



Applicability of the linear solvation energy relationships in the prediction for adsorption of aromatic compounds on activated carbons from aqueous solutions



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ABSTRACT

A correlation capable of predicting adsorption capacities from the commonly available physicochemical properties of an adsorbate is of great significance to the engineering design of adsorption process. Apart from van der Waals force, dipole–dipole, induced dipole–dipole, and hydrogen-bonding donor–acceptor interactions exist between aromatic compounds (AOCs) and activated carbons. Correlations between the solubility normalized Freundlich affinity coefficients (K_{FS}) of six AOCs on four activated carbons and the linear solvation energy relationship (LSER) variables of the AOCs were established. The modeling results demonstrate that the LSER model could be applied to predict the adsorption of AOCs on the activated carbons with K_{FS} as a measure of the relative interaction strengths between the adsorbents and the adsorbates. Although derived from the properties of the adsorbates, the LSER modeling parameters were correlated with the surface chemistry of the studied activated carbons, suggesting that the LSER models could also reflect the natures of the adsorbents.

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1. Introduction

Adsorption is one of the most widely used technologies for organic contaminant removal from aqueous streams in water treatment [1]. A large quantity of adsorbents has been produced to meet the demand for removal of the massive types of organic compounds in waste streams. However, there are only limited experimental adsorption isotherms being available for the preliminary design of adsorption process. Time, cost, and toxicity may prevent the extensive collection of experimental adsorption data [2]. Therefore, for the sake of preliminary design, a correlation capable of predicting adsorption equilibrium capacities from commonly available physicochemical properties of these compounds is highly needed. Up to now, most of the correlations are based either on the Polanyi adsorption potential theory or the linear solvation energy relationships (LSERs) [2–7].

The Polanyi potential theory assumes that there is a fixed space surrounding the adsorbent surface where adsorption occurs [3]. The van der Waals forces are assumed to be responsible for the adsorption. Therefore, it is only applicable to nonspecific adsorption, but not applicable in cases where dipole–dipole, induced dipole–dipole, and hydrogen-bonding donor–acceptor interactions exist. However, in aqueous adsorption, those interactions are ubiq-

uitous and play a significant role. Hence, LSERs were put forward by Kamlet and coworkers to consider the chemical properties including nonspecific dipolarity/polarizability, hydrogen bonding, and the free energy of solute partitioning into solvent cavities [4,5]. In late 1990s, the LSER model was developed with some new descriptors [6,7]. After that, to the best of our knowledge, research efforts have been mainly focused on the application of LSERs for prediction of solubility, partition coefficient, and toxicity of various organics [8–12], with little development in the model itself.

The use of LSERs in adsorption on activated carbon is very powerful in understanding both adsorption interactions [9,13,14] and adsorbent properties [15,16]. For example, Burg et al. concluded that the LSER approach could be used to assess the selectivity of activated carbons toward pollutants like volatile organic compounds in terms of gas–solid interactions [15,16].

In the LSER model, chemical properties are related to: (a) the molecular structure through the solvation energy of a solute with solvent molecules, and (b) the energy variation through formation of electrostatic and hydrogen bonds between the solute and the surrounding solvent molecules [5]. The formed electrostatic and hydrogen bonds stabilize the solvent molecule cavity and keep the solute inside it. The equation of one specific property (SP) that related with the solute–solvent interactions contains three simple and explicit terms:

$$SP = \text{cavity term} + \text{dipolar term} + \text{hydrogen-bonding terms} \quad (1)$$

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For adsorption, the overall adsorption energy may consist of five interaction energy (IE) components: IE between adsorbate and adsorbent, IE between solvent and adsorbent, IE between solvent and adsorbate, IE between adsorbed adsorbates, and IE between solvent molecules. If considering the adsorbent as a second solvent, the five IE terms correspond to the above three terms in Eq. (1) and can be represented by the four energy terms in the following equation:

$$SP = c + mV_i/100 + s\pi^* + z\beta + h\alpha \quad (2)$$

The symbols in Eq. (2), including c , m , s , z , h , are fitting constants. The definitions for the terms in Eq. (2) are as follows: “The endoergic term $mV_i/100$ represents the free energy required to separate the solvent molecules and provide a suitably configured cavity for the contaminant molecule. $V_i/100$ is the intrinsic (van der Waals) molecular volume scaled by a factor of 100 for magnitudes that are comparable to the other three variables. The dipolar-polarizability term, $s\pi^*$, represents the (typically) exoergic effects of solute–solvent dipole–dipole and dipole-induced dipole interactions and π^* is a measure of the molecule’s ability to stabilize a neighboring charge or dipole through nonspecific dielectric interactions [5].” The hydrogen-bonding term $z\beta$ represents the exoergic effects of hydrogen bonding involving the solvent as hydrogen bond donor acid (HBD) and the solute as hydrogen bond acceptor base (HBA). The term $h\alpha$ is the counterpart of the term $z\beta$, with the solute as HBD and the solvent as HBA.

Eq. (2) has been successfully applied to describe K_{ow} (octanol–water partition coefficient) and S_w (water solubility) with self-consistent rationale [4,17]. Similar approaches have been made to describe the adsorption coefficient. For example, the earlier work of Kamlet and coworkers on a small aliphatic compound set established the following equation [4]:

$$\log k = -1.93 + 3.065V_m/100 + 0.56\pi^* - 3.20\beta \quad (3)$$

where k represents the infinite dilution partition coefficient between the adsorbed solutes and the solutes in the solution phase, and V_m is the solute molar volume at 20 °C.

The lack of dependence on α in Eq. (3) might be explained by that the hydrogen bond acceptor ability of water is too weak to be noticeably enhanced by hydrogen bond donating strength of the solute. This is supported by the fact that the α value of pure water is 1.17 while the β value is only 0.48 [7,18]. For aliphatic compounds, Eq. (3) was of fair quality. When aromatic compounds (AOCs) were included, however, the quality of the correlations dropped dramatically. The question of aromatic adsorbates was left unanswered [4]. To solve this problem, Luehrs and coworkers developed another equation (Eq. (4)) by introducing two more index parameters to Eq. (3) [18].

$$\log k = -0.37 + 3.41V_i/100 - 1.07\beta + D + 0.65P \quad (4)$$

where D is an index parameter including the effects of the carbon types, the temperature, and the length of adsorption equilibrium time, and P is an index parameter for the flatness of the molecule. P is defined to be unity if there is an aromatic system in the system or if there is a double bond or series of conjugated double bonds with no more than one non-H atom beyond the double bond and zero otherwise [18].

Apparently, such a definition of P is rather coarse and cannot appropriately reflect the difference between planar and nonplanar compounds. Besides, it is hard to get the values of k and D . The lack of dependence on α and π^* in Eq. (4) might suggest that some interactions between the adsorbate and the adsorbent were masked by their stronger interactions with water.

By defining an adsorbate-adsorbent interaction index, $A = kS_w$, and combining Eq. (3) with a correlation equation for $\log S_w$, Kamlet

and coworkers established the following equation (Eq. (5)) which is independent of the nature of the second phase [4].

$$\log A = -1.50 - 0.15V_m/100 + 1.04\pi^* + 2.06\beta \quad (5)$$

The important difference and conceptual advantage of the A index over the k index is that A isolates the adsorbate-adsorbent interaction from the adsorbate-solvent interaction. Thus, the adsorbability, as measured by k , increases with increasing V_m because of the decrease in S_w with increasing V_m . With the adsorption and solubility effects being unraveled, the adsorbate-adsorbent interaction index A decreases with increasing V_m , which correctly reflects the molecular sieving effect. Being a product of the infinite dilution partition coefficient of the adsorbate between the adsorbent and the solvent and the saturated aqueous concentration of the adsorbate, A cannot be taken as an absolute measure of the adsorption capacity of the adsorbent to adsorbate, but an index of relative interaction strengths. For a given adsorbent, A reflects the relative adsorption susceptibilities of the adsorbates, whereas for a given adsorbate, A reflects the relative adsorption capabilities of the adsorbents.

As aforementioned, k as a descriptor of adsorption is not easily available. Assuming that the adsorbate is tested at a concentration low enough to be on the linear portion of the isotherm, k should have a reasonably constant value. However, in practice isotherm data often do not reach that portion of the curve due to either the difficulty in analytical determination or the high actual concentration level being concerned. Arbuckle [19] and Abe et al. [20] took the value at the equilibrium concentration of 1 mg/L as k , which is apparently not sufficiently low for some chemicals, whereas Blum et al. [21] used the partition coefficient at the minimum concentration tested as the k or got the k by back-calculation with the Freundlich K_F and n values at the lowest concentration tested. As pointed out by Blum et al. [21], some ambiguity regarding the correct interpretation of k is unavoidable when data are taken from literature sources. Therefore, a more universal and precise descriptor of the adsorbability is of great significance for the application of LSERs to describe the adsorption of various adsorbates according to their physicochemical properties.

In the present work, four activated carbons with different origins or surface chemistry were used for the adsorption of six AOCs with various physicochemical properties. Both single- and multiple-parameter LSERs were used for the modeling of adsorption isotherms. In our previous work, Freundlich adsorption affinity coefficients (K_F or K_{FS}) have been successfully applied to correlate the adsorption of organic solutes from aqueous solutions with the structural characteristics of activated carbons [22]. K_F or K_{FS} was also employed in this work as a practical descriptor to correlate the adsorption affinities of adsorbents to adsorbates with the physicochemical properties of the adsorbates. The developed correlations may help the preliminary design for removal of a large quantity of chemicals from water streams at a low cost and without time-consuming data collection.

2. Experimental

2.1. Materials

Phenol (PN, 99.5+%), nitrobenzene (NB, 99.0+%), biphenyl (BP, 99.5+%), 2-phenylphenol (2PP, 99+%) and 2-nitrobiphenyl (2NP, 97+%) were purchased from Sigma–Aldrich Chemical Co. Analytical standard grade 2-chlorobiphenyl (2CP) was purchased from Fluka Chemical Co. The physicochemical properties of the studied AOCs are listed in Table 1.

A coconut shell-based granular activated carbon, OLC (Calgon Carbon Co.), and a phenol formaldehyde-based activated carbon fi-

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