



Effect analysis of quantum chemical descriptors and substituent characteristics on Henry's law constants of polybrominated diphenyl ethers at different temperatures



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ABSTRACT

Twelve substituent descriptors, 17 quantum chemical descriptors and 1/T were selected to establish a quantitative structure-property relationship (QSPR) model of Henry's law constants for 7 polybrominated diphenyl ethers (PBDEs) at five different temperatures. Then, the $\lg H$ of 202 congeners at different temperatures were predicted. The variation rule and regulating mechanism of $\lg H$ was studied from the perspectives of both quantum chemical descriptors and substituent characteristics. The R^2 for modeling and testing sets of the final QSPR model are 0.977 and 0.979, respectively, thus indicating good fitness and predictive ability for Henry's law constants of PBDEs at different temperatures. The favorable hydrogen binding sites are the 5,5',6,6'-positions for high substituent congeners and the O atom of the ether bond for low substituent congeners, which affects the interaction between PBDEs and water molecules. $\lg H$ is negatively and linearly correlated with 1/T, and the variation trends of $\lg H$ with temperature are primarily regulated by individual substituent characteristics, wherein: the more substituents involved, the smaller the $\lg H$. The significant sequence for the main effect of substituent positions is *para* > *meta* > *ortho*, where the *ortho*-positions are mainly involved in second-order interaction effect (64.01%). Having two substituents in the same ring also provides a significant effect, with 81.36% of second-order interaction effects, particularly where there is an adjacent distribution (55.02%).

1. Introduction

Commonly added to various industrial materials and home furnishings as additive brominated flame retardants, polybrominated diphenyl ethers (PBDEs) are physically combined with pre-produced polymer and do not react with them via chemical bonds (Luo et al., 2013; Na et al., 2013; Wang et al., 2013). In addition, the relatively low water solubility and vapor pressures of PBDEs suggest they are likely to leach or volatilize from products and sorb onto sediment, soil, and atmospheric particles (Gajewicz et al., 2010; Palm et al., 2002). The widespread use of PBDEs means that they have a worldwide presence in various biotic and abiotic environments, even in the remote areas of the Arctic and Antarctica, producing significant negative effects on nervous systems, endocrine systems and immune systems of wildlife and humans (Darnerud et al., 2015; Möller et al., 2011; Wang et al., 2008). In addition, their strong lipophilicity, persistence, and bioaccumulation potential in the environment, showing similar environmental effects to dioxins (Darnerud et al., 2001; Ji et al., 2011; Lilienthal et al., 2006), means that PBDEs have gained significant attention. Some (penta-BDEs

and octa-BDEs) are classified as persistent organic pollutants (POPs) under the Stockholm Convention (Ashton et al., 2009; Palm et al., 2002).

Physicochemical parameters, particularly partitioning properties such as Henry's law constant (H), vapor pressure, and *n*-octanol/air partition coefficient (K_{OA}), play major roles in the transport and mobility of PBDEs' in the environment. Among these, Henry's law constant is an important indicator of the transfer of organic compounds transfer between the atmosphere and water (Parnis et al., 2015). Fewer than 40 PBDE congeners have been synthesized, which makes it difficult to detect the physical and chemical properties of each compound (Marsh et al., 1999). To assess the overall effect and variation rules of PBDEs more comprehensively, it is important to develop predictive models for physicochemical properties of PBDEs from their molecular structures.

A quantitative structure-property relationship (QSPR) model allows for the study of limited number of compounds to predict the properties of other unknown homologs (Blotvogel et al., 2011). Previous studies have shown that it is feasible to predict the properties or activities for PBDEs with QSPR models, such as the relative retention times (RRT),

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biological toxicity, and K_{OA} , among other properties (Liu et al., 2007; Papa et al., 2011; Roy et al., 2011) via quantum chemical descriptors, topological indices, weighted holistic invariant molecular (WHIM) descriptors, molecular electronegativity distance vectors, molecular connectivity or a combination of different kinds of descriptors. Among them, only the specific meanings of quantum chemical descriptors are direct and helpful for the optimization stage or regulating the environmental behaviors of PBDEs. Additionally, linear solvation energy relationship (LSER), theoretical LSER (TLSER), or poly-parameter linear free-energy relationship (pp-LFER) may be also reliable means for predicting partition coefficients of PBDEs, as demonstrated by Liu et al., in the case of PBDEs–partition coefficients of hydrophobic organic chemicals between low density polyethylene film and water (Liu et al., 2017) and by Hang et al. in the case of PBDEs–theoretical plate number (Hang et al., 2009), but have not been widely used in other properties of PBDEs, especially for Henry's law constants due to the remain limited experimental values.

Because of the large enthalpy change involved in octanol/water to air transfers, K_{OA} and Henry's law constant have strong temperature dependence. Unfortunately, the absence of H , K_{OA} and their temperature-dependence data for PBDEs were limited. Among previous studies, only Chen et al. (2003) has established a QSPR model for the K_{OA} of PBDEs in different temperature only via quantum chemistry descriptors and there is no further analysis. Compared with K_{OA} , Henry's law constant has only been measured for 7 PBDE congeners at five different temperatures, rather rarely. Although Xu et al. (2007) and Papa et al. (2011) have used different parameters to establish the QSPR model of Henry's law constants of 7 PBDE congeners, the existing conditions of less data, not taking temperature into consideration, most selected descriptors reflecting the overall performance of PBDEs molecule and no experimental data divided to testing sets, cannot guarantee the validity of model.

The logarithmic form of Henry's law constant ($\lg H$) was found to be negatively and linearly correlated with $1/T$, and the conventional square of the correlation coefficient (R^2) ranged from 0.92 to 0.99 (Cetin and Odabasi, 2005). However, the QSPR models referenced (Cetin and Odabasi, 2005) were different for each temperature. The good linear correlation between $\lg H$ and T in the work of Cetin and Odabasi (2005) is predominately regulated by the individual identity of each PBDE. Different from descriptors used in previous studies, the abstract and topology, energy, charge, and substituent descriptors are beneficial for explaining the differences in Henry's law constants between different PBDE congeners.

A failing of traditional QSPR models is that they can only provide the predicted equation and significant or influential descriptor. To understand the regulating mechanism of the Henry's law constants among PBDE congeners requires other analytical methods, particularly for the substituent characteristics. Full factor experiment design, which is an important statistical method for assessing the risk of hybrid compounds by the EPA (Svensgaard and Hertzberg, 1994), has become widely used during experimental design to assess the strength of single (major effects) and combined effects (second-order interaction effects) attributable to each experimental factor during target detection, such as the concentration effect in heavy metals and pesticides that affect the adsorption capacity of characteristic pollutants. However, to the best of our knowledge, this method has never before been applied to theoretical studies of substituent characteristics. Using full factorial experimental design to assess substituent position would provide a new approach for exploring the interaction effects between different substituent positions on the $\lg H$ of PBDEs. Therefore, the aim of this study is to develop an integral QSPR model to predict Henry's law constants of 209 PBDEs at different temperatures and then research the variation rule and regulating mechanism among 209 congeners from the perspectives of chemical quantum descriptors (energy, atom charge) and substituent characteristics.

2. Methods

2.1. Experimental data

Henry's law constants of 7 PBDE congeners (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-209) were measured at five different temperatures ranging from 5 to 40 °C using a gas-stripping technique (Cetin and Odabasi, 2005). In our study, the logarithmic form of Henry's law constants ($\lg H$) was treated as a dependent variable for conveniently analyzing the specific transformational $\lg H$ of 7 PBDE congeners listed in Table A1 (supplemental material).

The predicted $\lg H$ values of 209 PBDE congeners at 298.15 K (25 °C), using a full factorial experimental design referenced from the work of Xu et al. (2007), were obtained from an established QSPR model based on electrostatic potential parameters.

2.2. Computational methods and descriptors

The geometries of 7 PBDE congeners in water were fully optimized using a combination of density functional theory (DFT) (Hohenberg and Kohn, 1964) and the polarizable continuum model (PCM) (Cammi et al., 1996) at the B3LYP/6–311 + G(d,p) level. The PCM was used to consider the effect of bulk solvent on the interaction between PBDE congener and water molecules. The PCM-DFT model has been shown to be appropriate for describing some noncovalent interactions (Pan and Bian, 2013; Riley et al., 2007; Sang-Aroon and Ruangpornvisuti, 2008).

Based on the optimized geometries, 17 quantum chemical descriptors for QSPR modeling were obtained from the Gaussian output files (Worrall and Thomsen, 2004). The data obtained included: charge parameters, polarization parameters and energy parameters, and there have been validated via correlation with other properties of PBDEs effectively: the dipole moment (μ , Debye), energy of the highest occupied molecular orbital (E_{HOMO} , eV), energy of the lowest unoccupied molecular orbital (E_{LUMO} , eV), $E_{LUMO}-E_{HOMO}$ (ΔE , eV), $E_{LUMO}+E_{HOMO}$ (E_{SUM} , eV), total energy (TE , eV), most negative atomic partial Mulliken charge in the molecule (q , e), most positive partial Mulliken charge in H atom (qH^+ , e), the mean polarizability (α , 10^{-30} esu), the anisotropy polarizability ($\Delta\alpha$, 10^{-30} esu), the approx. polarizability (α_{xx} , α_{yy} , α_{zz} , α_{xy} , α_{xz} , and α_{yz}), the six components of which reflect perturbations of the polarizability in different coordinates, and the molar volume (V , cm^3/mol).

In addition, 12 substituent descriptors used for QSPR modeling were represented as follows: N_T (total Br atoms number); $N_{2(6)}$, N_2 , and N_6 (Br atoms at *ortho*-positions 2, 2', 6, and 6'); $N_{3(5)}$, N_3 , and N_5 (Br atoms at *meta*-positions 3, 3', 5, and 5'); $N_{(4)}$ (Br atoms at *para*-positions 4 and 4'); N_o (pairs of Br atoms at relative *ortho*-positions in a single phenyl ring); N_m (pairs of Br atoms at relative *meta*-positions in a single phenyl ring); N_p (pairs of Br atoms at relative *para*-positions in a single phenyl ring); N_D (different number of Br atoms between two phenyl rings); and $N_{2,4,6}$ (the sum of *ortho*-substituents and *para*-substituents). The concrete atom mark number was presented in Fig. 1.

All calculations were performed using the Gaussian 09 software package (Frisch et al., 2009). To analyze the interaction mechanism between the PBDE congeners and water molecule further, graphs of the HOMO, LUMO, and the potential energy surface (PES) of 7 congeners were calculated. Then, an explicit water solvent molecule was considered in the PCM-DFT model. Because the H-bonding between the Br atom of PBDE and the hydroxyl H of the water molecule is very weak

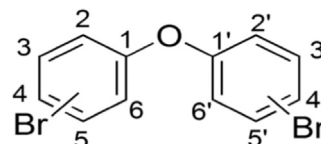


Fig. 1. Atom mark number and molecular geometry of PBDEs.

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