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Correlation of enthalpies of solvation of organic vapors and gases in ionic liquid solvents using a group contribution version of the Abraham solvation parameter model

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ABSTRACT

The cation and anion functional group contribution Abraham model that was previously proposed for mathematically correlating the partitioning coefficients of organic solutes and gases into anhydrous ionic liquid solvents has been extended to enthalpies of solvation. Numerical group values are determined for 10 cation functional groups and for 10 anion functional groups from regression analyses of 1077 experimental enthalpies of solvation. The derived correlations describe the 1077 experimental values to within a standard deviation of about 1.74 kJ/mole.

1. Introduction

This study continues our application of the Abraham solvation parameter model to describe the solubilization of organic solutes into ionic liquid (IL) solvents. Previously, we have developed a relatively simple method for predicting the logarithm of the gas-to-anhydrous IL partition coefficient, log *K*, [1–4]:

$$\begin{aligned}\log K &= c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})\mathbf{E} + (s_{\text{cation}} + s_{\text{anion}})\mathbf{S} \\ &\quad + (a_{\text{cation}} + a_{\text{anion}})\,\mathbf{A} + (b_{\text{cation}} + b_{\text{anion}})\mathbf{B} + (l_{\text{cation}} + l_{\text{anion}})\mathbf{L}\end{aligned} \tag{1}$$

and logarithm of the water-to-anhydrous IL partition coefficient, log *P*:

$$\begin{aligned}\log P &= c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})\mathbf{E} + (s_{\text{cation}} + s_{\text{anion}})\mathbf{S} \\ &\quad + (a_{\text{cation}} + a_{\text{anion}})\,\mathbf{A} + (b_{\text{cation}} + b_{\text{anion}})\mathbf{B} + (v_{\text{cation}} + v_{\text{anion}})\mathbf{V}\end{aligned} \tag{2}$$

by splitting the Abraham model equation coefficients into individual cation and anion contributions. The independent variables in the mathematical correlations are solute descriptors as follows: **A** and **B** are measures of the solute hydrogen-bond acidity and basicity solute descriptors of the solute, respectively, **E** and **S** refer to the excess molar refraction in units of $(\text{cm}^3\ \text{mol}^{-1})/10$ and dipolarity/polarizability descriptors, **V** is the McGowan volume in units of $(\text{cm}^3\ \text{mol}^{-1})/100$ and **L** is the logarithm of the gas-to-hexadecane partition coefficient 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 later 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 interactions are also related to solute size, hence both **V** and **L** will also describe the general solute–solvent interactions.

The regression coefficients and constants (*c*, *e*, *s*, *a*, *b*, *v* and *l*) are obtained by regression analysis of experimental data for a specific process (*i.e.*, a given partitioning process or a given chromatographic stationary phase and mobile phase combination, *etc.*). In the case of partition coefficients, where two solvent phases are involved, the *c*, *e*, *s*, *a*, *b*, *v* and *l* coefficients represent differences in the solvent phase properties. For any fully characterized system/process (those with calculated values for the equation coefficients) further values of log *K* and log *P* can be estimated with the known values for the solute descriptors. This is the major advantage of using Eqs. (1) and (2) to correlate solute properties, and the reason that prompted us to split the equation coefficients into ionic-specific coefficients in the case of IL solvents. To date we have reported numerical values for 19 cation-specific

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and 12 anion-specific equation coefficients based on experimental partition coefficient data for 1790 solute-IL pairs. The calculated equation coefficients described the observed log *K* and log *P* data to within overall standard deviations of 0.114 log units and 0.139 log units, respectively.

Sprunger et al. [5] and Grubbs et al. [6] later extended the ion-specific Abraham model to enthalpies of solvation, ΔH_{solv}:

$$\Delta H_{\text{solv}} = c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})\mathbf{E} + (s_{\text{cation}} + s_{\text{anion}})\mathbf{S} + (a_{\text{cation}} + a_{\text{anion}})\mathbf{A} + (b_{\text{cation}} + b_{\text{anion}})\mathbf{B} + (l_{\text{cation}} + l_{\text{anion}})\mathbf{L} \quad (3)$$

$$\Delta H_{\text{solv}} = c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})\mathbf{E} + (s_{\text{cation}} + s_{\text{anion}})\mathbf{S} + (a_{\text{cation}} + a_{\text{anion}})\mathbf{A} + (b_{\text{cation}} + b_{\text{anion}})\mathbf{B} + (v_{\text{cation}} + v_{\text{anion}})\mathbf{V} \quad (4)$$

of organic vapors and vapors in IL solvents. The enthalpy of solvation correlations allow predicted log *K* and log *P* values at 298 K to be corrected to other temperatures. Not all industrial and separation processes using IL solvents take place at 298 K. The Abraham model correlations that we have developed for partition coefficients for solute transfer to IL solvents pertain to 298 K.

The 12 cation-specific and 10 anion-specific equation coefficients that Grubbs et al. [6] determined can be combined to yield mathematical correlations capable of predicting ΔH_{solv} values of solutes in 120 (12 times 10) different IL solvents. The database used in developing the ΔH_{solv} correlations included inert gases, diatomic gas molecules, linear and cyclic alkanes and alkenes (up to dodecane), alkylbenzenes, linear and branched alcohols, linear and cyclic monoethers (plus 1,4-dioxane), chlorinated methanes and a few of the smaller aldehydes and ketones. The solute descriptor space defined by these compounds would be: $\mathbf{E} = 0.000–0.850$; $\mathbf{S} = 0.000–0.900$; $\mathbf{A} = 0.000–0.430$; $\mathbf{B} = 0.000–0.650$; $\mathbf{V} = 0.109–1.800$; and $\mathbf{L} = -1.200–5.700$.

Revelli et al. [7] extended the predictive applicability of the Abraham model by further splitting the cation-specific equation coefficients into functional group values:

$$\log K = \sum_{\text{group}} c_i n_i + \sum_{\text{group}} e_i n_i E + \sum_{\text{group}} s_i n_i S + \sum_{\text{group}} a_i n_i A + \sum_{\text{group}} b_i n_i B + \sum_{\text{group}} l_i n_i L + (c_{\text{anion}} + e_{\text{anion}} E + s_{\text{anion}} S + a_{\text{anion}} A + b_{\text{anion}} B + l_{\text{anion}} L) \quad (5)$$

and

$$\log P = \sum_{\text{group}} c_i n_i + \sum_{\text{group}} e_i n_i E + \sum_{\text{group}} s_i n_i S + \sum_{\text{group}} a_i n_i A + \sum_{\text{group}} b_i n_i B + \sum_{\text{group}} v_i n_i V + (c_{\text{anion}} + e_{\text{anion}} E + s_{\text{anion}} S + a_{\text{anion}} A + b_{\text{anion}} B + v_{\text{anion}} V) \quad (6)$$

while the anion-specific values remained intact. In Eqs. (5) and (6) n_i is the number of times the functional group appears in the cation. The authors were able to mathematically describe the 1450 available gas-to-IL partition coefficients (log *K* values) and 1410 water-to-IL partition coefficients (log *P* values) with 21 groups: 12 functional groups characterizing the cations (CH_3, CH_2, N_{cyclic}, C_{cyclic}, *etc.*) and 9 individual anions ($[PF_6]^-$, $[BF_4]^-$, $[SCN]^-$, *etc.*) to within 0.15 and 0.17 log units, respectively. The contributions of Revelli et al. represent a significant advance in extending the Abraham model to IL solvents. Once the cation and anion group values are known the model can be used as a purely predictive model.

In the present study we explore the applicability of the Abraham group contribution model proposed by Revelli et al. [7] in regards to describing enthalpies of solvation of organic vapors and gases into IL solvents. Experimental ΔH_{solv} data have been gathered from the published literature for solutes dissolved in 34 different IL solvents. The entire 1077 experimental value ΔH_{solv} database was analyzed in accordance with the enthalpic analogs of Eqs. (5) and (6). The calculated regression coefficients describe the experimental ΔH_{solv} data to within a standard deviation of 1.74 kJ/mole.

2. Enthalpy of solvation database

Through a search of the published literature we have assembled 1077 ΔH_{solv} values for organic vapors and gases dissolved in IL solvents. The experimental values were determined from gas-liquid chromatographic retention measurements on an IL stationary phase. The measured retention is related to the thermodynamic infinite dilution activity coefficient of the solute, $\gamma^{\infty}_{\text{solute}}$. As part of the published chromatographic studies, authors often perform the retention time measurements at several temperatures. The solute's molar enthalpy of solution in the IL is calculated from the variation of $\gamma^{\infty}_{\text{solute}}$ with temperature, *i.e.*, $\Delta H^{\text{ex},\infty} = R\partial \ln \gamma^{\infty}_{\text{solute}} / \partial(1/T)$. Enthalpies of solution determined in this fashion assume that $\Delta H^{\text{ex},\infty}$ is independent of temperature over the range of the experimental measurements. Most of the experimental $\gamma^{\infty}_{\text{solute}}$ measurements were performed over a 30 K temperature range, and we have taken the calculated $\Delta H^{\text{ex},\infty}$ values to be at the median temperature of the respective $\gamma^{\infty}_{\text{solute}}$ measurements. For he majority of measurements the median temperature corresponded to 323 ± 5 K.

The published $\Delta H^{\text{ex},\infty}$ values were converted to gas-to-RTIL enthalpies of transfer by:

$$\Delta H_{\text{Solv}} = \Delta H^{\text{ex},\infty} - \Delta H_{\text{Vap},323\,\text{K}} \quad (7)$$

subtracting the solute's enthalpy of vaporization $\Delta H_{\text{Vap},323\,\text{K}}$ [8]. The organic solutes were liquids at 323 K. Enthalpies of vaporization used in this conversion were based on the published $\Delta H_{\text{Vap},298\,\text{K}}$ data from the compilation by Chickos and Acree [8], and were converted to a common temperature of 323 K using the method recommended by the authors. The correction of ΔH_{Vap} from 298 K to 323 K amounted to less than 2.5 kJ/mole for the solutes considered here, which is believed to be less than the experimental uncertainty in the $\Delta H^{\text{ex},\infty}$ data.

Our enthalpy of solvation database was recently published [5,6] in connection with the calculation of cation-specific and anion-specific Abraham model equation coefficients for Eqs. (3) and (4). At the time of the publication the database contained 942 experimental values. Rather than republish the entire database again, we have tabulated in Table 1 recently added ΔH_{solv} data for organic solutes dissolved in 1-propyl-1-methylpiperidinium *bis*((trifluoromethyl)sulfonyl)-imide, ($[PMPip]^+[(Tf)_2N]^-$) [9], 1-(3-hydroxypropyl)pyridinium *tris*(pentafluoroethyl)trifluoro-phosphate, ($[1\text{-PrOHPy}]^+[FAP]^-$) [10], 4-methyl-N-butylpyridinium thiocyanate, ($[4\text{-MBPy}]^+[SCN]^-$) [11], and 1-butyl-1-methylpyrrolidinium thiocyanate, ($[BMPyrr]^+[SCN]^-$) [11]. Solute descriptors used in the calculations are of experimental origin, and came from our solute descriptor database, which now contains values for more than 4000 different organic and organometallic compounds. Solute descriptors for the compounds studied here can be found in the supporting information associated with our published ionic liquid papers [1–3] that proposed splitting the Abraham model equation coefficients into separate cation and anion contributions.

Table 1
Experimental enthalpies of solvation, ΔH_{solv} (in kJ/mole), of organic vapors in ($[\text{4-MBPy}]^+[\text{SCN}]^-$), ($[\text{BMPyrr}]^+[\text{SCN}]^-$), ($[\text{1-PrOHPy}]^+[\text{FAP}]^-$) and ($[\text{PMPip}]^+[(\text{Tf})_2\text{N}]^-$) at 323 K.

	($[\text{4-MBPy}]^+[\text{SCN}]^-$)	($[\text{BMPyrr}]^+[\text{SCN}]^-$)	($[\text{1-PrOHPy}]^+[\text{FAP}]^-$)	($[\text{PMPip}]^+[(\text{Tf})_2\text{N}]^-$)
Solute				
Pentane			−15.90	
Hexane	−21.52		−19.60	−21.98
Heptane	−27.03	−26.28	−23.30	−27.08
Octane	−31.78	−31.23	−27.30	−31.83
Nonane	−34.55	−35.64	−31.20	−36.18
Decane	−39.55	−40.14	−35.10	−40.47
Cyclopentane	−21.17	−21.06	−18.30	−20.00
Cyclohexane	−24.59	−24.78	−21.00	−23.88
Cycloheptane	−31.00	−31.12	−26.50	−30.48
Cyclooctane	−35.50	−35.65	−31.20	−35.43
1-Pentene		−19.44	−18.00	
1-Hexene	−24.55	−25.08	−22.90	−24.85
1-Heptene	−29.26	−29.75	−27.10	−29.77
1-Octene	−33.70	−34.57	−31.10	−34.77
1-Pentyne	−29.09			
1-Hexyne	−32.04	−33.08	−27.30	−30.72
1-Heptyne				−39.47
1-Octyne	−40.78	−41.25	−35.40	−39.70
Benzene	−33.41	−34.84	−34.10	−33.73
Toluene	−37.98	−39.41	−38.10	−38.33
Ethylbenzene	−40.86	−41.43	−40.83	−41.53
o-Xylene	−42.90	−43.41	−42.59	−43.09
m-Xylene	−42.07	−42.05	−42.07	−42.56
p-Xylene	−41.82	−41.78	−41.64	−42.39
Methanol	−35.20	−36.88	−34.00	−29.24
Ethanol	−38.38	−40.20	−38.40	−33.44
1-Propanol			−42.50	−37.96
1-Butanol			−45.80	−41.39
1-Pentanol				−48.73
Thiophene	−34.92	−36.52	−34.37	−34.44
Tetrahydrofuran	−31.11	−31.87	−39.80	−32.57
Methyl tert-butyl ether	−27.05	−28.00	−36.60	−27.94
Diethyl Ether	−23.49	−23.94	−32.70	−24.49
Dipropyl ether	−29.84	−30.35	−37.50	−31.47
Dibutyl ether	−37.66	−38.01	−44.17	−38.84
Acetone	−31.76	−32.10	−39.70	−32.51
2-Pentanone	−36.72	−37.47	−44.30	−38.35
3-Pentanone	−36.65	−38.44	−44.20	−39.07
2-Hexanone				−42.91
3-Hexanone				−42.27

3. Results and discussion

The 1077 experimental ΔH_{solv} values (in kJ/mole) were analyzed to yield the following correlations:

$$\Delta H_{\mathrm{solv}}(\text{in kJ/mole}) = \sum_{\text{group}} c_i n_i + \sum_{\text{group}} e_i n_i E + \sum_{\text{group}} s_i n_i S + \sum_{\text{group}} a_i n_i A + \sum_{\text{group}} b_i n_i B + \sum_{\text{group}} l_i n_i L + \sum_{\text{anion}} (c_{\text{anion}} + e_{\text{anion}} E + s_{\text{anion}} S + a_{\text{anion}} A + b_{\text{anion}} B + l_{\text{anion}} L) \quad (8)$$

$$(N = 1077,\ \mathrm{SD} = 1.73,\ R^2 = 0.998 \text{ and } F = 3612)$$

and

$$\Delta H_{\mathrm{solv}}(\text{in kJ/mole}) = \sum_{\text{group}} c_i n_i + \sum_{\text{group}} e_i n_i E + \sum_{\text{group}} s_i n_i S + \sum_{\text{group}} a_i n_i A + \sum_{\text{group}} b_i n_i B + \sum_{\text{group}} v_i n_i V + \sum_{\text{anion}} (c_{\text{anion}} + e_{\text{anion}} E + s_{\text{anion}} S + a_{\text{anion}} A + b_{\text{anion}} B + v_{\text{anion}} V) \quad (9)$$

$$(N = 1077,\ \mathrm{SD} = 1.74,\ R^2 = 0.998 \text{ and } F = 3550)$$

where N corresponds to the number of solutes, R^2 denotes the squared correlation coefficient, SD is the standard deviation and F corresponds to the Fisher F-statistic. Regression analyses were performed using SPSS statistical software. In accordance with the computation methodology that we recommended in our earlier papers [1–3] we have set the anion-specific equation coefficients of $[(\text{Tf})_2\text{N}]^-$ equal to zero. As noted previously when we first proposed splitting the Abraham model coefficients into individual cation-specific and anion-specific contributions, the ion-specific coefficients in Eqs. (1)–(4) are paired. Each cation-specific coefficient goes together with its anion-specific coefficient counterpart to make up a summed value that the five solute descriptors are multiplied by. The cation group contribution method proposed by Revelli et al. [7] is also based upon a similar separation of cation group value coefficients and anion-specific coefficients, and the same pairing still applies.

We have followed the method proposed by Revelli et al. [7] in splitting the organic cations into various functional groups. Four groups: (CH_3, CH_2, –O–, and OH) are defined to construct the alkyl-chain (or functionalized alkyl-chain) of the IL cation. The remaining six functional groups are needed to construct the imidazolium, pyridinium and piperidinium ring system ($CH_{2\text{cyclic}}$, CH_{cyclic}, C_{cyclic}, and N_{cyclic}), and the ammonium ($>N^+<$) and sulfonium ($>S^+-$) positively-charged headgroups. Ten groups are used for the anions: $[(\text{Tf})_2\text{N}]^-$ is the *bis*(trifluoromethylsulfonyl)imide anion; $[BF_4]^-$ is tetrafluoroborate anion; $[PF_6]^-$ is the hexafluorophosphate anion; $[NO_3]^-$ is nitrate anion; $[\text{Trif}]^-$ is the trifluoromethanesulfonate anion; $[F_3\text{Ac}]^-$ is the trifluoroacetate anion; $[\text{EtSO}_4]^-$ is the ethylsulfate anion; $[\text{SCN}]^-$ is the thiocyanate anion, $[B(CN)_4]^-$ is the tetracyanoborate anion; and $[\text{FAP}]^-$ is the *tris*(pentafluoroethyl)trifluoro phosphate anion.

The calculated group values for Eqs. (8) and (9) are listed in Tables 2 and 3, respectively. The standard errors in the coefficients are given in parenthesis directly below the respective values. Zeroes

Table 2
Cation-group and anion-specific equation coefficients for the Abraham model enthalpy of solvation correlation (Eq. (8)).

Group/ion	$c_{\text{group/ion}}$	$e_{\text{group/ion}}$	$s_{\text{group/ion}}$	$a_{\text{group/ion}}$	$b_{\text{group/ion}}$	$l_{\text{group/ion}}$
Cation groups						
CH_3	0.000	−52.943	0.000	−34.721	0.000	0.000
		(6.183)		(14.840)		
CH_2	−0.280	−0.382	1.940	0.479	−0.416	−0.049
	(0.167)	(0.337)	(0.402)	(0.478)	(0.440)	(0.049)
Ether, –O–	1.839	8.978	−14.745	−5.083	6.654	−0.455
	(1.027)	(2.102)	(2.623)	(2.532)	(2.509)	(0.304)
OH	−17.121	−69.687	44.812	−23.459	−31.510	−3.962
	(3.453)	(10.046)	(10.345)	(19.831)	(12.608)	(1.006)
$CH_{2\text{cyclic}}$	−0.872	12.431	−4.605	2.293	1.020	−1.047
	(0.329)	(1.441)	(0.609)	(3.224)	(0.606)	(0.093)
CH_{cyclic}	−1.292	−0.123	−3.952	−5.363	0.870	−0.756
	(0.576)	(0.870)	(0.970)	(1.113)	(0.928)	(0.163)
C_{cyclic}	2.533	55.618	−4.152	30.725	−0.092	−2.151
	(1.267)	(6.601)	(1.950)	(15.270)	(1.849)	(0.358)
N_{cyclic}	−0.332	54.191	−2.781	30.550	−4.312	−2.444
	(0.801)	(6.348)	(1.267)	(15.016)	(1.164)	(0.227)
$>N^+<$	−6.413	214.27	−15.225	114.729	−5.942	−6.503
	(1.140)	(24.74)	(3.121)	(59.28)	(3.581)	(0.290)
$>S^+–$	−2.072	175.04	−38.699	89.968	−4.301	−7.588
	(1.806)	(19.10)	(7.941)	(45.852)	(13.302)	(0.543)
Anions						
$[(Tf)_2N]^-$	0.000	0.000	0.000	0.000	0.000	0.000
$[BF_4]^-$	−1.261	−3.157	3.268	3.023	−1.489	0.636
	(0.719)	(1.543)	(1.877)	(2.217)	(2.088)	(0.207)
$[PF_6]^-$	−6.275	11.642	−22.161	14.830	13.204	1.063
	(0.743)	(2.618)	(3.232)	(3.263)	(3.312)	(0.231)
$[EtSO_4]^-$	−2.530	0.748	5.993	−14.328	−0.666	0.836
	(1.415)	(2.515)	(2.943)	(3.652)	(3.286)	(0.329)
$[Trif]^-$	0.597	4.412	−4.293	−13.537	3.864	−0.491
	(0.921)	(1.715)	(2.036)	(2.159)	(1.953)	(0.275)
$[F_3Ac]^-$	4.296	11.198	−5.827	−8.839	−17.442	−1.674
	(1.858)	(5.009)	(7.985)	(11.727)	(13.324)	(0.560)
$[NO_3]^-$	−4.776	2.670	0.000	−10.847	4.444	0.609
	(3.384)	(2.900)		(4.541)	(2.816)	(1.007)
$[SCN]^-$	5.650	8.543	−12.763	−22.391	5.737	−1.604
	(0.940)	(1.754)	(2.236)	(2.027)	(2.080)	(0.266)
$[B(CN)_4]^-$	19.277	7.413	−24.612	−35.894	20.736	−4.435
	(2.499)	(7.413)	(10.015)	(14.135)	(13.668)	(0.745)
$[FAP]^-$	24.639	20.148	−48.570	−1.581	8.943	−4.850
	(2.488)	(7.223)	(9.347)	(12.915)	(11.930)	(0.728)

are entered for the *c*, *s*, *b*, *l* and *v* values for the CH_3 functional group. The SPSS software used in the regression analyses eliminated these CH_3 values due to high colinearity. We also performed the analysis with Microsoft Solver software, which retained the CH_3 group values. The goodness-of-fit of both sets of analyses as measured by the standard deviation was essentially identical: SPSS analyses: SD = 1.73 kJ/mole for Eq. (8) and SD = 1.74 kJ/mole for Eq. (9) versus Microsoft Solver analyses: SD = 1.75 kJ/mole for Eq. (8) and SD = 1.76 kJ/mole for Eq. (9). No loss in descriptive ability resulted from the removal of the CH_3 group values. The colinearity issue will likely be eliminated as more ΔH_{solv} values are added to the database. All of the IL solvents in the ΔH_{solv} database contain an CH_2 alkyl-chain functional group, and all of the IL solvents, except for ($[1\text{-PrOHPy}]^+[FAP]^-$) possess a terminal CH_3 alkyl-chain functional group. The tabulated group values in Tables 2 and 3 are intended strictly for the prediction of ΔH_{solv} values for solute-IL combinations for which experimental data is not available. Since no physical significance is given to the calculated numerical values the removal of a few of the CH_3 group values by the SPSS software for colinearity reasons is not a concern.

Eqs. (8) and (9) are statistically very good, and describe the experimental ΔH_{solv} values that cover a 54 kJ/mole range to within standard deviations of 1.73 kJ/mole (Eq. (8)) and 1.74 kJ/mole (Eq. (9)) as shown in Figs. 1 and 2. This is comparable in magnitude to the standard deviations of SD = 1.62 kJ/mole and SD = 1.68 kJ/mole that Grubbs et al. [6] reported for Eqs. (3) and (4) using a slightly smaller data base of 942 experimental ΔH_{solv} values. Careful examination of the individual residuals between the calculated and observed values revealed that Eq. (8) described 67.4% (726 of 1077 values) of the enthalpy of solvation data to within 1.5 kJ/mole, 91.2% (982 of 1077 values) to within 3 kJ/mole. Only 8.8% of the predicted ΔH_{solv}

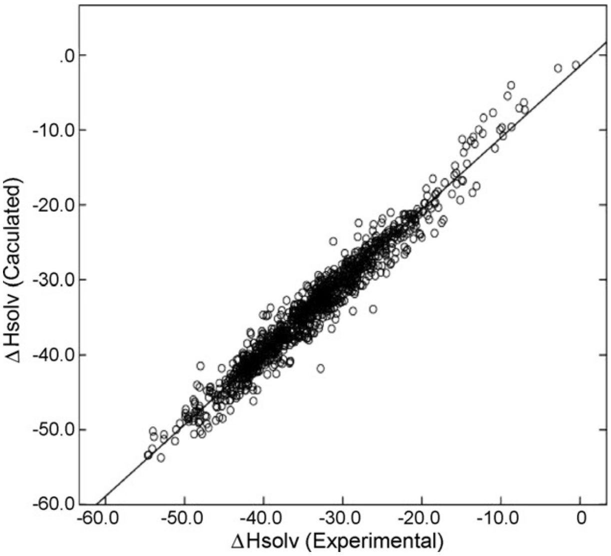

Fig. 1. Comparison of the experimental ΔH_{solv} data and calculated values based on Eq. (8) (using coefficients in Table 2).

Table 3
Cation-group and anion-specific equation coefficients for the Abraham model enthalpy of solvation correlation (Eq. (9)).

Group/ion	$c_{\text{group/ion}}$	$e_{\text{group/ion}}$	$s_{\text{group/ion}}$	$a_{\text{group/ion}}$	$b_{\text{group/ion}}$	$v_{\text{group/ion}}$
Cation groups						
CH_3	0.000	−50.338	0.000	−33.235	0.000	0.000
		(6.238)		(14.948)		
CH_2	−0.449	−0.878	2.372	1.285	−0.872	−0.078
	(0.205)	(0.324)	(0.412)	(0.485)	(0.443)	(0.177)
Ether, –O–	2.267	6.160	−11.541	−7.769	5.901	−1.739
	(1.254)	(2.036)	(2.647)	(2.561)	(2.542)	(1.089)
OH	−21.140	−42.496	19.209	−24.190	−14.567	14.472
	(4.145)	(10.391)	(10.581)	(20.069)	(12.567)	(3.539)
$CH_{2\text{cyclic}}$	0.311	9.680	−4.342	2.001	0.021	−4.056
	(0.393)	(1.449)	(0.622)	(3.251)	(0.614)	(0.328)
CH_{cyclic}	−0.196	−2.123	−3.338	−4.712	−0.644	−3.112
	(0.679)	(0.817)	(1.016)	(1.150)	(0.940)	(0.572)
C_{cyclic}	1.759	51.464	−5.613	27.335	2.798	−5.736
	(1.489)	(6.615)	(2.080)	(15.395)	(1.875)	(1.252)
N_{cyclic}	1.365	49.663	−5.799	26.235	−2.018	−8.602
	(0.940)	(6.390)	(1.338)	(15.129)	(1.180)	(0.793)
$>N^+<$	0.189	196.90	−22.137	103.60	−3.605	−24.437
	(1.379)	(24.96)	(3.206)	(59.72)	(3.616)	(1.062)
$>S^+–$	5.356	142.76	−24.146	72.137	−9.443	−28.360
	(2.276)	(19.28)	(7.969)	(46.220)	(13.396)	(1.992)
Anions						
$[(Tf)_2N]^-$	0.000	0.000	0.000	0.000	0.000	0.000
$[BF_4]^-$	−0.180	1.473	−1.929	−1.716	2.933	0.975
	(0.906)	(1.499)	(1.951)	(2.276)	(2.116)	(0.777)
$[PF_6]^-$	−3.422	14.191	−25.662	10.300	16.219	0.628
	(0.971)	(2.572)	(3.295)	(3.334)	(3.347)	(0.911)
$[EtSO_4]^-$	−1.916	5.515	1.178	−16.673	2.593	2.479
	(1.741)	(2.461)	(3.134)	(3.798)	(3.340)	(1.239)
$[Trif]^-$	0.486	1.891	−2.554	−12.985	3.043	−1.351
	(1.106)	(1.639)	(2.059)	(2.177)	(1.966)	(0.969)
$[F_3Ac]^-$	5.748	−7.910	16.791	−15.231	−25.088	−6.021
	(2.366)	(5.063)	(8.032)	(11.972)	(13.420)	(2.079)
$[NO_3]^-$	−8.452	4.499	−0.360	−8.584	7.767	4.585
	(3.655)	(2.512)	(3.242)	(4.536)	(2.809)	(3.205)
$[SCN]^-$	6.570	1.847	−7.516	−22.641	2.872	−5.525
	(1.140)	(1.761)	(2.251)	(2.057)	(2.115)	(0.956)
$[B(CN)_4]^-$	21.358	−15.452	−1.216	−37.228	9.261	−14.449
	(3.054)	(7.806)	(10.119)	(14.398)	(13.568)	(2.642)
$[FAP]^-$	27.162	−4.542	−23.828	−2.669	−3.828	−16.009
	(3.006)	(7.713)	(9.550)	(13.129)	(11.865)	(2.576)

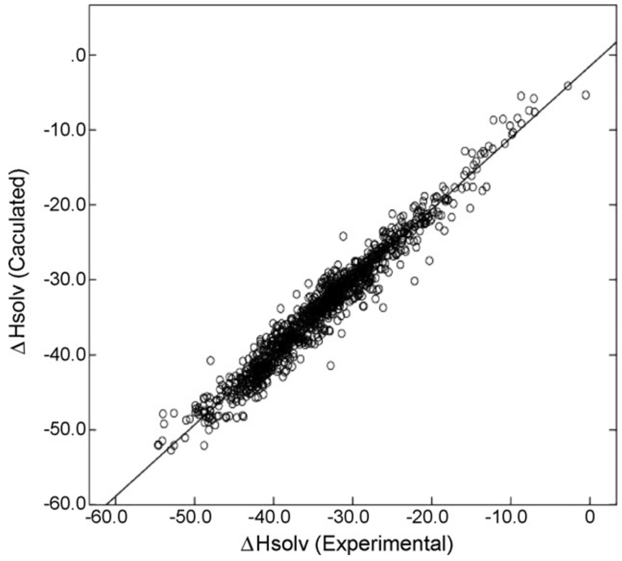

Fig. 2. Comparison of the experimental ΔH_{solv} data and calculated values based on Eq. (9) (using coefficients in Table 3).

values fell more than 3 kJ/mole from the experimental value, with the largest residual being −9.02 kJ/mole. The residual analysis is depicted graphically in Fig. 3. Similar results were noted for Eq. (9); 67.5% of the back-calculated enthalpies of solvation differed from the observed value by less than 1.5 kJ/mole and 91.7% differed by less than 3 kJ/mole. Less than 8.3% of the predicted ΔH_{solv} values were more than 3 kJ/mole from the observed value (see Fig. 4 for a graphical summary). The largest residual for the Eq. (7) correlation is −8.61 kJ/mole. We expect these values would be reflect the predictive ability that Eqs. (8) and (9) would exhibit in terms of predicting enthalpies of solvation for organic solutes dissolved in ILs containing the 9 cation functional groups and 10 anions given in Tables 2 and 3, provided that the solute descriptors of the compounds fall within the area of predictive chemical space defined by the calculated equation coefficients.

In order to assess further the predictive capabilities of Eq. (8) and (9), the 1077 data points were divided into a training set and a test set by selecting every other data point in the complete database. The selection ensured that each ion was equally represented in both the training and test sets. The selected data points became the training set, and the compounds that were left served as the test set. Analysis of the 539 experimental data points in the training set gave the cation-specific and anion-specific equation coefficients listed in Tables S1 and S2 (Supporting Material), with SD = 1.64 and SD = 1.64 kJ/mole, $R^2 = 0.998$ and $R^2 = 0.998$, and $F = 1785$ and $F = 1767$ for Eqs. (8) and (9), respectively. The training set equation coefficients were then used to predict ΔH_{solv} values for the

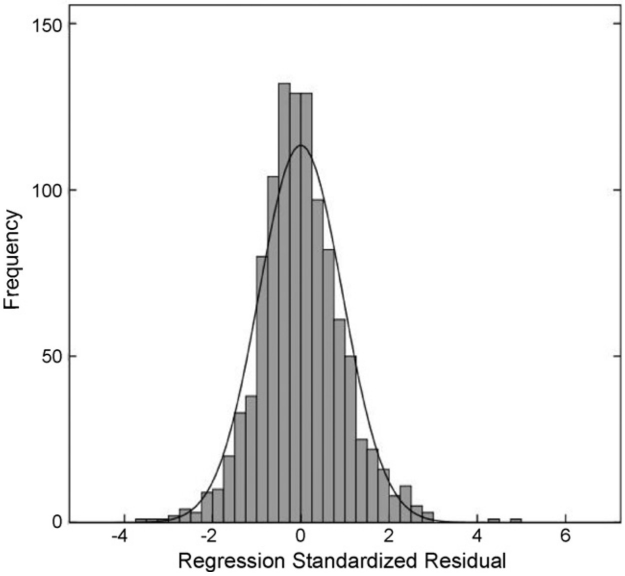

Fig. 3. Histogram of the frequency of occurrence of the regression standardized residuals for difference between observed ΔH_{solv} data and predicted values based on Eq. (8).

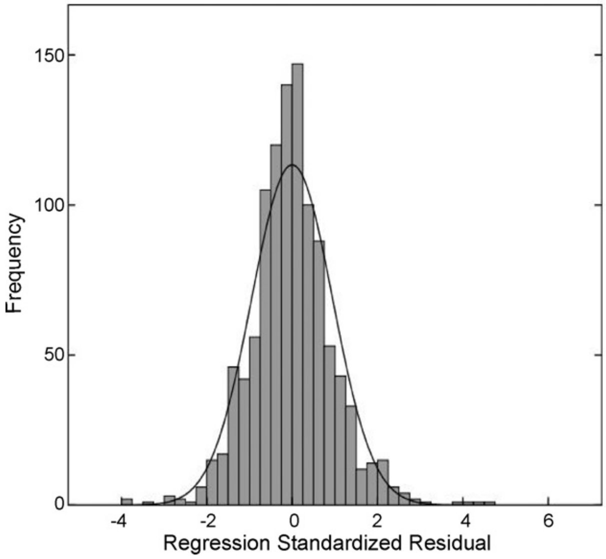

Fig. 4. Histogram of the frequency of occurrence of the regression standardized residuals for difference between observed ΔH_{solv} data and predicted values based on Eq. (9).

remaining 538 compounds in the test set. For the predicted and experimental values we find SD = 1.94 kJ/mole, average absolute error (AAE) = 1.47 kJ/mole, and average error (AE) = 0.11 kJ/mole for Eq. (8). Very similar results of SD = 1.90 kJ/mole, average absolute error (AAE) = 1.40 kJ/mole, and average error (AE) = 0.07 kJ/mole for Eq. (9). There is therefore very little bias in the predictions using Eq. (8) (coefficients in Table S1) with AE equal to 0.11 kJ/mole and Eq. (9) (coefficients in Table S2) with AE equal to 0.07 kJ/mole.

The correlations presented here further document the applicability of the group contribution version of the Abraham model recently proposed by Revelli et al. [7] The authors demonstrated that the model described the observed gas-to-IL partition coefficients and water-to-IL partition coefficients for a wide range of organic solutes and gases. We find in the present study that the model also provides a reasonably accurate mathematical description of enthalpy of solvation data for solutes dissolved in ionic liquids.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.07.030.

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