		7.0	5×10 <sup>-3</sup>	20~80	0.04	20.0
Run IV		7.0	6×10 <sup>-3</sup>	0.5	1.6~8.0	20.0
Run V		7.0	0	0	0.04	10~50

changed up to 50 minutes. The equilibrium was shown as preserving the constant concentration after 30 minutes of the contact time. At this moment, the equilibrium ozone concentrations (mgO<sub>3</sub>/L) are 0.68, 0.65, 0.63, 0.62, and 0.59 for the level of pH 5.0, 6.0, 6.5, 8.0, and 9.0 respectively and shows 0.69, 0.54, 0.35, and 0.27 for the water temperature(°C) 10, 15, 30, and 50 respectively. The equilibrium ozone concentration presents a remarkable difference for the changes of water temperature rather than that of pH. Figure 2(a) and 2(b) show the effect of pH and water temperature on the absorbed ozone concentration. The residual ozone concentrations decrease when the pH and water temperature are increased. That is, the equilibrium ozone concentration was decreased by following the higher pH and water temperature even though the dosage of gaseous ozone was increased. It is considered that the gaseous ozone mass transfer is reduced, and then the

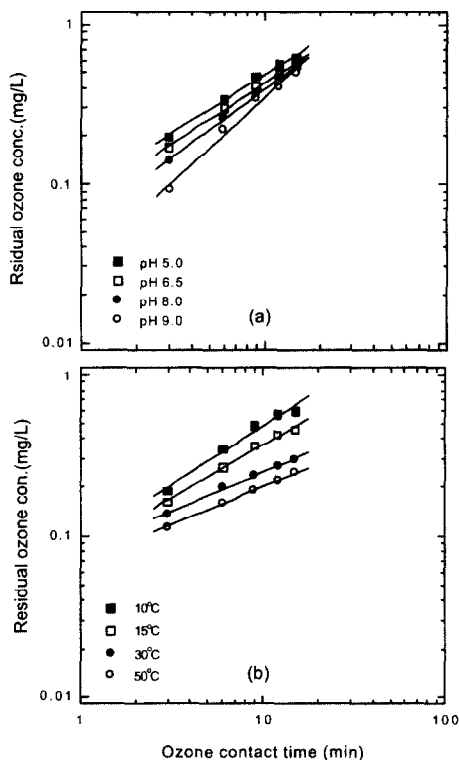


Fig. 2. Effect of (a) pH and (b) water temperature on residual ozone.

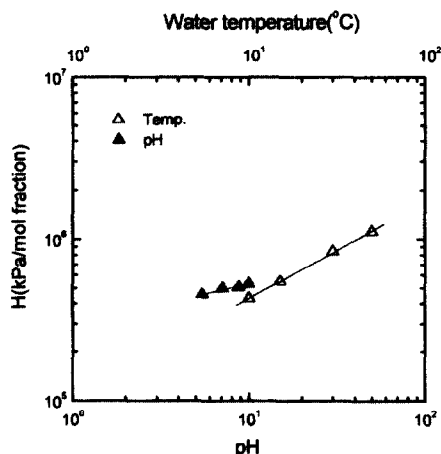


Fig. 3. Effect of pH and water temperature on Henry's law constant of dissolved ozone.

amount of discharged gaseous phase is much more than the dissolved ozone.<sup>8)</sup>

The effect of pH and water temperature on the Henry's law constant of dissolved ozone is shown in Figure 3. Henry's law constant in the state of equilibrium is calculated as the partial pressure(110 Pa, 1.09×10<sup>-3</sup> atm) divided by the molar fraction of the dissolved ozone for water as presented in Eq. (4).

$$C^* = \frac{[O_3]}{[O_3] + [H_2O]} \tag{4}$$

where C\* is the ozonic molar fraction(molf) in the state of equilibrium for water, [O<sub>3</sub>] is the molar concentration of ozone, [H<sub>2</sub>O] is the molar concentration of water. Henry's law constant was determined from correlations as a function of pH and temperature:

$$\ln H_{pH} = 0.23 \ln[pH] + 12.6 \tag{5}$$

$$\ln H_{Temp.} = 0.57 \ln[Temp] + 11.7 \tag{6}$$

The coefficient of determination for Eq. (5) and (6) are 0.946 and 0.999, and the standard deviation are 0.00774 and 0.00695, respectively. Henry's law constant of dissolved ozone(10<sup>6</sup>kPa/mol<sub>l</sub>) was 0.4~0.5 at pH 5~9, 0.4~1.0 at the water temperature 10~50(°C). It shows the

higher value for the higher water temperature and pH. This shows that the equilibrium ozone concentration is decreased in case of the higher water temperature and pH under the constant pressure, and Henry's law constant was to increase by Henry's law as presented in Eq. (1).<sup>8)</sup> Especially, Henry's law constant was remarkably changed by the water temperature rather than that of pH. This means that the control of the water temperature was a more effective way to preserve the high level of the equilibrium ozone of an aqueous solution.<sup>8)</sup>

### Effect of Ionic Strength, Alkalinity and Total Organic Carbon on Equilibrium Ozone Concentration and Henry's Law Constant

The residual ozone concentration before the equilibrium concentration as a function of the ionic strength, alkalinity, and total organic carbon are shown in Figure 4(a), 4(b), and 4(c). The equilibrium ozone concentrations(mgO<sub>3</sub>/L) according to the factors are 0.72, 0.68, 0.64, 0.62, and 0.53 for the ionic strength 0.05, 0.10, 0.15, 0.2, and 0.25M, respectively, and 0.63, 0.48, 0.24, and 0.16 for the alkalinity(mg/L) 20, 40, 60, and 80, respectively, and 0.15, 0.14, 0.12, and 0.11 for the total organic carbon(mgC/L) 1.6, 2.7, 5.0, and 8.3 respectively. The residual ozone concentrations decrease as ionic strength, alkalinity and total organic carbon grow, due to the fact that high these values are inducing the ozone decomposition.<sup>8)</sup>

Henry's law constant of the dissolved ozone as a function of the ionic strength, alkalinity, and total organic carbon was presented in Figure 5. Henry's law constants(10<sup>6</sup>kPa/mol<sub>r</sub>) for the ionic strength, alkalinity, and total organic carbon are 0.40~0.55, 4.7~18.5, and 2.0~2.8 respectively. Henry's law constant was determined from correlations as a function of ionic strength, alkalinity and total organic carbon:

$$\ln H_{I.S} = 1.4 [I.S] + 1.31 \quad (7)$$

$$\ln H_{Alk.} = 0.024 [Alk.] + 0.92 \quad (8)$$

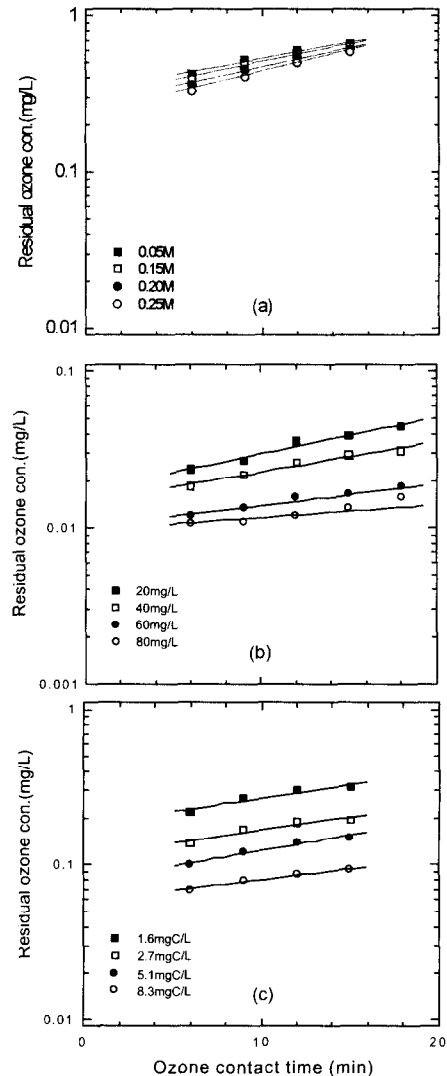


Fig. 4. Effect of (a) ionic strength (b) alkalinity and (c) TOC on residual ozone.

$$\ln H_{TOC} = 0.053 [TOC] + 0.58 \quad (9)$$

The coefficients of determination for Eq. (7), (8), and (9) are 0.929, 0.969, and 0.986 respectively, and the standard deviations are 0.01785, 0.0583, and 0.00979 respectively, where Eq. (9) is superior to the others. Several parameters can influence the Henry's law constant. The most relevant is ionic strength. That is, the larger ionic strength shows the higher Henry's law constant and is to decide the

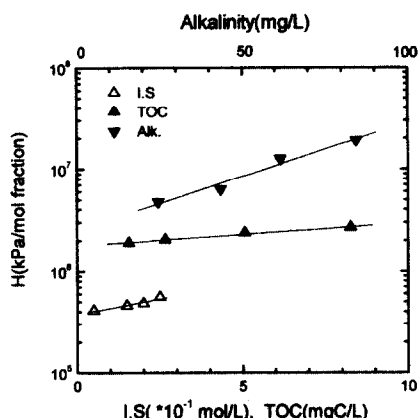


Fig. 5. Effect of ionic strength, alkalinity and TOC on Henry's law constant of dissolved ozone.

optimum ozone dosage because the equilibrium ozone concentration is not increased even though the gaseous ozone dosage is increased.<sup>8)</sup>

### Overall Henry's Law Constant of the Dissolved Ozone

The measurement of overall Henry's law constant ( $H_{01} \sim H_{05}$ ) under the operating conditions was presented in Table 3. The value  $H_{01}$  of Run VI was the smallest, and the value  $H_{05}$  of Run X was the largest. The small value of  $H_0$  means that the dissolved ozone concentration is large in

the dose of gaseous ozone to water, and the large value of  $H_0$  means that the ozone discharge in the air is much more than the dissolved ozone even though the large amount of the gaseous ozone is dosed to water.<sup>8,9)</sup>

The overall Henry's law constant equation calculated from the multiple regression analysis by using the measured values of  $H_{01} \sim H_{05}$  was shown in Eq. (10). The application ranges and units of  $H_0$  were presented in Table 4.

$$\ln H_0 = 0.23 \ln[\text{pH}] + 0.57 \ln[\text{Temp}] + 1.40[\text{I.S}] + 0.024[\text{Alk}] + 0.053[\text{TOC}] + 10.71 \quad (10)$$

Effect of pH, water temperature, ionic strength, alkalinity, and total organic carbon on  $H_0$ , the most relevant was ionic strength. Therefore, it showed that the control of the ionic strength was the most effective method to preserve the equilibrium ozone as the higher level with the lower Henry's law constant of the aqueous solution. Figure 6 shows the  $H_0$  and equilibrium ozone concentration by using the measurement and prediction with Eq. (10). The equations of line  $y = 0.890x + 0.13$ ,  $y = 0.831x + 0.044$  and the multiple correlation coefficients as 0.876 and 0.889 show the excellent results comparatively.

Table 3. Determination of overall Henry's law constants under the operating conditions

No of Run	Parameters	pH	Temp. (°C)	I.S. (mol/L)	Alk. (mg/L)	TOC (mgC/L)	$H_{01} \sim H_{05}$ ( $10^6 \text{ kPa/mol}_l$ )
VI		7.0	15	0.10	25	0.5	0.768
VII		7.0	20	0.15	20	0.2	0.818
VIII		8.0	20	0.15	25	1.0	0.989
IX		7.0	20	0.20	20	0.2	0.811
X		7.5	20	0.20	30	1.0	1.099

Table 4. Application ranges and units for overall Henry's law constant ( $H_0$ )

Parameters	Application	Units	Ranges	Variable type
pH			5.0 ~ 9.0	independent
Water temp.		°C	10 ~ 50	independent
Ionic strength		mol/L	0.05 ~ 0.25	independent
Alkalinity		mg/L	20 ~ 80	independent
TOC		mgC/L	0.2 ~ 8.3	independent
$H_0$		$10^6 \text{ kPa/mol}_l$	0.4 ~ 20	dependent

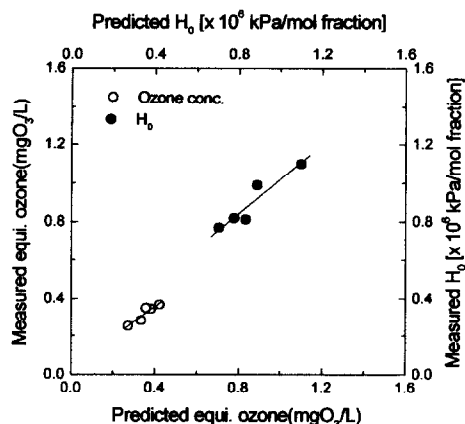


Fig. 6. Comparison of predicted equilibrium ozone profile and overall Henry's law constant with measurement.

## CONCLUSIONS

The purpose of this study are to evaluate Henry's law constants during ozonation in aqueous solution. The overall Henry's law constant ( $H_0$ ) calculated from the multiple regression analysis for a given operating conditions can be presented as follows.

$$\ln H_0 = 0.23 \ln[\text{pH}] + 0.57 \ln[\text{Temp}] + 1.40 [I.S.] \\ + 0.024 [Alk] + 0.053 [TOC] + 10.71$$

Several parameters can influence the Henry's law constants. The most relevant was ionic strength. The effect of parameters on  $H_0$  was in proportion to  $[\text{pH}]^{0.23} [\text{Temp}]^{0.57} e^{1.4[I.S.]} e^{0.024[Alk]}$ ,  $e^{0.053[TOC]}$  for pH, water temperature, the ionic strength, alkalinity and total organic carbon, respectively. The range of  $H_0$  (kPa/mol<sub>l</sub>) was  $0.4 \times 10^6 \sim 20 \times 10^6$ . If the value of  $H_0$  of the aqueous solution is large enough, the residual ozone concentration will not be increased by the large amount of the gaseous ozone dosage. This occurs due to a drop in the liquid phase ozone mass transfer and to a higher ozone discharge in the air. The equations of line  $y = 0.890x + 0.13$ ,  $y = 0.831x + 0.044$  for the value of  $H_0$  and measured value according to the predicted value of the equilibrium ozone

concentration relatively, and the the multiple correlation coefficients as 0.876 and 0.889 present the excellent results comparatively.

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