Henry’s law constants of volatile organic compounds in activated sludge and wastewater at 298 K
Jun-Hong Lin and Ming-Shean Chou
Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, R.O.C.

ABSTRACT. Henry’s law constant is an important equilibrium factor in volatile organic compounds (VOCs) mass transfer process. The air-water dimensionless Henry’s law constants ($K_H$) and the dimensionless apparent Henry’s law constants ($K'_H$) in air-activated sludge mixed liquor and air-wastewater system for volatile organic compounds (VOCs) were measured at 298K. Hydrophilic VOCs (isopropanol and acetone) and hydrophobic VOCs (toluene and $p$-xylene) were used as target compounds. Deionized (DI) water, a pasteurized wastewater with a maximum dissolved total organic carbon (TOC) content of 700 mg/L and DI water diluted pasteurized activated sludge (mixed liquor) with a maximum suspended solid concentration of 40,000 mg/L were used as liquids. $K'_H$ of the hydrophilic compounds in the mixed liquor with the maximum suspended solid concentration were 13 to 21% higher than those in DI water. Those for toluene and $p$-xylene decreased up to 69 and 86%, respectively, in the mixed liquor. $K_H$ 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.

1 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 (Zigmontiené and Baltrénas, 2004). For effective removal of the gaseous contaminants, equilibrium of organic compounds 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). The organic carbon-water partition constant \((K_{OC})\) has been correlated with the octanol-water partition coefficient \((K_{OW})\) in linear free energy relationship (Goss and Schwarzenbach, 1998). In addition, the existence of suspended organic solids in liquid can enhance the solubility of VOCs of low water solubility. The sorption of VOCs in activated sludge biomass has been an investigation topic in many studies. The accumulation of some VOCs or hazardous pollutions 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 concentration in wastewater (David et al., 2000). The apparent Henry’s law constant decreases or the apparent solubility increases by increasing 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. The target of this research was to discuss the partitioning equilibrium migration in gas-deionized water, gas-wastewater, and gas-water-activated sludge systems. This study provides phase equilibrium information for hydrophilic and hydrophobic VOC treatment by bioscrubbers or bubble column.

2 MATERIALS AND METHODS

2.1 Theoretical
The dimensionless Henry’s law constant \((K_{H})\) have been presented in eq 1 and called as an air-water partition coefficient in the environmental literature:

\[
K_{H} = \frac{C_{g}}{C_{w}} \quad (1)
\]

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 that the dissolved VOC exists both in the aqueous phase and combined with the dissolved organic carbon (DOC). The partition coefficient \((K_{OC})\) of VOC between the DOC and the aqueous phases can be expressed as eq 3.

\[
\frac{C_{d}}{C_{w}} \xleftrightarrow{DOC \rightarrow bound \ VOC} \frac{C_{d}}{S_{d}} \quad (2)
\]

\[
K_{OC} = \frac{DOC \text{-bound VOC}}{C_{w}} = \frac{C_{d}/S_{d}}{C_{w}} \quad (3)
\]

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). Equation 3 is based on the concept of partition of VOC between an organic liquid, such as octanol, and water by assuming that the dissolved organics 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).

In a liquid containing activated sludge (a mixed liquor), some VOC is adsorbed in 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 eqs 4 and 5:

$$C_S \xrightarrow{K_p} C_v \xrightarrow{SS-bound VOC}$$

$$K_p = \frac{SS-bound VOC}{C_v} C_s / S_s$$

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). Equation 5 was mentioned in literature for calculating the organic biosorption coefficient in activated sludge liquor (Grady Jr. et al., 1997). The total VOC concentration $C_T$ in the wastewater with suspended solids is the sum of that in aqueous, dissolved organic, and suspended solid phases as shown in the following equation:

$$C_T = C_w + C_d + C_S$$

With a system composed of water, DOC and SS, the apparent Henry’s law constant $K_H'$ can then be express as:

$$K_H' = \frac{C_T}{C_T} = \frac{C_T}{(C_w + C_d + C_S)} = \frac{K_T}{(1 + K_{oc}S_S + K_pS_S)}$$

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

$$C_T = \frac{C_T}{K_H'} = \frac{C_T}{(1 + K_{oc}S_S + K_pS_S)}$$

Equation 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’ knowledge, no SNOM-water and SIM-water partition coefficient have been published and no model has been proposed for modeling $K_H'$ with the activated sludge concentration.

2.2 Material and method

An 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 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 simultaneously with glucose as carbon sources. 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. 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 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 mixed liquor and the prepared filtrate were pasteurized at 80 °C for 2 hr to inactivate the biomass activity. The pasteurized samples were then diluted with deionized (DI) water (NANOpure, Barnstead, USA) to obtain the desired concentrations. Blank samples of wastewater and mixed liquor were analyzed after pasteurization, no target VOCs appeared in each chromatogram.

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 gas-tight 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:

$$K_H = \frac{C_g}{C_T} = \frac{C_g}{(m_T - C_T V_T)/V_T} = \frac{C_g V_T}{m_T - C_T V_T}$$ (9)

where $V_T$ is the bulk volume of the liquid phase injected with an initial mass of $m_T$ of the chemical compound to be tested, and $V_T$ is the overhead gas volume.

The standard SET procedures in this study were as follows. Target VOCs were 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 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 (abbreviated as 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. 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. 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 (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 be fixed. 3-9 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. After then, 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. Notably, the sampling period was kept as short as possible to prevent any possible disturbance of the gas-liquid equilibrium (Staudinger and Roberts, 1996; Cheng et al., 2004). For ensuring the effectiveness of
pasteurization, the chromatogram of the headspace gas sample was also checked if there was any by-product peak except 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). Suspended solids 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.

3 RESULTS AND DISCUSSION

3.1 $K'_H$ in wastewater and activated sludge mixed liquor

Using the SET method, experimental $K'_H$ data for isopropanol, acetone, toluene and $p$-xylene in mixed liquor and the synthetic wastewater at 298 K are shown in Figure 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 was maintained at around 40,000 mg/L.

$K'_H$ for all the test compounds in the mixed liquor have larger standard deviations than those in the wastewater. These deviations might be attributed to the greater variations of the structure and chemical compositions of the activated sludge biomass than the wastewater. Sludge age might be responsible for the greater variations.

For all the tested hydrophilic compounds, $K'_H$ increased with an increasing of MLSS at the experimental temperature of 298 K and in the MLSS range of 0-40,000 mg/L. At a MLSS of around 40,000 mg/L, $K'_H$ increased up to 21 and 13 % for 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. Apparently, the hydrophobic biomass in the mixed liquor accounts for the solubility decrease.

In general, biomass like activated sludge is surrounded with organic compounds in the mixed liquor. These extra-cellular polymeric substances (EPS) are composed mainly of proteins, carbohydrates and lipids (Liao et al., 2000). These EPS are much hydrophobic than the low-molecular alcohols and acetone. As the biomass concentration increases, the decrease of the bulk water volumetric fraction decreased the solubility and increases the $K'_H$ of these hydrophilic compounds in the mixed liquors as shown in Figs. 1(a)-1(b).

On the other hand, $K'_H$ decreased with an increase of MLSS for hydrophobic toluene and $p$-xylene as shown in Figure 1(c). The presence of biomass increased the partition of these compounds to the mixed liquor. At 298 K and a MLSS of 40,000 mg/L, it was observed that the $K'_H$ decreased up to 69 and 86 % for toluene and $p$-xylene, respectively, as compared with those in DI water. All $K'_H$ decreased significantly with increasing biomass concentration. Compared with DI water, the biomass in the mixed liquors would absorb or adsorb more hydrophobic compounds and increase the apparent solubility of these compounds (Wang et al., 1993). However, $K'_W/K_H$ 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 $K'_W/K_H$ might result from the partial removal of hydrophobic EPS from the biomass.
Somewhat different phenomena were observed for the solubility of organic compounds in biomass-free wastewater with some dissolved organics. As shown in Figure 1, $K'_{H}$ for all tested compounds decreased with increasing organic content in the wastewater. $K'_{H}$ of all the test compounds in the wastewater was only 1 to 11% smaller than those in DI water.

The above results indicate that a medium to high concentration of activated sludge can help in enhancing the water solubility of hydrophobic compounds such as benzene, toluene and xylenes (BTX). This solubility increase is essential to the increase in the removal of such compounds from waste air streams that are injected into the activated basin. On the other hand, the solubility increase attributed to the dissolved organics in wastewaters may be negligible as compared with that to the activated sludge biomass.

3.2 Verification of the $K'_{H}$ model

By referring to eq 7 and with 0 suspended solid concentration ($S_{S} = 0$) or 0 dissolved organic concentration ($S_{d} = 0$), $K'_{H}$ is either related to $S_{d}$ or $S_{S}$ by the following equations:

$$K'_{H} = K_{H} \frac{1}{1 + K_{P}S_{S}}$$

(10)

$$K'_{H} = K_{H} \frac{1}{1 + K_{OC}S_{d}}$$

(11)

Equation 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 $K_{P}$ were estimated from regressions of the experimental data by eqs 11 and 12, respectively, by the software. Data of experimental $K_{H}$ and calculated $K_{OC}$ and $K_{P}$ were listed in Table 1. For ensuring the significance of independency of $K'_{H}$ with $K_{H}$ on TOC at the tested temperature, the ANOVA was introduced for testing the independency. Result indicated the $K'_{H}$ was 99% significant than $K_{H}$ in the TOC range. The regressed lines were plotted in Figure 1 for all species.

Table 1. Experimental $K_{H}$, $K_{P}$ and $K_{OC}$ of target VOCs at 298K

<table>
<thead>
<tr>
<th>Compound</th>
<th>Log $K_{GW}$</th>
<th>$K_{H}$</th>
<th>$K_{P} \times 10^{6}$</th>
<th>$K_{OC} \times 10^{6}$</th>
<th>$R^{2}$</th>
<th>$R^{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropanol</td>
<td>0.05</td>
<td>(3.101±0.013)×$10^{-4}$</td>
<td>3.23×$10^{-4}$</td>
<td>-4.26</td>
<td>0.765</td>
<td>0.832</td>
</tr>
<tr>
<td>Acetone</td>
<td>-0.24</td>
<td>(1.408±0.016)×$10^{-3}$</td>
<td>1.59×$10^{-3}$</td>
<td>-2.66</td>
<td>0.844</td>
<td>0.806</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.73</td>
<td>0.272±0.004</td>
<td>2.24×$10^{-1}$</td>
<td>d 46.7</td>
<td>0.959</td>
<td>139.3</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>3.15</td>
<td>0.263±0.005</td>
<td>2.32×$10^{-1}$</td>
<td>d 82.9</td>
<td>0.957</td>
<td>191.8</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 10 with known experimental $K_{H}$.
f Regressed from eq 11 with known experimental $K_{H}$. 
Figure 1. Variations of $K'_n$ with MLSS and TOC concentrations in wastewater samples at 298 K for (a) isopropanol; (b) acetone; (c) toluene and $p$-xylene.

4 REFERENCES


