DETERMINATION OF HENRY'S LAW CONSTANTS OF POLYCHLORINATED NAPHTHALENES AS A FUNCTION OF TEMPERATURE

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Introduction

Polychlorinated naphthalenes (PCNs) have past uses and physical–chemical properties similar to polychlorinated biphenyls (PCBs) [1]. PCNs were manufactured commercially as technical mixtures with the trade names Halowax (United States), Seekay (UK), and Nibren (Germany). They were mainly used in applications requiring high thermal stability such as dielectric fluids in transformers and capacitors [2], and as wood preservatives, pesticides, plasticizers, and oil additives. They are also found as trace contaminants in PCBs mixtures [2,3].

Due to their potential for toxicity, bioaccumulation, persistence, and long-range atmospheric transport, PCNs have been targeted by Stockholm Convention on persistent organic pollutants (POPs). They are currently under review for listing under the Convention [4]. Unlike the other toxic organic chemicals, studies on atmospheric PCN concentrations are relatively scarce.

The Henry's law constant (*H*) is an important parameter that plays a fundamental role in predicting the transport, behavior and fate of PCNs in the environment and it is required to model gas-exchange in aquatic systems. The objective of this study was to measure the Henry's law constants of 32 PCN congeners as a function of temperature. Henry's law constants were measured at five different environmental temperatures in deionized water by a commonly used gas-stripping technique. The enthalpies and entropies of phase change were also determined.

Materials and methods

Gas-stripping experiments

Experiments were conducted at five different temperatures (5, 10, 15, 25 and 35ºC). The gas-stripping apparatus consisted of a 75 cm by 5 cm diameter water-jacketed glass vessel filled with 1 liter deionized water at a depth of 50 cm [5,6]. The water depth was selected based on previous studies indicating that the equilibrium between gas and water-phases is achieved at less than 50 cm of water depth [7,8]. PCNs were prepared in 1 ml methanol and spiked into the water in the vessel. The initial aqueous concentrations were set to 0.001-15.8% of the solubility of the 32 PCN congeners. The volume of methanol added to the vessel was 0.1% of the total water volume. The effect of methanol on the solubility of PCNs was assumed to be negligible based on a previous study demonstrating that spiking a solvent solution into the vessel versus coating the inside of the vessel with the solution and allowing the solvent to evaporate before adding water yields similar *H* values [9].

Then, 200 ml min^{-1} compressed chromatographic grade N_2 was passed through a 40-µm fritted glass diffuser from the bottom of the vessel. Prior to the vessel, the N_2 purge gas was saturated with water vapor using a gas washing bottle filled with deionized water. Flow rates of N_2 were measured using a flow meter (rotameter) and the temperature was controlled by a constant-temperature circulated water bath. The rotameter calibration was checked occasionally using a primary standard (soap-bubble meter).

A 5-cm section of the tube exiting the inner chamber was plugged with pre-baked silanized glass wool to prevent the escape of the water droplets that may be produced during the bubbling process. Vapor phase PCNs were captured by an XAD-2 resin filled glass column. Water samples (10 ml) were drawn through a valve located at the base of the vessel at the start and end of each sampling period (2 h).

Sample preparation and analysis

Water and gas-phase samples were spiked with 20 pg of a surrogate standard (PBDE-77, 3,3′,4,4′-tetrabromodiphenyl ether) prior to extraction. Gas-phase samples were extracted into acetone/hexane (50:50) in an ultrasonic bath for 30 min. Water samples were liquid-liquid extracted three times with 5 ml hexane using a separatory funnel. Then, the solvent for all samples was exchanged into hexane and sample volumes were reduced to 0.5 ml under a gentle stream of pure nitrogen.

PCNs were analyzed using negative chemical ionization (NCI). The capillary column was HP5-MS (30 m, 0.25 mm, 0.25 µm). Helium was the carrier gas and high purity methane was the reagent gas for NCI. Compounds were identified based on their retention times, target and qualifier ions, and were quantified using the internal standard calibration procedure. Further details for sample preparation and instrumental analysis could be found elsewhere [10].

Quality control

Average recovery for the surrogate standard (PBDE-77) was 102.4±20.4%. Instrumental detection limits (IDL) were determined from linear extrapolation, based on the lowest standard in calibration curve and using the area of a peak having a signal/noise ratio of 3. For 1 µl injection, IDLs were 0.01–0.37 pg for PCNs. Blank XAD-2 resin and water samples were also analyzed. The method detection limit (MDL) was defined as the mean blank mass plus three standard deviations (MDL=Mean blank value+3SD). IDL was used for the compounds that were not detected in blanks. Average analyte amounts in blanks were generally <1% of the sample amounts. Sample quantities exceeding the MDL were quantified and blank-corrected by subtracting the average blank amounts from sample amounts.

Five point calibration curves were used to calibrate the analytical system. In all cases the r^2 was >0.999. A mid-point calibration standard was used to confirm the GC performance for every 12-h period.

A backup column was also placed in series with the adsorbent column in order to determine possible breakthrough of gas-phase chemicals during the experiments at 35 and 25°C. The average amounts found on these backup columns were less than 1.0% indicating that the breakthrough of PCNs was not significant even at the highest gas-phase concentrations encountered at 35 and 25°C.

Data analysis

The Henry's Law constant is often expressed as [8]:

$$H = P_g/C_w \tag{1}$$

where P_g is the gas-phase partial pressure (Pa) and C_w is the dissolved concentration (mol m^{-3}).

Using the ideal gas law [$p = (nRT)/V$] to convert partial pressure to moles per cubic meter (mol m^{-3}) of air, dimensionless Henry's law constant (H') can be obtained as:

$$H' = H/RT \tag{2}$$

where R is the ideal gas constant (8.314 Pa m^3 mol^{-1} K^{-1}) and T is the absolute temperature (K).
The temperature dependence of H can be expressed as [8]:

$$\ln H = -\Delta H_H/RT + \Delta S_H/R \tag{3}$$

where ΔH_H (J mol^{-1}) and ΔS_H (J mol^{-1} K^{-1}) are the enthalpy and entropy of the phase change from the dissolved phase to the gas phase, respectively.

After directly measuring H at different temperatures, ln H versus $1/T$ can be plotted and ΔH_H and ΔS_H can be obtained from the slope and the intercept, respectively.

Experimental H' values were calculated as follows:

$$H' = C_g/[(C_{w(n)} + C_{w(n+1)})/2] \qquad (4)$$

where C_g (ng l^{-1}) is the time-integrated gas-phase PCN concentration and $C_{w(n)}$ and $C_{w(n+1)}$ are the aqueous PCN concentrations (ng l^{-1}) measured at the beginning and end of air sampling period, respectively.

Results and discussion

For each individual experiment at specific temperatures (5, 15, 20, 25 and 35°C) three H' values (n=3) were determined (Equation 4) using the PCN concentrations measured in aqueous (n=4) and gas-phase samples (n=3) that were collected over the experimental duration (2 h). The replicate determinations provide a measure of the precision of the experimental method. For most PCNs, the relative standard deviations associated with the mean H′ value were less than 30% and no systematic differences, within experimental variability were observed among the different temperatures (Table 1).

Table 1. The regression parameters for the equation $\ln H = A + B/T(K)$, enthalpies and entropies of phase change, and H values measured at 25°C for PCNs in dionized water.

	r^2	**A**	**B**	**ΔS_H (kj mol^{-1} K^{-1})**	**ΔH_H (kj mol^{-1})**	**H (Pa m^3 mol^{-1})**
PCN-19	0.99	20.97	-5488	0.17	45.6	14.04±1.65
PCN-24/14	0.99	21.51	-5703	0.18	47.4	12.00±0.95
PCN-15	0.99	20.02	-5320	0.17	44.2	9.11±1.01
PCN-16	0.99	23.61	-6496	0.20	54.0	5.96±1.15
PCN-17/25	0.99	20.32	-5530	0.17	46.0	6.79±0.90
PCN-23	0.99	19.46	-5364	0.16	44.6	4.46±0.39
PCN-42	0.98	21.65	-5633	0.18	46.8	18.01±0.69
PCN-33/34/37	0.98	19.39	-5056	0.16	42.0	12.79±0.20
PCN-47	0.98	21.76	-5810	0.18	48.3	10.91±0.14
PCN-36/45	0.97	20.97	-5606	0.17	46.6	10.02±0.27
PCN-28/43	0.98	21.90	-5931	0.18	49.3	8.56±0.09
PCN-32	0.95	21.48	-5873	0.18	48.8	6.61±0.08
PCN-35	0.95	21.86	-6041	0.18	50.2	5.52±0.22
PCN-38/40	0.98	23.15	-6499	0.19	54.0	4.47±0.26
PCN-46	0.99	20.14	-5729	0.17	47.6	2.82±0.34
PCN-52/60	0.91	29.29	-8059	0.24	67.0	14.50±0.09
PCN-58	0.93	31.27	-8728	0.26	72.6	11.22±0.26
PCN-61	0.92	31.20	-8755	0.26	72.8	9.86±0.33
PCN-50	0.92	32.30	-9016	0.27	75.0	12.90±0.47
PCN-57	0.92	33.43	-9545	0.28	79.4	7.20±0.77
PCN-62	0.92	32.03	-9180	0.27	76.3	5.79±0.62
PCN-53	0.93	33.64	-9659	0.28	80.3	5.94±0.78
PCN-59	0.93	31.31	-9079	0.26	75.5	3.80±0.55
PCN-66/67	0.97	43.87	-12800	0.36	106.4	3.95±0.98
PCN-64/68	0.96	42.12	-12394	0.35	103.0	2.67±0.85
PCN-69	0.95	40.33	-11906	0.34	99.0	2.35±0.76
PCN-71/72	0.95	38.89	-11500	0.32	95.6	2.24±0.72
PCN-63	0.98	39.80	-11897	0.33	98.9	1.29±0.43
PCN-65	0.94	33.52	-10094	0.28	83.9	1.07±0.31
PCN-73	0.99	33.31	-10293	0.28	85.6	0.28±0.08
PCN-74	0.98	34.13	-10474	0.28	87.1	0.42±0.13
PCN-75	0.94	25.64	-7845	0.21	65.2	0.82±0.26

H values (at 25°C) ranged between 0.28±0.08 Pa m^3 mol^{-1} (PCN-73) and 18.01±0.69 Pa m^3 mol^{-1} (PCN-42) in deionized water. To our knowledge there are no previously reported experimental Henry's law constant values for PCNs. Therefore, H values measured at 25°C were compared to those calculated as the ratio of octanol-water to octanol-air partition coefficients (K_{OW}/K_{OA}) [11,12,13] (Figure 1). The agreement between the measured and estimated values was good and measured/estimated ratios ranged between 0.47 and 2.31 (1.00±0.41), average±SD).

There is a strong correlation between the experimental *H* values of PCNs and temperature. For all PCNs, *H* increases with temperature more than 6 times (6 times for PCN-33/34/37 and 63 times for PCN-66/67) over the studied temperature range. The variation in *H* with temperature was expressed using the van't Hoff equation (Equation 3). Assuming enthalpy and entropy are independent of temperature over the experimental temperature range, the slope and intercept of the line were obtained from the plot of (ln H) vs. ($1/T$) yields the enthalpy (ΔH_H, kJ mol^{-1}) and entropy (ΔS_H, kJ mol^{-1}.K^{-1}) of phase change, respectively. The slopes (B) and the intercepts (A) for the Equation (3) [ln $H=A + B/T$(K)] are presented in Table 1. The r^2 values for the plots of (ln H) vs. ($1/T$) ranged between 0.91-0.99 (Table 1) indicating the assumption that ΔH_H and ΔS_H are constant over the experimental temperature range and that the temperature dependence of *H* can be accurately modeled by van't Hoff equation.

ΔH_H values ranged between 42 (PCN-33/34/37) and 106.4 kJ mol^{-1} (PCN-66/67) (Table 1). ΔH_H values for PCNs have not been reported previously. However, values determined in the present study were in the ranges reported for other compound groups like PBDEs (54.1-70.8 kJ mol^{-1}) [6], PCBs (14.5-167 kJ mol^{-1}) [14], PAHs (35.4-100 kJ mol^{-1}) [8] and OCPs (27.2-66.1 kJ mol^{-1}) [5].

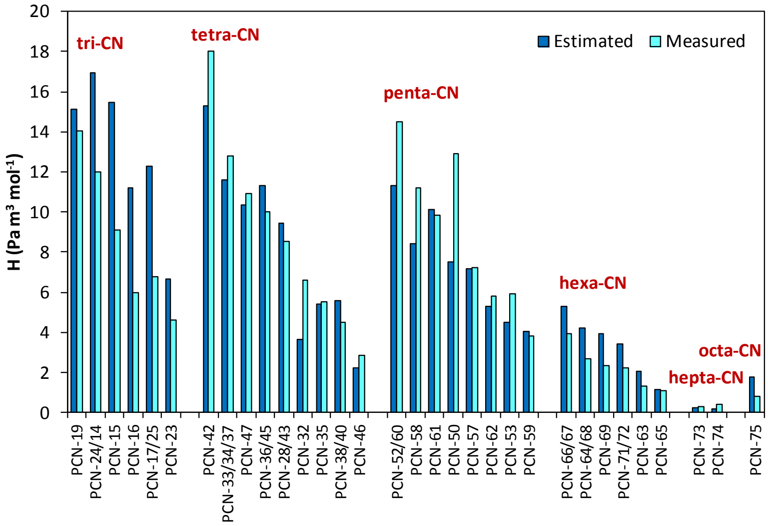

Figure 1. Comparison of *H* values measured at 25°C and those estimated as the ratio of octanol-water to octanol-air partition coefficients (K_{OW}/K_{OA}).

References:

1. Helm, P.A., Bidleman, T.F. (2003) *Environ Sci Technol* 37, 1075-1082.
2. Falandysz, J. (1998) *Environ Pollut* 101, 77-90.
3. Lee, S.C., Harner, T., Pozo, K., Shoeib, M., Wania, F., Muir, D.C.G., Barrie, L.A., Jones, K.C. (2007) *Environ Sci Technol* 41, 2680-2687.
4. Stockholm Convention (2015). http://chm.pops.int/Convention/ThePOPs/ChemicalsProposedforListing/tabid/2510/Default.aspx Accessed on April 20, 2015.
5. Cetin, B., Ozer, S., Sofuoglu, A., Odabasi, M. (2006) *Atmos Environ* 40, 4538-4546.
6. Cetin, B. and Odabasi, M. (2005) *Atmos Environ* 39, 5273-5280.
7. Jantunen L.M.M, Bidleman, T.F. (2000) *Chemosphere-Global Change Science* 2, 225-231.
8. Bamford, H.A., Poster, D.L., Baker, J.E. (1999) *Environ Toxicol Chem* 18, 1905-1912.
9. ten Hulscher, T.E.M., Van Der Velde, L.E., Bruggeman, W.A. (1992) *Environ Toxicol Chem* 11, 1595-1603.
10. Odabasi, M., Bayram, A., Elbir, T., Dumanoglu, Y., Kara, M., Altiok, H., Cetin, B. (2012) *Atmos Pollut Res* 3, 477-484.
11. Harner, T., Bidleman, T.F. (1998) *J Chem Eng Data* 43, 40-46.
12. Puzyn, T., Falandysz, J. (2005) *Atmos Environ* 39, 1439-1446.
13. Puzyn, T., Falandysz, J. (2005) *J Environ Sci Health, Part A* 40:9, 1651-1663.
14. Bamford, H.A., Poster, D.L., Baker, J.E. (2000) *J Chem Eng Data* 45, 1069-1074.