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Linear solvation energy relationships (LSER) for adsorption of organic compounds by carbon nanotubes

Gamze Ersan [a], Onur G. Apul [b], Tanju Karanfil [a, *]

[a] Department of Environmental Engineering and Earth Sciences, Clemson University, Anderson, SC 29625, USA
[b] Department of Civil, Environmental and Sustainable Engineering, Arizona State University, Tempe, AZ 85287, USA

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ABSTRACT

The objective of this paper was to create a comprehensive database for the adsorption of organic compounds by carbon nanotubes (CNTs) and to use the Linear Solvation Energy Relationship (LSER) technique for developing predictive adsorption models of organic compounds (OCs) by multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). Adsorption data for 123 OCs by MWCNTs and 48 OCs by SWCNTs were compiled from the literature, including some experimental results obtained in our laboratory. The roles of selected OCs properties and CNT types were examined with LSER models. The results showed that the r^2 values of the LSER models displayed small variability for aromatic compounds smaller than 220 g/mol, after which a decreasing trend was observed. The data available for aliphatics was mainly for molecular weights smaller than 250 g/mol, which showed a similar trend to that of aromatics. The r^2 values for the LSER model on the adsorption of aromatic and aliphatic OCs by SWCNTs and MWCNTs were relatively similar indicating the linearity of LSER models did not depend on the CNT types. Among all LSER model descriptors, V term (molecular volume) for aromatic OCs and B term (basicity) for aliphatic OCs were the most predominant descriptors on both type of CNTs. The presence of R term (excess molar refractivity) in LSER model equations resulted in decreases for both V and P (polarizability) parameters without affecting the r^2 values. Overall, the results demonstrate that successful predictive models can be developed for the adsorption of OCs by MWCNTs and SWCNTs with LSER techniques.

1. Introduction

Carbon nanotubes (CNTs) show a great affinity for adsorption of organic compounds (OCs) in water (Pan et al., 2008; Apul et al., 2013a,b; 2015). Adsorption of more than one hundred OCs by CNTs have been extensively investigated in the literature in more than 50 studies (e.g., Yang et al., 2006; Peng et al., 2003; Su et al., 2010; Yu et al., 2011; 2012a,b; Wang et al., 2012; Abdel Salam and Burk, 2010; Chen et al., 2009; Lin et al., 2008; Pyrzynska et al., 2007; Lu et al., 2006; Liu et al., 2014; Carabineiro et al., 2012; Long and Yang, 2001). Collecting OC adsorption data experimentally is a cost, labor and time intensive task. Therefore, linear solvation energy relationships (LSER) can be developed utilizing the available adsorption isotherms of the literature, and these models can be used for predicting the adsorption of untested OCs by CNTs. In addition, LSER models can be instrumental in examining the adsorption mechanism(s) of OCs onto CNTs.

LSER is a poly-parameter equation that is developed using ordinary linear regression and a predetermined set of solvatochromic descriptors as independent variables. In the past, LSER models have been developed for predicting OCs adsorption by activated carbons (ACs) (Kamlet et al., 1985; Blum et al., 1994; Shih and Gschwend, 2009; Dickenson and Drewes, 2010). In the last five years, they were also implemented for predicting adsorption of OCs by CNTs (Xia et al., 2010; Apul et al., 2013a,b; 2015; Zhao et al., 2014; Hüffer et al., 2014; Yu et al., 2015). These studies are summarized in Table 1. Of these studies, Xia et al (2010), Apul et al. (2013a,b)., and Zhao et al. (2014) investigated the predictive model development for adsorption of aromatic OCs by MWCNTs, Hüffer et al. (2014) focused on adsorption of aromatic and aliphatic OCs by MWCNTs. Recently, Apul et al. (2015) evaluated the predictive model development for adsorption of aliphatic OCs by MWCNTs and SWCNTs and Yu et al. (2015) examined the adsorption of aromatic OCs by MWCNTs and SWCNTs (Table 1). To date, no study has been

* Corresponding author.
E-mail address: tkaranf@clemson.edu (T. Karanfil).

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Table 1
Literature review on LSER models for adsorption of OCs by CNTs.

No	Authors	Type of OCs	Number of OCs	Type of CNT	Oxygen content (%)	Parameters used	Adsorption descriptors
1	Xia et al., 2010	Aromatic	28	MWCNTs	<5	A, B, V, P, C	logK
2	Apul et al., 2013a,b	Aromatic	29	MWCNTs	<5	A, B, V, P, C	$logK_{inf} - K_{0.01} - K_{0.1}$
		Aromatic	30	MWCNTs	<5	A, B, V, P, C	$logK_{inf}$
3	Zhao et al., 2014	Aromatic	16	MWCNT	–	A, B, V, P, R, C	C_e/C_s-(0–5)
		Aromatic	10	Oxidized-MWCNTs	–	A, B, V, P, R, C	C_e/C_s-(0–5)
4	Hüffer et al., 2014	Aromatic	14	MWCNT	<2	A, B, V, P, R, L, C	$logK_{d/a}$ at10^6 Cs
		Aliphatic	20	MWCNT	<2	A, B, V, P, R, L, C	$logK_{d0.01,0.001}$
5	Apul et al., 2015	Aliphatic	10	MWCNT	5	A, B, V, P, R, C	$logK_{d,500,750,1000}$[a]
		Aliphatic	10	SWCNT	9	A, B, V, P, R, C	$logK_{d,5,10,25,50,100,250,500,750,1000}$[a]
6	Yu et al., 2015	Aromatic	67	MWCNTs	<10	A, B, V, P, R, C	$logK_{d,0.00001,0.0001,0.001,0.01,0.1}$
		Aromatic	40	SWCNTs	<10	A, B, V, P, R, C	$logK_{d,0.00001,0.0001,0.001,0.01,0.1}$
7	This study	Aromatic	94	MWCNT	<5	A, B, V, P, R, C	$logK_{d,0.0001,0.001,0.01,}$
			36	SWCNT	<10	A, B, V, P, R, C	$logK_{d,0.0001,0.001,0.01,}$
		Aliphatic	29	MWCNTs	<5	A, B, V, P, R, C	$logK_{d,0.0001,0.001,0.01,}$
			12	SWCNTs	<10	A, B, V, P, R, C	$logK_{d,0.0001,0.001,0.01,}$

[a] Single point adsorption descriptors were used at different aqueous concentrations (ppb).

conducted to develop LSER models and compare the molecular interactions for adsorption of aromatic and aliphatic OCs by SWCNTs and MWCNTs simultaneously. In this study, adsorption data of 123 OCs by MWCNTs and 48 OCs by SWCNTs were compiled from the literature, including some experimental results obtained in our laboratory (Apul et al., 2013a,b; 2015) and predictive LSER models were trained and validated. To the best our knowledge, this study is currently the most comprehensive LSER modeling effort in the literature to elucidate the adsorption of OCs by CNTs (Table 1).

The main objectives of the study were to: (i) develop poly-parameter LSERs for adsorption of OCs by CNTs, (ii) evaluate the role of selected OC properties on LSER models, (iii) compare adsorption of OCs by MWCNTs and SWCNTs side-by-side, and (vi) compare the findings with the LSER models presented in the peer-reviewed literature.

2. Materials and methods

2.1. Data collection and organization

A comprehensive literature review was conducted to collect adsorption isotherm data for aromatic and aliphatic compounds by SWCNTs and MWCNTs. A database was created for adsorption of 123 OCs (i.e., 94 aromatic and 29 aliphatic compounds) on MWCNTs from 59 studies and 48 OCs (i.e., 36 aromatic and 12 aliphatic compounds) on SWCNTs from 19 studies (Tables S1–S4 in the Supporting Information (SI)). For MWCNTs, 70 out of 94 aromatic compounds had molecular weight lower than 200 g/mol, and the rest higher than 200 g/mol. Aliphatic compounds, except 1,2-dibromo-3-chloropropane and hexachloroethane, had molecular weight lower than 200 g/mol. For SWCNTs, 23 out of 36 aromatic compounds had molecular weight lower than 200 g/mol. Aliphatic compounds, except 1,2-dibromo-3-chloropropane, had molecular weight lower than 200 g/mol. The adsorption isotherm data for single solute OCs were collected from literature under similar experimental conditions (i.e., temperature was about at 25–30 °C and in distilled deionized water) for the LSER modeling. Type and surface chemistry of the carbonaceous adsorbents have been shown to impact the adsorption of OCs (e.g., Karanfil and Kilduff, 1999; Zhang et al., 2009, 2010). The adsorption data for MWCNTs and SWCNTs with less than 5% and 10% of oxygen content were used in the modeling, respectively, to be able to compare the data obtained from literature (as shown in Table 1).

2.2. Determination of single point adsorption descriptor (K_d)

Single point adsorption descriptors ($K = q_e/C_e$, where q_e is solid phase equilibrium concentration and Ce is liquid phase equilibrium concentration) at three different C_e values, 0.01%, 0.1%, and 1% of the aqueous solubility of each adsorbate were calculated and represented with $K_{d,0.0001}$, $K_{d,0.001}$ and $K_{d,0.01,}$ respectively. The details of $K_{d,0.0001}$, $K_{d,0.001}$ and $K_{d,0.01}$ determination were provided in the SI section and in one of our previous publications (Apul et al., 2013a,b).

2.3. LSER model training

Adsorption of OCs by CNTs is controlled by a number of physicochemical interactions, some of which are described with solvatochromic descriptors as independent variables in the LSER model (Apul et al., 2013a,b). Solvatochromic theory explains the adsorption interactions among adsorbate, adsorbent, and solvent with solute specific descriptors representing cavity formation, dipolar interactions and hydrogen bonding interactions. The LSER model has the following form:

$$\log K = aA + bB + vV + pP + rR + c$$

Briefly, A, B, V, P and R terms are adsorbate molecular descriptors. A is the hydrogen bond donating ability (acidity), B is the hydrogen bond accepting ability (basicity), V ((cm^3 mol^{-1})/100)) is the molecular volume, P is the polarizability and dipolarity term, R is the (cm^3/10) excess molar refractivity. The R descriptor is intercorrelated with the V descriptor to some extent because the cavity term also captures the size-dependent non-specific interactions. Although these two descriptors (V and R) cannot be distinctly separated, they encompass both the cavity formation and non-specific attraction energies. Lastly, c is the regression constant and a, b, v, p and r are the regression coefficients. All solvatochromic descriptors were obtained from Absolv module of ADME Suite 5.0 software.

2.4. Statistical methods

Multiple linear regression was employed to develop correlations between adsorption descriptors and solvatochromic descriptors. Fitting equations were obtained using SAS v.9.3 software. The goodness of the fit was examined by the coefficient of determination (r^2). The regression models were evaluated by the *p*-values presented in analysis of variance (ANOVA). The *p*-value less than