Examination of hydrogen-bonding interactions between dissolved solutes and alkylbenzene solvents based on Abraham model correlations derived from measured enthalpies of solvation

Mikhail A. Varfolomeev [a], Ilnaz T. Rakipov [a], William E. Acree Jr. [b,*], Michela Brumfield [b], Michael H. Abraham [c]

[a] Chemical Institute, Kazan Federal University, Kremlevskaya 18, Kazan 420008, Russia
[b] Department of Chemistry, 1155 Union Circle # 305070, University of North Texas, Denton, TX 76203-5017, USA
[c] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

ABSTRACT

Enthalpies of solution at infinite dilution of 48 organic solutes in mesitylene and 81 organic solutes in *p*-xylene were measured using isothermal solution calorimeter. Enthalpies of solvation for 92 organic vapors and gaseous solutes in mesitylene and for 130 gaseous compounds in *p*-xylene were determined from the experimental and literature data. Abraham model correlations are determined from the experimental enthalpy of solvation data. The derived correlations describe the experimental gas-to-mesitylene and gas-to-*p*-xylene solvation enthalpies to within average standard deviations of $1.87 \, \text{kJ} \, \text{mol}^{-1}$ and $2.08 \, \text{kJ} \, \text{mol}^{-1}$, respectively. Enthalpies of $X-H \cdots \pi$ ($X-O$, N, and C) hydrogen bond formation of proton donor solutes (alcohols, amines, chlorinated hydrocarbons etc.) with mesitylene and *p*-xylene were calculated based on the Abraham solvation equation. Obtained values are in good agreement with the results determined using conventional methods.

1. Introduction

Enthalpies of solvation provide valuable insight regarding solute–solvent interactions and molecular complexation in fluid solution. Measured enthalpies of solvation, $\Delta_{\text{solv}}H^\circ$, can be used to test solution models and quantum chemical computations [1,2]. Experimental $\Delta_{\text{solv}}H^\circ$ can be utilized to extrapolate gas-to-liquid partition coefficients to system temperatures slightly higher and/or lower than the measurement temperature through standard thermodynamic relationships [3]. Solvation enthalpies have also been applied in chemical kinetic studies to model solvent effects on reaction rate parameters [4,5].

The present study continues our systematic combined experimental and theoretical examination of the transfer of nonelectrolyte solutes from the gas phase to organic solvents and to water. To date enthalpies of solvation have been reported for organic solutes dissolved in both dichloromethane and 1,4-dioxane [6], for amines dissolved in aliphatic alcohols and *vice versa* [7–9], for formamide and methylformamide derivatives dissolved in organic solvents [10], and for select ketones, nitriles and alkyl acetates

dissolved in methanol and 1-octanol [11]. Results of the calorimetric measurements have provided thermodynamic functions pertaining to the formation of hydrogen-bonded complexes. Mathematical expressions have also been developed for calculating $\Delta_{\text{solv}}H^\circ$ values of organic vapors and gases dissolved in water [12] and 26 different organic solvents based on the Abraham solvation parameter model. The specific organic solvents studied include four alkanes (hexane [13], heptane [14], hexadecane [14] and cyclohexane [14]), two aromatic hydrocarbons (benzene [14] and toluene [15]), four chloroalkanes (chloroform [16], carbon tetrachloride [15], 1,2-dichloroethane [16], and dichloromethane [6]), three ethers (di-*n*-butyl ether [17], tetrahydrofuran [18] and 1,4-dioxane [6]), six primary alcohols (methanol [19], ethanol [19,20], propan-1-ol [18], butan-1-ol [19], octan-1-ol [12] and 2-methylpropan-1-ol [20]), two secondary alcohols (propan-2-ol [20] and butan-2-ol [20]), one tertiary alcohol (2-methylpropan-2-ol [21]), and six other organic solvents (acetonitrile [22], acetone [22], ethyl acetate [17], propylene carbonate [23], N,N-dimethylformamide [21], and dimethylsulfoxide [23]). The derived correlations back-calculate the observed $\Delta_{\text{solv}}H^\circ$ data to within an overall average standard deviation of less than $\pm 3 \, \text{kJ} \, \text{mol}^{-1}$.

The purpose of the present communication is to develop Abraham model correlations for enthalpies of solvation in mesitylene and *p*-xylene, and illustrate how the derived

correlations can be used to obtain hydrogen-bond enthalpies for proton donors with aromatic hydrocarbon solvents. We report experimental enthalpy of solution data, $\Delta_{soln}H°$ for 48 and 81 organic solutes dissolved in mesitylene and *p*-xylene, respectively. Enthalpies of solvation are calculated by combining the measured $\Delta_{soln}H°$ values with published enthalpy of vaporization, $\Delta_{vap}H$, and enthalpy of sublimation, $\Delta_{sub}H°$, data [24]. Abraham model correlations:

$$\Delta_{solv}H° = c_l + e_l \times \mathbf{E} + s_l \times \mathbf{S} + a_l \times \mathbf{A} + b_l \times \mathbf{B} + l_l \times \mathbf{L} \quad (1)$$

$$\Delta_{solv}H° = c_v + e_v \times \mathbf{E} + s_v \times \mathbf{S} + a_v \times \mathbf{A} + b_v \times \mathbf{B} + v_v \times \mathbf{V} \quad (2)$$

have been derived for calculating the gas-to-mesitylene and gas-to-*p*-xylene solvation enthalpies of organic solutes from available experimental $\Delta_{solv}H°$ data. The uppercase letters ($\mathbf{E}$, $\mathbf{S}$, $\mathbf{A}$, $\mathbf{B}$, $\mathbf{L}$ and $\mathbf{V}$) in Eqs. (1) and (2) represent a set of numerical descriptors that characterize the solute's ability to interact with surrounding solvent molecules, whereas the lowercase letters (c_l, e_l, s_l, a_l, b_l, l_l, c_v, e_v, s_v, a_v, b_v, v_v) are a set of system coefficients that describe the complementary properties of the process. In the present case the coefficients describe the properties of mesitylene and *p*-xylene in regards to enthalpic interactions governing the transfer of organic vapors and gases into the respective organic solvents.

Solute descriptors are defined as follows: $\mathbf{E}$ denotes the solute excess molar refraction that reflects the solute's ability to interact with the surrounding solvent molecules through π- and lone-electron pairs, $\mathbf{S}$ is the solute dipolarity/polarizability parameter, $\mathbf{A}$ and $\mathbf{B}$ are measures of the solute's hydrogen-bond acidity and basicity, $\mathbf{V}$ is the McGowan volume of the solute in units of $(dm^3\,mol^{-1})/100$, and $\mathbf{L}$ is the logarithm of the solute's gas phase dimensionless Ostwald partition coefficient into hexadecane at 298 K. The first four descriptors can be regarded as measures of the tendency of the given compound to undergo various solute–solvent interactions. The latter two descriptors, $\mathbf{V}$ and $\mathbf{L}$, are both measures of solute size, and so will be measures of the solvent cavity term that will accommodate the dissolved solute. General dispersion forces are also related to solute size; thus both $\mathbf{V}$ and $\mathbf{L}$ will also describe the general solute–solvent interactions.

The product of the solute and solvent coefficients describe a particular type of solute–solvent interaction. Hydrogen-bond interactions are given by the products $a \times \mathbf{A}$ and $b \times \mathbf{B}$ which take into account the possibility that the solute might be a H-bond donor ($a \times \mathbf{A}$) and/or a H-bond acceptor ($b \times \mathbf{B}$). Hydrogen-bond enthalpies, $\Delta_{HB}H$, have been calculated for select proton donor solutes with mesitylene and *p*-xylene using the calculated a and b Abraham model equation coefficients. The calculated $\Delta_{HB}H$ numerical values are compared to values based on Solomonov method [25], and to $\Delta_{HB}H$ values for respective proton donor solute-benzene and proton donor solute-toluene weak hydrogen-bond complexes.

2. Experimental

Mesitylene (Acros Organics, mass fraction purity min. 0.97) was dried with $CaCl_2$ and distillated from sodium. *p*-Xylene (Sigma–Aldrich, mass fraction purity min. 0.99) was used without further purification. Organic solutes studied in this work were of commercial origin with the mass fraction purity no less than 0.98. They were purified before use by standard methods [26]. Quality of chemicals was controlled using gas chromatograph with flame ionization detector. The purities of the chemicals, as determined by gas chromatographic analysis, were no less than 0.995 mass fraction. The residual water content was checked by Karl Fischer titration. In general it did not exceed 0.002.

Calorimetric measurements were carried out using isothermal solution calorimeter TAM III at $T = 298.15 \pm 0.01$ K. The detailed procedure of dissolution experiments was described previously [27]. The calorimetric cell is a glass vessel equipped with a gold stirrer, a Joule heater, and a thermistor. In each experiment it was charged with 100 mL of a solvent. Titration technique was used for measurements of solution enthalpies of liquid solutes. According to standard procedure small portions of liquid solute (10–20 μL) were added to the solvent using an electronically operated microliter syringe equipped with a long gold cannula with the tip immersed in the measuring cell. Obtained calorimetric curve was used for determination of heat effect of each addition. Cylindrical glass ampoules were used for dissolution of solid samples. In each experiment they were filled with the sample (0.01–0.05 g), sealed, weighed (± 0.01 mg), inserted in the sample holder, and immersed into the solvent. After thermal equilibration with the solvent the ampoule was broken and the temperature change in the cell was registered. Calorimeter apparatus was calibrated by the dissolution

Table 1
Enthalpies of solution $(kJ\,mol^{-1})$ at infinite dilution of different organic solutes in mesitylene measured in this work at 298.15 K and atmospheric pressure.

N	Solute	$\Delta_{soln}H°{,}^{A/Mes}/$ $(kJ\,mol^{-1})$
1	Acetonitrile	3.91 ± 0.02[a]
2	Acetophenone	1.33 ± 0.06
3	Anthracene	22.51 ± 0.21
4	Biphenyl	17.20 ± 0.04
5	Butyl acetate	-0.09 ± 0.01
6	Butyl benzoate	-0.21 ± 0.01
7	Butyronitrile	1.62 ± 0.02
8	2-Chlorophenol	3.80 ± 0.03
9	4-Chlorophenol	14.29 ± 0.16
10	Decane	1.45 ± 0.02
11	Decan-1-ol	14.95 ± 0.10
12	Dodecane	1.72 ± 0.02
13	Dichloromethane	-1.32 ± 0.05
14	*N,N*-Dimethylacetamide	1.92 ± 0.06
15	*N,N*-Dimethylformamide	2.50 ± 0.18
16	Ethanol	16.10 ± 0.03
17	Ethyl acetate	1.15 ± 0.06
18	Ethyl benzoate	1.02 ± 0.04
19	Heptane	1.14 ± 0.03
20	Hexane	1.05 ± 0.03
21	Hexan-1-ol	15.61 ± 0.15
22	Indole	13.60 ± 0.12
23	Methanol	15.03 ± 0.15
24	2-Methoxyphenol	6.78 ± 0.10
25	3-Methoxyphenol	5.28 ± 0.05
26	4-Methoxyphenol	24.71 ± 0.16
27	Methyl acetate	2.32 ± 0.11
28	Methyl benzoate	1.50 ± 0.03
29	*N*-Methylimidazole	5.87 ± 0.02
30	Naphthalene	18.20 ± 0.05
31	Nitromethane	4.33 ± 0.08
32	2-Nitrophenol	18.24 ± 0.03
33	Octane	1.19 ± 0.02
34	Octan-1-ol	15.56 ± 0.03
35	4-Picoline	1.54 ± 0.05
36	Piperidine	2.65 ± 0.03
37	Propan-1-ol	16.33 ± 0.11
38	Propionitrile	2.48 ± 0.07
39	Propyl acetate	0.95 ± 0.02
40	Propyl benzoate	0.39 ± 0.03
41	Pyrrole	5.18 ± 0.07
42	Pyrrolidine	2.17 ± 0.06
43	1,3-Diphenylbenzene	20.98 ± 0.06
44	1,4-Diphenylbenzene	25.64 ± 0.28
45	Tetrahydrofuran	-0.25 ± 0.02
46	Tri-*n*-butylamine	-0.32 ± 0.03
47	Triethylamine	-0.17 ± 0.01
48	1,3,5-Triphenylbenzene	19.06 ± 0.23

[a] Standard deviation of the mean of replicate measurements. The individual measurements are given in Table S1 of the Supplementary material.