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Alcohols as molecular probes in ionic liquids: evidence for nanostructuring†

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A comprehensive study of the solution and solvation of linear alcohols (propan-1-ol, butan-1-ol and pentan-1-ol) in ionic liquids (ILs) is presented. The effect of the alkyl chain size of both alcohols and ILs (1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_nC_{1im}][NTf_2]$, ionic liquid series) on the thermodynamic properties of solution and solvation was used to obtain insight into the interactions between alcohols and ILs. Alcohols were used as molecular probes to ascertain whether their solvation in ILs would reflect IL nanostructuring. A trend shift was found in the values of enthalpy of solution and solvation for the $[C_nC_{1im}][NTf_2]$ series at a critical alkyl size (CAS) of C_6 . Further, the effect of the hydrogen bond basicity of the anion in the solvation of alcohols was explored based on the comparative study of the solvation of propan-1-ol in two different IL series, 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_nC_{1im}][NTf_2]$ and hexafluorophosphate $[C_nC_{1im}][PF_6]$. The results obtained provide experimental support for the strength of hydrogen bonds between the alcohols and the NTf_2 and PF_6 anions, providing insights into the IL intermolecular interactions, namely by indicating the ability of the alcohols to discriminate the IL anion hydrogen bond basicity.

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Introduction

Ionic liquids (ILs) are a class of neoteric solvents^{1,2} typically composed of organic cations and organic or inorganic anions that cannot form an ordered crystal and thus remain liquid at or near room temperature. The interest in room temperature ionic liquids (RTILs) relies on their unique properties such as stability at high temperatures, negligible vapour pressure, non-flammability, wide electrochemical window, and wide liquid ranges.^{3–8} Moreover, the properties of an ionic liquid can be tuned for a specific application by adjusting the cation and/or anion family (and thus the structure). In addition, ionic liquids can be combined either with other ILs or with molecular solvents. The interesting properties and tunability of ILs make them alternatives to conventional solvents in the separation process,⁹ electrochemistry,^{10,11} media for chemical and biological reactions,^{12,13} catalysis,¹⁴ sensors¹⁵ and tribology.¹⁶

However, in order to easily select the ideal ionic liquid (or ionic liquid mixture) for a particular application, it is essential

to know the properties and structural organization of the pure compounds as well as to understand the solute–solvent interactions and possible changes in the structure induced by the dissolved species.

With regard to the study of structuration in pure ILs, there has been a theoretical study by Wang and Voth¹⁷ where the effect of cation's alkyl chain length is explored, and the existence of cation's tail domains is found, beyond a certain cation's chain length. Further, they found that the headgroup of the cation and the anion are rather homogeneously distributed. In 2006, Lopes and Pádua¹⁸ observed the existence of nanostructural organization in ILs characterized by the existence of non-polar domains and a three-dimensional continuous network of ionic channels constituted by the anion and the cation headgroups.

Structural evidence of nanostructuring was obtained for $[C_nC_{1im}][Cl]$,¹⁹ $[C_nC_{1im}][BF_4]$,¹⁹ $[C_nC_{1im}][PF_6]$ ²⁰ and $[C_nC_{1im}][NTf_2]$ ²¹ by Triolo *et al.*^{19,20} and Russina *et al.*²¹ Subsequent theoretical studies^{22,23} on the nanostructural organization of ILs have shown an increase in the distance between the same charge ions within the polar network as a result of the accommodation of larger non-polar domains as the alkyl side chain increases, until reaching a number of carbons in the alkyl chain of 6. This number was also found to be the threshold value for the percolation of island-like non-polar domains into a continuous non-polar sub-phase.²³ At the experimental level, experiments were conducted by our group leading to the measurement of vapour pressures, heat capacities,

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viscosities and refractive indices of symmetric and asymmetric ionic liquids. For all these properties, a trend shift^{24–31} was observed at the same critical value for the number of carbons in the alkyl chain (6). This value has been referred to as the critical alkyl size (CAS).

In systems with dissolved species, particularly molecular solvents in ILs, some studies are available on solubility,^{32–34} excess properties,^{35–45} phase behavior,^{37,39,40,46–50} structure^{42,51–55} and dynamics.^{56–58} In order to understand the specific location of the dissolved species and interactions with the ionic liquid, it is enlightening to determine the solution and solvation enthalpies of the chosen solutes in IL families. At present very little data are available, and in some cases the deviation between the values for the enthalpy of solution at infinite dilution obtained by different groups amount to 40%.^{45,59,60} Thus, direct (calorimetric) measurements of enthalpies of solution at infinite dilution for solutes in these systems are in great need, as they are much more accurate than the corresponding values derived from activity coefficients^{50,60–62} or excess enthalpies^{35,45} in concentration ranges not close to the infinite dilution.

Among the available studies reporting values calculated over a concentration range close to infinite dilution⁵⁹ up to 0.2 mole fraction,^{45,60} the work of Costa Gomes *et al.*⁴⁵ should be referred. They determined excess volumes and excess enthalpies using isothermal titration calorimetry (ITC) of methanol, ethanol, butan-1-ol and hexan-1-ol in $[C_nC_1im][NTf_2]$ IL series, and found a trend shift effect when varying the cation's alkyl chain length, but did not explore it extensively. On the other hand, the studies of Fumino *et al.*^{63,64} indicated a stronger solute–solvent (or anion–cation) interaction for an imidazolium-based ionic liquid with the more basic acetate anion.

These two studies inspired us to take up the present study of determining the enthalpies of solution and solvation, using alcohols as molecular probes to explore the effect of the size of the alkyl chain in both cations and alcohols as well as the effect of the hydrogen bond basicity of the anion. Therefore, ITC was used to obtain experimental values for the enthalpies of solution at infinite dilution of propan-1-ol, butan-1-ol and pentan-1-ol in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (asymmetric) series, $[C_nC_1im][NTf_2]$ and of propan-1-ol in 1-alkyl-3-methylimidazolium hexafluorophosphate series, $[C_nC_1im][PF_6]$, at 298.15 K. Alcohols were used as molecular probes in ILs due to their well-known amphiphilic nature: in one side the dispersive and H-bond ability of the hydroxyl functional group and on the other side the non-polar alkyl chain.

In fact, the idea was to address the effect of the three alcohols in the $[C_nC_1im][NTf_2]$ series, exploring the effect of the alkyl chain length of both alcohols and ILs to ascertain whether the solution/solvation properties would reflect the IL nanostructuring. This work was then complemented with the study of propan-1-ol in $[C_nC_1im][PF_6]$ in order to check for an anion differentiation effect. The study of the 1-alkyl-3-methylimidazolium hexafluorophosphate series is limited by the number of members in the series ($n = 4–9$) available in the liquid phase with suitable viscosity to be studied by ITC.

The study was performed at very low alcohol concentrations (≤ 0.06 mole fraction) in order to obtain the enthalpies of solution at infinite dilution. Using available data for the enthalpies of vaporization of the alcohols, the enthalpies of solvation at 298.15 K were derived. The data were further used to obtain insight into the interactions between alcohols and ILs as well as to study the influence of IL nanostructuring on the alcohol solvation process.

Experimental

Materials

Two different IL series were studied, $[C_nC_1im][NTf_2]$ with n from 2 to 11 and $[C_nC_1im][PF_6]$ with n from 4 to 9. In the abbreviation used, n represents the number of carbons in the cation's alkyl chain. A scheme of the structures of the ILs used is presented in Fig. 1 and the complete list of the studied ILs with the corresponding abbreviations is presented in the ESI† in Table S1. The study of the series of 1-alkyl-3-methylimidazolium hexafluorophosphate was limited by the number of members in the series that are available in the liquid phase with suitable viscosity to be studied by ITC.

The IL samples were acquired from IoLiTec GmbH with the highest purity available. Information concerning the Chemical Abstract Service registry number, purity and molar mass is provided in the ESI† in Table S2. The commercial IL samples were purified under vacuum (0.1 Pa) at moderate temperature (348 K) and constant stirring for 48 hours in order to remove the traces of volatile impurities.

The alcohols propan-1-ol, butan-1-ol and pentan-1-ol were acquired from Sigma-Aldrich Co. with a purity degree superior to 99% and were dried using molecular sieves of 0.3 nm, from Metrohm AG. The list of the three alcohols studied, together with their purity, molar mass, density and enthalpy of vaporization (from literature), is provided in Table 1.

The water mass fraction in alcohols and ILs was determined using a Metrohm Karl Fischer coulometer, model 737 KF, using a Hydranal® – Coulomat AG from Riedel-de Haën. The water

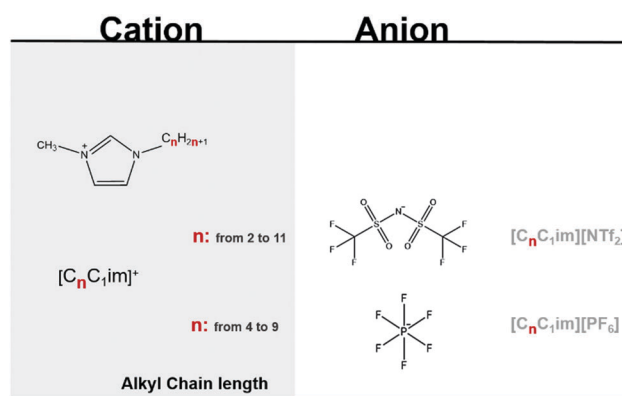


Fig. 1 Schematic representation of the IL series studied: $[C_nC_1im][NTf_2]$ with n from 2 to 11; $[C_nC_1im][PF_6]$ with n from 4 to 9.

Table 1 List of the studied alcohols, their purity, molar mass and literature data for density and enthalpy of vaporization at $T = 298.15$ K

| Source | Purity (%) | $M_w/g\ mol^{-1}$ | $\rho/kg\ m^{-3}$ | $\Delta_v^0 H_m^0/kJ\ mol^{-1}$ | |
|-------------|---------------|-------------------|-------------------|---------------------------------|--------------------|
| Propan-1-ol | Sigma Aldrich | 99.7 | 60.10 | 799.62 ^a | 47.45 ^b |
| Butan-1-ol | Sigma Aldrich | 99.8 | 74.12 | 805.87 ^a | 52.35 ^b |
| Pentan-1-ol | Sigma Aldrich | 99.0 | 88.15 | 811.04 ^a | 57.02 ^b |

^a Ref. 65. ^b Ref. 66.

content in all ILs (after purification) and in the alcohols (after drying using molecular sieves) was below 100 ppm.

Isothermal titration calorimetry (ITC)

The experiments were performed in a microcalorimetric system contained in a 100 L water bath, with a high precision temperature controller developed and constructed at Lund University, Sweden. Each channel consisted of a twin heat conduction calorimeter equipped with a 1 mL titration cell (Thermometric AB/TA) connected to a 7^{1/2} digit Agilent nanovoltmeter (model 344420A) and to a computer that performs data acquisition and controls the syringe pump (LABTERMO⁶⁷ software for ITC).

The calorimeter unit, as well as the experimental methodology, has been described in detail in the literature.⁶⁸ The calorimetric cell, the main titration cell tube where the stirrer shaft sits, and the needle conducting tube were all carefully dried before each experiment by passing a stream of nitrogen for 15 minutes. The alcohol additions were made using a modified 100 μ L gastight Hamilton syringe, through a stainless-steel capillary needle (inner diameter 0.15 mm), whose tip was immersed in the IL sample just before the experiment. The calorimetric titration experiments consisted of a series of seven consecutive injections of 1.6 μ L of pure propan-1-ol, butan-1-ol or pentan-1-ol (in the syringe) into 900 μ L of a pure ionic liquid sample contained in the calorimeter cell. A gold propeller stirrer was used at a stirring speed of 80 rpm to ensure proper mixing of the alcohols and ILs. The experiments were carried out at (298.15 ± 0.01) K in slow mode, *i.e.*, allowing the calorimetric signal to come back to the baseline before each new injection (see Fig. 2). Even so, in order to correct the

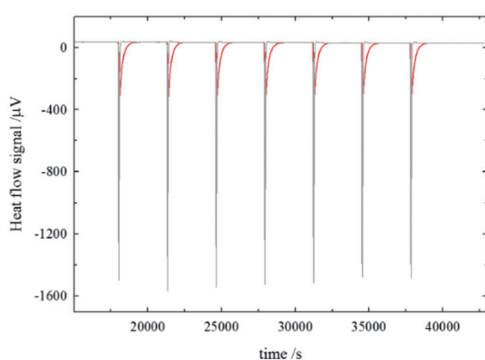


Fig. 2 Plot of the typical results obtained from ITC for the injection of alcohols in the ionic liquids studied: raw data (red line —); corrected data using the Tian equation (gray line —). Data obtained for the titration of 1.6 μ L of pure propan-1-ol into 900 μ L of $[C_7C_1im][PF_6]$.

instrumental calorimetric time delay and clear out the real time solution process in the calorimetry cell, the calorimetric signal was corrected to the instrument time constant using the Tian equation⁶⁹,

$$\frac{dQ}{dt} = \varepsilon \left(U + \tau \frac{dU}{dt} \right) \quad (1)$$

where dQ/dt stands for the thermal power, τ is the time constant of the calorimeter, U is the heat flow signal, dU/dt is the time derivative of the heat flow signal, and ε is the calibration constant of the calorimeter. Since no concentration dependence was observed for the enthalpies of solution in the concentration range (molar fraction of alcohol ≤ 0.06) used, the standard molar enthalpy of solution at infinite dilution ($\Delta_{soln}H_m^{0,\infty}$) was calculated according to

$$\Delta_{soln}H_m^{0,\infty} = \frac{\bar{Q}}{n} \quad (2)$$

where n stands for the molar quantity added per injection and \bar{Q} was taken as the average of the heat generated per injection in the calorimeter. In order to evaluate the repeatability of the results, the titration experiment was repeated independently at least twice. The quoted uncertainty is the extended standard deviation, considering the overall uncertainty for the 0.95 level of confidence.

The instrument (channels 1 and 2) was calibrated electrically using an insertion heater and varying power and energy. The values obtained for the calibration constant, ε , present an uncertainty of $\pm 0.3\%$. The dilution of a 10% (m/m) aqueous propanol solution in water⁷⁰ was performed as a test to ascertain the accuracy. The obtained values (-1.63 ± 0.02 kJ mol⁻¹ and -1.58 ± 0.02 kJ mol⁻¹) are in agreement with the accepted values^{70,71,72} for this process at 298.15 K. The standard molar enthalpy of solution of pure propan-1-ol in water at infinite dilution was also determined and the results (-10.16 ± 0.05 kJ mol⁻¹ and -10.13 ± 0.04 kJ mol⁻¹) are in excellent agreement with the recommended literature data (-10.16 ± 0.02 kJ mol⁻¹).⁷³

Results and discussion

The experimental results of the standard ($p^0 = 0.1$ MPa) molar enthalpies of solution at infinite dilution, $\Delta_{soln}H_m^{0,\infty}/kJ\ mol^{-1}$ at the reference temperature ($T = 298.15$ K), of propan-1-ol, butan-1-ol and pentan-1-ol in $[C_nC_1im][NTf_2]$ and $[C_nC_1im][PF_6]$ IL series are summarized in Table 2.

In Table 3, the experimental molar enthalpies of solution at infinite dilution of propan-1-ol, butan-1-ol and pentan-1-ol in $[C_nC_1im][NTf_2]$ and $[C_nC_1im][PF_6]$ ionic liquid series obtained in this work are compared with data available in the literature. Moreover, some data were found for the molar enthalpies of solution at infinite dilution of butan-1-ol and pentan-1-ol in $[C_nC_1im][PF_6]$.^{74–76}

An excellent agreement was obtained between our enthalpies of solution of propan-1-ol in $[C_8C_1im][NTf_2]$, propan-1-ol in $[C_6C_1im][NTf_2]$ and butan-1-ol in $[C_2C_1im][NTf_2]$ and the data reported by Kato *et al.*,⁵⁰ Dobryakov *et al.*⁷⁴ and Heintz *et al.*⁶¹

Table 2 Standard ($p^0 = 0.10 \pm 0.01$ MPa) molar enthalpy of solution at infinite dilution of propan-1-ol, butan-1-ol and pentan-1-ol in the ILs studied at the reference temperature ($T = 298.15$ K)

| Ionic liquid | $\Delta_{\text{soln}}H_m^{0,\infty}/\text{kJ mol}^{-1}$ | | |
|---|---|---------------------|---------------------|
| | Propan-1-ol | Butan-1-ol | Pentan-1-ol |
| [$C_nC_1\text{im}$][NTf₂] series | | | |
| [C ₂ C ₁ im][NTf ₂] | 8.72 (± 0.17) | 9.41 (± 0.19) | 9.86 (± 0.20) |
| [C ₃ C ₁ im][NTf ₂] | 8.58 (± 0.17) | 9.15 (± 0.18) | 9.44 (± 0.19) |
| [C ₄ C ₁ im][NTf ₂] | 8.37 (± 0.24) | 8.89 (± 0.25) | 9.19 (± 0.25) |
| [C ₅ C ₁ im][NTf ₂] | 8.34 (± 0.17) | 8.70 (± 0.17) | 8.81 (± 0.18) |
| [C ₆ C ₁ im][NTf ₂] | 8.13 (± 0.29) | 8.35 (± 0.24) | 8.53 (± 0.24) |
| [C ₇ C ₁ im][NTf ₂] | 8.38 (± 0.17) | 8.45 (± 0.17) | 8.32 (± 0.17) |
| [C ₈ C ₁ im][NTf ₂] | 8.42 (± 0.17) | 8.53 (± 0.17) | 8.15 (± 0.16) |
| [C ₉ C ₁ im][NTf ₂] | 8.47 (± 0.17) | 8.50 (± 0.17) | 8.11 (± 0.16) |
| [C ₁₀ C ₁ im][NTf ₂] | 8.45 (± 0.17) | 8.54 (± 0.17) | 8.18 (± 0.16) |
| [C ₁₁ C ₁ im][NTf ₂] | 8.57 (± 0.17) | 8.67 (± 0.17) | 8.10 (± 0.16) |
| [$C_nC_1\text{im}$][PF₆] series | | | |
| [C ₄ C ₁ im][PF ₆] | 11.02 (± 0.22) | — | — |
| [C ₅ C ₁ im][PF ₆] | 10.65 (± 0.15) | — | — |
| [C ₆ C ₁ im][PF ₆] | 10.49 (± 0.21) | — | — |
| [C ₇ C ₁ im][PF ₆] | 10.25 (± 0.38) | — | — |
| [C ₈ C ₁ im][PF ₆] | 10.16 (± 0.36) | — | — |
| [C ₉ C ₁ im][PF ₆] | 9.89 (± 0.35) | — | — |

The uncertainty is the extended standard deviation considering the overall uncertainty.

With regard to the remaining available literature results,^{45,50,60–62,74–76} most of our experimental values deviate from $\pm 5\%$ to $\pm 15\%$. For the values obtained for the enthalpies of solution of propan-1-ol in [C₂C₁im][NTf₂], in [C₆C₁im][NTf₂], in [C₄C₁im][PF₆], in [C₆C₁im][PF₆], in [C₈C₁im][PF₆], our data

deviate -20.6% , 40.2% , -43.4% , -78.9% and -32.1% from the previously published data,^{50,62,75,76} respectively. It is worth noting that a positive deviation was found towards some of the data presented by Heintz *et al.*,^{60,62} whereas a negative deviation was observed towards the data presented by Kato *et al.*,⁵⁰ Mutelet *et al.*⁷⁵ and Li *et al.*⁷⁶ The anterior observations show that the deviations found towards the literature data,^{45,50,60–62,74–76} even when considering the same group of authors, are not indicative of a systematic error in our values. The experimental results concerning the measurements of enthalpies of solution are very sensitive to the sample purity and the experimental procedure used in both titration and calibration experiments. Indeed this is particularly relevant in microcalorimetry, where the solution process involves measurements of very small heat flows.

In Fig. 3, a schematic representation of the difference between solution and solvation is presented. The standard enthalpy of solution at infinite dilution is the heat involved in the transfer of a solute molecule (in its condensed, pure phase) into a solvent, at zero concentration, at constant pressure. This property can thus be viewed hypothetically as a sum of three processes: breaking of solute–solute interactions (endothermic – related to the solute cohesive energy), creation of a solvent cavity (endothermic – related to the solvent cohesive energy) and solvent relaxation around the solute with concomitant solute–solvent interactions (exothermic). The standard enthalpy of solvation at infinite dilution, on the other hand, can be viewed as a two-step process: creation of a solvent cavity (endothermic) and solvent relaxation around the solute with concomitant solute–solvent interactions (exothermic).

Table 3 Comparison of experimental standard ($p^0 = 0.1 \pm 0.01$ MPa) molar enthalpies of solution at infinite dilution of propan-1-ol, butan-1-ol and pentan-1-ol in [C_nC₁im][NTf₂] and [C_nC₁im][PF₆] ionic liquid series at the reference temperature ($T = 298.15$ K) obtained in this work and data available from the literature

| System | Molecular solvent | $\Delta_{\text{soln}}H_m^{0,\infty}/\text{kJ mol}^{-1}$ | | | Ref. |
|---|-------------------|---|--|---------------------|----------------|
| | | This work ^a | Literature ^b | $\delta^c/\%$ | |
| [$C_nC_1\text{im}$][NTf₂] series | | | | | |
| [C ₂ C ₁ im][NTf ₂] | Propan-1-ol | 8.72 (± 0.17) | 7.946 (± 0.360) ^d 6.926 ^d | -8.9 -20.6 | 61 50 |
| | Butan-1-ol | 9.41 (± 0.19) | 8.518 (± 0.140) ^e 9.307 (± 0.420) ^d | -9.5 -1.1 | 45 61 |
| | Pentan-1-ol | 9.86 (± 0.20) | 11.217 (± 0.480) ^d | 13.8 | 61 |
| [C ₆ C ₁ im][NTf ₂] | Propan-1-ol | 8.13 (± 0.29) | 11.4 ^d 7.536 ^d | 40.2 -7.3 | 62 50 |
| | Butan-1-ol | 8.35 (± 0.24) | 8.1 ^d 9.201 (± 0.125) ^e 9.0 ^d | 0 10.2 7.8 | 74 45 62 |
| | | | 9.32 (± 0.01) ^e 9.6 (± 0.8) ^d 9.1 ^d | 11.6 15.0 9.0 | 60 60 74 |
| | | | 9.4 ^d 8.445 ^d | 10.2 0.3 | 62 50 |
| | Pentan-1-ol | 8.53 (± 0.24) | 9.4 ^d | 10.2 | 62 |
| | | | 8.42 (± 0.17) | 8.445 ^d | 0.3 |
| [$C_nC_1\text{im}$][PF₆] series | | | | | |
| [C ₄ C ₁ im][PF ₆] | Propan-1-ol | 11.02 (± 0.22) | 11.6 ^d 6.2385 ^d | 5.3 -43.4 | 74 75 |
| | | | 2.212 (± 0.0033) ^d 6.901 (± 0.0282) ^d | -78.9 -32.1 | 76 76 |
| [C ₆ C ₁ im][PF ₆] | | 10.49 (± 0.21) | | | |
| [C ₈ C ₁ im][PF ₆] | | 10.16 (± 0.36) | | | |

^a The uncertainty is the extended standard deviation considering the overall uncertainty. ^b The uncertainty is reported by the authors. ^c Relative deviation of literature data. ^d Obtained from activity coefficients at infinite dilution.^{50,60–62,74–76} ^e Obtained from the partial excess enthalpies/enthalpies of solution.^{45,60}

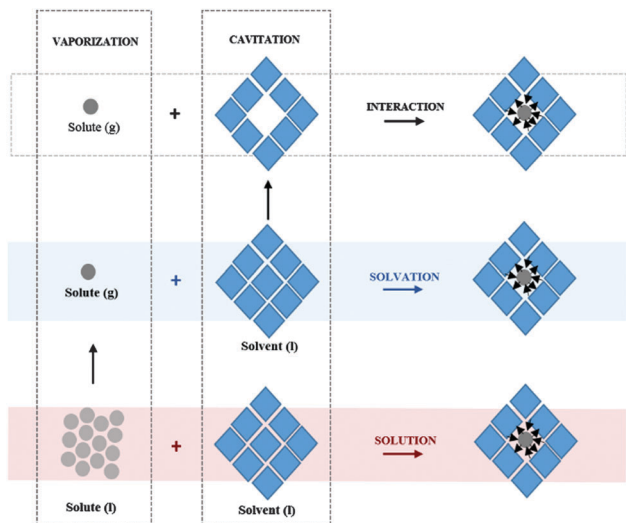


Fig. 3 Schematic diagram of the interplay between the enthalpies of solution, enthalpies of solvation, solute-solute interaction (vaporization), solvent-solvent interaction (cavitation) and solute-solvent interaction at infinite dilution.

The data concerning the enthalpies of solution of the alcohols in both series $[C_nC_1im][NTf_2]$ and $[C_nC_1im][PF_6]$ as a function of the number of carbons in the cation's alkyl chain are plotted in Fig. 4.

The endothermic enthalpy of solution (balance between the exothermic and endothermic contributions) reflects the interplay between the high volumic cohesive energy of the alcohols and the ionic liquids and their solute-solvent interaction. See the scheme in Fig. 3.

The standard molar enthalpies of solution at infinite dilution of each alcohol (propan-1-ol, butan-1-ol and pentan-1-ol) in $[C_nC_1im][NTf_2]$ ionic liquid series (Fig. 4) were found to initially

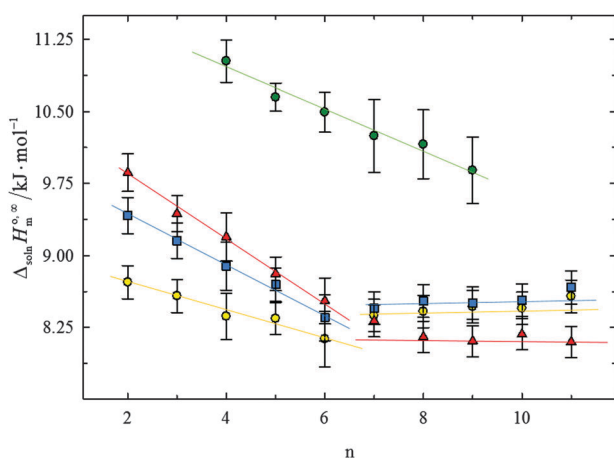


Fig. 4 Plot of the standard ($p^0 = 0.10 \pm 0.01$ MPa) molar enthalpy of solution ($T = 298.15$ K) at infinite dilution of alcohols in the $[C_nC_1im][anion]$ ionic liquid series as a function of the number of carbons in the alkyl side chain of the cation (n): propan-1-ol in $[C_nC_1im][NTf_2]$ (yellow ●); propan-1-ol in $[C_nC_1im][PF_6]$ (green ●); butan-1-ol in $[C_nC_1im][NTf_2]$ (blue ■); pentan-1-ol in $[C_nC_1im][NTf_2]$ (red ▲). The lines are intended as a guide to the eye.

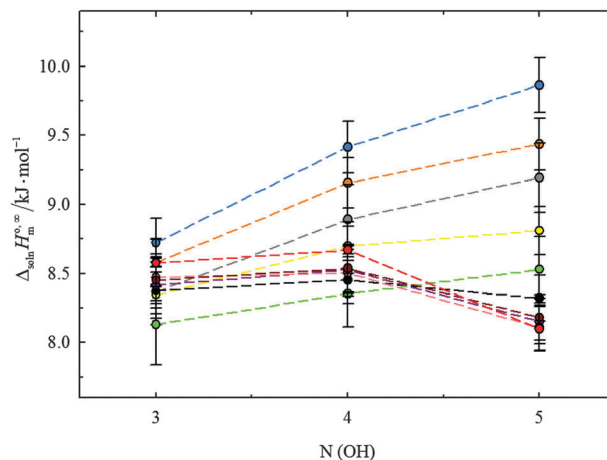


Fig. 5 Plot of the standard ($p^0 = 0.10 \pm 0.01$ MPa) molar enthalpy of solution ($T = 298.15$ K) at infinite dilution of alcohols in the $[C_nC_1im][NTf_2]$ ionic liquid series as a function of the number of carbons in the alkyl side chain of the alcohol ($N(OH)$): $[C_2C_1im][NTf_2]$ (blue ●); $[C_3C_1im][NTf_2]$ (orange ●); $[C_4C_1im][NTf_2]$ (grey ●); $[C_5C_1im][NTf_2]$ (yellow ●); $[C_6C_1im][NTf_2]$ (green ●); $[C_7C_1im][NTf_2]$ (black ●); $[C_8C_1im][NTf_2]$ (purple ●); $[C_9C_1im][NTf_2]$ (pink ●); $[C_{10}C_1im][NTf_2]$ (dark red ●); $[C_{11}C_1im][NTf_2]$ (red ●). The dashed lines are intended as a guide to the eye.

decrease with the increasing number of carbon atoms in the cation's alkyl chain, until C_6 ($n = 6$), and an almost constant value was obtained thereafter. The existence of a trend shift (at the CAS, $n = 6$) in the enthalpy of solution values for the $[C_nC_1im][NTf_2]$ ionic liquid series is in line with the experimental results^{26,27,31} for the other measured physical and chemical properties of this IL series.

It is worth noting that the decrease in enthalpy values is more pronounced for alcohols with larger alkyl chains.

A different presentation of the data for the $[C_nC_1im][NTf_2]$ series is shown in Fig. 5, where the standard molar enthalpies of solution at infinite dilution are represented as a function of the number of carbons in the alcohol's alkyl chain (propan-1-ol, butan-1-ol and pentan-1-ol). Fig. 5 highlights the decrease of the values of the standard molar enthalpy of solution at infinite dilution for each alcohol from $[C_1C_1im][NTf_2]$ to $[C_6C_1im][NTf_2]$ and then the stabilization of the value until $[C_{11}C_1im][NTf_2]$. Besides the alcohol's alkyl chain ($N(OH) = 3, 4$ and 5), the dependence of the molar enthalpy of solution on the alkyl chain length of the ILs is observed until $[C_6C_1im][NTf_2]$, increasing from propan-1-ol to pentan-1-ol. Beyond $[C_6C_1im][NTf_2]$ the differentiation effect disappears, evidencing the trend shift at the CAS ($n = 6$).

The observation of a trend shift for the $[C_nC_1im][NTf_2]$ series, from both perspectives (Fig. 4 and 5), is an evidence of nanostructuring in the ionic liquids. The decrease of the enthalpies of solution until C_6 , followed by a level-off for larger ILs of the same family, is an indication that the alcohols are preferentially located in the polar region.

This last observation is in accordance with the hydrogen bond interaction between associating solutes like water and methanol and anions.⁷⁷

It is known from the literature^{22,23} that as the number of carbons in the cation increases, the distance between the cation and the anion also increases, but only until C₆, and levels off thereafter. If we consider that the cavity in the ionic liquid occurs partially in its polar region, the increase in the distance between the cation and the anion until C₆ would lead to a progressive decrease in the volumic cavitation energy. Furthermore, a larger distance between the anion and the cation would also lead to a decrease of the dielectric constant of the media, favouring the alcohol-IL interaction. The interplay between these two effects could explain the decrease in the enthalpies of solution until C₆ followed by stabilization after this critical alkyl chain length. Moreover, the fact that the decrease in the enthalpies is more pronounced for longer chain alcohols supports the idea that the solution/solvation is influenced by the volumic cavitation energy.

The standard molar enthalpies of solution at infinite dilution of propan-1-ol in [C_nC₁im][PF₆] seem to present a continuous decrease along the ionic liquid series (see Fig. 4). No trend shift is apparent/evidenced in the enthalpies of solution of propan-1-ol in the [C_nC₁im][PF₆]. This observation, together with the fact that the enthalpies of solution of propan-1-ol in [C_nC₁im][PF₆] ionic liquid series are higher than in [C_nC₁im][NTf₂] IL series, suggests that propan-1-ol has a weaker interaction with the PF₆ anion (a smaller exothermic contribution at the 3rd step in the hypothetical process described in Fig. 3) when compared to the NTf₂ anion.

These observations are in accordance with the literature, where Kramer *et al.*⁵⁷ and Wong *et al.*⁵⁸ have studied the IR spectrum of water in [C₂C₁im][NTf₂] and in [C₄C₁im][PF₆], respectively, particularly the deuterated hydroxyl (HOD) stretch mode and found out that it is centred at 2645.9 cm⁻¹ and 2678 cm⁻¹. This difference in frequency is an indication that the H-bond between the PF₆ anion and the hydroxyl group of water is weaker than that with the NTf₂ anion. A similar study,⁷⁸ involving the IR spectrum of methanol in [C₄C₁im][BF₄] and in [C₄C₁im][PF₆], revealed a band at 3580 cm⁻¹ and 3620 cm⁻¹, respectively. Thus, the interaction of methanol was found to be weaker with the PF₆ anion than with the BF₄ anion⁷⁸ (which has an ability to form a hydrogen bond similar to the NTf₂ anion⁷⁹). The hydrogen bond basicity could also be evaluated based on the β solvatochromic parameters that are strongly anion dependent.⁷⁹

From the existing evidence in the literature of hydrogen bonding between the PF₆ anion and solutes like water or ethanol we would expect propan-1-ol to be preferentially located in the polar region, and thus to see a trend shift in our data, reflecting the nanostructuring of this IL. As mentioned earlier, in the case of the [C_nC₁im][PF₆] series, the evidence for the IL nanostructuring in the form of a trend shift could not be detected in our measurements. This fact is probably due to several reasons: the small number (five) of studied ILs, the increased uncertainty of the measurements related to the higher viscosity of the ILs, and the lower interaction of the alcohol with the anion. Future work involving the study of solution/solvation of water and long alcohols like heptan-1-ol or octan-1-ol or even alkanes along the [C_nC₁im][PF₆]

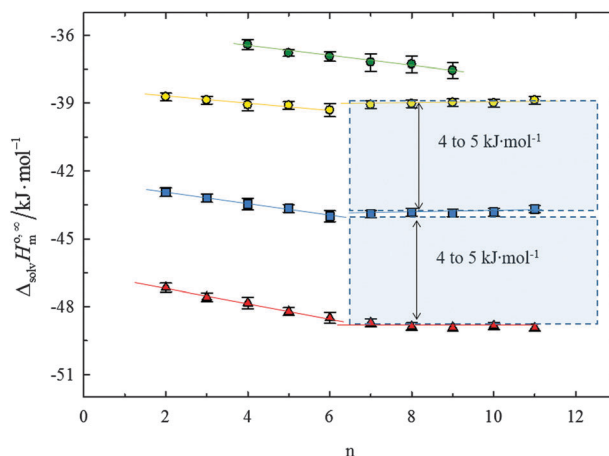


Fig. 6 Plot of the standard ($p^0 = 0.10 \pm 0.01$ MPa) molar enthalpy of solution ($T = 298.15$ K) at infinite dilution of alcohols in [C_nC₁im][anion] ionic liquid series as a function of the number of carbons in the alkyl side chain of the cation (n): propan-1-ol in [C_nC₁im][NTf₂] (yellow ●); propan-1-ol in [C_nC₁im][PF₆] (green ●); butan-1-ol in [C_nC₁im][NTf₂] (blue ■); pentan-1-ol in [C_nC₁im][NTf₂] (red ▲). The lines are intended as a guide to the eye.

IL series will probably shed new light on this topic and give new insights into the molecular understanding of this process.

Despite all this, it is clear from our data that (i) the anion has an important effect on the properties of solvation of ILs and (ii) there is stronger interaction between alcohols and imidazolium-based ILs with the NTf₂ anion (in comparison to the PF₆ anion).

The decrease of the enthalpy of solution with the increase of carbons in the cation's alkyl chain could be associated (like in the [C_nC₁im][NTf₂] IL series) with the overall decrease of the volumic cavitation energy in the PF₆ anion series.

From the experimental results obtained for the standard molar enthalpies of solution at infinite dilution and the data for the vaporization enthalpies available in the literature,⁶⁶ the standard molar enthalpies of solvation at infinite dilution ($\Delta_{\text{sol}}H_m^{0,\infty} = \Delta_{\text{soln}}H_m^{0,\infty} - \Delta_v^{\text{g}}H_m^0$) were derived and are represented in Fig. 6 as a function of the number of carbons in the alkyl side chain of the cation (and listed in the ESI† in Table S3).

The plot in Fig. 6 (solvation enthalpies) is similar to the one presented in Fig. 4. It is important to notice the change in the relative position of the enthalpies of solvation between the alcohol series. The cohesive interaction of the alcohols was now withdrawn and thus the enthalpies of solvation reflect the interplay between the cavitation energy of the ILs and the interaction between the alcohols and the ionic liquids (see scheme in Fig. 3). The obtained values are highest (more exothermic) for pentan-1-ol in [C_nC₁im][NTf₂], followed by butan-1-ol in [C_nC₁im][NTf₂] and finally the less exothermic values are found for propan-1-ol in [C_nC₁im][NTf₂] and propan-1-ol in [C_nC₁im][PF₆].

Considering that cavitation represents an endothermic contribution and that it must be larger for longer alcohols, the main effect reflected here is the solute-solvent interaction. Therefore, the results point to an increase in the interaction of

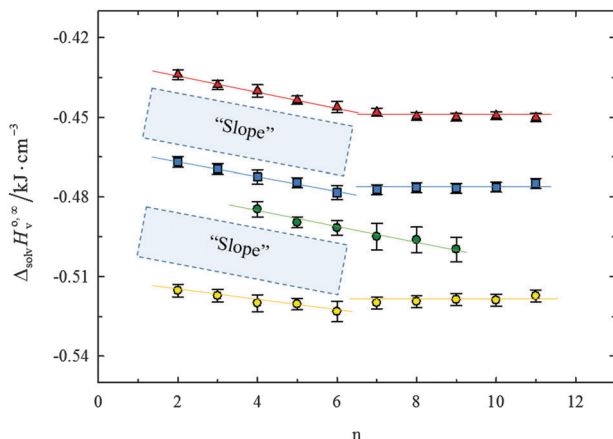


Fig. 7 Plot of the standard ($p^0 = 0.10 \pm 0.01$ MPa) volumic enthalpy of solvation ($T = 298.15$ K) of alcohols in $[C_{n-1}C_1\text{im}][\text{anion}]$ ionic liquid series as a function of the number of carbons in the alkyl side chain of the cation (n): propan-1-ol in $[C_nC_1\text{im}][\text{NTf}_2]$ (yellow ●); propan-1-ol in $[C_nC_1\text{im}][\text{PF}_6]$ (green ●); butan-1-ol in $[C_nC_1\text{im}][\text{NTf}_2]$ (blue ■); pentan-1-ol in $[C_nC_1\text{im}][\text{NTf}_2]$ (red ▲). The lines are intended as a guide to the eye.

the alcohols with the IL as the alkyl chain length increases (see Fig. 6). This conclusion is in line with the increase in favorable nonpolar alkyl-alkyl group interaction, amounting to 4–5 kJ mol^{-1} , typical for the methylene, $-\text{CH}_2-$, group contribution (e.g. in the alkanes, alcohols).⁸⁰

The standard enthalpies of solvation at infinite dilution per unit volume of the alcohol (instead of per mole) are presented in Fig. 7 and listed in the ESI† in Table S4 (calculated using available data for the densities⁶⁵). It is very interesting to note that when using the enthalpies of solvation per unit volume (Fig. 7), the relative position of the solvation data is inverted as compared with the plot in Fig. 6 that uses molar values. This observation highlights the significantly higher volumic interaction contribution of the hydroxyl group ($-\text{OH}$) in comparison with the methylene group ($-\text{CH}_2-$). Furthermore, it is interesting to observe (as expected) a similar dependence of the volumic enthalpies of solvation on the alkyl chain length of the ILs for the different alcohols and IL series (i.e. the same “slope” – see Fig. 7) due to cancelation of the cavitation energy, when the differential comparison analysis is done for the same alcohol volume. This indication of a similar dependence of the volumic enthalpies of solvation on the alkyl chain length of the ILs for the different IL series (NTf_2 and PF_6) is important as it suggests that the cohesive energy of both IL series is similar in the polar domains. According to this interpretation, the more endothermic enthalpy of solution/the less exothermic enthalpy of solvation is indeed an evidence for a lower interaction between the alcohol and the PF_6 anion (in relation to NTf_2).

Conclusions

The standard enthalpies of solution at infinite dilution of three alcohols in imidazolium-based IL series were measured and the corresponding enthalpies of solvation were derived. Analyzing the effect of the increase of the cation’s alkyl chain on the

enthalpies of solution of propan-1-ol, butan-1-ol and pentan-1-ol in $[C_nC_1\text{im}][\text{NTf}_2]$ ionic liquid series, a trend shift was found at CAS $n = 6$, as observed previously^{26,27,31} in several other physical properties of this IL series. In contrast, the enthalpies of solution of propan-1-ol in $[C_nC_1\text{im}][\text{PF}_6]$ showed no detectable trend shift. The results and overall discussion lead to the conclusion that propan-1-ol has a smaller interaction with the PF_6 anion as compared to the NTf_2 anion. Finally, it is found that the decrease in molar enthalpy of solution/solvation is more pronounced for longer chain alcohols, in agreement with the expected increased contribution of the IL cavitation energy. The higher volumic interaction contribution of the hydroxyl group as compared to the methylene group is evidenced in the volumic enthalpies of solvation. Furthermore, an intensification of the interaction of the alcohols with the IL was found as the alkyl chain length increased, approximately 4–5 kJ mol^{-1} per $-\text{CH}_2-$.

This work is, to the best of our knowledge, the most extensive experimental work dealing with the direct calorimetric (ITC) determination of enthalpies of solution at infinite dilution of molecular solvents in different and extensive IL series. It represents a contribution to the molecular understanding of the solvent properties of imidazolium-based ionic liquids and the effect of both the cation chain length and the basicity of the anion is explored. As such, it provides insight into the IL nanostructuration, the interactions present both in pure ILs and when molecular solvents are present, as well as the ability of these molecular probes to provide information on the hydrogen bond basicity of the anion.

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