PARTITIONING OF SOME VOLATILE ORGANIC COMPOUNDS BETWEEN AIR AND WASTEWATER FROM 288 To 303 K

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This study investigated effects of temperature and organic content in wastewater on the air-liquid partitions of isopropanol, acetone and *p*-xylene. A supernatant obtained from centrifugation of activated sludge as the test liquid. Dimensionless Henry's law constants (K_H) in a deionized water and dimensionless apparent Henry's law constants (K'_H) in the supernatant containing one of the VOCs were measured at 288 to 303 K. K'_H for all the three VOCs decrease with an increase in the dissolved total organic carbon (TOC) concentration in the wastewater. A model correlating K'_H with the organic carbon-water partition coefficient, TOC concentration and temperature was derived.

Keywords: *Henry's law constant, temperature effect, dissolved organic carbon*

INTRODUCTION

Emission control of volatile organic compounds (VOCs) is concerned in manufactories and wastewater plants for many years. The VOCs-contamination gases and wastewater lead negative impacts on human health and environment. Biodegradation is a popular technique for treatment of particular contaminants. In bioreactor, activated sludge is a group of suspended growth biomass that is acclimated for treating gaseous and liquid pollutants. Wastewater in the activated sludge mixed liquor serves as a competent character for affect the VOCs equilibrium between gases, organic compounds and water.

The involvement of organic carbon in wastewater avail the sorption capacity itself for bound VOCs. The dissolved and colloidal organic carbons provide sorption and binding site for hydrophobic organic compounds. Such mechanisms could improve the ability of a sorption unit to remove organic contaminants. In the sediment and wastewater environment, linear partition model can be described the sorption phenomena and quantified by the organic carbon-water partition coefficient (K_{OC}) [1]. Dissolved organic carbon (DOC) (e.g. fulvic and humic acid) in wastewater will increase the observed solubility of VOCs [2,3]. The polarity and molecular size of DOC participate in enhancing solute solubility [4,5]. Octanol-water partition coefficient (K_{OW}) of a VOC could be an indicator to evaluate the sorption ability from water to octanol. Linear free energy relationship can correlate K_{OW} with K_{OC} to predict the variation trend for particular VOCs [6,7]. A compound with a higher K_{OW} value has normally a higher degree hydrophobic character, therefore, a higher disposition with soluble organic matter.

Henry's law constant (H, atm m^3/mole) is an important factor, which is a ratio of vapor pressure and solubility for estimating the equilibrium of VOCs between air and liquid phases in environmental application. For environmental applications, the H usually expressed as a dimensionless form (K_H) and also called an air-water partition coefficient in environmental literature:

$$K_H = C_g / C_w \tag{1}$$

where C_g and C_w are the gas- and liquid-phase VOC concentrations (mg/L), respectively. The apparent dimensionless Henry's law constant (K'_H) can be an indicator for air-liquid equilibrium. The variation of K'_H has been observed in a close system with introducing of DOC in wastewater [8] and sediment system [9]. In organic-containing liquid, the K'_H of VOCs is decreased by the enhanced solubility of DOC.

K_H of environmental important compounds in pure water have been reported by a number of researchers and it is a temperature depended factor [10,11]. However, few studies discussed the K'_H in wastewater system. Furthermore, K_{OC} express thermal equilibrium between water-organic phases, but few literatures focus on the K_{OC} temperature effect in wastewater. This paper presents effects of temperature and DOC isolated from activated sludge on the K_H, K'_H and K_{OC} for some industrial VOCs. In addition, a thermodynamic analysis of the VOCs-DOC system is presented and discussed.

THEORETICAL

The K_H in pure water system has been defined as shown in Eq. (1) with C_w in pure water. In wastewater system, a model applied to VOC partitioning between vapor, water and liquid phase organic carbon has been developed [8]. In water containing organic matters, VOC is adsorbed on the DOC and related of K_{OC} can be expressed as following equations:

$$C_g \xleftrightarrow{K_H} C_w \xleftrightarrow{K_{OC}} DOC\text{–}bound\ \ VOC \tag{2}$$

$$K_{OC} = \frac{DOC\text{–}bound\ \ VOC}{C_w} = \frac{C_d / S_d}{C_w} \tag{3}$$

where C_d and S_d are the DOC-bound VOC and DOC concentrations, respectively, both based on the liquid-phase volume (mg/L). C_d/S_d represents the mass of VOC bound to that of DOC and has a unit of mg VOC/(mg DOC).

The total VOC concentration C_T with water containing DOC is the sum of aqueous VOC of concentration C_w and DOC-bound VOC of concentration C_d:

$$C_T = C_w + C_d \tag{4}$$

In the system, the sorption phenomenon for a specific VOC can be described as Eq. (5). With a system composed of water and DOC, K'_H can then be express as Eq. (6):

$$C_g \xleftrightarrow{K'_H} C_T \tag{5}$$

$$K'_H = \frac{C_g}{C_T} = \frac{C_g}{(C_w + C_d)} = K_H \frac{1}{1 + K_{OC} \times S_d} \tag{6}$$

The partition of a VOC between two phases is strongly temperature dependent. Thermodynamics can be introduced to analyze this temperature dependency. From theoretical consideration, the partition coefficient can be expected by Van't Hoff's equation [9,12] as:

$$\frac{-d\ lnK'_H}{d(1/T)} = \frac{\Delta H'_{gw}}{R} \tag{7}$$

$$\frac{-d\ lnK_{OC}}{d(1/T)} = \frac{\Delta H'_{OC}}{R} \tag{8}$$

where T is the system temperature (K); R is the universal gas constant (8.314 J mole^{-1} K^{-1}); $\Delta H'_{gw}$ and $\Delta H'_{OC}$ is the phase change enthalpy of gas-liquid and organic carbon-liquid (J/mole), respectively. $\Delta H'_{gw}$ and $\Delta H'_{OC}$ represent the energy required to overcome the attractive force in the transfer of molecules between the two phases. An average $\Delta H'_{gw}$ and $\Delta H'_{OC}$ over a certain temperature range can be estimated from a linear regression of the experimental ln K'_H or ln K_{OC} *vs.* 1/T according to Eqs. (7) and (8).

The Gibbs-Helmholtz equation can be introduced as the following equations to obtain the temperature dependence of K'_H and K_{OC} [13,14]:

$$ln\ K'_H = (-\Delta H'_{gw} / R)(1/T) + \Delta S'_{gw\,w}/R \tag{9}$$

$$ln\ K_{OC} = (-\Delta H'_{OC} / R)(1/T) + \Delta S'_{OC}/R \tag{10}$$

where $\Delta S'_{gw}$ and $\Delta S'_{OC}$ is the associated phase entropy change of gas-liquid and organic carbon-liquid (J mole^{-1} K^{-1}). By the regression of the experimental ln K'_H or ln K_{OC} at different temperatures versus 1/T, enthalpy and entropy change at interface can be obtained from the slope and intercept of the regressed straight line, respectively.

MATERIALS AND METHODS

An aeration tank was used for cultivation of the activated sludge for the present study. The seed sludge was obtained from a recycling line of an activated sludge system of a petrochemical wastewater plant of Kaohsiung Refinery, Chinese Petroleum Corp., Taiwan. A MLSS concentration in the range of 40,000-45,000 mg/L was kept in the laboratory aeration liquor with a pH value in the range of 6.8-7.2. The sludge was fed with glucose as a carbon source. A daily organic loading rate of 0.20 kg COD (chemical oxygen demand) per kg sludge (dry basis) was kept for the whole experimental period. In addition to the organics, urea, potassium dihydrogen phosphate, and ferric iron were added to the activated sludge liquor as supplemental nutrients with a constant mass ratio of COD:N:P:Fe of 100:5:1:0.5. For supplementing natural nutrients, dried food yeast powder (Taiwan Sugar Co., Taiwan) was added to the aeration tank at a rate of 0.2 g/L per day. A sludge retention time in the range of 10-15 days was kept by maintaining a proper sludge-wasting rate.

A simplified centrifugation method was used to separate the wastewater from the activated sludge mixed liquor. A fixed volume of the mixed liquor sample was centrifuged in a centrifuge (Universal 30F, Hettich, Germany) operated at 11,000 rpm (15,000 g) for 15 min. The centrifugation efficiently separated the mixed liquor into two parts: activated sludge biomass with bound water and supernatant wastewater. The supernatant was then filtered through a 4.7-cm diameter cellulose acetate membrane (Advantec MFS, Inc., USA) with an average pore size of 0.45 µm. The filtrate was then stored at 4 ^{o}C for subsequent experiments. Before the sorption experiment, the prepared filtrate was pasteurized at 80 ^{o}C for 2 hrs to inactivate the bacteria activity. The pasteurized samples were then diluted with deionized (DI) water (NANOpure, Barnstead, USA) to obtain the desired concentrations.

Static methods has usually been used in measuring Henry's law constant [11]. Several headspace analysis techniques have been applied for explain the variations of Henry's law constant in wastewater investigation [8,15]. In this work, a single equilibration technique (SET) was adopted for detecting the Henry's law constant change[16]. By the technique, an equilibrium of the tested VOC between the liquid and gas phases was established within a gas-tight vessel that contained a fixed volume activated sludge and the VOC at a constant temperature. K'_H could then be calculated from the headspace analysis result by the following relationship:

$$K'_H = \frac{C_g}{C_T} = \frac{C_g}{(m_T - C_g V_g)/V_L} = \frac{C_g V_L}{(m_T - C_g V_g)} \tag{11}$$

where V_L is the bulk volume of the liquid phase injected with an initial mass of m_T of the VOC and V_g the overhead gas volume.

The standard SET procedures in this study are as follows. Isopropanol (IPA), acetone and *p*-xylene were selected for the target VOCs. All the VOCs were analysis ACS grade obtained from E. Merck, Germany. A water-bath shaker could be operated at a shaking rate of 0-200 rpm and the water temperature be controlled to a constant value in 0-100 ^{o}C with a precision of 0.1 ^{o}C. Constant temperatures of 288, 293, 298 and 303 K, respectively, were adopted in the present study. The prepared samples were shaken at 150 rpm for 2 hours at the preset temperature and the shaker turned off for the following 2 hours in order to get equilibrium of the organic compound between phases. In the case of water-soluble IPA and acetone, vials of nearly 43 mL (Kimble Glass, USA) were used for the tests. 40 mL of one of the DI water and wastewater filtrate (abbreviated as wastewater) were used for each 43-mL vial with a screw cap and PTFE septa. For much less water-soluble *p*-xylene, Erlenmeyer flasks (Kimble Glass, USA) with an empty volume of around 310 mL were used. The flask was filled with 302 mL of one of the experimental liquids before sealed by a screw-fasten cap with a PTFE septum. Before the tests, the inner volume of each of the vials or flasks was determined by the water-replacement method. Every liquid sample volume in the vial or flask was obtained by weighting and modified by its density. After sealing of all the vials or flasks, a fixed volume (IPA 20 µL, acetone 5 µL and *p*-xylene 2 µL) of each liquid organic compound was injected into each of them by a syringe (Hamilton, USA). After completing the standard SET procedures, 1.0 mL of the overhead gas sample in each vial or flask was extracted using a gas-tight sampling syringe for analyzing the target compound concentration. 3-12 replicates of bottles were prepared for each liquid concentration. Notably, the sampling period was kept as short as possible to prevent any possible disturbance of the gas-liquid equilibrium.

C_g for each gas sample was analyzed by a gas chromatography (GC-14B, Shimadzu, Japan) equipped with a flame ionization detector (GC-FID). A 30 m x 0.53 mm ID x 5.0 µm film thickness capillary column (AT-1, Alltech, USA) was used in the GC-FID. K'_H for each compound in each liquid was then obtained from Eq. (11). Statistical analysis was then performed to obtain the mean and standard deviation (SD) for the estimated K'_H values. For regression works, the confidence interval was set to be 95%. Statistical analyses were carried out by using the SigmaPlot (SSI, USA) and Microsoft Excel.

RESULTS AND DISCUSSION

K'_H and K_{OC} in Wastewater

The K'_H/K_H decrease level associated with the dissolved organic can be plotted in Figure 1. The K'_H also can be predicted by TOC concentration and K_{OC}. Hydrophobic VOCs usually have high K_{OW} and K_{OC}. The lower K'_H is caused by higher TOC concentration and higher K_{OC} value. The hydrophobic VOCs will have higher sorption ability than hydrophilic ones to organic carbon in wastewater system, that is, less emission to gas phase. This relationship can applied to predicted the K'_H changes in wastewater system.

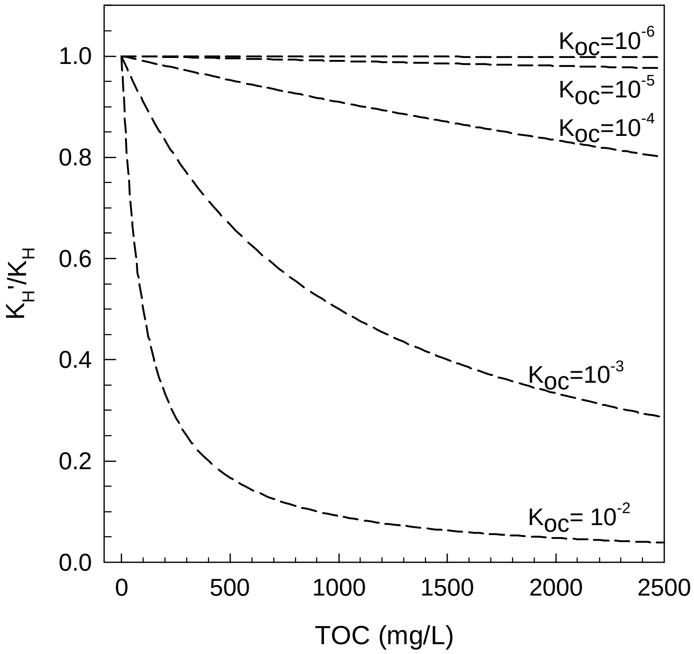

Figure 1. Prediction of K'_H / K_H changes with K_{OC} and total organic carbon (TOC) oncentration.

Using the SET method, experimental K'_H data for IPA, acetone and *p*-xylene in the wastewater at 293 to 303 K are shown in Figures 2 to 5. K'_H corresponding to 0 DOC (TOC = 0) are for compounds partitioning between air and DI water, i.e., $K'_H = K_H$. K'_H for all tested compounds decreased with increasing organic content in the wastewater. The maximum change of K'_H for all test compounds in the wastewater were 17% smaller than those in DI water. This indicates that all the tested compounds have a little greater affinity to the dissolved organics than to water, although the differences between K_H and K'_H are small because of the low TOC contents of the wastewater.

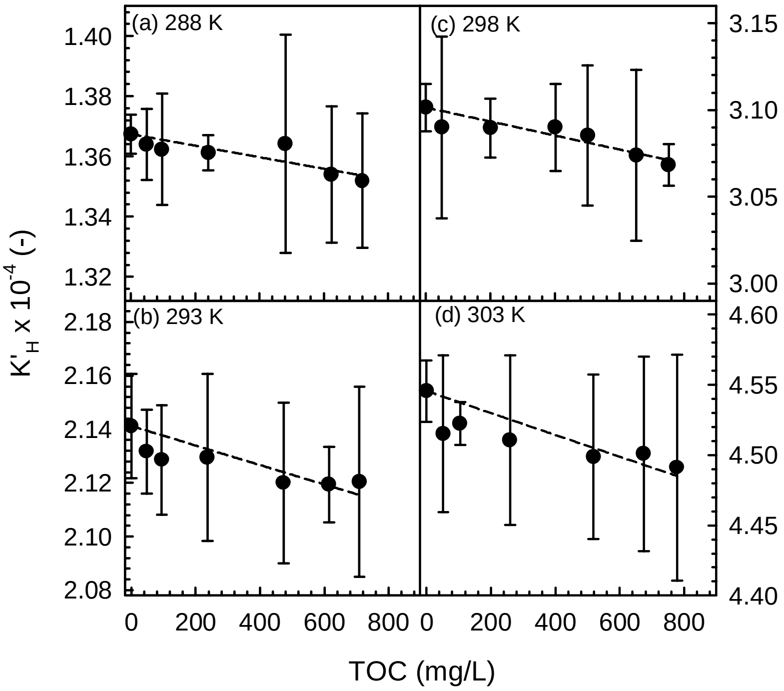

Figure 2. K'_H and SD of IPA varied with TOC concentration in wastewater samples at (a) 288 K, (b) 293 K, (c) 298 K and (d) 303 K.

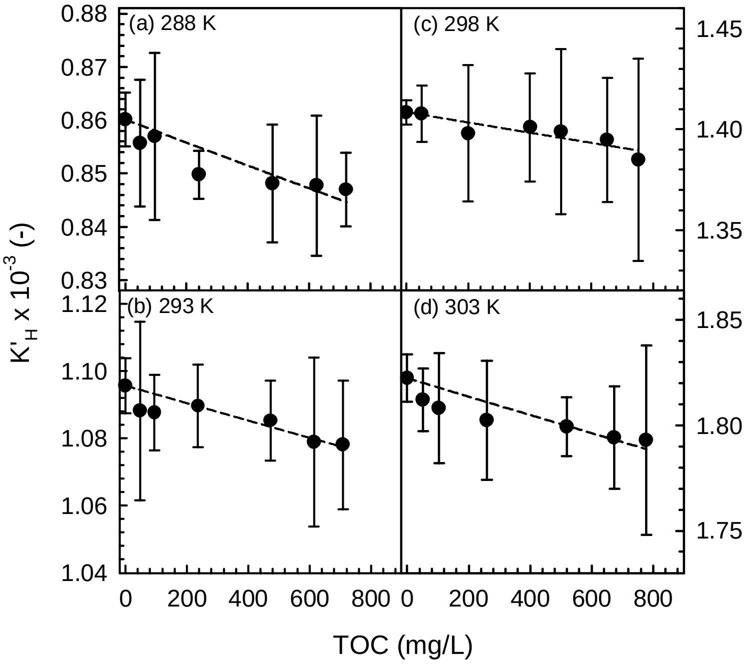

Figure 3. K'_H and SD of acetone varied with TOC concentration in wastewater samples at (a) 288 K, (b) 293 K, (c) 298 K and (d) 303 K.

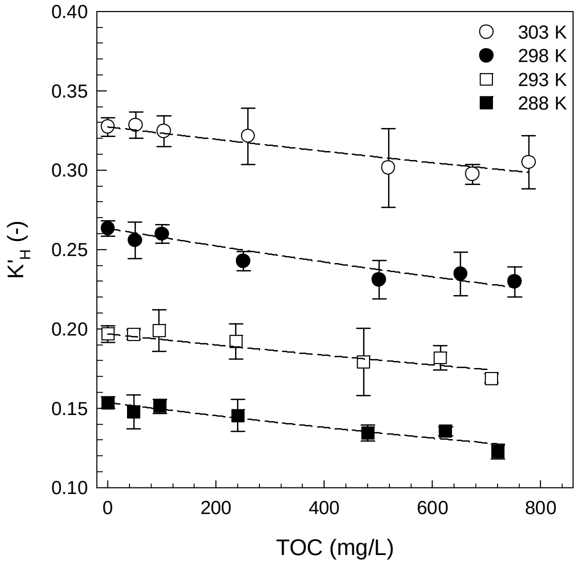

Figure 4. K'_H and SD varied with TOC concentration in wastewater samples for *p*-xylene.

K_{OC} values were estimated from regressions of the experimental data from Eq. (6). The regression lines were also plotted in ures. 2 to 5. Data of K_{OW}, cited K_{OC} at 298 K and experimental ones in this work at 288 to 303 K were listed in Table 1. For ensuring the significance of dependency between K'_H and K'_H at the tested temperature, the ANOVA was introduced for testing the independency. Results indicated most of the K'_H is independence from K_H with 95% ($F_{df} > F_{0.95}$) and 99% ($F_{df} > F_{0.95}$) significant in the TOC range. The SET method associated with ANOVA process can get KOC with in a small range of TOC concentrations.

Table 1. The experimental results of K_{OC} (L/mg) and analysis of variance (ANOVA) results of K'_H between DI water and wastewater samples in 288 to 303 K.

Compound	log K_{OW} [a]	Literature	Temp.	This work [e]		ANOVA [f]			
		$K_{OC} \times 10^6$	(K)	$K_{OC} \times 10^6$	R^2	*df*	F_{df}	$F_{0.95}$	$F_{0.99}$
IPA	0.05	30 [c]	288	14.0	0.968	6, 38	2.42	2.36	3.33
			293	12.8	0.847	6, 38	2.46	2.36	3.33
			298	11.3	0.832	6, 38	2.42	2.36	3.33
			303	11.2	0.758	6, 38	4.57	2.36	3.33
Acetone	-0.24	18 [c]	288	19.6	0.839	6, 38	4.23	2.36	3.33
			293	18.1	0.826	6, 38	2.41	2.36	3.33
			298	17.8	0.806	6, 38	2.43	2.36	3.33
			303	17.3	0.862	6, 38	3.89	2.36	3.33
p-xylene	3.15	1,230 [c]	288	290.2	0.891	6, 20	14.12	2.60	3.78
		65-324 [d]	293	216.7	0.891	6, 20	4.84	2.60	3.78
			298	191.8	0.895	6, 20	11.92	2.60	3.78
			303	130.9	0.870	6, 20	4.16	2.60	3.78

[a.] Recommended values [17]; [b.] Experimental value [18]; [c.] Calculated from log K_{OC} = 0.544 log K_{OW} + 1.377, which has been widely used chemical property estimation [18]; [d.] Experimental values [19]; [e.] Experimental results regressed from Eq (6); [f.] K'_H Replications for DI water n=9, TOC sample n=6 (for IPA and acetone) and n=3 (for *p*-xylene) at each TOC concentration; *df*: degree of freedom; F_{df} is the cumulative F distribution; $F_{0.95}$ and $F_{0.99}$ is F distribution at 95% and 99% confidence interval, respectively.

Thermodynamic Analysis

The temperature effect of K'_{H} in gas-liquid partition system for IPA, acetone, and *p*-xylene between 288 and 303 K were shows in Figures. 2 to 5 and Table 1. The K'_H is increased with increasing the system temperature but K_{OC} is decreased. The temperature dependence of K_{OC} is related to the temperature dependence of change in enthalpy of dissolution in water. The phase change enthalpy of VOC is temperature related should be considered. The relationship of VOC phase change enthalpy can be pressed as Eq. (12):

$$\Delta H'_g \xleftrightarrow{\Delta H'_{gw}} \Delta H'_w \xleftrightarrow{\Delta H'_{OC}} \Delta H'_d \tag{12}$$

where $\Delta H'_g$, $\Delta H'_w$ and $\Delta H'_d$ is phase change enthalpy of VOC dissolution in gas, water and organic carbon (J/mole), respectively. The $\Delta H'_{gw}$ and $\Delta H'_{OC}$ can be gotten from Eqs. (9) and (10) and be listed in Table 2.

By consequence the $\Delta H'_{OC}$, the sorption of VOCs from liquid phase to organic carbon phase release energy. For all VOCs partitioning into organic carbon phase releases energy, that is, the process is preferred lower temperature.

Table 2. Phase change enthalpy (kJ/mole) and entropy (J mole^{-1} K^{-1}) of target VOCs between gas, water and dissolved organic carbon.

	phase change enthalpy		phase entropy change	
VOCs	$\Delta H'_{gw}$	$\Delta H'_{OC}$	$\Delta S'_{gw}$	$\Delta S'_{OC}$
IPA	57.7	-11.8	126.5	-19.1
Acetone	36.3	-5.7	67.3	4.8
p-xylene	37.2	-36.4	113.5	-79.1

CONCLUSIONS

The SET is simple and reliable for determining the gas-liquid partition coefficients in water and wastewater system for both hydrophilic and hydrophobic VOCs. The introduction of DOC will decrease the K'_H by sorption effect and reduce VOCs emission from wastewater system. Temperature effects of partition coefficient (K'_H and K_{OC}) are observed to and thermodynamic analysis can get phase change enthalpy and entropy. The result indicated the system is preferred lower temperature.

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