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Predicting solvent-water partitioning of charged organic species using quantum-chemically estimated Abraham pp-LFER solute parameters

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HIGHLIGHTS

- Ion pp-LFER descriptors are obtained from molecular structure and quantum chemistry.
- Improved solvent-water partition predictions over direct quantum chemical calculations.
- Improved prediction of partition coefficients for anions vs. neutral descriptor pp-LFERs.
- Comparable prediction of partition coefficients for anions vs. neutral descriptor pp-LFERs.

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ABSTRACT

Methods for obtaining accurate predictions of solvent-water partitioning for neutral organic chemicals (e.g., K_{ow}) are well-established. However, methods that provide comparable accuracy are not available for predicting the solvent-water partitioning of ionic species. Previous methods for addressing charge contributions to solvent-water partitioning rely on charged solute descriptors which are obtained from regressions to neutral species descriptors as well as charged descriptors which are specific to unique charge-functionalities and structural moieties. This paper presents a method for obtaining Abraham poly-parameter linear free energy relationship (pp-LFER) descriptors using quantum chemical calculations and molecular structure, only. The method utilizes a large number of solvent-water systems to overcome large errors in individual quantum chemical computations of ionic solvent-water partition coefficients. The result is a single set of quantum-chemically estimated Abraham solute parameters (QCAP) which are solvent-independent, and can be used to predict the solvent-water partitioning of ionic species.

Predictions of solvent-water partition coefficients for ionic species using quantum-chemically estimated Abraham parameters (QCAPs) are shown to provide improved accuracy compared over both existing Absolv-estimated Abraham solute parameters (AAP) as well as direct a priori quantum chemical (QC) calculations for partitioning of anionic solutes in 4 organic solvent-water systems (RMS = 0.740, 2.48 and 0.426 for the Absolv, QC and QCAP methods, respectively). For quaternary amine cations in the octanol-water system the RMS errors of the solvent-water partition coefficients were larger and similar between the two Abraham models (RMSE = 0.997 and 1.16, for the AAP and QCAP methods, respectively). Both methods showed significant improvement over direct QC calculations (RMSE = 2.82).

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1. Introduction

Methods for obtaining accurate predictions of solvent-water partition coefficients for neutral species (e.g., K_{ow}) are well-established (EPA, 2014; Chiou et al., 2005; Endo and Goss, 2014; Hansch et al., 1968; Leo and Weininger, 1989; Platts et al., 2000; Schüürmann et al., 2006). Approaches exist which can be separated into several groups: (1) direct a priori quantum chemical (QC) calculation of the solvent-water partition coefficient (Klamt, 2011; Klamt et al., 2010; Lin and Sandler, 2002; Marenich et al., 2009) (e.g., using the programs COSMO-SAC, COSMO-RS, SMD), (2) polyparameter linear free energy relationships (pp-LFERs) (Endo and Goss, 2014; Platts et al., 2000; Liang, 2016; Xiong et al., 2014; Marenich et al., 2012) which utilize physical-chemical molecular

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descriptors of the solute and solvent species, and (3) fragment-based (EPA, 2014) models that rely on group additive (fragment) contributions and corrections.

For neutral species, the accuracies of these methods are comparable. RMS errors for octanol-water systems of 0.690, 0.560, and 0.476 for the three approaches have been observed, respectively (EPA, 2014; Liang, 2016; Xiong et al., 2014). Similar predictive accuracies, however, have not been observed for these methods for charged species. Direct quantum chemical computations of solvent-water partition coefficients for both anions and cations (Marenich et al., 2012) have been shown to result in significantly larger errors. Previous work by Marenich et al. (2012) has shown large errors in the QC computed partition coefficients for both anions and cations in acetonitrile-, methanol-, and dimethylsulfoxide-water systems (SMD (Marenich et al., 2009), RMSE = 4.35, N = 88, Table A.1-a in supplemental information). Even within the same QC method (e.g., SMD), errors have been shown to range over several orders of magnitude between different solvent-water systems (e.g., acetone-water vs. methanol-water) with significant evidence of solvent-based prediction bias (Table A.1-a,b in supplemental information).

1.1. *Abraham poly-parameter linear free energy relationship (pp-LFER)*

A popular model for predicting partitioning of neutral organic compounds between organic solvent phases and water is the Abraham poly-parameter linear free energy relationship (pp-LFER) (Endo and Goss, 2014; Hansch et al., 1968; Platts et al., 2000; Abraham and Zhao, 2004; Goss, 2006; Goss and Schwarzenbach, 2001). The model relies directly on the physical chemical properties of the solute and its individual interactions with the solvent and water phases (e.g., dispersion forces, hydrogen bond acidity, and cavitation energy). For neutral organic chemicals, the Abraham pp-LFER describing the partitioning between an organic phase (j) and water can be expressed as:

$$\log\left(K_{i,\,j}\right) = e_jE_i + s_jS_i + a_jA_i + b_jB_i + v_jV_i + c_j \tag{1}$$

where the upper case letters represent the solute (i) contributions to the binding energy; E_i, molar refractivity, S_i, polarizability, A_i, hydrogen bond donating; and B_i, hydrogen bond accepting capacities, and V_i, the energy required to form a cavity. The lower case letters represent the complementary solvent (j) contributions, relative to water; e_j, excess molar refractivity, s_j, polarizability, a_j, hydrogen bond accepting and b_j, donating, and v_j, cavitation energy terms, respectively. The c_j term accounts for any non-specific binding interactions and varies with the units of $K_{i,\,j}$.

Previous work by Zhao & Abraham (Abraham and Zhao, 2004; Zhao and Abraham, 2005) have attempted to predict the octanol-water partition coefficients of a set of quaternary amine cations using the Abraham solute descriptors for a comparable neutral species. They do this by neutralizing the molecule, replacing the charged nitrogen atom, $[N^+]$ with a neutral carbon atom, C. The solute descriptors are then estimated using the method of Platts (Platts et al., 2000) with the experimentally derived octanol-water solvent-system descriptors (Abraham et al., 2004). Octanol-water partition coefficients are then predicted, using the solute descriptors for the neutralized species and the experimental solvent-water system parameters (Eq. (1)). While a clear trend was demonstrated within homologous series and structurally similar solutes, the error in the predictions were large (RMSE = 2.66, N = 544)[18].

Alternatively, (Abraham and Zhao, 2004) propose a modification to the Abraham pp-LFER in which charge-group specific ion descriptors for ionic solutes (J^+ and J^-) are used to describe the additional charge-based hydrogen bond acidity/basicity of the ionic species. In a recent publication, (Abraham and Acree, 2010a) used this modification to the Abraham pp-LFER and applied it to a set of anionic solutes in multiple solvent-water systems. The modified pp-LFER for charged organic solute partitioning is:

$$\log\left(K_{i,\,j}\right) = e_jE_i^* + s_jS_i^* + a_jA_i^* + b_jB_i^* + v_jV_i^* + j_j^+J_i^+ + j_j^-J_j^- + c_j \tag{2}$$

where the asterisks denote the Abraham solute parameters for the charged species, which are either obtained using experimental partition coefficients and a multiple linear regression (as described by Platts et al. 2000) or are obtained using linear regressions for each solute descriptor which are functions of the neutral species solute descriptors (Abraham and Acree, 2010a).

The new product terms, $j_j^+J_i^+$ and $j_j^-J_i^-$, are included to account for the interaction of the charged moiety on the ionic solute with the solvent-water system, and is specific to the type of charge moiety (e.g., carboxylic (COO^-) acidic, pyridinium (Py^+) and amine (R_3NH^+) basic structural moieties) (Abraham and Acree, 2010a, 2010b). Abraham et al. propose that the solute parameters for the charged compounds (including the new J^+ and J^- terms) can be obtained directly from the Abraham solute parameters for the neutral species (Abraham and Acree, 2010a). For the excess molar refractivity, E, and the McGowan volume, V, it is assumed that they are constantly offset for the ionic species, with a slope of 1.00 and an intercept which is unique to the charge group structural moiety (Abraham and Acree, 2010a, 2010b). However, for the remaining descriptors (S, A, B, and $J^{+,-}$) the relevant regression parameters and their estimated equation coefficients for relating the neutral and charged Abraham solute parameters vary significantly and depend on the charged structural moieties of the ionic species (i.e., carboxylate-based anions vs. pyridinium-based cations) (Abraham and Acree, 2010a, 2010b). For example, for the carboxylic-functional acids, the polarizability, S, is a function of the excess molar refractivity, E, the polarizability, S, and the McGowan volume, V, of the neutral species, with a fitted slope for each parameter and a fitted intercept. However, for the amine cations the polarizability is a function of the polarizability, S, and the hydrogen bond basicity, B, of the neutral compound, with a different slope value for the neutral polarizability term.

Consequently, these relationships are not universally applicable to new organic ionic species with different charge sites (e.g., imidazolium-based cations, phenolic-based anions). Further, the number of fitting parameters is large, relative to the number of data points used to obtain the regression parameters. For 78 carboxylate ions and 26 amines, there are 20 and 13 fitted equation coefficients required, respectively, to obtain the charged solute parameters using this method. While the models perform well for each individual charge moiety type, they cannot be applied universally and new equations as well as equation constants must be derived for each unique charge moiety. Consequently, a method for obtaining the charged Abraham solute parameters which is independent of the chemical class and has universal applicability is desired.

Alternatively, (Zissimos et al., 2002) have shown that for neutral species, Abraham solute descriptors can be obtained through regressions to the sigma profile moments of the electron density of the molecule (computed from the COSMOTherm (Klamt, 2011; Klamt et al., 2010) program), with separate regressions for each Abraham solute descriptor (*E*, *S*, *A*, *B*, and *V*). (Cho et al., 2015) have extended this method to include charged species. However, predictions of the Abraham solute descriptors for *S*, *A*, and two new sorbate descriptors, J^+, and J^- (charged descriptors for cations and

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