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Solvation and Aggregation of *N,N'*-Dialkylimidazolium Ionic Liquids: A Multinuclear NMR Spectroscopy and Molecular Dynamics Simulation Study

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The solvation and aggregation of the ionic liquid (IL) 1-*n*-butyl-3-methylimidazolium chloride ([C₄mim]Cl) in water and dimethylsulfoxide (DMSO) were examined by analysis of ¹H and ^{35/37}Cl chemical shift perturbations and molecular dynamics (MD) simulations. Evidence of aggregation of the IL *n*-butyl chains in aqueous environments at IL concentrations of 75–80 wt% was observed both in the NMR experiments and in the MD simulations. The studies also show that [C₄mim]Cl behaves as a typical electrolyte in water, with both ions completely solvated at low concentrations. On the other hand, the data reveal that the interactions between the [C₄mim]⁺ and Cl⁻ ions strengthen as the DMSO content of the solutions increases, and IL-rich clusters persist in this solvent even at concentrations below 10 wt%. These results provide an experimentally supported atomistic explanation of the effects that these two solvents have on some of the macroscopic properties of [C₄mim]Cl. The implications that these findings could have on the design of IL-based solvent systems are briefly discussed.

1. Introduction

Arbitrarily defined as salts that liquefy at or below 100 °C, ionic liquids (ILs) represent a neoteric class of solvents with diverse and well-documented applications.¹ Much of the interest in ILs originated from their potential as environmentally affable alternatives to volatile organic compounds, and as a result, they have been employed extensively as green media for synthesis and liquid–liquid extractions.^{1–4} However, these materials have also led to improvements in chemical processes not well-suited for traditional molecular solvents. Indeed, ILs have been employed successfully as gas storage fluids and battery electrolytes, for the processing and analysis of polymers, and even as lubricants and fuels, to mention just a few examples.^{1,5–11} This versatility is not surprising, because the physical and chemical properties of these materials can be fine-tuned through judicious selection of their cation and anion moieties. Consequently, ILs can be made compatible with a wide range of materials, including ionic, polar, and nonpolar compounds, and are thus considered by many as designer media.

In most applications, ILs are employed together with or in the presence of other solvents which can significantly affect their properties. Of particular interest are the effects of water, because virtually all ILs are hygroscopic and thus absorb atmospheric moisture readily.^{12,13} Numerous studies on IL/H₂O systems have shown that hydrophilic and hydrophobic ILs behave similarly in the presence of water, although the latter often reach a saturation point at which phase separation occurs.^{1,4,14–17} In general, hydrophobic regions tend to aggregate whereas charged moieties interact with water, with anions usually acting as hydrogen-bond acceptors and cations as donors

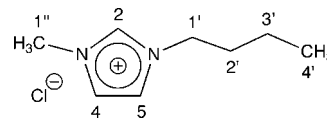


Figure 1. Structure and numbering of [C₄mim]Cl.

and becoming fully solvated at high dilution. Because of these interactions, water usually has deleterious effects on IL properties. For example, the presence of small amounts of moisture greatly reduces the solubility of cellulose in 1-*n*-butyl-3-methylimidazolium chloride ([C₄mim]Cl, Figure 1).⁵ On the other hand, and with counted exceptions,^{18,19} the effects of organic solvents on IL properties are not as extensively documented. Interestingly, some of these have been found to act as additives in IL-based processes, and this is best illustrated by results obtained for [C₄mim]Cl as well. As we have recently reported, dimethyl sulfoxide (DMSO) in concentrations of up to 15 wt% has no apparent effect on the ability of this IL to dissolve polysaccharide-rich biomass.^{8,9,20} However, the use of this cosolvent leads to substantial reductions in the viscosities of the mixtures and thus to improvements in parameters that are directly related to processing efficiency, including heat and mass transfer rates.^{1,21}

Taking into account just the two cases presented above, it is evident that gaining a detailed understanding of the behavior of IL-based binary mixtures as a function of the concentration of its components is critical for the development of new processes involving these materials. In this manuscript, we present a series of studies aimed at gathering this type of information for two such systems. Given its aforementioned potential for biomass processing, we concentrated our attention on binary mixtures of [C₄mim]Cl with either water or DMSO.

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TABLE 1: Details of the System Configurations Employed in the MD Simulations of [C₄mim]Cl/H₂O and [C₄mim]Cl/DMSO Solutions^a

[C ₄ mim]Cl/H ₂ O					[C ₄ mim]Cl/DMSO				
[H ₂ O]	<i>n</i> _{H₂O}	<i>n</i> _{[C₄mim]Cl}	χ_{IL}	<i>l</i>	[DMSO]	<i>n</i> _{DMSO}	<i>n</i> _{[C₄mim]Cl}	χ_{IL}	<i>l</i>
1.0	20	214	0.910	38.7	1.0	6	213	0.978	38.7
9.4	200	196	0.498	38.5	30.9	144	144	0.500	38.0
25.0	530	163	0.236	38.3	50.0	228	102	0.309	37.7
50.0	1080	108	0.093	38.7	70.0	312	60	0.161	37.4
99.0	2130	3	0.001	40.2	98.0	426	3	0.009	37.1

^a [H₂O] and [DMSO] represent the wt% of each solvent in the systems, *n*_{H₂O}, *n*_{DMSO}, and *n*_{[C₄mim]Cl} indicate, respectively, the number of water and DMSO molecules and [C₄mim]Cl ion pairs present in the simulation boxes, χ_{IL} is the [C₄mim]Cl mole fraction, and *l* corresponds to the size of the simulation boxes in angstrom.

The entire concentration range of the IL in each solvent was probed by analyzing ¹H and ^{35/37}Cl NMR chemical shift perturbations ($\Delta\delta$ s), and the results from these studies were corroborated and explained in atomic detail using molecular dynamics (MD) simulations on representative IL/solvent systems. Our findings show that although there is aggregation of the *n*-butyl chains in aqueous environments at high concentrations of [C₄mim]Cl, the IL behaves as a typical electrolyte in water with both ions completely solvated when diluted. Conversely, the data reveal that the interactions between the [C₄mim]⁺ and Cl⁻ ions strengthen as the solvent content increases in DMSO solutions, with IL-rich clusters persisting even at low salt concentration. As discussed herein, these results help explain the effects that these two solvents have on some of the macroscopic properties of [C₄mim]Cl.

2. Materials and Methods

2.1. NMR Experiments. The [C₄mim]Cl employed in the studies was prepared by following previously reported procedures and stored in vacuo prior to use.¹² The solutions were made by vortexing the appropriate weighed amounts of [C₄mim]Cl and either deionized H₂O or anhydrous DMSO in a capped vial for 2–5 min until a homogeneous mixture was obtained. The resulting solutions were then transferred to 5 mm NMR tubes, and these were subsequently fitted with 60 μ L coaxial inserts containing 0.5 M sodium 3-(trimethylsilyl)propionate-2,2,3,3-*d*₄ (TSP) and 0.5 M NaCl, used respectively as ¹H and ^{35/37}Cl references, in D₂O, which was required for field-frequency lock. Spectra were collected with standard one-dimensional acquisition sequences by using a 30° read pulse for ¹H and a 90°–90°–90° ARING pulse train to reduce acoustic ringing artifacts in ^{35/37}Cl measurements.²² Although the nominal concentrations of the solutions were in all cases within 1% from those determined by judicious integration of the IL and H₂O or DMSO signals, the latter values were used in all plots and analyses. All measurements were carried out at 60 °C on a Bruker AVANCE 400 MHz NMR with a 5 mm BBO probe operating at ¹H, ³⁵Cl, and ³⁷Cl frequencies of 400.13, 39.21, and 32.64 MHz, respectively.

2.2. Simulation Details. All MD simulations were performed by employing the CM3D software package and the OPLS-AA force field with optimized van der Waals parameters for the chloride ion described earlier.^{23–25} The modified SPC water model of Ahlborn and co-workers was used for all simulations of aqueous systems.²⁶ Partial charges for DMSO and [C₄mim]Cl were computed from fits to the electrostatic potential derived from ab initio calculations at the B3LYP/6-311+G* level of theory by using Gaussian 03.²⁷ The initial configurations of all systems were obtained from previously equilibrated [C₄mim]Cl simulation boxes.²⁵ The IL/solvent mixtures were created by

replacing sufficient [C₄mim]Cl ion pairs with H₂O or DMSO molecules to obtain the desired concentrations in a manner leading to an even distribution of IL and solvent molecules throughout the simulation box. In the case of [C₄mim]Cl/H₂O solutions, 10 H₂O molecules were used to replace each [C₄mim]Cl ion pair removed from the systems, whereas only two DMSO molecules were used per ion pair for [C₄mim]Cl/DMSO solutions. The configurations of all systems and their corresponding concentrations are summarized in Table 1. All simulations were carried out at the temperature employed in the NMR studies (363.15 K). Periodic boundary conditions were employed by using the Ewald method to treat long-range electrostatic interactions.^{28,29} The reversible reference system propagator algorithm (r-RESPA) with time steps of 0.5 and 2 fs was employed to evaluate short-range intramolecular forces and long-range interactions, respectively.³⁰ Each system was first equilibrated in the canonical ensemble (NVT) for 1 ns, followed by a 1–2 ns period in the isothermal–isobaric ensemble (NPT), in which the density of the system stabilized within 10% of the experimental value. Given the long equilibration times required to overcome the slow dynamics of ILs,³¹ the systems were equilibrated for an additional 5 ns period in the NVT ensemble. This was followed by 5 ns production runs carried out under the same conditions as those that were used for the analyses discussed below.

3. Results and Discussion

3.1. NMR Studies of IL/H₂O and IL/DMSO Solutions. ¹H $\Delta\delta$ s for the C-2 and C-4' protons of the [C₄mim]⁺ cation as a function of water concentration are shown in Figure 2. Although data for all ¹H nuclei of the IL were determined (see Supporting Information), these two protons are the most informative regarding the environment of the positively charged imidazolium ring and hydrophobic tail of the cation. Because the C-2 proton is the most acidic proton on the imidazolium ring and forms the strongest hydrogen bonds with the Cl⁻ ion,^{32–34} its chemical shift is the most affected by variations in the water content of the binary mixture. This is clearly depicted by the large negative $\Delta\delta$ observed for this proton, which is consistent with increased shielding at this position due to exchange of Cl⁻ ions for H₂O molecules around the five-membered ring. In agreement with the fact that the C-4 and C-5 protons form weaker hydrogen bonds with the anion,^{32–34} a similar but lesser effect is observed for these nuclei. Protons on positions C-1'' and C-1', both contiguous to the imidazolium ring nitrogens, exhibit small $\Delta\delta$ s upon addition of water, shifting upfield less than 0.3 ppm over the whole concentration range. Although the $\Delta\delta$ s for protons on the C2'–C4' fragment indicate deshielding at high dilution, these positions exhibit an increase in shielding up to H₂O concentrations of 20 wt%, which is consistent with packing of

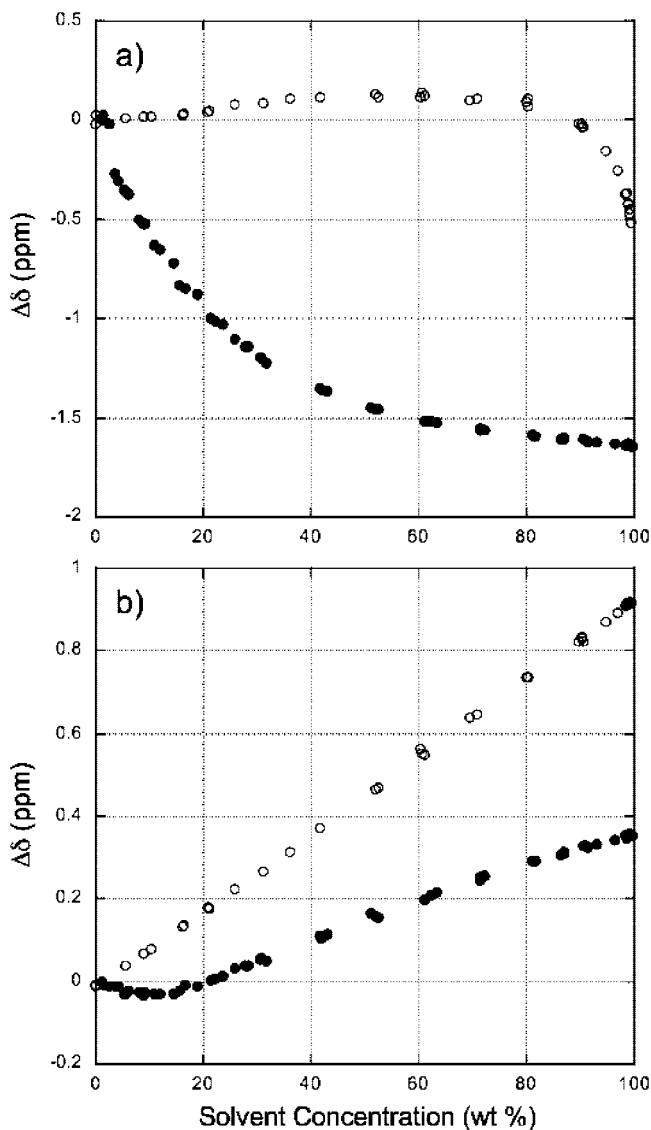


Figure 2. ¹H $\Delta\delta$ for the C-2 (a) and C-4' (b) protons relative to neat [C₄mim]Cl as a function of IL concentration in H₂O (solid circles) and DMSO (open circles).

the aliphatic chains. This suggests that the alkyl groups aggregate when water is initially introduced into the system but become gradually solvated as the IL content of the mixture decreases (vide infra). A comparison of the data obtained for the imidazolium protons and those on the *n*-butyl group also reflects that the positively charged ring is solvated prior to the alkyl chain. Indeed, the $\Delta\delta$ for the C-2 proton at H₂O concentrations as low as 5 wt% is larger than 0.3 ppm but is only 0.03 ppm for protons on C-4'. Similar conclusions regarding the solvation of imidazolium ILs by water have been obtained through measurement of intermolecular nuclear Overhauser effects (NOEs) and rotating frame NOEs on aqueous [C₄mim]BF₄ solutions.³⁵

The results for [C₄mim]Cl/DMSO systems present an interesting contrast to those obtained in aqueous environment (Figure 2). First, the $\Delta\delta$ for the C-2 proton in the most dilute [C₄mim]Cl/DMSO solution is \sim 1.1 ppm smaller than that observed for the corresponding aqueous system, and similar trends are observed for the C-4 and C-5 protons. These results suggest that the imidazolium ring is not as strongly solvated in DMSO as it is in water and are in agreement with the lower hydrogen bond acceptor ability of this organic solvent.³⁶ In addition, DMSO

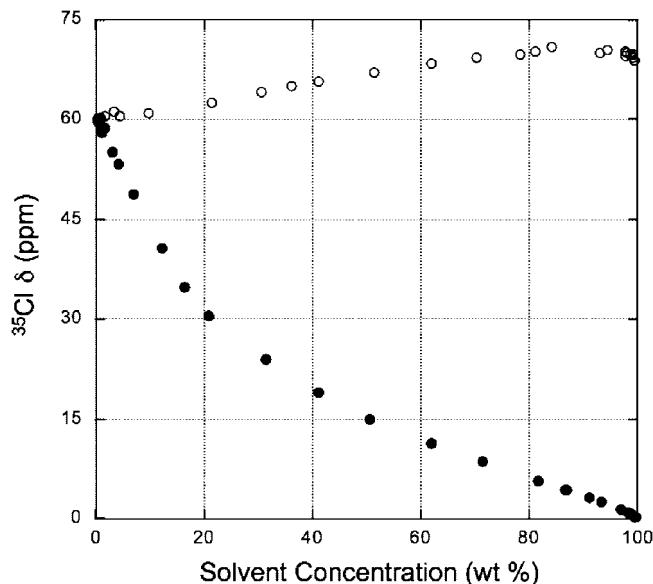


Figure 3. ³⁵Cl δ for the [C₄mim]Cl chloride ion as a function of IL concentration in H₂O (solid circles) and DMSO (open circles).

lacks a hydrogen-bond donor, which would be required to solvate the Cl⁻ ions, making it less likely for this solvent to disrupt interionic hydrogen bonds. Conversely to what was observed for the imidazolium protons, the $\Delta\delta$ s for protons on the *n*-butyl chains are larger in water, being, for example, \sim 0.5 ppm larger for protons on the C-4' position. This indicates that the alkyl group becomes solvated long before the imidazolium ring in this medium. Furthermore, aggregation of the nonpolar chains does not appear to occur in [C₄mim]Cl/DMSO solutions, because there is merely a linear dependence of the C-4' proton chemical shifts with solvent content. Solvation of the ring does eventually occur, and this is depicted by the sharp drop in the chemical shift of the C-2, C-4, and C-5 protons seen at DMSO concentrations approaching 95 wt%.

The changes in the environment around the Cl⁻ ion as a function of IL concentration in both solvents were also examined, using for this purpose ^{35/37}Cl measurements (Figure 3). In the case of aqueous systems, the anion becomes increasingly shielded as the IL concentration drops. For the most dilute solution studied, the ^{35/37}Cl δ was within 0.2 ppm of that of a fully solvated Cl⁻ ion,³⁷ indicating clearly that water solvates the [C₄mim]Cl anion. This finding is also consistent with the previously suggested replacement of Cl⁻ ions around the imidazolium ring with H₂O molecules that occurs as the water content of the system increases. Analogous to what was observed for the imidazolium protons, the changes in ^{35/37}Cl δ in [C₄mim]Cl/DMSO systems were not only smaller in magnitude than those measured in aqueous systems but also indicate deshielding of the anion as the IL concentration decreases. This suggests a strengthening of the interionic interactions as the content of DMSO in the binary mixtures increases. Indeed, because of its lower hydrogen-bond acceptor ability and dielectric constant,³⁶ DMSO is unlikely to break and replace the hydrogen bonds between the imidazolium protons and the Cl⁻ ion. These observations are also, to some extent, consistent with results from NOE experiments which reveal that DMSO does not exchange with the anion around the imidazolium cation.³⁵ As was the case for the imidazolium ring, an increase in the ^{35/37}Cl shielding of the anion indicates that it also becomes solvated at DMSO concentrations above 95 wt%.

3.2. MD Simulations. In order to further explain the results from ¹H and ^{35/37}Cl chemical shift perturbation studies and

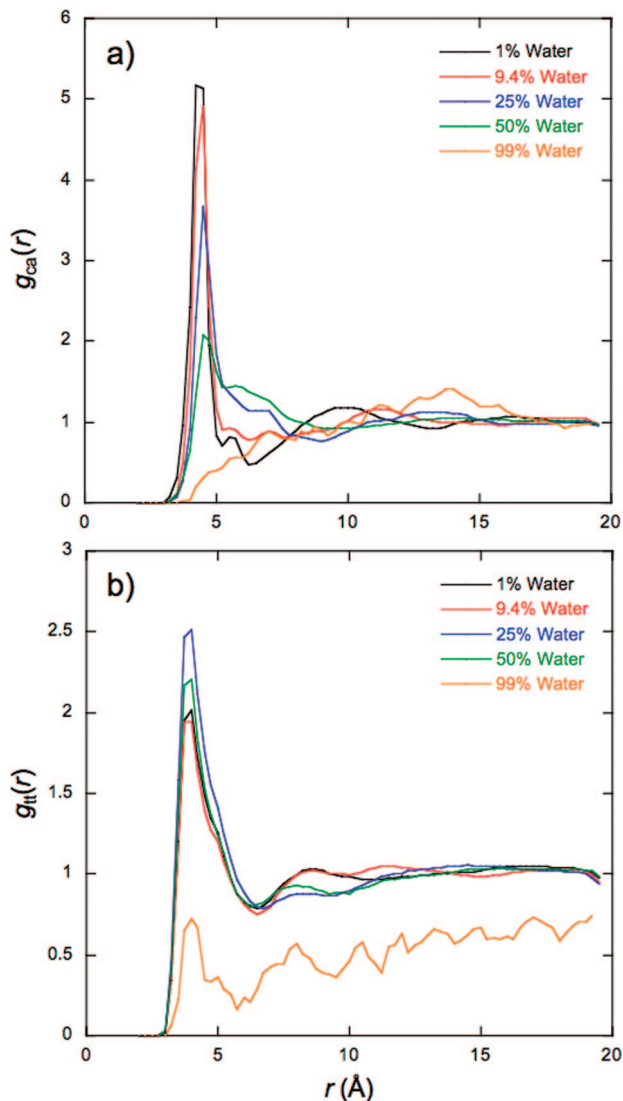


Figure 4. Cation–anion ($g_{ca}(r)$, a) and tail–tail ($g_{tt}(r)$, b) RDFs for all [C₄mim]Cl/H₂O systems considered in the studies.

corroborate our preliminary conclusions, MD simulations were carried out on a series of representative IL/solvent systems (Table 1). We concentrated initially on the analysis of radial distribution functions (RDFs) from the MD trajectories, as the information derived from these relates to ensemble averages that can be compared to experimental NMR data. Figure 4 shows the cation–anion and tail–tail RDFs for the [C₄mim]Cl/H₂O systems. In this and all other cases presented here, the center of mass of the imidazolium ring and the C-4' carbon were taken to represent the cation and tail sites, respectively. The first peak of the cation–anion RDFs, which corresponds to the first shell of chloride ions surrounding the cation, loses intensity and shifts to larger distances as the water content of the system increases until it becomes virtually undetectable (Figure 4a). As expected, these results indicate that interactions between cations and anions weaken as the IL is progressively diluted in water and are consistent with an exchange of Cl[−] ions for H₂O molecules around the imidazolium ring. On the other hand, the general shape of the tail–tail RDFs remains unchanged as the water content increases. However, the intensity of the first peak grows up to water concentrations of 25 wt%. This shows that the interactions between the *n*-butyl groups strengthen as water is introduced into the systems and is clearly indicative of aggregation of the hydrophobic tails. More importantly, the trends in

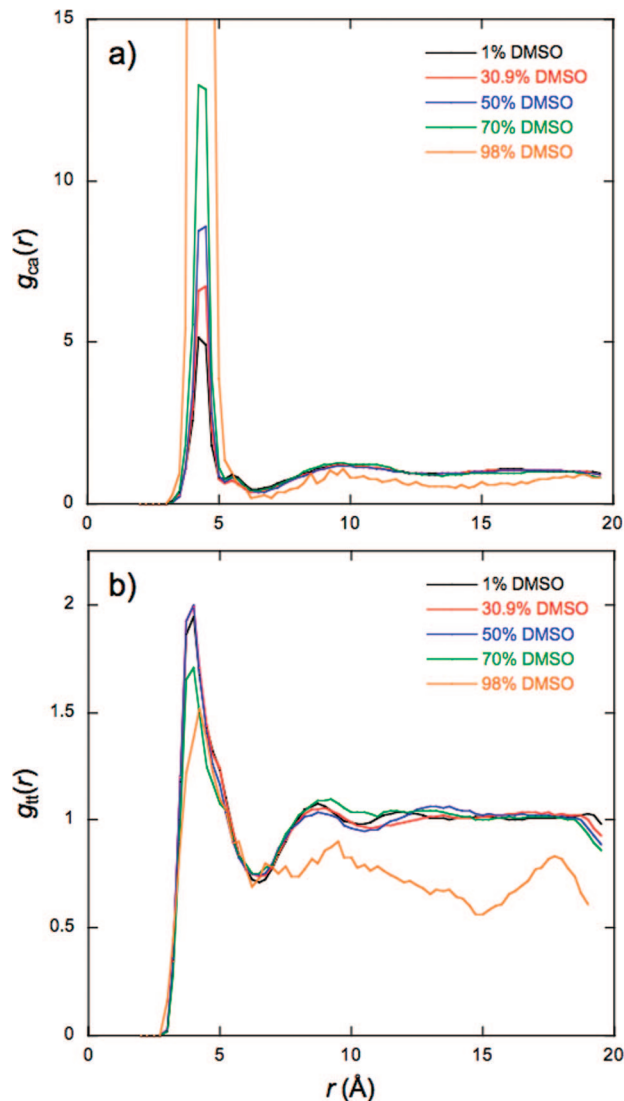


Figure 5. Cation–anion ($g_{ca}(r)$, a) and tail–tail ($g_{tt}(r)$, b) RDFs for all [C₄mim]Cl/DMSO systems considered in the studies.

the tail–tail RDFs correlate remarkably well with the trends in the $\Delta\delta$ s measured for the C-4' protons in aqueous solutions discussed earlier. Although aggregation of the alkyl groups is still evident at water concentrations of 50 wt%, the tail–tail interactions decrease considerably at high dilution as a result of the complete solvation of the imidazolium cation.

A similar RDF analysis was performed for the MD trajectories of the [C₄mim]Cl/DMSO systems, and the results are presented in Figure 5. A progressive growth of the first peak in the cation–anion RDFs as a function of the DMSO concentration can be clearly observed (Figure 5a). In agreement with our tentative interpretation of the ^{35/37}Cl δ data, this indicates that the interactions between the cationic and anionic IL moieties strengthen as the DMSO content of the systems increases. Opposite to what was observed in aqueous systems, the tail–tail RDFs exhibit only a gradual decrease in the intensity of the first peak with increasing DMSO content. These results are consistent with the solvation of the lipophilic chains and correlate well with our findings from ¹H chemical shift perturbation studies.

Three-dimensional (3D) probability density distributions of Cl[−] ions and solvent molecules around the [C₄mim]⁺ cation were computed to examine the average 3D structure and ordering of the different systems at the atomic level. Among

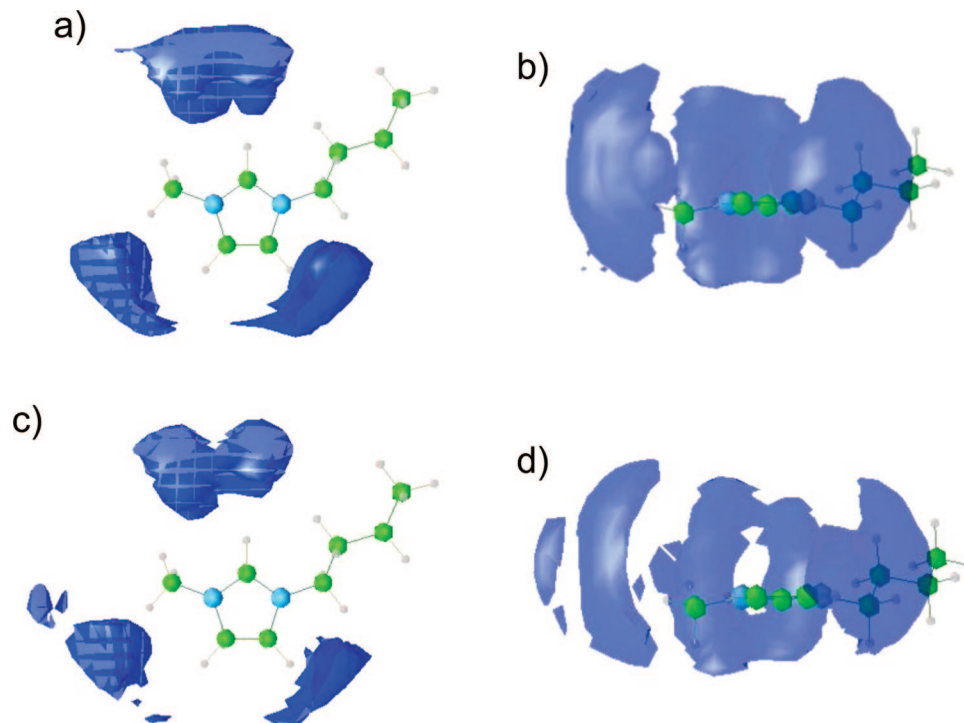


Figure 6. 3D probability distributions of Cl⁻ ions (a, top view and b, side view) and H₂O molecules (c, top view and d, side view) around the [C₄mim]⁺ ion computed for the 9.4 wt% H₂O solution. The isosurfaces are drawn at five times the average density of Cl⁻ or H₂O.

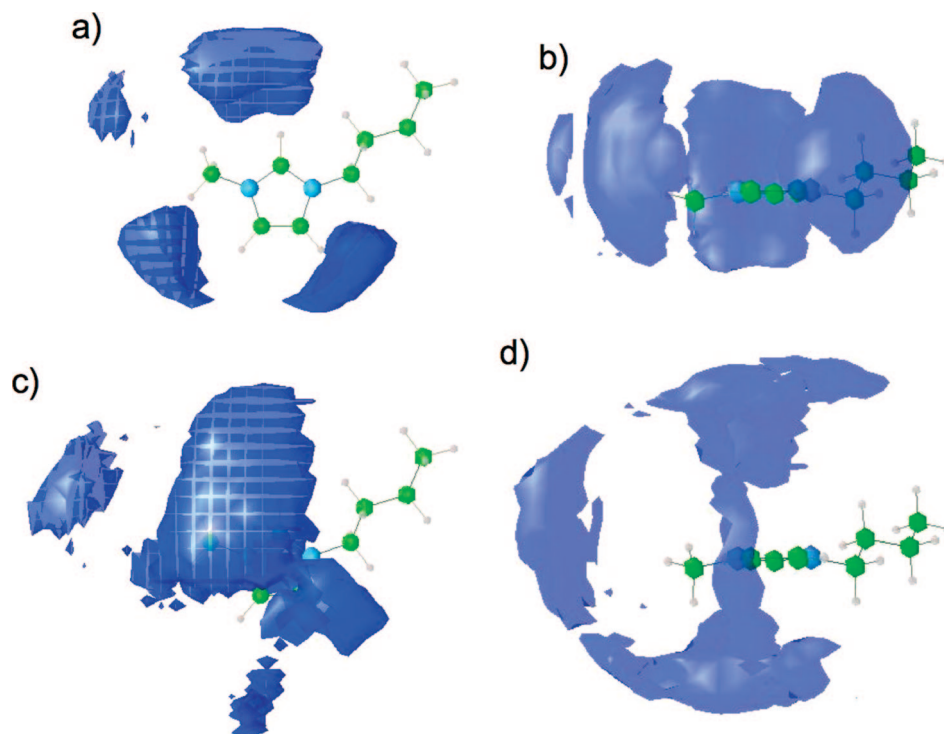


Figure 7. 3D probability distributions of Cl⁻ ions (a, top view and b, side view) and DMSO molecules (c, top view and d, side view) around the [C₄mim]⁺ ion computed for the 30.9 wt% DMSO solution. The isosurfaces are drawn at five times the average density of Cl⁻ and 2.25 times the average density of DMSO.

the different aqueous systems studied, there were only minor variations in the distributions of Cl⁻ ions and H₂O molecules around the cation obtained, and thus, only results for the solution containing 9.4 wt% water, shown in Figure 6, are discussed here. In agreement with findings from numerous experimental and theoretical studies,^{32–35,38–42} the high Cl⁻ ion density found around the imidazolium ring indicates the presence of hydrogen bonds between the anion and the C-2, C-4, and C-5 protons

(Figure 6a,b). In order for water molecules to exchange with the anions and interact with the cation, they would have to reside at virtually the same positions around the ring. Figure 6c,d clearly demonstrates that this is indeed the case, and further inspection reveals that the water oxygens are, as expected, within hydrogen-bonding distance from the imidazolium protons.

As was the case with the aqueous systems, the 3D distributions of Cl⁻ and DMSO molecules around the [C₄mim]⁺ cation

obtained for all [C₄mim]Cl/DMSO solutions were similar, and only results obtained for the 30.9 wt% DMSO system are discussed here. Figure 7a,b shows that the Cl⁻ ions interact with the cation through the formation of hydrogen bonds in a manner similar to that observed in aqueous media. Consistent with the stronger interionic interactions in this medium (vide supra), higher anion density can be found near the C-1'' position. On the other hand, there are marked differences with the aqueous systems regarding the distribution of solvent around the imidazolium cation (Figure 7c,d). It is clear that DMSO molecules do not replace the anions around the ring but instead occupy the space devoid of Cl⁻ ion density. This agrees with the analysis of the cation–anion RDFs presented above for these systems and further supports our earlier interpretation of the NMR data obtained for [C₄mim]Cl/DMSO solutions. Combined, these findings indicate that DMSO dissolves this IL by solvating ion pairs or clusters as opposed to isolated ions. Furthermore, the results suggest that these ion pairs or clusters persist in DMSO solution even at IL concentrations below 10 wt%.

4. Conclusions

The information detailed in this manuscript provides experimental and theoretical evidence regarding the effects of water and DMSO on the structure of [C₄mim]Cl at the atomic level. Our data reveal that water solvates the Cl⁻ ion and the imidazolium ring of the cation prior to solvating the *n*-butyl tails. Indeed, these hydrophobic groups were found to aggregate up to water concentrations of 20–25 wt%. Furthermore, the exchange of Cl⁻ ions by H₂O molecules suggested by the NMR data was readily observed upon inspection of the MD trajectories. On the other hand, the interactions between ions appear to strengthen in the presence of DMSO. As a matter of fact, our results show that this solvent is unable to effectively disrupt the interactions between ions and indicate that ion pairs or clusters exist in this environment even at low concentrations of the IL.

As proposed earlier, these results shed light on the effects that water and DMSO have on the solvent properties of [C₄mim]Cl. The fact that both ions become rapidly solvated in the presence of low amounts of water explains why this and other polysaccharide-dissolving ILs, all of which owe their potential as carbohydrate solvents to the presence of nonhydrated, noncoordinating anions in high concentration, are adversely affected by residual moisture. In the case of DMSO, the persistence of IL-rich clusters at low salt concentrations agrees with earlier findings indicating that this solvent has negligible effects on the dissolution of polysaccharides by [C₄mim]Cl. Although additional studies will be required to corroborate them, our results are likely representative of the effects of polar protic and polar aprotic solvents on imidazolium ILs. The approach applied here to the [C₄mim]Cl/H₂O and [C₄mim]Cl/DMSO systems could be employed to investigate the validity of this hypothesis, as well as to predict how different solvents and solutes modulate the macroscopic properties of other relevant ILs. Work in these areas is underway and will be reported in due course.

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Supporting Information Available: Complete ¹H and ^{35/37}Cl NMR chemical shift data as a function of solvent concentration for IL/H₂O and IL/DMSO solutions and partial charges used in the MD simulations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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