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# Enthalpies of Solution and Enthalpies of Solvation in Water: The Anion Effect in Ionic Liquids with Common 1-Ethyl-3-methyl-imidazolium Cation

**Mikhail A. Varfolomeev[1] · Artashes A. Khachatrian[1] · Bulat S. Akhmadeev[1] · Boris N. Solomonov[1] · Andrei V. Yermalayeu[2] · Sergey P. Verevkin[1,2]**

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**Abstract** Thermochemical studies of ionic liquids (ILs) in aqueous solution were carried out using solution calorimetry. Heat effects of dissolution in water at 298.15 K and molar limiting enthalpies of solution were measured for ILs having a common cation, 1-ethyl-3-methyl-imidazolium, connected with different anions: diethylphosphate, ethylsulfate, tetracyanoborate, thiocyanate, and trifluoroacetate. Molar enthalpies of solvation of ILs in water were derived from experimental data for solution and vaporization enthalpies. Enthalpic data were correlated with ionic liquid specific parameters and descriptors. The best correlation was observed with hydrogen-bonding interaction energies. This result confirmed that hydrogen bonding is one of the main types of intermolecular interactions inherent for ILs in aqueous solutions.

**Keywords** Ionic liquid · Solution calorimetry · Enthalpy of solution · Enthalpy of solvation · Anion · Structure–property relations · Intermolecular interactions

## 1 Introduction

Ionic liquids (ILs) belong to a class of molten salts which are liquid below the decomposition temperature. They usually consist of bulky asymmetric organic cations and different anions. Unique properties of ionic liquids such as high thermal stability, negligible vapor pressure, non-flammability, and good solvation ability for different types of chemicals allow their use in various fields of chemical industry such as organic synthesis,

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✉ Mikhail A. Varfolomeev
vma.ksu@gmail.com; mikhail.varfolomeev@kpfu.ru

[1] Department of Physical Chemistry, Kazan Federal University, Kremlevskaya 18, Kazan 420008, Russia

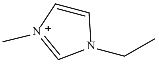
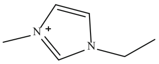
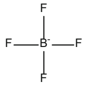
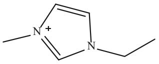
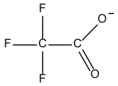
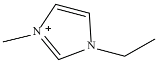
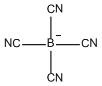
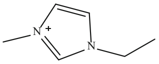
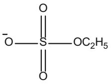
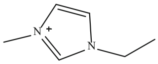
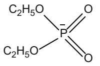
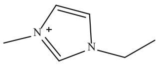
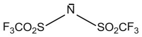
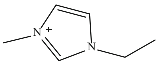
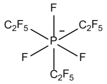
[2] Department of Physical Chemistry, University of Rostock, Dr-Lorenz-Weg 1, 18059 Rostock, Germany

pharmacy, electrochemistry, and cellulose processing [1, 2]. ILs can be also applied to separation processes, biphasic transfer, and extraction. In practical applications, water is often used as the second solvent. It was shown that ILs were effective for the removal of organics from aqueous streams [3]. Moreover, water as a co-solvent additionally increases the solubility of organic compounds in ILs [4]. Thus, areas of practical applications of IL–water mixtures significantly depend on their mutual solubility. Many solubility data of ILs in water can be found in the literature [5]. As a rule, separation and extraction processes are usually realized at different temperatures. The knowledge of enthalpies of solution or enthalpies of solvation of ionic liquids in water could be a useful tool for the prediction of solubility at any desired temperature. These data are also of importance in the evaluation of the risk of penetration of IL traces in the environment.

From a general point of view, special physical chemical properties of IL–water mixtures are determined by the intensity of intermolecular interactions. Ionic liquids can be hydrophobic or hydrophilic depending on the structures of the constituent cation and anion. Knowledge of the type and the strength of intermolecular interactions of ILs with water is important to predict their behavior in aqueous solution. Also, this knowledge could be used for synthesis of ionic liquids with desired properties. As an example, in Ref. [6] the authors have prepared three novel dianionic ILs with an enhanced water absorption capacity, based on the information about hydrogen bond acceptor ability of anion and strength of cation–anion interactions. In this work, we have focused on solution calorimetry as a well-established, direct method for quantification of intermolecular interactions in solution. In addition, we collected literature data on limiting solution enthalpies measured by solution calorimetry [7] and indirectly derived from the temperature dependence of solubility of ILs in water [8].

Brennecke et al. [9] were the first who applied UV–Vis spectroscopy to determine solubility of three imidazolium based ILs with hexafluorophosphate and tetrafluoroborate anions in water in the temperature range (283.15–323.15) K and determined their enthalpies of solution at infinite dilution. Coutinho and co-workers studied the chain length effects [4, 10–12] as well as influence of the cation [4] on the water solubility and solution enthalpies of numerous imidazolium and pyridinium based ILs with bis(trifluoromethylsulfonyl)imide and hexafluorophosphate anions. However, using UV–Vis spectroscopy for studies of ILs solubility in water has some restrictions. Firstly, an IL should have some characteristic absorption bands in the UV–Vis spectra. This limitation excludes this method for studies of ammonium and phosphonium based ILs. Secondly, an IL should be sparingly miscible with water. As a useful alternative approach, the temperature dependence of the conductivity [13, 14] could be applied. Another approach is the dynamic method, based on visual detection of two phases disappearance with increasing temperature. This approach was applied in works of Królikowska et al. [15, 16]. Authors have studied effect of cation and anion structure on mutual solubilities of ILs–water mixtures. However, all these methods significantly suffer from the difficulty of proving the saturation condition. Moreover, solubility with these methods is usually studied at measurable concentrations, thus, the extrapolation to infinite dilution is possibly thwarted by uncertainties. For example, solution enthalpies of three ILs in water derived using UV–Vis spectroscopy [9] are two times smaller than those derived from the same measurements by other research groups [10, 17]. In contrast, the direct calorimetric measurements of solution enthalpies are free from the aforementioned disadvantages. Thus solution calorimetry can be used in combination with different indirect techniques to predict the temperature effect on the solubility of IL-water mixtures. Previously [18–22] calorimetric methods were applied for measurements of excess enthalpies and heat capacities of aqueous solutions of different ILs

**Table 1** Structure and molar mass of studied ionic liquids

| Solute | Abbreviation | Cation | Anion | Molar mass (g·mol$^{-1}$) |
|---|---|---|---|---|
| 1-ethyl-3-methylimidazolium thiocyanate | ([EMIM][SCN]) |  | $^{-}S—C\equiv N$ | 169.3 |
| 1-ethyl-3-methylimidazolium tetrafluoroborate | ([EMIM][BF$_4$]) |  |  | 198.0 |
| 1-ethyl-3-methylimidazolium trifluoroacetate | ([EMIM][CF$_3$CO$_2$]) |  |  | 224.2 |
| 1-ethyl-3-methylimidazolium tetracyanoborate | ([EMIM][B(CN)$_4$]) |  |  | 226.1 |
| 1-ethyl-3-methylimidazolium ethylsulfate | ([EMIM][EtSO$_4$]) |  |  | 236.3 |
| 1-ethyl-3-methylimidazolium diethylphosphate | ([EMIM][diEtPO$_4$]) |  |  | 264.3 |
| 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide | ([EMIM][(Tf)$_2$N]) |  |  | 391.3 |
| 1-ethyl-3-methylimidazolium *tris*(pentafluoroethyl)trifluorophosphate | ([EMIM][FAP]) |  |  | 556.2 |

covering a wide composition range, but concentrations of these ILs usually were far from limiting dilution conditions. In order to get solution enthalpies at infinite dilution conditions different extrapolation methods were required.

In this work we have studied dissolution of several imidazolium based ionic liquids in water using solution calorimetry at 298.15 K. We selected ILs with a common cation (1-ethyl-3-methylimidazolium) connected to eight different anions (see Table 1). The focus of our study was to assess the impact of the anion on the values of limiting enthalpies of solution and enthalpies of solvation in terms of the intensity of intermolecular interactions in the aqueous solutions. Some regularities between thermochemical data and IL parameters responsible for different types of intermolecular interactions were analyzed.

# 2 Experimental

## 2.1 Materials

Samples of the 1-ethyl-3-methylimidazolium based ILs studied in this work were of commercial origin with mass fraction purities no less than 0.98 according to specifications. Ionic liquids were additionally purified before measurements by vacuum evaporation at low pressure, $5 \times 10^{-2}$ Pa, and $T = 333.15$ K to remove traces of water and volatile compounds. The residual mass fraction of water in the ionic liquids measured by Karl Fischer titration on the automatic titrator C20 (Mettler Toledo) did not exceed 0.0005. Water used in calorimetric measurements was twice distilled and additionally deionized by an EasyPure II (Thermo Scientific) system. Its final resistivity before experiments was 18.2 MΩ·cm at 298.15 K.

### 2.2 Solution Calorimetry Experiments (Rostock)

Calorimetric measurements at the University of Rostock were carried out at $T = 298.15 \pm 0.01$ K using an upgraded commercial LKB 8700-2 isoperibol solution calorimeter. The detailed description of apparatus was published elsewhere [23]. Accuracy of the calorimetric device was tested by determining the solution enthalpy of potassium chloride in water. The experimentally measured value (17.41 ± 0.04) kJ·mol$^{-1}$ is in a good agreement with the recommendation of ICTAC (International Confederation for Thermal Analysis and Calorimetry) working group (17.47 ± 0.07) kJ·mol$^{-1}$ [24].

The ampoule technique was used for measurements of heat effects of dissolution. A sample amount of 0.025–0.12 g of an IL was weighed in a cylindrical glass ampoule with an accuracy ±0.01 mg. The ampoule was sealed and placed into the calorimetric cell filled with 100 mL of water. After equilibration the ampoule was broken. The heat effect was derived from the temperature change in the measuring system. The detailed experimental procedure was described elsewhere [25].

### 2.3 Solution Calorimetry Experiments (Kazan)

Calorimetric measurements at the Kazan Federal University were carried out at $T = 298.15 \pm 0.01$ K using a commercial TAM III precision isothermal solution calorimeter. In each experiment, a constant volume (100 mL) of water was placed in a glass calorimetric cell equipped with a stirrer, a thermistor, and a calibration heater. The setup was tested by measuring the solution enthalpy of propan-1-ol in water. The average experimental value of the solution enthalpy (−10.16 ± 0.03) kJ·mol$^{-1}$ measured in this work is in good agreement with the recommended data [26]. Detailed description of experimental technique and procedure was published previously [27, 28]. For ILs we used two methods (ampoule and titration) to introduce a sample into the calorimetric system. In the case of ampoule breaking technique we used about of 0.03–0.05 g (±0.1 mg) of a solute for each dissolution experiment. An ampoule containing solute was sealed, weighed and introduced into the solvent. It was found experimentally that the contribution to the heat effect due to breaking of an empty ampoule can be considered negligible. In the case of titration technique, small portions of solute (10 μL) were dropped automatically into the solvent using the electronically operated microliter syringe filled with 100 or 250 μL of solute. The syringe was equipped with a long gold cannula immersed in the calorimetric cell. The heat effect from addition of each portion of solute was calculated from a calorimetric curve. From our experience, the titration technique seems to be more convenient, because it gives the option of analyzing the concentration dependence of solution enthalpies within one dissolution experiment. However, the titration technique was not always optimal for measurements with ILs, due to their high viscosity. Experiments with each IL were repeated at least four times.

All experimental values of solution enthalpies measured in this work are given in Table 2.

**Table 2** Enthalpies of solution of ionic liquids in water measured in this work at 298.15 K and atmospheric pressure

| Solute | Solvent | Mass of sample[a] (g) × $10^3$ | Molality[b] (mol·kg$^{-1}$) × $10^3$ | $\Delta_{soln}H^{IL/H_2O}$ (kJ·mol$^{-1}$) |
|---|---|---|---|---|
| [EMIM][SCN][c] | Water | 21.4 | 5.1 | 7.88 |
| | Water | 38.0 | 9.0 | 7.85 |
| | Water | 61.8 | 14.6 | 7.86 |
| | Water | 72.1 | 17.0 | 7.83 |
| | Water | 106.7 | 25.2 | 7.80 |
| [EMIM][SCN][d] | Water | 35.5 | 1.90 | 9.07 |
| | Water | 39.4 | 4.01 | 8.66 |
| | Water | 46.4 | 6.50 | 8.77 |
| | Water | 47.8 | 9.06 | 8.74 |
| | Water | 54.4 | 11.98 | 8.83 |
| [EMIM][$CF_3CO_2$][c] | Water | 25.9 | 4.63 | −20.82 |
| | Water | 50.6 | 9.06 | −20.69 |
| | Water | 59.2 | 10.60 | −20.54 |
| | Water | 103.4 | 18.51 | −20.94 |
| | Water | 126.4 | 22.63 | −20.94 |
| [EMIM][$B(CN)_4$][c] | Water | 26.2 | 4.65 | 19.75 |
| | Water | 46.6 | 8.28 | 19.64 |
| | Water | 65.0 | 11.53 | 19.23 |
| | Water | 120.3 | 21.35 | 19.67 |
| [EMIM][$B(CN)_4$][e] | Water | 12.36 | 0.31 | 18.80 |
| | Water | 12.36 | 0.62 | 18.47 |
| | Water | 12.36 | 0.93 | 18.73 |
| | Water | 12.36 | 1.24 | 18.82 |
| | Water | 12.36 | 1.55 | 18.93 |
| | Water | 12.36 | 1.86 | 18.78 |
| | Water | 12.36 | 2.17 | 18.70 |
| [EMIM][$EtSO_4$][c] | Water | 39.3 | 6.65 | −10.70 |
| | Water | 43.1 | 7.29 | −10.97 |
| | Water | 43.7 | 7.39 | −10.87 |
| | Water | 51.5 | 9.79 | −10.64 |
| | Water | 95.7 | 16.20 | −10.84 |
| | Water | 104.4 | 17.67 | −10.85 |
| [EMIM][$EtSO_4$][e] | Water | 12.39 | 1.05 | −10.70 |
| | Water | 12.39 | 1.57 | −10.82 |
| | Water | 12.39 | 2.10 | −10.78 |
| | Water | 12.39 | 2.62 | −10.78 |
| | Water | 12.39 | 3.14 | −10.76 |
| | Water | 12.39 | 3.67 | −10.72 |
| | Water | 12.39 | 4.19 | −10.82 |
| | Water | 12.39 | 4.72 | −10.66 |
| | Water | 12.39 | 5.24 | −10.68 |
| | Water | 12.39 | 5.76 | −10.68 |

**Table 2** continued

| Solute | Solvent | Mass of sample[a] (g) × $10^3$ | Molality[b] (mol·kg$^{-1}$) × $10^3$ | $\Delta_{\mathrm{soln}}H^{\mathrm{IL/H_2O}}$ (kJ·mol$^{-1}$) |
|---|---|---|---|---|
| | Water | 12.39 | 6.29 | −10.70 |
| | Water | 12.39 | 6.81 | −10.82 |
| | Water | 12.39 | 7.34 | −10.80 |
| | Water | 12.39 | 7.86 | −10.82 |
| | Water | 12.39 | 8.38 | −10.74 |
| | Water | 12.39 | 8.91 | −10.72 |
| | Water | 12.39 | 9.43 | −10.59 |
| | Water | 12.39 | 9.96 | −10.68 |
| | Water | 12.39 | 10.48 | −10.78 |
| | Water | 12.39 | 11.00 | −10.72 |
| | Water | 12.39 | 11.53 | −10.68 |
| | Water | 12.39 | 12.05 | −10.64 |
| [EMIM][diEtPO$_4$][c] | Water | 30.8 | 4.67 | −49.36 |
| | Water | 61.7 | 9.37 | −47.70 |
| | Water | 82.3 | 12.49 | −47.15 |
| | Water | 123.1 | 18.70 | −45.69 |

[a] Mass of the solute sample which was added in each injection experiment

[b] Molality of the solute in the solution after experiments

[c] Measured in Rostock using the ampoule breaking technique

[d] Measured in Kazan using the ampoule breaking technique

[e] Measured in Kazan using the titration technique

## 3 Results and Discussion

We have studied the thermochemistry of dissolution of 1-ethyl-3-methylimidazolium based ionic liquids with five various anions (see Table 1) in water at 298.15 K. Molar solution enthalpies, $\Delta_{\mathrm{soln}}H^{\mathrm{IL/H_2O}}$, of [EMIM][EtSO$_4$], [EMIM][B(CN)$_4$], [EMIM][SCN], [EMIM][CF$_3$CO$_2$], and [EMIM][diEtPO$_4$] in water at $T = 298.15$ K and at different concentrations of the solute are given in Table 2. It is important to note, that all ILs were in the liquid state at $T = 298.15$ K. Analysis of the experimental data given in Table 2 shows that, in spite of the fact that we used two different solution calorimeters and also two charging techniques to measure solution enthalpies, results for the same ionic liquids were in good agreement proving the reliability of our results.

For each solute, calorimetric experiments were carried out in a reasonably wide concentration range. However, the molar enthalpy change remained constant (see Fig. 1). Such independence of solution enthalpies on concentration in the studied range supported the assumption that our systems were sufficiently dilute that the molar enthalpies of solution are equal to the infinite dilution values. The only exception was observed for [EMIM][diEtPO$_4$] where the solution enthalpies into water became less exothermic with increasing of sample weight (see Table 2). In order to obtain $\Delta_{\mathrm{soln}}H^{\mathrm{IL/H_2O}}$ at infinite dilution for [EMIM][diEtPO$_4$], we used a well-known linear extrapolation to the zero concentration. There are a lot of approaches to obtain limiting solution enthalpies.

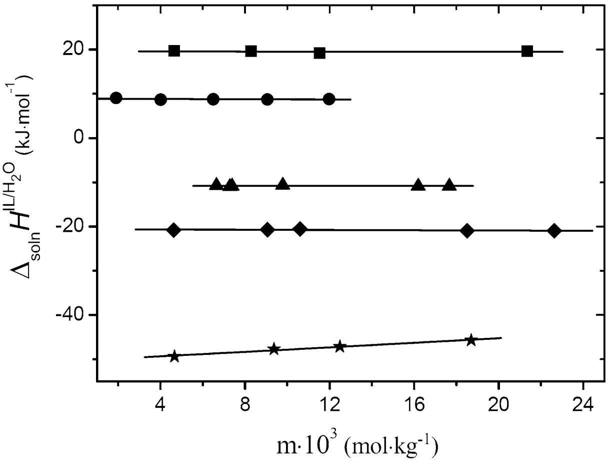


**Fig. 1** Solution enthalpies of 1-ethyl-3-methylimidazolium based ionic liquids as a function of molality of ionic liquids in water: *filled square* ([EMIM][B(CN)$_4$]), *filled circle* ([EMIM][SCN]), *filled triangle* ([EMIM][EtSO$_4$]), *filled diamond* ([EMIM][CF$_3$CO$_2$]), *asterisk* ([EMIM][diEtPO$_4$])

However, previously [29] it was shown that application of these approaches for the one system usually gave difference in enthalpy values no more than 0.5–1 kJ·mol$^{-1}$.

Limiting enthalpies of solution of 1-ethyl-3-methylimidazolium based ionic liquids in water are presented in Table 3. Three additional values of $\Delta_{soln}H^{IL/H_2O}$ for the related, 1-ethyl-3-methylimidazolium based ionic liquids [EMIM][(Tf)$_2$N], [EMIM][BF$_4$] and [EMIM][FAP] were taken from the literature [7, 8]. As can be seen in Table 3, solution enthalpies are significantly different depending on the structure of the anion. Values of $\Delta_{soln}H^{IL/H_2O}$ range from −50 kJ·mol$^{-1}$ for [EMIM][diEtPO$_4$] to 23 kJ·mol$^{-1}$ for [EMIM][FAP]. For the five ILs considered in this study, the enthalpies of solution in water are positive. Consequently, the dissolution processes were endothermic, following with a rising temperature the solubility of these ILs in water will increase, especially for [EMIM][FAP]. For another three ILs the values of $\Delta_{soln}H^{IL/H_2O}$ are negative. The largest exothermic effect was observed for dissolution of [EMIM][diEtPO$_4$].

From the general point of view, the value of the solution enthalpy is determined by three main factors: breaking of solute–solute intermolecular interactions in order to reach infinite dilution condition (endothermic term); cavity formation in the solvent, which includes breaking of solvent–solvent intermolecular interactions (endothermic term); and the last one is the formation of solute–solvent intermolecular interactions (exothermic term) [30]. We shall try to understand the interplay and extend these three factors using the experimental enthalpies of solvation of ILs in water, $\Delta_{solv}H^{IL/H_2O}$, given in Table 3. Solvation is defined as a process of transfer of any solute from the ideal gas state to the solvent at 298.15 K. The enthalpy of solvation, $\Delta_{solv}H^{IL/H_2O}$, does not include the contribution of solute–solute intermolecular interactions in contrast to the values of solution enthalpies. Generally, the solvation enthalpy is considered as an overall measure of solute–solvent interactions. Equation 1 was used for determination of $\Delta_{solv}H^{IL/H_2O}$ from available enthalpies of solution and vaporization:

$$\Delta_{solv}H^{IL/H_2O} = \Delta_{soln}H^{IL/H_2O} - \Delta_{vap}H^{IL} \quad (1)$$

**Table 3** Enthalpies of solution, $\Delta_{\text{soln}}H^{\text{IL}/\text{H}_2\text{O}}$, and enthalpies of solvation, $\Delta_{\text{solv}}H^{\text{IL}/\text{H}_2\text{O}}$, of ionic liquids in water at 298.15 K, their vaporization enthalpies, $\Delta_{\text{vap}}H^{\text{IL}}$, molar volume, $V_{\text{m}}$, Abraham–Acree descriptors, *a*, *l* and *b*, and hydrogen bond energies, $E_{\text{HB}}$

| IL | $\Delta_{\text{soln}}H^{\text{IL}/\text{H}_2\text{O}}$ (kJ·mol$^{-1}$) | $\Delta_{\text{vap}}H^{\text{IL}}$ (kJ·mol$^{-1}$) [31] | $\Delta_{\text{solv}}H^{\text{IL}/\text{H}_2\text{O}}$ (kJ·mol$^{-1}$) | $V_{\text{m}}$ (cm·mol$^{-1}$) | *a* [33] | *b* [33] | *l* [33] | $E_{\text{HB}}$ (kJ·mol$^{-1}$) [36] |
|---|---|---|---|---|---|---|---|---|
| [EMIM][SCN] (l) | 8.8 ± 0.2 | 153.7 | −145.4 | 151.6 | −22.391 | 5.737 | −1.604 | −17.03 |
| | 7.84 ± 0.03 | | | | | | | |
| | 8.32 ± 0.68[a] | | | | | | | |
| [EMIM][$BF_4$] (l) | 17.33 ± 0.27 [7] | 135.5 | −118.2 | 148.1 | 3.023 | −1.489 | 0.636 | −9.79 |
| [EMIM][$CF_3CO_2$] (l) | −20.79 ± 0.17 | 129.3 | −150.1 | 173.7 | −8.839 | −17.442 | −1.674 | −24.38 |
| [EMIM][$B(CN)_4$] (l) | 18.75 ± 0.14 | 135.6 | −116.4 | 217.4 | −35.894 | 20.736 | −4.435 | −12.48 |
| | 19.58 ± 0.23 | | | | | | | |
| | 19.17 ± 0.59[a] | | | | | | | |
| [EMIM][$EtSO_4$] (l) | −10.73 ± 0.07 | 155.9 | −166.7 | 191.0 | −14.328 | −0.666 | 0.836 | −22.10 |
| | −10.83 ± 0.12 | | | | | | | |
| | −10.78 ± 0.07[a] | | | | | | | |
| [EMIM][$diEtPO_4$] (l) | −50.38 ± 1.52 | 146.1 | −196.5 | 231.8 | – | – | – | −33.41 |
| [EMIM][$(Tf)_2N$] (l) | 7.81 ± 0.47[a] [8] | 121.8 | −114.0 | 258.9 | 0 | 0 | 0 | −9.86 |
| | 7.1 ± 1.5 [10] | | | | | | | |
| [EMIM][FAP] (l) | 23.2 ± 0.4 [8] | 125.8 | −102.6 | 325.9 | −1.581 | 8.943 | −4.85 | −0.74 |

[a] Average values

Molar vaporization enthalpies, $\Delta_{\mathrm{vap}}H^{\mathrm{IL}}$, of ILs required for calculation of $\Delta_{\mathrm{solv}}H^{\mathrm{IL/H_2O}}$ (see column 3, Table 3) were taken from the literature [31]. Enthalpies of solvation calculated according to Eq. 1 are given in column 4, Table 3.

The largest exothermic effect and as a consequence the strongest intermolecular interactions were observed in the aqueous solution of [EMIM][diEtPO$_4$]. For the set of ILs under study the enthalpy of solvation of [EMIM][FAP] in water was the least negative despite the high molar mass. Apparently, [EMIM][FAP] exhibited the weakest intermolecular interactions in comparison to the other studied ILs.

The set of $\Delta_{\mathrm{solv}}H^{\mathrm{IL/H_2O}}$-values (column 4, Table 3) can also be compared with different structure related parameters in order to derive some "structure–property" relations and to evaluate factors responsible for their intermolecular interactions in the aqueous solutions. Similar to structure–property correlations performed with vaporization enthalpies in our previous study [31], there were no correlation between solvation enthalpies and molar masses, or with the molar volume $V_{\mathrm{m}}$. Following from this, the size and the mass of ILs are hardly responsible for the strength of intermolecular interactions of ILs with water.

Acree et al. [32, 33] and later Mutelet with co-authors [34] used the well-known LSER (linear solvation energy relationships) approach for interpretation of experimental data and describing the intermolecular interactions in solutions of ILs. This approach is based on application of Abraham solvation multi-parameter Eq. 2 for the gas-to-solvent partition coefficient, solvation enthalpies or other solvation properties (SP). This equation has the following expression:

$$\mathrm{SP} = c + e * \mathrm{E} + s * \mathrm{S} + a * \mathrm{A} + b * \mathrm{B} + l * \mathrm{L}, \tag{2}$$

here E and S refer to the excess molar refraction and a dipolarity/polarizability description of the solute, respectively; A and B are measures of the solute hydrogen-bond acidity and basicity; L is the logarithm of the gas-to-hexadecane partition coefficient at 298 K. The coefficients *c*, *e*, *s*, *a*, *b* and *l* are not simply fitting coefficients, but they reflect complementary properties of the solvent phase. Solvent hydrogen bond descriptors (*a*—basicity and *b*—acidity) have opposite meanings to the solute descriptors (A—acidity and B—basicity).

In works [32, 33], the authors collected and analyzed enthalpies of solvation of different organic compounds in ILs. Based on this collection they evaluated the Abraham solute specific descriptors for 10 cation functional groups and for 10 anion functional groups of ILs. Each of these descriptors was responsible for a certain type of intermolecular interactions with an IL used as the solvent (but not as the solute as in this work). Thus, it is reasonable to discuss our thermochemical data using the descriptors *a*, *b* and *l* developed by Acree et al. [33] (see Figs. 2, 3, 4). Parameter *a* is responsible for the basicity of ILs, the parameter *b* is ascribed for acidity, and the parameter *l* takes into account the van der Waals interactions term. Unfortunately, none of the parameters developed by Acree et al. correlated with solvation enthalpies derived in this work. For the *a*-descriptor correlation (Fig. 2) we observed a *v*-shaped dependence with a minimum for [EMIM][EtSO$_4$]. In the case of the *b*-descriptor two series of points can be observed (Fig. 3). Ionic liquids [EMIM][EtSO$_4$], [EMIM][SCN], [EMIM][B(CN)$_4$] exhibited a separated series, and another four ILs [EMIM][CF$_3$CO$_2$], [EMIM][BF$_4$], [EMIM][(Tf)$_2$N], [EMIM][FAP] were included in the second series. An irregular pattern was observed by comparison of $\Delta_{\mathrm{solv}}H^{\mathrm{IL/H_2O}}$ and the *l*-descriptor (see Fig. 4). The trends shown on Figs. 3 and 4 are even opposite with their slopes. Increasing of the *l*-descriptor values leads to the decrease of solvation enthalpies, and the *b*-descriptor values of solvation enthalpies increased. Absence

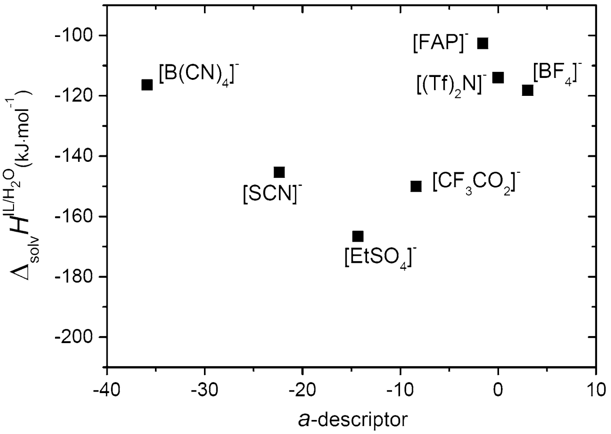


**Fig. 2** Correlation of solvation enthalpies of 1-ethyl-3-methyl-imidazolium based ionic liquids in water with the Abraham solute descriptor *a*

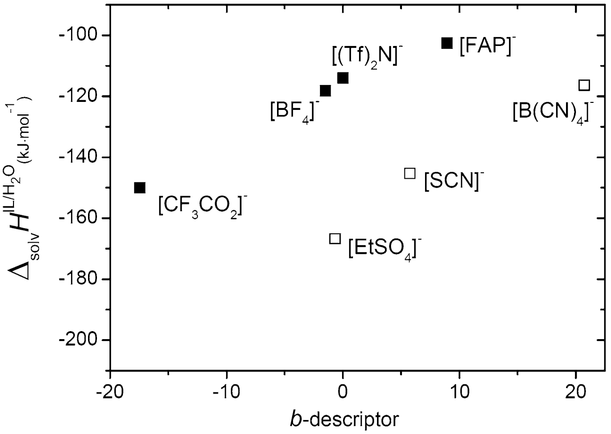


**Fig. 3** Correlation of solvation enthalpies of 1-ethyl-3-methyl-imidazolium based ionic liquids in water with the Abraham solute descriptor *b*

of reasonable correlations of the descriptors defined by Acree et al. [33] with values of solvation enthalpies could be rationalized by some intrinsic reasons. First of all, the value of $\Delta_{\mathrm{solv}}H^{\mathrm{IL/H_2O}}$ is a bulk property and it combines different types of intermolecular interactions. Thus, the failing correlations of $\Delta_{\mathrm{solv}}H^{\mathrm{IL/H_2O}}$ with *a*, *b* and *l*—descriptors seem to be an evidence of the complex nature of intermolecular interactions in ILs under study. Secondly, the descriptors *a*, *b,* and *l* were derived for the mixtures where ILs were used as the solvent, and not as the solute as in in the current work.

Intermolecular hydrogen bonding is often discussed as a main type of interaction in aqueous solutions for molecular solutes [35]. How important is the hydrogen bonding for ionic liquids in water? To answer this question we correlated solvation enthalpies derived in this work with the hydrogen-bonding interaction energies, $E_{\mathrm{HB}}$, estimated by using the

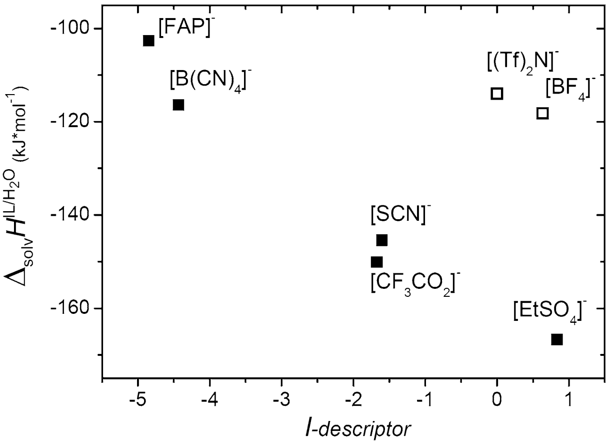


**Fig. 4** Correlation of solvation enthalpies of 1-ethyl-3-methyl-imidazolium based ionic liquids in water with the Abraham solute descriptor *l*

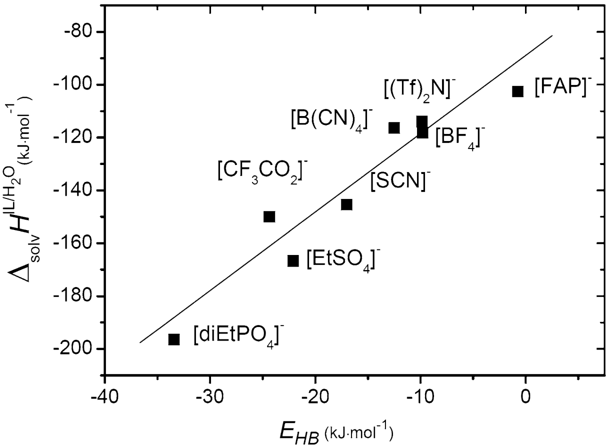


**Fig. 5** Correlation of solvation enthalpies of 1-ethyl-3-methyl-imidazolium based ionic liquids in water with the hydrogen-bonding interaction energies $E_{HB}$

COSMO-RS method for the equimolar cation–anion mixtures [36]. We have observed that the correlation of solvation enthalpies $\Delta_{solv}H^{IL/H_2O}$ (298.15 K) with the interaction energies $E_{HB}$ fit very well (see Fig. 5) in the linear correlation:

$$\Delta_{solv}H^{IL/H_2O}(298.15\ K)/kJ{\cdot}mol^{-1} = -\ 35.99 + 2.24 \times E_{HB}\ \text{with}$$

$$\left(R^2 = 0.94\right). \tag{3}$$

This correlation can serve as evidence that hydrogen bonding is also very important intermolecular interaction in aqueous solutions of ionic liquids. This conclusion confirms the results of work [37], there the authors have shown that differences in excess properties of ionic liquids in aqueous solutions are ascribed to their capability to form hydrogen bonds with water molecules. Moreover, Eq. 3 can be used to assess enthalpies of solvation of unknown ILs using interaction energies estimated by COSMO-RS.

## 4 Conclusion

In this work we systematically studied the thermochemistry of dissolution of ILs in water. Highly accurate and consistent values of solution enthalpies for five ionic liquids in water were directly measured at 298.15 K using two different calorimeters. These results could be useful for prediction of solubility of ILs in aqueous solutions at elevated temperatures and validation of solution enthalpies calculated indirectly from the solubility temperature dependence. Enthalpies of solvation were calculated from solution enthalpies measured in this work and vaporization enthalpies available from the literature. The linear correlation of solvation enthalpies with the hydrogen-bonding interaction energies revealed the importance of this type of intermolecular interactions in aqueous solutions of ionic liquids, as well as provided an useful empirical equation for a quick appraisal of solvation enthalpies.

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