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# Mathematical correlations for describing enthalpies of solvation of organic vapors and gaseous solutes into ionic liquid solvents

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ABSTRACT

Previously reported ion-specific equation coefficients for the Abraham general solvation model are updated using recently published enthalpy of solution data for organic solutes dissolved in room temperature ionic liquids (RTILs). Reported for the first time are equation coefficients for 1-hexyloxymethyl-3-methylimidazolium, 1,3-dihexyloxymethylimidazolium, 3-methyl-N-butylpyridinium, *tris*(pentafluoroethyl)trifluoro phosphate, and tetracyanoborate ions. In total 12 sets of cation-specific and 10 sets of anion-specific equation coefficients have been determined for each model. The derived correlations describe the 942 experimental enthalpies of solvation to within a standard deviation of about 1.65 kJ/mol.

## 1. Introduction

New generation ionic liquids (ILs) have become an increasing popular solvent choice in manufacturing applications involving synthesis of new organic materials, construction of electrochemical-based and optical-based sensing devices, extractive distillations and chromatographic separations, capture of acidic flue gases, and high-temperature lubrication of metallic contacts. Select alkylimidazolium-based ILs have exhibited large benzene versus cyclohexane vapor selectivities [1], carbon dioxide versus nitrogen gas selectivities [2], and large carbon dioxide versus methane gas selectivities [2]. Ionic liquids have also shown high selectivity in the extractive separation of heavy metal ions from waste water effluents produced by metal-plating, ceramic, metallurgical and photographic film manufacturing processes. The applicability of ionic liquids for so many manufacturing processes results from the fact that the ionic liquid's chemical and physical properties can be judiciously modified by simply changing the cation–anion combination. Currently there are more than 1000 different ILs that are commercially available. It is not economically feasible to experimentally study every possible cation–anion combination, and predictive methods need to be developed to aid researchers in selecting the most appropriate IL for a given application.

The present study continues our examination of the solubilizing properties that ionic liquids exhibit towards organic solutes and gases. Previously we [3–7] have developed mathematical correlations for describing solute transfer from the gas phase

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

$$\begin{aligned}\Delta H_{\text{solv}} = {} & c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})E + (s_{\text{cation}} + s_{\text{anion}})S \\ & + (a_{\text{cation}} + a_{\text{anion}})A + (b_{\text{cation}} + b_{\text{anion}})B \\ & + (l_{\text{cation}} + l_{\text{anion}})L \qquad (2)\end{aligned}$$

$$\begin{aligned}\Delta H_{\text{solv}} = {} & c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})E + (s_{\text{cation}} + s_{\text{anion}})S \\ & + (a_{\text{cation}} + a_{\text{anion}})A + (b_{\text{cation}} + b_{\text{anion}})B \\ & + (v_{\text{cation}} + v_{\text{anion}})V \qquad (3)\end{aligned}$$

and for the partitioning of solutes between water and an IL

$$\begin{aligned}\log P = {} & c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}})E + (s_{\text{cation}} + s_{\text{anion}})S \\ & + (a_{\text{cation}} + a_{\text{anion}})A + (b_{\text{cation}} + b_{\text{anion}})B \\ & + (v_{\text{cation}} + v_{\text{anion}})V \qquad (4)\end{aligned}$$

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based on the ion-specific equation coefficient version of the Abraham general solvation model. The dependent variables in Eqs. (1)–(4) are the logarithm of the solute's gas-to-IL partition coefficient, log *K*, the solute's enthalpy of solvation in the IL, $\Delta H_{\text{solv}}$, and the logarithm of the solute's water-to-IL partition coefficient. 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 cation-specific and anion-specific regression coefficients and constants (lowercase letters) are determined by regression analyses of the experimental data for the given partition process. In the case of partition coefficients involving two condensed solvent phases, the lower case equation 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*, $\Delta H_{\text{solv}}$, and log *P* can be estimated with known values for the solute descriptors.

The major advantage of splitting the equation coefficients into individual cation-specific and anion-specific contributions is that one can make predictions for many more ILs. The 19 cation and 12 anion coefficients that we have calculated thus far for the log *K* and log *P* equations were based on experimental partition coefficient data for 36 different ILs. [6] It takes approximately 40–50 experimental log *K* values (or log *P* values) to develop an Abraham model specifically for a given IL. We have developed very few IL-specific Abraham model correlations. On the other hand, the 19 cation and 12 anion coefficients that we have calculated can be combined to give predictive linear solvation energy relationships (LSERs) for 228 ILs (19 × 12). The predictive log *K* and log *P* correlations pertain to 298 K. The number of calculated equation coefficients for the enthalpy of solvation correlations is considerably less. Only 9 cation-specific and 8 anion-specific equation coefficients have been calculated for $\Delta H_{\text{solv}}$ equations. [7] The calculated coefficients allow one to make $\Delta H_{\text{solv}}$ predictions in 72 different ILs. Enthalpy of solvation predictions are important in that the $\Delta H_{\text{solv}}$ values allow one to extrapolate the predicted log *K* and log *P* values based on Eqs. (1) and (4) to other temperatures. Manufacturing and separation processes are not restricted to 298 K, and there is a growing need to estimate partitioning properties at other temperatures as well.

In the present communication we have extended our earlier enthalpy of solvation study to include ionic liquids containing additional cations and anions. Experimental enthalpy of solution data have been gathered from the recently published literature for solutes dissolved in 1-hexyloxymethyl-3-methylimidazolium *bis*(trifluoromethyl-sulfonyl)imide, ($[\text{HxomMIm}]^+$ $[(\text{Tf})_2\text{N}]^-$) [8], 1,3-dihexyloxymethylimidazolium *bis*(trifluoromethyl sulfonyl)imide, ($[(\text{Hxom})_2\text{Im}]^+[(\text{Tf})_2\text{N}]^-$) [8], 4-methyl-N-butylpyridinium *bis*(trifluoromethyl sulfonyl)imide, ($[\text{4-BMPy}]^+[(\text{Tf})_2\text{N}]^-$) [9], 1-methyl-3-ethylimidazolium *tris*(pentafluoroethyl)trifluoro phosphate, ($[\text{MEIm}]^+[\text{FAP}]^-$) [10], 1-methyl-3-ethylimidazolium tetracyanoborate ($[\text{MEIm}]^+$ $[\text{B(CN)}_4]^-$) [11], and 3-methyl-N-butylpyridinium triflate ($[\text{3-MBPy}]^+[\text{Trif}]^-$) [12]. The newly compiled $\Delta H_{\text{solv}}$ values were added to our existing enthalpy of solvation database for ionic liquid solvents, and the entire 942 experimental value database was regressed in accordance with Eqs. (2) and (3) to yield ion-specific equation coefficients for 12 cations and for 10 anions. Only 675 experimental values were used in our earlier study [7]. Reported for the first time are ion-specific equation coefficients for $[\text{HxomMIm}]^+$, $[(\text{Hxom})_2\text{Im}]^+$, $[\text{3-MBPy}]^+$, $[\text{B(CN)}_4]^-$ and $[\text{FAP}]^-$.

## 2. Experimental enthalpy of solvation data set

Thermodynamic properties of solutes dissolved in ionic liquid solvents are often determined from gas–liquid chromatographic retention time measurements using the IL as the stationary phase solvent. Through standard thermodynamic relationships the measured retention time is related to the 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. Our search of the published literature found recently published $\Delta H^{\text{ex},\infty}$ data for solutes dissolved in six more ionic liquids. 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 the 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

$$\Delta H_{\text{solv}} = \Delta H^{\text{ex},\infty} - \Delta H_{\text{Vap},323\,\text{K}} \tag{5}$$

subtracting the solute's enthalpy of vaporization $\Delta H_{\text{Vap},323\,\text{K}}$ [13] 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 [13], and were converted to a common temperature of 323 K using the method recommended by the authors. The correction of $\Delta H_{\text{Vap}}$ from 298 to 323 K amounted to less than −2.5 kJ/mol for the solutes considered here, which is believed to be less than the experimental uncertainty in the $\Delta H^{\text{ex},\infty}$ data. Including the enthalpy of solvation data from our earlier paper [7], we have $\Delta H_{\text{solv}}$ values for 942 different solute-IL pairs. For convenience, we have compiled in Table S1 (Supporting Information) the $\Delta H_{\text{solv}}$ values for solutes dissolved in ($[\text{HxomMIm}]^+[(\text{Tf})_2\text{N}]^-$), $[(\text{Hxom})_2\text{Im}]^+[(\text{Tf})_2\text{N}]^-$), ($[\text{4-BMPy}]^+[(\text{Tf})_2\text{N}]^-$), ($[\text{MEIm}]^+[\text{FAP}]^-$), ($[\text{MEIm}]^+[\text{B(CN)}_4]^-$), and ($[\text{3-MBPy}]^+[\text{Trif}]^-$) at 323 K, along with the values of the respective solute descriptors. The latter values are of experimental origin and came from our solute descriptor database, which now contains values for more than 4000 different organic and organometallic compounds.

## 3. Results and discussion

The newly published experimental data has significantly increased our enthalpy of solvation data for solutes dissolved in ionic liquids. Updated values of the cation-specific and anion-specific equation coefficients were determined by regression analysis of the 942 $\Delta H_{\text{solv}}$ values (in kJ/mol) to yield the following two LSERs

$$\begin{aligned}\Delta H_{\text{solv}}\ (\text{kJ/mol}) = {} & \sum_{\text{cation}} (c_{\text{cation}} + e_{\text{cation}}E + s_{\text{cation}}S \\ & + a_{\text{cation}}A + b_{\text{cation}}B + l_{\text{cation}}L) \\ & + \sum_{\text{anion}} (c_{\text{anion}} + e_{\text{anion}}E + s_{\text{anion}}S \\ & + a_{\text{anion}}A + b_{\text{anion}}B + l_{\text{anion}}L)\end{aligned} \tag{6}$$

$(N = 942,\ R^2 = 0.998,\ R^2_{\text{adj}} = 0.998,\ \text{SD} = 1.619,\ F = 3036)$

and

$$\begin{aligned}\Delta H_{\text{solv}}\ (\text{kJ/mol}) = {} & \sum_{\text{cation}} (c_{\text{cation}} + e_{\text{cation}}E + s_{\text{cation}}S \\ & + a_{\text{cation}}A + b_{\text{cation}}B + v_{\text{cation}}V) \\ & + \sum_{\text{anion}} (c_{\text{anion}} + e_{\text{anion}}E + s_{\text{anion}}S \\ & + a_{\text{anion}}A + b_{\text{anion}}B + v_{\text{anion}}V) \end{aligned} \tag{7}$$

($N = 942$, $R^2 = 0.998$, $R^2_{\text{adj}} = 0.997$, SD = 1.677, $F = 2826$)

In accordance with the computation methodology that we recommended in our earlier papers [3–5] we have set the anion-specific equation coefficients of $[(\text{Tf})_2\text{N}]^-$ equal to zero. As noted previously the cation-specific and anion-specific coefficients in Eqs. (6) and (7) paired. Each cation-specific coefficient goes together with its anion-specific counterpart to make up a summed value that the five solute descriptors are multiplied by. If one were to perform a regression analysis on Eqs. (6) and (7) the statistical software would generate numerical equation coefficients based on some reference point. The reference point would likely depend on the particular database used and the software's built-in convergence routine. Calculation of additional ion values at some later time would be difficult as there is no guarantee that the next regression analyses would find the same reference point. To circumvent this problem we have defined a set reference for the calculated ion-specific equation coefficients. In many respects our fixed reference point is analogous to how the chemical potentials of the individual ions are determined. By convention the chemical potential of the hydrogen ion is defined to be zero, and the values of all other ions are computed relative to this defined thermodynamic reference state.

The calculated cation-specific and anion-specific equation coefficients for Eqs. (6) and (7) are listed in Tables 1 and 2, respectively. Reported for the first time are ion-specific equation coefficients for $[\text{HxomMIm}]^+$, $[(\text{Hxom})_2\text{Im}]^+$, $[\text{3-MBPy}]^+$, $[\text{B(CN)}_4]^-$ and $[\text{FAP}]^-$. The standard errors in the coefficients are given again in parenthesis directly below the respective values. For the most part, the larger standard errors are noted in the equation coefficients for those ions for which experimental data is limited. The number of data points for the individual ions ranged from 22 $\Delta H_{\text{solv}}$ values for the $[\text{B(CN)}_4]^-$ anion to 394 $\Delta H_{\text{solv}}$ values for the $[(\text{Tf})_2\text{N}]^-$ anion. Both LSERs are statistically very good, and describe experimental $\Delta H_{\text{solv}}$ values that cover a 54 kJ/mol range to within standard deviations of 1.62 kJ/mol (Eq. (6)) and 1.68 kJ/mol (Eq. (7)) as shown in Figs. 1 and 2. Each calculation uses only the values for the cation and anion in the given RTIL. For example, to predict the enthalpies of solvation of organic vapors and gases in 4-methyl-N-butylpyridinium *bis*(trifluoromethyl sulfonyl)imide one would use only the six equation coefficients for the $[\text{4-BMPy}]^+$ and the six equation coefficients for the $[(\text{Tf})_2\text{N}]^-$ anion.

Careful examination of the individual residuals between the calculated and observed values revealed that Eq. (6) described 70.6% (665 of 942 values) of the enthalpy of solvation data to within 1.5 kJ/mol, 92.6% (872 of 942 values) to within 3 kJ/mol. Only 7.4% of the predicted $\Delta H_{\text{solv}}$ values fell more than 3 kJ/mol from the experimental value, with the largest residual being −7.65 kJ/mol. The residual analysis is depicted graphically in Fig. 3. Similar results were noted for Eq. (7); 70.3% of the back-calculated enthalpies of solvation differed from the observed value by less than 1.5 kJ/mol and 92.3% differed by less than 3 kJ/mol. Less than 7.7% of the predicted $\Delta H_{\text{solv}}$ values were more than 3 kJ/mol from the observed value (see Fig. 4 for a graphical summary). The largest residual for Eq. (7) correlation is −8.56 kJ/mol. We expect these values would be reflect the predictive ability that Eqs. (6) and (7) would exhibit in terms of predicting enthalpies of solvation for new compounds dissolved in ILs containing the 12 cations and 10 anions given in Tables 1 and 2, provided that the solute descriptors of the compounds fall within the area of predictive chemical space defined by the calculated equation coefficients. Solutes studied have typically been 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: $E = 0.000$ to $E = 0.850$; $S = 0.000$ to $S = 0.900$; $A = 0.000$ to $A = 0.430$; $B = 0.000$ to $B = 0.650$; $V = 0.109$ to $V = 1.800$; and $L = -1.200$ to $L = 5.700$.

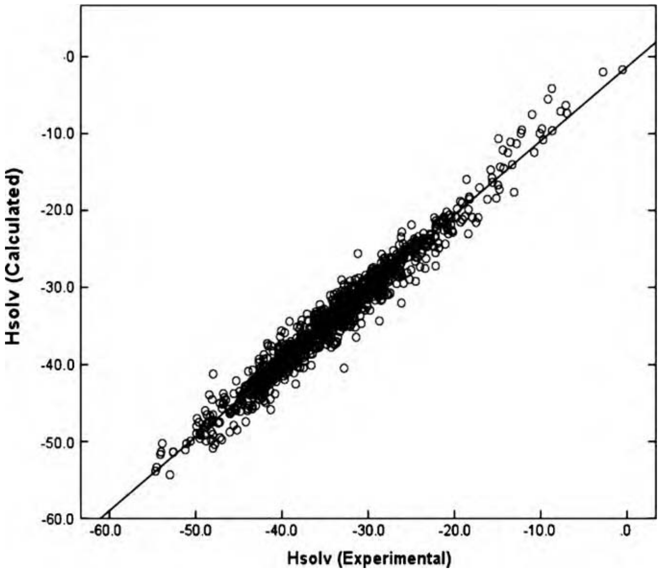

**Fig. 1.** . Comparison of experimental $\Delta H_{\text{solv}}$ data (kJ/mol) to calculated values based on Eq. (6).

In order to assess further the predictive capabilities of Eqs. (6) and (7), the 942 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

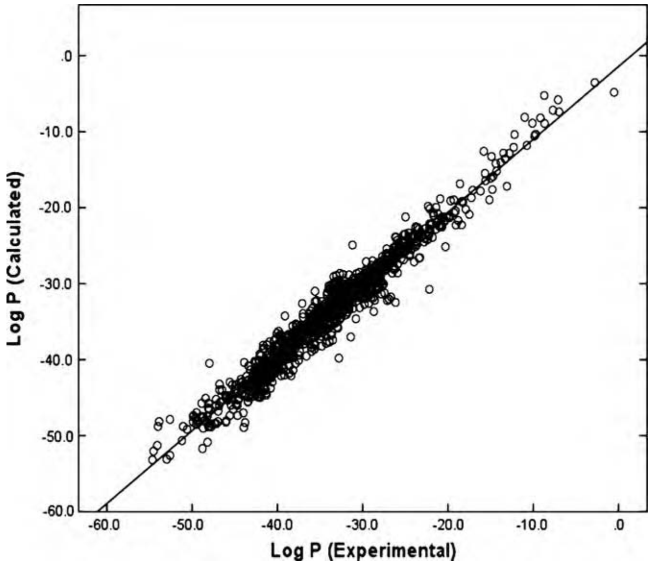

**Fig. 2.** . Comparison of experimental $\Delta H_{\text{solv}}$ data (kJ/mol) to calculated values based on Eq. (7).

**Table 1**
Cation-specific and anion-specific equation coefficients for the Abraham model enthalpy of solvation correlation (Eq. (6)).

| Ion | $c_{\text{ion}}$ | $e_{\text{ion}}$ | $s_{\text{ion}}$ | $a_{\text{ion}}$ | $b_{\text{ion}}$ | $l_{\text{ion}}$ |
|---|---|---|---|---|---|---|
| Cations[a] | | | | | | |
| [MEIm]$^+$ | −6.007 | 3.914 | −15.247 | −20.601 | −7.607 | −7.153 |
| ($N$ = 257)[b] | (0.829) | (1.578) | (1.765) | (2.167) | (1.720) | (0.251) |
| [BMIm]$^+$ | −6.223 | −1.307 | −8.699 | −20.815 | −9.869 | −7.072 |
| ($N$ = 179) | (0.648) | (1.420) | (1.944) | (2.189) | (2.350) | (0.175) |
| [MHIm]$^+$ | −5.543 | 0.111 | −6.842 | −19.484 | −10.780 | −7.795 |
| ($N$ = 101) | (0.691) | (1.591) | (2.032) | (2.384) | (2.379) | (0.188) |
| [MOIm]$^+$ | −7.758 | 1.088 | −4.778 | −21.886 | −6.993 | −7.448 |
| ($N$ = 86) | (0.915) | (2.174) | (2.656) | (2.711) | (2.612) | (0.277) |
| [M$_3$BAm]$^+$ | −7.255 | 1.352 | −9.405 | −22.715 | −7.191 | −6.761 |
| ($N$ = 51) | (0.978) | (2.060) | (2.750) | (3.096) | (3.180) | (0.240) |
| [M$_2$EIm]$^+$ | −0.592 | 4.122 | −15.849 | −23.339 | −7.193 | −8.667 |
| ($N$ = 37) | (1.584) | (2.117) | (2.242) | (2.654) | (2.034) | (0.446) |
| [4-BMPy]$^+$ | −2.796 | 5.802 | −19.743 | −27.272 | −2.956 | −8.378 |
| ($N$ = 69) | (1.138) | (2.113) | (2.578) | (2.364) | (2.231) | (0.337) |
| [3-BMPy]$^+$ | −6.188 | 5.800 | −18.460 | −20.302 | −2.050 | −7.565 |
| ($N$ = 36) | (2.011) | (3.441) | (4.331) | (4.419) | (4.416) | (0.594) |
| [E$_3$S]$^+$ | −2.913 | 15.064 | −32.880 | −15.755 | −5.551 | −7.845 |
| ($N$ = 28) | (1.658) | (4.644) | (7.498) | (11.076) | (12.644) | (0.500) |
| [BMPyr]$^+$ | −5.800 | 10.249 | −25.046 | −16.107 | −3.629 | −7.191 |
| ($N$ = 30) | (1.726) | (4.482) | (5.736) | (4.769) | (4.783) | (0.544) |
| [HxomMIm]$^+$ | −3.748 | 13.318 | −24.942 | −27.250 | 1.260 | −8.645 |
| ($N$ = 34) | (1.603) | (3.161) | (4.056) | (3.085) | (3.265) | (0.483) |
| [(Hxom)$_2$Im]$^+$ | −4.547 | 13.240 | −21.422 | −28.533 | 0.734 | −8.833 |
| ($N$ = 34) | (1.603) | (3.161) | (4.056) | (3.085) | (3.265) | (0.483) |
| Anions[c] | | | | | | |
| [(Tf)$_2$N]$^-$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| ($N$ = 394) | | | | | | |
| [BF$_4$]$^-$ | −0.520 | −3.920 | 3.391 | 1.969 | −1.162 | 0.494 |
| ($N$ = 136) | (0.759) | (1.822) | (2.245) | (2.325) | (2.164) | (0.229) |
| [PF$_6$]$^-$ | −5.420 | 12.391 | −24.092 | 13.322 | 14.997 | 0.806 |
| ($N$ = 54) | (0.821) | (2.672) | (3.401) | (3.495) | (3.650) | (0.256) |
| [EtSO$_4$]$^-$ | −3.021 | −2.344 | 6.454 | −16.911 | 1.412 | 1.106 |
| ($N$ = 42) | (1.565) | (2.658) | (3.065) | (3.782) | (3.306) | (0.383) |
| [Trif]$^-$ | 2.171 | 2.471 | −5.152 | −19.614 | 6.577 | −0.696 |
| ($N$ = 132) | (1.265) | (2.245) | (2.822) | (3.225) | (3.161) | (0.381) |
| [F$_3$Ac]$^-$ | 5.481 | 9.027 | −6.060 | −12.187 | −16.266 | −1.763 |
| ($N$ = 27) | (1.867) | (4.910) | (7.721) | (11.294) | (12.767) | (0.566) |
| [NO$_3$]$^-$ | −3.591 | 0.499 | −0.226 | −14.195 | 5.620 | 0.520 |
| ($N$ = 28) | (3.284) | (2.980) | (3.008) | (4.571) | (2.869) | (0.980) |
| [SCN]$^-$ | 7.978 | 14.895 | −23.862 | −26.264 | 12.733 | −2.220 |
| ($N$ = 84) | (1.113) | (2.467) | (3.285) | (2.714) | (2.989) | (0.319) |
| [B(CN)$_4$]$^-$ | 20.462 | 5.485 | −24.845 | −39.242 | 21.911 | −4.524 |
| ($N$ = 22) | (2.457) | (7.166) | (9.642) | (13.579) | (13.094) | (0.736) |
| [FAP]$^-$ | 25.824 | 17.977 | −48.802 | −4.930 | 10.119 | −4.938 |
| ($N$ = 23) | (2.428) | (6.987) | (9.009) | (12.421) | (11.439) | (0.720) |

[a] Cation abbreviations: [4-BMPy]$^+$ is 4-methyl-N-butylpyridinium cation; [3-BMPy]$^+$ is 3-methylpyridinium cation; [MEIm]$^+$ is 1-methyl-3-ethylimidazolium cation; [M$_2$EIm]$^+$ is 1,2-dimethyl-3-ethylimidazolium cation; [MBIm]$^+$ is 1-methyl-3-butylimidazolium cation; [MHIm]$^+$ is 1-methyl-3-hexylimidazolium cation; [M$_3$BAm]$^+$ is trimethylbutylammonium cation; [MOIm]$^+$ is 1-methyl-3-octylimidazolium cation; [BMPyr]$^+$ is 1-butyl-1-methylpyrrolidinium cation; [E$_3$S]$^+$ is triethylsulphonium cation; [HxomMIm]$^+$ is the 1-hexyloxymethyl-3-methylimidazolium cation; and [(Hxom)$_2$Im]$^+$ is the 1,3-dihexyloxymethylimidazolium cation.

[b] Number of experimental data points associated with the specified ion.

[c] Anion abbreviations: [(Tf)$_2$N]$^-$ is *bis*(trifluoromethyl-sulfonyl)imide anion; [BF$_4$]$^-$ is tetrafluoroborate anion; [PF$_6$]$^-$ is hexafluorophosphate anion; [NO$_3$]$^-$ is nitrate anion; [Trif]$^-$ is the trifluoromethanesulfonate anion; [F$_3$Ac]$^-$ is the trifluoroacetate anion; [EtSO$_4$]$^-$ is ethylsulfate anion; [SCN]$^-$ is thiocyanate anion, [B(CN)$_4$]$^-$ is the anion; and [FAP]$^-$ is the anion.

became the training set, and the compounds that were left served as the test set. Analysis of the 471 experimental data points in the training set gave the cation-specific and anion-specific equation coefficients listed in Tables S2 and S3 (Supporting Material), with SD = 1.52 and SD = 1.68 kJ/mol, $R^2 = 0.998$ and $R^2 = 0.998$, and $F = 1456$ and $F = 1180$ for Eqs. (6) and (7), respectively. The training set equation coefficients were then used to predict $\Delta H_{\text{solv}}$ values for the remaining 471 compounds in the test set. For the predicted and experimental values we find SD = 1.94 kJ/mol, average absolute error (AAE) = 1.43 kJ/mol, and average error (AE) = 0.101 kJ/mol for Eq. (6). Very similar results of SD = 1.87 kJ/mol, average absolute error (AAE) = 1.35 kJ/mol, and average error (AE) = 0.103 kJ/mol for

**Table 2**
Cation-specific and anion-specific equation coefficients for the Abraham model enthalpy of solvation correlation (Eq. (7)).

| Ion[a] | $c_{ion}$ | $e_{ion}$ | $s_{ion}$ | $a_{ion}$ | $b_{ion}$ | $v_{ion}$ |
|---|---|---|---|---|---|---|
| Cations | | | | | | |
| $[MEIm]^+$ | −0.522 | −8.710 | −15.755 | −24.770 | −7.602 | −25.280 |
| ($N$ = 257)[b] | (1.040) | (1.487) | (1.860) | (2.298) | (1.787) | (0.925) |
| $[BMIm]^+$ | 0.671 | −10.742 | −13.978 | −23.150 | −10.347 | −26.260 |
| ($N$ = 179) | (0.803) | (1.426) | (2.029) | (2.266) | (2.425) | (0.654) |
| $[MHIm]^+$ | 0.103 | −12.846 | −7.474 | −16.018 | −15.782 | −27.380 |
| ($N$ = 101) | (0.861) | (1.603) | (2.108) | (2.451) | (2.441) | (0.706) |
| $[MOIm]^+$ | −3.094 | −14.937 | −1.923 | −21.742 | −10.249 | −25.306 |
| ($N$ = 86) | (1.161) | (2.148) | (2.779) | (2.833) | (2.705) | (1.033) |
| $[M_3BAm]^+$ | −1.158 | −7.091 | −15.020 | −25.483 | −6.221 | −24.671 |
| ($N$ = 51) | (1.212) | (2.084) | (2.902) | (3.241) | (3.299) | (0.902) |
| $[M_2EIm]^+$ | 4.006 | −5.855 | −21.604 | −28.854 | −3.145 | −29.304 |
| ($N$ = 37) | (1.904) | (1.986) | (2.494) | (2.864) | (2.125) | (1.595) |
| $[4\text{-}BMPy]^+$ | 1.375 | −11.008 | −16.169 | −28.921 | −5.933 | −27.874 |
| ($N$ = 69) | (1.389) | (2.049) | (2.686) | (2.484) | (2.308) | (1.210) |
| $[3\text{-}BMPy]^+$ | 1.324 | −6.735 | −20.274 | −23.121 | −4.582 | −28.299 |
| ($N$ = 36) | (2.465) | (3.457) | (4.496) | (4.560) | (4.584) | (2.132) |
| $[E_3S]^+$ | 4.009 | −10.891 | −17.029 | −23.710 | −12.059 | −28.593 |
| ($N$ = 28) | (2.150) | (4.839) | (7.724) | (11.598) | (13.078) | (1.883) |
| $[BMPyr]^+$ | 2.509 | −6.665 | −20.110 | −20.750 | −9.554 | −27.793 |
| ($N$ = 30) | (2.167) | (4.220) | (5.820) | (4.945) | (4.901) | (1.985) |
| $[HxomMIm]^+$ | 2.168 | −5.927 | −19.612 | −27.547 | −4.531 | −30.045 |
| ($N$ = 34) | (2.001) | (3.150) | (4.161) | (3.205) | (3.439) | (1.753) |
| $[(Hxom)_2Im]^+$ | 1.063 | −6.379 | −15.883 | −28.570 | −5.017 | −30.303 |
| ($N$ = 34) | (2.001) | (3.150) | (4.161) | (3.205) | (3.439) | (1.753) |
| Anions | | | | | | |
| $[(Tf)_2N]^-$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| ($N$ = 394) | | | | | | |
| $[BF_4]^-$ | 0.525 | 3.258 | −5.021 | −0.272 | 3.289 | 0.404 |
| ($N$ = 136) | (0.980) | (1.796) | (2.375) | (2.457) | (2.252) | (0.872) |
| $[PF_6]^-$ | −3.055 | 14.791 | −27.034 | 9.240 | 18.214 | 0.108 |
| ($N$ = 54) | (1.087) | (2.695) | (3.558) | (3.652) | (3.779) | (1.019) |
| $[EtSO_4]^-$ | −1.724 | 5.034 | −1.145 | −17.689 | 4.040 | 2.461 |
| ($N$ = 42) | (1.988) | (2.616) | (3.349) | (4.054) | (3.447) | (1.466) |
| $[Trif]^-$ | 0.513 | −0.513 | −2.324 | −16.775 | 5.462 | −0.738 |
| ($N$ = 132) | (1.544) | (2.185) | (2.943) | (3.321) | (3.259) | (1.357) |
| $[F_3Ac]^-$ | 7.964 | −7.797 | 13.304 | −17.312 | −24.326 | −7.359 |
| ($N$ = 27) | (2.433) | (5.064) | (7.981) | (11.848) | (13.208) | (2.149) |
| $[NO_3]^-$ | −6.235 | 4.613 | −3.847 | −10.664 | 8.528 | 3.247 |
| ($N$ = 28) | (3.660) | (2.654) | (3.423) | (4.713) | (2.947) | (3.216) |
| $[SCN]^-$ | 9.842 | 1.469 | −11.336 | −31.443 | 8.565 | −8.113 |
| ($N$ = 84) | (1.439) | (2.542) | (3.396) | (2.865) | (3.168) | (1.220) |
| $[B(CN)_4]^-$ | 23.574 | −15.339 | −4.703 | −39.309 | 10.023 | −15.787 |
| ($N$ = 22) | (3.084) | (7.722) | (10.008) | (14.211) | (13.353) | (2.679) |
| $[FAP]^-$ | 29.378 | −4.429 | −27.315 | −4.750 | −3.066 | −17.347 |
| ($N$ = 23) | (3.038) | (7.631) | (9.455) | (12.974) | (11.687) | (2.617) |

[a] Cation and anion abbreviations are given in the footnote to Table 1.
[b] Number of experimental data points associated with the specified ion.

Eq. (7). There is therefore very little bias in the predictions using Eq. (6) (coefficients in Table 2S) with AE equal to 0.101 kJ/mol and Eq. (7) (coefficients in Table 3S) with AE equal to 0.103 kJ/mol.

The list of ion-specific equation coefficients that we have provided in Tables 1 and 2 can be easily updated or increased to include more cations/anions as experimental data for more RTILs becomes available. Should one wish to calculate additional ion-specific equation coefficients for the Abraham model there are calculation methods that can be used that would not significantly change the values that have already been calculated. One simple method would be to redefine the regressed "dependent experimental value" as

$$\text{Regressed value} = \Delta H_{solv} - c_{ion} - e_{ion}E - s_{ion}S - a_{ion}A - b_{ion}B - v_{ion}V \quad (8)$$

$$\text{Regressed value} = \Delta H_{solv} - c_{ion} - e_{ion}E - s_{ion}S - a_{ion}A - b_{ion}B - l_{ion}L \quad (9)$$

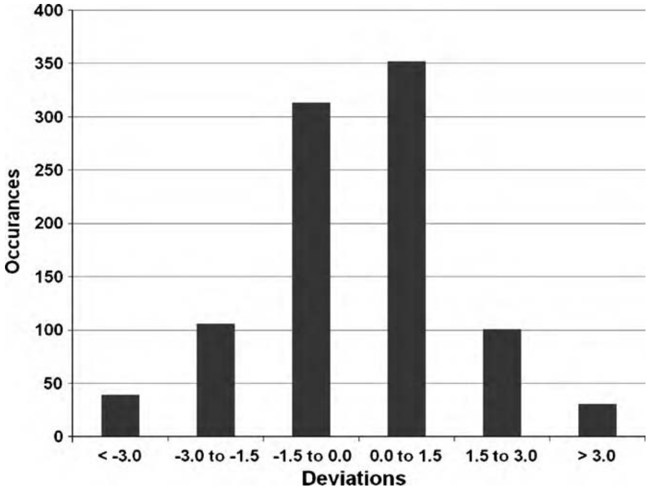

**Fig. 3.** Differences between the experimental $\Delta H_{\text{solv}}$ (kJ/mol) and back-calculated values based on Eq. (6).

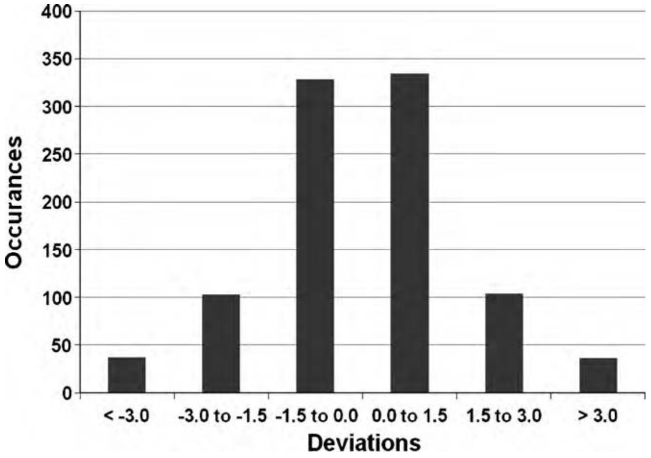

**Fig. 4.** Differences between the experimental $\Delta H_{\text{solv}}$ (kJ/mol) and back-calculated values based on Eq. (7).

the difference between the experimental $\Delta H_{\text{solv}}$ value and the calculated contribution for the ion whose equation coefficients are known. Equation coefficients of the other counter ion could then be computed by regression analysis without altering the values that have already been determined. The ability to compute (or revise) equation coefficients of a given ion without affecting the numerical values that have been calculated for other ions is highly desirable. The popularity of RTILs as solvent media continues to grow, and new ionic liquids continue to be synthesized in response to the growing industrial demand for these rather novel liquid organic compounds.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2010.06.008.

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