Enthalpies of Solution of 1-Butyl-3-methylimidazolium Tetrafluoroborate in 15 Solvents at 298.15 K[†]

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Enthalpies of solution of 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIm]BF_4, are reported at 298.15 K in a set of 15 hydrogen bond donor and hydrogen bond acceptor solvents, chosen by their diversity, namely, water, methanol, ethanol, 1,2-ethanediol, 2-choroethanol, 2-methoxyethanol, formamide, propylene carbonate, nitromethane, acetonitrile, dimethyl sulfoxide, acetone, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, and aniline. These values are shown to be largely independent of [BMIm]BF_4 concentration. The obtained enthalpies of solution vary from very endothermic to quite exothermic, thus showing a very high sensitivity of the enthalpies of solution of [BMIm]BF_4 to solvent properties. Solvent effects on the solution process of this IL are analyzed by a quantitative structure−property relationship methodology, using the TAKA equation and a modified equation, which significantly improves the model's predictive ability. The observed differences in the enthalpies of solution are rationalized in terms of the solvent properties found to be relevant, that is, π^* and E_T^N.

Introduction

Ionic liquids (ILs) are low-temperature molten salts (T_f of typically < 373.15 K) obtained by the combination of (usually) bulky organic cations with a variety of small organic or inorganic anions. Because of their peculiar properties, such as negligible vapor pressure, high thermal stability, low melting temperature, and the ability to dissolve many organic and inorganic substances, ILs have gained attractiveness as "green" alternatives to volatile organic solvents (VOCs) and have found applications in a myriad of fields (e.g., synthesis, catalysis, biocatalysis, separation technology, electrochemistry, analytical chemistry, and nanotechnology).[1−3] Nevertheless, their thermochemical properties have not been extensively studied. Moreover, these properties may differ considerably from those of conventional molecular liquids (MLs). One such property, the enthalpy of solution, $\Delta_{sol}H$, is particularly important since it provides valuable information about molecular interactions in solution.[4−6] The enthalpy of solution is a sum of three major energetic components due to the (a) breaking of solute−solute interactions (endothermic effect), (b) formation of a cavity in the solvent to accommodate the solute, with the corresponding breaking of solvent−solvent interactions (endothermic effect), and (c) establishment of new solute−solvent interactions as a result of the accommodation of the solute in the formed cavity (exothermic effect). Consequently, $\Delta_{sol}H$ values provide an insight into the solvation process: in this case, into IL-solvent interactions, which are strongly influenced by the physicochemical properties of the medium. To quantify these solvent effects we used a quantitative structure−property relationship (QSPR) methodology. QSPRs are among the most powerful tools used to probe solvent effects on physicochemical processes. One widely used QSPR is the TAKA equation[7] (eq 1), which applied to enthalpies of solution assumes the form:

$$\Delta_{sol}H = a_0 + a_1\pi^* + a_2\alpha + a_3\beta + a_4C \qquad (1)$$

According to the above equation, solvents are characterized by their dipolarity/polarizability, π^*, taken as a measure of nonspecific solute−solvent interactions related with the solvent's ability to induce charge polarization in the solute's cybotactic region; their hydrogen bond donor (HBD) acidity, α, and hydrogen bond acceptor (HBA) basicity, β, regarded as measures of Lewis like specific solute−solvent interactions and their structure, given by the cohesive energy density parameter, C, which accounts for solvent−solvent interactions due to the disruption and/or reorganization of solvent structure associated with the formation of a cavity to accommodate the solute. The a_i coefficients are the solute-dependent counterparts of the referred solvent parameters.

In the present work we intend to evaluate the dominant solute−solvent interactions involved in the solvation process of 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIm]BF_4, a member of a widely studied family of room temperature ionic liquids (RTILs). For this purpose, the enthalpies of solution of [BMIm]BF_4 in a set of 15 different solvents were determined at 298.15 K using a precision solution calorimeter.

Experimental Section

Solvents, with a water mass fraction below 0.1 %, were obtained commercially (purity > 99 %) and were used without further drying or purification.

[BMIm]BF_4, from a freshly opened bottle, supplied by Fluka (purity ≥ 97 % and water mass fraction < 0.05 %, according to the product's certificate of analysis), was weighed in a Precisa

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Table 1. Enthalpies of Solution and Respective 95 % Level of Confidence Values, *L*, as a Function of [BMIm]BF$_4$ Molality, *m*, for Five Solvents, at 298.15 K

water		methanol		acetonitrile		formamide		dimethylsulfoxide	
m	$\Delta_{sol}H \pm L$	m	$\Delta_{sol}H \pm L$	m	$\Delta_{sol}H \pm L$	m	$\Delta_{sol}H \pm L$	m	$\Delta_{sol}H \pm L$
mol·kg^{-1}	kJ·mol^{-1}	mol·kg^{-1}	kJ·mol^{-1}	mol·kg^{-1}	kJ·mol^{-1}	mol·kg^{-1}	kJ·mol^{-1}	mol·kg^{-1}	kJ·mol^{-1}
0.003	16.60 ± 0.31	0.003	18.92 ± 0.05	0.004	−4.70 ± 0.05	0.003	6.94 ± 0.12	0.002	−6.58 ± 0.04
0.004	16.71 ± 0.08	0.006	18.88 ± 0.03	0.006	−4.756 ± 0.005	0.004	7.07 ± 0.11	0.004	−6.52 ± 0.03
0.005	16.73 ± 0.14	0.008	18.58 ± 0.03	0.007	−4.67 ± 0.09	0.005	7.10 ± 0.11	0.005	−6.45 ± 0.04
0.006	16.58 ± 0.02	0.009	18.95 ± 1.24	0.009	−4.74 ± 0.01	0.006	6.83 ± 0.08	0.007	−6.58 ± 0.03
0.008	16.65 ± 0.02	0.012	18.74 ± 0.03	0.012	−4.72 ± 0.01	0.008	6.92 ± 0.02	0.009	−6.58 ± 0.05
0.009	16.72 ± 0.05	0.013	18.87 ± 0.02	0.013	−4.67 ± 0.02	0.010	6.83 ± 0.01	0.010	−6.46 ± 0.01
0.012	16.56 ± 0.02	0.015	18.58 ± 0.03	0.014	−4.68 ± 0.05	0.011	6.85 ± 0.04	0.011	−6.50 ± 0.01

Table 2. Enthalpies of Solution at 298.15 K and Infinite Dilution ($\Delta_{sol}H^\infty$) of [BMIm]BF$_4$ in 15 Different Solvents, Respective 95 % Level of Confidence Values, *L*, and Solvent Parameters

		$\Delta_{sol}H^\infty \pm L$	solvent parameters				
solvent	N^a	kJ·mol^{-1}	π^{*b}	α^b	β^b	$C_{calc}{}^b$	E_T^{Nc}
water	11	16.64 ± 0.06	1.09^c	1.17^c	0.47^c	2.29^c	1.000
methanol	7	18.79 ± 0.24	0.60	1.09	0.73	0.86	0.762
ethanol	3	23.03 ± 0.52	0.55	0.88	0.80	0.68	0.654
1,2-ethanediol	4	16.54 ± 0.25	0.89	0.88	0.72	1.17	0.790
2-chloroethanol	3	26.96 ± 0.17	1.03^d	1.04^d	0.53^c	0.43^c	0.753
2-methoxyethanol	3	−4.18 ± 0.08	0.74^d	0.77^d	0.63^d	0.54^e	0.657
formamide	8	6.95 ± 0.10	0.97^f	0.71^f	0.60^f	1.57^e	0.775
propylene carbonate	3	−2.29 ± 0.07	0.83	0.00	0.40	0.74^c	0.472
nitromethane	3	−3.74 ± 0.27	0.85	0.22	0.25	0.66	0.481
acetonitrile	8	−4.72 ± 0.04	0.75^f	0.19^f	0.37^f	0.58^e	0.460
dimethyl sulfoxide	7	−6.52 ± 0.05	1.00	0.00	0.76^f	0.71	0.444
acetone	4	−9.95 ± 0.04	0.71^f	0.08^f	0.48^f	0.39^e	0.355
N,*N*-dimethylformamide	4	−13.31 ± 0.13	0.88	0.00	0.69	0.58	0.386
N,*N*-dimethylacetamide	3	−13.49 ± 0.07	0.85^d	0.00^f	0.76^f	0.50^e	0.377
aniline	3	−15.87 ± 0.20	1.18^d	0.26^c	0.50^c	0.58^e	0.420

[a] Number of individual experiments. [b] From ref 10. [c] From ref 11. [d] From ref 12. [e] From ref 13. [f] From ref 14.

XT 120A analytical balance with a precision of ± 0.1 mg, and its concentration was 0.010 ± 0.003 mol·kg^{-1}. For five solvents, namely, water, methanol, formamide, acetonitrile, and dimethylsulfoxide, the variation of the enthalpy of solution, Δ_{sol}H, with [BMIm]BF$_4$ molality was assessed. All operations involving IL manipulation were performed in a glovebox under a nitrogen atmosphere.

Enthalpies of solution were measured at 298.15 ± 0.01 K in a Thermometric 2225 precision solution calorimeter.[6,8,9] This equipment operates under semiadiabatic conditions and has a temperature resolution of about 1 μK, corresponding to an enthalpy resolution of (1 to 4) mJ.

Cylindrical ampules were filled with solute and sealed. Each sealed ampule was immersed into 100 mL of solvent, inside the glass reaction vessel, and stirred at (500 to 600) rpm. Two electrical calibrations were performed before and after breaking each ampule. For each solvent, the enthalpy data reported correspond to an average of at least three individual experiments, with an average relative standard deviation of 0.9 %. Heats of empty ampule breaking, measured in the less unfavorable solvent, that is, in the solvent with the higher vapor pressure (acetone), lead to a value of 0.467 ± 0.014 J and can thus be considered negligible.

The performance and accuracy of the calorimetric system was tested by measuring the enthalpy of solution of tris(hydroxymethyl)aminomethane (TRIS) in both 0.05 mol·dm^{-3} NaOH and 0.1 mol·dm^{-3} HCl. The measured enthalpies of solution are 17.16 ± 0.02 kJ·mol^{-1} in NaOH and −29.73 ± 0.04 kJ·mol^{-1} in HCl, at 298.15 K, which are in good agreement with the corresponding published data, within experimental uncertainty, that is, within 0.1 %: (17.19 ± 0.02 and −29.75 ± 0.02) kJ·mol^{-1}, respectively.[6]

Results and Discussion

Results for the dependence of the enthalpy of solution on [BMIm]BF$_4$ molality for water, methanol, formamide, acetonitrile, and dimethyl sulfoxide are given in Table 1, together with the 95 % level of confidence, *L*, for each reported value.

Analysis of data in Table 1 reveals that $\Delta_{sol}H$ values are largely independent of [BMIm]BF$_4$ molality and, thus, measured $\Delta_{sol}H$ are regarded as enthalpies of solution at infinite dilution, $\Delta_{sol}H^\infty$.

$\Delta_{sol}H^\infty$ values obtained for the whole set of solvents are assembled in Table 2, together with the solvent parameters used in the subsequent analysis.

Solvents were chosen to ensure a large variability in the parameters depicted in Table 2. Enthalpies of solution show a wide span, with values ranging from ≈ −16 kJ·mol^{-1} in aniline to ≈ 27 kJ·mol^{-1} in 2-chloroethanol, reflecting a high sensitivity to the solvents' properties.

[BMIm]BF$_4$ enthalpies of solution in water, methanol, and acetonitrile listed in Table 2 are in good agreement with those determined by Waliszewski et al., (15.81 ± 0.31, 18.50 ± 0.22, and −5.15 ± 0.15) kJ·mol^{-1}, respectively.[15] There is an additional literature value for the enthalpy of solution of [BMIm]BF$_4$ in water, 26.82 ± 0.26 kJ·mol^{-1},[16] which differs considerably from this work and Waliszewski et al.. However, those authors report that this enthalpy of solution in water varies with the solute's molality. This is in disagreement with what was found in this work and the conclusions of Waliszewski et al. and may be the cause for the observed discrepancy.

Correlations of $\Delta_{sol}H^\infty$ with TAKA Parameters. Solvent effects on the enthalpy of solution of [BMIm]BF$_4$ were analyzed using the TAKA equation (eq 1) using a backward stepwise procedure, that is, starting with all parameters and successively

Table 3. Correlations of $\Delta_{sol}H^{\infty}$ versus Various Combinations of Solvent Parameters, Using Equation 1

equation number	$a_0 \pm s(a_0)$ L^a (%)	$a_1 \pm s(a_1)$ L (%)	$a_2 \pm s(a_2)$ L (%)	$a_3 \pm s(a_3)$ L (%)	$a_4 \pm s(a_4)$ L (%)	sd_{fit}^b	R^{2c}	F^d	N^e
2	-2.58 ± 14.81	-9.49 ± 13.78	27.97 ± 5.88	-0.35 ± 13.50	-0.39 ± 5.51	8.0	0.7831	9	15
	13	49	100	2	6				
3	-2.82 ± 10.76	-9.43 ± 12.95	27.94 ± 5.49	–	-0.38 ± 5.24	7.6	0.7831	13	15
	20	52	100	–	6				
4	-2.67 ± 10.09	-9.85 ± 11.12	27.71 ± 4.29	–	–	73	0.7830	21	15
	20	61	100	–	–				
5	–	-12.67 ± 2.98	27.42 ± 3.99	–	–	7.0	0.7875	24	15
	–	100	100	–	–				
6	–	-12.73 ± 2.05	27.55 ± 2.96	–	–	4.8	0.8874	43	13^f
	–	100	100	–	–				

[a] Level of confidence. [b] Standard deviation of the fit. [c] Determination coefficient. [d] Fisher's F value. [e] Number of solvents used in the correlation. [f] Correlation performed over 13 solvents, that is, excluding 2-methoxyethanol and 2-chloroethanol.

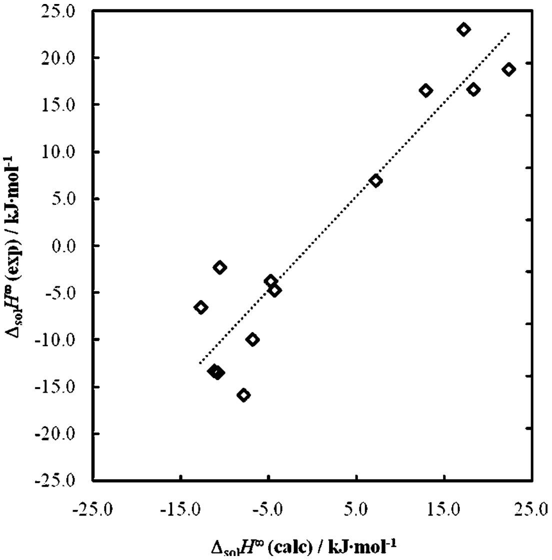

Figure 1. ◇, experimental vs calculated $\Delta_{sol}H^{\infty}$ values for [BMIm]BF_4, using eq 6; dotted line indicates $\Delta_{sol}H^{\infty}$ (exp) = $0.9989\Delta_{sol}H^{\infty}$ (calc) + 0.2357 ($R^2 = 0.8872$).

removing from those with a level of confidence, L, lower than 95 %, the least significant one. The best equation to describe the process under study was chosen according to several other statistical criteria, namely, the standard deviation of the fit, sd_{fit}, the determination coefficient, R^2, and Fisher's F value. A given data point was regarded as an outlier whenever $|Y_{calc} - Y_{exp}| > 2\ sd_{fit}$. Intercorrelations among solvent parameters were always tested and found to be negligible ($R^2 < 0.3$).

The obtained regression coefficients, a_i, are listed in Table 3, together with the associated standard deviations, s, and the referenced statistical figures of merit.

Initially, the TAKA equation was applied to all solvents (eq 2). However, the intercept, a_0, and also the β and C terms (a_3 and a_4) were found to have no statistical meaning since $L \ll 95$ %. They were, therefore, removed sequentially and the data refitted, leading to eq 5. In this equation, both parameters have statistical significance, but 2-methoxyethanol was identified as an outlier; 2-chloroethanol showed a very high residual error, yet it was less than 2 sd_{fit}. Since literature α and π^* values for the latter[11,12] are quite divergent, we decided to remove this solvent from the solvent matrix, even though, strictly speaking, it would not be an outlier, according to the statistical criterion used. After removal of these two solvents the data was again refitted, and a better model equation, with a smaller sd_{fit}, higher F, and higher adjusted determination coefficient R^2_{adj} (0.6943 vs 0.7863), was obtained (eq 6). The latter statistical parameter allows a direct comparison among regressions involving dissimilar numbers of points since this quantity corrects R^2 for different degrees of freedom.

In Figure 1, experimental $\Delta_{sol}H^{\infty}$ values are plotted against calculated values obtained through eq 6.

Correlations of $\Delta_{sol}H^{\infty}$ with π^* and E_T^N Parameters. A close scrutiny of Figure 1 shows that the predictive ability of eq 6 is not entirely satisfactory. In our quest for a better, more robust, model to interpret and predict the enthalpy of solution behavior of [BMIm]BF_4 in this set of solvents, we evaluated the effect of substituting α by E_T^N (eq 7):

$$\Delta_{sol}H^{\infty} = a_0 + a_1\pi^* + a_2E_T^N \qquad (7)$$

E_T^N is the well-known normalized Dimroth−Reichardt polarity parameter which is defined as the excitation energy (in kcal·mol^{-1}) of the solvatochromic indicator, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate, also known as $E_T(30)$ dye,[17−19] in a given solvent, calculated from its longest-wavelength intramolecular charge-transfer absorption band. This parameter reflects both the hydrogen bond acidity and the dipolarity characteristics of the solvent. The fact that the dye used for its determination is a large compound with a considerable charge separation might make it better suited for the description of ILs, particularly if they are as bulky as [BMIm]BF_4. For the set of solvents under study, no correlation was found between E_T^N and π^* ($R^2 = 0.012$).

The a_i coefficients together with the associated standard deviations and values for the standard deviation of the fit, the determination coefficient, the F statistic, and the level of confidence of each regression coefficient for the correlations involving the two descriptors π^* and E_T^N are listed in Table 4. The choice of the best model was carried out according to the same statistical criteria described above.

Equation 7 was applied to the full set of solvents leading to eq 8. Once again, 2-chloroethanol and 2-methoxyethanol were consecutively removed from the data set for the same reasons as before. In addition, the intercept was found to have no statistical meaning, and in the new fitting the regression was forced to pass through the origin, leading to a more robust model (eq 11).

In Figure 2, experimental $\Delta_{sol}H^{\infty}$ values are plotted against calculated values from eq 11.

A comparison between both equations shows that in either case the independent term has no statistical significance. This might mean that in the present case the energy required to overcome solute−solute interactions is negligible.

Although both equations were obtained for the same set of solvents and have the same number of parameters, differing only by one descriptor (α and E_T^N), eq 11 is clearly statistically more

Table 4. Correlations of $\Delta_{sol}H^{\infty}$ versus π^* and E_T^N (Equation 7)

	$a_0 \pm s(a_0)$	$a_1 \pm s(a_1)$	$a_2 \pm s(a_2)$				
equation number	L^a (%)	L (%)	L (%)	sd_{fit}^b	R^{2c}	F^d	N^e
8	-16.31 ± 11.39 82	-21.53 ± 11.72 91	63.48 ± 10.45 100	7.6	0.7614	19	15
9	-7.75 ± 8.44 62	-29.16 ± 8.60 99	57.64 ± 7.61 100	5.4	0.8581	33	14^f
10	-4.70 ± 5.90 56	-33.24 ± 6.06 100	60.17 ± 5.31 100	3.8	0.9375	75	13^g
11	– –	-37.31 ± 3.21 100	58.29 ± 4.68 100	3.7	0.9339	78	13^g

[a] Level of confidence. [b] Standard deviation of the fit. [c] Determination coefficient. [d] Fisher's F value. [e] Number of solvents used in the correlation. [f] Correlation performed on 14 solvents, that is, excluding 2-chloroethanol. [g] Correlation performed on 13 solvents, that is, excluding 2-chloroethanol and 2-methoxyethanol.

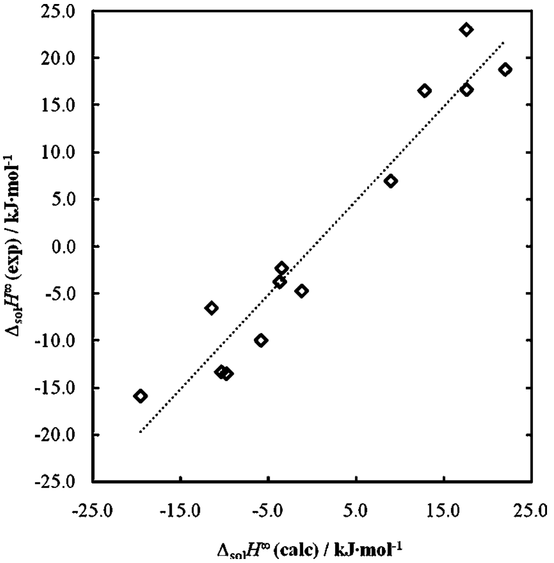

Figure 2. ◇, experimental vs calculated $\Delta_{sol}H^{\infty}$ values for [BMIm]BF$_4$, using eq 11; dotted line indicates $\Delta_{sol}H^{\infty}$ (exp) = 1.001 $\Delta_{sol}H^{\infty}$ (calc) − 0.1479 ($R^2 = 0.9337$).

robust than eq 6 which derives from the TAKA equation. This indicates that E_T^N seems to provide a better description of the effects involved in the dissolution process of [BMIm]BF$_4$ than α, as already mentioned.

A close inspection at the magnitude and sign of $\Delta_{sol}H^{\infty}$ shows that both α and E_T^N contribute endothermically to the dissolution process of this IL, and their coefficients have a higher magnitude than that of π^*. This means that specific solute−solvent interactions as measured by α and E_T^N do not seem to favor the solution process of [BMIm]BF$_4$, and this is particularly evident in the case of HBD solvents (i.e., solvents with a high α value) with the exception of 2-methoxyethanol: that is, HBD solvent molecules seem to prefer to interact with each other rather than with [BMIm]BF$_4$. The reason why 2-methoxyethanol is an exception to the general behavior shown by HBD solvents might be linked to its ability to form intramolecular hydrogen bonding,[20] thereby weakening the overall solvent hydrogen-bonding network. As a consequence, the formation of a cavity to accommodate the IL solute requires the breaking of less solvent−solvent bonds and thus leads to a more exothermic dissolution process than in the case of the other HBD solvents.

Conversely, non-HBD solvents give rise to exothermic processes. α and E_T^N are much lower in non-HBD solvents, and therefore, in these solvents their endothermic contribution is less perceptible in the overall enthalpy of solution of [BMIm]BF$_4$.

On the other hand, both equations show a negative π^* coefficient, corresponding to an exothermic contribution: that is, the solvent's ability to induce charge polarization in the solute's cybotactic region appears to facilitate the dissolution of [BMIm]BF$_4$. This is even more so in non-HBD solvents where α and E_T^N are considerably smaller than in HBD solvents, while π^* is of the same order of magnitude (see above).

Conclusions

In this work, we studied the enthalpy of solution of 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIm]BF$_4$, in a set of 15 HBD and HBA solvents. The obtained enthalpy values showed a very unusual variation, spanning over 43 kJ·mol^{-1}.

The data was analyzed through a QSPR methodology using two approaches: the TAKA equation and an alternative equation in which α was substituted by E_T^N. The dipolarity/polarizability descriptor, π^*, and the hydrogen bond acidity parameter, α, were found to be relevant for the analysis of the [BMIm]BF$_4$ dissolution process in the context of the TAKA equation. All remaining descriptors were excluded because of lack of statistical significance. Both the TAKA and the alternative two-parameter equations were found to provide an adequate description and interpretation of the solvent effects involved in the dissolution process of this IL. However, the latter was found to be statistically more robust. Hence, for [BMIm]BF$_4$, and eventually for other ILs, E_T^N may provide a more suitable description of the solvent effects involved in the dissolution process than α.

The equations obtained from this QSPR analysis provided an insight into the thermochemistry of an IL dissolution process. In particular, the hydrogen bond acidity of the media (measured by E_T^N in eq 11 and α in eq 6) was found to contribute endothermically to the dissolution process, while solvent dipolarity/polarizability, responsible for nonspecific solute−solvent interactions (measured by π^*), was found to contribute exothermically to the same process.

Although the present work is of exploratory character, it clearly indicates that the methodology chosen and the same solvent descriptors used to probe solvent effects of other, simpler, organic solutes can also easily encompass ILs. However, (a) the extension of the solvent matrix and (b) the use of other, more appropriate, solvent descriptors might improve the statistical quality of the regressions and lead to better model equations, thus permitting a deeper understanding of the thermochemistry of this important class of compounds.

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