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Research article

Development and evaluation of MTLSER and QSAR models for predicting polyethylene-water partition coefficients

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ABSTRACT

Current study was aimed to make further improvements in measuring low density polyethylene (LDPE) -water partition coefficient (K_{PE-w}) for organic chemicals. Modified theoretical linear solvation energy relationship (MTLSER) model and quantitative structure activity relationship (QSAR) model were developed for predicting K_{PE-w} values from chemical descriptors. With the MTLSE model, α (average molecular polarizability), μ (dipole moment) and q^- (net charge of the most negative atoms) as significant variables were screened. With the QSAR model, main control factors of K_{PE-w} values, such as *CrippenLogP* (Crippen octanol-water partition coefficient), *CICO* (neighborhood symmetry of 0-order) and *GATS2p* (Geary autocorrelation-lag2/weighted by polarizabilities) were studied. As per our best knowledge, this is the first attempt to predict polymer-water partition coefficient using the MTLSE model. Statistical parameters, correlation coefficient (R^2) and cross-validation coefficients (Q^2) were ranging from 0.811 to 0.951 and 0.761 to 0.949, respectively, which indicated that the models appropriately fit the results, and also showed robustness and predictive capacity. Mechanism interpretation suggested that the main factors governing the partition process between LDPE and water were the molecular polarizability and hydrophobicity. The results of this study provide an excellent tool for predicting $\log K_{PE-w}$ values of most common hydrophobic organic compounds, within the applicability domains to reduce experimental cost and time for innovation.

1. Introduction

Passive sampling has become a widely used technique in measuring the concentration of hydrophobic organic compounds (HOCs) in urban air, water bodies or sediment pore water (Moodley et al., 2011; Perks et al., 2017; Zhu et al., 2015). Many different materials have been used as sorbents in various passive sampling devices, including semipermeable membrane devices (SPMD) (Turgut et al., 2017), polyoxymethylene (POM) devices (Beckingham and Ghosh, 2013), low density polyethylene (LDPE) film (Carls et al., 2004; Cornelissen et al., 2008; Zhu et al., 2015), polydimethylsiloxane (PDMS) fibers (Zhang et al., 2014) and polyurethane foam (PUF) device (Bartkow et al., 2004; Nabi and Arey, 2017). Among them, previous studies have shown that thin sheet of LDPE is the cheapest, simplest and effective material for measuring many different classes of HOCs in field and in laboratory

experiments (Liu et al., 2017; Zhu et al., 2015).

The partition coefficients of HOCs between polymer and water (K_{PE-w}) are significant for designing passive sampler devices and calculating chemical concentrations of aqueous phase from LDPE. The partition coefficients are often determined by equilibrating the LDPE with the aqueous phase containing the chemicals. The water phase concentrations of chemicals of interest are often too low and difficult to calculate accurately, especially for very hydrophobic organic compounds, with high octanol-water partition coefficient (K_{ow} , $\log K_{ow} > 6$). As our previous studies have reported that, as the diffusive flux from the aqueous phase to the LDPE strip was very low, the polymer film had to be equilibrated with water or sediment samples for a period of 119–365 days in laboratory (Bao et al., 2011; Cornelissen et al., 2008; Zhu et al., 2015). Therefore, it is difficult to measure K_{PE-w} values for all hydrophobic organic compounds since experimental determination of K_{PE-w}

Abbreviations: HOCs, hydrophobic organic compounds; K_{PE-w} , low density polyethylene-water partition coefficient; MTLSE, modified theoretical linear solvation energy relationship; QSAR, quantitative structure activity relationship; AD, applicability domain; OECD, Organization for Economic Cooperation and Development; K_{ow} , octanol-water partition coefficient; α , average molecular polarizability; q^- , highest formal negative charge; μ , dipole moment; q^+ , most positive atoms; E_{LUMO} , lowest unoccupied molecular orbital of the solute; E_{HOMO} , highest occupied molecular orbital of the solute; *MLR*, stepwise multiple linear regression; *CrippenLogP*, crrippen octanol-water partition coefficient; *CICO*, neighborhood symmetry of 0-order; *GATS2p*, geary autocorrelation-lag2/weighted by polarizabilities; R_{adj}^2 , determination coefficient; Q_{LOO}^2 , leave one out cross-validated; Q_{BOOT}^2 , bootstrap method; *RMSE*, root mean squared error; *VIF*, variance inflation factor; δ , standardized residuals; *h*, leverage values; *MAE*, mean absolute error

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values is generally laborious, time-consuming and expensive (Choi et al., 2013; Zhu et al., 2015).

For organic chemicals, it would be helpful to establish mathematical models for predicting K_{PE-w} values with the physicochemical properties of chemicals of interest. Until now, few models have been reported for accurate calculation of partition coefficient of HOCs. A linear relationship of $\log K_{PE-w}$ values with the logarithm of $\log K_{ow}$, subcooled liquid aqueous solubility ($\log C_{w,sat}$), solubility ($\log S$) and hexadecane-water partitioning coefficient ($\log K_{hdw}$) have been reported, but their results for polymer-water partition coefficient were only applicable to hydrophobic organic compounds with low $\log K_{ow}$ values ($\log K_{ow} < 7.0$) (Hale et al., 2010; Liu et al., 2017; Lohmann, 2012). In addition, a curvilinear relationship between $\log K_{PE-w}$ and the $\log K_{ow}$ was also investigated, with the turning point at 8.0 for K_{ow} (Liu et al., 2017). These models were only related to one or two parameters (variables), reflecting only one adsorption mechanism in partition process. Whereas, a weaker linear relationship was also reported by Liu et al. (2017), who argued that there would be other factors or mechanisms involved in partition process in LDPE for some compounds.

Quantitative structure-activity relationship (QSAR) and quantitative structure-property relationship (QSPR) studies are unquestionably of great importance in modern chemistry and biochemistry (Gadaleta et al., 2016). The concept of QSAR/QSPR is to transform investigations for compounds with desired properties using chemical intuition and experience into a mathematically quantified and computerized form (Dearden, 2016; Karelson et al., 1996). QSAR/QSPR method provides a convenient tool to predict physico-chemical properties of chemicals from their structure descriptors, and it also can provide insight into the main factors that influence physicochemical properties of chemicals (Zhu et al., 2011).

The linear solvation energy relationship (LSER) and the theoretical linear solvation energy relationship (TLSER) are considered as useful modeling methods for predicting partition coefficients or toxicity of solutes (Lyakurwa et al., 2014). The LSER parameters are usually obtained from experimental measurements which are not readily available for most of the polar and non-polar neutral organic chemicals. While, the TLSER parameters can be calculated by quantum chemical methods which is more convenient to develop a model. Nevertheless, most of the TLSER models are developed for predicting toxicity for the aquatic chemical species and only one paper focused on TLSER models for predicting K_{PE-w} values with a low correlation coefficient ($R^2 = 0.78$), which is most likely due to the fact that the average molecular polarizability (α) was not considered in the TLSER model. To make further improvements in measuring K_{PE-w} values, the aim of this study was to develop a modified TLSER (MTLSER) model and a QSAR model by chemical descriptors for predicting polymer-water partition coefficients according to the Organization for Economic Cooperation and Development (OECD) principles for the validation of QSAR models (OECD., 2007). Both the MTLSE models and QSAR models were based on a large data set, including 239 compounds, including most common HOCs, within the applicability domains to reduce experimental cost and time for innovation.

2. Materials and methods

2.1. Data sets

The Experimental values of K_{PE-w} were compiled from previous literature (Tables S1–S7) for seven different classes of HOCs, including 21 polycyclic aromatic hydrocarbons (PAHs) congeners (Adams et al., 2007; Belles et al., 2016; Booij et al., 2003; Choi et al., 2013; Cornelissen et al., 2008; Fernandez et al., 2009; Hale et al., 2010; Müller et al., 2001; Reitsma et al., 2013; Smedes et al., 2009; Zhu et al., 2015), 35 alkylated-PAHs (Adams et al., 2007; Choi et al., 2013; Fernandez et al., 2009; Reitsma et al., 2013), 12 Perdeuterated Parent-PAHs (Adams et al., 2007; Choi et al., 2013; Smedes et al., 2009), 8

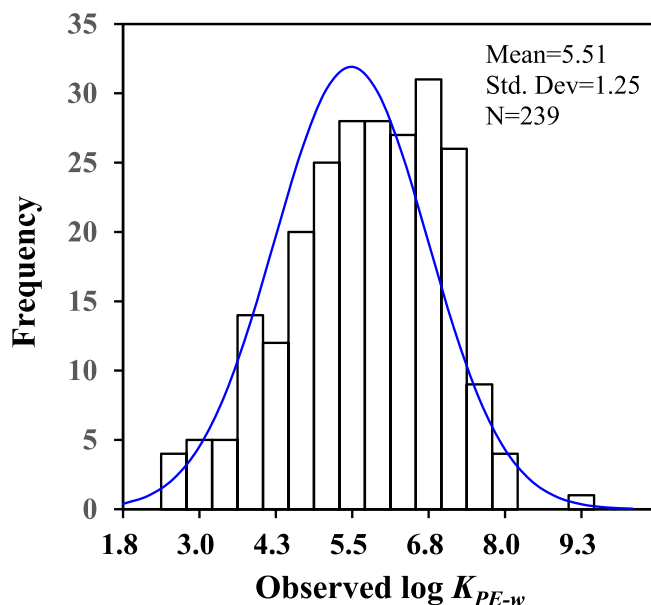


Fig. 1. Distribution of observed $\log K_{PE-w}$ values of data set.

Nitro-PAHs (Belles et al., 2016), 117 polychlorinated biphenyl (PCBs) congeners (Adams et al., 2007; Booij et al., 2003, 2014; Choi et al., 2013; Fernandez et al., 2009; Smedes et al., 2009; Zhu et al., 2015), 19 polybrominated diphenyl ethers (PBDEs) congeners (Bao et al., 2011; Joyce et al., 2015; Sacks, 2010; Zhu et al., 2015) and 27 different organochlorine pesticides (OCPs) (Hale et al., 2010; Joyce et al., 2015; Khairy and Lohmann, 2014; Thompson et al., 2015). Since, K_{PE-w} values were collected from different labs using different laboratory techniques, the average of $\log K_{PE-w}$ values were calculated for the same compound, which are presented in Tables S1–S7 of the Supporting information. 239 chemicals in data sets were collected in current study, with the $\log K_{PE-w}$ values ranging from 2.22 to 8.85. All data were followed a significant normal distribution ($p < 0.05$) and the standard deviation (Fig. 1). To obtain reliable MTLSE and QSAR models, the data set was randomly divided into two parts, training and validation sets in the ratio of 4:1.

2.2. Calculation of molecular descriptors

The molecular structures of the chemicals were obtained from the EPI Suit™ Version 4.11 (EPA, 2015) and were optimized with the MM2 method by the ChemBio3D software (Liu et al., 2016; Schnur et al., 1991). Then, MOPAC 2016 software was applied to generate molecular descriptors (MTLSER parameters) with the minimize energy/geometry method, using keywords: PM7, Dielectric Constant = 78.6, EF, GNORM = 0.01, MULLIK POLAR SHIFT = 80 (MOPAC 2016, 2016). Based on the optimized geometric structures from MOPAC 2016, 1875 molecular descriptors were calculated by using the PaDEL-Descriptor software (Version 2.21) (Yap, 2011). As a result, 1074 descriptors were retained in final set, with the screening methods mentioned in previous study (Liu et al., 2017). According to experience, the calculation of polarizability would fail for the chemical with sulfur atom in its molecular structure. In present study, the parameters of polarizability (α) for three chemicals (EndosulfanI, EndosulfanII and Endosulfan sulfate) were calculated by the equation ($\alpha = 9.81 + 89.1Vi/100$) (Chen et al., 1996; Chen and Wang, 1997). The descriptor of intrinsic molecular volume (Vi) were calculated by using the PaDEL-Descriptor software. By comparing the present results with the reference results and experimental data, it has been proved that the equation is reliable, and it can be used to calculate the polarizability (α) for EndosulfanI, EndosulfanII and Endosulfan sulfate (Table S9 in the Supporting information).

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