



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



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## ARTICLE INFO

### Article history:

Received 20 June 2014

Received in revised form 19 August 2014

Accepted 23 August 2014

Available online 27 August 2014

### Keywords:

Enthalpy of solution

Enthalpy of solvation

Mesitylene

*p*-Xylene

Molecular interactions

Hydrogen bonding

## 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 kJ mol<sup>-1</sup> and 2.08 kJ mol<sup>-1</sup>, respectively. Enthalpies of X–H···π (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.

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## 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  $\pm 3$  kJ mol<sup>-1</sup>.

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

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

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

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

have been derived for calculating the gas-to-mesitylene and gas-to-*p*-xylene solvation enthalpies of organic solutes from available experimental  $\Delta_{\text{soln}}H^\circ$  data. The uppercase letters (**E**, **S**, **A**, **B**, **L** and **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: **E** denotes the solute excess molar refraction that reflects the solute's ability to interact with the surrounding solvent molecules through  $\pi$ - and lone-electron pairs, **S** is the solute dipolarity/polarizability parameter, **A** and **B** are measures of the solute's hydrogen-bond acidity and basicity, **V** is the McGowan volume of the solute in units of ( $\text{dm}^3 \text{mol}^{-1}$ )/100, and **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, **V** and **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 **V** and **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,  $\Delta_{\text{HB}}H$ , 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  $\Delta_{\text{HB}}H$  numerical values are compared to values based on Solomonov method [25], and to  $\Delta_{\text{HB}}H$  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  $\text{CaCl}_2$  and distilled 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  $\mu\text{L}$ ) 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 ( $\pm 0.01$  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 ( $\text{kJ mol}^{-1}$ ) at infinite dilution of different organic solutes in mesitylene measured in this work at 298.15 K and atmospheric pressure.

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

<sup>a</sup> Standard deviation of the mean of replicate measurements. The individual measurements are given in Table S1 of the Supplementary material.

**Table 2**

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

N	Solute	$\Delta_{\text{soln}}H^{\circ, A/Xyl}/(\text{kJ mol}^{-1})$
1	Acetone	$1.87 \pm 0.01^a$
2	Acetonitrile	$0.49 \pm 0.01$
3	Acetophenone	$1.66 \pm 0.03$
4	Adamantane	$12.10 \pm 0.15$
5	Aniline	$6.22 \pm 0.03$
6	Anthracene	$24.48 \pm 0.04$
7	Benzonitrile	$0.98 \pm 0.02$
8	Butyl acetate	$-0.33 \pm 0.02$
9	Biphenyl	$16.99 \pm 0.13$
10	Butan-1-ol	$14.97 \pm 0.03$
11	Butyl benzoate	$0.23 \pm 0.01$
12	Butyronitrile	$0.77 \pm 0.01$
13	Butanone	$0.95 \pm 0.01$
14	1-Chlorobutane	$-1.07 \pm 0.01$
15	1-Chloronaphthalene	$0.00 \pm 0.01$
16	2-Chlorophenol	$3.97 \pm 0.04$
17	12-Crown-4	$1.49 \pm 0.05$
18	15-Crown-5	$2.27 \pm 0.04$
19	Decane	$1.95 \pm 0.01$
20	Decan-1-ol	$14.20 \pm 0.05$
21	Diethyl ether	$0.90 \pm 0.02$
22	Dibutyl ether	$-0.09 \pm 0.001$
23	1,4-Dichlorobenzene	$15.56 \pm 0.18$
24	Dichloromethane	$-1.82 \pm 0.02$
25	1,2-Dichloropropane	$-0.79 \pm 0.01$
26	<i>N,N</i> -Dimethylacetamide	$2.18 \pm 0.01$
27	<i>N,N</i> -Dimethylformamide	$2.97 \pm 0.01$
28	Dimethyl sulfoxide	$6.75 \pm 0.01$
29	2,6-Dimethoxyphenol	$25.01 \pm 0.37$
30	1,4-Dioxane	$1.33 \pm 0.01$
31	1,3-Diphenylbenzene	$22.44 \pm 0.08$
32	Docosane	$81.85 \pm 0.63$
33	Dodecane	$2.20 \pm 0.06$
34	Eicosane	$71.89 \pm 0.17$
35	Ethanol	$15.56 \pm 0.01$
36	Ethyl acetate	$0.59 \pm 0.01$
37	Ethyl benzoate	$0.49 \pm 0.01$
38	Ethyl salicylate	$1.07 \pm 0.02$
39	Fluoranthene	$17.32 \pm 0.07$
40	Hexane	$1.29 \pm 0.03$
41	Hexadecane	$3.06 \pm 0.04$
42	Heptane	$1.44 \pm 0.02$
43	Heptan-2-one	$-0.24 \pm 0.01$
44	Hexan-1-ol	$15.17 \pm 0.09$
45	Iodobenzene	$-0.04 \pm 0.01$
46	Indole	$13.71 \pm 0.03$
47	Mesitylene	$0.11 \pm 0.02$
48	Methanol	$14.82 \pm 0.03$
49	2-Methoxyphenol	$6.37 \pm 0.01$
50	3-Methoxyphenol	$8.32 \pm 0.01$
51	4-Methoxyphenol	$27.62 \pm 0.06$
52	Methyl acetate	$1.87 \pm 0.01$
53	<i>N</i> -Methylaniline	$3.06 \pm 0.01$
54	Methyl benzoate	$1.23 \pm 0.02$
55	2-Methylpropan-2-ol	$16.05 \pm 0.43$
56	<i>N</i> -Methylimidazole	$5.57 \pm 0.03$
57	Methyl propionate	$0.74 \pm 0.01$
58	Methyl salicylate	$1.93 \pm 0.03$
59	Naphthalene	$18.15 \pm 0.05$
60	Nitromethane	$3.56 \pm 0.06$
61	Nonan-2-one	$-0.50 \pm 0.02$
62	Octan-2-one	$-0.46 \pm 0.01$
63	Octan-1-ol	$14.72 \pm 0.13$
64	Pentan-1-ol	$14.88 \pm 0.03$
65	Pentan-2-one	$0.17 \pm 0.01$
66	2-Picoline	$1.00 \pm 0.01$
67	3-Picoline	$0.92 \pm 0.01$
68	4-Picoline	$1.33 \pm 0.01$
69	Piperidine	$3.52 \pm 0.05$
70	Propan-1-ol	$15.30 \pm 0.06$
71	Propionitrile	$0.67 \pm 0.01$
72	Propyl acetate	$-0.05 \pm 0.001$
73	Propyl benzoate	$-0.09 \pm 0.01$
74	Propylene carbonate	$5.97 \pm 0.03$
75	Pyrazole	$25.72 \pm 0.69$

**Table 2** (Continued)

N	Solute	$\Delta_{\text{soln}}H^{\circ,A}/\text{Xyl}/(\text{kJ mol}^{-1})$
76	Pyridine	1.62 ± 0.01
77	Pyrrole	4.20 ± 0.04
78	Pyrrolidine	2.79 ± 0.01
79	Tri- <i>n</i> -butylamine	1.47 ± 0.05
80	Triethylamine	-0.03 ± 0.001
81	Tri- <i>n</i> -propylamine	1.11 ± 0.04

<sup>a</sup> Standard deviation of the mean of replicate measurements. The individual measurements are given in Table S2 of the Supplementary material.

of potassium chloride and propan-1-ol in water. The averaged values obtained were  $\Delta_{\text{soln}}H^{\text{KCl}/\text{H}_2\text{O}} = 17.41 \pm 0.04 \text{ kJ mol}^{-1}$  ( $T = 298.15 \text{ K}$ ,  $m = 0.02783 \text{ mol kg}^{-1}$ ) and  $\Delta_{\text{soln}}H^{\text{PrOH-1}/\text{H}_2\text{O}} = -10.16 \pm 0.03 \text{ kJ mol}^{-1}$  ( $T = 298.15 \text{ K}$ ) which corresponds to the standard data [28,29]. Dissolution experiments for every solute–solvent system were reproduced at least 4 times (see Supplementary material Tables S1 and S2). Analysis of solution enthalpies measured at different concentrations of solutes did not show any concentration dependencies (at the concentrations used). Consequently calorimetric experiments were carried out under infinite dilution conditions. Averaged values of solution enthalpies of organic solutes at infinite dilution in mesitylene and *p*-xylene are presented in Tables 1 and 2, respectively.

### 3. Results and discussion

A search of the published literature found gas-to-mesitylene solvation enthalpy data,  $\Delta_{\text{soln}}H^{\circ,A}/\text{Mes}$ , for an additional 46 solutes [30–38], which when combined with our measured data in Table 1 gives a total of 94 solutes for which solute descriptors and  $\Delta_{\text{soln}}H^{\circ,A}/\text{Mes}$  are known. The experimental  $\Delta_{\text{soln}}H^{\circ,A}/\text{Mes}$  values of the 94 solutes are compiled in Table 3 along with the numerical values of the Abraham solute descriptors. A preliminary regression analysis identified both 2,2,4,4-tetramethylpentanon-3-one and tetracyanoethylene to be outliers. The experimental  $\Delta_{\text{soln}}H^{\circ,A}/\text{Mes}$  values for 2,2,4,4-tetramethylpentanon-3-one and tetracyanoethylene differed from the values calculated from the preliminary correlation equations by more than four standard deviations. The likely reason that these two solutes are outliers is that the calculated solute descriptors were based on very limited experimental data. The two compounds are seldom used in partitioning studies. Preliminary regression analysis also yielded a very small numerical value for the *b*-coefficients and the standard error in the *b*-coefficient was larger than the actual numerical value. A negligible *b* coefficient is not unexpected for mesitylene. The *b* coefficient measures the solvent's ability to act as a hydrogen-bond donor, and mesitylene does not possess any acidic hydrogens. Tetracyanoethylene and 2,2,4,4-tetramethylpentanon-3-one were removed from the dataset, and the *b*-coefficients were set equal to zero. The final derived Abraham model correlations for the gas-to-mesitylene solvation enthalpies

$$\Delta_{\text{soln}}H^{\circ,A}/\text{Mes}(\text{kJ mol}^{-1}) = -5.488(0.490) + 6.646(0.657)\mathbf{E} \\ - 9.602(0.617)\mathbf{S} - 10.828(0.913)\mathbf{A} \\ - 9.538(0.130)\mathbf{L} \quad (3)$$

(with  $N = 92$ ,  $SD = 1.55$ ,  $R^2 = 0.992$ ,  $F = 2876$ )

$$\Delta_{\text{soln}}H^{\circ,A}/\text{Mes}(\text{kJ mol}^{-1}) = 2.940(0.829) - 3.805(0.814)\mathbf{E} \\ - 18.981(0.916)\mathbf{S} - 14.011(1.294)\mathbf{A} \\ - 34.238(0.660)\mathbf{V} \quad (4)$$

(with  $N = 92$ ,  $SD = 2.18$ ,  $R^2 = 0.986$ ,  $F = 1452$ ) described the experimental values to within overall standard deviations of  $SD = 1.55$

$\text{kJ mol}^{-1}$  and  $SD = 2.18 \text{ kJ mol}^{-1}$ . The experimental data covers a fairly large interval of  $\Delta_{\text{soln}}H^{\circ,A}/\text{Mes}$  values that ranges from  $\Delta_{\text{soln}}H^{\circ,A}/\text{Mes} = -15.42 \text{ kJ mol}^{-1}$  for perfluoroheptane to  $\Delta_{\text{soln}}H^{\circ,A}/\text{Mes} = -128.74 \text{ kJ mol}^{-1}$  for 1,3,5-triphenylbenzene. No loss descriptive ability was observed from the elimination of the  $b_l \times \mathbf{B}$  and  $b_v \times \mathbf{B}$  terms. Figs. 1 and 2 compare the experimental  $\Delta_{\text{soln}}H^{\circ,A}/\text{Mes}$  data versus calculated values based on Eqs. (3) and (4) derived from the Abraham solvation parameter model. Intercorrelations between most of the descriptors are negligible, and even the largest intercorrelation between  $\mathbf{E}$  and  $\mathbf{S}$ , 0.521 (Eq. (3)) and 0.567 (Eq. (4)), are not too significant. The intercorrelation between the  $\mathbf{E}$  and  $\mathbf{S}$  solute descriptors has been noted in several earlier publications. [16,39,40]

The associated statistical information for each correlation includes the number of experimental values used in the regression analysis ( $N$ ), the standard deviation ( $SD$ ), the squared correlation coefficient ( $R^2$ ), and the Fisher  $F$ -statistical ( $F$ ). Standard errors in the equation coefficients are given in parenthesis immediately following the respective coefficient. As an informational note, Eq. (3) is the enthalpic derivative of the Abraham model's gas-to-condensed phase transfer equation. Eq. (4) might be more useful in some predictive applications in instances where the  $\mathbf{L}$ -descriptor is not known. Eq. (4) uses the McGowan volume,  $\mathbf{V}$ -descriptor, which is easily calculable from the individual atomic sizes and numbers of bonds in the molecule [41]. The change in sign in both the *c* and *e* equation coefficients is rationalized using the mathematical correlation proposed by Van Noort and co-workers [42]

$$\mathbf{L} = -0.882 + 1.183\mathbf{E} + 0.839\mathbf{S} + 0.454\mathbf{A} + 0.157\mathbf{B} \\ + 3.505\mathbf{V} \quad (5)$$

for estimating the  $\mathbf{L}$  descriptor from numerical values of the  $\mathbf{E}$ ,  $\mathbf{S}$ ,  $\mathbf{A}$ ,  $\mathbf{B}$  and  $\mathbf{V}$  descriptor based on  $\mathbf{V}$  and  $\mathbf{L}$  values for 4785 compounds. If one substitutes the mathematical correlation for  $\mathbf{L}$  into Eq. (3) one obtains the following Abraham model correlation:

$$\Delta_{\text{soln}}H^{\circ,A}/\text{Mes}(\text{kJ mol}^{-1}) = 2.925 - 4.637\mathbf{E} - 17.604\mathbf{S} \\ - 15.158\mathbf{A} - 1.497\mathbf{B} - 33.431\mathbf{V} \quad (6)$$

for estimating  $\Delta_{\text{soln}}H^{\circ,A}/\text{Mes}$  using the  $\mathbf{V}$  descriptor. The coefficients of Eq. (6) differ slightly from those of Eq. (4) as would be expected. The dataset used in deriving the  $\mathbf{L}$  descriptor correlation contained far more compounds, and in the case of the enthalpy of solvation correlation the *b* coefficient was set equal to zero because of its small numerical value and its much larger respective standard error. To our knowledge, Eqs. (3) and (4) are the first expressions that allow a prediction of the gas-to-mesitylene solvation enthalpy.

In order to assess the predictive ability of Eq. (3) we divided the 92 data points into a training set and a test set by allowing the SPSS software to randomly select half of the experimental points. The selected data points became the training set and the compounds that were left served as the test set. Analysis of the experimental data in the training set gave

**Table 3**Values of the gas-to-mesitylene solvation enthalpy,  $\Delta_{\text{solv}}H^{\text{A/Mes}}$ , in  $\text{kJ mol}^{-1}$  at 298.15 K for 94 solutes together with the solute descriptors.

Solute	E	S	A	B	L	V	$\Delta_{\text{solv}}H^{\text{0A/Mes}}$	Ref
Pentane	0.000	0.000	0.000	0.000	2.162	0.8131	-25.19	[30]
2-Methylbutane	0.000	0.000	0.000	0.000	2.013	0.8131	-23.62	[30]
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	-30.45	[30]
2,2-Dimethylbutane	0.000	0.000	0.000	0.000	2.352	0.9540	-25.98	[30]
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	-35.46	[31]
3-Ethylpentane	0.000	0.000	0.000	0.000	3.091	1.0949	-33.61	[32]
Octane	0.000	0.000	0.000	0.000	3.677	1.2358	-40.31	[33]
2,2,4,4-Tetramethylpentane	0.000	0.000	0.000	0.000	3.512	1.3767	-36.91	[34]
Decane	0.000	0.000	0.000	0.000	4.686	1.5176	-50.05	[30]
Dodecane	0.000	0.000	0.000	0.000	5.696	1.7994	-60.38	This work
Hexadecane	0.000	0.000	0.000	0.000	7.714	2.3630	-79.22	[30]
Cyclohexane	0.310	0.100	0.000	0.000	2.964	0.8454	-31.03	[31]
1-Hexene	0.080	0.080	0.000	0.070	2.572	0.9110	-30.18	[30]
1-Octene	0.094	0.080	0.000	0.070	3.568	1.1928	-39.88	[30]
Dichloromethane	0.390	0.570	0.100	0.050	2.019	0.4943	-30.12	This work
Diiodomethane	1.200	0.690	0.050	0.170	3.857	0.7659	-42.38	[34]
Trichloromethane	0.430	0.490	0.150	0.020	2.480	0.6167	-34.66	This work
Tetrachloromethane	0.460	0.380	0.000	0.000	2.823	0.7391	-31.94	[34]
1-Chlorobutane	0.210	0.400	0.000	0.100	2.722	0.7946	-34.29	[38]
1-Chlorooctane	0.191	0.400	0.000	0.090	4.708	1.3580	-52.86	[33]
Perfluoroheptane	-1.080	-1.400	0.000	0.430	1.331	1.3781	-15.42	[34]
1-Fluorooctane	-0.020	0.350	0.000	0.100	3.850	1.2538	-50.79	[33]
Diethyl ether	0.041	0.250	0.000	0.450	2.015	0.7309	-26.72	[30]
Dibutyl ether	0.000	0.250	0.000	0.450	3.924	1.2945	-44.92	[33]
Butyl methyl ether	0.045	0.250	0.000	0.440	2.658	0.8718	-32.23	[30]
tert-Butyl methyl ether	0.024	0.210	0.000	0.590	2.380	0.8718	-27.47	[30]
Heptyl methyl ether	0.048	0.250	0.000	0.450	4.088	1.2945	-47.40	[33]
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	-33.15	This work
Propanone	0.179	0.700	0.040	0.490	1.696	0.5470	-28.37	[31]
Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	-33.17	[31]
Heptan-2-one	0.123	0.680	0.000	0.510	3.760	1.1106	-47.40	[31]
Heptan-4-one	0.110	0.660	0.000	0.510	3.705	1.1106	-47.16	[30]
Nonan-2-one	0.113	0.680	0.000	0.510	4.735	1.3924	-56.57	[31]
Nonan-5-one	0.103	0.660	0.000	0.510	4.698	1.3924	-54.90	[31]
2,2,4,4-Tetramethyl pentan-3-one <sup>a</sup>	0.099	0.560	0.000	0.520	4.370	1.3924	-44.60	[31]
Cyclohexanone	0.403	0.860	0.000	0.560	3.792	0.8610	-44.31	[31]
Methyl acetate	0.142	0.640	0.000	0.450	1.911	0.6057	-29.98	This work
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	-33.85	This work
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	-36.75	This work
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	-42.79	This work
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	-29.09	This work
Propionitrile	0.162	0.900	0.020	0.360	2.082	0.5451	-34.22	This work
Butyronitrile	0.188	0.900	0.000	0.360	2.548	0.6860	-37.58	This work
Tetracyanoethylene <sup>a</sup>	0.800	2.02	0.00	1.02	5.330	0.9662	-83.90	[35]
Triethylamine	0.101	0.150	0.000	0.790	3.040	1.0538	-35.57	This work
Tri-n-butylamine	0.051	0.150	0.000	0.790	6.050	1.8998	-63.02	This work
Nitromethane	0.313	0.950	0.060	0.310	1.892	0.4237	-34.17	This work
Nitrobenzene	0.871	1.110	0.000	0.280	4.557	0.8906	-53.37	[30]
N,N-Dimethylformamide	0.367	1.310	0.000	0.740	3.173	0.6468	-44.20	This work
N,N-Dimethylacetamide	0.363	1.380	0.000	0.800	3.639	0.7877	-48.78	This work
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	-22.98	This work
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	-26.30	This work
Propan-1-ol	0.236	0.420	0.370	0.480	2.031	0.5900	-31.17	This work
Butan-1-ol	0.224	0.420	0.370	0.480	2.601	0.7309	-35.47	[36]
2-Methylbutan-2-ol	0.194	0.300	0.310	0.600	2.630	0.8718	-36.56	[36]
Pentan-1-ol	0.219	0.420	0.370	0.480	3.106	0.8718	-41.13	[36]
Hexan-1-ol	0.210	0.420	0.370	0.480	3.610	1.0127	-45.89	This work
Octan-1-ol	0.199	0.420	0.370	0.480	4.619	1.2945	-56.04	[33]
Decan-1-ol	0.191	0.420	0.370	0.480	5.628	1.5763	-66.75	This work
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	-32.21	[32]
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	-37.46	[30]
Mesitylene	0.649	0.520	0.000	0.190	4.344	1.1391	-47.50	This work
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	-54.40	This work
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3242	-65.70	This work
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4540	-77.69	This work
1,3-Diphenylbenzene	1.950	1.390	0.000	0.350	9.718	1.9320	-97.22	This work
1,4-Diphenylbenzene	1.950	1.430	0.000	0.350	9.814	1.9320	-98.16	This work
1,3,5-Triphenylbenzene	2.440	1.820	0.000	0.410	12.787	2.5398	-128.74	This work
Methyl benzoate	0.733	0.850	0.000	0.460	4.704	1.0726	-54.10	This work
Ethyl benzoate	0.689	0.850	0.000	0.460	5.075	1.2135	-57.78	This work
Propyl benzoate	0.675	0.800	0.000	0.460	5.718	1.3544	-64.41	This work
Butyl benzoate	0.668	0.800	0.000	0.460	6.210	1.4953	-68.61	This work
Anisole	0.710	0.750	0.000	0.290	3.890	0.9160	-45.01	[30]
Acetophenone	0.818	1.010	0.000	0.480	4.501	1.0140	-54.07	This work
Benzaldehyde	0.820	1.000	0.000	0.390	4.008	0.8730	-47.32	[37]
4-Fluoroanisole	0.571	0.740	0.000	0.280	3.904	0.9337	-48.49	[38]



Table 3 (Continued)

Solute	E	S	A	B	L	V	$\Delta_{\text{solv}}H^{0,A/\text{Mes}}$	Ref
Trifluoromethylbenzene	0.225	0.480	0.000	0.100	2.894	0.9104	-37.10	[30]
Phenol	0.805	0.890	0.600	0.300	3.766	0.7751	-49.37	[30]
<i>m</i> -Cresol	0.822	0.880	0.570	0.340	4.310	0.9160	-52.92	[30]
2-Methoxyphenol	0.837	0.910	0.220	0.520	4.449	0.9747	-54.62	This work
3-Methoxyphenol	0.879	1.170	0.590	0.380	4.803	0.9747	-66.88	This work
4-Methoxyphenol	0.900	1.170	0.570	0.480	4.773	0.9747	-65.09	This work
2-Chlorophenol	0.853	0.880	0.320	0.310	4.178	0.8976	-48.50	This work
4-Chlorophenol	0.915	1.080	0.670	0.200	4.775	0.8975	-62.81	This work
2-Nitrophenol	1.015	1.050	0.050	0.370	4.760	0.9493	-57.16	This work
4-Fluorophenol	0.670	0.970	0.630	0.230	3.844	0.7928	-53.90	[38]
Pyrrole	0.613	0.730	0.410	0.290	2.865	0.5570	-40.02	This work
Indole	1.200	1.260	0.440	0.180	5.310	0.9464	-64.00	This work
Aniline	0.955	0.960	0.260	0.410	3.934	0.8160	-47.00	[32]
Pyridine	0.631	0.840	0.000	0.520	3.022	0.6753	-37.49	[32]
4-Picoline	0.630	0.820	0.000	0.540	3.640	0.8162	-43.26	This work
<i>N</i> -Methylimidazole	0.589	0.950	0.000	0.800	3.805	0.6772	-49.13	This work
Piperidine	0.422	0.460	0.100	0.690	3.304	0.8043	-36.75	This work
Pyrrolidine	0.406	0.670	0.120	0.630	2.893	0.6634	-36.23	This work

<sup>a</sup> Not used in the regression analysis.

$$\Delta_{\text{solv}}H^{0,A/\text{Mes}}(\text{kJ mol}^{-1}) = -5.324(0.673) + 6.133(0.904)\mathbf{E} - 9.615(0.785)\mathbf{S} - 10.984(1.357)\mathbf{A} - 9.462(0.200)\mathbf{L} \quad (7)$$

(with  $N=46$ ,  $SD=1.34$ ,  $R^2=0.991$ ,  $F=1107$ ).

Again the  $b_l \times \mathbf{B}$  term was set equal to zero. There is very little difference in the equation coefficients for the full dataset and the training dataset correlations, thus showing that the training set of compounds is a representative sample of the total data set. The training set equation was then used to predict  $\Delta_{\text{solv}}H^{0,A/\text{Mes}}$  values for the 46 compounds in the test set. For the predicted and experimental values, we find  $SD=1.69$ ,  $AAE$  (average absolute error)=1.25 and  $AE$  (average error)=-0.39  $\text{kJ mol}^{-1}$ . There is therefore very little bias in using Eq. (7) with  $AE$  equal to -0.39  $\text{kJ mol}^{-1}$ . The training set and test set analyses were performed two more times with similar results. In each repetition the data set was split into new training and test sets using the SPSS randomization software. The ranges of solute descriptors covered

by the respective training and test sets were approximately the same. Training and test validations were also performed for Eq. (4). To conserve journal space, we give only the test set results (see Table S3 in the Supplementary material for the training set). The derived training set correlation for Eq. (4) predicted the 46 experimental  $\Delta_{\text{solv}}H^{0,A/\text{Mes}}$  values in the test set to within a  $SD=1.93$ ,  $AAE=1.63$  and  $AE=-0.56 \text{ kJ mol}^{-1}$ . Again, there is very little bias in the predictions using Eq. (4) with  $AE$  equal to -0.56  $\text{kJ mol}^{-1}$ . An error/uncertainty of  $\pm 2 \text{ kJ mol}^{-1}$  in the enthalpy of solvation results in an error of slightly less than  $\pm 0.04$  log units in extrapolating a log  $K$  value measured at 298.15 K to a temperature of 313.15. This level of predictive error will be sufficient for most practical chemical and engineering applications. Eqs. (3) and (4) are expected to provide reasonably accurate predictions of the gas-to-mesitylene solvation enthalpies for additional organic solutes whose solute descriptors fall within the area of predictive space defined by the solute descriptors used in deriving both Abraham model correlations. The solute descriptors in the regression dataset spanned the range of:  $\mathbf{E}=-1.080$  to  $\mathbf{E}=2.440$ ;  $\mathbf{S}=-1.400$  to  $\mathbf{S}=2.020$ ;  $\mathbf{A}=0.000$  to  $\mathbf{A}=0.670$ ;  $\mathbf{B}=0.000$  to  $\mathbf{B}=1.020$ ;  $\mathbf{L}=0.970$  to  $\mathbf{L}=12.787$ ; and  $\mathbf{V}=0.3082$  to  $\mathbf{V}=2.5398$ .

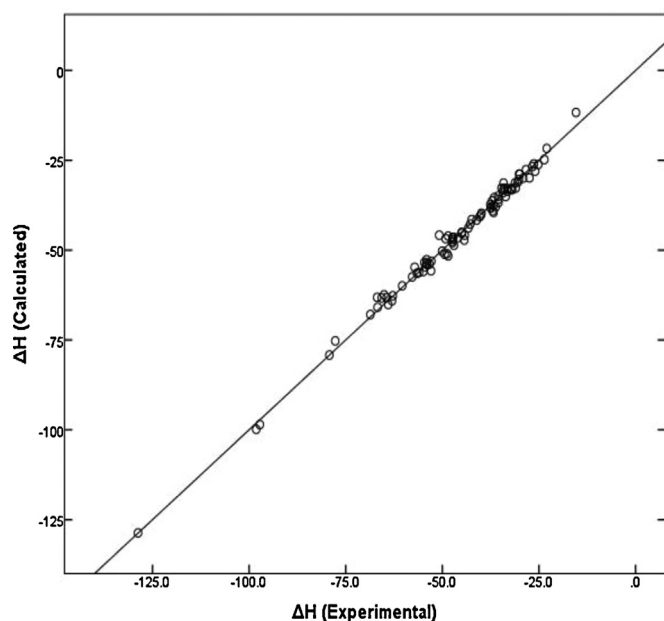


Fig. 1. Comparison between experimental  $\Delta_{\text{solv}}H^{0,A/\text{Mes}}$  data and values calculated based on Eq. (3).

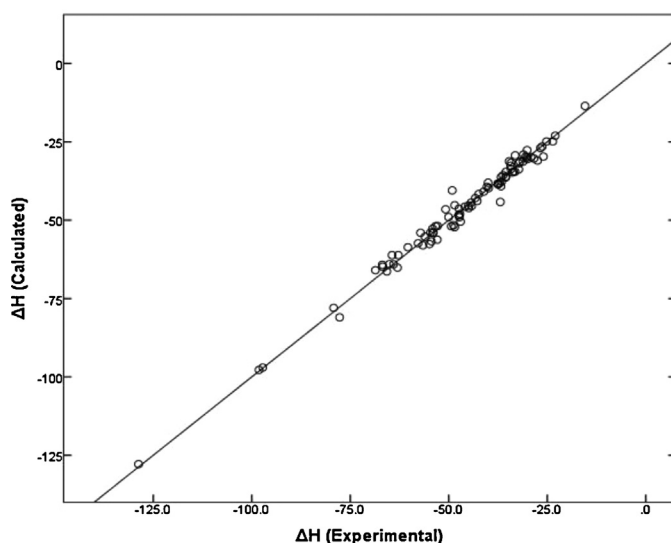


Fig. 2. Comparison between experimental  $\Delta_{\text{solv}}H^{0,A/\text{Mes}}$  data and values calculated based on Eq. (4).

**Table 4**Values of the gas-to-*p*-xylene solvation enthalpy,  $\Delta_{\text{solv}}H^{\text{A/Xyl}}$  in  $\text{kJ mol}^{-1}$  at 298.15 K for 136 solutes together with the solute descriptors for 132 solutes

Solute	E	S	A	B	L	V	$\Delta_{\text{solv}}H^{\text{A/Xyl}}$	Ref
Helium	0.000	0.000	0.000	0.000	-1.741	0.0680	10.50	[43]
Argon	0.000	0.000	0.000	0.000	-0.688	0.1900	-0.05	[43]
Carbon dioxide	0.000	0.280	0.050	0.100	0.058	0.2809	-9.52	[43]
Tetrafluoromethane	-0.580	-0.260	0.000	0.000	-0.817	0.3203	1.04	[43]
Sulfur hexafluoride	-0.600	-0.200	0.000	0.000	-0.120	0.4643	-5.08	[43]
Chlorine	0.360	0.320	0.100	0.000	1.193	0.3534	-17.10	[44]
Methane	0.000	0.000	0.000	0.000	-0.323	0.2495	-3.33	[43]
Propane	0.000	0.000	0.000	0.000	1.050	0.5313	-16.11	[45]
2-Methylpropane	0.000	0.000	0.000	0.000	1.409	0.6722	-18.01	[45]
Butane	0.000	0.000	0.000	0.000	1.615	0.6722	-20.08	[45]
Propene	0.100	0.080	0.000	0.070	0.946	0.4883	-15.94	[45]
2-Methylpropene	0.120	0.080	0.000	0.080	1.579	0.6292	-20.58	[45]
Butene-1	0.100	0.080	0.000	0.070	1.491	0.6292	-20.40	[45]
<i>cis</i> -2-Butene	0.140	0.080	0.000	0.050	1.737	0.6292	-22.19	[45]
<i>trans</i> -2-Butene	0.126	0.080	0.000	0.050	1.664	0.6292	-21.37	[45]
1,1-Difluoroethane	-0.250	0.470	0.040	0.070	0.570	0.4258	-17.96	[45]
Chloroethane	0.227	0.400	0.000	0.100	1.678	0.5128	-24.73	[45]
1,3-Butadiene	0.320	0.230	0.000	0.100	1.543	0.5862	-21.07	[45]
Hexane	0.000	0.000	0.000	0.000	2.668	0.9540	-30.21	This work
Heptane	0.000	0.000	0.000	0.000	3.173	1.0949	-35.16	This work
Decane	0.000	0.000	0.000	0.000	4.686	1.5176	-49.45	This work
Dodecane	0.000	0.000	0.000	0.000	5.696	1.7994	-59.20	This work
Hexadecane	0.000	0.000	0.000	0.000	7.714	2.3630	-78.34	This work
Cyclopentane	0.263	0.100	0.000	0.000	2.477	0.7045	-27.87	[46]
Cyclohexane	0.310	0.100	0.000	0.000	2.964	0.8454	-31.16	[62]
Adamantane	0.760	0.570	0.000	0.040	4.934	1.1918	-53.50	This work
Dichloromethane	0.390	0.570	0.100	0.050	2.019	0.4943	-30.62	This work
Trichloromethane	0.430	0.490	0.150	0.020	2.480	0.6167	-34.32	[47]
Tetrachloromethane	0.460	0.380	0.000	0.000	2.823	0.7391	-31.02	[48]
1,2-Dichloropropane	0.369	0.630	0.000	0.170	2.836	0.7761	-36.99	This work
1-Chlorobutane	0.210	0.400	0.000	0.100	2.722	0.7946	-34.57	This work
Dimethyl ether	0.000	0.270	0.000	0.410	1.285	0.4491	-19.71	[45]
Diethyl ether	0.041	0.250	0.000	0.450	2.015	0.7309	-26.20	This work
Di- <i>n</i> -butyl ether	0.000	0.250	0.000	0.450	3.924	1.2945	-44.79	This work
Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636	0.6223	-34.03	[46]
Tetrahydropyran	0.296	0.490	0.000	0.480	3.013	0.7632	-37.46	[49]
1,4-Dioxane	0.329	0.750	0.000	0.640	2.892	0.6810	-37.27	This work
Propanone	0.179	0.700	0.040	0.490	1.696	0.5470	-29.43	This work
Butanone	0.166	0.700	0.000	0.510	2.287	0.6879	-33.85	This work
Pentan-2-one	0.143	0.680	0.000	0.510	2.755	0.8288	-38.23	This work
Heptan-2-one	0.123	0.680	0.000	0.510	3.760	1.1106	-47.64	This work
Octan-2-one	0.108	0.680	0.000	0.510	4.257	1.2515	-52.46	This work
Nonan-2-one	0.113	0.680	0.000	0.510	4.735	1.3924	-56.90	This work
Undecan-2-one	0.101	0.680	0.000	0.510	5.732	1.6742	-67.84	[50]
Acetophenone	0.818	1.010	0.000	0.480	4.501	1.0140	-53.74	This work
Methyl acetate	0.142	0.640	0.000	0.450	1.911	0.6057	-30.43	This work
Ethyl acetate	0.106	0.620	0.000	0.450	2.314	0.7466	-34.41	This work
Propyl acetate	0.092	0.600	0.000	0.450	2.819	0.8875	-37.75	This work
Butyl acetate	0.071	0.600	0.000	0.450	3.353	1.0284	-43.03	This work
Isobutyl acetate	0.052	0.570	0.000	0.470	3.161	1.0284	-40.73	[51]
Cyclohexyl acetate	0.283	0.690	0.000	0.470	4.310	1.2020	-52.65	[52]
Methyl propionate	0.128	0.600	0.000	0.450	2.431	0.7466	-34.86	This work
Propyl propionate	0.070	0.560	0.000	0.450	3.338	1.0284	-43.20	[53]
Acetonitrile	0.237	0.900	0.070	0.320	1.739	0.4042	-32.51	This work
Propionitrile	0.162	0.900	0.020	0.360	2.082	0.5451	-36.03	This work
Butyronitrile	0.188	0.900	0.000	0.360	2.548	0.6860	-38.43	This work
Benzonitrile	0.742	1.110	0.000	0.330	4.039	0.8710	-49.12	This work
Triethylamine	0.101	0.150	0.000	0.790	3.040	1.0538	-35.43	This work
Tri- <i>n</i> -propylamine <sup>a</sup>							-49.90	This work
Tri- <i>n</i> -butylamine	0.051	0.150	0.000	0.790	6.050	1.8998	-61.23	This work
Nitromethane	0.313	0.950	0.060	0.310	1.892	0.4237	-34.94	This work
Nitroethane	0.270	0.950	0.020	0.330	2.414	0.5646	-36.11	[54]
1-Nitropropane	0.242	0.950	0.000	0.310	2.894	0.7055	-42.95	[55]
<i>N,N</i> -Dimethylformamide	0.367	1.310	0.000	0.740	3.173	0.6468	-43.73	This work
<i>N,N</i> -Dimethylacetamide	0.363	1.380	0.000	0.800	3.639	0.7877	-48.52	This work
Methanol	0.278	0.440	0.430	0.470	0.970	0.3082	-23.18	This work
Ethanol	0.246	0.420	0.370	0.480	1.485	0.4491	-26.84	This work
Propan-1-ol	0.236	0.420	0.370	0.480	2.031	0.5900	-32.20	This work
Butan-1-ol	0.224	0.420	0.370	0.480	2.601	0.7309	-36.73	This work
2-Methylpropan-1-ol	0.217	0.390	0.370	0.480	2.413	0.7309	-35.45	This work
Pentan-1-ol	0.219	0.420	0.370	0.480	3.106	0.8718	-42.52	This work
Hexan-1-ol	0.210	0.420	0.370	0.480	3.610	1.0127	-46.33	This work
Octan-1-ol	0.199	0.420	0.370	0.480	4.619	1.2945	-56.88	This work
Decan-1-ol	0.191	0.420	0.370	0.480	5.628	1.5763	-67.50	This work
Water	0.000	0.450	0.820	0.350	0.260	0.1673	-19.60	[56]
Benzene	0.610	0.520	0.000	0.140	2.786	0.7164	-33.17	[57]

Table 4 (Continued)

Solute	E	S	A	B	L	V	$\Delta_{\text{solv}}H^{\circ, A/Xyl}$	Ref
Toluene	0.601	0.520	0.000	0.140	3.325	0.8573	−37.96	[46]
Ethylbenzene	0.613	0.510	0.000	0.150	3.788	0.9980	−42.40	[58]
o-Xylene	0.623	0.520	0.000	0.160	3.839	0.9982	−43.40	[59]
m-Xylene	0.613	0.520	0.000	0.160	3.839	0.9982	−42.70	[59]
p-Xylene	0.613	0.520	0.000	0.160	3.839	0.9982	−42.40	This work
Mesitylene	0.649	0.520	0.000	0.190	4.344	1.1391	−47.39	This work
Naphthalene	1.340	0.920	0.000	0.200	5.161	1.0854	−54.45	This work
Biphenyl	1.360	0.990	0.000	0.260	6.014	1.3242	−64.81	This work
Anthracene	2.290	1.340	0.000	0.280	7.568	1.4540	−75.72	This work
Pyrene	2.808	1.710	0.000	0.280	8.833	1.5846	−86.74	[60]
1,3-Diphenylbenzene	1.950	1.390	0.000	0.350	9.718	1.9320	−96.16	This work
Chlorobenzene	0.718	0.650	0.000	0.070	3.657	0.8388	−41.68	[61]
Iodobenzene	1.188	0.820	0.000	0.120	4.502	0.9746	−49.54	This work
Fluorobenzene	0.477	0.570	0.000	0.100	2.788	0.7341	−35.07	[62]
Bromobenzene	0.882	0.730	0.000	0.090	4.041	0.8914	−44.87	[62]
1,2-Dichlorobenzene	0.872	0.780	0.000	0.040	4.518	0.9612	−50.02	[63]
1,3-Dichlorobenzene	0.847	0.730	0.000	0.020	4.410	0.9612	−48.10	[64]
1,4-Dichlorobenzene	0.825	0.750	0.000	0.020	4.435	0.9612	−49.24	This work
1-Chloronaphthalene	1.417	1.000	0.000	0.140	5.856	1.2078	−63.80	This work
Methyl benzoate	0.733	0.850	0.000	0.460	4.704	1.0726	−55.17	This work
Ethyl benzoate	0.689	0.850	0.000	0.460	5.075	1.2135	−59.91	This work
Propyl benzoate	0.675	0.800	0.000	0.460	5.718	1.3544	−64.89	This work
Butyl benzoate	0.668	0.800	0.000	0.460	6.210	1.4953	−69.16	This work
Anisole	0.710	0.750	0.000	0.290	3.890	0.9160	−45.76	[46]
Phenol	0.805	0.890	0.600	0.300	3.766	0.7751	−48.49	[46]
2,6-Dimethylphenol	0.850	0.820	0.510	0.370	4.495	1.0569	−53.06	[66]
2-Chlorophenol	0.853	0.880	0.320	0.310	4.178	0.8976	−48.33	This work
Methyl salicylate	0.850	0.840	0.020	0.470	5.025	1.1313	−55.37	This work
Ethyl salicylate	0.802	0.910	0.030	0.430	5.509	1.2722	−61.33	This work
2-Methoxyphenol	0.837	0.910	0.220	0.520	4.449	0.9747	−55.03	This work
3-Methoxyphenol	0.879	1.170	0.590	0.380	4.803	0.9747	−66.48	This work
4-Methoxyphenol	0.900	1.170	0.570	0.480	4.773	0.9747	−62.18	This work
2,6-Dimethoxyphenol <sup>a</sup>							−73.39	This work
Pyrrrole	0.613	0.730	0.410	0.290	2.865	0.5570	−41.00	This work
Aniline	0.955	0.960	0.260	0.410	3.934	0.8160	−47.98	This work
2-Methylaniline	0.966	0.920	0.230	0.450	4.442	0.9571	−56.07	[67]
Pyridine	0.631	0.840	0.000	0.520	3.022	0.6753	−38.88	This work
2-Picoline	0.598	0.750	0.000	0.580	3.422	0.8162	−42.00	This work
3-Picoline	0.631	0.810	0.000	0.540	3.631	0.8162	−43.68	This work
4-Picoline	0.630	0.820	0.000	0.540	3.640	0.8162	−43.47	This work
N-Methylimidazole	0.589	0.950	0.000	0.800	3.805	0.6772	−49.43	This work
Piperidine	0.422	0.460	0.100	0.690	3.304	0.8043	−35.88	This work
Indole	1.200	1.260	0.440	0.180	5.310	0.9464	−63.89	This work
Pyrrrolidine	0.406	0.670	0.120	0.630	2.893	0.6634	−35.61	This work
Dimethyl sulfoxide	0.522	1.740	0.000	0.880	3.459	0.6126	−46.55	This work
12-Crown-4	0.420	0.990	0.000	1.390	5.135	1.3620	−64.11	This work
15-Crown-5	0.410	1.200	0.000	1.750	6.779	1.7025	−77.33	This work
Pyrazole	0.620	1.000	0.540	0.450	3.151	0.5363	−48.28	This work
N-Methylaniline	0.948	0.900	0.170	0.430	4.478	0.9571	−52.24	This work
Iodine	1.398	0.670	0.280	0.000	3.6810	0.6250	−44.30	[65]
Dimethyl carbonate	0.142	0.540	0.000	0.370	2.328	0.6644	−35.42	[68]
Diethyl carbonate	0.060	0.580	0.000	0.530	3.412	0.9462	−43.38	[69]
Propylene carbonate <sup>a</sup>							−55.43	This work
Eicosane	0.000	0.000	0.000	0.000	9.731	2.9266	−98.51	This work
Docosane	0.000	0.000	0.000	0.000	10.740	3.2084	−104.75	This work
Fluoranthene	2.377	1.550	0.000	0.240	8.827	1.5850	−83.18	This work
Cholesterol <sup>a</sup>							−124.70	[70]
Diethylphosphite	0.142	0.980	0.100	0.900	3.912	1.0529	−47.00	[71]
Tetracyanoethylene <sup>a</sup>	0.800	2.020	0.000	1.020	5.330	0.9662	−83.34	[35]
Ethylene oxide	0.250	0.740	0.070	0.320	1.371	0.3405	−23.02	[72]

<sup>a</sup> Not used in the regression analysis.

Assembled in Table 4 data are experimental gas-to-*p*-xylene solvation enthalpies,  $\Delta_{\text{solv}}H^{\circ, A/Xyl}$ , values and solute descriptors for 132 organic compounds and inorganic gases. The  $\Delta_{\text{solv}}H^{\circ, A/Xyl}$  were calculated from the enthalpy of solution data tabulated in Table 2 or were obtained from published literature data [35,43–72]. The source of the experimental values is indicated in the last column of Table 4. Also listed in the table data are  $\Delta_{\text{solv}}H^{\circ, A/Xyl}$  values for

tri-*n*-propylamine, 2,6-dimethoxyphenol, propylene carbonate, and cholesterol. At the present time we have only very preliminary numerical values for the solute descriptors of these four compounds which were based on only a limited number of experimental data points. These four compounds are excluded from the regression analysis. Our preliminary regression analysis identified tetracyanoethylene to be an outlier, and helium to be an



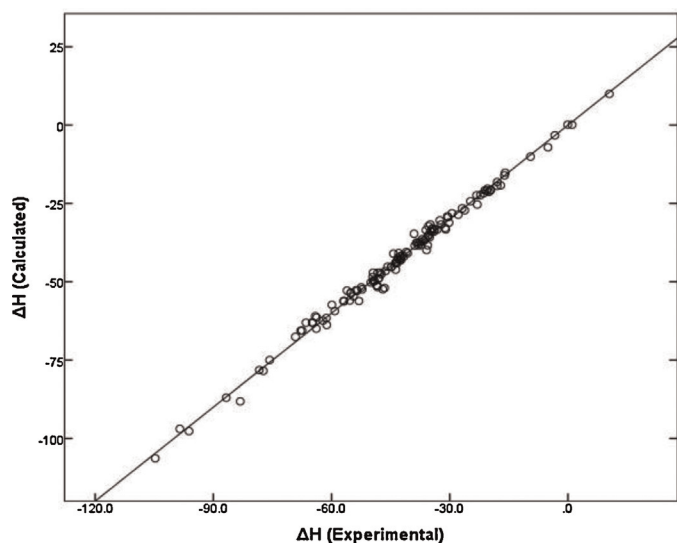


Fig. 3. Comparison between experimental  $\Delta_{\text{solv}}H^{\circ, A/\text{Xyl}}$  data and values calculated based on Eq. (8).

outlier for only Eq. (9) correlation. The outliers were removed from the data set and the regression analysis was performed one final time to yield:

$$\Delta_{\text{solv}}H^{\circ, A/\text{Xyl}} (\text{kJ mol}^{-1}) = -6.265(0.355) + 6.460(0.467)\mathbf{E} \\ - 9.862(0.542)\mathbf{S} - 10.775(0.964)\mathbf{A} \\ - 9.318(0.091)\mathbf{L} \quad (8)$$

(with  $N = 131$ ,  $\text{SD} = 1.68$ ,  $R^2 = 0.992$ ,  $F = 4080$ )

$$\Delta_{\text{solv}}H^{\circ, A/\text{Xyl}} (\text{kJ mol}^{-1}) = 1.703(0.639) - 3.466(0.668)\mathbf{E} \\ - 18.074(0.839)\mathbf{S} - 14.109(1.495)\mathbf{A} \\ - 33.618(0.519)\mathbf{V} \quad (9)$$

(with  $N = 130$ ,  $\text{SD} = 2.47$ ,  $R^2 = 0.982$ ,  $F = 1700$ ).

The  $b_1 \times \mathbf{B}$  and  $b_v \times \mathbf{B}$  terms were removed from the correlations because the standard error in the  $b$ -coefficient was significantly larger than the coefficient itself. Removal of the term is consistent with structural considerations as  $p$ -xylene does not contain an acidic hydrogen capable of involvement in hydrogen-bond

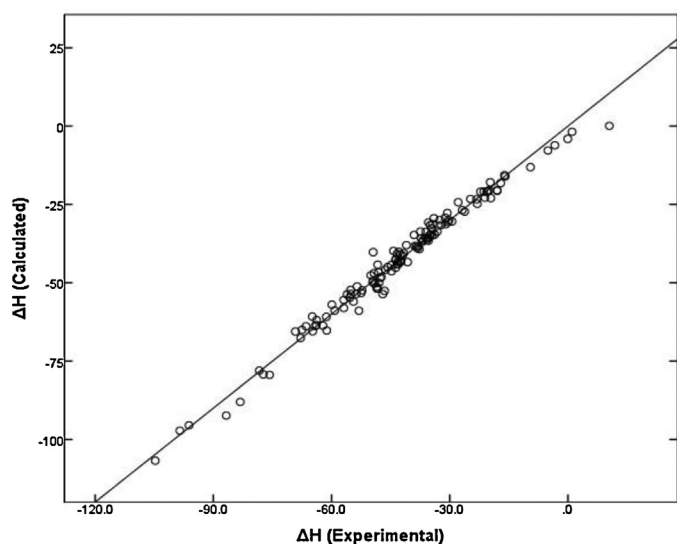


Fig. 4. Comparison between experimental  $\Delta_{\text{solv}}H^{\circ, A/\text{Xyl}}$  data and values calculated based on Eq. (9).

formation. Eqs. (8) and (9) provide a reasonably accurate mathematical description of the observed  $\Delta_{\text{solv}}H^{\circ, A/\text{Xyl}}$  data. Standard deviations between the measured and back-calculated values are  $\text{SD} = 1.68 \text{ kJ mol}^{-1}$  (Eq. (8)) and  $\text{SD} = 2.47 \text{ kJ mol}^{-1}$  (Eq. (9)) for a dataset that spans a range of approximately  $124 \text{ kJ mol}^{-1}$ . Figs. 3 and 4 compare the experimental  $\Delta_{\text{solv}}H^{\circ, A/\text{Xyl}}$  data versus calculated values based on the derived Abraham model correlations. This is the first time that expressions have been reported for estimating the gas-to- $p$ -xylene solvation enthalpies. Stephens and co-workers [73] have published Abraham model correlations for predicting the logarithm of the gas-to- $p$ -xylene partition coefficient,  $\log K$ , and the logarithm of the water-to- $p$ -xylene partition coefficient,  $\log P$ , at 298 K. The derived  $\Delta_{\text{solv}}H^{\circ, A/\text{Xyl}}$  correlations given above will expand the predictive capability of the published partition coefficients by allow researchers to extrapolate predicted  $\log K$  and  $\log P$  values to slightly higher and slightly lower temperatures.

The predictive ability of Eq. (8) was assessed as before by allowing the SPSS software to randomly divide the 131 experimental data points into training and test sets. Analysis of the experimental data in the training set gave

$$\Delta_{\text{solv}}H^{\circ, A/\text{Xyl}} (\text{kJ mol}^{-1}) = -6.390(0.500) + 6.346(0.787)\mathbf{E} \\ - 8.582(0.745)\mathbf{S} - 10.922(1.585)\mathbf{A} \\ - 9.380(0.159)\mathbf{L} \quad (10)$$

(with  $N = 66$ ,  $\text{SD} = 1.77$ ,  $R^2 = 0.992$ ,  $F = 1866$ ).

There is very little difference in the equation coefficients for the full dataset and the training dataset correlations, thus showing that the training set of compounds is a representative sample of the total data set. The training set equation was then used to predict  $\Delta_{\text{solv}}H^{\circ, A/\text{Xyl}}$  values for the 65 compounds in the test set. For the predicted and experimental values, we find  $\text{SD} = 1.63 \text{ kJ mol}^{-1}$ ,  $\text{AAE}$  (average absolute error) =  $1.27 \text{ kJ mol}^{-1}$  and  $\text{AE}$  (average error) =  $-0.54 \text{ kJ mol}^{-1}$ . There is therefore very little bias in using Eq. (10) with  $\text{AE}$  equal to  $-0.54 \text{ kJ mol}^{-1}$ . The training set and test set analyses were performed two more times with similar results. Training and test validations were also performed for Eq. (9). To conserve journal space, we give only the test set results. The derived training set correlation for Eq. (9) predicted the 65 experimental  $\Delta_{\text{solv}}H^{\circ, A/\text{Xyl}}$  values in the test set to within a  $\text{SD} = 2.45$ ,  $\text{AAE} = 1.89$  and  $\text{AE} = -0.38 \text{ kJ mol}^{-1}$ . Again, there is very little bias in the predictions using Eq. (9) with  $\text{AE}$  equal to  $-0.38 \text{ kJ mol}^{-1}$ .

Each term in the Abraham model represents a different type of solute–solvent interaction. For aprotic organic solvents, including benzene and alkylbenzenes, the terms  $a_1 \times \mathbf{A}$  and  $a_v \times \mathbf{A}$  in Eqs. (1) and (2) give the total contribution of hydrogen bond formation to the enthalpy of solvation (because the  $b_1 \times \mathbf{B}$  and  $b_v \times \mathbf{B}$  should be nearly zero). It must be noted that H-bonds play a crucial role in the effect of solvents on the reactivity of solute molecules. In accordance with the Abraham model correlations derived above, the enthalpy of hydrogen bond formation of organic substances with mesitylene,  $\Delta H_{\text{HB}}^{A/\text{Mes}}$ , is calculated by:

$$\Delta H_{\text{HB}}^{A/\text{Mes}} (\text{kJ mol}^{-1}) = -10.828(0.913)\mathbf{A} \quad (11)$$

$$\Delta H_{\text{HB}}^{A/\text{Mes}} (\text{kJ mol}^{-1}) = -14.011(1.294)\mathbf{A} \quad (12)$$

and with  $p$ -xylene,  $\Delta H_{\text{HB}}^{A/\text{Xyl}}$ , is calculated by:

$$\Delta H_{\text{HB}}^{A/\text{Xyl}} (\text{kJ mol}^{-1}) = -10.775(0.964)\mathbf{A} \quad (13)$$

$$\Delta H_{\text{HB}}^{A/\text{Xyl}} (\text{kJ mol}^{-1}) = -14.109(1.495)\mathbf{A} \quad (14)$$

Data on  $\Delta H_{\text{HB}}^{A/\text{Mes}}$  and  $\Delta H_{\text{HB}}^{A/\text{Xyl}}$  for several hydrogen bond acid solutes calculated using Eqs. (11)–(14) are presented in Table 5, along with enthalpy of hydrogen bond formation of several

**Table 5**Enthalpies of weak X–H... $\pi$  (X=O,N, and C) hydrogen bonding of aromatic solvents with different proton donors calculated by Abraham–Acree and Solomonov methods.

Solute (A)	$\Delta_{\text{HB}}H^{A,S}$			$\Delta_{\text{HB}}H^{A,S}$			$\Delta_{\text{HB}}H^{A,S}$			$\Delta_{\text{HB}}H^{A,S}$		
	Benzene			Toluene			Mesitylene			<i>p</i> -Xylene		
	L <sup>a</sup>	V <sup>b</sup>	S <sup>c</sup>	L	V	S	L	V	S	L	V	S
Methanol	–	–	–	–2.7	–4.3	–	–4.7	–6.0	–3.3	–4.6	–6.1	–3.2
Ethanol	–3.6	–4.4	–3.4	–2.3	–3.7	–	–4.0	–5.2	–2.0	–4.0	–5.2	–2.4
Propan-1-ol	–	–	–	–2.3	–3.7	–	–4.0	–5.2	–1.9	–4.0	–5.2	–2.6
Butan-1-ol	–3.6	–4.4	–0.9	–2.3	–3.7	–0.9	–4.0	–5.2	–2.5	–4.0	–5.2	–3.6
Pentan-1-ol	–3.6	–4.4	–	–2.3	–3.7	–1.2	–3.4	–4.4	–2.3	–4.0	–5.2	–3.5
Hexan-1-ol	–3.6	–4.4	–0.7	–	–	–	–4.0	–5.2	–2.4	–4.0	–5.2	–2.7
Octan-1-ol	–3.6	–4.4	–0.2	–2.3	–3.7	–0.6	–4.0	–5.2	–2.2	–4.0	–5.2	–2.8
Decan-1-ol	–3.6	–4.4	–	–	–	–	–4.0	–5.2	–2.0	–4.0	–5.2	–2.7
2-Propanol	–	–	–	–2.1	–3.3	–	–	–	–	–	–	–
2-Methylpropan-2-ol	–3.0	–3.7	–1.0	–2.0	–3.1	–	–3.4	–4.3	–	–4.0	–5.2	–1.6
2-Ethoxyethanol	–3.0	–3.7	–	–	–	–	–	–	–	–	–	–
2-Methoxyphenol	–	–	–	–	–	–	–2.4	–3.1	–1.4	–2.4	–3.1	–1.6
3-Methoxyphenol	–	–	–	–	–	–	–6.4	–8.3	–8.0	–6.4	–8.3	–7.0
4-Methoxyphenol	–	–	–	–	–	–	–6.2	–8.0	–11.6	–6.1	–8.0	–8.2
2-Chlorophenol	–	–	–	–	–	–	–3.5	–4.5	–2.6	–3.5	–4.4	–
4-Chlorophenol	–	–	–	–	–	–	–7.3	–9.4	–12.1	–	–	–
2-Nitrophenol	–	–	–	–	–	–	–0.5	–0.7	–4.2	–	–	–
4-Fluorophenol	–	–	–	–	–	–	–6.8	–8.8	–8.8	–	–	–
Pyrrrole	–4.0	–4.8	–3.2	–2.6	–4.1	–3.6	–4.4	–5.8	–3.8	–4.4	–5.6	–4.5
Piperidine	–	–	–	–	–	–	–1.1	–1.4	1.8	–1.1	–1.4	–2.4
Indole	–	–	–	–	–	–	–4.8	–6.2	–4.7	–4.7	–6.2	–4.3
Pyrrrolidine	–	–	–	–	–	–	–1.3	–1.7	0.2	–1.3	–1.6	–1.7
Dichloromethane	–	–	–	–	–	–	–1.1	–1.4	–3.0	–1.1	–1.4	–3.3
Chloroform	–1.5	–1.8	–2.5	–	–	–	–1.6	–2.1	–4.0	–1.6	–2.1	–3.7
Acetonitrile	–0.7	–0.8	–	–0.4	–0.8	–	–0.7	–1.0	–2.2	–0.8	–1.0	–0.6
Nitromethane	–0.6	–0.7	–	–	–	–	–0.7	–0.8	–3.0	–0.6	–0.8	–1.3
Aniline	–2.5	–3.1	–	–	–	–	–2.8	–3.6	–0.2	–2.8	–3.7	–1.7
<i>m</i> -Cresol	–	–	–	–	–	–	–6.2	–8.0	–7.6	–	–	–
Phenol	–5.9	–7.1	–	–3.8	–6.0	–	–6.5	–8.4	–5.5	–6.5	–8.5	–5.3
3-Methylphenol	–5.6	–6.7	–	–3.6	–5.7	–	–	–	–	–	–	–
2,6-Dimethylphenol	–5.0	–6.0	–	–3.2	–5.1	–	–	–	–	–5.5	–7.2	–
1-Naphthol	–5.9	–7.1	–	–	–	–	–	–	–	–	–	–
Water	–	–	–	–	–	–	–	–	–	–6.4	–8.3	–5.3

<sup>a</sup> Calculated from the Abraham–Acree multi-parameter correlations with **L** descriptor, values are in kJ mol<sup>–1</sup>.<sup>b</sup> Calculated from the Abraham–Acree multi-parameter correlations with **V** descriptor, values are in kJ mol<sup>–1</sup>.<sup>c</sup> Calculated using Solomonov method [25], values are in kJ mol<sup>–1</sup>.

organic substances with benzene,  $\Delta_{\text{HB}}H^{A/\text{Ben}}$ , and with toluene,  $\Delta_{\text{HB}}H^{A/\text{Tot}}$ . Abraham model a-equation coefficients used in the latter computations were taken from published studies by Mintz and co-workers [14,15].

Solomonov et al. method [25] was used for validation of proposed equations for calculation of weak X–H... $\pi$  hydrogen bonding enthalpies. This method is based on Eq. (15). It was successfully applied for calculations hydrogen bond enthalpies in different solute–solvent systems [7,25,74–76]. All data necessary for using Eq. (15) are presented in the Supplementary material (Table S4).

$$\Delta_{\text{HB}}H^{A/S} = \Delta_{\text{soln}}H^{A/S} - (\delta_{\text{cav}}h^S - \delta_{\text{cav}}h^{C_6H_{12}}) \times V^A - \Delta_{\text{soln}}H^{A/C_6H_{12}} - (a_R + b_R) \times \sqrt{\delta_{\text{cav}}h^S} \times [(\Delta_{\text{soln}}H^{A/S_R} - \Delta_{\text{soln}}H^{A/C_6H_{12}}) - (\delta_{\text{cav}}h^{S_R} - \delta_{\text{cav}}h^{C_6H_{12}}) \cdot V^A] \quad (15)$$

Here  $\Delta_{\text{soln}}H^{A/S}$ ,  $\Delta_{\text{soln}}H^{A/S_R}$ ,  $\Delta_{\text{soln}}H^{A/C_6H_{12}}$  are the solution enthalpies of solute A in studied solvent S, standard solvent S<sub>R</sub>, and in cyclohexane, respectively;  $\delta_{\text{cav}}h^S$ ,  $\delta_{\text{cav}}h^{S_R}$ , and  $\delta_{\text{cav}}h^{C_6H_{12}}$  are the specific relative cavity formation enthalpies for each solvent; V<sup>A</sup> is the McGowan volume of solute. As a standard solvent which does not form hydrogen bonding with a solvent carbon tetrachloride was selected. The specific relative cavity formation enthalpy  $\delta_{\text{cav}}h^S$  is the enthalpy of transfer of an alkane from imaginary solvent S<sub>0</sub>, where the solution enthalpy of an alkane is zero ( $\Delta_{\text{soln}}H^{C_nH_{2n+2}/S}$ ), to the solvent S, divided by the alkane's McGowan volume  $V^{C_nH_{2n+2}}$ .

It is evident (Table 5) that hydrogen bonding enthalpies determined by two independent methods are in good agreement with each other. Consequently, enthalpies of solvation correlations based on the Abraham model provide a good tool for the prediction of hydrogen bonding enthalpies in aprotic solvents.

#### 4. Conclusion

The correlations presented in this paper further document the applicability of the Abraham solvation parameter model to describe gas-to-organic solvent solvation enthalpies for both organic and inorganic solutes. The derived  $\Delta H_{\text{Solv}}^{A/S}$  correlations for mesitylene and *p*-xylene permit extrapolations of gas-to-mesitylene (or *p*-xylene) and water-to-mesitylene (or *p*-xylene) partition coefficients measured at 298.15 K to other temperatures. Since not all manufacturing processes occur at 298.15 K, there is a growing need in the chemical industry to know solute transfer and partition properties at other temperatures as well. The Abraham model can also be useful for analysis of intermolecular interactions, such as hydrogen bonding between an aprotic solvent molecule and a proton donor solute.

#### Acknowledgement

M.V. and I.R. gratefully acknowledge the Russian Government Program of Competitive Growth of Kazan Federal University.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tca.2014.08.024>.

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