Henry’s Law Constant Variations of Volatile Organic Compounds in Wastewater and Activated Sludge

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Abstract

Henry’s law constant is an important equilibrium factor in the mass transfer process of volatile organic compounds (VOCs). A single equilibration technique (SET) was adopted to measure the air-water dimensionless ($K_H$) and the dimensionless apparent ($K'_H$) of Henry’s law constant in an air-wastewater system and air-activated sludge for VOCs at 298 K. Hydrophilic VOCs (methanol, isopropanol and acetone) and hydrophobic VOCs (toluene and $p$-xylene) were used as target compounds. Deionized (DI) water, (DI-water diluted and pasteurized wastewater (abbreviated as wastewater) with a maximum dissolved total organic carbon (TOC) content of 700 mg/L) and DI-water diluted and pasteurized activated sludge (abbreviated as mixed liquor) with a maximum suspended solid concentration of 40,000 mg/L were used as liquids.

$K'_H$ of the target hydrophilic compounds in the mixed liquor with a maximum-suspended solid concentration were 8.9 to 19.9% higher than those in DI water. Those for toluene and $p$-xylene decreased up to 70.8 and 88.3% in the mixed liquor, respectively. $K'_H$ of all the test compounds in the wastewater was only 1 to 11% smaller than those in DI water. A model was proposed for correlating $K'_H$ with wastewater TOC and activated sludge concentration using an organic carbon-water partition coefficient ($K_{OC}$) and activated sludge-water partition coefficient ($K_P$) as model parameters.

Keywords: Partition coefficient, phase equilibrium, mixed liquor suspended solid, total organic carbon, bioscrubbing.

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INTRODUCTION

Emissions of volatile organic compounds (VOCs) from wastewaters and exhaust gases are often overlooked as sources of exposure to hazardous substances. The biological treatment of gaseous pollutants has been popularized in the recent two decades for the emission control of biodegradable pollutants. In general, a suspended-growth system includes a sorption unit which utilizes an activated sludge liquid as a scrubbing liquor followed by an aerated activated sludge reactor for further oxidation of the scrubbed contaminants (Overcamp et al., 1993; Burgess et al., 2001). High concentration recirculated activated sludge has been applied to remove gas stream VOCs by a Venturi tube bioreactor (Zigmontiene and Baltenas, 2004).

For effective removal of the gaseous contaminants, equilibrium of VOCs between air, wastewater and activated sludge has become an important topic. The appearance of dissolved organic compounds (e.g., humic and fulvic acids) in water will affect the water solubility. The magnitude of the equilibrium constant can be described by a linear partition coefficient model (Haas and Kaplan, 1985). In addition, the existence of suspended organic solids in liquid can enhance the solubility of VOCs of low water solubility. Between water and biomass, the accumulation of some VOCs or hazardous pollutants by live (Smith et al., 1993; Wang and Grady, Jr., 1995), dead (Dobbs et al., 1989; Tsezos and Wang, 1991), and pasteurized (Moretti and Neufeld, 1989; Dobbs et al., 1995) microorganisms has been investigated. By the sorption of the biomass, the total VOC contents in the liquor will be raised; that is, the existence of biomass will increase the apparent solubility of VOCs in the liquor.

Many Henry’s law constant values of environmental significant compounds in pure water phase have been published (Mackay and Shiu, 1981). Even though these data are important for understanding the fate and transport of VOCs, they could not satisfactorily be used for liquids containing other components, such as non-volatile organic compounds or activated sludge. The apparent Henry’s law constants of some hydrophobic organic compounds could be changed by dissolved organic carbon (DOC) concentration in wastewater (David et al., 2000). The apparent Henry’s law constant decreases, or the apparent solubility increases by raising the pasteurized biomass concentration in the liquid (Davison et al., 2000; Barton et al., 2003).

Although many studies have investigated the VOC equilibrium change between two phases, little attention has been paid to that in three phase systems, especially for hydrophilic VOCs. The target of this research was to discuss the partitioning equilibrium migration in gas-deionized water, gas-wastewater, and gas-water-activated sludge systems. High concentration of biomass would improve the dissolution of hydrophobic VOCs from contaminated air streams. This study provides phase equilibrium information for hydrophilic and hydrophobic VOC treatment by bioscrubbers or bubble column.
THEORETICAL

The dimensionless Henry’s law constant \( (K_H) \) has been presented in Eq. (1) and called as an air-water partition coefficient in the environmental literature:

\[
K_H = \frac{C_g}{C_w}
\]  

(1)

where \( C_g \) and \( C_w \) are the gas- and aqueous-phase VOC concentrations (mg/L), respectively.

A model describing the partitioning of a VOC between vapor, water and dissolved organics has been applied in wastewater system (David et al., 2000). In wastewaters with some dissolved organics, the sorption phenomenon for a specific VOC can be described as Eq. (2) in which the dissolved VOC exists both in the aqueous phase and combined with the DOC. The partition coefficient \( (K_{OC}) \) of VOC between the DOC and the aqueous phases can be expressed as Eq. (3).

\[
C_g \xrightarrow{K_H} C_w \xrightarrow{K_{OC}} \text{DOC-bound VOC}
\]  

(2)

\[
K_{OC} = \frac{\text{DOC-bound VOC}}{C_w} = \frac{C_d / S_d}{C_w}
\]  

(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 bounded to that of DOC and has a unit of mg VOC/(mg DOC).

In a liquid containing activated sludge (i.e., mixed liquor), the VOC is adsorbed on the suspended solids (SS) and the partition coefficient \( (K_p) \) of the VOC between the solid and the aqueous phases can be expressed similar to Eq. (4-5):

\[
C_g \xrightarrow{K_H} C_w \xrightarrow{K_p} \text{SS-bound VOC}
\]  

(4)

\[
K_p = \frac{\text{SS-bound VOC}}{C_w} = \frac{C_S / S_S}{C_w}
\]  

(5)

where \( C_S \) and \( S_S \) are the SS-bound VOC and suspended-solid (SS) concentrations, both based on the liquid-phase volume (mg/L). \( C_S / S_S \) represents the mass of VOC absorbed in and/or adsorbed on the suspended solids and has a unit of mg VOC/(mg SS). The total VOC
concentration in the wastewater ($C_T$, mg/L) with SS is the sum of that in aqueous, DOC, and SS phases as shown in the following equation:

$$C_T = C_w + C_d + C_S$$ (6)

In this system, the dimensionless apparent Henry’s law constant ($K'_H$) can then be expressed as:

$$K'_H = \frac{C_g}{C_T} = \frac{C_g}{(C_w + C_d + C_S)} = K_H \frac{1}{1 + K_{OC}S_d + K_pS_S}$$ (7)

Then the apparent solubility of the VOC in the liquor can be drawn:

$$C_T = \frac{C_g}{K'_H} = \frac{C_g}{K_H}(1 + K_{OC}S_d + K_pS_S)$$ (8)

Eq. (8) indicates that $C_T$ varies with both dissolved organics and suspended solids in liquids.

A model similar to Eq. (7) has been cited in literature for the partitioning of VOCs between gas and liquids containing suspended natural organic matter (SNOM) and suspended inorganic matter (SIM) (Staudinger and Roberts, 1996). As far as the authors know, no SNOM-water and SIM-water partition coefficient has been published and no model has been proposed for modeling $K'_H$ with the activated sludge concentration.

**MATERIAL AND METHOD**

An 80-L aeration tank was used for cultivation of 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 mixed-liquor, suspended-solid (MLSS) concentration was kept in 40,000-45,000 mg/L, with a pH value in the range of 6.8-7.2. The sludge was fed simultaneously with glucose as a carbon source. At a daily organic loading rate of 0.20 kg COD (chemical oxygen demand) per kg, MLSS 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 ratio of COD:N:P:Fe of 100:5:1:0.5, respectively. 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 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 mix into two parts: activated sludge biomass with bound water and supernatant wastewater (Jin et al., 2003). The supernatant was then filtered through a cellulose acetate membrane (Advantec MFS, USA) with an average pore size of 0.45 μm. The filtrate was then stored at 4 °C for subsequent experiments. Before the sorption experiment, both the activated sludge mixture and the prepared filtrate were pasteurized at 80 °C for 2 hours to inactivate the biomass activity. The pasteurized samples were then diluted with deionized water (NANOpure, Barnstead, USA) to obtain the desired concentrations.

The single equilibration technique (SET) has usually been used for water-gas partition analysis (Staudinger and Roberts, 1996; Cheng et al., 2004). The SET measures $C_g$ at an equilibrium of VOC between the aqueous and gas phases with the equilibrium being established within a gastight vessel that contains VOC solution of a given initial mass at a constant temperature. By the SET, $K'_H$ in Eq. (7) can be calculated by the following relationship:

$$
K'_H = \frac{C_g}{C_T} = \frac{C_g}{(m_T - C_g V'_g)/V_L} = \frac{C_g V_L}{(m_T - C_g V'_g)}
$$

where $V_L$ (L) is the bulk volume of the liquid phase injected with an initial mass of $m_T$ (mg) of the chemical compound to be tested, and $V'_g$ (L) is the overhead gas volume.

The standard SET procedures in this study were as follows. Target VOCs were methanol, isopropanol, acetone, toluene, and $p$-xylene (analysis ACS grade, Merck, Germany), and the tested temperature was fixed at 298 K (25 °C). In the case of water soluble methanol, isopropanol, and acetone, vials of nearly 43 mL (Kimble Glass, USA) were used for the tests. 40 mL of one of the pasteurized deionized water (DI water), wastewater filtrate (abbreviated as wastewater), and DI water mixed with a known amount of activated sludge (abbreviated as mixed liquor) was used for each 43-mL vial with a screw cap and PTFE septa. For much less water-soluble toluene and $p$-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. After sealing of all the vials or flasks, a fixed volume (methanol 30 μL, isopropanol 20 μL, acetone 5 μL, toluene 2 μL and $p$-xylene 2 μL) of each liquid organic compound was injected into a vial by a syringe (Hamilton, USA). The concentration of each VOC in the liquid phase would then be fixed. Three to nine replicates were prepared for each compound and each liquid.

The prepared samples were then shaken in a 298 K water-bathed shaker with a rate of 150 rpm for 2 hours, and the shaker turned off for the following 2 hours in order to obtain a phase and
temperature equilibrium. Afterwards, 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. For ensuring the effectiveness of pasteurization, the chromatogram of the headspace gas sample was also checked to see if there was any by-product peak other than the target VOC.

Total organic carbon (TOC) contents in the collected wastewater samples were measured by a TOC analyzer (Model 700, O. I. Analytical, USA). SS in the activated sludge liquors were determined by the traditional gravimetric method. For obtaining $C_g$, 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. (9). Statistical analysis was then performed to obtain the mean and standard deviation (SD) of the estimated $K'_H$. All statistical analyses were carried out with the software SigmaPlot (SPSS, USA) and Microsoft Excel.

RESULTS AND DISCUSSION

$K'_H$ Variation in Mixed Liquor and Wastewater

Using the SET method, experimental $K'_H$ data for methanol, isopropanol, acetone, toluene and $p$-xylene in mixed liquor at 298 K are shown in Fig. 1 $K'_H$ corresponding to MLSS = 0 was for compounds partitioning between air and DI water, i.e., $K'_H = K_H$. The maximum MLSS concentration was maintained at around 40,000 mg/L.

In the mixed liquor, all $K'_H$ of the tested hydrophilic VOCs rose with increasing MLSS concentration at the experimental temperature in Figs. 1(a-c). At the MLSS concentration around 40,000 mg/L, $K'_H$ increased up to 8.9%, 19.9% and 12.2% for methanol, isopropanol and acetone, respectively, compared with those in DI water. The increase corresponds to a decrease in solubility of the hydrophilic compound in the mixed liquor.

On the other hand, $K'_H$ decreased with an increase of MLSS for hydrophobic toluene and $p$-xylene as shown in Fig. 1(d). At the MLSS concentration around 40,000 mg/L, $K'_H$ decreased up to 70.8 and 88.3% for toluene and $p$-xylene, respectively, as compared with those in DI water. The presence of biomass increased the partition of these compounds to the mixed liquor. At a MLSS of around 2,000-4,000 mg/L, the typical wastewater treatment-plant operation range, $K'_H$ is not significantly different from $K_H$. The effect of biomass in the low MLSS concentration range could be ignored for both hydrophilic and hydrophobic VOCs.

In wastewater, somewhat different phenomena and trends were observed for the solubilities of hydrophilic VOCs than in mixed liquor. As shown in Fig. 1, both $K'_H$ of hydrophilic and hydrophobic VOCs decreased with DOC concentration. $K'_H$ of all the test compounds in the wastewater were only 1 to 11% smaller than those in DI water. This indicated that all the tested
compounds have little affinity for the dissolved organics, although the differences between $K_H$ and $K'_H$ were small because of the low DOC contents of the wastewater.

In the wastewater, the DOC could be treated as a pseudo-solvent for nonionic compounds. The physical properties of the dissolved organics control the partition of the dissolved VOC compound in the wastewater (Grathwohl, 1990).

![Graphs showing variations of $K'_H$ with MLSS and TOC concentrations in wastewater samples at 298 K for different compounds](image)

**Fig. 1.** Variations of $K'_H$ with MLSS and TOC concentrations in wastewater samples at 298 K for (a) methanol; (b) isopropanol; (c) acetone; (d) toluene and $p$-xylene.

In the mixed liquor, the biomass would absorb or adsorb more hydrophobic VOCs and increase the apparent solubility of these compounds. As the biomass concentration increases, the decrease of the bulk-water volumetric fraction excludes hydrophilic VOCs by the hydrophobic biomass, then is
distributed in bulk water and headspace phases. That would decrease the apparent solubility and increase the $K'_{H}$ of these hydrophilic compounds in the mixed liquors; i.e. $K'_{H}>K_{H}$. Zhu et al. also observed an increase of the Henry’s law constant of methanol in pulping spent liquors with high total solids content (Zhu et al., 2000).

The biomass is surrounded with extra-cellular polymeric substances (EPS) in the mixed liquor. These EPS are composed mainly of different kinds of proteins, carbohydrates and lipids that are soluble in water or bounded by the solid biomass (Liao et al., 2000). The soluble EPS are contained in wastewater. The bound ones surrounding the biomass are more hydrophobic than the low-molecular alcohols and acetone (Jorand et al., 1998; Laspidou and Rittmann, 2002). The inert biomass also includes solid components besides EPS that would make the mixed liquor heterogeneous.

Variations of $K'_{H}$ for toluene with biomass and dissolved compounds are shown and compared with literature-cited data in Table 1. All $K'_{H}$ decreased significantly with increasing biomass concentration. However, $K'_{H}$ for liquids with washed biomass were higher than those with unwashed biomass, such as the present study. $K'_{H}/K_{H}$ of toluene in mixed liquors with MLSS = 35,000 mg/L are around 0.41 and 0.52 for unwashed (this work) and DI-washed biomass (Barton et al., 2003), respectively. Higher $K'_{H}/K_{H}$ might result from the partial removal of hydrophobic EPS from the biomass; that is, a loss of EPS due to the washing could be a reason for the resulting higher $K'_{H}$. The unwashed biomass contains bound EPS that lead lower $K'_{H}$ for hydrophobic VOCs. Table 1 also shows the effect of dissolved TOC concentration on $K'_{H}$ for toluene is less than 10% within a TOC of less than 700 mg/L.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$K'_{H}$ (K)</th>
<th>MLSS, $S_{S}$ (mg/L)</th>
<th>TOC, $S_{d}$ (mg/L)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>2,500</td>
<td>35,000</td>
</tr>
<tr>
<td>298</td>
<td>0.272</td>
<td>0.260</td>
<td>0.085</td>
<td>0.270</td>
</tr>
<tr>
<td>296</td>
<td>0.263</td>
<td>0.233</td>
<td></td>
<td>0.250</td>
</tr>
<tr>
<td>295</td>
<td>0.268</td>
<td>0.248</td>
<td>0.140</td>
<td></td>
</tr>
</tbody>
</table>

*Note a.* This work. Biomass: Unwashed and pasteurized activated sludge. TOC: glucose and soluble metabolites from activated sludge.


*Note c.* Cited. DI-water washed and pasteurized pure strain biomass (Barton et al., 2003).
**Verification of the $K'_H$ Model**

By referring to Eq. (7) and zero suspended solids concentration $(S_S = 0)$, or zero dissolved organic concentration $(S_d = 0)$, $K'_H$ is either related to $S_d$ or $S_S$ by the following equations.

\[
K'_H = K_H \frac{1}{1 + K_P S_S} \quad (10)
\]

\[
K'_H = K_H \frac{1}{1 + K_{OC} S_d} \quad (11)
\]

Eq. (11) has been reported to describe the variation of $K'_H$ of VOCs to $S_d$ in wastewater (David et al., 2000). In this study, $K_{OC}$ and $K_P$ are estimated from regressions of the experimental data by Eqs. (10) and (11), respectively. Data of experimental $K_H$ and calculated $K_{OC}$ and $K_P$ are listed in Table 2. The regressed lines are plotted in Fig. 1 for all species.

The negative $K_P$ is physically unreasonable in Table 1, which indicates that the models are only suitable for $K_H \geq K'_H$ (Staudinger and Roberts, 1996). Nevertheless, $K_P$ shown in Eq. (10) is only a correction factor for relating $K'_H$, $K_H$, and $S_S$; both positive and negative $K_P$ values could be a mathematical reference index for $K'_H$ prediction by the equation.

Comparisons of the $K_{OC}$ data with those estimated from literature-cited models and experimental values are shown in Table 3. It indicates that $K_{OC}$ values are different for the same kind of VOC, because there were some differences in the adopted prediction models or experimental methods. Furthermore, the variation could be also the causes of the different molecular size and polarity of dissolved organic matter participated in enhancing the solubility. Although these factors would affect the $K_{OC}$ values, the data are within a narrow range for the same kind of VOC.

$K'_H$ for all the test compounds in the mixed liquor have larger SD than those in the DI water and wastewater, as shown in Fig. 1. These deviations might be attributed to the complex composition of the EPS and the high heterogeneity of the biomass in the activated sludge than to those in wastewater. Thus, the variation of $K'_H$ could be attributed mainly to the complexity of the physicochemical properties of the mixed liquor. The phenomena of smaller SD for the hydrophobic, rather than hydrophilic, VOCs might also be attributed to the hydrophobicity of the biomass. Hydrophobic VOCs partition on biomass easily, thus making the SD smaller.

For ensuring the significance of the relationship between $K'_H$, DOC and MLSS concentration at the tested temperature, ANOVA was introduced for testing the dependency. Results indicated the $K'_H$ of methanol was greater than 95% level of confidencesignificant, and other VOCs were more than 99% level of confidence in the DOC range. For the mixed-liquor samples, all tested VOCs were 99% significant in the SS range by ANOVA.
Table 2. Experimental Henry’s law constants in DI water ($K_H$), calculated partition coefficients of VOC in suspended solids ($K_P$), and calculated partition coefficients of VOC in dissolved organic carbon ($K_{OC}$) at 298 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Log $K_{OW}$</th>
<th>$K_H$</th>
<th>$K_P \times 10^6$</th>
<th>$K_{OC} \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>This work $^a$</td>
<td>Literature</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>-0.74</td>
<td>(1.859±0.017)$\times 10^{-4}$</td>
<td>1.82$\times 10^{-4}$</td>
<td>-2.22</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>0.05</td>
<td>(3.101±0.013)$\times 10^{-4}$</td>
<td>3.23$\times 10^{-4}$</td>
<td>-4.26</td>
</tr>
<tr>
<td>Acetone</td>
<td>-0.24</td>
<td>(1.408±0.016)$\times 10^{-3}$</td>
<td>1.59$\times 10^{-3}$</td>
<td>-2.66</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.73</td>
<td>0.272±0.004</td>
<td>2.24$\times 10^{-1}$</td>
<td>46.7</td>
</tr>
<tr>
<td>$p$-Xylene</td>
<td>3.15</td>
<td>0.263±0.005</td>
<td>2.32$\times 10^{-1}$</td>
<td>82.9</td>
</tr>
</tbody>
</table>

| |                     |                     |                     |                     |
| |                      |                     |                     |                     |

- a. Recommended value (Sangster, 1989).
- b. Results from data of 9 replicates with standard deviation.
- c. Headspace and aqueous concentration analysis data (Snider and Dawson, 1985).
- d. Experimental value by equilibrium partitioning in closed system (EPICS) technique (Dewulf et al., 1995).
- e. Regressed result of Eq. (11) with known experimental $K_H$.
- f. Regressed from Eq. (10) with known experimental $K_H$.

Table 3. Comparison experimental and literature-cited values of $K_{OC}$ for the five compounds at 298 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Log $[K_{OC}\times 10^6$ (L/mg)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.01</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>1.05</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.25</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.14</td>
</tr>
<tr>
<td>$p$-xylene</td>
<td>2.28</td>
</tr>
</tbody>
</table>

- a. Calculate from log $K_{OC} = 0.544 \log K_{OW} + 1.377$, which has been a widely used estimation of chemical property (Meylan et al., 1992).
- b. Experimental value (Meylan et al., 1992).
- c. Experimental value (Zytner, 1994).

CONCLUSIONS

The above results indicate that a medium to high concentration of activated sludge can enhance the apparent water solubility of hydrophobic compounds, such as benzene, toluene and xylenes (BTX). This increase in solubility is essential to increasing the removal of such compounds from waste-air streams. The results also provide information for selecting a suitable scrubbing liquor to remove VOC by bioscrubber. For the hydrophilic VOCs, water and organic-rich wastewater could be the scrubbing liquor; for the hydrophobic VOCs, high biomass-activated sludge could be the scrubbing liquor. A model has been presented to correlate $K_H$ with wastewater TOC and...
MLSS concentration using $K_{OC}$ and $K_P$ as model parameters. This consistency implies that SET is a rather reliable approach for getting these partition coefficients.

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