Experimental Method for Estimating Henry's Law Constant of Volatile Organic Compound

W. Zhang, L. Huang, C. Yang and W. Ying[*]

State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, East China University of Science and Technology, Shanghai, P.R. China

*Corresponding author: Fax: +86 21 64252978; Tel: +86 21 64252978; E-mail: wcying@yahoo.com

A simple experimental method for estimating the Henry's law constant of a volatile organic compound in water is presented. Based on the Henry's law constant definition, measuring the equilibrium liquid phase concentration of a closed system partially filled with the volatile organic compound solution provides the necessary data for calculating its Henry's law constant of the test conditions. The experimental Henry's law constants of methyl-*tert*-butyl ether, benzene, toluene, ethyl benzene, xylene were reproducible; the experimental Henry's law constants of those volatile organic compounds, nitrobenzene and trichloroethylene were in general agreements with corresponding estimates of the empirical methods of ratio of vapour pressure to water solubility, the Yaws method and the HENRYWIN program methods as well as the literature data. The Henry's law constants of several volatile organic compounds confirmed the expected effects of temperature and non volatile solvent methanol. The method of this study can be employed to estimate the Henry's law constant of a volatile organic compound at a specific temperature and sample composition.

Key Words: Henry's law constant, Water solubility, Vapour pressure, Volatile organic compound, Methyl-*tert*-butyl ether.

INTRODUCTION

Volatile organic compounds (VOCs) present in contaminated groundwater and soil are often lost due to volatilization during the remediation operations. The degree of volatilization loss of a volatile organic compound may be estimated from its Henry's law constant (HLC). There are indeed available Henry's law constants for most common volatile organic compounds[1-3]; however, large differences are found for some of them and that many others were reported for specific temperature, initial concentration, ionic strength, solution composition, making it difficult to choose the best Henry's law constant for the case of interest. The experimental procedures given in the literature are often complicate and time consuming[4-6]. The paper presents a simple, fast and reliable experimental method for estimating Henry's law constants of volatile organic compounds in aqueous samples and compares its estimates for many volatile water pollutants with the same of several empirical methods and available literature data.

EXPERIMENTAL

Simple experimental method for Henry's law constant estimation

Principle: The Henry's law constant (H, MPa-m³/mol) of a volatile organic compound in a liquid-vapour closed system at equilibrium is defined by:

$$p = H \times S = H \times \left(\frac{C_l}{mw} \right) \tag{1}$$

According to the ideal gas law,

$$p = C_v \times \frac{RT}{mw} \tag{2}$$

$$H = \frac{C_v}{C_l} \times RT \tag{3}$$

from conservation of mass for the volatile organic compound:

$$C_i \times V_l = C_v \times V_v + C_l \times V_l \tag{4}$$

therefore,

$$H = \left(\frac{C_i}{C_l - 1} \right) \times \frac{RT}{(V_v / V_l)} \tag{5}$$

where: p: partial pressure of the volatile organic compound (MPa); S: molar concentration (mol/m³); mw: molecular weight; R: the ideal gas constant, 8.32E-6 MPa-m³/mol-K; T: absolute temperature (K); C_i, C_l and C_v: initial and equilibrium concentrations of the liquid phase and equilibrium concentration of the vapour phase, respectively, mg/L; C_v/C_l: dimensionless Henry's law constant; V_v, V_l: volumes of the vapour and liquid phases, respectively, L.

H, the experimental Henry's law constant, can be calculated by C_i and C_l measured for each test run (H_1). If the test runs are conducted using a newly prepared volatile organic

compound solution, the theoretical C_i may be employed to obtain the estimated Henry's law constant (H_0) without measuring the initial concentration.

Experimental estimation of Henry's law constant for several volatile organic compounds: Aqueous solutions of methyl-*tert*-butyl ether (MTBE), benzene, toluene, ethyl-benzene, *o*-xylene, nitrobenzene, trichloroethylene (TCE) and chlorobenzene were prepared using pure water. The test runs employed single solute solutions of 20 mg/L for estimation of Henry's law constant of the volatile organic compound. The test runs employed small (42 mL) glass bottles which were filled with 20 mL of the test solutions ($V_v/V_1 = 1.1$) and capped immediately after filling. The bottles were shaken for 20 min in a rotating drum (10 rpm) and then left in a temperature controlled environment for 2 h or longer to establish the equilibrium condition for the liquid-vapour system of the capped bottles. Three series of identical test runs were performed sequentially in the reproducibility and method comparison studies. Each series of test runs were conducted in duplicate. The final liquid phase concentration was then measured by UV (benzene, toluene, ethylbenzene, xylene, nitrobenzene and chlorobenzene) or gas chromatography (methyl-*tert*-butyl ether and trichloroethylene). The experimental Henry's law constants were calculated according to eqn. 5. H_1 is the average of all duplicates. H_0 is obtained in the same manner as H_1 using the theoretical initial concentration.

Empirical methods for Henry's law constant estimation

Ratio of vapour pressure to water solubility: The ratio of vapour pressure to water solubility of a volatile organic compound is a recognized simple estimation of its Henry's law constant[7-9]. The experimental data of vapour pressure and water solubility may be obtained from a chemical handbook[3] or the MPBPWIN[10] program and WATERNT[11] program components, respectively, of the free EPI Suite v3.20 (Feb. 2007)[12], a collection of 13 estimation programs, downloadable from the United States EPA website (http://www.epa.gov/oppt/exposure/pubs/episuite.htm). Alternatively, the calculated Henry's law constant can be obtained using the Yaws program[8,9] which employs literature and calculated vapour pressure and water solubility and an activity coefficient values in the model calculations.

HENRYWIN estimates: The HENRYWIN program[13] is another component of EPI Suite v3.20 for estimating the Henry's law constant of a volatile organic compound over the temperature range of 0-50 ºC; it also includes a large Henry's law constant database of 1650 compounds (H_{Ref}). Its estimated 25 ºC Henry's law constant is obtained using one of the two empirical methods, the bond contribution method[14] (H_{Bond}) and the group contribution method[15] (H_{Group}), while its estimated Henry's law constant at another temperature is obtained using the 25 ºC H_{Ref} and the empirical van't Hoff equation:

$$\ln(H) = \frac{a}{T} + b \ ^{13}.$$ The HENRYWIN Bond and Group methods produce values of LWAPC (log water-to-air partition coefficient) which is the logarithm of the reciprocal dimensionless Henry's law constant. The bond method estimated LWAPCs for the 345-compound data set were well correlated with the experimental values ($r^2 = 0.94$); it has been further validated

for a set of 74 diverse and structurally complex compounds that were not included in the least-square analysis ($r^2 = 0.96$). When reliable experimental data are available, H_{Ref} is usually better than H_{Bond} and H_{Group} as an estimate of the actual Henry's law constants.

RESULTS AND DISCUSSION

Reproducibility of the experimental Henry's law constant estimation method: Table-1 presents the experimental Henry's law constant (H_1, average of the H_1 of 6 replicate samples), standard deviation (SD) and the relative standard deviation (RSD). The RSDs of 2.81-5.24 % is close to the RSD (0.60-8.98 %)of the well-known Robbins' method[16]. This simplified method is sufficiently reproducible for estimating Henry's law constants of volatile organic compounds in aqueous samples.

TABLE-1
REPRODUCIBILITY OF THE EXPERIMENTAL HENRY'S
LAW CONSTANT (HLC) ESTIMATION METHOD (H_1)

Volatile organic compound	HLC[a] (MPa-m³/mol)	Standard deviation[b] (SD)	Relative standard deviation[c] % (RSD)
Methyl-*tert*-butyl ether	3.13×10^{-5}	1.64×10^{-6}	5.24
Benzene	2.83×10^{-4}	1.08×10^{-5}	3.80
Toluene	3.58×10^{-4}	1.73×10^{-5}	4.83
Ethylbenzene	7.04×10^{-4}	3.49×10^{-5}	4.96
o-Xylene	4.58×10^{-4}	1.29×10^{-5}	2.81

Comparisons of Henry's law constants of 7 volatile organic compounds estimated by the method of this study and others: The Henry's law constants calculated from the ratio of vapour pressure to water solubility (VP/WS) are generally good estimates of the volatile organic compound in water at the given temperature. However, large variations may result when the actual vapour pressure and water solubility are unknown and that the calculated or the reported values are incorrect. Many researchers have employed the Yaws empirical Henry's law constants, the tabulated values for 362 volatile organic compounds in water[8] and the model predictions[9], when desired experimental Henry's law constant is unavailable. Such estimates are of limited applicability because of the cost and availability and, furthermore, are inaccurate for a volatile organic compound present at a different temperature and in a wastewater sample. Their utility are largely replaced by the free HENRYWIN program. USEPA RREL Treatability Database[17] and several other references[16,18,19] also provide many experimental Henry's law constants reliable for the specific test conditions.

Table-2 presents the empirical and experimental Henry's law constants for 7 common volatile water pollutants. Although there are differences among the calculated Henry's law constants of the four empirical methods, they are all adequate to obtain quick estimates when the desired Henry's law constants are unavailable. Given the variable test conditions for measuring the Henry's law constants of the 7 volatile organic compounds, experimental Henry's law constants of the two databases, literature reports and this study are indeed in general agreements.

TABLE-2
SUMMARY OF EMPIRICAL AND EXPERIMENTAL HENRY'S LAW CONSTANT (HLC)
FOR VOLATILE ORGANIC COMPOUND (VOC) AT 25 ºC (MPa-m^3/mol)[a]

VOC	Empirical					Experimental database and literature		Experimental this study	
	VP/WS[b]	Yaws [8]	H_{Bond}[c13]	H_{Group}[c13]	H_{Ref}[c13]	RREL[17]	Literature	H_0	H_1
MTBE	5.77×10^{-5}	–	2.05×10^{-4}	1.46×10^{-4}	5.95×10^{-5}	–	$5.35\times10^{-5\ 16}$, $7.23\times10^{-5\ 19}$	4.14×10^{-5}	3.13×10^{-5}
Benzene	5.51×10^{-4}	5.64×10^{-4}	5.46×10^{-4}	5.42×10^{-4}	5.62×10^{-4}	5.62×10^{-4}	$5.35\times10^{-4\ 19}$, $2.73\times10^{-4\ 18}$	3.61×10^{-4}	2.83×10^{-4}
Toluene	6.64×10^{-4}	6.45×10^{-4}	6.03×10^{-4}	5.81×10^{-4}	6.73×10^{-4}	6.00×10^{-4}	$6.52\times10^{-4\ 16}$, $5.95\times10^{-4\ 18}$	3.79×10^{-4}	3.58×10^{-4}
Ethylbenzene	8.05×10^{-4}	8.15×10^{-4}	7.99×10^{-4}	9.00×10^{-4}	7.98×10^{-4}	6.73×10^{-4}	$7.88\times10^{-4\ 16}$	5.13×10^{-4}	7.04×10^{-4}
o-Xylene	5.26×10^{-4}	4.24×10^{-4}	6.65×10^{-4}	6.22×10^{-4}	6.72×10^{-4}	5.34×10^{-4}	$5.06\times10^{-4\ 16}$	3.73×10^{-4}	4.58×10^{-4}
Nitrobenzene	1.93E-6	–	2.16E-6	4.51E-6	2.43E-6	2.41E-6	$8.67\times10^{-7\ 18}$	7.02×10^{-6}	6.93×10^{-6}
TCE	9.44×10^{-4}	1.19×10^{-3}	2.33×10^{-3}	1.88×10^{-3}	9.98×10^{-4}	1.19×10^{-3}	$1.04\times10^{-3\ 16}$	6.25×10^{-4}	7.54×10^{-4}

[a]HLC (Mpa- m^3/mol) = HLC (atm-m^3/mol) × 0.101325. [b]VP (vapour pressure in mmHg) and WS (water solubility in mg/L) were obtained from the MPBPWIN program and WATERNT program components, respectively, of the EPI Suite v3.20. [c]HENRYWIN empirical estimates of the bond method (H_{Bond}) and the group method (H_{Group}) and HENRYWIN database (H_{Ref}); MTBE = Methyl-tert-butyl ether.

Fig. 1 shows the good correlations of the experimental Henry's law constants of this study (H_0 and H_1) with the HENRYWIN estimates (H_{Bond}, H_{Group} and H_{Ref}). Two criteria are used to verify the accuracy of the estimations i.e., the averaged absolute error (AE) and the bias (BI) (Table-3). Table-2 shows that H_0 and H_1 are well correlated with H_{Bond} and H_{Group} and even better correlated with the more desired H_{Ref}. The closeness of H_0 with H_1 for those runs employing newly prepared volatile organic compound solution has validated using the theoretical initial concentration for calculation of Henry's law constant (eqn. 5).

TABLE-3
AVERAGED ABSOLUTE ERRORS (AE) AND BIAS (BI) OF
HENRY'S LAW CONSTANT (HLCS) OF THIS STUDY

	AE[a]	BI[b]
H_0-H_{Bond}	0.372	-0.226
H_0-H_{Group}	0.292	-0.237
H_0-H_{Ref}	0.244	-0.113
H_1-H_{Bond}	0.363	-0.218
H_1-H_{Group}	0.283	-0.230
H_1-H_{Ref}	0.236	-0.106

[a] $AE = \sum \dfrac{abs(\log H_a - \log H_b)}{n}$. [b] $BI = \sum \dfrac{(\log H_a - \log H_b)}{n}$ where,
H_a: H_0 or H_1; H_b: H_{bond}, H_{group} or H_{Ref}; n: number of samples.

Examples of Henry's law constant estimates

Effect of temperature on Henry's law constant and non-volatile solvent: Table-4 presents H_0 of 5 volatile organic compound at different temperatures (5, 25 and 40 ºC) and the corresponding HENRYWIN estimates. The observed Henry's law constants confirmed the known temperature effect that a high temperature would result in a higher Henry's law constant because of the higher vapour pressure and the lower water solubility. As experimentally determined values, the results of this study are better estimates of the actual Henry's law constants at 5 and 40 ºC than the HENRYWIN estimates.

Effect of non-volatile solvent: Preparing a volatile organic compound solution on demand is easy by dilution of a volatile organic compound-in-methanol mixture. Fig. 2 illustrates the effect of a small amount of methanol on Henry's law constants for 4 volatile organic compounds. The Henry's law constants (H_0) of benzene, toluene, ethylbenzene and o-xylene in methanol based solutions are smaller than in the respective pure water solutions; the Henry's law constants
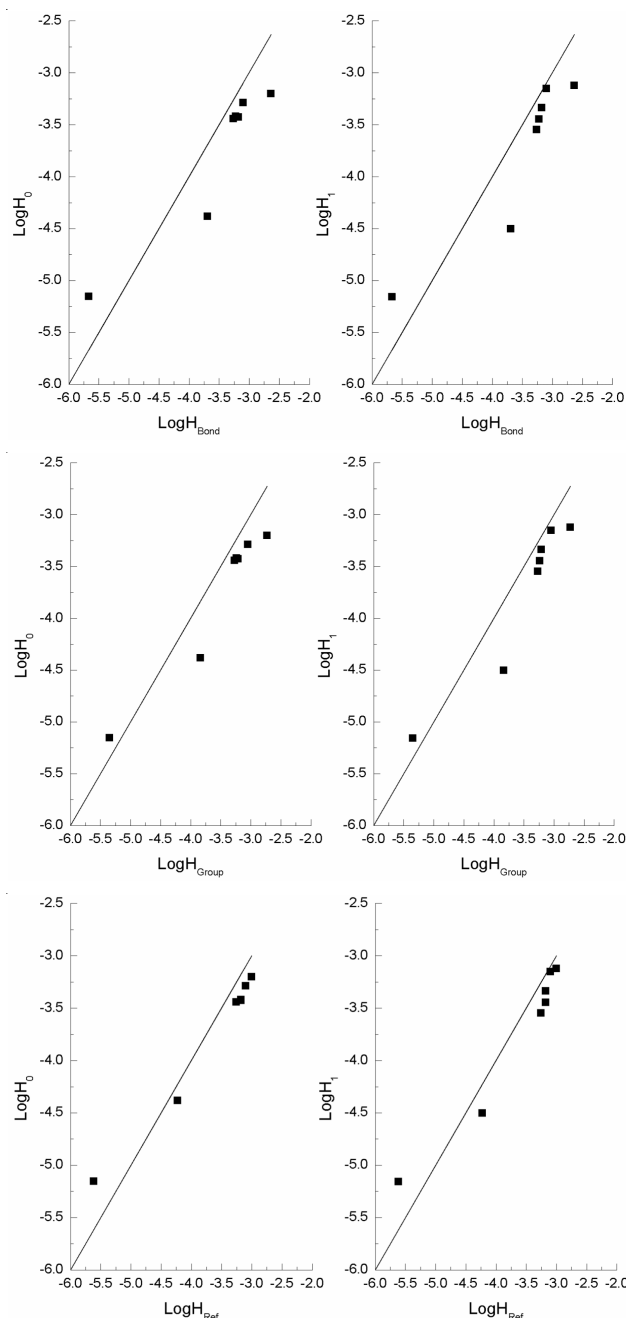

Fig. 1. Correlations of Henry's law constants of this study with the HENRYWIN estimates for 7 volatile organic compounds (l to r: nitrobenzene, methyl-tert-butyl ether, benzene, toluene, o-xylene, ethylbenzene and trichloroethylene)

TABLE-4
HENYR'S LAW CONSTANT (HLCs) OF VOLATILE
ORGANIC COMPOUND (VOC) AT DIFFERENT
TEMPERATURE (H_0, MPa-m³/mol)

VOC	Temp. (°C)	HENRYWIN[a]	H_0
Benzene	5	2.15×10^{-4}	2.71×10^{-4}
	25	5.62×10^{-4}	3.61×10^{-4}
	40	1.05×10^{-3}	4.71×10^{-4}
Trichloroethylene	5	3.02×10^{-4}	3.17×10^{-4}
	25	9.58×10^{-4}	6.25×10^{-4}
	40	2.07×10^{-3}	9.57×10^{-4}
Methyl-*tert*-butyl ether	25	5.95×10^{-5}	4.14×10^{-5}
	40	1.56×10^{-4}	7.22×10^{-4}
Ethylbenzene	25	7.92×10^{-4}	5.13×10^{-4}
	40	1.64×10^{-3}	1.01×10^{-3}
o-Xylene	25	5.25×10^{-4}	3.73×10^{-4}
	40	1.11×10^{-3}	1.46×10^{-3}

[a]Based on the 25 °C H_{Ref} and the empirical van't Hoff equation.
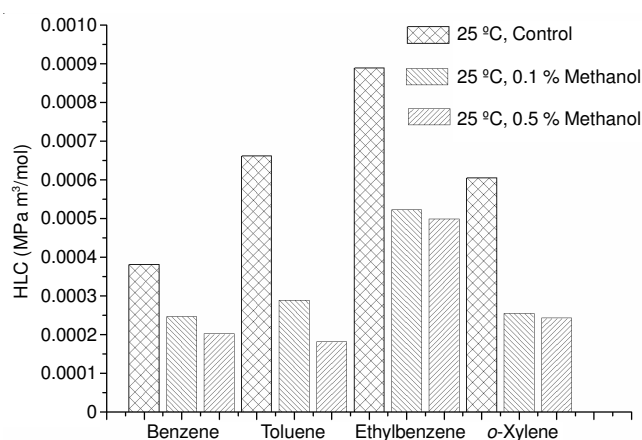

Fig. 2. Henry's law constants of volatile organic compounds with different methanol concentrations

reductions increased with the higher concentration of methanol from 0.1-0.5 %. The lower Henry's law constant was due to the reduced partial pressure of the volatile organic compound in the presence of the non volatile methanol. Methanol can be beneficially used as a solvent to prepare a volatile organic compound solution quickly while reducing its volatilization loss during the solution preparation and experiments.

Conclusion

Henry's law constants of volatile organic compounds in water can be estimated simply from the initial and the equilibrium liquid phase concentration of a partially filled bottle; the estimated Henry's law constants of several volatile organic compounds were in fair agreements with the existing methods and available experimental data. For test runs employing newly prepared volatile organic compound solution, the theoretical initial concentration can be used for calculating the Henry's law constant. The observed Henry's law constants confirmed the known temperature effect that a higher temperature would result in a higher Henry's law constant because of the higher vapour pressure and the lower water solubility. The presence of methanol lowered the Henry's law constant of a volatile organic compound; methanol can be beneficially used as a solvent to prepare a volatile organic compound solution quickly at a smaller volatilization loss. The simple, fast and reliable experimental method of this study can be employed to estimate the Henry's law constants of a volatile organic compound in an aqueous sample of specific temperature and composition.

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