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Enthalpy of solvation correlations for gaseous solutes dissolved in dibutyl ether and ethyl acetate

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Abstract

Data have been assembled from the published literature on the enthalpies of solvation for 68 compounds dissolved in dibutyl ether and for 79 compounds dissolved in ethyl acetate. It is shown that an Abraham solvation equation with five descriptors can be used to correlate the experimental enthalpies of solvation in dibutyl ether and ethyl acetate to within standard deviations of 1.88 and 2.16 kJ/mol, respectively. The derived correlations provide very accurate mathematical descriptions of the measured enthalpy of solvation data at 298 K, which in the case of ethyl acetate span a range of about 71 kJ/mol. Mathematical correlations have also been derived for predicting the enthalpies of solvation in dibutyl ether, ethyl acetate, water and 15 additional organic solvents based on the Goss modified version of the Abraham model. Expressions based on this latter model were found to correlate the experimental enthalpies of solvation to within an overall average standard deviation of 2.29 kJ/mol for the 18 solvents studied.

Keywords: Enthalpy of solvation; Linear free energy relationships; Molecular solute descriptors; Predictive methods

1. Introduction

Quantitative structure-property relationship (QSPR) models represent a consolidated computational method to mathematically correlate physical and thermodynamic properties of chemical compounds to molecular features (called molecular descriptors) that range from structural and topological indices to electronic and quantum-chemical properties. Properties that have been correlated include solute solubilities in both water and in organic solvent media, solute partitioning between water and an immiscible (or partly miscible) organic solvent, enthalpies of solvation, oral bioavailability, human and rat intestinal adsorption of drug molecules, drug distribution from blood to the various body organs, toxicities of organic compounds to several aquatic organisms, and the minimum alveolar concentration for inhalation anesthesia to rats. The molecular descriptors may

be of either experimental origin or calculated based solely on molecular structure considerations.

Previously, we have applied the Abraham solvation parameter model to describe the enthalpies of solvation of organic solutes and gases in water, $\Delta H_{\text{Solv,W}}$, [1]

$$\Delta H_{\text{Solv,W}} \text{ (kJ/mol)} = -13.310(0.457) + 9.910(0.814)\mathbf{E} \\ + 2.836(0.807)\mathbf{S} - 32.010(1.102)\mathbf{A} \\ - 41.816(0.781)\mathbf{B} - 6.354(0.200)\mathbf{L}$$

(1)

with $N = 368$, S.D. $= 3.68$, $R^2 = 0.964$, $R_{\text{adj}}^2 = 0.964$, $F = 1950.5$.

$$\Delta H_{\text{Solv,W}}(\text{kJ/mol}) = -6.952(0.651) + 1.415(0.770)\mathbf{E} \\ - 2.859(0.855)\mathbf{S} - 34.086(1.225)\mathbf{A} \\ - 42.686(0.850)\mathbf{B} - 22.720(0.800)\mathbf{V}$$

(2)

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(with $N = 369$, S.D. = 4.04, $R^2 = 0.959$, $R^2_{adj} = 0.958$, $F = 1688.2$) and in methanol, $\Delta H_{Solv,MeOH}$, [2]

$$\Delta H_{Solv,MeOH}(kJ/mol) = -6.366(0.454) - 2.506(0.898)\mathbf{E}$$
$$- 1.807(0.907)\mathbf{S} - 37.692(1.163)\mathbf{A}$$
$$- 15.466(0.904)\mathbf{B} - 7.674(0.140)\mathbf{L}$$
(3)

(with $N = 188$, S.D. = 2.749, $R^2 = 0.982$, $R^2_{adj} = 0.982$, $F = 2039.707$)

$$\Delta H_{Solv,MeOH}(kJ/mol) = 1.636(0.737) - 11.797(1.103)\mathbf{E}$$
$$- 9.336(1.161)\mathbf{S} - 41.378(1.504)\mathbf{A}$$
$$- 15.984(1.165)\mathbf{B} - 27.891(0.668)\mathbf{V}$$
(4)

(with $N = 188$, S.D. = 3.549, $R^2 = 0.971$, $R^2_{adj} = 0.970$, $F = 1211.855$) and in hexane [3], heptane [4], hexadecane [4], cyclohexane [4], benzene [4], toluene [5], carbon tetrachloride [5], chloroform [6], 1,2-dichloroethane [6], ethanol [2], 1-butanol [2], 1-octanol [1], propylene carbonate [7], and dimethyl sulfoxide [7]. Numerical values in parenthesis give the standard error for the respective equation coefficient. Each correlation was based on experimental enthalpy of solvation data for 90 or more different solutes. Here and elsewhere, N corresponds to the number of solutes, R denotes the correlation coefficient, S.D. is the standard deviation and F corresponds to the Fisher F-statistic.

The independent variables in Eqs. (1)–(4) are as follows: $\mathbf{E}$ is the solute excess molar refraction modeling the solute polarizability due to the n- and/or π-electrons in excess of that of a n-alkane of comparable size, $\mathbf{S}$ is the solute descriptor for the dipolar/polarizability character of the molecule, $\mathbf{A}$ and $\mathbf{B}$ are the solute overall or summation hydrogen bond acidity and basicity, $\mathbf{V}$ is the McGowan volume, and $\mathbf{L}$ is the logarithm of the gas phase dimensionless Ostwald coefficient of solute into hexadecane at 298.15 K. The first four descriptors can be regarded as measures of the tendency of the given solute to undergo various solute–solvent interactions. The last descriptor, $\mathbf{L}$, is a measure of the solvent cavity term that will accommodate the dissolved solute, and will thus be a measure of solute size. General dispersion interactions are also related to solute size, hence $\mathbf{L}$ will also describe the general solute–solvent interactions. The model considers solute descriptors to be temperature independent values. In fact the $\mathbf{E}$ and $\mathbf{L}$ solute descriptors are defined by experimental properties measured at specified temperatures of 293.15 and 298.15 K, respectively. The regression coefficients and constants were obtained by regression analysis of the experimental data for a given process, which in the case of Eqs. (1)–(4) was the enthalpic change resulting from the transfer of the gaseous solute into the respective liquid solvent

In the present communication, we report the Abraham model correlations for enthalpies of solvation of organic solutes and gases in both ethyl acetate and dibutyl ether. Predictive correlations are also derived for a second QSPR model, namely the Abraham model as modified by Goss [8–12]

$$\Delta H_{Solv}(kJ/mol) = c + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + l \cdot \mathbf{L} + v \cdot \mathbf{V}$$
(5)

where the lower case letters c, s, a, b, l and v represent the properties of the solvent. The latter model uses the five Abraham solute descriptors $\mathbf{S}$, $\mathbf{A}$, $\mathbf{B}$, $\mathbf{V}$ and $\mathbf{L}$. The Abraham $\mathbf{E}$ solute descriptor in equations such as Eqs. (1) and (3) is replaced by the McGowan volume (Abraham $\mathbf{V}$ solute descriptor), which is easily calculable from the individual atomic sizes and number of bonds in the molecule [13]. In the Abraham model, the $\mathbf{V}$ descriptor generally appears in the expression for solute transfer between two condensed phases

$$SP = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + v \cdot \mathbf{V}$$
(6)

where SP is some property of a series of solutes in a fixed phase. Eq. (6) has been used on few occasions to describe gas-to-condensed phase transfer processes in predictive applications where the $\mathbf{L}$-descriptors were not known.

2. Data sets and computational methodology

Our search of the chemical literature found a compilation of the enthalpy of solvation data for 59 solutes dissolved in dibutyl ether [14], plus a large number of papers [15–48] that reported experimental enthalpies of solution of liquid and crystalline organic compounds in the two solvents of interest. The latter data were determined by either direct calorimetric methods or calculated based on the temperature dependence of measured infinite dilution activity coefficient data, and the published values were converted to gas-to-organic solvent enthalpies of transfer by

Liquid solutes : $\quad \Delta H_{Solv} = \Delta H_{Soln} - \Delta H_{Vap,298K}$ (7)

Crystalline solutes : $\quad \Delta H_{Solv} = \Delta H_{Soln} - \Delta H_{Sub,298}$ (8)

subtracting the solute's standard molar enthalpy of vaporization [49], $\Delta H_{Vap,298K}$, or standard molar enthalpy of sublimation [50], $\Delta H_{Sub,298K}$, at 298.15 K.

Based on an initial assessment of the available experimental data, we eliminated from consideration all experimental data that pertained to temperatures outside of the temperature range of 283–318 K. Enthalpies of solvation are temperature dependent, and we did not want to introduce large errors in the database by including experimental data far removed from 298 K. Also excluded were values based on solubility measurements where the equilibrium solid phase might be a solvated form of the solid solute. For several solutes there were multiple, independently determined values. In such cases, we selected direct calorimetric data over indirect values based on the temperature dependence of measured solubilities or infinite dilution activity coefficients. Using the fore-mentioned criteria, 68 molar enthalpies of solvation in dibutyl ether and 79 molar enthalpies of solvation in ethyl acetate were selected for regression analysis. The experimental $\Delta H_{Solv,BE}$ and $\Delta H_{Solv,EA}$ values are listed in Tables 1 and 2, respectively.