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Dynamic Permeation Method To Determine Partition Coefficients of Highly Hydrophobic Chemicals between Poly(dimethylsiloxane) and Water

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Measurement of partition coefficients between poly(dimethylsiloxane) (PDMS) and water (K_{PDMSw}) becomes more and more difficult as the hydrophobicity of the compound increases. Experimental challenges include long extraction times, sorption to various surfaces and materials, and incomplete dissolution of the compound in the aqueous phase. In order to avoid these artifacts and to shorten experimental time, a dynamic permeation method was developed. According to steady-state diffusion theory, K_{PDMSw} is inversely proportional to the permeation rate through the aqueous boundary layer (ABL) from the donor PDMS to the acceptor PDMS. A simple ABL permeation reactor can thus be applied to determine K_{PDMSw} values of hydrophobic chemicals within a few days. The obtained values were in good agreement with those obtained using a conventional shaking method and the partition controlled delivery system. A good linear correlation was obtained between the logarithm of the 1-octanol/water partition coefficient (log K_{ow}) from the literature and log K_{PDMSw} over 6 orders of magnitude.

Poly(dimethylsiloxane) (PDMS) has been widely used as a common coating material of solid-phase microextraction (SPME) for solventless extraction.[1−9] More recently, its use has been extended to a passive sampling/dosing system to evaluate the bioavailability and fate of hydrophobic organic pollutants.[10−13] Thus, it is of critical importance to know equilibrium partition coefficients of target analytes between PDMS and water (K_{PDMSw}), because mass distribution is explained by a partitioning process between two liquid phases.[14−16] However, experimental determination of K_{PDMSw} becomes more and more difficult as the hydrophobicity of the chemical increases. In a conventional batch stirring/shaking method, aqueous volume should be much higher than PDMS volume in proportion to K_{PDMSw} of a selected chemical.[2] This is similar for chromatographic determination of partition coefficients, such as countercurrent chromatography (CCC).[17−19] In addition to the volume issue, equilibrium time or retention time in the CCC method increases with increasing hydrophobicity.[17]

Many researchers determined K_{PDMSw} for highly hydrophobic chemicals by measuring concentrations in PDMS and water after the apparent equilibrium is obtained.[3−6,12] Using a typical stirring/shaking method, it takes a very long time to observe an apparent equilibrium. For example, Yang et al.[6] extracted polychlorinated biphenyls spiked into water using fibers with PDMS coating for up to 40 days, and Ter Laak et al.[12] depleted SPME fibers with PDMS coating preloaded with polycyclic aromatic hydrocarbons (PAHs) in water up to 4 weeks. However, in many cases, it is difficult to say that the system is at or close to equilibrium due to relatively large errors associated with the measurement, especially the measurement of aqueous concentration. In addition, prolonged

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experimental time may make the system highly vulnerable to potential experimental artifacts such as volatilization, degradation, and adsorption to surfaces. Thus, there is a need for developing fast experimental methods to obtain K_{PDMSw} for highly hydrophobic chemicals.

Recently, partition controlled delivery systems have been used to determine the partition coefficient between water and the sorbing phase as well as to maintain a stable dissolved concentration in a toxicity assay.[10,20] In these systems, chemicals are initially loaded in the sorbing phase, such as PDMS, and delivered to aqueous solution. The time required to reach equilibrium can be very short (e.g., 1 h), because of the limited mass transfer that is needed. Although this method allows fast measurement of K_{PDMSw}, it may be limited by the analytical detection limits in small aqueous samples.

In this regard, we developed a novel method for determining K_{PDMSw} of highly hydrophobic compounds in a short time using information of the aqueous permeability in the boundary layer. In this method, the rate of mass transfer from a PDMS disk preloaded with chemicals to a clean PDMS disk is measured. This transfer rate is used to estimate K_{PDMSw} with an estimated aqueous diffusion coefficient and a calibrated thickness of the aqueous boundary layer (ABL). Here, K_{PDMSw} values were measured using a conventional shaking method, using a partition controlled delivery system and the above-described kinetic (ABL permeation) method. The results of all methods were compared with each other as well as compared with literature log K_{PDMSw} and log K_{ow} values.

THEORY

For a hydrophobic chemical, the overall mass transfer is not limited by internal diffusion in PDMS but by steady-state diffusion in the ABL.[11,21] The changes in concentration in a batch system containing water and PDMS can then be described by two differential equations

$$\frac{dC_w}{dt} = -k_a \frac{V_{PDMS}}{V_w} C_w + k_d \frac{V_{PDMS}}{V_w} C_{PDMS} \quad (1)$$

$$\frac{dC_{PDMS}}{dt} = k_a C_w - k_d C_{PDMS} \quad (2)$$

where C_w (mol/m^3_w) and C_{PDMS} (mol/m$^3_{PDMS}$) are the concentrations in water and PDMS, V_w and V_{PDMS} are the volumes of water and PDMS (m^3), and k_a (m^3_w/m$^3_{PDMS}$·s^{-1}) and k_d (s^{-1}) are the absorption and the desorption rate constants. The kinetic partition coefficient is defined as $K_{PDMSw} = k_a/k_d$. The analytical solutions for eqs 1 and 2 are (cf. Supporting Information A for derivation)

$$C_w = k_d c_1 + c_2 \frac{V_{PDMS}}{V_w} \exp\left[-\left(k_a \frac{V_{PDMS}}{V_w} + k_d\right)t\right] = k_d c_1 + c_2 \frac{V_{PDMS}}{V_w} \exp\left[-\left(K_{PDMSw} \frac{V_{PDMS}}{V_w} + 1\right)k_d t\right] \quad (3)$$

$$C_{PDMS} = k_a c_1 - c_2 \exp\left[-\left(k_a \frac{V_{PDMS}}{V_w} + k_d\right)t\right] \quad (4)$$

where $c_1 = (C_{w,0} + C_{PDMS,0} \times V_{PDMS}/V_w)/(k_d + k_a \times V_{PDMS}/V_w)$, $c_2 = (k_a C_{w,0} \times C_{w,0} - k_d \times C_{PDMS,0})/(k_d + k_a \times V_{PDMS}/V_w)$, and $C_{w,0}$ and $C_{PDMS,0}$ represent the initial concentrations in water and PDMS. The experimental time should be sufficiently long in order to obtain a thermodynamic equilibrium between water and PDMS. In most experiments, the volumes of water and PDMS are adjusted to hold approximately equal amounts of chemicals to avoid analytical difficulties.[3−6,12] To achieve this, the volume ratio (V_{PDMS}/V_w) should be equal to the inverse of K_{PDMSw}. For example, 1 L of water should be equilibrated with a PDMS volume of 1 μL if K_{PDMSw} equals to 10^6. In this condition, the exponential term, $\exp(-2k_d t)$, should be small enough to satisfy equilibrium criteria. The logarithm of the desorption rate constant (log k_d) decreases with a negative unit slope as log K_{PDMSw} increases whereas the absorption rate constant (k_a) remains relatively invariant for hydrophobic chemicals as shown by Verbruggen et al.[22] using polyacrylate-coated SPME fibers. This implies that we have to increase the experimental time by a factor of 10 as K_{PDMSw} increases by one log unit.

In order to make equilibrium time shorter, one must increase the rate constants or increase the volume ratio (eqs 3 and 4). Assuming that the diffusion occurs in a thin stagnant film of water and PDMS, the uptake rate constant, k_a, is expressed by the mass-transfer resistances in both phases. For hydrophobic solutes, the aqueous resistance predominantly determines the overall mass-transfer resistance and thus the resistance in the membrane can be neglected (eqs 5 and 6).

$$k_a = \frac{1}{\frac{\delta_w}{D_w} + \frac{\delta_{PDMS}}{D_{PDMS}K_{PDMSw}}} \frac{A}{V_{PDMS}} \cong \frac{D_w}{\delta_w} \frac{A}{V_{PDMS}} \quad (5)$$

$$k_d = \frac{k_a}{K_{PDMSw}} = \frac{1}{\frac{\delta_w}{D_w} + \frac{\delta_{PDMS}}{D_{PDMS}K_{PDMSw}}} \frac{A}{V_{PDMS}K_{PDMSw}} \cong \frac{D_w}{\delta_w} \frac{A}{V_{PDMS}K_{PDMSw}} \quad (6)$$

D_w and D_{PDMS} are the molecular diffusion coefficients of the solute in water and PDMS (in m^2/s), δ_w and δ_{PDMS} are the ABL thickness and the thickness of PDMS (in m), and A is the interface area (in m^2). Equations 5 and 6 indicate that larger surface to volume ratio shortens equilibrium time as was shown with different thicknesses of PDMS coating on SPME fibers.[6,23] With a given surface to volume ratio, the only way to shorten equilibrium time is to reduce the ABL thickness. However, it is very difficult to decrease it sufficiently using conventional stirring devices. Jeannot and

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Cantwell[24] estimated ABL thickness of 10.7 μm at the interface between water and *n*-octane at 1500 rpm. Even with tumble stirrers, one cannot reach less than a few micrometers.[25,26] Thus, we may increase the constant associated with time in the exponential term of the analytical solution (eqs 3 and 4) by making V_{PDMS}/V_w significantly greater than $1/K_{PDMSw}$. Figure 1a describes a schematic experimental setup for the partition controlled delivery system. With the specific experimental condition used in this study, it requires less than a few hours to reach equilibrium.

Diffusive mass transfer in the aqueous boundary layer is related to the partition coefficient between water and the sorbing phases.[11,26] Changes in concentrations in the three-phase system (ABL permeation method) shown in Figure 1b are described by three differential equations:

$$dC_{PDMS,donor}/dt = k_a C_w - k_d C_{PDMS,donor} \quad (7)$$

$$dC_{PDMS,acceptor}/dt = k_a C_w - k_d C_{PDMS,acceptor} \quad (8)$$

$$dC_w/dt = -2k_a \frac{V_{PDMS}}{V_w} C_w + k_d \frac{V_{PDMS}}{V_w} (C_{PDMS,donor} + C_{PDMS,acceptor}) \quad (9)$$

Due to the symmetry of the system, the absorption and desorption rate constants to the donor and acceptor PDMS are identical and can be expressed by the same as eqs 5 and 6. Since the water phase holds only a negligible fraction of the hydrophobic chemicals and K_{PDMSw} (equal to k_a/k_d) is much greater than V_w/V_{PDMS}, the simplified analytical solutions are (cf., Supporting Information B for derivation)

$$C_{PDMS,donor}(t) = C_0/2\ [1 + \exp(-k_d t)] \quad (10)$$

$$C_{PDMS,acceptor}(t) = C_0/2\ [1 - \exp(-k_d t)] \quad (11)$$

$$C_w(t) = C_0/2K_{PDMSw} \quad (12)$$

where C_0 is the initial concentration in the preloaded PDMS disk. Although it is not possible to observe changes in the donor disk within a short experimental time especially for a chemical having high K_{PDMSw}, it is not difficult to measure the concentration in the acceptor disk against an initial concentration of zero. Therefore, the desorption rate constant, k_d, can be easily obtained using a linearized form of eq 11 by measuring $C_{PDMS,acceptor}(t)$.

$$\ln(1 - 2C_{PDMS,acceptor}(t)/C_0) = -k_d t \quad (13)$$

The measured k_d can be used for the determination of K_{PDMSw} using the estimated ABL thickness (δ_w) and the diffusion coefficient in water (D_w) as shown in eq 6. The aqueous diffusion coefficient (D_w) can be estimated from the molecular weight (M; g/mol) of the chemical,[27]

$$D_w\ (m^2 s^{-1}) = \frac{2.7 \times 10^{-8}}{M^{0.71}} \quad (14)$$

EXPERIMENTAL SECTION

Materials. The chemicals used for determining K_{PDMSw} were of high purity and were purchased from Fluka (Buchs, Switzerland), Riedel-de Haën (Seelze, Germany), Sigma-Aldrich (St. Louis, MO), or Supelco (Bellefonte, PA) except for three pesticides (aldicarb, cabaryl, and carbofuran; from Institute of Industrial Organic Chemistry, Warsaw, Poland) and pentachlorophenol (from EGA Chemie, Steinheim, Germany). Water for organic trace analysis (≤0.000 003% trace organics, Fluka) was used as a medium in the ABL permeation method. Medical grade PDMS sheeting with a thickness of 1 mm and density of 1,170 kg/m^3 was purchased from Specialty Silicone Products, Inc. (Ballston Spa, NY). It was cut into 10 mm × 10 mm squares for the partition controlled delivery method and into 6-mm-diameter disks for the ABL permeation method. Custom-cut PDMS squares and disks were cleaned in a Soxhlet extractor using *n*-hexane followed by methanol for 3 h each. After the cleanup, the PDMS cuts were stored in methanol until use.

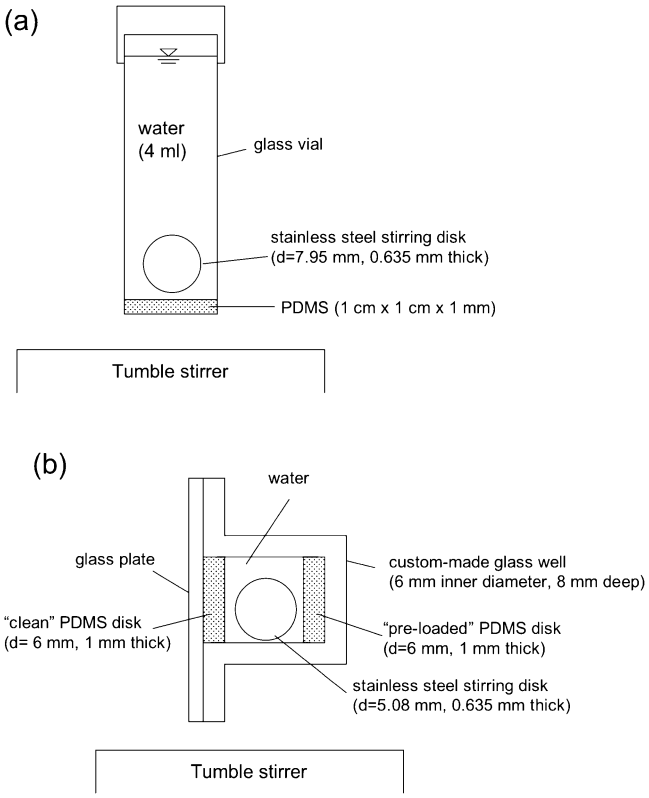

Figure 1. Cross sections of the experimental apparatus for (a) the partition controlled delivery system and (b) the ABL permeation method. A preloaded PDMS square serves as a source in the partition controlled delivery system. A preloaded PDMS disk serves as a donor and a "clean" PDMS disk as an acceptor in the ABL permeation method.

Determination of K_{PDMSw}. Partition coefficients between water and PDMS were determined using three methods, the conventional shaking method, the partition conttion controlled delivery

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system, and the ABL permeation method. All the partitioning experiments were performed at 25 °C.

In the conventional shaking method, a precleaned custom-cut PDMS disk (1.24×10^{-9}, 5.4×10^{-9}, or 24×10^{-9} m^3) was placed in a vial containing water spiked with methanol containing a chemical. Methanol fraction did not exceed 0.05%. Phosphate buffer solution (10 mM KH_2PO_4, pH 3.0) replaced distilled water for acidic phenols in order to measure K_{PDMSw} of neutral species. Vials were shaken for 1 or 3 days using a two-dimensional shaker at 240 rpm depending on their K_{PDMSw}. Equilibrium was ascertained by an extraction time profile (cf. Supporting Information Figure S-1). After shaking, the aqueous concentration was analyzed directly and PDMS concentration was analyzed by extracting PDMS disks with acetonitrile by shaking for 2 h, except for chlorinated benzenes and toluene, where both aqueous solution and PDMS were extracted using *n*-hexane. Sequential extraction of a PDMS disk showed that at least 98% of the analytes were extracted at the first extraction under given experimental condition. Extraction recovery of chlorinated benzenes and toluene was 90−105% from aqueous solution. In most cases, the volume ratio (V_w/V_{PDMS}) was close to measured K_{PDMSw} to ensure that the analyte is evenly distributed between both phases. K_{PDMSw} was calculated from the slope of the linear regression between measured C_{PDMS} and C_w ($n = 6$).

For the partition controlled delivery system, a PDMS square was placed in a vial containing methanol/water (50/50 v/v), in which a mixture of four to six compounds was dissolved. Each vial was shaken for at least 24 h to reach equilibrium. Each preloaded PDMS square was placed at the bottom of a glass vial and filled with 4 mL of distilled water and a stainless steel stirring disk (7.95-mm diameter, 0.635 mm thick, V&P Scientific, Inc., San Diego, CA) (Figure 1a). The initial concentration in PDMS squares ranged between 1.2 and 600 $mmol/m^3_{PDMS}$. After stirring using a tumble stirrer (VP710, V&P Scientific, Inc.) at 200 rpm, the aqueous solution was transferred into an extraction vial containing a clean PDMS disk (6-mm diameter, 2.83×10^{-8} m^3) and extracted for 24 h. Although the extraction time may not be sufficient to reach equilibrium between water and PDMS, almost all chemicals partition into the PDMS disk because of the high PDMS volume. The PDMS disk was then extracted using acetonitrile (*n*-hexane for chlorinated benzenes) as described previously. For chlorinated benzenes and toluene, the aqueous solution was extracted using *n*-hexane as was done in the conventional shaking method. Measured C_w values at different times were used to calculate kinetic K_{PDMSw} values. Nonlinear regression analysis was performed using GraphPad Prism (Version 4.0 for Mac, GraphPad Software, San Diego, CA).

In the ABL permeation method, a PDMS disk (6-mm diameter, 2.83×10^{-8} m^3) preloaded with a mixture of four to six compounds and a clean PDMS disk were separated by ~160 μL of ultrapure water as shown in Figure 1b. The initial concentration in the donor PDMS was between 10 and 160 $mmol/m^3_{PDMS}$. A stainless steel stirring disk (5.08-mm diameter, 0.635 mm thick, V&P Scientific, Inc.) was placed in the water to reduce ABL thickness (δ_w). After stirring at 300 rpm, both PDMS disks were taken and extracted using acetonitrile or *n*-hexane for HPLC or GC analysis. Mass balance was mostly 90−105%, indicating that system loss was negligible for all compounds tested with this method. The desorption rate constant (k_d) was obtained using eq 13. Then, K_{PDMSw} values were calculated from eq 6 using the ABL thickness. ABL was set to 12.5 μm as estimated by minimizing the square sum of residuals between log K_{PDMSw} values obtained by the ABL permeation method and those obtained by the partition controlled delivery system.

Chemical Analyses. All the chemicals except for chlorinated benzenes were analyzed using an HPLC system equipped with a Dionex P680 HPLC pump and an ASI-100 automated sample injector (Dionex Softron GmbH, Germering, Germany). PAHs were separated on a C18 Supelcosil LC-PAH column (150 mm × 4.6 mm, 5 μm, Supelco, Bellefonte, PA) at 40 °C and detected using an RF-2000 fluorescence detector (Dionex) with the excitation wavelength (λ_{ex}) of 275 nm and the emission wavelength (λ_{em}) of 350 nm for naphthalene, acenaphthene, and phenanthrene, λ_{ex} = 260 nm and λ_{em} = 420 nm for anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, and chrysene, and λ_{ex} = 290 nm and λ_{em} = 430 nm for perylene, benzo[*a*]pyrene, dibenz[*a*,*c*]anthracene, dibenz[*a*,*h*]anthracene, and benzo[*ghi*]perylene. All other compounds were separated on Nucleodur C18 Gravity column (125 mm × 4 mm, 5 μm, Macherey-Nagel GmbH & Co., Oensingen, Switzerland) at ambient temperature and detected using a UVD 340U diode array detector (Dionex) at their optimal wavelengths. Water and acetonitrile were used as the mobile phase either in a gradient mode or in an isocratic mode, depending on analytes, with the flow rate of 1 mL/min. For the analysis of organic acids, phosphate buffer solution (20 mM KH_2PO_4, pH 2.5) was used instead of water.

For chlorinated benzenes and toluene, concentrations of *n*-hexane extracts were measured by GC/MS with a Fisons HRGC 8000 Series GC (Milan, Italy) equipped with a Fisons MD800 mass spectrometer. The detector was operated in electron impact ionization mode (70 eV) with selective ion monitoring. Ions monitored at m/z = 146, 180, 194, 216, 250, and 284 for dichlorobenzenes, trichlorobenzenes, trichlorotoluene, tetrachlorobenzenes, pentachlorobenzene, and hexachlorobenzene. Recoveries of all analytes from water and PDMS extraction were between 90 and 110%. One microliter of *n*-hexane extract was injected in a split/splitless mode (splitless for 72 s followed by split ratio of 1:10) onto a DB-5MS column (15 m × 0.25 mm i.d., 0.25-μm film thickness, J&W Scientific, Folsom, CA). Helium was used as a carrier gas at a constant pressure of 50 kPa. Injector and transfer line temperatures were 250 and 280 °C, respectively. Column temperature was held at 50 °C for the initial 7.5 min, followed by a ramp of 5 °C/min to 150 °C without hold, followed by a ramp of 20 °C/min to 300 °C, and held for 2 min for simultaneous analysis of all chlorinated benzenes and toluene selected. A shortened temperature program was used for a specific mixture.

RESULTS AND DISCUSSION

Figure 2 shows typical aqueous concentration obtained from the partition controlled delivery system (Figure 1a) for naphthalene and benzo[*a*]anthracene as examples (cf. Supporting Information, Figure S-2 for all analytes). As V_{PDMS}/V_w is much higher than $1/K_{PDMSw}$, 95% equilibrium between two phases is obtained in less than 1 h. This short equilibrium time is consistent with those presented in the literature.[10,20] A nonlinear regression analysis was performed to obtain K_{PDMSw} and k_d values using eq

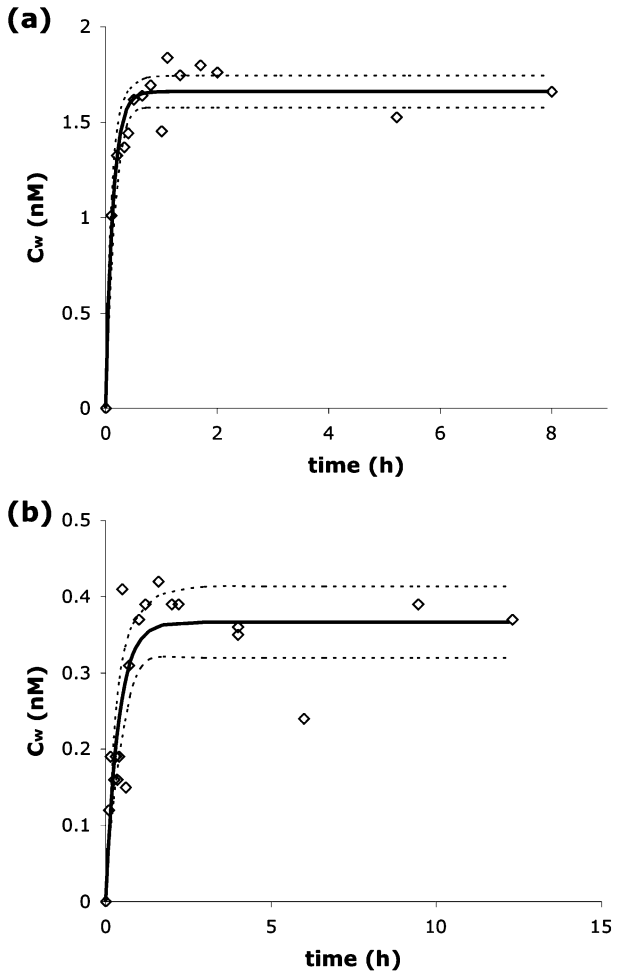

Figure 2. Release of (a) naphthalene and (b) benz[*a*]anthracene from PDMS to aqueous solution. Dashed lines denote 95% confidence interval.

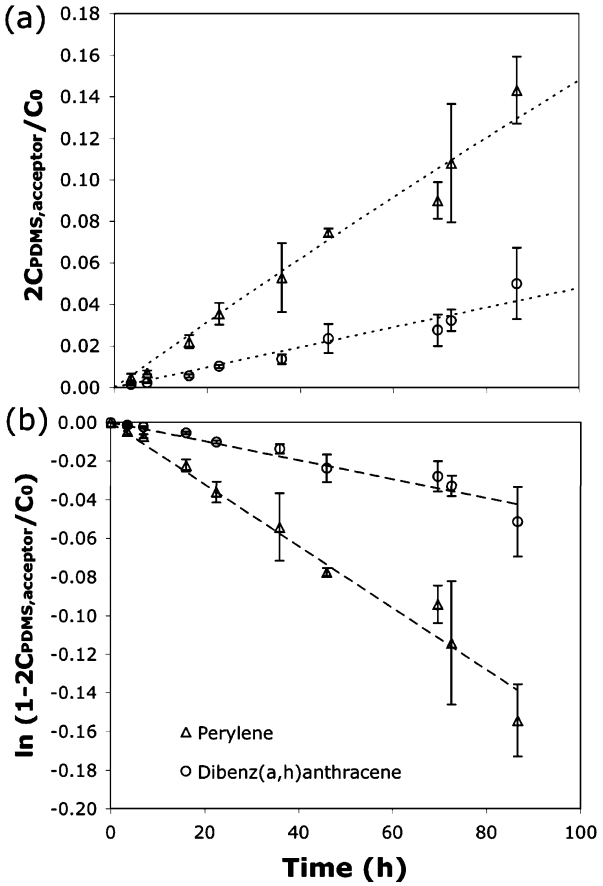

Figure 3. Permeation kinetics of perylene and dibenz[*a*,*h*]anthracene as examples using (a) normal scale and (b) linearized scale. Error bars denote standard deviation ($n = 3$) at each time, and dashed lines denotes best fit using eqs 11 and 13.

3. As mentioned previously, this method could not be applied for more hydrophobic chemicals (from perylene) because the aqueous concentration from a small volume of water needs to be measured.

Figure 3 shows permeation kinetics from the donor PDMS disk to the acceptor PDMS disk in a normal scale and in a linearized scale (cf. Supporting Information, Figure S-3 for all analytes). Dashed lines describe predicted kinetics using eqs 11 and 13. Although the system is far from equilibrium as $2C_{PDMS,acceptor}/C_0$ is less than 0.1 for most chemicals (Figure 3), the concentration extracted from the acceptor PDMS disk can be much higher than typical analytical limits. For example, the $2C_{PDMS,acceptor}/C_0$ value after 3.5 h for dibenz[*a*,*h*]anthracene, having the highest K_{PDMSw} in this study, was only 0.0014. Nevertheless, C_0 in our experiment was ~20 mmol/m^3 in PDMS and $C_{PDMS,acceptor}$ is ~30 μmol/m$^3_{PDMS}$, which is above the detection limit using HPLC fluorescence detection of ~10 μmol/m$^3_{PDMS}$. In addition, it would be possible to increase the initial loading concentration by at least a factor of 10. Mayer et al.[11] loaded fluoranthene at 2 mol/m^3 in PDMS. These considerations promise that this method can be applied to measure K_{PDMSw} for even more hydrophobic chemicals within a few days.

A crucial assumption of the method is that the mass-transfer resistance in the aqueous solution (δ_w/D_w) is much higher than the mass-transfer resistance in PDMS ($\delta_{PDMS}/D_{PDMS}K_{PDMSw}$). This assumption is certainly fulfilled for highly hydrophobic chemicals, whereas the assumption limits the applicability domain of the method with regard to more polar chemicals. Rusina et al.[21] reported D_{PDMS} of 1.1×10^{-10}, 1.5×10^{-11}, and 7.2×10^{-12} m^2/s for naphthalene, fluoranthene, and benzo[*a*]pyrene, respectively. These values are lower than calculated D_w using eq 14 by a factor of 7.7−63. If we assume that D_{PDMS} is 1 order of magnitude lower than D_w, two resistances are equal when K_{PDMSw} is ~2000 in our experimental system. Thus, this method may overestimate K_{PDMSw} for chemicals with a log K_{PDMSw} less than 4.0. This may explain the slightly higher log K_{PDMSw} values obtained using the ABL permeation method for trichlorinated benzenes compared to those obtained by the shaking method (Table 1). However, one can adjust stirring intensity and increase δ_w to overcome this limitation. Even if δ_w is increased by a factor of 10, the experiment can be done in 1 day because the mass-transfer rate is still fast enough for those chemicals.

Table 1 summarizes log K_{ow} values, calculated aqueous diffusion coefficients (D_w), and log K_{PDMSw} values measured in this study with experimental values reported in the literature. Values in parentheses are 95% confidence intervals obtained by linear regression and nonlinear regression for the conventional shaking method and the partition controlled delivery system, respectively. For the ABL permeation method, values analogous to 95% confidence intervals were calculated using an error propagation

Table 1. Summary of K_{PDMSw} Values of the Selected Chemicals Measured Using Three Different Methods with Values Reported in the Literature

chemicals	CAS regist no.	log K_{ow}[b]	D_w[c] ($\times 10^{-10}$ m^2/s)	log K_{PDMSw} shaking method	partition controlled delivery method	ABL permeation method[d]	lit.
terbutryn	886-50-0	3.74[e]		2.66 (2.57, 2.73)			2.80[9]
diuron	330-54-1	2.68[e]		1.10 (1.06, 1.14)			
carbofuran	1563-66-2	2.32		0.77 (0.72, 0.82)			
carbaryl	63-25-2	2.36		1.09 (1.06, 1.13)			
aldicarb	116-06-3	1.13		0.35 (0.28, 0.41)			
aniline	62-53-3	0.90		0.01 (−0.03, 0.05)			
2-chloroaniline	95-51-2	1.90		1.04 (1.02, 1.06)			
3-chloroaniline	108-42-9	1.88		0.83 (0.82, 0.84)			
3,4-dimethylaniline	95-64-7	1.86		1.07 (1.05, 1.09)			
2,4-dichloroaniline	554-00-7	2.78		1.69 (1.67, 1.71)			
3,4-dichloroaniline	95-76-1	2.68		1.39 (1.37, 1.40)			
2,3,5,6-tetrachloroaniline	3481-20-7	4.10		3.25 (3.24, 3.26)			
phenol	108-95-2	1.50		−0.53 (−0.56, −0.51)			
2-chlorophenol	95-57-8	2.15		0.56 (0.53, 0.58)			
4,6-dinitro-*o*-toluene	534-52-1	2.22		1.23 (1.21, 1.24)			
2,4,6-trichlorophenol	88-06-2	3.69		1.73 (1.70, 1.75)			
pentachlorophenol	87-86-5	5.18		2.65 (2.64, 2.65)			
1,2-dichlorobenzene	95-50-1	3.38		2.92 (2.90, 2.94)	2.81 (2.77, 2.85)		
1,4-dichlorobenzene	106-46-7	3.45		2.91 (2.88, 2.94)	2.95 (2.91, 2.99)		
1,2,3-trichlorobenzene	87-61-6	4.05	6.7	3.33 (3.30, 3.36)	3.42 (3.39, 3.45)	3.46 (3.36, 3.54)	
1,2,4-trichlorobenzene	120-82-1	4.02	6.7	3.33 (3.29, 3.37)	3.46 (3.43, 3.49)	3.51 (3.41, 3.59)	
1,3,5-trichlorobenzene	108-70-3	4.15	6.7	3.36 (3.31, 3.40)	3.61 (3.58, 3.64)	3.67 (3.57, 3.75)	
2,4,5-trichlorotoluene	6639-30-1	4.56[e]	6.4		4.12 (4.08, 4.15)	4.21 (4.12, 4.30)	
1,2,3,5-tetrachlorobenzene	634-90-2	4.63	5.9		4.24 (4.18, 4.29)	4.12 (4.02, 4.30)	
1,2,4,5-tetrachlorobenzene	95-94-3	4.63	5.9		4.14 (4.11, 4.17)	4.03 (3.93, 4.11)	
pentachlorobenzene	608-93-5	5.17	5.3		4.69 (4.64, 4.73)	4.56 (4.46, 4.64)	3.92−4.27[4,15]
hexachlorobenzene	118-74-1	5.31	4.9		5.12 (5.07, 5.16)	4.91 (4.82, 5.00)	4.33−4.75[4,15]
naphthalene	91-20-3	3.35		2.75 (2.73, 2.77)	2.85 (2.83, 2.87)		2.73−3.26[1−3,8]
acenaphthene	83-32-9	3.92		3.46 (3.45, 3.47)	3.46 (3.44, 3.48)		3.63[3]
phenanthrene	85-01-8	4.52	6.8		3.74 (3.71, 3.76)	3.87 (3.77, 3.96)	3.25−4.14[3,4,8,10,12,15]
anthracene	120-12-7	4.50	6.8		3.93 (3.88, 3.98)	3.98 (3.88, 4.06)	3.20−4.29[1−4,8,10]
fluoranthene	206-44-0	5.20	6.2		4.21 (4.17, 4.25)	4.32 (4.21, 4.41)	3.72−4.71[2−4,8,10,12,15]
pyrene	129-00-0	5.00	6.2		4.27 (4.24, 4.29)	4.36 (4.26, 4.45)	3.80−4.86[2−4,8,10,12]
chrysene	218-01-9	5.86	5.7		4.81 (4.76, 4.86)	4.74 (4.63, 4.83)	3.97−5.69[3,8]
benz[*a*]anthracene	56-55-3	5.91	5.7		4.90 (4.84, 4.95)	4.85 (4.75, 4.93)	3.83−5.26[1,3,8,12]
perylene	198-55-0	6.25	5.3			4.98 (4.88, 5.07)	
benzo[*a*]pyrene	50-32-8	6.35	5.3		5.36 (5.26, 5.44)	5.09 (4.98, 5.18)	4.14−5.47[1−4,10]
dibenz[*a*,*c*]anthracene	215−58-7	6.17	5.0			5.41 (5.30, 5.50)	
dibenz[*a*,*h*]anthracene	53-70-3	6.75	5.0			5.47 (5.35, 5.56)	4.86[3]
benzo[*ghi*]perylene	191-24-2	6.90	5.0			5.36 (5.23, 5.46)	4.28[3], 5.39[12]

[a] Values in parentheses are the lower and the upper 95% confidence limits of regression. [b]Values of log K_{ow} are recommended values in LOGKOW database.[28] [c] Calculated using eq 14. [b] Confidence limits for ABL permeation method were calculated using error propagation. [e]Recommended experimental values in KOWWIN Ver. 1.67 program.[29]

analysis assuming that the lower and the upper limits of ABL thickness are 10 and 15 μm, within 20% of the mean value (12.5 μm). Uncertainty associated with the determination of diffusion coefficient is not very significant among different estimation equations.[27] Thus, this range of ABL thickness may incorporate uncertainties associated with diffusion coefficients. This uncertainty term dominated the overall confidence interval because experimental k_d values had narrow confidence intervals. The partition coefficients obtained in this study did not depend on the method of determination. The difference between one method and the other typically do not exceed 0.1 log unit. The values obtained in this study fall in the range of partition coefficients obtained in the literature (Table 1) although literature values vary sometimes by more than 1 order of magnitude. The results in this study are correlated consistently with most literature[1,2,10,12,15] whereas a weak consistency is found with some references[3,4,8] (cf., Supporting information Figure S-4). Scrutinizing literature values revealed that the experimental K_{PDMSw} values obtained in this study correlate better with literature values obtained using a thinner PDMS coating[8] and deviate less when log K_{PDMSw} is lower than 5.0.[3] Improper volume ratio of V_w to V_{PDMS}, insufficient equilibrium time, or incomplete mass balance due to adsorption to surfaces might be the major reasons for disagreement as discussed earlier.[2]

Figure 4 shows a correlation between log K_{ow} and log K_{PDMSw}. When multiple K_{PDMSw} values were available, a selection priority was in the order of the shaking method, the ABL permeation method, and partition controlled delivery system. Although each value may deviate from the regression line up to 1 order of magnitude, two partition coefficients linearly correlate well over 6 orders of magnitude ($r^2 = 0.92$). The slope of regression is close to unity and the intercept was ~ -1. Experimental log K_{PDMSw} values increase with increasing log K_{ow} up to the compounds investigated in this study (log $K_{PDMSw} = 5.5$, log $K_{ow} = 6.9$).

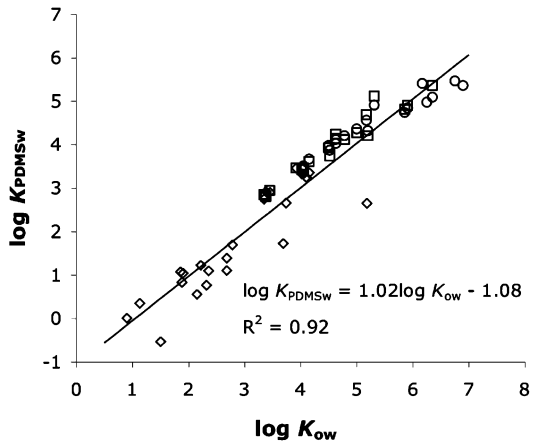

Figure 4. Relationship between log K_{PDMSw} and log K_{ow}. Open diamonds, open squares, and open circles represent K_{PDMSw} values obtained using the shaking method, the partition controlled delivery system, and the ABL permeation method, respectively.

CONCLUSION

Partition coefficients between PDMS and water (K_{PDMSw}) were measured for very hydrophobic chemicals using a simple ABL permeation reactor. These values are in good agreement with those obtained using the shaking method and the partition controlled delivery system. Time required to measure robust K_{PDMSw} values using the ABL permeation method is less than a few days for highly hydrophobic chemicals. Experimental log K_{PDMSw} values correlate well with literature log K_{ow} values over 6 orders of magnitude. The ABL permeation method used in this study can be extended to determine K_{PDMSw} values of superhydrophobic chemicals to evaluate the bioavailability and to determine compound properties for the application of SPME and other polymer-based sampling techniques. In addition, using PDMS as the passive dosing/sampling phase, one can establish dynamic exposure conditions, more relevant to "real" environmental conditions, for in vitro exposure/toxicity assays.

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SUPPORTING INFORMATION AVAILABLE

Derivations of the analytical solutions for eqs 1 and 2 and eqs 7−9, example time extraction profiles for the shaking method, kinetic data for the determination of individual K_{PDMSw} using the partition controlled delivery system and the ABL permeation method, and comparisons of the experimental K_{PDMSw} values to the literature values. This material is available free of charge via the Internet at http://pubs.acs.org.

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