Deep eutectic solvents: A structural point of view on the role of the cation

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HIGHLIGHTS

- The structural properties of two DESs, namely reline and UBTMAC, have been studied.
- The effect of the different cations on reline and UBTMAC structure was highlighted.
- Strong chloride-urea hydrogen bonds are found in both DES systems.
- The hydroxyl group on the cation strongly affects the DES hydrogen bond network.
- Different cations induce different 3D arrangements of all DES constituents.

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ABSTRACT

The structural properties of two different deep eutectic solvents (DESs), namely a 1:2 mixture of choline chloride and urea and a 1:2 mixture of butyltrimethylammonium chloride and urea, have been investigated by means of Molecular Dynamics simulations. The presence or not of a hydroxyl group on the organic cation has been found to strongly affect the DES hydrogen bond network, giving rise to a different three dimensional arrangement of all the species present in the mixtures. These findings can have important implications in the future development of DESs for specific applications.

1. Introduction

In the past decade, a new generation of designer solvents has emerged as promising green media for multiple applications: the deep eutectic solvents (DESs) [1]. Fundamentally, the term "eutectic" is used to describe a mixture of two or more compounds that, at a well-defined composition, displays a unique and minimum melting point in the phase diagram. In particular, DESs consist of a mixture of a salt and one or more hydrogen bond donors, having a melting point significantly lower than that of each individual component. The term DES was coined in 2003, when Abbott and co-workers first reported that by mixing choline chloride and urea at a ratio of 1:2, both solid starting materials with high melting points, an eutectic mixture (called reline) was formed with a melting point of 12 °C [1]. Thereby, many kinds of DESs have been reported, composed mostly of substituted ammonium salts and uncharged hydrogen bond donors, such as amines, amides, carboxylic acids, and alcohols [2,3]. DESs show interesting properties similar to those of ionic liquids (ILs), including negligible volatility, high conductivity, non-flammability. It is well known that even if ILs received tremendous attention in the literature due to their peculiar characteristics and many potential uses [4–10], commercial scale applications of ILs are limited by the high synthesis cost. On the other hand, DESs show many advantages over ILs, as they are less expensive, more synthetically accessible, nontoxic, and biodegradable. Furthermore, common components of DESs are naturally occurring biocompatible compounds that are not hazardous if they are released back into nature. Due to their exceptional properties, DESs can be used in many applications such as in electrochemistry, catalysis, polymer synthesis, purifications, extraction processes [11]. Another interesting application is the practical use of enzymes in these solvents, as many enzymes exhibit both high activity and unexpected promising stability in DESs [12]. Moreover, DESs can dissolve a wide range of solutes including metal oxides that are insoluble in most molecular solvents and are generally only soluble in aqueous acid or alkali [13]. The dissolution of metal oxides is essential in several processes such as metal extraction, waste recycling, and catalyst preparation.

A growing body of theoretical and experimental research is attempting to understand the molecular keys that unlock the deep eutectic behavior. Molecular Dynamics (MD) simulations and IR measurements of reline have been performed at different temperatures and, based on the theoretical and experimental results, a strong interaction between the $-NH_2$ group of urea and the chloride ion has been

suggested [14]. On the other hand, an ab initio study by Ashworth et al. explored the many possible hydrogen bonding interactions among reline constituents showing evidence for a tripodal CH···Cl doubly ionic hydrogen bond motif [15]. In a MD investigation of mixtures of choline chloride and urea with different urea concentrations, the insertion of urea molecules was found to disrupt the long-range ordered structure of choline chloride [16]. The effect of water on DES characteristics has been also investigated by combining MD and densities, viscosities and conductivities measurements of choline chloride/urea aqueous solutions, showing that in the presence of water the anion is preferentially hydrated as compared to urea or the cation [17].

Abbot et al. stated that the melting point depression upon mixing choline chloride with hydrogen bond donors rises from the interaction between the hydrogen bond donor molecules and the chloride ion, with additional effects such as cation molecular symmetry [1]. The key physical driving force for the formation of DESs has been also related to the charge delocalization process resulting from the intermolecular hydrogen bonding [18–20]. This view has been disputed by Zahn and co-workers, whose ab initio MD simulations of DES systems show negligible charge transfer from the chloride ion to the hydrogen bond donor molecule [21]. On the other hand, using DFT calculations Garcia et al. showed that there is a linear relationship between the melting temperatures and the change in electron density at the cage critical points of the hydrogen bond networks in cholinium-based DESs [22].

It is clear that even if research on DESs has made great progress, our understanding of their properties is at an early stage, especially of the very large depression of melting points, and a complete knowledge of their microstructures is still lacking. In this work, we use the MD technique, which has been profitably employed to characterize the structure of many liquid systems [23–32], to explore the interactions in DESs in order to gain a more thorough understanding of their behavior. In particular, we investigate and compare the structural properties of the most studied DES, namely reline, with the analogous DES composed of a different cation, namely butyltrimethylammonium (BTMA). The molecular structures of choline and BMTA differ for the presence of a hydroxyl group on the choline cation instead of an unsubstituted alkyl chain, and their simultaneous study will allow us to assess the effects on DES properties of the hydrogen bonds formed by the cation. This is a very important aspect that deserves further studies as also suggested by two recent neutron scattering investigations on reline showing that the choline hydroxyl group plays an important role in the DES hydrogen bond network [33,34].

2. Molecular dynamics details

MD simulations of reline and of a mixture composed of BTMA chloride and urea at a ratio of 1:2 (hereafter called UBTMAC) were carried out using the GROMACS software package [35]. The force field used in the simulations were taken from Canongia Lopes and Padua and from OPLS. In particular, the force field parameters of BTMA, cholinium, chloride ions and urea can be found in Refs. [36, 37, 38 and 39], respectively. Note that the Lopes-Padua force field is the most widely used force field in MD simulations of ILs and has been built on the OPLS one. The two systems were composed of 350 salt and 700 urea molecules placed in a cubic box. The simulations were performed in the NVT ensemble at 300 and 343 K for reline and UBTMAC, respectively, using the Nosé-Hoover thermostat [40] with a relaxation constant of 0.5 ps and a timestep of 1 fs. Note that different simulation temperatures have been chosen based on the different melting points of the two DESs: the melting point of UBTMAC is 55 °C and we have simulated both mixtures 15 °C above the melting points in order to properly compare the system properties. Initial configurations were obtained by generating a low density cubic box that was then compressed in the NPT ensemble in order to match the experimental densities of the mixtures at the simulation temperatures (1.197 and 1.070 g cm^{-3} with a final box edge of 50.15 and 52.85 Å for reline and UBTMAC, respectively). The

systems were then equilibrated in the NVT ensemble at 500 K for 20 ns, followed by a final NVT equilibration at the simulation temperature of 10 ns. The final production time in the NVT ensemble was of 100 ns, in which the configurations were saved every 100 timesteps. Intermolecular interactions were evaluated explicitly inside a 12 Å cutoff, while electrostatic long-range effects were treated with the Particle Mesh Ewald method.[41] All stretching vibrations involving hydrogen atoms were constrained by means of the LINCS algorithm. In order to check if the force fields used in the simulations are able to reproduce the experimental densities of the systems at the simulation temperatures, we have also carried out two MD simulations of reline and UBTMAC in the NPT ensemble using the Parrinello-Rahman barostat (5 ns long, P = 1 atm, T = 300 and 343 K for reline and UBTMAC, respectively) and we have calculated the average densities of the systems from these new simulations. The calculated average density values are 1.156 and 1.076 g cm^{-3} for reline and UBTMAC, respectively. These values are in good agreement with the experimental densities (percentage differences of 3.4% and 0.5% for reline and UBTMAC, respectively).

3. Results

To develop new understanding of DES behavior, we have carried out MD simulations of two DES systems containing different cations, namely reline and UBTMAC, and we have analyzed and compared their structural properties. Hammond and co-workers recently performed wide Q-range neutron diffraction measurements of reline isotopically-substituted samples and by interpreting the experimental data with the empirical potential structure refinement (EPSR) technique, they determined the reline liquid structure [33]. In the first step of this investigation we have checked the capability of the force fields to properly describe the reline system from a structural point of view by comparing our structural results with those of Hammond et al. To this end, we calculated the radial distribution functions g(r)'s of a selected subset of atoms from the MD trajectory, focusing on the interactions among different species present in the mixture, namely urea molecules, choline cations and chloride anions. We also computed a series of coordination numbers, N, by integration of the g(r)'s up to a cutoff, which has been chosen as the position of the first minimum of the corresponding g(r). The atom names used throughout the paper for the choline and BTMA cations and for the urea molecule are shown in
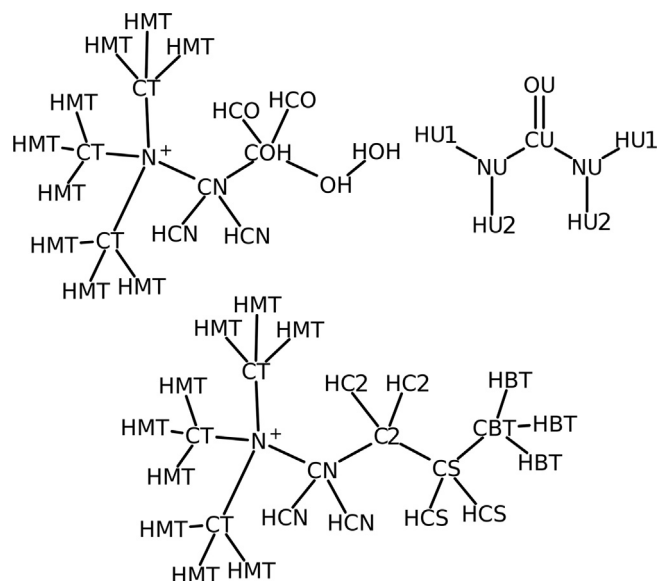

Fig. 1. Atom labeling used in this work for the choline cation (top left), urea molecule (top right) and BTMA cation (bottom).
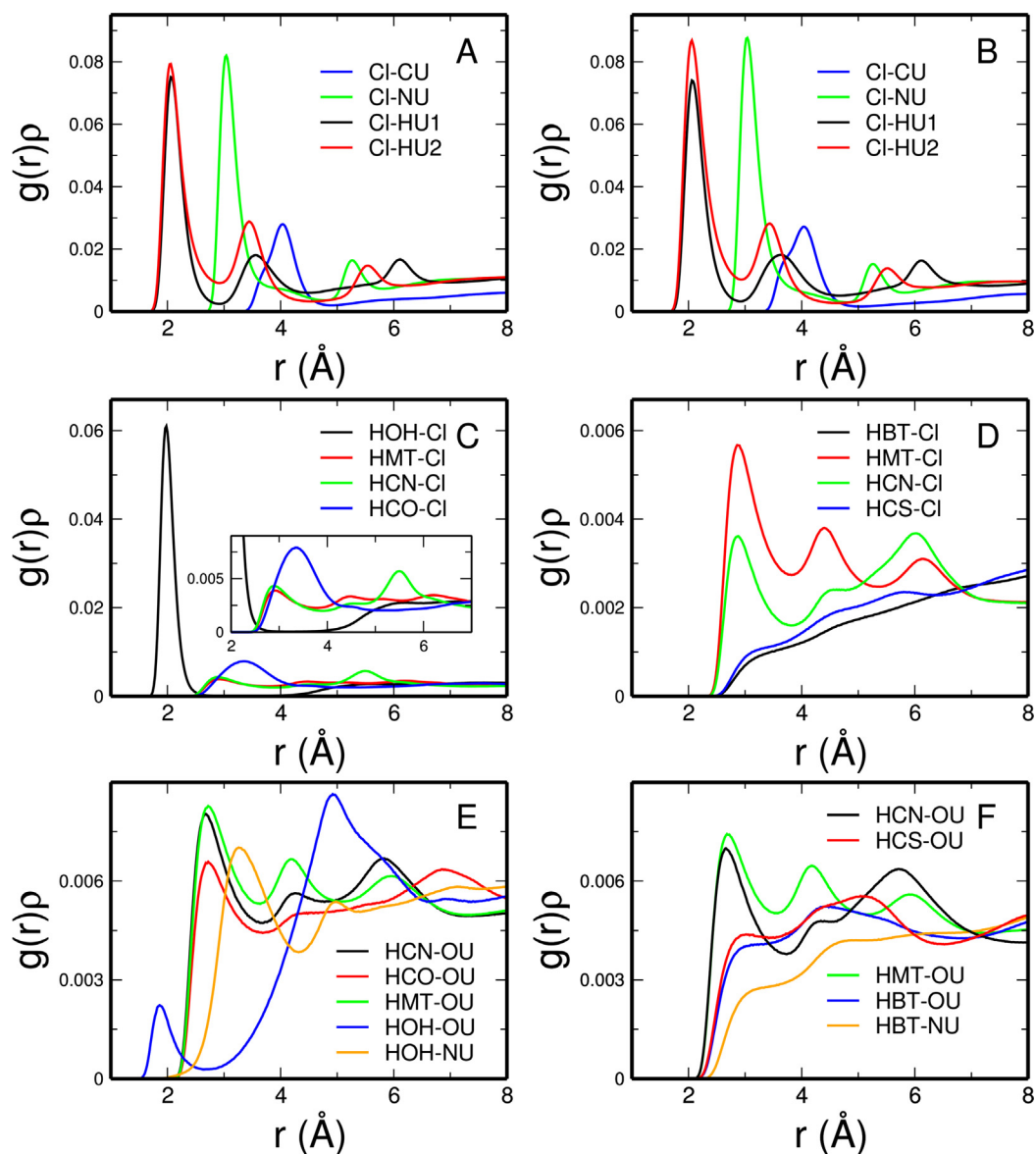
Fig. 2. Radial distribution functions multiplied by the numerical densities of the observed atoms, g(r)ρ's, calculated from the MD simulations of the reline (left panels) and UBTMAC (right panels) DESs for the chloride-urea (top), cation-chloride (middle) and cation-urea (bottom) interactions. Note that in the case of the cation-urea interactions the g(r)ρ functions involving the NU atoms have been divided by a factor of two for better visualization.

Fig. 1. The calculated g(r)'s are depicted in the left panels of Fig. 2 multiplied by the numerical density of the observed atoms (ρ). We have decided to show these functions to properly compare the reline and UBTMAC structural properties since the simple comparison of the g(r)'s can be misleading when treating systems with different densities, as already pointed out in the literature [42–46]. Several experimental and computational studies reported strong interactions between chloride and urea in the reline system [1,14,21,33], as also shown by the high intensity peaks of the chloride-urea g(r)ρ's calculated from our MD simulation (panel A of Fig. 2). On average each chloride is coordinated by 3.6 urea molecules (see the Cl-CU coordination number reported in Table 1): the interactions take place through the chloride ion forming hydrogen bonds with the urea hydrogen atoms and the Cl-HU1 and Cl-HU2 g(r)ρ's are similar, with a similar position of the first peak and a slight preference for the HU2 atom. This is in line with the results of a quantum mechanical MD study [47] and of a combined MD and IR investigation [14], while our results differ from those of Hammond and coworkers who found a preferential interaction with the HU1 atom [33]. Besides interacting with urea molecules, the chloride ion forms

strong hydrogen bonds with the hydroxyl group of the choline cation, as evidenced by the high intensity peak found in the HOH-Cl g(r)ρ (panel C of Fig. 2). On average 0.9 chloride ions are coordinated by each hydroxyl group of the choline cation. This result suggests that the hydrogen bond interaction present in the choline chloride crystal structure, where each chloride ion interacts with one hydroxyl group [48], is preserved also when the reline DES is formed. The g(r)ρ's between chloride and the other hydrogen atoms of choline are much less structured and the chloride interactions with the hydrogen atoms near the cationic core (HMT and HCN) are very similar. Conversely, the HCO-Cl g(r)ρ first peak is broader and more intense with a higher coordination number (1.9). However, this coordination number is not only due to specific interactions between HCO and the anion, but rather it originates from the chloride interactions with all of the other choline hydrogen atoms. The g(r)ρ's calculated for the choline-urea interactions are much less intense and more unstructured than both chloride-urea and choline-chloride g(r)ρ's (panel E of Fig. 2). Even if a low-distance peak is visible in the HOH-OU g(r)ρ, the calculated coordination number is negligible (0.1), meaning that the urea molecules do not form

Table 1
Structural parameters of the radial distribution functions g(r) calculated from the MD simulations of the reline and UBTMAC systems. R is the position of the g(r) first peak and N is the coordination number calculated by integration of the g(r) up to the cutoff distance. The cutoff distances used in the calculation of N are also reported. Note that peak positions larger than 8.00 Å have not been listed in the table.

g(r)	Atom A	Atom B	R (Å)	N	Cutoff (Å)
Reline system					
Chloride-Urea	Cl	CU	4.04[a]	3.6[a]	4.91
			(3.3–5.2)[b]	(3.76±2.27)[c]	
	Cl	NU	3.04[a]	5.6[a]	4.80
			(2.8–4.3)[b]	(4.10±2.63)[c]	
	Cl	HU1	2.06[a]	1.8[a]	2.94
			(1.7–3.1)[b]	(1.73±1.58)[c]	
	Cl	HU2	2.05[a]	2.4[a]	2.94
			(1.7–3.1)[b]	(1.25±1.15)[c]	
Choline-Chloride	HOH	Cl	1.98[a]	0.9[a]	3.24
			(1.6–3.4)[b]	(0.66±0.50)[c]	
	HMT	Cl	2.92[a]	0.4[a]	3.76
			(2.6–4.0)[b]	(0.70±0.66)[c]	
	HCN	Cl	2.90[a]	0.5[a]	3.90
			(2.6–4.2)[b]	(0.73±0.67)[c]	
	HCO	Cl	3.34[a]	1.9[a]	5.26
			(2.6–4.0)[b]	(0.70±0.66)[c]	
Choline-Urea	HCN	OU	2.68[a]	0.9[a]	3.68
			(2.2–3.5)[b]	(0.41±0.60[c])	
	HCO	OU	2.72[a]	0.8[a]	3.68
			(2.2–3.6)[b]	(0.45±0.64[c])	
	HMT	OU	2.72[a]	1.0[a]	3.64
			(2.2–3.4)[b]	(0.48±0.66[c])	
	HOH	OU	1.86[a]	0.1[a]	2.64
			(1.3–2.6)[b]	(0.16±0.38[c])	
	HOH	NU	3.26[a]	2.7[a]	4.32
			(1.8–4.2)[b]	(2.08±1.68[c])	
Urea-Chloride	CU	Cl	4.04	1.8	4.91
Choline-Chloride	CN	Cl	3.77	0.7	4.40
Choline-Urea	CN	CU	3.97	1.9	4.81
Choline-Choline	CN	CN	7.22	6.8	8.66
Urea-Urea	CU	CU	4.62	5.4	6.40
Chloride-Chloride	Cl	Cl	5.38	1.9	6.40
UBTMAC system					
Chloride-Urea	Cl	CU	4.04	4.0	5.06
	Cl	NU	3.04	5.9	4.80
	Cl	HU1	2.06	1.9	2.90
	Cl	HU2	2.06	2.7	2.92
BTMA-Chloride	HBT	Cl	–	–	–
	HMT	Cl	2.86	0.6	3.82
	HCN	Cl	2.88	0.4	3.82
	HCS	Cl	5.81	2.0	6.43
BTMA-Urea	HCN	OU	2.66	0.8	3.74
	HCS	OU	3.02	0.4	3.42
	HMT	OU	2.68	0.8	3.52
	HBT	OU	4.50	5.7	6.80
	HBT	NU	–	–	–
Urea-Chloride	CU	Cl	4.04	2.0	5.06
BTMA-Chloride	CN	Cl	3.80	0.5	4.36
BTMA-Urea	CN	CU	5.72	10.3	7.96
BTMA-BTMA	CN	CN	7.70	15.6	11.80
Urea-Urea	CU	CU	4.65	4.6	6.40
Chloride-Chloride	Cl	Cl	5.32	2.4	6.70

[a] This work.
[b] g(r) first peak range obtained in Ref. [33].
[c] Coordination numbers obtained in Ref. [33].

hydrogen bonds with the hydroxyl group of the choline cation, in agreement with the results of a previous ab initio MD simulation [49]. The urea oxygen atoms prefer to be located near the cationic core and to interact with all of the other choline hydrogen atoms, namely HCN, HCO and HMT, with a slight preference for the methyl groups.

In order to establish if the structural results obtained from our MD simulation of reline are reliable we have compared the g(r) structural parameters with those of Hammond et al. [33] (see Table 1). In general, the peak position and coordination numbers of our g(r)'s are in good agreement with the neutron diffraction results of Ref. [33]. Indeed, all the values are within the range reported by Hammond and co-workers with the only exception of the HCO-Cl coordination number that in our simulation is higher. However, as pointed out above, the high value we obtained is not due to specific interactions and therefore the disagreement could be ascribed to a larger orientational freedom of our choline cation as compared to the model of Hammond et al. From the overall good agreement found we can conclude that the force fields we used are able to provide a reliable description of the reline structure. To the best of our knowledge, an accurate determination of the UBTMAC liquid structural properties has not yet been carried out in the literature. However, since the force fields employed for UBTMAC and reline are part of the same generalized force field developed by Canongia Lopes and Padua, which is based on the OPLS one, we are confident in its ability to properly reproduce also the UBTMAC structural properties.

If we consider the melting points of choline chloride (302 °C) and BTMA chloride (220 °C) and the melting points of reline (12 °C) and UBTMAC (55 °C) we see that the depression of reline melting temperature is much larger than the UBTMAC one. This behavior suggests that the interactions in reline are much favored allowing it to be liquid also at ambient temperature at variance with UBTMAC which is solid. The comparison of the structural properties of the two systems can thus be useful to provide a deeper insight into the origin of the very large depression of melting points observed in DESs. Since the reline melting point depression has been ascribed to the interactions between the hydrogen bond donor and acceptor [1], one could suppose that these interactions are reduced in the UBTMAC system but our results show that this is not the case. Conversely, the chloride-urea g(r)ρ's calculated from our MD simulation of UBTMAC (panel B of Fig. 2) have a general trend similar to those calculated for reline but showing more intense first peaks and higher coordination numbers (see Table 1). Moreover, in this case the preference of chloride to form hydrogen bonds with the HU2 hydrogen atom is more pronounced as compared to the reline system. As one could expect, the biggest differences between the two DES systems are found in the interactions involving the cations and this is particularly true for the cation-chloride interactions (BTMA-chloride g(r)ρ's are reported in Panel D of Fig. 2). Due to the absence of the hydroxyl group in the BTMA cation, chloride prefers to interact with the cationic core. No peak at distances shorter than 5.00 Å is found in the g(r)ρ's of the hydrogen atoms belonging to the cation tail (HBT and HCS), while the HMT-Cl and HCN-Cl g(r)ρ's show a first peak at 2.86 and 2.88 Å with an average coordination number of 0.6 and 0.4, respectively, indicating a preference of chloride to be positioned near the methyl groups. The BTMA-urea g(r)ρ's depicted in panel F of Fig. 2 show a degree of structuring similar to the BTMA-chloride ones, at variance with the reline system where the cation-chloride functions were much more structured due to the presence of hydroxyl-chloride hydrogen bonds. In analogy with the behavior of the chloride ion, also in the case of urea the oxygen atom has a preference to interact with the BTMA cationic core: the favored interactions are the HCN-OU and HMT-OU ones while moving towards the end of the butyl chain the g(r)ρ functions become less and less intense.

In order to have a more global picture of the interactions taking place in DESs, we have calculated the molecularly centered g(r)ρ's among all of the species in the mixtures (panel A and B of Fig. 3 for reline and UBTMAC, respectively). Molecular centers are defined as the CU atom of urea and the CN atom of the cation. The structural parameters of all the molecularly centered g(r)'s are listed in Table 1. The strongest interaction found is that between urea molecules and chloride anions: the urea-chloride first shell distance is the same in both systems (4.04 Å) while a higher coordination number of chloride ions per urea molecule is found in UBTMAC (2.0) as compared to reline (1.8). Besides forming hydrogen bonds with chloride ions, urea molecules also form
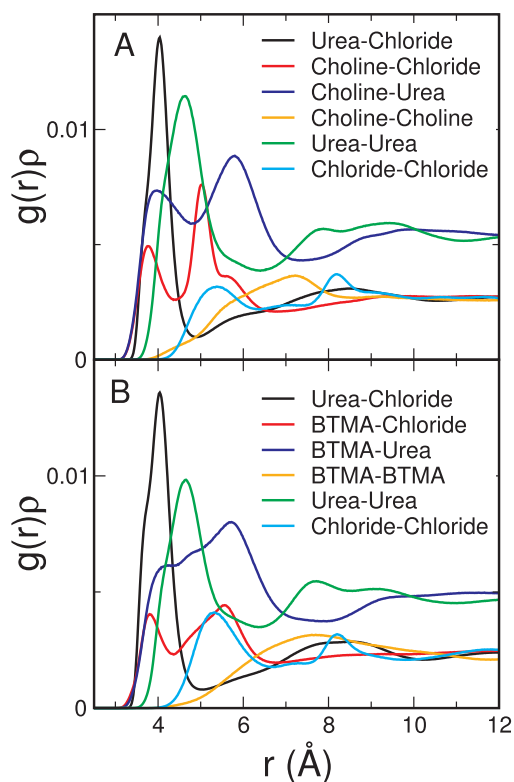
Fig. 3. Molecularly centered radial distribution functions multiplied by the numerical densities of the observed molecule, g(r)ρ's, calculated from the MD simulations of the reline (A) and UBTMAC (B) DESs. Molecular centers are defined as the CU atom of urea and the CN atom of the cation.

hydrogen bonds with other urea molecules and these interactions give rise to a sharp urea-urea g(r)ρ first peak with maximum position at 4.62 and 4.65 Å in reline and UBTMAC, respectively. The urea-urea co-ordination is more favored in reline as shown by the urea-urea co-ordination numbers which are 5.4 and 4.6 in reline and UBTMAC, respectively. Due to the more complex molecular structure of the cations as compared to urea, the g(r)ρ's involving cations show several low-distance peaks due to interactions with different cationic groups. As concerns the choline-chloride functions, the g(r)ρ's show two distinct peaks at 3.77 and 5.02 Å and an additional low intensity peak can be observed at about 5.70 Å. The first peak is due to chloride ions directly interacting with the HCN atoms, while the second peak to chloride ions interacting either with the hydroxyl group or with the cationic core via the methyl groups. The third peak can be instead ascribe to anions which interact with the cationic core but positioning themselves along the CN-N direction on the opposite side with respect to the hydroxyl group. Looking at the choline-urea g(r)ρ's we see that they are much broader than those involving chloride. As mentioned above, the urea molecules do not form hydrogen bonds with the hydroxyl group but rather interact with the methyl substituents on the ammonium nitrogen atoms: these contributions give rise to a broad peak at 5.80 Å, while urea molecules directly interacting with the HCN atoms bonded to CN generate the first peak with maximum position at 3.97 Å. Major differences between the reline and UBTMAC systems can be observed in the interactions involving the cations: the g(r)ρ functions of BTMA-chloride interactions are less structured as compared to the choline-chloride ones, and show two peaks at 3.80 and 5.56 Å due to chloride ions interacting with the HCN atoms and with the cationic core via the methyl groups, respectively. The BTMA-urea interactions are instead characterized by two shoulders at 4.28 and 4.82 Å and a broad peak at 5.72 Å as a result of diffuse interactions with the methyl groups bonded to the BTMA nitrogen atom and with the $-CH_2-$ groups of the butyl

chain. Finally, cations-cations and chloride-chloride g(r)ρ's have no short distance peaks (maximum positions below 5 Å) and exhibit very broad features indicating that ions with the same sign do not directly interact with each other but their interactions are rather mediated by the other species present in the mixtures. Previous studies on imidazolium-based ILs found pronounced oscillations in cation-anion distribution out of phase with weaker oscillations in the cation-cation one, showing a strong charge ordering whose effect extends at least two cation shells from a central imidazolium ring [7,50]. If we look at the general trend of the molecularly centered g(r)ρ's found for the DES systems investigated in this work we can conclude that while ILs have a structure of concentric solvation shells, in DESs the shell separation is not so neat and strong close-range interactions are found between both choline and urea with chloride, and between urea molecules, in agreement with previous results reported in the literature [33]. Therefore, while differentially charged solvation shells are found in ILs, in reline and UBTMAC a complex structure is formed, driven by hydrogen bond interactions.

Finally, the three-dimensional arrangement of the different species present in the DES mixtures can be obtained by looking at the spatial distribution functions (SDFs) calculated from the MD simulations. The upper panels of Fig. 4 displays the SDFs computed for chloride, urea and choline around the urea molecule in reline and UBTMAC (left and right panels, respectively). Note that these functions have been calculated in an internal reference system integral with the urea molecular
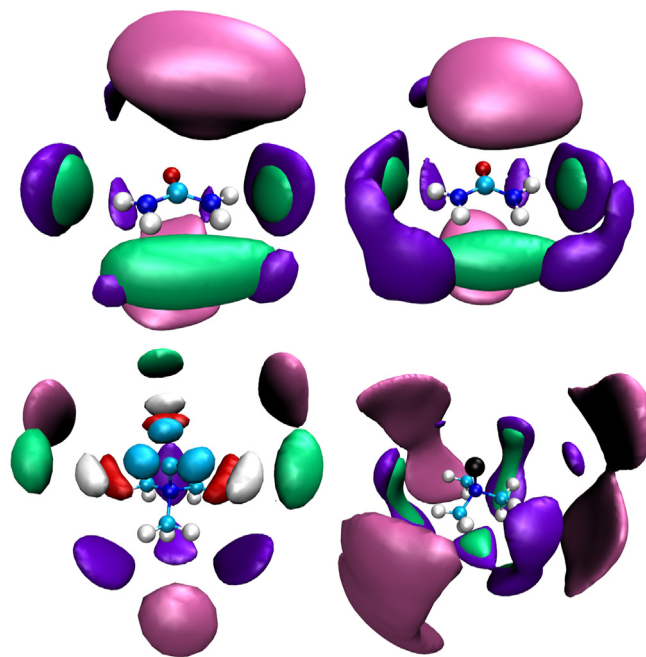

Fig. 4. Spatial distribution functions (SDFs) of the chloride anions (green surfaces), urea molecules (violet surfaces) and cations (mauve surfaces) around the urea molecule (top panels) and the cation (bottom panels) calculated from the MD simulations of the reline (left) and UBTMAC (right) systems. The carbon, nitrogen, hydrogen and oxygen atoms are colored cyan, blue, white and red, respectively. The 2-hydroxyethyl substituent of the choline cation is represented by intramolecular SDFs of the terminal carbon (cyan surface), oxygen (red surface) and hydrogen (white surface) atoms. The butyl chain of the BTMA cation is represented by a big black sphere. The isosurfaces have been drawn at the isovalues reported below in nm^{-3}. In the SDFs around the urea molecule: chloride (18.8 and 19.2 in reline and UBTMAC, respectively), urea (11.2 and 8.9 in reline and UBTMAC, respectively) and cations (6.3 and 6.2 in reline and UBTMAC, respectively). In the SDFs around the cations: chloride (13.5 and 9.1 in reline and UBTMAC, respectively), urea (14.4 and 12.2 in reline and UBTMAC, respectively) and cations (4.9 and 3.6 in reline and UBTMAC, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

plane and, in order to properly compare the results obtained for the two systems, SDFs with the same ratio density/maximum density have been shown. The favorite sites of interaction of the chloride ions are clearly the hydrogen atoms of the urea molecule and the high probability distributions obtained for reline and UBTMAC are very similar. The urea-urea interactions are also driven by hydrogen bonds: the distributions near the HU1 atoms are very similar to those of chloride, while in proximity of the HU2 atoms urea prefers to be located on the external side of the two NU-HU2 directions and not between them. Moreover, in the UBTMAC system these urea distributions are broader as compared to the reline ones, and extend towards the high-probability regions close to the HU1 atoms. Conversely, choline cations tend to occupy regions of space which are occupied neither by chloride nor by urea, namely above and belove the urea molecular plane, with very similar distributions in both DESs. Besides slight differences in the urea SDF, overall our results show that the three-dimensional arrangement of the different species around the urea molecule is similar in reline and UBTMAC. On the contrary, the spatial distributions around the choline and BTMA cations (lower left and right panels of Fig. 4, respectively) are very different in the two DESs. The SDFs have been calculated in both cases in an internal reference system integral with the tetrahedral structure of the quaternary nitrogen atom. However, in order to properly identify the most relevant interactions, in the case of choline we have also computed in the same reference system the intramolecular SDFs of the hydroxy-substituted carbon atom and of the oxygen and hydrogen atoms of the hydroxyl group. The results clearly show the orientation of the hydroxyl group in the three most probable rotamers of the cation. Three well defined high-probability spots for the chloride SDFs are found along the direction of the hydroxyl group, confirming the strong hydrogen bonding between choline and chloride. Due to the absence of the hydroxyl, in the UBTMAC system the chloride ions do not interact with the BTMA cation tail, but prefer to position themselves close to the methyl and $-CH_2-$ groups bonded to the nitrogen atom. In particular, three distributions of chloride ions extend parallel to the N-CN direction and an additional spot is also found along the N-CN direction on the opposite side with respect to the butyl chain. The SDFs of urea around choline show that, at variance with chloride, urea prefers to interact with the cationic core, in three high probability regions positioned between the three N-CT directions and along the N-CN direction opposed to the hydroxyl group. Also in the case of the UBTMAC system the urea molecules tend to interact with the cationic core but with a different spatial distribution which perfectly mimics the chloride one. Moreover, the cation SDFs show that cations tend to fill spaces not occupied by the chloride ions, generating different cation distributions around choline and BTMA whose shape resembles the anion distributions but at longer distances.

All together, our results show that the presence of a hydroxyl group on the cation which allows the formation of strong cation-anion hydrogen bonds gives rise to a different three-dimensional arrangement of all DES constituents. This effect that at a local level can be clearly observed from the SDFs generates a different motif of cage-like structures extending throughout the liquid. It is important to stress that besides the structural arrangements obtained from the SDF analysis, the reline and UBTMAC DESs sample many different structural configurations, due to the high disorder of these systems. While forming specific local structures DESs tend to maximize their hydrogen bond and Coulombic interactions reaching a delicate balance of forces which prevents the crystallization.

4. Conclusions

Here, we present a structural characterization of two DES systems having different organic cations, namely reline and UBTMAC, carried out by means of the MD technique. The structural results obtained for reline have been compared with the results of a recent neutron diffraction and EPSR modelling study [33] and the good agreement found

allowed us to assess the ability of the force fields used in the simulations to properly reproduce the DES structural properties. Since the depression in melting points as compared to pure substances is larger in reline than in UBTMAC, the interactions in reline seem to be more favorite and the comparison of the two DES structures allowed us to shed light on important differences that can be crucial to determine the different DES behavior. Strong hydrogen bond interactions between chloride ions and urea molecules are found in both systems and our results show that these interactions are even more favorite in UBTMAC, suggesting that the formation of anion-urea hydrogen bonds cannot be the only factor at the origin of the large melting point depression observed in DESs. The presence or not of a hydroxyl group on the organic cation seems to have an important role in the DES behavior. The choline-chloride hydrogen bonds via the hydroxyl group are largely retained when the reline DES is formed, and the establishment of these interactions gives rise to a three-dimensional arrangement of all the species in the mixture which is very different from that found in UBTMAC, where the cation is not able to form such hydrogen bonds due to the lack of the hydroxyl group. At variance with traditional molecular solvents which typically have a homogeneous hydrogen bond character, in DESs a variety of different hydrogen bonds exists and the system packs in a manner to maximize its hydrogen bond network between the different moieties. Therefore, a complex network of interactions is formed resulting from the delicate balance among all of the different forces into play. Our results show that the change of even a small part of one of the constituents alters this balance by forming a different supramolecular cage-like structure with different melting points and a different depression in melting points as compared to pure substances. These findings can help in the rationalization of DES behavior based on the structure at a molecular level, which is a key step to design DES systems for specific applications.

conflict of interest

The authors declare no conflict of interest.

Acknowledgments

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