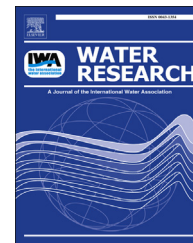




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Prediction of sorption of aromatic and aliphatic organic compounds by carbon nanotubes using poly-parameter linear free-energy relationships

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ABSTRACT

The accurate prediction of distribution coefficients of organic compounds from water to carbon-based nanomaterials (CNM) is of major importance for the understanding of environmental processes and a risk assessment of released CNM. Poly-parameter linear free-energy relationships (ppLFER) have previously been shown to offer such an accurate prediction of sorption processes. The aim of this study was to identify and quantify the contribution of individual molecular interactions to overall sorption by multi-walled carbon nanotubes (MWCNTs). To this end, a large data set of experimental sorption isotherms by MWCNTs of 20 aliphatic and 14 aromatic compounds covering various relevant molecular interactions was produced. A thermodynamic cycle was used to obtain MWCNT-air distribution coefficients ($K_{\text{MWCNT/a}}$) for the interpretation of direct sorbate-MWCNTs interactions. The thereby derived ppLFER $\log K_{\text{MWCNT/a}} = (0.59 \pm 0.59)E + (2.23 \pm 0.59)S + (3.90 \pm 0.67)A + (3.23 \pm 0.71)B + (0.98 \pm 0.17)L - (0.05 \pm 0.50)$ shows the contribution of non-specific interactions, represented by the hexadecane-air partitioning constant (L), and specific interactions related to the solute polarity (S) as well as the H-bond interactions (A , B). Measured MWCNT-water distribution coefficients were clearly more accurately calculated by the ppLFER equations (R^2 0.85–0.86) compared to the classical prediction by single parameter model based on the octanol–water partitioning constant (R^2 0.64–0.78). In addition, the ppLFER presented here allow a more accurately prediction of sorption by MWCNTs compared to literature ppLFER, especially for aliphatic compounds and at environmentally relevant concentrations.

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1. Introduction

In recent years, research on the environmental behaviour of carbon-based nanomaterials (CNM) has received growing attention, while, among others, the impact of CNM on the fate and transport of organic contaminants has been in the focus of researchers. In general, CNM are characterized by strong interactions with organic compounds (Pan and Xing, 2008); however, the influence of molecular structure on overall sorption are yet poorly understood. For example, specific π - π -electron donor-acceptor interactions have been discussed to be responsible for the strong interaction (Pan et al., 2008; Chen et al., 2008, 2007), while sorption of cyclohexane, which can only undergo non-specific interactions, was found to be stronger than of aromatic benzene (Chen et al., 2007). These contradictory observations emphasize the need for a more comprehensive approach to investigate sorption by CNM.

There have been few attempts for the quantitative and qualitative determination of the contribution of multiple types of interactions to overall sorption by CNM (Apul et al., 2013; Xia et al., 2010; Zhao et al., 2014). However, such an approach would be required for *a priori* prediction of sorption of diverse organic compounds by CNM. Poly-parameter linear free-energy relationships (ppLFER) present a promising approach, as they offer the opportunity to capture all relevant molecular interactions that influence the sorption coefficient. Thus, they have higher predictive power than commonly used one-parameter LFER (opLFER) based, e.g., on the octanol–water partitioning constant (K_{ow}) (Goss and Schwarzenbach, 2001). Abraham's ppLFER equations consist of terms describing the individual contributions of molecular interactions using both the properties of the sorbate (solute descriptors) and the sorbent (phase descriptors) (Abraham, 1993; Abraham et al., 2004), which are given by:

$$\log K_{i,1/a} = e_{1a}E_i + s_{1a}S_i + a_{1a}A_i + b_{1a}B_i + l_{1a}L_i + c_{1a} \quad (1)$$

$$\log K_{i,1/w} = e_{1w}E_i + s_{1w}S_i + a_{1w}A_i + b_{1w}B_i + v_{1w}V_i + c_{1w} \quad (2)$$

where $\log K_{i,1/a}$ and $\log K_{i,1/w}$ represent the logarithmic distribution coefficients of a given sorbate *i* between phase 1 and air and between phase 1 and water, respectively. The uppercase letters in Eqs. (1) and (2) denote the solute descriptors representing the solute's capability of exerting individual types of interactions: E_i , the excess molar refraction; S_i , dipolarity/polarizability; A_i , solute hydrogen (H)-bond acidity; B_i , solute H-bond basicity; L_i , logarithmic hexadecane-air partitioning constant; and V_i , McGowan volume of the solute. E_i , V_i , and L_i are descriptors representing non-specific interactions as the cavity formation energy and dispersive van-der-Waals interactions, whereas S_i , A_i , and B_i indicate specific interaction (Goss and Schwarzenbach, 2001). It should be noted that non-specific interactions cannot be fully separated by the ppLFER model, because of inherent correlations between the descriptors. The corresponding lowercase letters denote the phase descriptors and are derived by multiple regression analysis (MRA), and *c* denotes the regression constant. Sorption mechanisms have successfully been determined by ppLFER, for example, from the aqueous phase to activated carbon (Shih and Gschwend, 2009) and to natural organic

matter in soils and sediment (Endo et al., 2008a; Bronner and Goss, 2011).

Most recently, Apul et al. developed a ppLFER model for the prediction of sorption of aromatic compounds by multi-walled carbon nanotubes (MWCNTs) (Apul et al., 2013). However, the developed ppLFER has certain drawbacks. Firstly, only aromatic compounds have been used for the model development. Inaccurate description of sorption properties of MWCNTs can result from the use of a biased probe sorbate set that does not include aliphatic compounds. Secondly, the reported ppLFER did not contain the term for excess molar refraction (E), which also accounts for the contribution of non-specific interactions (Nguyen et al., 2005). A comprehensive discussion of the relevant interactions may not be possible without taking all descriptors into account. As a consequence, there is still improvement necessary for a comprehensive ppLFER development.

Thus, the aim of the study presented here was to derive ppLFER for sorption by MWCNTs in order to investigate the contribution of individual intermolecular interactions to overall sorption and, furthermore, to characterize the sorption properties of MWCNTs. For ppLFER modelling, a probe set of 34 compounds was selected including aliphatic and aromatic compounds featuring various functionalities.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes (C150HP) were purchased from Bayer Material Science (Leverkusen, Germany). Properties of MWCNTs are given elsewhere (Hüffer et al., 2013a). Amorphous carbon was removed by heating MWCNTs to 350 °C for 1 h (Chen et al., 2007). Thirty-four sorbates were selected as probe compounds based on previous publications (Endo et al., 2008a, 2009a) covering a broad range of various substance classes including the following: apolar aliphatics (alkanes), monopolar aliphatics (ethers and halogenated alkenes), bipolar aliphatics (alcohols), non-polar aromatics (BTEX and PAHs), monopolar aromatics (e.g., anisole), and bipolar aromatics (phenols). Note that the present study vastly extends the diversity of chemicals from previous works (Apul et al., 2013; Xia et al., 2010). The probe compound set used in this study did not cover very large hydrophobic compounds, multifunctional polar compound (e.g., pesticides), and poly-fluorinated chemicals, which are thus out of the calibration domain of the resulting models from this study. Basic physico-chemical properties and ppLFER descriptors of used sorbates are given in Tables S1 and S2 of the Supplementary Material, respectively. Stock solutions of sorbates were prepared weekly in methanol by dissolving the pure compound and kept at 4 °C in the dark.

2.2. Sorption batch experiments

MWCNTs (2–5 mg) were weighted into 20-mL amber head-space screw vials. Then, 10–20 mL of 10 mM CaCl_2 as background solution were added into the vials, which were then closed with screw caps with butyl/PTFE-lined septa. After the

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