Measurement of Low Air−Water Partition Coefficients of Organic Acids by Evaporation from a Water Surface

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A novel system is described for the determination of the air−water partition coefficient (K_{AW}) for substances that have low air−water partition coefficients, i.e., $K_{AW} < 10^{-3}$, and may aggregate in solution, ionize, and display surface activity. The compound is evaporated isothermally from solution through an undisturbed air−water interface at a known gas flow rate, and its concentrations in the water and gas phases are measured. Although equilibrium is not achieved, the extent of departure from equilibrium can be determined using estimated mass transfer coefficients. K_{AW} was determined for formic, acetic, benzoic, and perfluorooctanoic acids (PFOA), and assuming an approximately 50 % approach to equilibrium, which is in accord with theoretical prediction. Agreement with available literature data was satisfactory. The experimentally determined K_{AW} of PFOA was $1.02 \cdot 10^{-3}$ with a standard deviation of 9.1 % ($n = 9$). The method is suitable for fluorinated surfactants, aggregating and ionizing substances for which K_{AW} may not be readily measured with existing techniques.

Introduction

The air−water partition coefficient K_{AW} or Henry's law constant is an important determinant of a chemical's environmental behavior and fate. These coefficients are measured experimentally by a variety of techniques including direct measurement of the concentrations of both phases. Improved accuracy is generally obtained if the concentration measurements are made in only one phase and a mass balance is applied to calculate the concentration in the other. This can be accomplished by the gas stripping method[1] in which the concentration in the water phase is followed in time as the solute is stripped under equilibrium conditions from solution by a known flow rate of air. It is also possible to measure the solute concentrations in the exit air. In the EPICS method (equilibrium partitioning in closed systems),[2,3] the vapor-phase concentrations are measured at various air−water volumetric ratios. The wetted-wall method developed by Fendinger and Glotfelty[4] has also been used for pesticides by flowing air over a wetted surface. In the absence of a direct measurement, K_{AW} is often estimated from solubility and vapor pressure. This can be problematic for substances that may associate, dissociate, or aggregate in solution or have very low vapor pressures. For example, there are few reports of K_{AW} data for fluorinated compounds that are of environmental concern.[5]

Experimental difficulties are encountered when the air−water partition coefficient is very low and especially if the solute is polar or surface active. The low equilibrium concentration in the air can be difficult to measure accurately. The gas stripping method can require very long stripping times to achieve a significant change in the concentration in the water phase. If the air-phase concentration is measured, it is essential that there be no aerosol particles of water present. For example, if K_{AW} is 10^{-6}, then water particles present at a low volumetric concentration of 1 part in 10^6 will double the total concentration in air. This issue is particularly problematic if the solute is surface active and the air−water interface is turbulent as occurs during gas stripping. These and related issues have been discussed by Goss et al.[6] and Baker et al.[7]

We suggest here a novel method of determining K_{AW} in which the air−water interface is quiescent, eliminating the potential for aerosol formation. The proposed method utilizes a low velocity jet of gas which impinges on a horizontal water surface, and an experimental value of K_{AW} is determined from the concentration in the air after contact with the water. The obvious difficulty in this approach is that equilibrium is not achieved under these conditions, but it is possible to account for the degree of nonequilibrium and to obtain an estimate of the partition coefficient that may be sufficiently accurate for environmental assessment purposes. The method is thus suitable for substances that are surface active or ionize or are susceptible to aerosol formation. The method can also be used to assess environmental water samples for their potential to emit chemicals by evaporation. In this study, we illustrate the method by applying it to formic acid, acetic acid, benzoic acid, and a fluorinated carboxylic acid.

Air−Water Partitioning Apparatus. The apparatus shown in Figure 1 consists of a polypropylene vessel of an inside diameter of 7.23 cm containing 100 mL of an aqueous solution of the solute at a concentration of less than 4 % of saturation. Aqueous solutions of the acids being tested were acidified with 10 % H_2SO_4 to a pH of 0.6 to suppress dissociation and thus ensure that the acids were fully protonated. Nonvolatile sulfuric acid has no significant vapor pressure over the aqueous solution. Regulated nitrogen gas from a compressed cylinder was saturated with water vapor using a gas washing bottle filled with Milli-Q water. The gas stream then flowed down a tube with an internal diameter of 4 mm at a flow rate of 66.65 $mL \cdot min^{-1}$ to form a low velocity jet. A glass flow meter (Gilmont Instruments, Inc., GF-1160) at the entrance of the saturation bottle was used to maintain a constant nitrogen flow through the system. The tube was 5.4 cm above the water surface. The temperature was controlled by constant temperature water baths to 20 ± 1 °C. The nitrogen gas exiting the system

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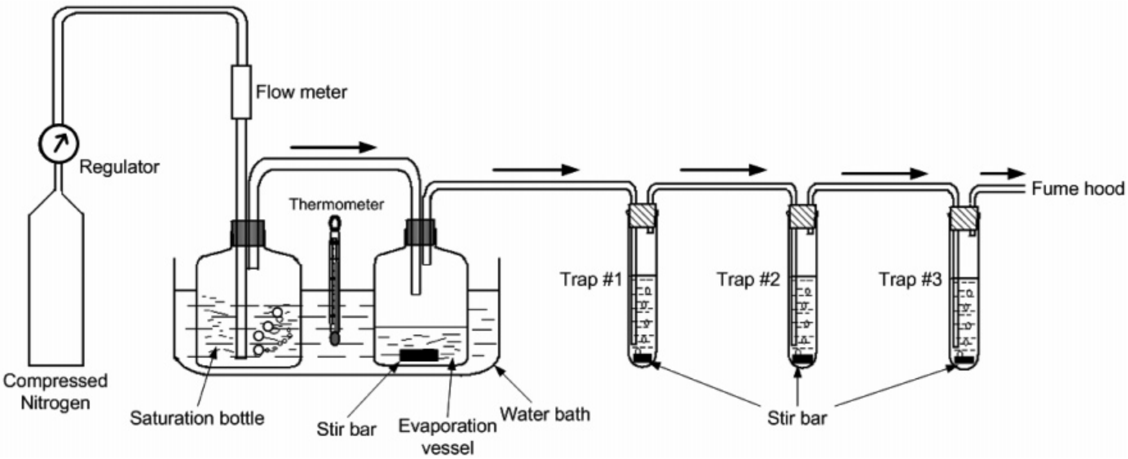

Figure 1. Experimental design for the determination of Henry's law constants by evaporation from a water surface.

passed through a series of three liquid traps to capture the solute for later determination of the quantity of solute evaporated. The contents of the evaporation vessel and each trap were gently mixed with a magnetic stirrer. From the total volume of air passed over the water surface and the mass trapped, the concentration in the gas phase, C_A, is calculated. K_{AW} is then calculated from this concentration, the known concentration in the water phase, C_w, and an estimated efficiency of approach to equilibrium, E. C_w remains essentially constant if K_{AW} is low, but a correction can be applied for the decrease in C_w if necessary. K_{AW} is then calculated as $C_A/(C_wE)$.

To initiate an experimental measurement, the test chemical was thoroughly mixed with water and allowed to thermally equilibrate in the water bath for 2 h. To avoid errors resulting from adsorption of PFOA on the vessel walls, a conditioning period was used in which the N_2 gas was allowed to flow through the vessel into the atmosphere without connecting the receiver traps with the apparatus. After this conditioning period, each receiver trap was filled with 40 mL of 0.05 M KOH (in the case of the reference acids, KCl solutions were used) and connected to the system. Two additional traps were placed in series with the first trap to determine possible solute breakthrough during the experiments. The average amount found in these backup traps was less than 1 % of the amount in the first trap, indicating that breakthrough was insignificant. Hourly samples of 400 μL were taken from each trap. The aqueous concentration in the evaporation vessel was determined at the beginning and the end of the experiment. Over this time period, the loss of solute acid from the water was insignificant.

Calibration. The principal challenge with this experimental method is to determine the equilibrium efficiency E. In the following discussion, we suggest three approaches. It is, however, first necessary to clarify how the mass transfer resistance to evaporation is distributed between the gas and liquid phases.

Generally, liquid-phase mass transfer coefficients k_L are about 100 times smaller than corresponding gas-phase coefficients k_G for similar geometries. Applying the two-phase resistance model for evaporation,[8] the overall gas-phase mass transfer coefficient k will be given by

$$\frac{1}{k} = \frac{1}{k_G} + \frac{K_{AW}}{k_L} \sim \frac{1}{k_G}(1 + 100K_{AW})$$

The liquid-phase resistance is thus negligible provided that 100 $K_{AW} < 1$. If K_{AW} is 10^{-4} or less, the liquid-phase resistance provides less than 1 % of the total resistance to mass transfer and evaporation is entirely controlled by gas-phase resistance due to the relatively low concentration in the gas phase. If it is assumed that the gas over the water surface is well mixed with a solute concentration C_A, then the solute flux from the water can be equated to the flux in the gas leaving the surface, namely, flux $= kA(C_wK_{AW} - C_A) = GC_A$, where G is the gas flow rate. Rearranging gives

$$\frac{C_A}{C_w} = K_{AW}\left[\frac{1}{1 + G/kA}\right]$$

It follows that the efficiency of saturation of the gas E is $1/(1 + G/kA)$. Clearly, a low gas flow rate G and a high mass transfer coefficient area group favor an approach to equilibrium. In the current experimental apparatus, G is approximately 1.0 $cm^3 \cdot s^{-1}$ and A is approximately 40 cm^2. If k is, for example, 0.025 $cm \cdot s^{-1}$, then the group G/kA is 1.0 and E is expected to be approximately 50 %. Given the uncertainties in k, an accurate value of E cannot be deduced from theory, but if, for example, k ranges from the above value by a factor of 2, i.e. (0.0125 to 0.05) $cm \cdot s^{-1}$, then E will range from 33 % to 67 %.

The first method of determining appropriate values of k and E is to calibrate with a solute of known K_{AW}, preferably similar in K_{AW} and molecular mass to the solute being studied. The results of calibrations using formic, acetic, and benzoic acids are discussed later.

A second way to determine k and E values is to directly measure the gas-phase mass transfer coefficient by flowing a gas over a liquid of known vapor pressure and determining the evaporation rate gravimetrically. The flux is $kA(C_S - C_A)$, where C_S is the saturated gas-phase concentration at the interface, and is P^s/RT, where P^s is the vapor pressure. C_A, the gas concentration at the exit, can be determined from the gas flow rate and the measured evaporation rate. Thus, kA can be determined from the measured flux, C_S and C_A.

A third method to estimate k and E is to develop a correlation of k as a function of the specific geometry and chemical diffusivity. The fluid mechanical regime in this case is a radial wall jet as studied by Scholtz and Trass.[9] These authors developed correlations for the mass transfer coefficient in the fluid phase for laminar flow conditions in which the fluid jet impinges vertically on a solid surface. Because the surface in the present system is a liquid and is deformable, an identical solution is not expected. However, the original correlation remains valuable by indicating the potential dependence of k on solute diffusivity and by providing insights into the likely range of mass transfer coefficients. The Scholtz−Trass correlation (their eq 43)[9] can be rearranged and simplified to the dimensionless form

$$\mathrm{Sh} = 0.1590\mathrm{Re}^{0.75}\mathrm{Sc}^{0.67}$$

Here, Sh is the Sherwood number (kL/D); Re is the jet Reynolds number ($\rho v d/\mu$); and Sc is the Schmidt number ($\mu/\rho D$). Using CGS units, k is the mass transfer coefficient ($\mathrm{cm \cdot s^{-1}}$); L is a length parameter (cm); D is diffusivity ($\mathrm{cm^2 \cdot s^{-1}}$); ρ is the fluid density ($\mathrm{g \cdot cm^{-3}}$); v is the jet velocity ($\mathrm{cm \cdot s^{-1}}$); d is the jet diameter (cm); and μ is the fluid viscosity ($\mathrm{g \cdot cm^{-1} \cdot s^{-1}}$ or Poise).

In the present experimental system, ρ is $1.16 \cdot 10^{-3}$ $\mathrm{g \cdot cm^{-3}}$ (the density of nitrogen at STP); v is 8.83 $\mathrm{cm \cdot s^{-1}}$; d is 0.4 cm; and μ is $1.8 \cdot 10^{-4}$ $\mathrm{g \cdot cm^{-1} \cdot s^{-1}}$. Thus, Re is 22.8, and laminar flow conditions prevail. The length parameter L and hence k depend on radial distance x from the central stagnation point and the jet diameter d as follows

$$L = (x^5/d)^{1/4}$$

This implies that L equals 1 when x equals d. L increases as x increases toward the wall. The result is that for a constant Sherwood number k decreases as expected at greater radial distances because of the decrease in velocity over the surface as the jet spreads. A complication arises in this case because the jet is constrained by the walls of the vessel, thus exact prediction is not expected. At a radial distance of 2 cm from the center, L is $(2^5/0.4)^{1/4}$ or 3.0 cm. At a radial distance of 3 cm, L is 5.0 cm. Thus, for a constant Sherwood number, k is expected to fall by a factor of 1.7 over these radial distances.

If a typical value of 0.1 $\mathrm{cm^2 \cdot s^{-1}}$ is assumed for D, Sc = 1.6. Using Sc = 1.6 and Re = 23, an order of magnitude estimate of the Sherwood number is then Sh = 2.3. For an L value of 5 cm, k is thus 0.046 $\mathrm{cm \cdot s^{-1}}$. The resulting value of G/kA is 0.54, and E is then 65 %. In this correlation, as asserted above, the mass transfer coefficient is that in the gas phase.

For both methods of estimating k, a diffusivity correction should be applied to k when correcting for each evaporated solute. The Sherwood and Schmidt numbers both contain the gas-phase diffusivity D, and thus the mass transfer coefficient k is proportional to $D^{0.33}$. Reid et al.[10] reviewed methods of estimating D, but in this case, all that is required is a correction factor for D as a function of molar mass of the nitrogen and the solute. Reid et al.[10] suggest that D is proportional to $M_{AB}{}^{-0.5}$, where M_{AB} is determined from the molar masses of the gas M_A and solute M_B; namely

$$M_{AB} = 2(1/M_A + 1/M_B)^{-1}$$

In this case, M_A for nitrogen is 28 $\mathrm{g \cdot mol^{-1}}$, and M_B is 46 $\mathrm{g \cdot mol^{-1}}$ for formic acid, 60 $\mathrm{g \cdot mol^{-1}}$ for acetic acid, and 414 $\mathrm{g \cdot mol^{-1}}$ for PFOA. The M_{AB} values are thus 38.2 for acetic acid, 34.8 for formic acid, and 52.5 for PFOA. Because k is proportional to $D^{0.33}$ and D is proportional to $M_{AB}{}^{-0.5}$, k is proportional to $M_{AB}{}^{-0.165}$ and G/kA is then proportional to $M_{AB}{}^{0.16}$. This correction factor is small but can be significant for large molar mass solutes.

To test the feasibility of the method and to determine E, the system was calibrated with two solutes of known K_{AW}, acetic acid and formic acid, whose Henry's law constants had been previously determined using different experimental techniques.[11]

Using the same experimental conditions, the concentrations in the aqueous phase and air phase of the acids were measured. From these concentrations, E and then k can be calculated using the reported K_{AW}. Using the same experimental conditions, the K_{AW} of PFOA can be calculated from the measured PFOA concentrations in water and air after correction for diffusivity differences. This was also applied to a fourth acid, benzoic acid, with an established K_{AW}.

Experimental

Standards and Reagents. Perfluorooctanoic acid (PFOA) (96 %), ammonium acetate (Sigma Ultra, > 98 %), acetic acid (> 99.7 %), benzoic acid (> 99 %), potassium chloride (> 99 %), and potassium hydroxide (> 85 %) were obtained from Sigma-Aldrich (Oakville, ON, Canada). Formic acid (88 %) and HPLC-grade methanol and acetonitrile were purchased from Fisher Scientific (Ottawa, ON). PFOA was used as received without further purification. All other reagents and solvents were used as received. Milli-Q water was used in all experiments.

Direct pH measurement was used to analyze acetic and formic acid.[11] 1.5 % acetic acid (pK_a = 4.756) or formic acid (pK_a = 3.745)[12] was acidified to pH 1.84 with dilute sulfuric acid (10 %) prior to the experiment to ensure that the organic acids were fully protonated. The Millipore water and nitrogen carrier gas were shown to be free of formic and acetic acid contamination. The gas passed through 10 mL of 1.0 $\mathrm{mol \cdot L^{-1}}$ unbuffered KCl solution, and the resulting pH change of the solution was recorded as a function of gas volume. The amount of acid present in the gas stream was then calculated using the results of separate calibration experiments which relate change in pH caused by the direct addition of each acid to the acid concentration in the aqueous KCl. The pH in the second and third KCl traps did not change, thus the gas-phase acids are believed to be totally absorbed by the KCl solution. The experiment lasted for 2 h. The decrease in the concentration of the acid in the test solution over the course of the experiment was negligible.

An AB15 Plus digital pH meter having an Accumet glass electrode and an automatic temperature compensation probe (Fisher Scientific) was used to record the pH of the KCl solution every hour during the experimental runs. Buffer solutions of pH 7 and pH 4 were used for electrode calibration prior to the experiments. The pH change over the course of a partial pressure measurement was about 0.3 units.

Preparation of a Standard Solution and Test Solutions. A standard stock solution of PFOA (1 $\mathrm{mg \cdot mL^{-1}}$) was prepared by dissolving solid standards in methanol. Six working standard solutions ranging from (2 to 500) $\mathrm{pg \cdot \mu L^{-1}}$ were prepared by serial dilution in methanol to final concentrations. All stock solutions and standards were stored in polypropylene bottles or vials. Samples were stored at 4 °C prior to analysis.

The aqueous solutions of acids were prepared by adding the required amount of acid into Millipore water and filtered using a 0.45 μm nylon filter. Laboratory grade acids purchased from Sigma-Aldrich and Fisher Scientific were used without any further treatment.

LC-MS/MS Analysis. The identification and quantification of the single substances were carried out using external standards. The concentrations of PFOA or benzoic acid in the vessel and trap solutions were analyzed by LC-MS/MS. The LC measurements were performed using a Waters 2695 LC instrument (Waters, MA), at room temperature using a Genesis lightning C8 column (50 × 2.1 mm, 4 μm, Chromatographic Specialties) and a C18 guard column (4.0 × 2.0 mm, Phenomenex, Torrance, CA). For PFOA, isocratic elution was used. The mobile phase consisted of 50 % acetonitrile and water (10 mM ammonium acetate) for PFOA and 75 % acetonitrile and water (10 mM ammonium acetate) for benzoic acid. The flow

Table 1. Reported Measured K_{AW} Literature Values for Formic and Acetic Acids[14]

reported K_{AW}, (20 to 25) °C	
formic acid	acetic acid
6.858·E−06	1.222·E−05
3.066·E−06 to 7.181·E−06	1.230·E−05
1.134·E−05	4.075·E−06
7.262·E−06	4.397·E−06 to 6.374·E−06
7.383·E−06	7.342·E−06
3.715·E−06 to 4.760·E−06	5.850·E−06 to 9.884·E−06

rate was 0.2 mL·min^{-1} without split before entering the source. The injection volume was set to 10 μL.

Mass spectrometric measurements were performed using a Micromass Quattro Triple Quadrupole Mass Spectrometer (Micromass; Manchester, UK) equipped with an electrospray ion source operated in negative ionization mode. A standard with a concentration of 1.0 ng·μL^{-1} in methanol was infused through a syringe pump (Harvard Apparatus) at a flow rate of 10 μL·min^{-1} for position of the ion sprayer and tuning of the mass spectrometer. The MS conditions were similar to the previously reported method[13] with minor modifications.

Before LC-MS/MS analysis, trap solutions were acidified with 2 M HCl to pH = 3∼4, and aqueous solutions from the evaporation vessel were adjusted with 0.05 M KOH to pH 3∼4.

Results

E and k Values Determined by Measuring the Air−Water Partition of Acetic and Formic Acids. The K_{AW} of acetic acid is reported[11] to be 7.41·10^{-6} (other literature values for formic and acetic acids are presented in Table 1). After 2 h, the concentration ratio in the air and liquid phases (C_A/C_W) of acetic acid is 3.64·10^{-6}; therefore E is estimated to be 49 %, and G/kA is 1.04. Using the same procedure for formic acid, the concentration ratio in air and water, C_A/C_W, was 4.86·10^{-6}. The reported[11] K_{AW} of formic acid is 7.37·10^{-6}; therefore E is 66 %, and G/kA is 0.515. A complete listing of the reported K_{AW} values for formic and acetic acids is presented in Table 1. Overall, the E values for acetic (49 %) and formic (66 %) acid are comparable to the 65 % predicted using the Scholtz−Trass correlation.

The diffusivity correction suggests that G/kA for formic acid should be lower than that of acetic acid by a factor of $(38.2/34.8)^{0.16}$ or 1.015. Experimentally, this factor is approximately 2.0, thus the diffusivity correction is small and cannot account for the difference in E. Until further values of E are available, it is suggested that a simple expedient is to assume that G/kA averages 0.78 and E is 56 % with an error limit of ± 10 %. This value is applied later to benzoic acid and PFOA.

Method Validation. The Determination of the K_{AW} Value of Benzoic Acid. To validate this method, a reference compound of higher molecular weight than formic or acetic acid and with a previously published K_{AW} was employed. Benzoic acid was chosen as this reference compound. From the ratios of the concentrations of benzoic acid in the gas phase, C_G, to the concentrations in the liquid phase, C_w, and E, the dimensionless partition coefficients $K_{AW} = C_G/(EC_w)$ are calculated. Using an E value of 56 %, the mean K_{AW} value of three experimental runs is 1.39·10^{-6} ± 6.95·10^{-8}. The single reported literature value[11] for benzoic acid is 2.86·10^{-6}. Given the limited reported values for the K_{AW} of benzoic acid and that well-established reported K_{AW} values for other compounds often differ similarly, if not in greater amounts, the experimental value obtained here is reasonable.

Determination of the K_{AW} Value of PFOA. From the ratios of the concentrations of PFOA in the gas phase, C_G, to the concentrations in the liquid phase, C_w, and E, the dimensionless partition coefficients $K_{AW} = C_G/(EC_w)$ are calculated. The concentration of PFOA in the liquid phase (C_w) was ∼ 700 ng·mL^{-1}. The concentration in the gas phase ranged from (0.30 to 0.55) ng·mL^{-1}. Using an E value of 56 %, the mean K_{AW} value of nine experimental runs is 1.02·10^{-3} and ranges between 7.65·10^{-4} and 1.39·10^{-3}. The standard deviation is 9.1 % (n = 9). An acceptable level of precision corresponding to a standard deviation of less than 10 % in the air−water concentration ratios was achieved. As more data become available for the efficiency E, the accuracy of the method can be improved. It is also noted that the pH of 0.6 used to necessitate complete protonation of PFOA in solution may have an impact on the measured K_{AW}. Further work is being conducted at higher pHs where partial ionization occurs and allowance of this effect must be included. Initial results suggest that the ionic strength of the solution does not significantly alter the measured K_{AW}.

Conclusions

A technique has been devised, tested, and verified for the measurement of the air−water partition coefficient for PFOA. The method is particularly suitable for low solubility, low vapor pressure solutes, ionizing substances in which K_{AW} is pH dependent, and especially compounds that are active and thus susceptible to aerosol formation, such as long-chain fluorinated acids. For such compounds, the estimation of K_{AW} from solubility and vapor pressure is not feasible. The method is also suitable for determining the water−air transport characteristics of water samples from rivers, lakes, or environments in which there may be other substances in solution or suspension that may influence the substance's partial pressure or fugacity and hence the evaporation rate.

Note Added in Proof: Since acceptance of this paper, Shunthirasingham et al. have critically reviewed the possibility of bias in K_{AW} by the inert gas stripping method.[15]

Literature Cited

(1) Mackay, D.; Shiu, W. Y.; Sutherland, R. P. Determination of air−water Henry's law constants for hydrophobic pollutants. *Environ. Sci. Technol.* **1979**, *13*, 333−337.

(2) Lincoff, A. H.; Gossett, J. M. The determination of Henry's Law for volatile organics by equilibrium partitioning in close systems. In *Gas Transfer at Water Surfaces*; Brutsaert, W., Jirka, G. H., Eds.; D. Reidel Publishing Company: Dordrecht, 1984; pp 17−25.

(3) Gossett, J. M. Measurement of Henry's law constants for C1 and C2 chlorinated hydrocarbons. *Environ. Sci. Technol.* **1987**, *21*, 202−208.

(4) Fendinger, N. J.; Glotfelty, D. E. A laboratory method for the experimental determination of air/water Henry's law constants for several pesticides. *Environ. Sci. Technol.* **1988**, *22*, 1289−1293.

(5) Mackay, D.; Shiu, W. Y. A critical review of Henry's law constants for chemicals of environmental interest. *J. Phys. Chem. Ref. Data* **1981**, *10*, 1175−1199.

(6) Goss, K. U.; Wania, F.; Mclachlan, M. S.; Mackay, D.; Schwarzenbach, R. P. Comment on "Reevaluation of Air−Water Exchange Fluxes of PCBs in Green Bay and Southern Lake Michigan". *Environ. Sci. Technol.* **2004**, *38*, 1626−1628.

(7) Baker, J. E.; Totten, L. A.; Gigliotti, C. L.; Offenberg, J. H.; Eisenreich, S. J.; Bamford, H. A.; Huie, R. E.; Poster, D. L. Response to Comment on "Reevaluation of Air−Water Exchange Fluxes of PCBs in Green Bay and Southern Lake Michigan". *Environ. Sci. Technol.* **2004**, *38*, 1629−1632.

(8) Whitman, W. G. *Chem. Metal. Eng.* **1923**, *29*, 146−150.

(9) Scholtz, M. T.; Trass, O. Mass transfer in the laminar radial wall jet. *AIChE J.* **1963**, *9*, 548−554.

(10) Reid, R. C.; Prausnitz, J. M; Poling, B. E. *The Properties of Gases and Liquids,* 4th ed.; McGraw-Hill: New York, 1987.

(11) (a) Khan, I.; Brimblecombe, R.; Clegg, S. L. Solubilities of Pyruvic Acid and the Lower (C1−C6) Carboxylic Acids. Experimental Determination of Equilibrium Vapour Pressures Above Pure Aqueous and Salt Solutions. *J. Atmos. Chem*. **1995**, *22*, 285−302. (b) Howard, P. H. *Handbook of Fate and Exposure Data for Organic Chemicals. Vol. I. Large Production and Priority Pollutants*; Lewis Publishers: Chelsea, MI.

(12) Bacarella, A. L.; Grunwald, E.; Marshall, H. P.; Purlee, E. L. The potentiometric measurement of acid dissociation constants and pH in the system methanol−water. pKa values for carboxylic acids and anilinium ions. *J. Org. Chem*. **1955**, *20* (6), 747−762.

(13) Moody, C. A.; Kwan, W. C.; Martin, J. W.; Muir, D. C. G.; Mabury, S. A. Determination of Perfluorinated Surfactants in Surface Water Samples by Two Independent Analytical Techniques: Liquid Chromatography/Tandem Mass Spectrometry and 19F NMR. *Anal. Chem*. **2001**, *73*, 2200−2206.

(14) Mackay, D.; Shiu, W. Y.; Ma, K.-C.; Lee, S. C. *Handbook of Physical−Chemical Properties and Environmental Fate for Organic Chemicals*, 2nd ed; CRC Press: Boca Raton, 2005; Vol. III.

(15) Shunthirasingham, C.; Lei, Y. D.; Wania, F. Evidence of Bias in Air−Water Henry's Law Constants for Semivolatile Organic Compounds Measured by Inert Gas Stripping. *Environ. Sci. Technol.* **2007**, *41* (11), 3807−3814.

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