VAPOR PRESSURES OF SIX BROMINATED DIPHENYL ETHER CONGENERS

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Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of flame-retardants used in large quantities for a variety of consumer products[1,2]. In 1992, the estimated world annual consumption was 40 kT[2]. The environmental fate of PBDEs has been an issue of concern due to their similarity in structure to PCBs, and especially due to the fact that their levels in human breast milk have increased exponentially from 1972-97[3]. Because of their intrinsic persistence/resistance to degradative processes[5] and their lipophilicity[1], PBDEs are considered to be a threat to the marine environment.

Even though individual PBDEs congeners have been detected in a variety of environmental media[4,6] little is known about their physical-chemical properties. Early work in this area relied on commercial mixtures, since individual congeners were unavailable[2,7]. One drawback to this approach is that commercial formulations contain a mixture of brominated homologues. Here we report for the first time the liquid subcooled vapor pressures (P^o_L) of six PBDE congeners of varying bromine content. The congeners used in this study represent those observed in biota. Values of P^o_L were determined by the method developed by Hinckley *et al.*[8]

In this method, P^o_L is related to retention time (relative to a reference compound) obtained during an isothermal GC run according to the following equations:

$$\ln\left(\frac{t}{t_{ref}}\right) = \left[1 - \left(\frac{\Delta H}{\Delta H_{ref}}\right)\right] \ln P^o_{L,ref} - C$$

$$\ln P^o_L = \left(\frac{\Delta H}{\Delta H_{ref}}\right) \ln P^o_{L,ref} + C$$

Methods and Materials

PBDE congeners used in this study were 2,4,4'-tribromodiphenyl ether (BDE-28), 2,2',4,4'-tetrabromodiphenyl ether (BDE-47), 2,2',3,4,4'- and 2,2',4,4',5-pentabromodiphenyl ether (BDE-85 and 99, respectively), 2,2',3,4,4',5'-hexabromodiphenyl ether (BDE-138) and 2,3,3',4,4',5,6-heptabromodiphenyl ether (BDE-190). Nomenclature of PBDE congeners follows those for

PCBs[9]. Mirex, *t*-chlordane, CB-15, CB-28, CB-52, CB-118, CB-153, CB-180, CB-187, CB-194, CB-206, and CB-209 were all used as standards. Standard compounds were selected to represent a range of vapor pressures. *p,p'*-DDT was used as the reference compound. Solutions of all standards and PBDEs were made in isooctane in the 100 – 300 pg/μL range.

Retention times for all compounds were determined using a 2 m x 0.250 mm DB5-MS column (J&W Scientific). The column was fitted in a Hewlett Packard 5890 GC equipped with a ^{63}Ni electron capture detector kept at 280°C. Injections of 2 μL were made at 280°C in the split/splitless mode using a Hewlett Packard 7673A autoinjector. Ten isothermal runs were performed at oven temperatures ranging from 130°C to 175°C at 5°C intervals. The three higher brominated PBDEs could only be chromatographed at the eight highest oven temperatures.

Results and Discussion

Experimentally determined subcooled liquid vapor pressures, $P^{o}_{L,exp}$, were calculated for all standards and PBDEs at 25°C. Values of $P^{o}_{L,exp}$ for the standards were then compared to literature values, $P^{o}_{L,lit}$, determined in other gas-liquid chromatography-retention time vapor pressure studies. There was a slight deviation of the regression line from the 1:1 ideal correlation. The deviation resulted in the lower vapor pressure compounds, such as CB-194, CB-206, and CB-209, to be overestimated. This deviation, observed in similar studies[8,10,11], may be caused by inaccuracies in $P^{o}_{L,lit}$ values of the standards. $P^{o}_{L,lit}$ values, especially for low vapor pressure compounds, can often vary by at least 2 to 3 times[10]. Vapor pressure-related changes in activity coefficients could also cause the deviation observed[8].

Table 1. Experimentally determined PBDE liquid subcooled vapor pressures.

PBDE Congener	Bromine Number	log $P^{o}_{L,exp}$ (25°C, Pa)
BDE-28	3	-3.84
BDE-47	4	-4.84
BDE-99	5	-5.11
BDE-85	5	-5.81
BDE-118	6	-6.12
BDE-190	7	-7.02

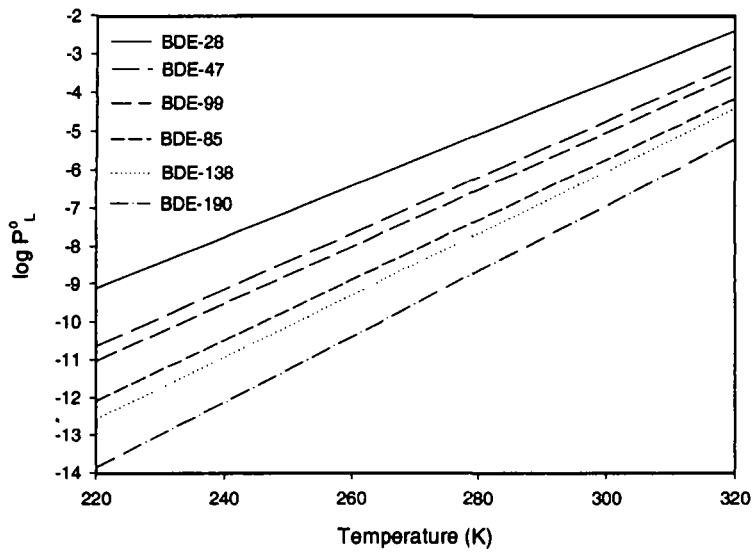
The experimentally derived $P^{o}_{L,exp}$ values for the PBDEs were adjusted for deviations due to changes in activity coefficients by using the regression line equation obtained from the $P^{o}_{L,lit}$ / $P^{o}_{L,exp}$ comparison. The corrected $P^{o}_{L,exp}$ values are listed in Table 1. The correction assumes that the activity coefficients of the PBDEs varied in the same manner as the standard compounds, resulting in an overestimation of $P^{o}_{L,exp}$. This is likely a valid assumption since molecular structures govern physical properties, and the PBDEs are structurally similar to PCBs, which comprised the majority of the standards.

There are few data on PBDE vapor pressures, and those available refer to homologue groups rather than individual congeners. The $P^{o}_{L,exp}$ values determined in this experiment are about ten times greater than P^{o}_{L} determined for tri-, tetra-, penta-, and hexabrominated BDEs by Watanabe and Tatsukawa[7]. However, it is unclear which method was used to obtain P^{o}_{L} values in their study.

Values of $P^{o}_{L,25}$ were found to decrease with an increase in the number of bromine atoms on the

PBDE molecule. Substitution of a bromine for a hydrogen atom resulted in a 5.8-fold decrease in $P^{o}_{L,25}$. Similar values for the slope of log P^{o}_{L} versus chlorine number have been observed for PCBs (slope = -0.655)[9], chlorinated *n*-alkanes (slope = -0.645)[11], and chlorinated benzenes (slope = -0.641)[12]. By comparing the magnitude of the slopes, it appears that addition of a bromine atom causes a greater decrease in P^{o}_{L} than addition of a chlorine. Bromine's greater effect may be explained by its larger size, which causes an increase in intermolecular attractions in organobromine as compared to organochlorine compounds.

Figure 1. Effect of temperature on PBDE vapour pressures.



The variation of P^{o}_{L} with temperature is described by the Clausius-Clapeyron equation, which takes the form:

$$\log P^{o}_{L} = \frac{B}{T} + A$$

where $B = -\Delta H_{vap}/2.303R$. A graphical representation of the Clausius-Clapeyron equation indicates that P^{o}_{L} of PBDEs will increase up to four orders of magnitude over environmentally relevant temperatures (Figure 1).

The results of this experiment show that PBDEs have very low P^{o}_{L}, which are in some instances even lower than CB-209. As found with organochlorine compounds, there is a trend of decreasing P^{o}_{L} with increasing halogen content. In the case of PBDEs, there is approximately a 5.8 fold decrease in P^{o}_{L} for each additional bromine atom. The Clausius-Clapeyron relationship also demonstrates that P^{o}_{L} varies with temperature, with the higher brominated PBDEs showing the greatest variation. All of these results imply that atmospheric transport will not be as significant in the movement of higher brominated PBDEs through the environment as compared to analogous

PCBs. The results also show that there is a need for more work on physical properties of organobromine compounds, since the effect of bromination on physical properties appears to be more extreme than chlorination.

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