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Order in the chaos: The secret of the large negative entropy of dissolving 1-alkyl-3-methylimidazolium chloride in trihexyltetradecylphosphonium chloride†

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The dissolution of 1-alkyl-3-methylimidazolium chloride ILs with short alkyl chains in tetradecylphosphonium chloride does not only exhibit a large negative entropy. Also, in the resulting mixtures, the phosphonium cation diffuses faster than the much smaller imidazolium cation. Both unexpected features originate from the formation of a large symmetric ion cluster cage in which the imidazolium cation is caught by three chloride anions and four phosphonium cations.

Understanding the source of the physico-chemical properties of ionic liquids on a molecular level is a challenging task for several reasons, including the multitude of possible interactions and the sheer number of potential anion-cation combinations. It was hence quite surprising to find that in most cases, little deviation from ideal behavior occurs for binary ionic liquid mixtures,[1–5] i.e. mixtures of three ions, as defined by Welton and co-workers.[6] Nevertheless, some sporadic and rather unexpected observations were made, pointing to non-ideal behavior, such as increased conductivities of binary ionic liquid electrolytes,[7,8] or enhanced reactivity of organic reactants dissolved in binary ionic liquid solvents.[9–13] Driven by the idea that non-ideal mixture behavior might be beneficial for certain applications, we and others groups have set out to comprehend the structure-property relationship of binary mixtures of ionic liquids.[1–4,14–22] The meta-analysis of empirical data demonstrated that non-ideal behavior can often be observed if the two ions of the same charge in the mixture differ considerably in size and hydrogen-bond forming ability.[19] Furthermore, and in disagreement to the intuitive rule of thumb *similia similibus solvuntur*, some

mutually immiscible binary mixtures of ionic liquids have been reported.[7,23–26] For example, two phases are obtained at room temperature if 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_2C_1im][NTf_2]$)) is mixed with trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl)imide ($[C_6C_6C_6C_{14}P][NTf_2]$).[23,24] If water and pentane are added to this mixture, stable tetraphasic mixtures can be obtained.[23] Mutually immiscible binary mixtures are also obtained if the anion of $[C_nC_1im]_X[C_6C_6C_6C_{14}P]_{1-X}[NTf_2]$ ($0 \leq X \leq 1$; $n \leq 5$) is replaced by chloride.[23,24] Most interestingly, a large negative entropy of dissolving 1-alkyl-3-methylimidazolium chlorides in trihexyltetradecylphosphonium chloride ($[C_6C_6C_6C_{14}P]Cl$) was observed for imidazolium cations with short alkyl chains,[23] see table 1. Arce *et al.* speculated that the addition of $[C_1C_1im]Cl$ to $[C_6C_6C_6C_{14}P]Cl$ leading to "the formation of new stronger hydrogen bonds results in the exotherm and an increase in the degree of ordering in the phosphonium layer (and hence a large entropy decrease). As the alkyl chain length increases, this introduces a degree of asymmetry and hence the entropy of dissolution is less negative."[23] From these intriguing results, the following questions arise: What is the structure resulting in the high order of the liquid state, and which new hydrogen bonds are formed by the addition of $[C_1C_1im]Cl$ to $[C_6C_6C_6C_{14}P]Cl$?

Table 1 The enthalpy and entropy[23] of dissolving 1-alkyl-3-methylimidazolium chlorides in $[C_6C_6C_6C_{14}P]Cl$

Alkyl group	ΔH_{solv} in kJ/mol	ΔS_{solv} in J/K·mol
Methyl	−21.7	−100.3
Ethyl	−2.29	−39.1
n-Propyl	1.03	−25.5
n-Butyl	1.35	−20.3
n-Pentyl	1.51	−15.7

The large negative entropy of dissolving $[C_1C_1im]Cl$ in $[C_6C_6C_6C_{14}P]Cl$ might be induced by an ion cluster similar to **cage-Im** which is illustrated in Fig. 1. Please note,

cage-Im is only a static picture of a simplified isolated ion cluster which is discussed first to introduce the reader to the structure which is found in the classical molecular dynamics simulations subsequently. The phosphonium cation preferably arranges chloride as shown in Fig. 2 where the position along the C-P vector is most preferred. Two chloride anions of this tetrahedral solvation can link via hydrogen bonding at H4 and H5 on the backside of the imidazolium cation without a significant rearrangement compared to pure $[C_6C_6C_6C_{14}P]Cl$ and pure $[C_1C_1im]Cl$. This two ion pair cluster can be extended if a second phosphonium cation resides in front of the most acidic proton of the imidazolium ring (H2) which results in a linear arrangement of three cations. Furthermore, two additional phosphonium cations can link to the chloride ions which are hydrogen bonded at H4 or H5. This results finally in the ion cluster **cage-Im** with a mirror plane where the imidazolium cation is enclosed by three chloride anions and four phosphonium cations. The anions of cluster **cage-Im** reside only in places where they can be found in the pure imidazolium[27–29] or in the pure phosphonium compounds. Thus, no new type of hydrogen bond is formed in **cage-Im** which would contribute to the negative enthalpy of dissolving $[C_1C_1im]Cl$ in $[C_6C_6C_6C_{14}P]Cl$. Therefore, the negative enthalpy originates from an increased hydrogen bond strength in the $[C_1C_1im]_X[C_6C_6C_6C_{14}P]_{1-X}Cl$ mixtures while the large negative entropy stems from the symmetric shape of **cage-Im** and the decreased flexibility of the polar domains.
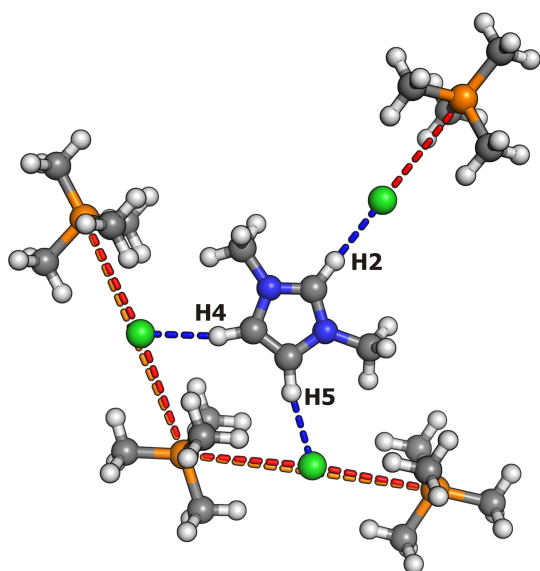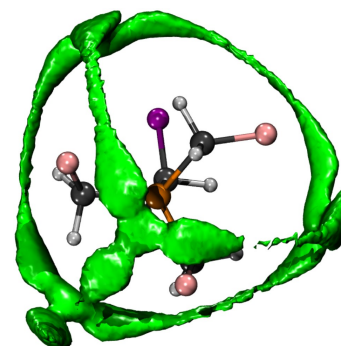

Fig. 2 Spatial distribution of Cl around the phosphonium cation of $[C_6C_6C_6C_{14}P]Cl$

To identify the role of **cage-Im** for the liquid structure, we have carried out classical molecular dynamics simulations of five IL systems, i.e. pure 1-ethyl-3-methylimidazolium chloride ($[C_2C_1im]Cl$; **pure-E**), pure 1-hexyl-3-methylimidazolium chloride ($[C_6C_1im]Cl$; **pure-H**), pure trihexyltetradecylphosphonium chloride ($[C_6C_6C_6C_{14}P]Cl$; **pure-P**), $[C_2C_1im]_{0.125}[C_6C_6C_6C_{14}P]_{0.875}Cl$ (**mix-E**), and $[C_6C_1im]_{0.125}[C_6C_6C_6C_{14}P]_{0.875}Cl$ (**mix-H**). In all simulations, we employed the force field developed for ionic liquids by Canongia Lopes *et al.*,[30–32] see ESI† for computational details.

The distances obtained from a static quantum chemistry calculation of the ion cluster **cage-Im** are only slightly smaller than those determined from the maximum of the first solvation shell in the radial pair distribution functions (RDFs) of **pure-E** and **pure-P**, see table 2 for comparison of distances and supporting information for illustration of the RDFs. Significant differences are also not visible in the position of the RDF maxima in **mix-E** compared to either **pure-E** or **pure-P**. Thus, the structure of $[C_2C_1im]Cl$ should fit nearly perfectly into the liquid structure of $[C_6C_6C_6C_{14}P]Cl$ at low imidazolium concentrations, indicating that a structure similar to **cage-Im** is important for the liquid structure of **mix-E**. Indeed, the spatial distribution of neighboring ions of an imidazolium cation shows strong similarities to **cage-Im**, see Fig. 4a. Nicely visible is the position of the two chloride anions in front of H4 and H5 as well as the phosphonium cations arranged behind. Only the ion positions in front of the acidic proton H2 show small differences compared to **cage-Im**. It is known that the chloride anion resides mainly close to the C2-H2 vector but not in front of the most acidic proton H2 in the force field model of Canongia Lopes *et al.* while it prefers a position in front of the acidic proton H2 in ab initio molecular dynamics simulations.[27,33] Nonetheless, the liquid structure is only slightly affected by this drawback of the

Fig. 1 Ion cluster **cage-Im** formed by one 1,3-dimethylimidazolium cation ($[C_1C_1im]$), three chloride anions (Cl) and four tetramethylphosphonium cations ($[C_1C_1C_1C_1P]$) optimized with 6-31++G**/BLYP-D2(RI).

employed force field. Besides the structures of the charged centers, another interesting structural feature is visible in Fig. 4a: The imidazolium core of **cage-Im** is surrounded by the nonpolar alkyl chains of phosphonium cations. Thus, the imidazolium cation is accommodated within the structure of the phosphonium cations, introducing a larger degree of order.

Table 2 Comparison of distances d_{QC}, d_{pure} and d_{mix-E} in pm between two atoms. d_{QC}: **cage-Im** of Fig. 1 optimized with 6-31++G**/BLYP-D2(RI); d_{pure}: Maximum of the first solvation shell peak in the RDFs of **pure-E** or **pure-P**; d_{mix-E}: Maximum of the first solvation shell peak in the RDFs of **mix-E**. Atom labels are shown in Fig. 3.

atoms	color in Fig. 1	d_{QC}	d_{pure}	d_{mix-E}
HX···Cl ($X = 2, 4, 5$)	blue	238–241	265	260–265
P···Cl	red	393–401	420	420
P···P	orange	792	805	795

Fig. 4 Spatial distribution of chloride (*green*), Rc (*red*), P (*orange*), and CP6 (*blue*) around the imidazolium plane of **mix-E** (*a*) and of **mix-H** (*b*). Atom labels can be found in Fig. 3.
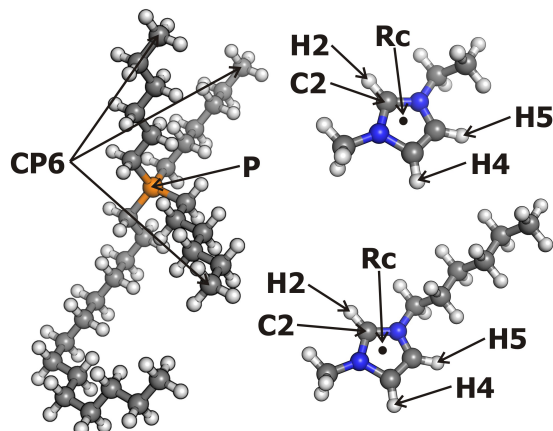

Fig. 3 Ball-and-stick model of all cations in the investigated systems with the atom labels used throughout this work. Rc is the geometric ring center of the imidazolium cation.

Extending the alkyl side chain attached to the imidazolium cation has three effects, compare Fig. 4a and 4b:

1. The preferred position of the anion in front of the acidic hydrogen atom H2 will move toward the methyl group side of the imidazolium cation affecting the position of the phosphonium cation in front of the imidazolium cation as well. Thus, the linear arrangement of the three central cations is perturbed.

2. The extended alkyl chain on the imidazolium cation competes for free space with the nonpolar alkyl chains of the phosphonium cations. Since this interaction is asymmetric, the linear arrangement of the three central cations is perturbed.
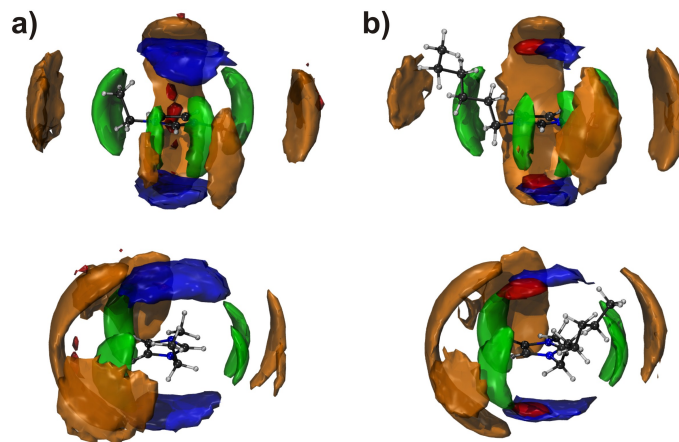
3. Extending the alkyl chain on the imidazolium significantly enhances π-π-stacking of the imidazolium cations, see spatial distribution function (SDF) of Rc in Fig. 4 and Rc-Rc radial distribution function (RDF) in Fig. 5a. As a result, the available space for the alkyl side chains of the phosphonium cations is significantly reduced and two preferred structural motifs for imidazolium solvation can be found in the liquid, one with π-π-stacking and one similar to **cage-Im**.

Overall, these three aspects lead to the smaller negative entropy of dissolution, if the alkyl chain on the imidazolium cation is increased.

The capability of 1-alkyl-3-methylimidazolium cations to arrange in a **cage-Im**-type fashion affects also dynamical properties. In its pure state, $[C_2C_1im]^+$ possesses a significant larger diffusion coefficient than either $[C_6C_1im]^+$ or $[C_6C_6C_6C_{14}P]^+$, see table 3. In the mixtures, however, the translational motion of $[C_2C_1im]^+$ is severely reduced, and the large and bulky $[C_6C_6C_6C_{14}P]^+$ cation possesses the highest diffusion coefficient in **mix-E**. This originates from the imidazolium cation being caught in an ionic cage similar to **cage-Im** which prevents a fast, surrounding-independent diffusion of $[C_2C_1im]^+$. The phosphonium cations form the outer shell of **cage-Im** and, therefore, can link to the cluster or leave the cluster most easily. Of course, the diffusion coefficents of $[C_6C_6C_6C_{14}P]^+$ and $[C_2C_1im]^+$ do not match each other because the ratio of them is 7:1 in **mix-E** while the ratio in the cluster is only 4:1. Thus, several phosphonium ions exist in the mixture which do not participate in the **cage-Im**-like structure. Nevertheless, all ion diffusion coefficients are close to each other in **mix-E**. In **mix-H**, $[C_6C_1im]^+$ is somewhat
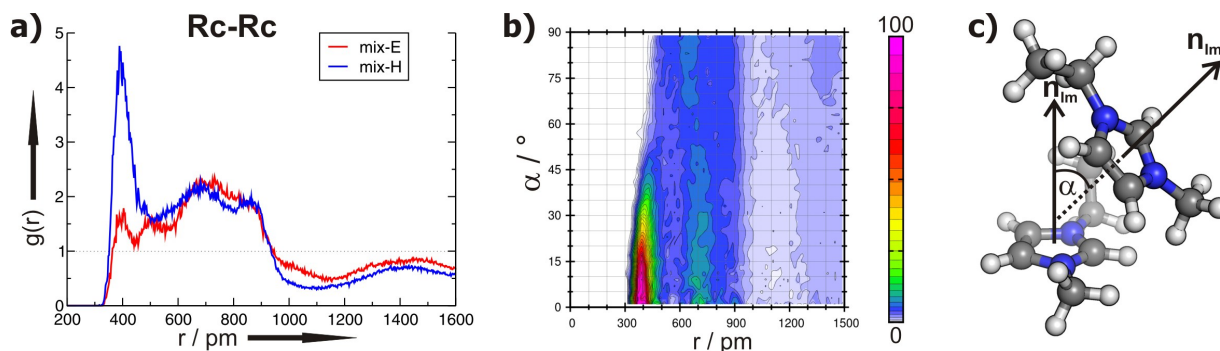
Fig. 5 a): Rc-Rc-RDFs of **mix-E** and **mix-H**; b): Combined distribution function (CDF) of the Rc-Rc radial distribution function (RDF) and the angle distribution function (ADF) of α for **mix-H**; c): Illustration of α which is the angle enclosed by the two normal vectors of the imidazolium planes

faster than $[C_6C_6C_6C_{14}P]^+$. The long alkyl chain attached to the imidazolium ring significantly perturbs the formation of the **cage-Im**-like structure in **mix-H**. Therefore, the imidazolium cation can move more freely and faster in **mix-H** than in **mix-E**.

In summary, we have shown the important role of the structural motif illustrated by the ion cluster shown in Fig. 1, **cage-Im**, for the unexpected large negative entropy of dissolving 1-alkyl-3-methylimidazolium chloride ILs with short alkyl chains in trihexyltetradecylphosphonium chloride ($[C_6C_6C_6C_{14}P]$Cl). The results clearly demonstrate that the positions of the atoms involved in hydrogen bonding in the binary mixtures remain nearly the same as those of the pure components, because the polar domains of $[C_1C_1im]$Cl and of $[C_6C_6C_6C_{14}P]$Cl fit nearly perfectly to each other. In agreement to the hypothesis of Acre et al.,[23] the strength of these hydrogen bonds is increased in the mixtures. Thus, the phosphonium ionic liquid can easily take up the imidazolium cations by the formation of a structure similar to **cage-Im** which introduces a high degree of order into the liquid. Extending the alkyl chain on the imidazolium cation disturbs the formation of **cage-Im** and enhances π-π-stacking of the imidazolium cations as additional preferred solvation structure of the imidazolium cations. Both aspects decrease the order of the liquid. Furthermore, we uncovered the impact of **cage-Im** on ion dynamics which results in an unexpected faster ion diffusion of the large and bulky phosphonium cation than the significantly smaller imidazolium cation in $[C_2C_1im]_{0.125}[C_6C_6C_6C_{14}P]_{0.875}$Cl.

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Table 3 Calculated diffusion coefficient D([X]) of ion [X] in pm^2/ps at 400 K

	D($[C_2C_1im]^+$)	D($[C_6C_1im]^+$)	D($[C_6C_6C_6C_{14}P]^+$)	D(Cl^-)
pure-E	30.40	—	—	22.87
pure-H	—	3.71	—	4.90
pure-P	—	—	0.99	0.74
mix-E	0.95	—	1.05	0.93
mix-H	—	1.24	1.13	0.96

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