

SUPPLEMENTARY MATERIAL

Solvent effects of 1-Ethyl-3-methylimidazolium acetate: Implications for the solvation properties and the dynamic behavior of polar and apolar solutes in ionic liquids

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Dynamic structure factor

The dynamic structure factor is given by

$$F(\vec{k}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} S(\vec{k}, t) e^{i\omega t} dt \quad (1)$$

with the intermediate scattering

$$S(\vec{k}, t) = \int G(\vec{r}, t) e^{-i\vec{k}\vec{r}} d\vec{r} \quad (2)$$

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and the van Hove function,

$$G(\vec{r}, t) = \frac{1}{N} \left\langle \sum_i^N \sum_j^N \delta(\vec{r} + \vec{r}_j(t_0) - \vec{r}_i(t)) \right\rangle \quad (3)$$

which is defined as the probability to find a particle at position \vec{r} at time t given that there was a particle at the origin at t_0 with the Dirac delta function δ .

The evaluation of the intermediate scattering function $S(\vec{k}, t)$ gives important hints with regard to the time evolution of wave vectors \vec{k} and the related inverse length scales. The

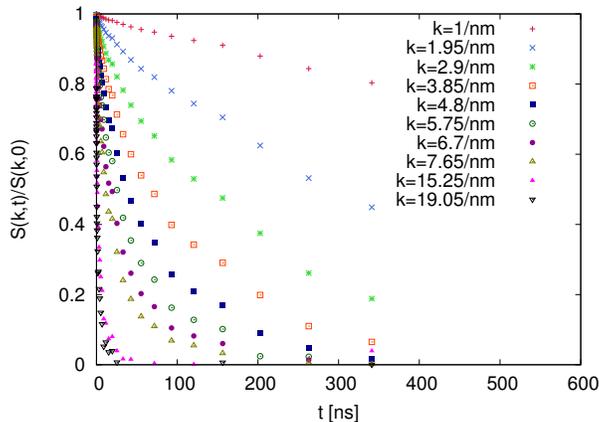


Figure 1: Decay of the normalized incoherent scattering function $S(\vec{k}, t)/S(\vec{k}, 0)$ for different wave vector values on timescales smaller than 350 ns.

values for the normalized incoherent scattering function at different times are shown in Fig. 1 where we have taken all EMIM ions except the spheres into account.

It can be clearly seen that the intermediate scattering function for all wave vectors decays on very long time scales. Specifically for small wave vectors ($k \leq 1.95 \text{ nm}^{-1}$), it becomes obvious that all values are not exponentially relaxed within 200 ns. With respect to the obtained values, we can conclude that very long equilibration times ($t \geq 200 \text{ ns}$) are necessary to study the system in full detail. With regard to our chosen equilibration time of 200 ns, the validity of equilibrated wave vector values $k \geq 1.95 \text{ nm}^{-1}$ which corresponds to length scales $r \leq 0.5 \text{ nm}$ is guaranteed. It can be therefore summarized, that the first two solvent shells

around the molecules as well as the spheres can be regarded as exponentially relaxed and therefore equilibrated. The properties that are determined by these length scales are in the main focus of our study.

Translational order parameter and excess entropies

The integration of the radial distribution function $g_{\alpha\beta}$ further allows us to evaluate the translational order parameter^{1,2}

$$t^*(r) = \int |g_{\alpha\beta} - 1| dr \quad (4)$$

which yields quantitative insights into the structure of the solution as it has been previously used for aqueous systems. In addition, the calculation of the excess entropies^{3,4}

$$s_{\beta}^{(2)}(r) = -2\pi\rho_{\beta}k_B \int r^2 [(g_{\alpha\beta}(r) \log g_{\alpha\beta}(r)) - (g_{\alpha\beta}(r) - 1)] dr \quad (5)$$

offers the possibility to calculate the deviations to an ideal solution.

The corresponding translational order parameters and the excess entropies according to Eqn. 4 and Eqn. 5 are presented in Fig. 2 and Fig. 3. With regard to the values in Fig. 2, it becomes obvious that the charged spheres obey the strongest ordering effect on the solution. It is evident that the translational order parameter for acetate ions around positively charged spheres indicates the strongest ordering effect compared with all other systems. This finding can be mainly related to the strong accumulation and high packing density as discussed in the main article. The degree of order for the acetate ions around negatively charged spheres is comparable with the magnitude of the t-factor for EMIM ions around both charged spheres. A slightly increased order can be also found for the acetate ions around the uncharged solute in comparison to the corresponding results for the EMIM ions. Hence, all these values indicate a high degree of order for both ion species around the solutes.

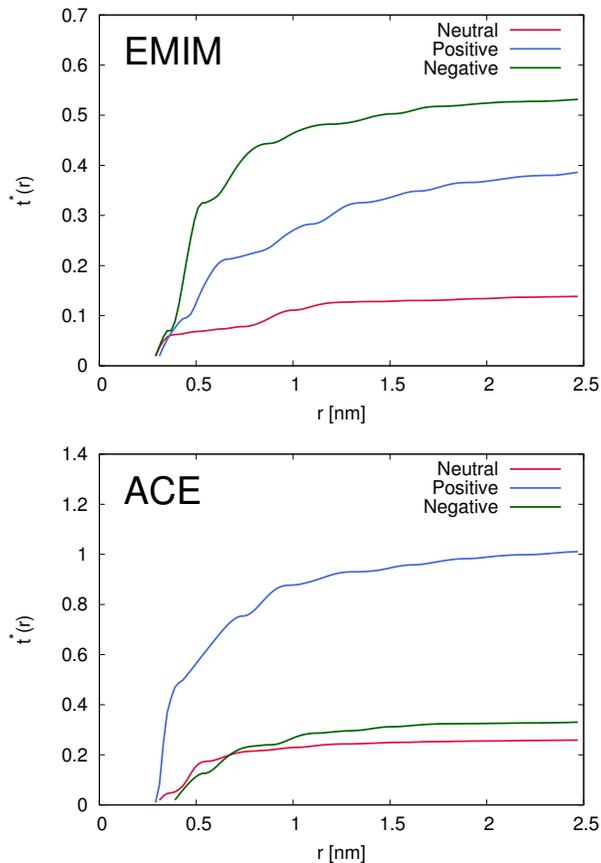


Figure 2: **Top:** Translational order parameter $t^*(r)$ according to Eqn. 4 for EMIM around the negatively (green line), the positively charged (blue line) and uncharged solute (red line). **Bottom:** Translational order parameter $t^*(r)$ according to Eqn. 4 for ACE around the negatively (green line), the positively charged (blue line) and uncharged solute (red line).

This behavior is also strongly reflected by the calculated excess entropies in Fig. 3. The calculation of the excess entropy $s^{(2)}$ provides a quantitative evaluation for the deviation of the actual solvent composition to an ideal gas state in terms of the entropic penalty. Herewith, it can be easily seen that the smallest entropic loss due to ordering effects can be related to both ion species around the uncharged solute. In contrast, the strongest decrease in entropy can be again observed for acetate ions around positively charged spheres. With respect to the obtained values, it can be concluded that the overall electrostatic interaction energy at room temperature between the solute and the ions has to compensate the order-induced entropic loss. Hence, the pronounced values for the excess entropy clearly validate

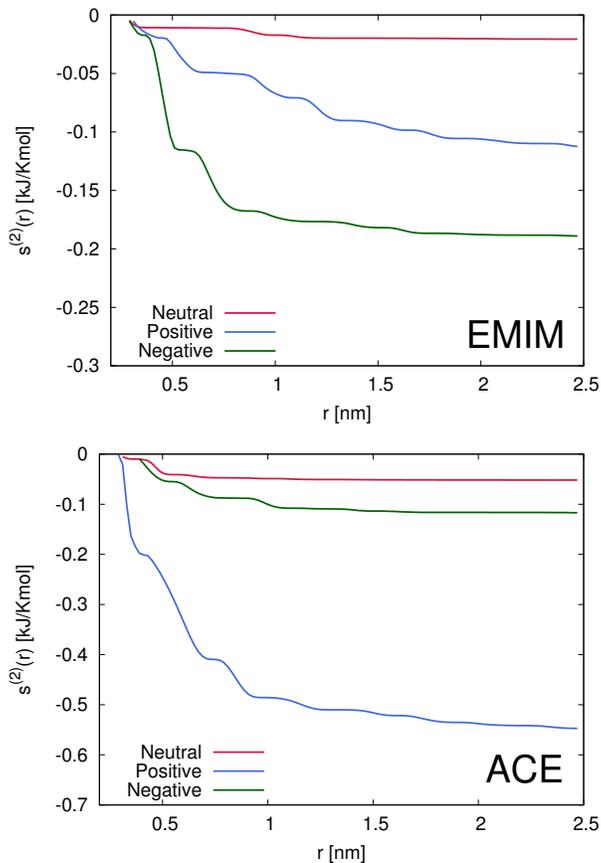


Figure 3: **Top:** Excess entropy $s^{(2)}(r)$ according to Eqn. 5 for EMIM around the negatively (green line), the positively charged (blue line) and uncharged solute (red line). **Bottom:** Excess entropy $s^{(2)}(r)$ according to Eqn. 5 for ACE around the negatively (green line), the positively charged (blue line) and uncharged solute (red line).

the presence of strong electrostatic contributions in terms of a favorable solvation process for the charged solutes. In addition, the long range order effect around the charged spheres becomes also evident with regard to the decreasing entropy values for distances $r \leq 2.5$ nm and beyond.

Energetic contributions for conservative solvent-solute interactions

We studied the energetic contributions according to the conservative potentials with respect to Lennard-Jones and Coulomb interactions between the ionic liquid species and the spheres. The corresponding results are presented in Fig. 4 where all ions of the simulation box have

been taken into account for the calculation of the energetic contributions. It becomes clearly

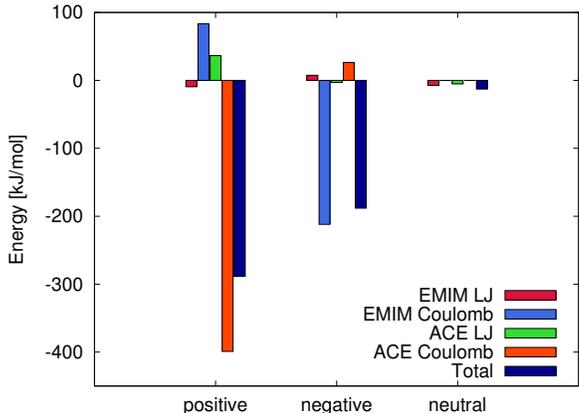


Figure 4: Order of Lennard-Jones (LJ) and electrostatic interactions (Coulomb) between EMIM, respectively acetate ions and the differently charged spheres (positive, negative and neutral). The deep blue bar for each solute denotes the total conservative energy which is the sum over the four independent Lennard-Jones and electrostatic contributions with the solvent.

evident that the most favorable interaction energy is given for the Coulomb forces between the acetate ions and the positively charged sphere. We can relate this finding to the large packing density of acetate ions around the sphere which can be easily seen with regard to the height of the first acetate peak in the radial distribution function in the main text. In addition, the strong dominance of electrostatic interactions between the positive solute and the acetate ions even explains the corresponding occurrence of a slightly positive Lennard-Jones interaction due to a short distance interaction between the acetate ions and the positively charged sphere. For EMIM ions, the Lennard-Jones interactions with the positive sphere are slightly attractive whereas the Coulomb interactions are reasonably repulsive. Nevertheless, the summation of all contributions leads to the most negative total energy which hints towards a good solubility of positive solutes in 1-ethyl-3-methylimidazolium acetate. An identical mechanism may be also responsible for the good solubility of glucose with polar hydrogen atoms in a comparable solvent as reported in Refs.^{5,6}.

The dominance of electrostatic interactions is also present for the negatively charged solute.

However, due to the smaller amount of EMIM ions in the first solvation shell (*c. f.* the height of the first peak in the radial distribution function (data in main article)), the total net order of Coulomb interaction contributions between EMIM and the negatively charged sphere is smaller compared with acetate ions around positively charged solutes. The lower packing density of EMIM ions as discussed in the main article becomes even visible with respect to the smaller value for the positive Lennard-Jones interaction energies.

The presence of attractive Lennard-Jones interactions which favor the solvation of the solute becomes also evident with regard to the results for the uncharged solute. We observe that both ion species favorably interact with the spheres, although with a negligible amount compared to the charged solutes, but nevertheless in terms of a stabilizing effect.

With respect to the overall order of the total interaction energy ($E_{tot} \approx -400$ to -200 kJ/mol for the charged spheres), one can clearly conclude that the solvation of charged solutes is driven by enthalpic contributions. This becomes evident with respect to the results for the excess entropy as presented in Fig. 3, where the largest contribution for the positively charged solute even at room temperature remains negligible compared to the enthalpic electrostatic contributions. Hence, the strong ordering effect which results in a significant increase of the entropic contributions does not severely influence the good solvation properties as they have been found for polar solutes like cellulose or glucose^{5,6}. Therefore, the prominent compensation of electrostatic and enthalpic contributions, as it was often proposed for biomolecular solvation⁷⁻¹⁰ is not applicable for the description of charged solute solvation in ionic liquids. In contrast, the entropy-enthalpy compensation principle seems to be more important for the solvation of uncharged or apolar solutes due to comparable orders of magnitude for the van-der-Waals and the entropic contributions. Therefore, we can assume, based on our findings for the model spheres, that positively charged solutes in 1-ethyl-3-methylimidazolium acetate should be most favorably solvated compared to negatively charged or uncharged solutes. One reason for this finding can be related to the smaller molecular size of the ionic liquid anion which forms a strongly accumulated first solvation shell. In addition, it can be

stated that, although uncharged, the solvation of apolar solutes should be merely influenced by the strength of the van-der-Waals interactions. If these contributions exceed the entropic loss due to a strong ordering effect, the solvation of apolar solutes should be favorable.

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