

Measurements of water solubility and 1-octanol/water partition coefficient of three hexabromocyclododecane diastereoisomers

Hidetoshi Kuramochi¹, Shigeru Suzuki², Katsuya Kawamoto¹, Masahiro Osako¹, Shin-ichi Sakai³

¹National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba 305-8506, Japan

²Chubu University, 1200, Matsumoto-cho, Kasugai 487-8501, Japan

³Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan

Introduction

Recently, hexabromocyclododecane (HBCD) is attracting increased attention as an alternative brominated flame retardant to decabromodiphenylether. However, HBCD is very hydrophobic, not readily biodegradable, and expected to be persistent in the environment. In recent work, HBCD has been detected in a number of environmental samples such as sediment and aquatic biota (e.g. Morris et al. 2004, Janák et al. 2005, and Marvin et al. 2006). The technical product of HBCD is mainly composed of α -, β -, and γ -diastereoisomers. Although γ -HBCD is the predominant isomer in the technical product, α -HBCD has often emerged as the most abundant isomer in aquatic biota samples (e.g. Morris et al. 2004, and Janák et al. 2005).

To gain a better understanding of the environmental fate and behavior of HBCD, the physicochemical properties of the three HBCD isomers such as water solubility S_w , 1-octanol/water partition coefficient K_{ow} , and Henry's law constant H_w are of fundamental importance. Unfortunately, there is little reliable experimental data on such properties. In addition, it is unclear whether there is any difference in physicochemical properties among the diastereoisomers. In this work, therefore, S_w and K_{ow} of α -, β -, and γ -HBCD isomers were measured using the generator column and slow-stirrer method, respectively. To evaluate the difference in both properties between the pure isomer and mixture of the three isomers, the present measurements dealt with the following two solutes; a diastereoisomer alone and a mixture of all isomers, respectively. Furthermore, H_w of HBCD was estimated using the obtained S_w data. Finally, these physicochemical property data were compared with our previous experimental data for PBDEs with 4 to 6 bromines, and then the environmental partitioning properties of HBCD were briefly discussed.

Materials and Methods

Chemicals: Two kinds of HBCD samples were used in this study. The first was a single isomer. The used isomers were α -, β -, and γ -diastereoisomers purchased from Cambridge Isotope Laboratories Inc., with purities ranging from 97.3% to 100%. The other was a mixture of the three isomers purchased from Wako Pure Chemical Industries, Ltd. The composite had a reported purity of 97.1%, and was composed of 8.8%, 7.6% and 83.6% of the α -, β -, and γ -diastereoisomers, respectively. Pure water (18.2 $\mu\text{M}\Omega\text{-m}$) was supplied by Elix 10 followed by Synthesis A10 (Millipore). 1-Octanol

solution for K_{ow} measurement was a reagent used to determine 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. Details of the experimental apparatus were described in our previous work (Kuramochi et al. 2004a and b).

The generator column incorporated two 4.5×250-mm stainless columns, packed with 60-80 mesh glass beads coated with sample compound. The weight ratio of solid to glass beads was about 1%. Pure water was pumped into the generator column in a thermostated water bath at a constant flow rate of 1.0 ml/min. In the generator column, a solid-liquid equilibrium was 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 directly injected into a Waters HPLC system with an

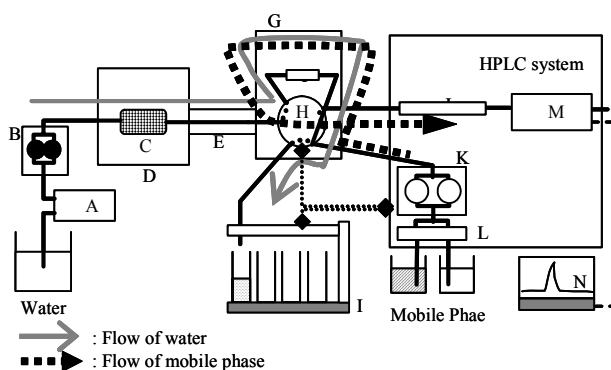


Fig.1.Schematic apparatus of DCCLC method.

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: ELSD Detector, N: Integrator.

ODS-type analytical column, followed by an ELSD detector to determine the concentration of the solute. S_w was determined by dividing the concentration by the weight of the eluted solution. In the case of the S_w determination for γ -HBCD, however, the eluate from the generator column was analyzed using another analysis method (Suzuki & Hasegawa 2006), in which the eluate was concentrated by solvent extraction and then analyzed by a Waters LC/MS system with a ZQ2000 Mass Spectrometer.

1-Octanol/water partition coefficient (K_{ow}) measurement: According to an early work (Tolls et al. 2003), K_{ow} measurement was carried out by the slow-stirrer method. As shown in Fig. 2, the experimental apparatus consisted of a jacketed glass vessel with a cock at the bottom, a thermostatically controlled circulating water bath, and a magnetic stirrer. Firstly, 800 mL of 1-octanol-saturated water was poured into the vessel, including a magnetic stirrer. Next, the 1-octanol solution with 0.5 g·L⁻¹ of HBCD was also poured into the vessel, and the two-phase sample was incubated without disturbing the 1-octanol layer for three weeks at 298K. The stirring rate was controlled as the vortex depth did not exceed 20 mm. Before sampling, the stirrer was turned off and the material was allowed to settle overnight. The concentration of HBCD

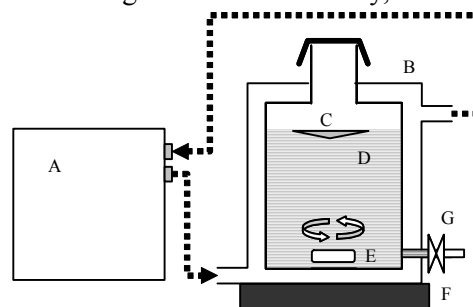


Fig.2.Schematic apparatus of slow-stirrer method.

A: Circulation Water Bath, B: Glass Vessel with Water Jacket, C: Octanol Phase, D: Water Phase, E: Stirrer Bar, F: Magnetic Stirrer, G: Cock for Sampling

during the 1-octanol phase was analyzed via the aforementioned HPLC-ELSD method, while that in the aqueous phase recovered from the cock at the bottom was analyzed via dichloromethane extraction and the same LC/MS system as the S_w determination for γ -HBCD. K_{ow} was determined by the ratio of the concentration in the 1-octanol phase to that in the aqueous phase. For each isomer, three independent experiments were performed.

Results and Discussion

S_w measurement: Table 1 shows the S_w values measured in the presence of only a single isomer. The S_w values of α -, β -, and γ -HBCD were 13.7, 2.8, and 1.5 $\mu\text{g}\cdot\text{L}^{-1}$, respectively. The value of α -HBCD was higher than that of the others by one order of magnitude. Thus, α -HBCD is considered to be easier to partition from its solid form to water. In recent literature (Hunziker et al. 2004), the S_w values of the three isomers at 298 K were 48.8, 14.7, and 2.08 $\mu\text{g}\cdot\text{L}^{-1}$, respectively. Although the temperatures in the present experiment were slightly higher than those in the literature, the S_w values of α - and β -isomers in this study were about five times lower than those in the literature. Since the literature values had been observed in the presence of all isomers at a composition ratio; 8.0% α -, 5.4% β -, and 86.6% γ -isomers, this indicates that the mixing of isomers or the isomer composition in the solid phase significantly increased S_w of α - and β -HBCD. This effect was first observed in this study. Therefore, the S_w values of each isomer in the presence of other isomers were examined. The same S_w measurement for a technical product of HBCD with 8.8% α -, 6.9% β -, and 83.6% γ -isomers was performed. The measured results for the technical product are given in Table 1. The S_w values for α - and β -isomers were much higher than those in the absence of other isomers. This demonstrated that the solid composition has a significant effect on S_w of α - and β -isomers, which is expected to be attributable to the following two phenomena. The first is the formation of a solid solution in the solid phase. The second is the formation of an intermolecular association in the liquid phase. In future, the reason will be clarified by spectroscopic and thermal analysis studies.

K_{ow} measurement: Firstly, $\log K_{ow}$ measurement was carried out in the presence of other isomers. As shown in Table 1, the $\log K_{ow}$ values of α -, β -, and γ -HBCD were measured as 5.65, 6.05, and 6.34, respectively. Based on these experimental results, $\log K_{ow}$ of total HBCD was estimated to be 6.16. The literature data for a technical product of HBCD was available, and thus was compared with our experimental value of total HBCD. Although the measured value was slightly higher than that in literature (Am. Chem. Council 2001), the two were almost comparable. From this comparison, our measurement method is considered reasonable. Similarly to S_w measurement, the $\log K_{ow}$ of each isomer were measured for single isomers, and are listed in Table 1. The $\log K_{ow}$ values of α -, β -, and γ -HBCD were 5.75, 5.79, and 6.25, respectively. Furthermore, the effect of the presence of other isomers on $\log K_{ow}$ was examined. Table 1 showed the presence of other isomers did not affect $\log K_{ow}$ unlike the results of S_w measurement. This indicates that the intermolecular association described above may not occur in the liquid phase.

Estimation of H_w and partition characteristics in comparison with PBDEs: Based on the obtained

S_w data of the technical product and a reported vapor pressure (p^0) value of 6.27×10^{-5} Pa (Am. Chem. Council 2001), Henry constant (H_w) values of each isomer in the technical product were estimated by the following equation; $H_w = p^0/S_w$, and are subsequently given in Table 2. The physicochemical properties presented here were compared with those of PBDEs with 4 to 6 bromines (Kuramochi et al. in press), as shown in Table 2. The properties resembled those of TeBDE and PeBDE on the whole. Therefore, the environmental partition characteristics of HBCD are expected to be roughly similar to PBDEs with 4 or 5 bromines. Due to the higher H_w value of γ -HBCD, however, γ -HBCD may have a higher partitioning potential from water to air than both PBDEs. In contrast, due to a higher S_w value of α -HBCD, α -HBCD has a higher partitioning potential to water.

Table 1. Experimental results for S_w and $\log K_{ow}$ of α -, β -, and γ -HBCD and literature data

Properties	This work ^I	This work ^{II}	Literature
$S_w, \Sigma\alpha\beta\gamma / \mu\text{g}\cdot\text{L}^{-1}$	-	116.5	65.6 [*]
$S_w (\alpha) / \mu\text{g}\cdot\text{L}^{-1}$	13.7	81.0	48.8 [*]
$S_w (\beta) / \mu\text{g}\cdot\text{L}^{-1}$	2.8	33.3	14.7 [*]
$S_w (\gamma) / \mu\text{g}\cdot\text{L}^{-1}$	1.5	1.6	2.08 [*]
$\log K_{ow, \Sigma\alpha\beta\gamma}$	-	6.16	5.625 [†]
$\log K_{ow} (\alpha)$	5.75	5.65	-
$\log K_{ow} (\beta)$	5.79	6.05	-
$\log K_{ow} (\gamma)$	6.25	6.34	-

I : an isomer, II : a mixture of isomers (a technical product),
 $S_w, \Sigma\alpha\beta\gamma$: S_w of total HBCD, $\log K_{ow, \Sigma\alpha\beta\gamma}$: $\log K_{ow}$ of total HBCD,
^{*}: literature data at 293 K (Hunziker et al. 2004), [†]: a technical product of HBCD of which the major component is γ -HBCD (Am. Chem. Council, 2001.)

Table 2. S_w , $\log K_{ow}$, and H_w for HBCD and PBDEs with 4-6 bromines

	HBCD	2,2',4,4'-	2,2',4,4',5-	2,2',4,4',5,5'-
Properties	(Technical product)	TeBDE	PeBDE	HxBDE
$S_w / \mu\text{g}\cdot\text{L}^{-1}$	See Table 1	14.7	4.37	5.04×10^{-2}
$\log K_{ow}$	See Table 1	6.78	7.39	8.05
$H_w / \text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$	0.496 ^{α} , 1.21 ^{β} , 18 ^{γ}	2.24	0.791	2.37

Superscripts α , β , and γ denote α -, β -, and γ -diastereomers, respectively. Property data for PBDEs (Kuramochi et al. in press)

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