Water Solubility and Partitioning Behavior of Selected Brominated Flame Retardants

On-line-number 936

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ABSTRACT

To understand the distribution behavior of brominated flame retardants (BFRs) such as polybromodiphenylethers, polybromophenols, and hexabromobenzene, and their related compounds in the environment, their physico-chemical properties are required. In this study, the water solubilities ($S_w$) at various temperatures and 1-octanol/water partition coefficients ($K_{ow}$) for selected BFRs and their related compounds (brominated diphenylethers and brominated benzenes) were measured. These solubility data revealed not only the temperature dependence of $S_w$, namely enthalpy of solution, but also the effect of bromine substitution on $S_w$ and the enthalpy of solution. Furthermore, the enthalpy of fusion and melting point for each of BFRs were measured by a differential scanning calorimetry method. These properties were used to determine the activity coefficients of these compounds in water using the measured $S_w$ data. Henry’s law constants of BFRs were also derived by assuming the obtained activity coefficients represent the infinite dilution activity coefficient. Finally, some additional physico-chemical characteristics of BFRs including brominated phenols were also discussed on the basis of basic structure and bromine substitution.

KEYWORDS

brominated flame retardants, water solubility, octanol/water partition coefficient

INTRODUCTION

Brominated flame retardants (BFRs) such as brominated phenols (BPhs), polybromodiphenylethers (PBDEs), tetrabromobisphenol A, and hexabromobenzene given in Figure 1, are often used as brominated flame retardants (BFRs), and are included in the plastics of industrial products as well as household appliances. Recently, BFRs and their related compounds are attracting increased attention due to their environmental contamination effects, toxicities, and dioxin precursors released during thermal treatment (e.g., de wit, 2002; Sakai et al., 2001). The physicochemical properties (aqueous solubility

![Figure 1. The chemical structures of BFRs](image)

(a) PBDEs, (b) BPhs, (c) tetrabromobisphenol-A, (d) hexabromobenzene.
(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 and their temperature dependence. In this study, S_w and K_{ow} of four PBDEs and four brominated benzenes (BBzs) with 2-6 bromines were measured by the following methods; the shake-flask or the generator-column method for S_w and the high-performance liquid chromatography (HPLC) or 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 of BPhs (Kuramochi et al., 2004) but also with the literature data of polychlorinated dibenzo-p-dioxins PCDDs (Shiu and Ma, 2000). From these comparisons, the physicochemical characteristics of BFRs were discussed with respect to structural differences and bromine substitution effects.

**EXPERIMENTAL SECTION**

**Materials**

The following PBDEs and BBzs were used in this study: 4,4’-dibromodiphenylether (D2BDE) 99%, 2,2’,4,4’-tetabromodiphenylether (T4BDE) 100%, 2,2’,4,4’,5-pentabromodiphenylether (P5BDE) 98%, 2,2’,4,4’,5,5’-hexabromodiphenylether (H6BDE) 99.3%, 1,4-dibromobenzene (D2BBz) 97%, 1,2,4,5-tetrabromobenzene (T4BBz) 97%, and hexabromobenzene (H6BBz) 98%. D2BDE and BBzs, and the others were purchased from Sigma-Aldrich Co. and AccuStandard Inc., respectively. Those compounds were used without further purification. Pure water (<0.1 μS 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 accord with the US-EPA Test Guidelines (US-EPA, 1996), in the case of a water solubility higher than 10 mg/L, the well-known shake-flask method was used. For a water solubility lower than 10 mg/L, the generator-column method was used, and are described below. **Generator-column method:** The generator-column method was used for PBDEs and BBzs except for D2BBz. In this work, a DCCLC (Direct Coupled Column Linked Chromatographic) technique was used as the generator-column as shown in Figure 2. The generator column was a 4.5×250-mm stainless

![Figure 2. Schematic apparatus of our DCCLC method.](image)

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 3 %, 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.

1-Octanol/water partition coefficient ($K_{ow}$) measurement

**HPLC method:** According to the US-EPA Product Properties Test Guidelines (US-EPA, 1996), $K_{ow}$ values of BBzs were determined by measuring the retention time $t_R$ of BBzs at a fixed HPLC analytical condition. The HPLC condition was as follows: analytical column: a Waters 39×300-mm µ-Bondapack C18 column, mobile phase: water/methanol (25/75). First, $t_R$ of standard samples, such as chlorinated benzenes with 1-6 chlorines 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:

$$\log K_{ow} = 2.764\log k + 3.092 \quad (1)$$

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

**Generator-column method:** In accordance with the US-EPA Product Properties Test Guidelines (US-EPA, 1996), $K_{ow}$ 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 $\times$ 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 $S_w$**

In Figure 3, $S_w$ of PBDEs and BBzs at 298 K is plotted as a function of bromine substitution number compared with $S_w$ data of BPhs (Kuramochi et al., 2004) and PCDDs (Shiu and Ma, 2000). The $S_w$ values of PBDEs at 298 K ranged from 0.223 mg/L for D2BDE to 5.05×10^{-5} mg/L for H6BDE, and those of BBzs from 17.0 mg/L for D2BBz to 1.10×10^{-4} mg/L for H6BBz, 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 phenols (Kuramochi et al., 2004). The effect of halogen substitution on $S_w$ is dependent on the basic structure and halogen to be substituted.

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 constructed. The slope of this plot is related with the enthalpy of solution $\Delta_{sol}H$ (slope = $-\Delta_{sol}H/R$). Values of $\Delta_{sol}H$ for all compounds were positive, and so the dissolution process of solid PBDEs was endothermal, thus the solubility increased with higher temperature. $\Delta_{sol}H$ for BBzs and BPhs increased with an increase in bromine content, whereas the $\Delta_{sol}H$ values for PBDEs up to 5 bromines decreased with an increase in bromine substitution. Furthermore, the variation of $\Delta_{sol}H$ as a function of bromine content for PBDEs was smaller than that for BBzs as well as BPhs.

**Measurement of $K_{ow}$**

Figure 4 shows the experimental results for $K_{ow}$ of PBDEs, BBzs and the other aromatic compounds. $K_{ow}$ increased with an increase in bromine content. 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.

**Figure 3. Effect of bromine substitution number on $S_w$ of PBDEs and BBzs at 298 K, and comparison with that BPhs and PCDDs.**

- PBDEs (this work), BBzs (this work), BPhs (Kuramochi et al., 2004), PCDDs (Shiu and Ma, 2000).

**Figure 4. $\log K_{ow}$ of BPDEs and BBzs at 298 K as a function of bromine substitution, compared with those of BPhs and PCDDs.**

- PBDEs (this work), BBzs (this work), BPhs (Kuramochi et al., 2004), PCDDs (Shiu and Ma, 2000).
the $K_{ow}$ measurement, the physicochemical characteristic was affected by structural differences, rather than by the halogen content to be substituted.

**Determination of activity coefficient in water**

In order to determine the activity coefficient ($\gamma$) of PBDEs and BBzs 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. The relationship between activity coefficient and aqueous solubility by use of $T_m$ and $\Delta_{fus}H$ can be expressed as (Sandler, 1996)

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

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. (2), $\gamma$ of each compound $i$ in water was determined at various temperatures. As shown in Figure 5, the $\gamma$ value significantly increased with an increase in bromine substitution number. This figure is 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. In the $K_{ow}$ results, for example, the analysis based on Figure 5 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.

**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 $i$ $\gamma^\infty$ can be converted to Henry’s Law constant ($H_w$) by the following equation

$$H_w = 18.015 \times 10^{-4} \gamma^\infty p_i^{\alpha_L} = 18.015 \times 10^{-4} \gamma^\infty p_i^{\alpha_S} \exp \left( \frac{\Delta_{fus}H}{RT_m} \left( \frac{T}{T_m} - 1 \right) \right)$$

where $p_i^{\alpha_L}$ and $p_i^{\alpha_S}$ are the vapor pressures of pure compound $i$ at the subcooled liquid state and at the solid state, respectively. 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 $\gamma^\infty$, the Henry’s Law constant of PBDEs and BBzs at 298 K was calculated using the literature vapor pressure data (Howard and Melyan, 1997; Tittlemier and Tomy, 2002; Shibata). The relationship between the $\gamma^\infty$-derived $H_w$ and halogen substitution is shown 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. In the comparison with PCDDs, the $H_w$ of PBDEs...
was roughly similar to that of PCDDs. 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 conclusion, 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. However, the variations of the properties except for $S_w$ as a function of bromine substitution are similar and not significantly dependent on the basic structure.

REFERENCES


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