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Henry's Law Constants of Polychlorinated Biphenyl Congeners and Their Variation with Temperature

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The Henry's law constants for 26 polychlorinated biphenyl (PCB) congeners were measured using a gas-stripping apparatus at five environmentally relevant temperatures between (4 and 31) °C. The Henry's law constants ranged between (0.079 ± 0.003) Pa·m^3·mol^{-1} for 2,2′,3,3′,4,4′,5,6-octachlorobiphenyl (IUPAC congener #195) at 4 °C and (308 ± 29) Pa·m^3·mol^{-1} for 2,2′,3,3′,4,5′,6,6′-octachlorobiphenyl (IUPAC congener #201) at 31 °C. The temperature dependence of each PCB congener's Henry's law constant was modeled to calculate the enthalpy and entropy of the phase change between the gaseous and dissolved phases. For many PCB congeners, this study reports the first experimentally measured temperature variations of their Henry's law constants. The enthalpies of phase change (ΔH_H) ranged between (14.5 ± 3.4) kJ·mol^{-1} for 2,2′,4,6,6′-pentachlorobiphenyl (IUPAC congener #104) and (167 ± 13) kJ·mol^{-1} for 2,2′,3,3′,4,4′,5,6-octachlorobiphenyl (IUPAC congener #195). These data can be used to predict PCB congener Henry's law values within the experimental temperature range within a relative standard error of less than 10%.

Introduction

The Henry's law constant (K_H) plays a fundamental role in describing many important industrial, toxicological, and environmental processes which transport chemicals between gaseous and aqueous phases.[1,2] From an environmental standpoint, the K_H is a key parameter used to model the diffusive exchange of semivolatile chemicals such as polychlorinated biphenyls (PCBs) between surface waters and the atmosphere.[3−10] Accurate knowledge of a chemical's K_H and how it changes with environmental conditions, including temperature and ionic strength, is essential to predict the environmental behavior, transport, and fate of many classes of organic chemicals.

The K_H is required to model the chemical transfer between air and water.[11−13] These models are used to predict chemical behavior under various environmental conditions, including a wide range of temperatures. However, the lack of accurate K_H measurements and information regarding how they vary with temperature is a major limitation in predicting the environmental distribution and transport of chemicals such as PCBs.[14−16] For various PCB congeners, Burkhard et al.[17] predicted an order of magnitude increase in K_H with a 25 °C increase in temperature. Mackay and Shiu[18] estimated that the K_H of organic compounds will approximately double between 10 °C and 65 °C. Staudinger and Roberts[16] estimated that the PCB K_H will increase by 220% as temperature rises from 12 °C to 25 °C. From these earlier studies, the temperature dependence of K_H for PCBs can be estimated. However, the variation in K_H with temperature for individual congeners has not been systematically studied. The effect of temperature may be compounded within a specific class of compounds. For example, the temperature dependence of K_H for polycyclic aromatic hydrocarbons (PAHs) varied as much as 65% between different PAH compounds.[19] A quantitative understanding of the temperature dependence of K_H for individual compounds is required to accurately model air−water exchange. Furthermore, a consistent data set of experimentally measured values for a wide range of congeners determined using a single method is needed in order to accurately assess the variability of K_H among PCB congeners.

The objective of this study is to use a modified gas-stripping technique[19,20] to measure K_H for a wide range of PCBs at various environmental temperatures. The 26 PCB congeners ranged between 2-monochlorobiphenyl (IUPAC congener #1) and 2,2′,3,3′,4,5′,6,6′-octachlorobiphenyl (IUPAC congener #201; Table 1). The Henry's law constants were measured at (4, 11, 18, 25, and 31) °C, and both the enthalpy and entropy of phase change were calculated using the Gibbs−Helmholtz equation (Table 2). From these data, the temperature dependence was modeled for each individual congener.

Background

A thorough discussion of the theoretical background of K_H and its temperature dependence is presented elsewhere[19] and is summarized here. The Henry's law constant is often expressed either with dimensions of (pressure·volume)/mass

$$K_H = p_g/C_w \tag{1}$$

where p_g is the gas-phase partial pressure and C_w is the dissolved concentration in units of mass of chemical per volume of water, or as the dimensionless Henry's law constant (K_H')

$$K_H' = C_g/C_w \tag{2}$$

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Table 1. Henry's Law Constants (K_H) at Different Temperatures in the Range between (4 and 31) °C[a,b] (K_H/Pa·m^3·mol^{-1})

congener[c]	4 °C	11 °C	18 °C	25 °C	31 °C	lit. 25 °C
1	5.13 ± 0.15	8.32 ± 0.18	13.17 ± 0.25	20.43 ± 0.52	29.3 ± 1.1	28.9,[d] 30.2[e]
8	6.010 ± 0.086	9.87 ± 0.10	15.85 ± 0.14	24.89 ± 0.29	36.07 ± 0.60	20.3,[f] 24.9,[d] 30.7[e]
18	8.11 ± 0.14	12.07 ± 0.15	17.64 ± 0.18	25.35 ± 0.34	34.14 ± 0.65	58.1,[d] 25.3,[h] 38.5,[g] 32.0[e]
28	13.13 ± 0.15	19.06 ± 0.15	27.18 ± 0.19	38.14 ± 0.37	50.39 ± 0.71	22.8,[d] 32.0,[g] 29.0,[e] 20.3[h]
29	12.12 ± 0.19	18.04 ± 0.21	26.37 ± 0.27	37.89 ± 0.53	51.03 ± 1.0	25.3,[d] 30.0,[e] 20.3[h]
44	11.86 ± 0.14	16.02 ± 0.13	21.33 ± 0.15	28.05 ± 0.27	35.13 ± 0.48	24.3,[f] 32.8,[d] 23.3[e]
50	28.86 ± 0.72	38.18 ± 0.67	49.84 ± 0.78	64.3 ± 1.4	79.3 ± 2.4	138,[d] 61.8[e]
52	11.34 ± 0.19	16.13 ± 0.19	22.56 ± 0.23	31.07 ± 0.42	40.43 ± 0.77	22.3,[f] 53.2,[d] 34.7,[g] 32.3[e]
66	14.17 ± 0.22	19.80 ± 0.22	27.25 ± 0.26	36.97 ± 0.48	47.51 ± 0.87	84.2,[f] 13.7,[d] 20.5[e]
77	4.46 ± 0.14	6.99 ± 0.16	10.75 ± 0.21	16.20 ± 0.41	22.69 ± 0.81	4.37,[d] 9.52,[g] 10.4[e]
87	12.97 ± 0.29	18.83 ± 0.30	26.86 ± 0.37	37.71 ± 0.69	49.8 ± 1.3	33.4,[f] 19.9,[d] 18.6[e]
101	15.75 ± 0.31	22.20 ± 0.31	30.78 ± 0.34	42.07 ± 0.70	54.4 ± 1.3	32.7,[d] 25.4,[g] 24.9,[e] 9.1[h]
104	39.4 ± 1.0	47.17 ± 0.88	56.00 ± 0.88	66.0 ± 1.4	75.5 ± 2.1	185,[d] 90.9,[g] 75.1[e]
105	3.09 ± 0.12	7.10 ± 0.22	15.73 ± 0.44	33.6 ± 1.3	62.5 ± 3.9	10.1,[e] 5.68[d]
118	7.34 ± 0.23	12.81 ± 0.30	21.79 ± 0.44	36.2 ± 1.0	54.8 ± 2.3	40.5,[f] 12.7,[e] 9.35[d]
126	0.958 ± 0.038	2.82 ± 0.087	7.88 ± 0.22	21.02 ± 0.83	47.0 ± 3.0	8.29,[e] 2.78[d]
128	0.890 ± 0.031	3.224 ± 0.091	10.99 ± 0.30	35.4 ± 1.5	92.3 ± 6.6	50.7,[f] 6.85,[d] 1.3,[h] 3.04,[g] 10.5[e]
138	2.88 ± 0.11	7.50 ± 0.22	18.68 ± 0.49	44.6 ± 1.7	91.1 ± 5.6	48.6,[f] 11.0,[d] 13.2,[e] 2.1[h]
153	6.50 ± 0.19	13.52 ± 0.31	27.2 ± 0.58	52.8 ± 1.6	91.2 ± 4.3	35.5,[f] 17.9,[d] 2.3,[h] 13.4,[g] 16.7[e]
154	17.34 ± 0.50	29.18 ± 0.63	47.85 ± 0.96	76.7 ± 2.2	113.1 ± 4.8	72.1,[e] 58.5[d]
170	0.128 ± 0.004	0.760 ± 0.018	4.139 ± 0.096	20.84 ± 0.80	78.5 ± 5.5	19.3,[d] 8.85,[e] 0.91[h]
180	0.425 ± 0.012	2.025 ± 0.046	8.96 ± 0.20	37.0 ± 1.3	118.5 ± 7.8	30.4,[d] 10.9,[e] 1.01[h]
187	3.034 ± 0.099	8.72 ± 0.23	23.84 ± 0.57	62.2 ± 2.2	136.7 ± 8.2	42.2,[d] 20.5[e]
188	15.77 ± 0.47	31.39 ± 0.74	60.5 ± 1.4	113.1 ± 4.0	188.6 ± 10.4	44.9,[e] 113[d]
195	0.079 ± 0.003	0.485 ± 0.015	2.724 ± 0.088	14.13 ± 0.78	54.5 ± 5.5	12.0,[e] 12.8,[d] 1.1[h]
201	1.069 ± 0.032	5.14 ± 0.13	22.98 ± 0.59	95.8 ± 4.4	308 ± 29	13.2,[e] 64.5,[d] 1.7[h]

[a] Predicted Henry's law constants from the linear regression analysis of measured ln $K_{H'}$ versus the reciprocal temperature. [b] 95% Working−Hotelling simultaneous confidence bounds[27] for linearly predicted Henry's law constants. [c] Congeners are listed in order of IUPAC number. [d] Burkhard et al., 1985.[17] [e] Dunnivant et al., 1992.[32] [f] Murphy et al., 1983.[31] [g] Dunnivant et al., 1988.[34] [h] Brunner et al., 1990.[33]

Table 2. Measured Enthalpy (ΔH_H) and Entropy (ΔS_H) of K_H, along with Enthalpy of K_H, Vaporization (ΔH_{VAP}), Solubility (ΔH_{SOL}), and the Enthalpy Associated with the Transition from Octanol Solution to Air ($\Delta H_{O/A}$), Taken from the Literature[a]

congener	r^2	ΔH_H[b] (kJ·mol^{-1}) this study	ΔS_H[c] (kJ·mol^{-1}·K^{-1}) this study	ΔH_H (kJ·mol^{-1}) [references]	ΔH_{VAP} (kJ·mol^{-1}) [references]	ΔH_{SOL} (kJ·mol^{-1}) [references]	$\Delta H_{O/A}$ (kJ·mol^{-1}) [references]
1	0.83	42.7 ± 5.8	0.104 ± 0.020	52[d]	64[e]		
8	0.96	44.1 ± 2.6	0.110 ± 0.010	56[d]	72[e]		
18	0.92	34.9 ± 3.0	0.079 ± 0.010	57[d]	75[e]		80[f]
28	0.96	32.5 ± 1.9	0.074 ± 0.006	50 ± 6[g] 60[d]	78[e]	18.7[h]	
29	0.94	34.9 ± 2.8	0.082 ± 0.010	59[d]	77[e]		72.6[i]
44	0.94	25.8 ± 2.2	0.049 ± 0.008	61[d]	81[e]		86[f]
50	0.81	23.8 ± 3.6	0.049 ± 0.012	59[d]			
52	0.91	30.5 ± 2.8	0.066 ± 0.010	52 ± 5[g] 61[d]	81[e]	16.6[h]	86[f]
66	0.92	29.0 ± 2.6	0.062 ± 0.008	64[d]	83[e]		73.3[j]
77	0.81	39.8 ± 6.0	0.092 ± 0.020	67[d]	87[e]	25.6[h] 50.7[k]	73.3[j]
87	0.88	32.5 ± 3.6	0.074 ± 0.012	65[d]	87[e]		
101	0.89	29.7 ± 3.2	0.066 ± 0.010	65[d]	86[e]	18.8[h] 31.9[k]	73.5[j]
104	0.63	14.5 ± 3.4	0.018 ± 0.012	61[d]			
105	0.88	75.6 ± 8.4	0.218 ± 0.028	69[d]	90[e]	22.2[h]	89.6[j]
118	0.87	49.8 ± 5.8	0.132 ± 0.018	68[d]	89[e]	21.6[h]	89.9[j]
126	0.91	98.5 ± 9.4	0.291 ± 0.032	71[d]	95[e]	21.5[h]	93.3[j]
128	0.95	118.0 ± 8.4	0.360 ± 0.028	70[d]	93[e]		
138	0.93	87.1 ± 7.4	0.259 ± 0.026	69[d]	92[e]	20.0[h]	87.8[j]
153	0.93	66.1 ± 5.4	0.190 ± 0.018	69[d]	91[e]	21.3[h]	89.9[j]
154	0.91	46.2 ± 4.6	0.126 ± 0.016	66[d]	90[e]		
170	0.97	164.0 ± 8.8	0.510 ± 0.030	70[d]	98[e]		
180	0.97	143.6 ± 7.4	0.447 ± 0.026	69[d]	97[e]	21.7[h]	86.8[j]
187	0.95	96.3 ± 6.8	0.293 ± 0.022	69[d]	94[e]		89[f]
188	0.95	62.0 ± 4.8	0.182 ± 0.016	67[d]	88[e]		
195	0.93	167 ± 13	0.518 ± 0.046	73[d]	100[e]		
201	0.97	144.5 ± 7.4	0.458 ± 0.026	70[d]	93[e]		

[a] $K_H' = \exp(-\Delta H_H/RT + \Delta S_H/R)$. This equation, along with ΔH_H and ΔS_H values from this table can be used to calculate K_H' for each compound at any temperature within the experimental temperature range. [b] ±2 standard errors of the slope. [c] ±2 standard errors of the intercept. [d] Burkhard et al., 1985.[17] [e] Falconer and Bidleman, 1994.[36] [f] Komp and McLachlan, 1997.[40] [g] ten Hulscher et al., 1992.[26] [h] Paasivirta et al., 1999.[42] [i] Harner and Mackay, 1995.[43] [j] Harner and Bidleman, 1996.[39] [k] Dickhut et al., 1986.[44]

where the gas-phase concentration (C_g) is expressed in units of mass of chemical per volume of air. Both forms are approximations of the Henry's law constant which assume that C_w is equal to a compound's mole fraction at infinite dilution. Using the ideal gas law to convert partial pressure to moles per cubic meter of air [$p_i = (n_i/V)RT$], K_H and K_H' are related by

$$K_H' = K_H/RT \tag{3}$$

where R is the ideal gas constant (8.314 $J\cdot K^{-1}\cdot mol^{-1}$) and T is the absolute temperature. The temperature dependence of K_H is described by the equation

$$-RT \ln K_H' = \Delta H_H - T\Delta S_H \tag{4}$$

where ΔH_H and ΔS_H are the enthalpy and entropy of the phase change from the dissolved phase to the gas phase. Solving for ln K_H' yields the Gibbs–Helmholtz equation:

$$\ln K_H' = -\Delta H_H/RT + \Delta S_H/R \tag{5}$$

Assuming ΔH_H and ΔS_H are independent of temperature (a reasonable assumption over small temperature ranges), this equation describes the dependence of K_H on temperature. By directly measuring K_H at different temperatures and plotting ln K_H' versus $1/T$, ΔH_H and ΔS_H are determined from the slope and intercept, respectively.

Experimental Section

The method used here employs a gas-stripping apparatus where the gas-phase concentration of a chemical in the air passing through a column of water is in equilibrium with the dissolved concentration.[19,20] The gas-stripping apparatus consists of a 122 cm by 15.2 cm diameter glass reactor filled with 10 L of Nanopure deionized water to a depth of 83 cm. Once the reactor was filled, between 130 $mL\cdot min^{-1}$ and 160 $mL\cdot min^{-1}$ of compressed air was passed through a hydrocarbon trap (R&D Separations, Rancho Corbova, CA) to remove possible contaminants and through a 500 mL glass, gas washing bottle to saturate the air with water vapor prior to entering the reactor through two 5 μm pore size air stones mounted at the bottom of the reactor. An in-line flow controller (Cole-Palmer Instrument, Vernon Hills, IL) maintained constant air flow (±1.0 $mL\cdot min^{-1}$) through the system during each experiment. Gas exiting the reactor first passed through a 5 μm glass impactor to remove possible aerosols created by breaking bubbles,[21] which may potentially interfere with hydrophobic organic contaminant gas-phase estimates,[22,23] and then through a cylindrical polyurethane foam plug (PUF, 25 mm diameter by 75 mm) housed in a glass column (i.d. 25 mm, length 150 mm; Ace Glass, Vineland, NJ) to capture vapor-phase PCBs. Instantaneous flow rates and the total volume of air passing through the reactor were recorded using a flow meter (Cole-Parmer Instrument, Vernon Hills, IL) located after the PUF plug. The volumes of air collected ranged from 14 L to 150 L, resulting in less than 2% of gas-phase PCBs breaking through the PUF trap (as determined by analyzing two traps in series) even at the higher sampling volumes.

Water samples (50 mL) were drawn through a Teflon stopcock located at the base of the reactor. Dissolved congener concentrations measured in replicate water samples differed by less than 10% for most of the PCBs studied. The entire system was located in a temperature-controlled room (Climate Technologies, Laytonsville, MD). The temperature was monitored both from the digital control panel and from a thermometer attached to the wall of the apparatus (±0.1 °C).

During each experiment, simultaneous air and water samples were collected every 4 h to 24 h for 3 days to 6 days. The time intervals between samples were dictated by the amount of gas-phase PCB mass collected in the PUF over time. K_H was calculated as the ratio of the time-integrated gas-phase concentration and the average of the two dissolved concentrations (i.e., those measured at the start and end of each air sample):

$$K_H/RT = C_g/\{(C_{w(n)} + C_{w(n+1)})/2\} \tag{6}$$

where C_g ($ng\cdot L^{-1}$) is the time-integrated gas-phase PCB concentration and $C_{w(n)}$ and $C_{w(n+1)}$ are the dissolved PCB concentrations measured at the beginning and end of the air sampling period, respectively. An integrated mass balance equation for the loss of PCBs from solution over time can also be used to calculate K_H.[24] However, the rate of PCB loss from the dissolved phase over such short time periods of an experiment in our system was small, and changes in the masses of less volatile compounds were close to the analytical detection limits. This suggests evidence of PCB analytes initially absorbing to the glass reactor and over time dissolving off the glass into the water column, buffering the change of PCB concentrations in the water column. Of the initial mass added to the reactor, about 15% of the lighter molecular weight PCB congeners and 60% of the heavier molecular weight PCB congeners absorbed onto the glass reactor. This would result in inaccurate K_H measurements if an integrated mass balance equation was used; however, at equilibrium, such buffering does not affect the ratio measurements of K_H from both air and water concentrations.

Chemicals. The PCB congeners used in this study were the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2262, a solution of 28 PCB congeners in 2,2,4-trimethylpentane (isooctane) at certified concentrations ranging from (2.00 to 2.14) $\mu g\cdot mL^{-1}$.[25] An aliquot (≈1 mL) of this solution was spiked into the reactor, resulting in initial dissolved PCB concentrations in the reactor ranging from (200 to 214) $ng\cdot mL^{-1}$. Initial PCB concentrations were less than 15% of their aqueous solubilities. The volume of solution added to the reactor was 0.01% of the total volume of water in the reactor, and the effect of isooctane on PCB solubility at this level should be negligible. ten Hulsher et al.[26] demonstrated that spiking a solvent solution into the reactor versus coating the inside of the reactor with the solution and allowing the solvent to evaporate before adding water yields similar K_H values. After adding the PCB aliquot solution to the reactor, the system was purged with air for 2 to 3 days to allow the analytes to become well mixed and equilibrate with the apparatus prior to sampling.

Sample Analysis and Quality Control. Gas-phase (PUF) samples were Soxhlet extracted for 24 h with 150 mL of chromatographic grade petroleum ether. Extracts were reduced in volume by rotary evaporation to 3 mL and then reduced under nitrogen to a final volume of 1 mL in hexane. Each water sample was solvent extracted three times with 10 mL of hexane in a separatory funnel, and the combined extracts were dried with Na_2SO_4 and reduced as above to 1 mL in hexane. PCB congeners were analyzed using a Hewlett-Packard 5890 gas chromatograph with a 5% diphenyl-methyl-polysiloxane capillary column (J&W Scientific) and a ^{63}Ni electron capture detector (GC-ECD). All analyte peaks were baseline resolved, and their levels were in the linear range of the detector. Internal standards (Ultra Scientific) consisting of 2,4,6-trichlorobiphenyl (IUPAC congener #30) and 2,2′,3,4,4′,5,6,6′-octachlorobiphenyl (IUPAC congener #204) were added to each sample prior to analysis to calculate relative response factors for each congener by comparing a known mass of a congener in the calibration standard to the known mass of each internal standard.

Two PCB congeners (2,3,5,6-tetrachlorobiphenyl, IUPAC congener #65, and 2,3,4,4′,5,6-hexachlorobiphenyl, IUPAC congener #166) were added as surrogates to each sample prior to extraction to monitor analytical recovery. For each sample, concentrations of PCB congeners were corrected by the recovery of the nearest eluting surrogate within that sample. The average surrogate recoveries for the dissolved samples were (78 ± 9)% (average ± std. dev., $n = 66$) for IUPAC congener #65 and (81 ± 9)% ($n = 66$) for IUPAC congener #166. Surrogate recoveries for gas-phase samples were (90 ± 14)% ($n = 54$) for IUPAC congener #65 and (101 ± 15)% ($n = 54$) for IUPAC congener #166.

Results and Discussion

Tests were performed to ensure that equilibrium was achieved between the gas-phase PCB concentrations in the rising bubbles and those in the dissolved phase by comparing the K_H values obtained at various purge heights in the reactor.[19] These studies showed that equilibrium was reached for these compounds at a water column height of between (53 and 83) cm, and all experiments were conducted in this study at a height of 83 cm.

Two independent K_H experiments were conducted at each temperature (three at 25 °C). Several K_H values ($n = 5$) were calculated from air and water pairs collected over the duration of the experiment. These replications provide a measure of the precision of the experimental method. For most compounds, the relative standard deviations associated with the mean K_H value ($n = 5$) observed for each PCB congener were less than 15%, and no systematic differences, within experimental variability, were observed among the different temperatures. After five measurements had been made for each experiment, the entire system was broken down, cleaned, set up, and started again to repeat the above measurements over the range of given temperatures. This was done in an effort to measure the variability of K_H between two independent experiments (three at 25 °C) and examine the repeatability of the first mean K_H. Again, as with the first experiment, relative standard deviations associated with the mean K_H value ($n = 5$) observed for each PCB congener in the second experiment were less than 15%. More importantly, the percent coefficient of variation between the mean K_H measured in the first experiment and that measured in the second experiment at each temperature was less than 20% for most compounds.

All of the K_H values calculated from the experiments described above were pooled and analyzed using linear regression of ln K_H' versus the reciprocal of temperature (K) (eq 5) to predict the K_H values and provide estimates of the uncertainty (95% Working−Hotelling confidence limits for the predicted values) at each temperature (Table 1).[27] The expected dominant Type B (systematic) error component of ±0.1 °C was shown to have no effect on the estimates and uncertainties presented in Tables 1 and 2. The uncertainties presented can thus be interpreted as expanded uncertainties, with a $k = 2$ expansion factor, compliant with the ISO/NIST method of reporting.[28,29]

Experiments at 25 °C. Henry's law constants at 25 °C for PCBs have been previously reported.[14,16,30] Literature values range from (1 to 190) Pa·m^3·mol^{-1}, including PCB congeners with one to eight chlorine atoms. Results from our study range from (14.13 to 113.1) Pa·m^3·mol^{-1} and are mostly within the range of literature values for each congener (Table 1). The literature values listed in Table 1 were measured by various indirect and direct methods to calculate K_H. Burkhard et al.[17] and Murphy et al.[31] estimated K_H from the ratio of the subcooled liquid vapor pressure and the aqueous solubility, and Dunnivant et al.[32] used the quantitative structure−property relationship (QSPR) model to estimate K_H. Direct methods were employed by Brunner et al.,[33] who used the concurrent flow technique, and Dunnivant et al.,[34] who used the batch-stripping technique. At 25 °C, K_H varied by a factor of 10 between the 26 congeners; however, there was no strong relationship between K_H and molecular weight. The data reported by Dunnivant et al.,[34] Burkhard et al.,[17] and Atlas et al.[35] also support this observation. However, Brunner et al.[33] did observe a relationship between molecular weight and K_H for 58 congeners. Examination of a larger data set by Burkhard et al.[17] exhibited no systematic trend between K_H and molecular weight when all PCB congeners were considered. However, there is a significant variation in K_H with the number of *ortho*-chlorine substitutions within the same molecular weight class (Figure 1). *Ortho* substitutions refer to the four positions adjacent to the biphenyl bond. As the number of *ortho*-chlorine substitutions increases on the biphenyl rings, the K_H increases. This effect has also been discussed before by Burkhard et al.,[17] Dunnivant et al.,[34] and Brunner et al.[33] The effects of *ortho*-chlorine substitution may be related to steric hindrance, where the planarity between the two biphenyl rings decreases, resulting in lower solute/solvent interactions compared to those for non-*ortho* substitution PCBs.[34] Within the same homologue group non- and mono-*ortho*-chlorine PCBs have a

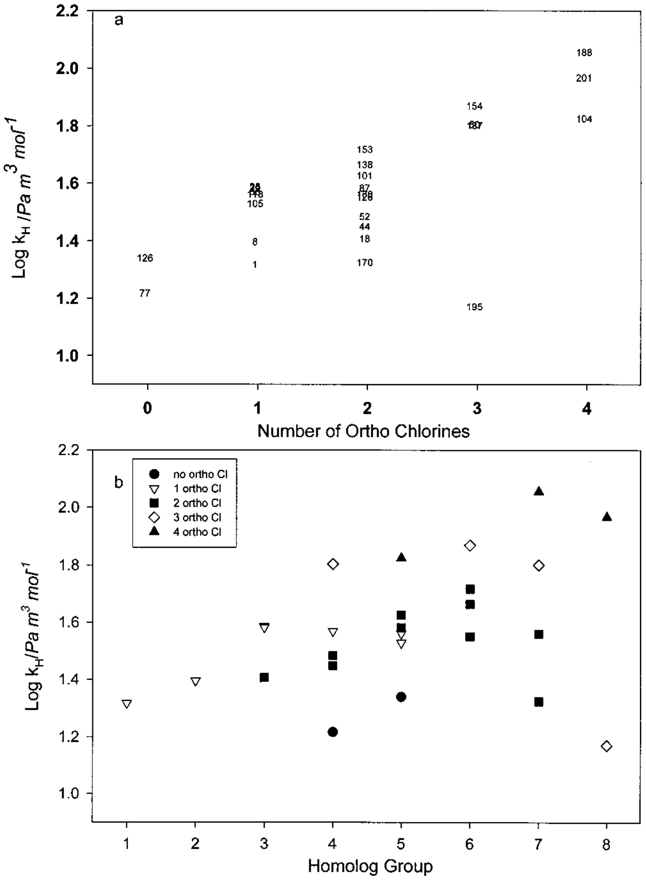

Figure 1. (a) Systematic variation in PCB congener (IUPAC #) Henry's law constant with the number of *ortho*-chlorines at 25 °C. (b) Dependence of Henry's law constants on PCB homologue group at 25 °C.

lower K_H than congeners with two or more *ortho*-chlorine substitutions (Figure 1b). For example, K_H for PCB congeners in the pentachlorobiphenyl homologue group (IUPAC congeners #126, 105, 118, 87, 101, and 104) increase with an increase in the number of *ortho* substitutions on the biphenyl ring.

Structure activity relationships have been used to estimate physicochemical constants of organic chemicals, including K_H. Examining the correlations among PCB structure and the measured K_H is part of our ongoing work to develop techniques in predicting the physical properties of organic contaminants.

Variation in PCB K_H with Temperature. In this study, the K_H of each congener was measured at five different temperatures ranging between (4 and 31) °C (Table 1). The K_H of 2,2′,4,6,6′-pentachlorobiphenyl (IUPAC congener #104) almost doubles between (4 and 31) °C, while the K_H of 2,2′,3,3′,4,4′,5,6-octachlorobiphenyl (IUPAC congener #195) increased by almost 3 orders of magnitude over the same temperature range, indicating a wide range in the temperature dependence among different PCB congeners. Burkhard et al.[17] also reported an increase in the temperature dependence for more chlorinated congeners such as decachlorobiphenyl compared to heptachlorobiphenyls. The slope and intercept of the line obtained from the plot of ln K_H' versus $1/T$ yield ΔH_H and ΔS_H, respectively, assuming ΔH_H and ΔS_H are independent of temperature over the experimental range (Table 2). These data are compared to literature values for ΔH_H, the enthalpy of volatilization (ΔH_{VAP}), the enthalpy of solvation (ΔH_{SOL}), and the enthalpy of octanol/air partitioning ($\Delta H_{O/A}$) in Table 2. For each congener measured, K_H can be calculated at any temperature within the experimental temperature range with a relative standard error of less than 10% using eq 5 and ΔH_H and ΔS_H values from Table 2.

Among the 26 PCBs measured, ΔH_H varied from (14.5 ± 3.4) kJ·mol^{-1} for 2,2′,4,6,6′-pentachlorobiphenyl (IUPAC congener #104) to (167 ± 13) kJ·mol^{-1} for 2,2′,3,3′,4,4′,5,6-octachlorobiphenyl (IUPAC congener #195; Table 2). ten Hulsher et al.[26] measured the K_H temperature dependence of two of the same PCB congeners examined in this study (2,4,4′-trichlorobiphenyl, IUPAC congener #28, and 2,2′,5,5′-tetrachlorobiphenyl, IUPAC congener #52). The calculated ΔH_H for congener #28 was 50 kJ·mol^{-1} in ten Hulsher's study[26] and (32.5 ± 1.9) kJ·mol^{-1} (35% lower) here. For congener #52, ΔH_H was 52 kJ·mol^{-1} in ten Hulsher's study[26] and (30.5 ± 2.8) kJ·mol^{-1} (45% lower) here. Indirect estimates of the temperature dependence of K_H for the homologous series of chlorobiphenyls have also been calculated by Burkhard et al.[17] using the predicted temperature dependence of vapor pressure and solubility. The data presented by Burkhard et al.[17] were recalculated to ln K_H' and $1/T$ to obtain estimates for ΔH_H for each individual congener. Enthalpies of phase change for the 26 PCBs ranged from 52 kJ·mol^{-1} to 73 kJ·mol^{-1}, although these values can vary substantially depending on which vapor pressure and solubility data are used to calculate K_H. The temperature dependencies determined from this study show a greater range of dependency on temperature than values estimated from the data presented in Burkhard et al.;[17] however, both data sets demonstrate an increase in the average ΔH_H with an increase in the homologue series.

Table 2 also summarizes literature values of ΔH_{VAP}, ΔH_{SOL}, and $\Delta H_{O/A}$. ΔH_{VAP} values were estimated from gas chromatographic retention data,[36] ΔH_{SOL} values were either estimated from thermodynamic equations[37] or experimentally measured by a generator column, and $\Delta H_{O/A}$ values were measured using a generator column or a fugacity meter.[38−40] The mean value of ΔH_{VAP} for these PCBs is (86.8 ± 8.8) kJ·mol^{-1} ($n = 24$), of ΔH_{SOL} is (20.8 ± 2.5) kJ·mol^{-1} ($n = 10$), of $\Delta H_{O/A}$ is (83.6 ± 7.5) kJ·mol^{-1} ($n = 14$), and of ΔH_H from this study is (66.6 ± 46) kJ·mol^{-1} ($n = 26$). This is consistent with thermodynamic principles, which suggests the effect of temperature on K_H (ΔH_H) should be lower than ΔH_{VAP} by an amount close to or equal to ΔH_{SOL}.[41] For individual congeners, the difference between ΔH_H and ΔH_{VAP} ranges from (2 to 68)%, the difference between ΔH_H and ΔH_{SOL} ranges from (36 to 85)%, and the difference between ΔH_H and $\Delta H_{O/A}$ ranges from 1% (i.e., nearly equal) to 70%. On average, ΔH_H is 24% lower than ΔH_{VAP}. It is unknown why the ΔH_H values are higher than those of ΔH_{VAP} for some of the heavier weight congeners.

Conclusions

To date, the data presented here are the most comprehensive list of experimentally determined K_H values over various temperatures for a wide range of PCBs. K_H values ranged between (0.079 ± 0.003) Pa·m^3·mol^{-1} for 2,2′,3,3′,4,4′,5,6-octachlorobiphenyl (IUPAC congener #195) at 4 °C and (308 ± 29) Pa·m^3·mol^{-1} for 2,2′,3,3′,4,5′,6,6′-octachlorobiphenyl (IUPAC congener #201) at 31 °C. On average, K_H values for individual PCBs from this study were within the range of previously reported values. These data suggest that K_H values for PCBs are not directly related to the molecular weight of the congeners but rather to the *ortho*-chlorine substitution within a homologue series. This observation may be useful in developing a model for the estimation of other K_H values for PCBs not measured in this study. Enthalpies of phase change ranged from (14.5 ± 3.4) kJ·mol^{-1} for 2,2′,4,6,6′-pentachlorobiphenyl (IUPAC congener #104) to (167 ± 13) kJ·mol^{-1} for 2,2′,3,3′,4,4′,5,6-octachlorobiphenyl (IUPAC congener #195). The differences between the enthalpies of phase change for individual congeners are as high as 91%, demonstrating the considerable variability in the K_H temperature dependence among individual congeners. Therefore, it is important to use experimentally determined enthalpies and entropies of individual congeners to accurately predict the temperature-specific Henry's law constants of PCB congeners.

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Disclaimer. Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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