Determination of log Kow values for polybromo diphenyl ether (PBDEs) by Capillary Gas Chromatography and by Total Surface Area (TSA) Correlation

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Introduction

Polybrominated diphenyl ether (PBDEs) flame retardants have emerged as a pollution problem of global dimensions. Like the PCBs they reached even the most remote areas[1,2,3]. PBDEs are structurally similar to PCBs and DDT; therefore their chemical properties on persistance and distribution in the environment follow similar patterns. Like other lipophilic compounds they are easily removed from the aqueous environment and adsorb onto sediments and particulate matter or accumulate in fatty tissue. Understanding their transport behaviour and the partitioning between the environmental compartments requires extensive knowledge of their physico-chemical properties such as water solubility (s_wH_2O) and octanol-water partitioning coefficent (K_{ow}).
In this work we report the estimation of log K_{ow} values that are usually derived by liquid chromatography solely from capillary gas chromatography (GC) data by selective correlation with PCB congeners as secondary standards and as a second method by a correlation to the total surface area (TSA). The log K_{ow} (GC) method based on values of the retention factor was recently validated[4]. The total surface area (TSA) is the area of the geometric structure of a molecule. So TSA is a function of the molar volume, which has been found to give a linear relationship with log K_{ow} for compounds such as halobenzenes, PCBs and polyaromatic hydrocarbons[5]. The TSA values of PBDEs are calculated by molecular modeling. The log K_{ow} values directly determind for distinct PBDEs[6] are correlated with their TSA values. This relationship provides a estimation of log K_{ow} (TSA) values for all 209 PBDE congeners on the basis of their TSA values.

Methods and Materials

The PCB standard solution SRM 2262 (28 PCB congeners Cl_1-Cl_{10}) is used as a reference for calculating the log K_{ow} (GC). The log K_{ow} (HPLC) values of the standard PCBs are taken from the work of Brodsky and Ballschmiter[7]. Capillary colum and temperature programm used for all GC measurements: Chrompack Sil 5 (25 m x 0,25 mm, 0,12 µm film thickness); 80 °C (1min) at 20 °C/min → 160 °C at 2 °C /min → 250 °C at 2 °C/min → 290 °C (15 min). The TSA values for the 209 PBDE congeners were calculated with Spartan 02. We used a Semi Empirience PM 3 method for the calculation.

Results

To obtain the log K_{ow} values of PBDEs by measuring the GC retention factor t_R/t_M we used the equation as suggested by Miller et al.[8], Hawker and Connell[5] and reviewed by James[9] and recently evaluated by Hackenberg et al.[4] (equation 1)

$$\log K_{ow} = a \log (t_R/t_M - 1) + C \qquad (1)$$

t_R being the retention time of the compound and t_M being the dead time in the chromatographic system. Using reference compounds with known log K_{ow} values (e.g. specific PCB congeners), the constants a and C can be derived by a linear correlation[4].
With the PCB derived constants of equation 1, we are able to calculate the log K_{ow} (GC) values of PBDEs that are components of Bromkal 70-5 (PBDE 47, PBDE 66, PBDE 85, PBDE 99, PBDE 100, PBDE 138, PBDE 153, PBDE 154) [10,11,12] (Table 1).

Table 1. Determination of log K_{ow} (GC) of PBDEs based on the GC retention factors and PCB SRM 2262 (28 PCB congeners Cl_1-Cl_{10}) as correlation standard. Directly determined log Kow values of ref 6 are given for comparison.

PBDE Nr	Structure	Retention factor	log K_{ow} (GC)	log K_{ow} ref 6
47	2,2',4,4'	11.67	7.3	6.81
66	2,3',4,4'	12.35	7.4	nd
85	2,2',3,4,4'	18.51	8.0	7.37
99	2,2',4,4',5	16.68	7.9	7.32
100	2,2',4,4',6	15.50	7.8	7.24
138	2,2',3,4,4',5'	23.74	8.4	nd
153	2,2',4,4',5,5'	21.79	8.3	7.90
154	2,2',4,4',5,6'	20.08	8.2	7.82
209	2,2',3,3'4,4',5,5',6,6'	43.72	9.3	nd

nd: not determind

We correlated directly determined log K_{ow} values of PBDEs[6] with their TSA data. With this correlation ($R^2 = 0.996$) we were able to calculate the log K_{ow} values of all 209 PBDEs (Table 3). The resulting log K_{ow} (TSA) values do correspond to the range of published data and the log K_{ow} (GC) data of distinct PBDEs (Tables 2 and 3). We also correlated the log K_{ow} values of reference 6 with the log K_{ow} (HPLC) values determind for PCDE and used this correlation to calculate the log K_{ow} (Cl/Br) values of PBDEs (Table 2)[13].

Table 2. Range of TSA values of PBDEs and the log K_{ow} (TSA) derived therefrom by correlation

PBDE Nr	Bromination	TSA [Å^2]	log K_{ow} (TSA)	log K_{ow} (Cl/Br)
1-3	mono	241.01 - 242.93	6.1 - 6.2	4.8 - 5.2
4 - 15	di	250.88 - 267.4	6.3 - 6.7	5.1 - 5.9
16 - 39	tri	263.21 - 289.9	6.6 - 7.1	5.5 - 6.8
40 - 81	tetra	289.43 - 313.07	7.1 - 7.6	6.5 - 7.4
82 - 127	penta	307.86 - 331.35	7.5 - 8.0	6.9 - 8.1
128 - 169	hexa	324.91 - 347.89	7.9 - 8.4	7.6 -8.5
170 - 193	hepta	350.99 - 364.25	8.3 - 8.7	8.3 - 9.1
194 - 205	octa	360.01 - 378.03	8.6 – 9.0	9.2 - 9.5
205 - 208	nona	378.53 - 381.37	8.9 - 9.0	9.5
209	deca	397.52	9.4	9.9

The log K_{ow} (TSA) values of all 209 PBDE congeners are available at our homepage: http://www.uni-ulm.de/uni/fak/natwis/anachem/

Table 3: TSA values of distinct PBDEs and the log K_{ow} values derived by correlation.

PBDE Nr	Structure	TSA [Å^2]	log K_{ow} ref 6	log K_{ow} (TSA)	log K_{ow} (Cl/Br)	log K_{ow} (GC)	log K_{ow} ref 14
17	2,2',4	268.92	5.74 ± 0.22	5.7	5.5	6.6	5.41 -5.77
28	2,4,4'	280.16	5.94 ± 0.15	6.0	6.3	6.8	5.98 -6.34
47	2,2',4,4'	307.56	6.81 ± 0.08	6.8	nd	7.4	6.55 - 7.03
66	2,3',4,4'	305.47	nd	6.8	6.8	7.3	nd
85	2,2',3,4,4	323.16	7.37 ± 0.12	7.3	7.1	7.7	7.03 - 7.63
99	2,2',4,4',5	325.09	7.32 ± 0.14	7.4	7.4	7.7	7.13 - 7.73
100	2,2',4,4',6	322.68	7.24 ± 0.16	7.3	7.1	7.7	6.86 - 7.46
138	2,2',3,4,4',5'	340.68	nd	7.8	8.3	8.0	nd
153	2,2',4,4',5,5'	342.65	7.90 ± 0.14	7.9	7.9	8.0	7.62 - 8.34
154	2,2',4,4',5,6	340.16	7.82 ± 0.16	7.8	7.6	8.0	7.39 - 8.11
180	2,2',3,4,4',5,5'	359.74	nd	8.4	8.9	8.4	nd
183	2,2',3,4,4',5',6	356.31	8.27 ± 0.26	8.3	nd	8.4	nd
206	2,2',3,3'4,4',5,5',6	378.53	nd	8.9	9.4	8.8	nd
209	2,2',3,3'4,4',5,5',6,6'	397.52	nd	9.5	9.9	9.2	nd

nd: not determined

The results obtained indicate that the calculation and correlation of TSA values is an easy way to get the log K_{ow} (TSA) values of all the PBDE congeners. Our semi-experimental log K_{ow} (GC) approach is a further independent procedure to derive log Kow (GC) values of distinct PBDEs. On this basis approximated physicochemical properties relevant to the environmental distribution of distinct compounds can be calculated[4].

The two approaches presented here can be generally applied to other compounds because GC retention data and total surface area values (TSA) are easily obtainable.

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