

Measurements of the Aqueous Solubility and 1-Octanol/Water Partition Coefficient of Selected Brominated Phenols and Estimation of Henry's Law Constant Using Activity Coefficient in Water

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Introduction

Brominated flame retardants (BFRs) such as polybromophenols, polybromodiphenylethers, and tetrabromobisphenol A, are attracting increased attention due to their environmental contamination effects, toxicities, and dioxin precursors released during thermal treatment. The physico-chemical properties (aqueous solubility (S_w), 1-octanol/water partition coefficient (K_{ow}), Henry's law constant, and so on) of BFRs and their related compounds are of fundamental importance in understanding the distribution behavior of BFRs in the environment and manufacturing or waste treatment processes of products containing BFRs. However, there is little experimental data available on such properties. In this study, S_w and K_{ow} of brominated phenols (4-bromophenol, 2,4-dibromophenol, 2,4,6-tribromophenol, and pentabromophenol) were measured by the generator column or shake flask method, and the HPLC method, respectively. Especially, the physico-chemical properties of nonionic form were investigated by adjusting the pH of water to 3.0. The experimental temperature for S_w measurement ranged from 283 to 308 K in view of the application of the experimental data for assessing the environment or chemical fate. To determine the activity coefficients of those compounds in water, their enthalpies of fusion and melting points were also measured by the differential scanning calorimetry (DSC) method. Based on the determined activity coefficients and vapor pressure data, the Henry's law constant was estimated. These physico-chemical property data for brominated phenols are systematically reported in the present study for the first time.

Experimental Section

Materials. The following brominated phenols (BPhs) were used in this study: 4-bromophenol (M1BP) 99%, 2,4-dibromophenol (D2BPh) 95%, 2,4,6-tribromophenol (T3BPh) 99%, and pentabromophenol (P5BPh) 96%. All the compounds were purchased from Sigma-Aldrich Corporation, and were used without further purification. Pure water was adjusted to pH 3.0 by dissolving a small amount of sodium dihydrogen phosphate and hydrochloric acid.

Apparatus and Procedure. In the present S_w measurement, two methods were used on the basis of solubility value. In the case of an aqueous solubility of higher than 100 mg/L, the shake flask method was used, whereas in the case of lower than 100 mg/L, the generator column method was used. The apparatus and procedure for the generator column method are described below.

Generator Column Method. In this work, a DCCLC (Direct Coupled Column Linked Chromatographic) technique was employed as the generator column method, as shown in Figure 1. The generator column was a 250-mm stainless column (4.0 mm i.d.) packed with 60-80 mesh glass beads (Chromosorb AWA; Chromatography Research Supplies) coated with solids of the compound to be measured. The weight ratio of solid to glass beads ranged from 1-8%, depending on S_w value. Pure water adjusted to pH 3.0 was pumped to the generator column in a thermostated water bath at a constant flow rate of 0.5-1.0 ml/min. In the generator column, solid-liquid

equilibrium is reached. The solute in the saturated solution generated by the generator column was extracted with a 20-mm C18 extractor column. After extraction, by switching the six-port valve, the adsorbed solute was eluted with HPLC mobile phase (methanol and 0.05 M NaClO₄ solution at pH 3.0). The eluate was directly injected into an analytical column. The solute concentration in the extractor column was determined by a UV detector, while the weight of the eluted solution passed through the extractor column was measured by a gravimetric method. From the results of HPLC assay and gravimetric measurement, S_w was determined.

HPLC method. According to the US-EPA Product Properties Test Guidelines¹⁾, K_{ow} values of BPhs were determined by measuring the retention time t_R of BFRs at a fixed HPLC analytical condition. The HPLC condition was as follows: analytical column: a Waters 39×300-mm μ -Bondapak C18 column, mobile phase: pH 3.0 NaClO₄ solution/methanol (25/75). First, t_R of standard samples, such as chlorophenols and triphenylamine, was measured, and thus the capacity factor k ($= (t_R - t_0) / t_0$) of each standard was calculated using the dead time of the column t_0 . By plotting $\log K_{ow}$ versus $\log k$ for all reference standards, the following linear relationship between $\log K_{ow}$ and k was obtained:

$$\log K_{ow} = 2.91 \log k + 3.84 \quad (1)$$

Next, t_R of BPhs was measured under the same HPLC analytical condition. Finally, K_{ow} of BPhs was obtained by substituting the measured t_R in Eq. (1).

Results and Discussion

In Figure 2, S_w of BPhs at 298 K is plotted as a function of bromine substitution number compared with S_w of nonionic form of chlorinated phenols (CPhs)²⁾. The solubility of BPhs decreased by one order of magnitude as the bromine content increased. This decrement of solubility was larger than that of CPhs. Regarding the effect of halogen content of phenols on S_w , bromine had a more intense effect than chlorine.

To examine quantitatively the temperature dependence of S_w , the logarithm of S_w was plotted against reciprocal temperature, namely a van't Hoff plot was drawn as shown in Figure 3. The slope of this figure is related with the enthalpy of

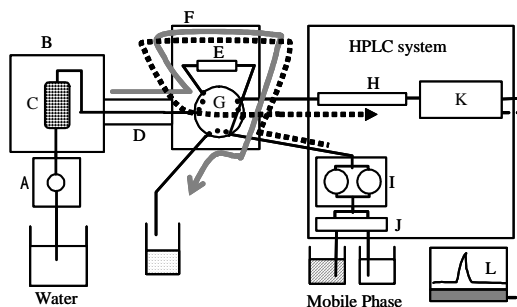


Figure 1. Schematic apparatus of our DCCLC method.

—:Flow of water - - - ->:Flow of mobile phase

A: Pump, B: Thermostated Water Bath, C: Generator Column, D: Thermostated Tape Heater, E: Extractor Column, F: Thermostated Air Oven, G: Two-Position Six-Port Switching Valve, H: Analytical Column, I: HPLC Pump, J: HPLC Degassor, K: UV Detector, L: Integrator

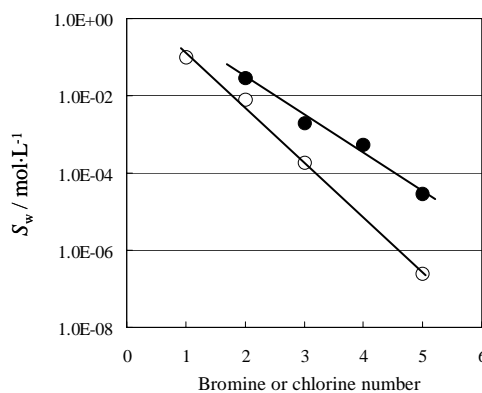


Figure 2. Effect of bromine substitution number on S_w of BPhs at 298 K, and comparison with that of chlorinated phenols (CPhs)²⁾.

•BPhs; 4-M1BPh, 2,4-D2BPh, 2,4,6-T3BPh, P5BPh.

○CPhs; 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, pentachlorophenol.

solution $\Delta H_{\text{solution}}$ (slope = $-\Delta H_{\text{solution}}/R$). Values of $\Delta H_{\text{solution}}$ for all compounds were positive, and so the dissolution process of solid BPhs was endothermic, thus the solubility increased with higher temperature. $\Delta H_{\text{solution}}$ also increased with an increase in bromine substitution number. Especially, $\Delta H_{\text{solution}}$ of pentabromophenol was much higher than that of the others. $\Delta H_{\text{solution}}$ is the sum of enthalpy of fusion ΔH_{fusion} and enthalpy of mixing ΔH_{mixing} . Since ΔH_{fusion} of pentabromophenol is not much higher than the others in the measurement of melting point T_m and ΔH_{fusion} section described below, ΔH_{mixing} of pentabromophenol is considered to be so large. Therefore, such high ΔH_{mixing} is responsible for the higher value of $\Delta H_{\text{solution}}$ of pentabromophenol. In addition, the high positive value of ΔH_{mixing} indicates that the interaction between pentabromophenol and water may be significantly repulsive.

Figure 4 shows the experimental results for K_{ow} of BPhs. K_{ow} increased with an increase in bromine content or a decrease in S_w . From the comparison between our experimental data and the literature, it is deduced that $\log K_{\text{ow}}$ value by the present HPLC method is considered to be reasonable. To evaluate a general hydrophobicity level for BPhs, K_{ow} 's of polycyclic aromatic hydrocarbons (PAHs), polybrominated benzenes (PBBzs), and CPhs, which have the same S_w level as BPhs, are plotted in Figure 4. This figure suggests that the bioconcentration and soil adsorption for BPhs with high bromine content ranging from 3 to 5, are as high as those of the PAHs with 2 to 4 rings as well as PBBzs with 2 to 4 bromines. A further characteristic is that halogenated phenols have relative high K_{ow} in spite of relatively high S_w .

In order to determine the activity coefficient of BPhs in water, T_m and ΔH_{fusion} were measured by DSC method. In this study, a SII DSC 6200 (Seiko Instruments, Chiba, Japan) was used. The

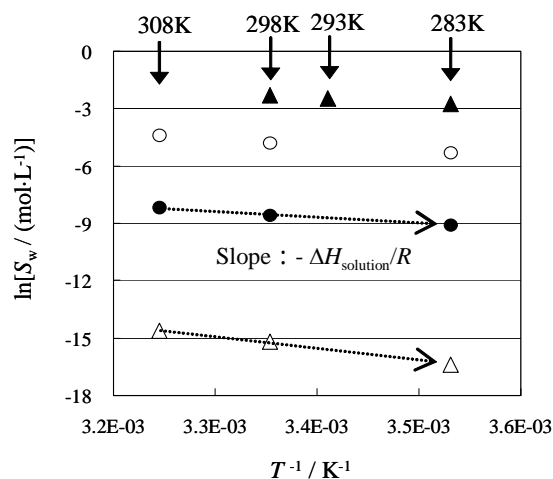


Figure 3. Dependence of S_w of BPhs on temperature T .

○ : 4-M1BPh, ▲ : 2,4-D2BPh, ● : 2,4,6-T3BPh, △ : P5BPh.

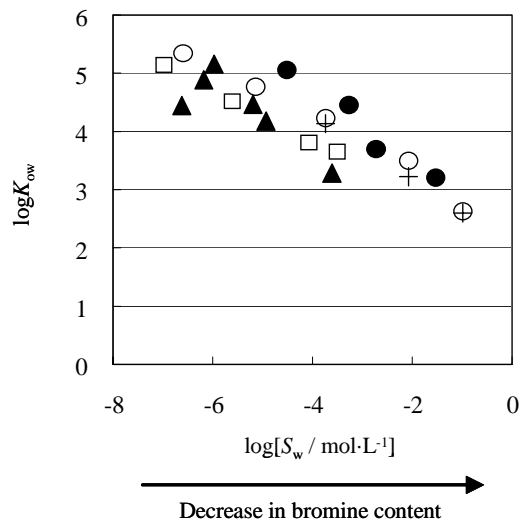


Figure 4. $\log K_{\text{ow}}$ of BPhs as a function of $\log S_w$, compared with that of polycyclic aromatic hydrocarbons (PAHs), polybrominated benzenes (PBBzs), and CPhs..

○ : BPhs (This work [exp. value]), ● : BPhs (lit. data [exp. value]), △ : CPhs (lit. data [exp. value]⁴), ▲ : PAHs (lit. data [exp. value]⁴), □ : PBBzs (lit. data [exp. value]⁴)

relationship between activity coefficient and aqueous solubility by use of T_m and ΔH_{fusion} can be expressed as³⁾

$$\gamma_i = \frac{1}{x_i} \exp \left[-\frac{\Delta H_{\text{fusion}}}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \right] \quad (2)$$

where x_i denotes aqueous solubility in units of mole fraction.

By substituting the measured ΔH_{fusion} , T_m , and x_i into Eq. (2), the activity coefficient of each compound in water was determined at various temperatures. The activity coefficient increased by one order of magnitude with an increase in bromine substitution number. In the case that the saturated solution is near a dilute solution, the activity coefficient may be regarded as the infinite dilution activity coefficient. The infinite dilution activity coefficient of a compound i γ_i^∞ is a useful parameter because it can be used to derive Henry's law constant H_w from the following equation³⁾

$$H_w = 18.015 \times 10^{-6} \times \gamma_i^\infty \times p_i^\circ \quad (3)$$

where p_i° denotes the vapor pressure of pure compound i .

In the present study, assuming that the obtained activity coefficient is regarded as γ_i^∞ , the Henry's law constant of BPhs at 298 K was calculated using the literature vapor pressure data⁴⁾. The relationship between the γ_i^∞ -derived H_w and S_w is shown in Figure 5. Although S_w decreased with an increase in bromine substitution

number, H_w was roughly similar for all BFRs. Comparing the H_w values with those of the same PAHs and PBBzs as the K_{ow} comparison, the distribution of BPhs from water to air is very weak by two to four orders of magnitude and may be independent of bromine content in the molecule. This characteristic is very different from that of the other hydrophobic compounds. The difference in H_w may be attributed to the relatively low vapor pressure of BPhs.

References

1. US-EPA, OPPTS *Product Properties Test Guidelines*: 830.7570 Partition Coefficient (n-Octanol/Water), Estimation by Liquid Chromatography 1996.
2. Huang, G.-L., Xiao, H., Chi, J., Shiu, W.-Y., Mackay, D. E. (2000) *J. Chem. Eng. Data* 45, 411-414.
3. Sandler, S. I. (1996) *Fluid Phase Equilibria* 116, 343-353.
4. Howard, P. H., Melyan, W. M., Ed. (1997) *Handbook of Physical Properties of Organic Chemicals*, CRC Press Inc.: Boca Raton FL.
5. Alaei, M., Whittall, R. M., Strach, W. M.J. (1996) *Chemosphere*, 32, 1153-1164.
6. Bamford, H. A., Poster, D. L., Baker, J. E. (1999) *Environ. Toxicol. Chem.* 18, 1905-1912.

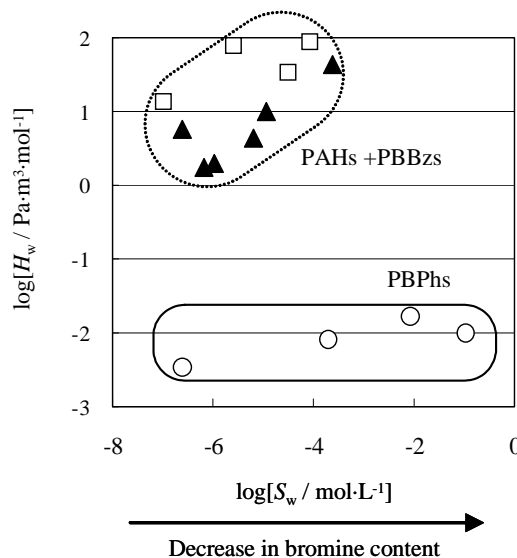


Figure 5. $\log H_w$ of BPhs at 298 K as a function of $\log S_w$, compared with those of PAHs, PBBzs with the same solubility range as BPhs .

○ : BPhs (This work [γ^∞ -derived value]), ○ : PAHs (lit. data [exp. value]⁴⁻⁶), ○ : PBBzs (literature data [est. value]⁴)