Journal of chemical & engineering data

Article

pubs.acs.org/jced

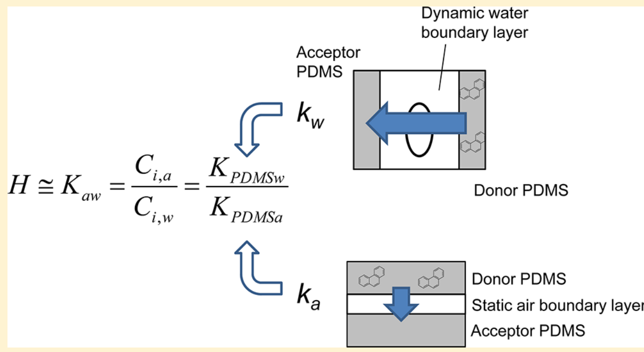
Determination of Henry's Law Constant Using Diffusion in Air and Water Boundary Layers

Hwang Lee,[†] Hyo-Jung Kim,[‡] and Jung-Hwan Kwon*[,†,‡]

[†]Department of Environmental Engineering and [‡]Environmental Research Institute, Ajou University, Woncheondong, Yeongtonggu, Suwon 443-742, Republic of Korea

Supporting Information

ABSTRACT: A simple and precise method for determining the Henry's law constant for hydrophobic organic chemicals was developed. Henry's law constants were obtained as air–water partition coefficients in a dilute solution from the two partition coefficients between polydimethylsiloxane (PDMS) and air (K_{PDMSa}) and between PDMS and water (K_{PDMSw}). Measurements of the low concentrations in air or water at phase equilibrium were avoided. Instead, the K_{PDMSa} and K_{PDMSw} values were obtained by measuring the mass transfer rate constants in a boundary layer and relating them with K_{PDMSa} and K_{PDMSw} using a film diffusion model. Twenty hydrophobic chemicals (11 polycyclic aromatic hydrocarbons, 5 chlorinated benzenes, 2 phthalate esters, and 2 aromatic nitro musks) with literature values of the Henry's law constant ranging from 10^{-2} to 10^{2} Pa·m^3·mol^{-1} were chosen to evaluate the method. The Henry's law constants derived in this study agreed very well with the experimentally determined values from the literature. Because the proposed method provides a fast and simple method for measuring the Henry's law constant within three days, it is a very promising method for generating the Henry's law constants widely used in the assessment of the environmental fate of hydrophobic chemicals.



INTRODUCTION

The Henry's law constant (H) is one of the most important parameters used in determining the fate and transport of organic chemicals in both natural and engineered environments. Although the original definition of H is the ratio of the vapor pressure to the aqueous solubility of a chemical at saturation, an equilibrium partition coefficient between air and water below saturation is often used in environmental sciences because the solubilities of hydrophobic organic chemicals in both phases are, in many cases, very low.

According to the original definition, H values are often calculated from the measured or estimated saturated vapor pressure and the water solubility at a specific temperature. However, low values of both quantities for many hydrophobic organic chemicals make it difficult to derive an accurate and reliable H value. The typical variation in both parameters is often larger than 1 order of magnitude.[1−3] For example, the water solubility, vapor pressure, and calculated or experimentally determined H values for dibutyl phthalate (DBP) at 25 °C ranged over (3.2 to 4500) mg·L^{-1}, (0.0013 to 0.047) Pa, and (0.028 to 0.46) Pa·m^3·mol^{-1}, respectively.[3] The ranges tend to become even wider for more hydrophobic chemicals because of experimental difficulties associated with the quantification of chemicals at low concentrations. Thus, it is sometimes difficult for researchers to select an appropriate H value, even though it is frequently used for the estimation of emissions and environmental fate modeling.[4,5] In this regard, several experimental techniques for determining precise values of H have been developed by many researchers, including equilibrium partitioning in closed systems (EPICS),[6−8] batch air stripping,[9] gas stripping,[4,10,11] the wetted-wall column technique,[12] the static headspace method,[13,14] the counterflow method,[15] and the gas chromatographic method.[16,17] The aforementioned methods determine the equilibrium distribution ratios or mass transfer rates between air and water. Alternatively, H can be obtained from equilibrium partition coefficients between a third phase and air or water. For example, H can be calculated from the 1-octanol/water partition coefficients (K_{ow}) and 1-octanol/air partition coefficients (K_{oa}) although this relationship is more often used for the derivation of K_{oa}, because the K_{ow} and H values are more readily available.[18,19]

Recently, simple methods for obtaining the partition coefficients between passive sampling/dosing phases and the medium separating them were developed. The partition coefficients between polydimethylsiloxane (PDMS) and water (K_{PDMSw}) were obtained using a dynamic permeation method,[20] and the K_{oa} values were obtained using a liquid phase extraction

Received: September 2, 2012
Accepted: October 16, 2012
Published: October 25, 2012

   dx.doi.org/10.1021/je300954s | J. Chem. Eng. Data 2012, 57, 3296−3302

using an octanol drop at the tip of a microsyringe needle.[21] The rate of mass transfer in the boundary layer separating the passive sampling and dosing phases was determined experimentally, and this value was used to determine the partition coefficient using a film diffusion model. The main advantages of these methods are that (1) the experimental systems are very simple, (2) precise measurements can be made because it is not necessary to measure low chemical concentrations in media such as water or air, and (3) the measurement can be made in a short time because the mass transfer coefficients are measured instead of the equilibrium ratios. Because the difficulty in measuring H lies in the low concentrations of hydrophobic chemicals in both air and water, the use of kinetically obtained partition coefficients would be very helpful in the determination of H.

In this study, H values were obtained from the partition coefficient between PDMS and air (K_{PDMSa}) and K_{PDMSw}. Twenty hydrophobic organic chemicals (11 polycyclic aromatic hydrocarbons (PAHs), 5 chlorinated benzenes, 2 phthalate esters, and 2 aromatic nitro musks) were chosen for a proof of the principle. The mass transfer rate constants experimentally measured in this study or those reported in earlier studies were used to derive the H values. The obtained H values were then compared with those reported in the literature obtained using various experimental and calculation methods.

■ THEORY

The transfer of a chemical through the air or water boundary layer shown in Figure 1 can be described using a film diffusion model. Because PDMS disks have a much higher holding capacity for hydrophobic chemicals than air or water, it is reasonable to neglect the mass of chemicals stored in the air or water boundary layers and to consider them as mass transfer barriers that do not accumulate chemicals. A rigorous derivation of the partition coefficient between PDMS and the medium is found in our earlier study.[20] Briefly, the transport of a chemical from the donor disk to the acceptor disk is described by

$$\frac{dC_{acceptorPDMS}}{dt} = -k(C_{acceptorPDMS} - C_{donorPDMS}) \quad (1)$$

where $C_{acceptorPDMS}$ and $C_{donorPDMS}$ are the concentrations of a chemical in the acceptor and the donor PDMS and k is the transfer rate constant (s^{-1}), which is dependent on the chemical and the medium between the two PDMS disks. The analytical solution of eq 1 for $C_{acceptorPDMS}$ is given by

$$C_{acceptorPDMS} = \frac{C_0}{2}[1 - \exp(-kt)] \quad (2)$$

$$\ln\left(1 - \frac{2C_{acceptorPDMS}}{C_0}\right) = -kt \quad (3)$$

where C_0 is the initial concentration in the donor disk. Thus, the mass transfer rate constant k can easily be obtained by a linear regression. In a film diffusion model, k is determined from four mass transfer resistances, namely, those in the donor PDMS, in the boundary layers both on the donor and the acceptor side, and in the acceptor PDMS. The K_{PDMSa} or K_{PDMSw} values are large enough for the chemicals chosen, and the diffusion coefficients of many organic chemicals are sufficiently large in PDMS that it can be further assumed that the mass transfer resistances in the donor and the acceptor PDMS are negligibly small compared to that in the medium (air or water). Under these assumptions, k can be approximated as

$$k \approx \frac{D_{medium}}{K_{PDMSmedium}\delta_{medium}} \frac{A}{V_{PDMS}} \quad (4)$$

where D_{medium} represents the diffusion coefficient in the medium ($m^2 \cdot s^{-1}$), δ_{medium} is the thickness of the mass transfer boundary layer (m), A is the interface area between the PDMS and the medium (m^2), and V_{PDMS} is the volume of the PDMS disk (m^3). While the air boundary layer thickness (δ_a) is equal to the physical distance between the two PDMS disks because a fixed stagnant air layer is used (Figure 1a), the water boundary layer in the dynamic permeation method (δ_w) was estimated as 12.5 μm because the experiment was performed under exactly the same experimental conditions used in the earlier studies.[20] The molecular diffusion coefficients in air and water were estimated using the Fuller−Schettler−Giddings correlation[22] and Hayduk−Laudie correlation,[23] respectively. The molar liquid volume of each chemical was estimated using the LeBas method.[24]

$$D_a(m^2 s^{-1}) = \frac{10^{-7}T^{1.75}(1/M_a + 1/M)^{1/2}}{P(V_a^{1/3} + V^{1/3})^2} \quad (5)$$

$$D_w(m^2 \cdot s^{-1}) = \frac{13.26 \cdot 10^{-9}}{\eta^{1.14}MLV^{0.589}} \quad (6)$$

where D_a and D_w are diffusion coefficients in air and water, respectively, T is temperature (K), M_a and M are the molecular weights ($g \cdot mol^{-1}$) of air and the chemical, V_a and V are molar volume of air and the chemical ($cm^3 \cdot mol^{-1}$), η is the viscosity of water (0.89 mP·s at 25 °C), and MLV is the LeBas molar liquid volume ($cm^3 \cdot mol^{-1}$). Given the thickness of the air or the water boundary layer and the estimated molecular diffusion

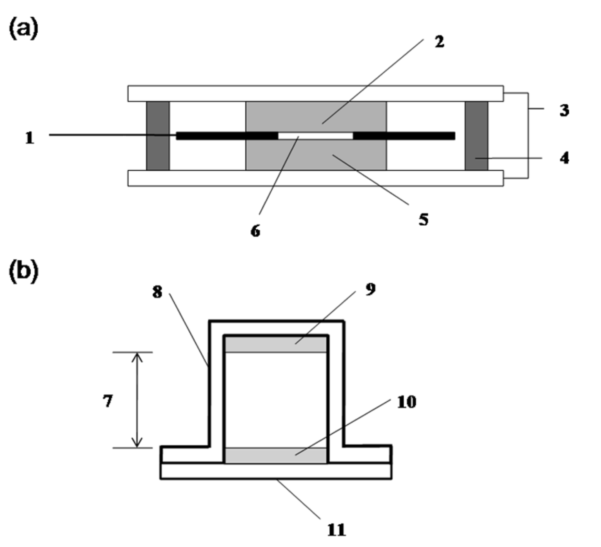


Figure 1. Experimental device used for the determination of K_{PDMSa} for (a) less volatile compounds and (b) more volatile compounds. (1) steel spacer (o.d. 15 mm, i.d. 6 mm); (2) "pre-loaded" PDMS disk (d = 8 mm, 0.5 mm thick); (3) glass plate; (4) stainless steel ring (5) "clean" PDMS disk (d = 8 mm, 0.5 mm thick); (6) air boundary layer (100 μm); (7) air boundary layer (6 mm); (8) custom-made glass wall (i.d. 6 mm, depth = 8 mm); (9) "pre-loaded" PDMS disk (d = 6 mm, 1 mm thick); (10) "clean" PDMS disk (d = 6 mm, 1 mm thick); (11) glass plate.

coefficient, K_{PDMSa} or K_{PDMSw} can be calculated from experimentally measured values of k.

EXPERIMENTAL SECTION

Materials and Chemicals. For the evaluation of the proposed method, we chose 20 chemicals, namely, 11 PAHs (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*k*]fluoranthene, and benzo[*a*]pyrene), five chlorinated benzenes (1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,2,4,5-trichlorobenzene, pentachlorobenzene, and hexachlorobenzene), two phthalate esters (DBP and benzylbutyl phthalate (BBP)), and two nitro musks (1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (musk xylene) and 1-(4-*tert*-butyl-2,6-dimethyl-3,5-dinitrophenyl) ethanone (musk ketone)), whose H values ranged between 10^{-2} and 10^2 $Pa \cdot m^3 \cdot mol^{-1}$. All test chemicals and solvents were of high purity (over at least 98 %) and were purchased from Sigma-Aldrich (St. Louis, MO, USA) or Fluka (Buchs, Switzerland). The sources and purity of chemicals used in this study are summarized in Table 1. Medical grade PDMS sheets with a thickness of 1 mm or 0.5 mm and a density of 1170 $kg \cdot m^{-3}$ were purchased from Specialty Silicone Products, Inc. (Ballston Spa, NY, USA). The PDMS was cut into disks with diameters of 6 mm (1 mm thick) or 8 mm (0.5 mm thick) and cleaned in a Soxhlet extractor using hexane followed by methanol for 2 h each. The cleaned PDMS disks were stored in methanol until use.

Table 1. Sources and Initial Mass Fraction Purity of Chemicals Used in This Study

chemical	source	initial mass fraction purity
methanol	B&J	≥ 0.999
hexane	Fluka	≥ 0.99
naphthalene	Sigma	≥ 0.99
1,2,3-trichlorobenzene	Fluka	≥ 0.999
1,2,4-trichlorobenzene	Fluka	≥ 0.99
1,2,4,5-tetrachlorobenzene	Fluka	0.99
pentachlorobenzene	Sigma	0.98
hexachlorobenzene	Fluka	≥ 0.99
dibutyl phthalate	Fluka	0.998
benzylbutyl phthalate	Sigma	0.98
1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene	Fluka	0.999
1-(4-*tert*-butyl-2,6-dimethyl-3,5-dinitrophenyl) ethanone	Sigma	0.98

Determination of K_{PDMSa} and K_{PDMSw}. The K_{PDMSa} and K_{PDMSw} values were determined using the unstirred boundary layer (UBL) diffusion method[25,26] and the aqueous boundary layer (ABL) permeation method,[20] respectively. Detailed experimental procedures are described in earlier publications,[20,25,26] and the schematic designs of the experimental device are shown in Figure 1. Briefly, the donor PDMS disks were loaded with test chemicals to the desired initial concentrations using a methanol:water mixture (4.7:4, m/m) containing the test chemical(s). The initial concentrations in the PDMS donor disks ranged from 200 $\mu mol \cdot kg_{PDMS}{}^{-1}$ (1,2,4-trichlorobenzene) to 29 $mol \cdot kg_{PDMS}{}^{-1}$ (naphthalene), considering the sensitivity of the detectors used. The initial concentrations of all test chemicals are listed in Table S1, Supporting Information. For all PAHs except for naphthalene, the kinetic rate constants reported by Mayer et al.[26] and Kwon et al.[20] were used for the calculation of K_{PDMSa} and K_{PDMSw}.

In the UBL method, two different experimental designs were used depending on the volatility of the chemical mixtures. For the phthalate esters and nitro musks, the experimental setup was very close to that used by Mayer and co-workers,[26] except that both the donor and the acceptor PDMS disks were placed in a closed vessel (Figure 1a). Although the mass transfer boundary layer may not be the same as the physical distance used in our devices, we assumed that the thickness of boundary layer equals to the physical distance between two PDMS disks because bulk motion of air was limited. The thickness of the PDMS disks was 0.5 mm, and δ_a was 100 μm. For the chlorobenzenes and naphthalene, δ_a was extended to 6 mm because of their high volatility (Figure 1b). After a predetermined time interval, both the donor and the acceptor disks were removed and extracted with 1 mL of hexane for gas chromatography analyses. The mass transfer rate constants (k) were obtained using eq 3 and the K_{PDMSa} values were obtained using eq 4.

The ABL permeation method was employed for the determination of K_{PDMSw}. A PDMS disk (6 mm in diameter) preloaded with a mixture of compounds and a clean PDMS disk were separated by water. A stainless steel stirring disk (5.08 mm in diameter, 0.635 mm thick) was placed in the water and stirred at 300 rpm to reduce the ABL thickness (δ_w) to 12.5 μm.[20] The extraction and analysis of chemicals in PDMS were performed in the same way as in the UBL method. All experiments were conducted at 25 ± 2 °C.

Instrumental Analyses. The hexane extracts were quantified using a gas chromatographic system equipped with a Hewlett-Packard 5890 Series II gas chromatograph, an electronic pressure control (EPC), a split/splitless capillary inlet, and a flame ionization detector (FID) or an electron-capture detector (ECD). The chemical mixtures were separated on an HP-5 column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent J&C Scientific, Folsom, CA). Naphthalene and phthalate esters were detected using the FID, and chlorinated benzenes and nitro musks were detected using the ECD. The detailed analytical conditions for chromatographic separation and detection are listed in Table S2, Supporting Information.

RESULTS AND DISCUSSION

Determination of Mass Transfer Rate Constants and Partition Coefficients. Figure 2 shows example plots used for the determination of the mass transfer rate constant k according to eq 3 for (a) chlorinated benzenes and (b) nitro musks in fixed air boundary layers of 6 mm and 100 μm, respectively, and for (c) nitro musks in the dynamic ABL. The experimental plots used for the determination of the k values for all other chemicals are presented in Figure S1, Supporting Information. As shown in Figure 2 and Figure S1, the experimental data fitted well with the model equation (eq 3) and resulted in a narrow range of k values. The 95 % confidence intervals for H were calculated using error propagation from the confidence intervals for K_{PDMSw} and K_{PDMSa}. For the ABL permeation method, it was not possible to derive a 95 % confidence interval because the ABL thickness cannot be measured. Instead, analogous values were obtained assuming that the range of ABL thickness corresponding to the 95 % confidence interval is (10 to 15) μm.[20] Typical 95 % confidence intervals were within 15 % of the fitted value neglecting potential uncertainties

dx.doi.org/10.1021/je300954s | J. Chem. Eng. Data 2012, 57, 3296−3302

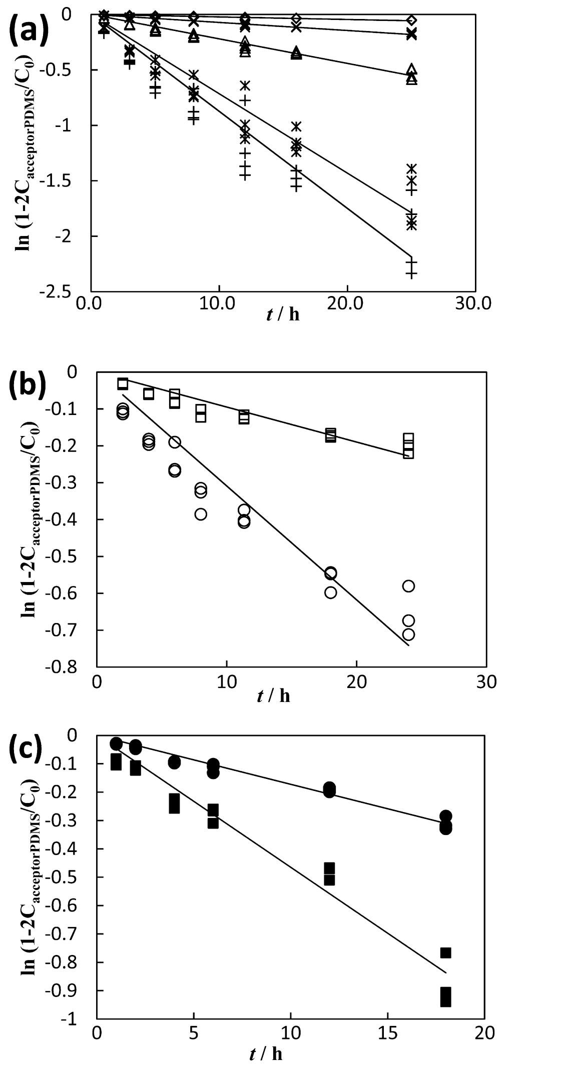


Figure 2. Plots for the determination of the mass transfer rate constant k using a linearized equation (eq 3) for (a) chlorinated benzenes and nitro musks (b) in the fixed air boundary layer and (c) in the dynamic water boundary layer: +, 1,2,3-trichlorobenzene; ∗, 1,2,4-trichlorobenzene; △, 1,2,4,5-tetrachlorobenzene; ×, pentachlorobenzene; ◇, hexachlorobenzene; □, 1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene; ○, 4-*tert*-butyl-2,6-dimethyl-3,5-dinitroacetophenone; ■, 1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene; ●, 1-(4-*tert*-butyl-2,6-dimethyl-3,5-dinitrophenyl) ethanone.

associated with the estimation of diffusion coefficient (eq 6). The increase in the concentration in the acceptor PDMS exceeded the analytical limit for quantification and was easily measurable after a few hours for all chemicals except for BBP with the fixed air boundary layer of 100 μm.

Table 2 lists all k values in the air and water boundary layers determined experimentally in this study, along with those reported by Mayer et al.[26] and Kwon et al.[20] and the calculated molecular diffusivities. The values of K_{PDMSa} and K_{PDMSw} calculated from the k values and the Henry's law constants are also given. For naphthalene, the k value obtained in this study was used to derive K_{PDMSa}, because the experimental setup used for a mixture of PAHs by Mayer et al.[26] was not suitable for highly volatile compounds such as naphthalene, which has a vapor pressure of approximately 10 Pa at 25 °C.[1] The mass transfer rate constant obtained by Mayer et al.[26] was much lower than that obtained in this study in a closed system. Potential evaporation of naphthalene during the experiment may be significant even if the experiment is completed within a few hours. For the determination of K_{PDMSw}, the k values obtained using the dynamic permeation method were preferred, because the measured rate constant may be significantly affected by the potential evaporation of water captured between the two PDMS disks.[26]

As shown in Table 2, the ranges of log K_{PDMSa} and log K_{PDMSw} were 4.6 to 9.3 and 2.4 to 5.1, respectively, and the resulting range of H was between (0.00969 and 179) $Pa \cdot m^3 \cdot mol^{-1}$.

Comparisons with Literature Values. Figure 3 shows a comparison of the Henry's law constants obtained from K_{PDMSa} and K_{PDMSw} in this study with values reported in the literature obtained using various methods. Because of the narrow range of the 95 % confidence intervals of values obtained in this study, the horizontal error bars are not shown. The symbols for PAHs and penta- and hexa-chlorobenzenes represent the final adjusted values suggested by Wania and co-workers.[27,28] For all other chemicals, median experimental values of H compiled by Mackay et al.[1−3] were used. The vertical bars represent the entire range of experimental values for all chemicals except for two phthalate esters and two nitro musks. For the two phthalate esters (DBP and BBP), the values compiled by Mackay et al.[3] only include values estimated from the water solubility and the vapor pressure, resulting in a range of calculated H values over 1 order of magnitude. Thus, the H values recommended by Staples et al.[29] were used as representative literature values. No experimental values for the Henry's law constants were available for the two nitro musks. Instead, the H values were calculated using measured or estimated solubility and vapor pressure values.[30−34] In Figure 3, the recommended values in the EU risk assessment report[30,31] were taken as the representative literature values for the two nitro musks instead of the median values because of the wide range of values reported in the literature and their great uncertainties.

The range of experimental values was within at most a factor of 5 (1,2,4-trichlorobenzene) when H was above 1 $Pa \cdot m^3 \cdot mol^{-1}$, and the aqueous solubility and vapor pressure were both relatively high. However, the deviation in experimental values became larger with increasing hydrophobicity of the chemicals. This is likely due to the fact that the low aqueous solubility and low vapor pressure of those chemicals posed difficulties in the precise determination of both quantities. However, the experimentally measured H values in general agree well with the median or representative values from the literature, except for those for BBP and the two nitro musks.

In spite of the structural similarity of DBP and BBP, the measured log K_{PDMSa} value of BBP was much smaller than that of DBP (Table 2), resulting in an H value lower than those reported in literature. In the earlier calculation of the vapor pressure of BBP, the evaporation of BBP might have been overestimated. On the other hand, the H values for the two nitro musks determined in this study were greater than the reference literature values by approximately an order of magnitude (Figure 3). Their vapor pressure at room temperature was estimated using values measured at higher temperatures according to the modified Grain method[32] and the aqueous solubility measured using a high-performance liquid chromatography (HPLC) method.[35] Two possible explanations for the discrepancy are the underestimation of the vapor

Table 2. Summary of Mass Transfer Rate Constants k_a and k_w Measured Experimentally in This Study and from the Literature and Derived K_{PDMSa}, K_{PDMSw}, and H Values[a]

	D_a[b]	D_w[b]	$k_a/10^{-3}$ h^{-1}			$k_w/10^{-3}$ h^{-1}				H
chemical	10^{-6} m^2·s^{-1}	10^{-10} m^2·s^{-1}	δ_a = 6 mm	δ_a = 100 μm	δ_a = 100 μm[26]	δ_w = 100 μm[26]	ABL permeation method[20]	log K_{PDMSa}	log K_{PDMSw}	Pa·m^3·mol^{-1}
naphthalene	6.94	7.99	113			85.7		4.57 ± 0.03	2.40 ± 0.11	16.7 ± 3.4
acenaphthene	6.52	7.26			217	15.6		5.90 ± 0.05	3.09 ± 0.10	3.84 ± 0.75
fluorene	6.24	7.01			129	11.5		6.11 ± 0.05	3.21 ± 0.07	3.12 ± 0.52
phenanthrene	5.93	6.70			48.6		26.2	6.51 ± 0.04	3.87 ± 0.08	5.61 ± 1.24
anthracene	5.93	6.70			43.1		20.6	6.56 ± 0.04	3.97 ± 0.08	6.33 ± 1.38
fluoranthene	5.73	6.36			8.66		8.62	7.25 ± 0.04	4.33 ± 0.09	2.98 ± 0.72
pyrene	5.73	6.42			6.36		7.80	7.38 ± 0.05	4.37 ± 0.10	2.44 ± 0.03
benz[a]anthracene	5.26	5.85			0.472		2.34	8.47 ± 0.01	4.86 ± 0.10	0.600 ± 0.129
chrysene	5.26	5.85			0.477		2.98	8.47 ± 0.04	4.75 ± 0.09	0.478 ± 0.115
benzo[k]fluoranthene	5.12	5.61			0.0639	0.181		9.33 ± 0.04	4.92 ± 0.03	0.0958 ± 0.0102
benzo[a]pyrene	5.12	5.66			0.0681		1.25	9.30 ± 0.31	5.12 ± 0.11	0.161 ± 0.074
1,2,3-trichlorobenzene	6.84	7.66	71.6				33.8	4.76 ± 0.03	3.46 ± 0.10	125 ± 27
1,2,4-trichlorobenzene	6.84	7.66	87.4				29.9	4.67 ± 0.04	3.51 ± 0.10	171 ± 37
1,2,4,5-tetrachlorobenzene	6.44	7.12	22.1				7.99	5.24 ± 0.02	4.03 ± 0.10	152 ± 32
pentachlorobenzene	6.10	6.67	7.27				2.12	5.70 ± 0.02	4.56 ± 0.10	179 ± 38
hexachlorobenzene	5.81	6.29	2.28				0.865	6.18 ± 0.04	4.91 ± 0.09	132 ± 27
dibutyl phthalate	4.60	4.83		2.55			43.8	7.86 ± 0.04	3.50 ± 0.10	0.108 ± 0.025
benzylbutyl phthalate	4.42	4.66		0.225			43.1	8.90 ± 0.06	3.49 ± 0.09	0.00969 ± 0.00247
1-*tert*-butyl-3,5-dimethyl-2,4,6-trinitrobenzene	4.88	4.98		30.9			17.9	6.81 ± 0.03	3.90 ± 0.10	3.11 ± 0.70
1-(4-*tert*-butyl-2,6-dimethyl-3,5-dinitrophenyl) ethanone	4.79	4.97		9.50			51.6	7.31 ± 0.04	3.44 ± 0.10	0.336 ± 0.076

[a]Uncertainties were calculated based on 95 % confidence intervals and error propagation. [b]Calculated using eqs 5 and 6.

dx.doi.org/10.1021/je300954s | J. Chem. Eng. Data 2012, 57, 3296−3302

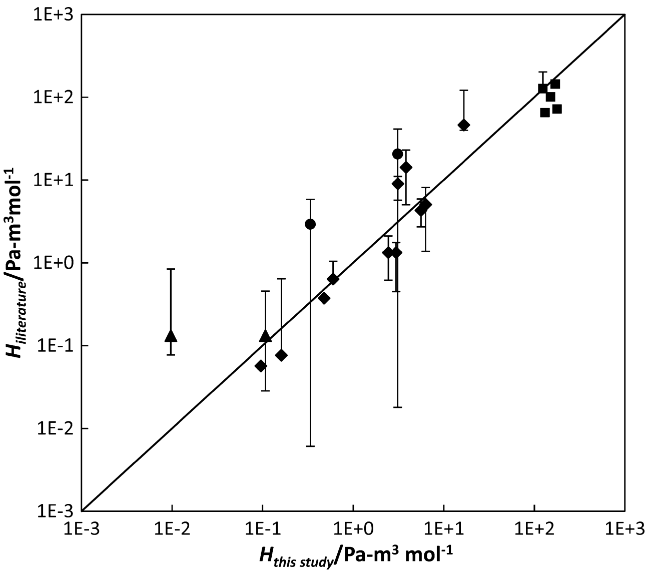


Figure 3. Comparison of the Henry's law constants determined kinetically in this study with values reported in the literature: ♦, polycyclic aromatic hydrocarbons; ■, chlorinated benzenes; ▲, phthalate esters; ●, nitro musks. Symbols represent the median or selected Henry's law constant values, and bars denote the range of literature values. The solid line indicates the 1:1 relationship.

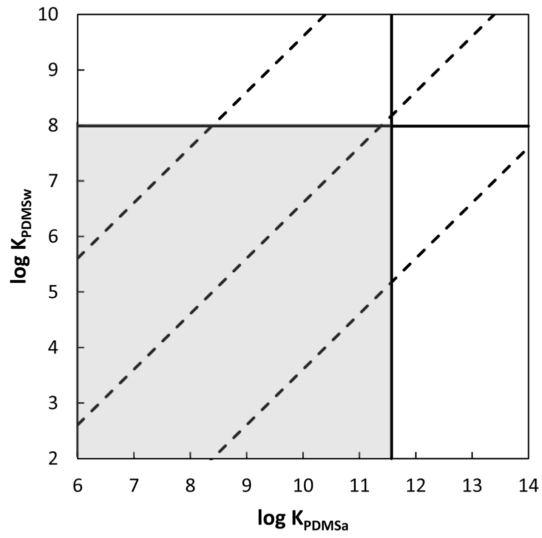


Figure 4. Applicability domain for the determination log K_{PDMSa} and log K_{PDMSw} for a hypothetical chemical. The shaded area indicates the range of values that can be determined within 10 *d* for K_{PDMSa} and 3 *d* for K_{PDMSw} assuming that $C_{acceptorPDMS}/C_0 = 10^{-4}$, $\delta_a = 100$ μm, $\delta_w = 12.5$ μm, and $A/V_{PDMS} = 2000$ m^{-1}. Dashed lines indicate Henry's law constants equal to (10^3, 1, and 10^{-3}) Pa·m^3·mol^{-1}, respectively.

pressure and the overestimation of the water solubility. Because the vapor pressure was extrapolated to the values at 20 °C,[32] the real values at 25 °C would be higher because of the great sensitivity of vapor pressure to temperature changes. The water solubility might be also overestimated using an HPLC retention time method. Because the Henry's law constant was derived from the ratio of the relative mass transfer rates in the air and water boundary layers, it is likely that this comparison would result in a more precise estimation of *H* if the boundary layer diffusion theory holds. Although further confirmation of the method is needed, the results in this study show that the volatility of the two nitro musks at the air–water interface might have been underestimated in the earlier evaluation.

Applicability Domain of the Method. The K_{PDMSw}, K_{PDMSa}, and *H* values were obtained from the mass transfer rate in the boundary layers measured using a simple experimental device in a short time, suggesting that the method should be useful for the determination of partition coefficients when the values are very low or very high. As discussed earlier, the K_{PDMSw} or K_{PDMSa} value is inversely proportional to the appropriate mass transfer rate constant *k* if all other parameters are unchanged (eq 4). The parameters *A*, V_{PDMS}, and δ_{medium} are physical variables independent of the chemicals, and D_{medium} varied less than a factor of 2 for the selected chemicals (Table 2). In addition, $C_{acceptorPDMS}$ should be sufficiently higher than the analytical detection limit to obtain *k* (eq 3). Thus, the range of K_{PDMSw} or K_{PDMSa} values that can be estimated within a reasonable experimental time, less than 3 days for K_{PDMSw} and 10 days for K_{PDMSa}, can be estimated using the lower bound values of D_a and D_w in this study. The thicknesses of air and water boundary layer were (100 and 12.5) μm, respectively. The area-to-volume ratio was assumed to be $2\cdot10^3$ m^{-1}, and the lowest detection limit of $C_{acceptor}/C_0$ was assumed to be 0.0001.

Figure 4 shows a diagram of the applicability domain of the method. Because of the many practical constraints such as the analytical detection limits, the values of K_{PDMSw} and K_{PDMSa} that could be determined using the proposed method would be limited to 10^8 and $10^{11.6}$, respectively. The shaded area in Figure 4 is the experimentally feasible domain of the method. The proposed method may not be applicable when K_{PDMSw} or K_{PDMSa} is sufficiently small because eq 4 does not hold anymore. However, partition coefficients for those less hydrophobic chemicals can be measured without difficulties using equilibrium partitioning methods. The dashed lines in Figure 4 represent *H* values of a hypothetical chemical. Because the Henry's law constants of many organic chemicals of environmental concern fall in the range that could be covered by the method, it is very promising for generating quick and simple experimental data on air–water partitioning with great precision.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Initial concentrations of the test chemicals in PDMS, detailed analytical conditions for gas chromatography, and compiled literature values of Henry's law constants are presented in Tables S1, S2, and S3. Figure S1 presents the plots used for the experimental determination of the mass transfer rate constants *k* for all chemicals chosen. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +82 31 219 1942, fax: +82 31 215 5145, and e-mail: jhkwon@ajou.ac.kr.

Funding

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2009-0065352 and 2012R1A1B4000841).

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Mackay, D.; Shiu, W. Y.; Ma, K.-C.; Lee, S. C. *Handbook of Organic Chemicals: Properties and Environmental Fate for Organic Chemicals. Vol. I. Introduction and Hydrocarbons*, 2nd ed.; CRC Press: New York, NY, 2006.

(2) Mackay, D.; Shiu, W. Y.; Ma, K.-C.; Lee, S. C. *Handbook of Organic Chemicals: Properties and Environmental Fate for Organic Chemicals. Vol. II. Halogenated Hydrocarbons*, 2nd ed.; CRC Press: New York, NY, 2006.

(3) Mackay, D.; Shiu, W. Y.; Ma, K.-C.; Lee, S. C. *Handbook of Organic Chemicals: Properties and Environmental Fate for Organic Chemicals. Vol. III. Oxygen Containing Compounds*, 2nd ed.; CRC Press: New York, NY, 2006.

(4) Lau, F. K.; Charles, J.; Cahill, T. M. Evaluation of gas-stripping methods for the determination of Henry's law constants for polybrominated diphenyl ethers and polychlorinated biphenyls. *J. Chem. Eng. Data* **2006**, *51*, 871−878.

(5) Diaz, A.; Ventura, F.; Galceran, M. T. Determination of Henry's law constants for low volatile mixed halogenated anisoles using solid-phase microextraction. *Anal. Chim. Acta* **2007**, *589*, 133−136.

(6) Gosset, R. M. Measurement of Henry's law constants for C_1 and C_2 chlorinated hydrocarbons. *Environ. Sci. Technol.* **1987**, *21*, 202−208.

(7) Ashworth, R. A.; Howe, G. B.; Mullins, M. E.; Rogers, T. N. Air-water partitioning coefficients of organics in dilute aqueous solutions. *J. Hazard. Mater.* **1988**, *18*, 25−36.

(8) Allen, J. M.; Balcavage, W. X.; Ramachandran, B. R.; Shrout, A. L. Determination of Henry's law constants by equilibrium partitioning in a closed system using a new in situ optical absorbance method. *Environ. Toxicol. Chem.* **1998**, *17*, 1216−1221.

(9) Alaee, M.; Whittal, R. M.; Strachan, W. M. J. The effect of water temperature and composition on Henry's law constant for various PAH's. *Chemosphere* **1996**, *32*, 1153−1164.

(10) Mackay, D.; Shiu, W.-Y.; Sutherland, R. P. Determination of air-water Henry's law constants for hydrophobic pollutants. *Environ. Sci. Technol.* **1979**, *14*, 333−337.

(11) Li, H.; Ellis, D.; Mackay, D. Measurement of low air-water partition coefficients of organic acids by evaporation from a water surface. *J. Chem. Eng. Data* **2007**, *52*, 1580−1584.

(12) Brunner, S.; Hornung, E.; Santl, S.; Wolff, E.; Pringer, O. G.; Altschuh, J.; Bruggemann, R. Henry's law constant for polychlorinated biphenyls: Experimental determination and structure-property relationships. *Environ. Sci. Technol.* **1990**, *24*, 1751−1754.

(13) Miller, M. E.; Stuart, J. D. Measurement of aqueous Henry's law constants for oxygenates and aromatics found in gasolines by the static headspace method. *Anal. Chem.* **2000**, *72*, 622−625.

(14) Robbins, G. A.; Wang, S.; Stuart, J. D. Using the static headspace method to determine Henry's law constants. *Anal. Chem.* **1993**, *65*, 3113−3118.

(15) Caires, J. P.; Suzuki, M.; Kibbey, T. C. G. Counterflow method for measurement of Henry's law constants. *J. Environ. Eng.* **2003**, *129*, 1169−1175.

(16) Tse, G.; Orbey, H.; Sandler, S. I. Infinite dilution activity coefficients and Henry's law coefficients of some priority water pollutants determined by a relative gas chromatographic method. *Environ. Sci. Technol.* **1992**, *26*, 2017−2022.

(17) Schoene, K.; Steinhanses, J. Determination of Henry's law constant by automated head space-gas chromatography: Determination of dissolved gases. *Fresenius J. Anal. Chem.* **1987**, *321*, 538−543.

(18) Shoeib, M.; Harner, T. Using measured octanol-air partition coefficients to explain environmental partitioning of organochlorine pesticides. *Environ. Toxicol. Chem.* **2002**, *21*, 984−990.

(19) Li, X.; Chen, J.; Li, Z.; Qiao, X.; Huang, L. The fragment constant method for predicting octanol-air partition coefficients of persistent organic pollutants at different temperatures. *J. Phys. Chem. Ref. Data* **2006**, *35*, 1365−1384.

(20) Kwon, J.-H.; Wuethrich, T.; Mayer, P.; Escher, B. I. Dynamic permeation method to determine partition coefficients of highly hydrophobic chemicals between poly(dimethylsiloxane) and water. *Anal. Chem.* **2007**, *79*, 6816−6822.

(21) Ha, Y.; Kwon, J.-H. Determination of 1-octanol-air partition coefficient using gaseous diffusion in the air boundary layer. *Environ. Sci. Technol.* **2010**, *44*, 3041−3046.

(22) Fuller, E. N.; Schettler, P. D.; Giddings, J. C. A new method for prediction of binary gas-phase diffusion coefficient. *Ind. Eng. Chem.* **1966**, *58*, 19−27.

(23) Hayduk, W.; Laudie, H. Prediction of diffusion coefficients for non-electrolytes in dilute aqueous solutions. *AIChE J.* **1974**, *20*, 611−615.

(24) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, NY, 1977.

(25) Mayer, P.; Karlson, U.; Christensen, P. S.; Johnsen, A. R.; Trapp, S. Quantifying the effect of medium composition on the diffusive mass transfer of hydrophobic organic chemicals through unstirred boundary layers. *Environ. Sci. Technol.* **2005**, *39*, 6123−6129.

(26) Mayer, P.; Fernqvist, M. M.; Christensen, P. S.; Karlson, U.; Trapp, S. Enhanced diffusion of polycyclic aromatic hydrocarhons in artificial and natural aqueous solutions. *Environ. Sci. Technol.* **2007**, *41*, 6148−6155.

(27) Ma, Y.-G.; Lei, Y. D.; Xiao, H.; Wania, F.; Wang, W.-H. Critical review and recommended values for the physical-chemical property data of 15 polycyclic aromatic hydrocarbons at 25 °C. *J. Chem. Eng. Data* **2010**, *55*, 819−825.

(28) Shen, L.; Wania, F. Compilation, evaluation, and selection of physical-chemical property data for organochlorine pesticides. *J. Chem. Eng. Data* **2005**, *50*, 742−768.

(29) Staples, C. A.; Peterson, D. R.; Parkerton, T. F.; Adams, W. J. The environmental fate of phthalate esters: a literature review. *Chemosphere* **1997**, *35*, 667−749.

(30) European Communities European Union Risk Assessment Report on 4′-tert-butyl-2′,6′-dimethyl-3′,5′-dinitroacetophenone (musk ketone); European Chemicals Bureau: Ispra, Italy, 2005.

(31) European Communities European Union Risk Assessment Report on 5-tert-butyl-2,4,6-trinitro-m-xylene (musk xylene); European Chemicals Bureau: Ispra, Italy, 2005.

(32) Tas, J. W.; Balk, F.; Ford, R. A.; van de Plassche, E. J. Environmental risk assessment of musk ketone and musk xylene in the Netherlands in accordance with the EU-TGD. *Chemosphere* **1997**, *35*, 2973−3002.

(33) Paasivirta, J.; Sinkkonen, S.; Rantalainen, A.-L.; Broman, D.; Zebühr, Y. Temperature dependent properties of environmentally important synthetic musks. *Environ. Sci. Pollut. Res.* **2002**, *9*, 345−355.

(34) Peck, A. M.; Hornbuckle, K. C. Synthetic musk fragrances in Lake Michigan. *Environ. Sci. Technol.* **2004**, *38*, 367−72.

(35) Schramm, K.-W.; Kaune, A.; Beck, B.; Thumm, W.; Behechti, A.; Kettrup, A.; Nickolova, P. Acute toxicities of five nitromusk compounds in Daphnia, algae and photoluminescent bacteria. *Water Res.* **1996**, *30*, 2247−2250.