Physicochemical properties of selected polybrominated diphenylethers and comparison with some brominated aromatics and PCDDs

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Introduction

Brominated flame retardants (BFRs) such as polybromodiphenylethers (PBDEs), brominated phenols (BPhs), and hexabromobenzene, and their related compounds are attracting increased attention due to their environmental contamination effects, toxicities, and dioxin precursors released during thermal treatment. The physicochemical properties (aqueous solubility (S_w), 1-octanol/water partition coefficient (K_{ow}), and Henry's Law constant (H_w)) of these compounds are of fundamental importance in understanding the distribution 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 of PBDEs and their temperature dependence. In this study, S_w and K_{ow} of four PBDEs with 2-6 bromines were measured by the generator column method. The experimental temperature for S_w measurement ranged from 283 to 308 K to enable the experimental data to be used 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. On the basis of the determined activity coefficients and literature vapor pressure data, the Henry's Law constant was estimated. We compared these physicochemical property data not only with our previous experimental data[1,2] of BPhs and brominated benzenes (BBzs) but also with the literature data[3,4] of polychlorinated dibenzo-*p*-dioxins (PCDDs). From these comparisons, the effects of structural difference and bromine substitution on the physicochemical properties of BFRs and the environmental partitioning properties of PBDEs were discussed.

Experimental Section

Materials: The following PBDEs were used in this study: 4,4'-dibromodiphenylether (D2BDE) 99%, 2,2',4,4'-tetrabromodiphenylether (T4BDE) 100%, 2,2',4,4',5-pentabromodiphenylether (P5BDE) 98%, and 2,2',4,4',5,5'-hexabromodiphenylether (H6BDE) 99.3%. D2BDE and the others were purchased from Sigma-Aldrich Co. and AccuStandard Inc., respectively. Those compounds were used without further purification. Pure water (<0.1 $\mu S \cdot cm^{-1}$) was supplied by Milli-RX 45 (Millipore). 1-Octanol solution for K_{ow} measurement was a reagent used for the determination of K_{ow} (Tokyo Kasei).

Solubility (S_w) measurement: In this work, a DCCLC (Direct Coupled Column Linked Chromatographic) technique was used as the generator column as shown in Figure 1. The generator column was a 4.5×250-mm stainless column packed with 60-80 mesh glass beads (Chromosorb AWA; Chromatography Research Supplies) coated with sample compound. The weight ratio of solid to glass beads ranged from 0.5 to 1%, depending on the S_w value. Pure water was pumped to the generator column in a thermostated water bath at a constant flow rate of 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/water = 90/10). The eluate was directly injected into an ODS-type analytical column. The solute concentration in the extractor column was determined by a UV detector, while the weight of the eluted solution that passed through the extractor column was measured by a gravimetric method. From the results of HPLC assay and gravimetric measurement, S_w was determined.

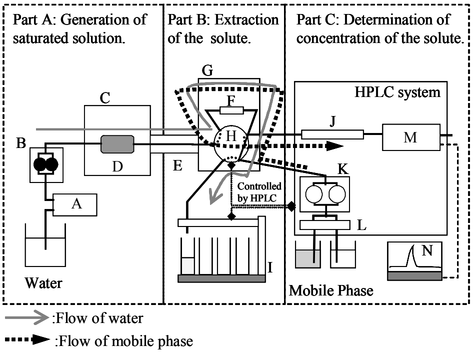

Figure 1. Schematic apparatus of our DCCLC method.

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

1-Octanol/water partition coefficient (K_{ow}) measurement: In accordance with the US-EPA Product Properties Test Guidelines[5], K_{ow} values of PBDEs were determined by the generator column method similar to the S_w measurement. The measurement procedure and difference between S_w and K_{ow} measurements are briefly described. The silanized glass beads were packed in the generator column and were coated with water-saturated 1-octanol containing sample compound. The concentration of sample was fixed at about 1 g/L. The pure water used in the S_w measurement was replaced with 1-octanol-saturated water. In the generator column, the distribution equilibrium of sample compound between 1-octanol and water phases is reached. The generator column was followed by a mini-column packed with silanized glass beads and wool to remove micro-emulsions in the water phase eluted from the generator column. The concentration of sample in the eluate was analyzed with the same HPLC system with the extraction column as the S_w measurement. K_{ow} was determined from the ratio of the molar concentration of sample in 1-octanol and water phases. In the case of PBDEs with 2 or 4 bromines, the DCCLC method was used. For the others with higher bromine content, the HPLC system is insufficient for analysis of the eluate due to the very low concentration of sample in the water phase. Therefore, the eluate from the extractor column was collected into a sample vial and then was analyzed by another analysis method. The analyses were performed with a 30 m × 0.25-mm DB-17 capillary column (J&W Scientific) fitted into an Agilent 6890 GC equipped with a ^{63}Ni electron-capture detector.

Results and Discussion

Measurement of S_w: Experimental S_w values at 298 K ranged from 6.57×10^{-7} mol·L^{-1} (0.216 mg·L^{-1}) for D2BDE to 7.82×10^{-11} mol·L^{-1} (5.04×10^{-5} mg·L^{-1}) for H6BDE shown in Table 1. In Figure 2, S_w of PBDEs at 298 K is plotted as a function of bromine substitution number compared with S_w data of BBzs and BPhs[1,2], clearly showing a significant decrease in S_w with increasing bromine substitution. The substitution effect of bromine for PBDEs was weaker than those for BBzs and BPhs. The variation of S_w of PBDEs was –0.92 log units per one bromine substitution, while those of BBzs and BPhs were –1.42 and –1.47, respectively. It is interesting to note that the effect of substitution on the S_w of PBDEs is similar to that of PCDDs, although the substitution effect of bromine is more intense than that of chlorine for halogenated benzenes and phenols[2]. The effect of halogen substitution on S_w is dependent on the basic structure and halogen to be substituted.

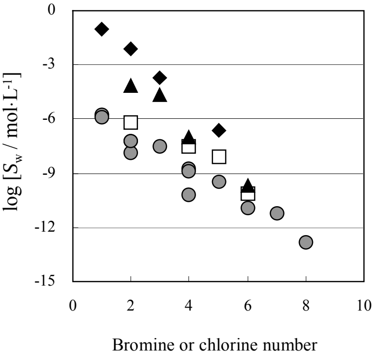

Figure 2. Effect of bromine substitution number on S_w of polybromodiphenylethers (PBDEs) at 298 K, and comparison with that of brominated phenols (BPhs)[1] and benzenes (BBzs)[2], ploychlorinated dibenzo-*p*-dioxin (PCDDs)[3].

□ : PBDEs, ◆ : BPhs, ▲: BBzs, ●: PCDDs.

To examine quantitatively the temperature dependence of S_w, the logarithm of S_w was plotted against the reciprocal of temperature, namely a van't Hoff plot was performed. The slope of this plot is related with the enthalpy of solution $\Delta_\mathrm{sol}H$ (slope = $-\Delta_\mathrm{sol}H/\mathrm{R}$). Values of $\Delta_\mathrm{sol}H$ are summarized in Table 1. The $\Delta_\mathrm{sol}H$ values for all compounds were positive, and so the dissolution process of solid PBDEs was endothermal, thus the solubility increased with higher temperature. In our previous works[1,2] $\Delta_\mathrm{sol}H$ for BBzs and BPhs increased with an increase in bromine content, whereas the $\Delta_\mathrm{sol}H$ values for PBDEs up to 5 bromines decreased with an increase in bromine substitution number.

Measurement of K_ow: The results for log K_ow of PBDEs are given in Table 1, and then are compared with the literature data of other aromatic compounds in Figure 3. K_ow increased with an increase in bromine content, as shown in Figure 3. Contrary to the S_w comparison, the bromine substitution effect of PBDEs was similar to the halogen substitution effect of the others. Moreover, this behavior was also observed in additional plots of K_ow versus halogen content for halogenated benzenes and phenols. Regarding the absolute value of K_ow, however, K_ow values for PBDEs were as high as those of the PCDDs with the same chlorine contents, and were much higher than those of BBzs and BPhs by two orders of magnitude. In the K_ow measurement, the physicochemical characteristic was affected by structural differences, rather than by the halogen content to be substituted.

To evaluate an environmental partitioning property for PBDEs, all K_ow values are plotted as a function of S_w in Figure 4. Generally, positive linear correlations between log of bioconcentraion factor or log of organic carbon sorption coefficient and log K_ow are observed by many investigators. Therefore, Figure 4 suggests that the bioconcentration and soil adsorption for PBDEs are as high as those for PCDDs and much higher than BBzs at the same S_w level. A further characteristic is that

PBDEs with low bromine content have high bioconcentration and soil adsorption in spite of relatively high S_w.

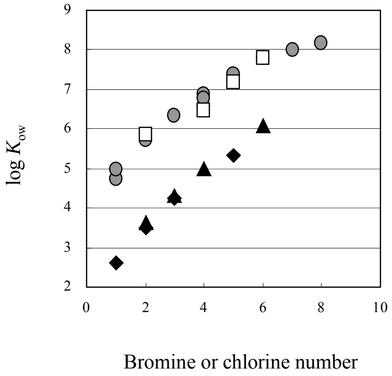

Figure 3. log K_{ow} of BPDEs at 298 K as a function of bromine substitution, compared with those of BPhs[1], BBzs[2], and PCDDs[4].

□ : PBDEs, ◆ : BPhs, ▲: BBzs, ●: PCDDs.

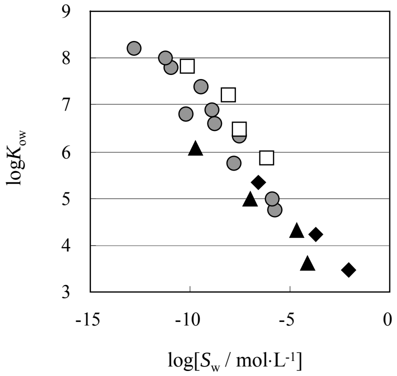

Figure 4. log K_{ow} of BPhs as a function of log S_w, compared with those of BPhs[1], BBzs[2], and PCDDs[3,4].

□ : PBDEs, ◆ : BPhs, ▲: BBzs, ●: PCDDs.

Table 1. Physicochemical Properties of PBDEs Determined in This Study

PBDEs	4,4'-dibromo diphenylether (D2BDE)	2,2'4,4'-tetrabromodiphenhylethr (T4BDE)	2,2',4,4',5-pentabromodiphenylether (P5BDE)	2,2',4,4',5,5'-hexabromodiphenylether (H6BDE)
S_w (298 K) / mol•L^{-1}	6.57×10^{-7}	3.04×10^{-8}	7.74×10^{-9}	7.82×10^{-11}
S_w (298 K) / mg•L^{-1}	0.216	1.47×10^{-2}	4.37×10^{-3}	5.04×10^{-5}
$\Delta_{sol}H$ / kJ•mol^{-1}	40.5	32.2	30.6	38.8
log K_{ow}	5.86	6.48	7.21	7.83
$\Delta_{fus}H$ / kJ•mol^{-1}	19.6	17.3	27.5	30.2
T_m / K	331.7	356.9	355.0	436.6
log γ_w (298 K) / -	7.58	8.76	9.08	10.2
$p_i^{o,L}$ (298 K)$^+$ / Pa	0.0173	1.86×10^{-4}	1.76×10^{-5}	2.09×10^{-6}
H_w (298 K) / Pa•m^3•mol^{-1}	11.8	1.94	0.383	0.559

+ denotes the literature data[7].

Determination of activity coefficient in water: In order to determine the activity coefficient (γ_i) of PBDEs in water, the melting temperature (T_m) and enthalpy of fusion ($\Delta_{fus}H$) were measured by the DSC method. In the present measurement, a SII DSC 6200 (Seiko Instruments, Chiba, Japan) was used. Experimental values of $\Delta_{fus}H$ and T_m are listed in Table 1. The relationship between activity coefficient and aqueous solubility by use of T_m and $\Delta_{fus}H$ can be expressed as[6]

$$\gamma_i = \frac{1}{x_i}\exp\left[-\frac{\Delta_{fus}H}{R}\left(\frac{1}{T}-\frac{1}{T_m}\right)\right] \qquad (1)$$

where x_i denotes aqueous solubility in units of mole fraction.

By substituting the measured $\Delta_{fus}H$, T_m, and x_i into Eq. (1), γ_i of each compound i in water was determined at various temperatures. The determined γ_i values at 298 K are given in Table 1. Similar to the other brominated aromatic compounds, the γ_i value significantly increased with an increase in bromine substitution number as shown in Figure 5. This figure is very useful for discussing the physicochemical differences among the other aromatics, since the physicochemical properties examined in this paper were thermodynamically related with the activity coefficient in water. For example, K_{ow} is related as follows:

$$\log K_{ow} = \log\gamma_w - \log\gamma_o + C \qquad (2)$$

where the subscripts w and o denote water-rich phase and 1-octanol-rich phase, respectively. C is a constant and derived from the molar volumes of both liquid phases. In the present K_{ow} results, the analysis based on Figure 5 and Eq. (2) indicates that the difference in the activity coefficient of PBDEs in 1-octanol may be responsible for the higher K_{ow} value for PBDEs than that for BBzs and BPhs.

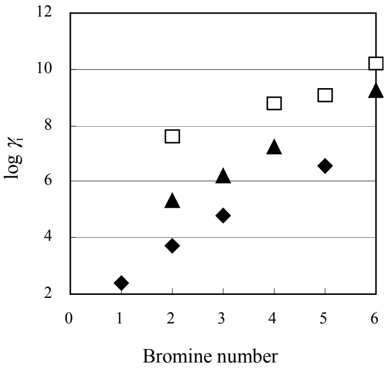

Figure 5. log γ_i of PBDEs as a function of bromine substitution, compared with those of BPhs[1] and BBzs[2].
□: PBDEs, ◆: BPhs, ▲: BBzs,

Estimation of Henry's Law constant (H_w): If it can be assumed that the saturated solution is almost 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^∞ can be converted to Henry's Law constant (H_w) by the following equation[5]

$$H_w = 18.015\times10^{-6}\times\gamma_w^\infty\times p_i^{o,L} \qquad (3)$$

where $p_i^{o,L}$ is the vapor pressure of pure compound i at the subcooled liquid state. The exponential term denotes the liquid-solid fugacity ratio of pure compound. In the present study, assuming that the obtained activity coefficient is regarded as γ_i^∞, the Henry's Law constant of PBDEs at 298 K was calculated using the literature vapor pressure data[7]. The literature values of $p_i^{o,L}$ and calculated values of H_w are summarized in Table 1. The γ_i^∞-derived H_w is plotted as a function of halogen substitution number in Figure 6. H_w decreased with an increase in bromine substitution number. Comparing the H_w values of PBDEs with those of the other halogenated aromatics, the H_w values were lower than those of BBzs due to the lower vapor pressures of PBDEs and were much higher than those of BPhs due to the higher activity coefficients of PBDEs. The H_w value is different among basic structures, whereas the variations of H_w against bromine substitution are not so different for all compounds except for BPhs. In the comparison with PCDDs, the H_w of PBDEs was roughly similar to that of PCDDs.

The relationship between the γ_1^∞-derived H_w and S_w is shown in Figure 7. In terms of the air-water partitioning, this figure shows that PBDEs have the same distribution from the aqueous phase to air as PCDDs for the same S_w values. The distribution of PBDEs is weaker than that of BBzs, but much higher than that of BPhs.

In summary, the series of measured and estimated results of the physicochemical properties of PBDEs did not differ from those of PCDDs, and thus PBDEs have lower S_w and H_w, and higher K_{ow} than other brominated aromatics such as BBzs and BPhs.

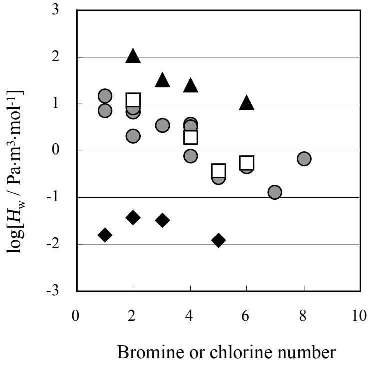

Figure 6. log H_w of BPDEs at 298 K as a function of bromine substitution, compared with those of BPhs[1], BBzs[2], and PCDDs[3]. (all data: γ^∞-derived value)

□ : PBDEs, ◆ : BPhs, ▲: BBzs, ●: PCDDs.

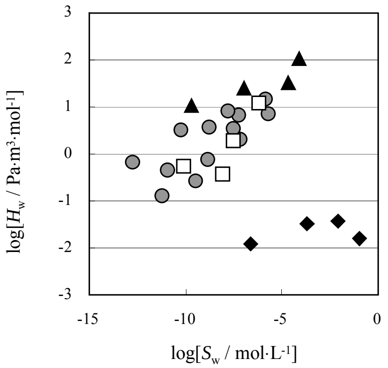

Figure 7. log H_w of BPDEs as a function of logS_w, compared with those of BPhs[1], BBzs[2], and PCDDs[3]. (all data: γ^∞-derived value)

□ : PBDEs, ◆ : BPhs, ▲: BBzs, ●: PCDDs.

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