SOFT MATTER

INTERACTION OF DIMETHYLIMIDAZOLIUM CHLORIDE WITH WATER MOLECULE AT $T = 400$ K

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The work presents data on the structure and the energy characteristics in the case of the interaction of a water molecule with dimethylimidazolium chloride $(dmim^+/CL^-)$ at the temperature $T = 400$ K calculated using the molecular dynamics method. We established the existence of hydrogen bonds between a water molecule and molecules of dimethylimidazolium $(dmim^+)$ and chlorine (CL^-) and determined the orientation position of the water molecule with respect to those of chlorine and dimethylimidazolium.

1. Introduction

Recently, the more and more attention is paid to the investigation of properties of ionic liquids consisting of large organic anions and small inorganic cations. Such ionic liquids are of great practical importance for the chemical industry and other fields of national economies [1, 2]. At room temperature, such solvents have a high application potential determined by an extremely low evaporation pressure and the possibility of reprocessing after their use in organic reactions. These unusual physical-chemical properties of ionic liquids determine the great interest to these objects.

One of the simplest representatives of the class of ionic liquids is dimethylimidazolium chloride $dmim^+/CL^-$. The general form of the molecule of dimethylimidazolium $(dmim^+)$ cation is given in Fig. 1.

This work presents the results of calculations of the radial distribution functions (RDFs) for an ionic liquid consisting of relatively large dimethylimidazolium cations $(dmim^+)$, anions (CL^-), and water performed with the use of the free energy perturbation method.

2. Model and Calculations

Investigating the properties of the three-component liquid system "dimethylimidazolium chloride $dmim^+/CL^-$ – solvent", we used various types of potentials for the description of intermolecular interactions. For example, the "ionic liquid – ionic liquid" interaction was described with the help of the Buckingham potentials obtained in [4–6]. Table 1 presents the values of charges and Lennard-Jones parameters for a dimethylimidazolium cation, chlorine anion, and water molecule.

The intermolecular interaction "ionic liquid – water" was described with the use of the potentials for water given in [7]. According to this model, each hydrogen atom of the system has the positive charge $+q$, whereas the negative charge $+2q$ is located on the bisector of two OH bonds, whose length equals 0.945 Å, while the angle
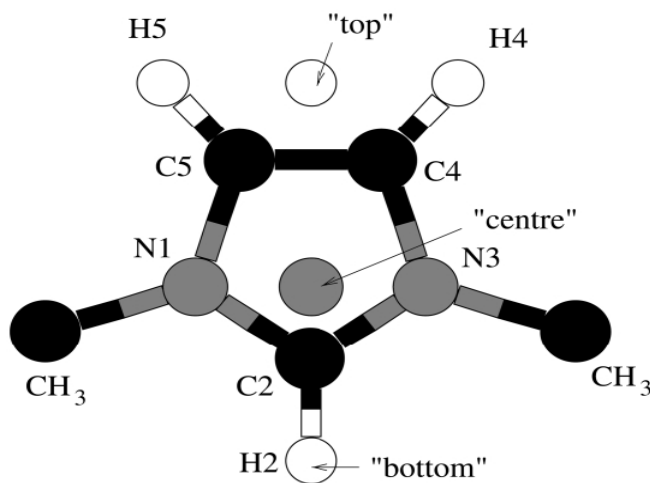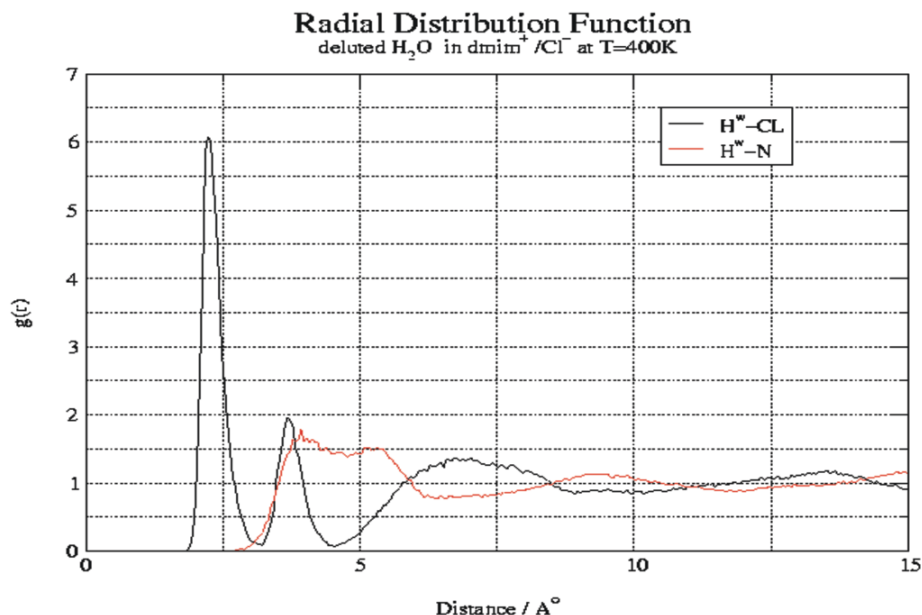

Fig. 1. Dimethylimidazolium molecule $(dmim^+)$

Fig. 2. Radial distribution function for a water molecule dissolved in dimethylimidazolium chloride (dmim$^+$/CL$^-$) at $T = 400$ K

$\angle$(HOH) amounts to 108° [6]. The parameters of the interaction between molecules of a dimethylimidazolium chloride dmim$^+$/CL$^-$ solution and a water molecule were determined with the help of the Lorentz–Berthelot mixing rule [8]. It is also worth noting that, in calculations, the methyl group in the dimethylimidazolium molecule was represented by a single atom, whose characteristic parameters were also determined according to the Lorentz–Berthelot rule. The electrostatic interaction at large dimensions was taken into account with the help of the Ewald summation [8].

All calculations were performed at the constant temperature $T = 400$ K for the ensemble consisting of 192 molecules of dimethylimidazolium, 192 chlorine molecules and only one water molecule, which gave a possibility to estimate the influence of water on the structure of the ionic liquid in detail.

3. Obtained Results and Their Analysis

The information on the liquid local structure can be obtained in two ways – experimentally, namely using the neutron scattering method, and theoretically with the help of calculations of the radial distribution function.

We calculated the radial distribution functions for the most interesting separate interacting atoms. Based upon the analysis of the Coulomb interaction, it is worth expecting the strongest repulsive interaction between negatively charged atoms of dimethylimidazolium and

the negatively charged oxygen atom (-0.8476 un.q) of the water molecule. The strongest attractive interaction should be expected between the positively charged hydrogen atoms of water ($+0.4238$ un.q) and negatively charged chlorine atoms (-1.0 un.q).

In addition, one should expect a strong attractive interaction between the positively charged hydrogen atoms of water and negatively charged atoms of dimethylimidazolium, which will determine, in turn, the position of the water molecule with respect to dimethylimidazolium ones. The given assumptions were widely used in [10]. Based on this analysis, one can expect that the water molecule will be located, most probably, close to the methyl group of dimethylimidazolium. Figure 2 presents the radial distribution functions calculated for the interaction

T a b l e 1. Charges and Lennard-Jones parameters for a dimethylimidazolium cation, chlorine anion, and water molecule

species	atom	charge	ε_{jj}	σ_{jj}
[dmim$^+$]	C$_2$	0.407	0.3598	3.4
	N$_1$, N$_3$	-0.267	0.7113	3.25
	C$_4$, C$_5$	0.105	0.3598	3.4
	H$_2$	0.097	0.0628	2.42
	H$_4$, H$_5$	0.094	0.0628	2.42
	Me(united)	0.316	0.8665	3.775
Cl_	Cl	-1.000	4148	4.401
H$_2$O	H	0.4238	0.0	–
H$_2$O	O	-0.8476	0.6502	3.169

683

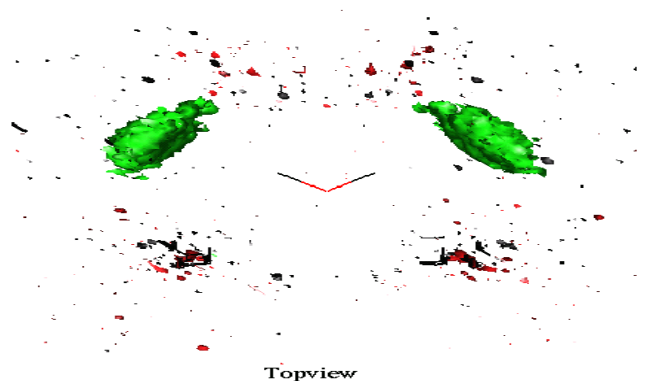**Local environment of a water molecule in dmim / Cl**

Topview

Fig. 3. Probability density distribution around the water molecule dissolved in dimethylimidazolium chloride (dmim$^+$/CL$^-$) at $T = 400$ K

4. Results and Conclusions

The mean energy of the interaction between the water molecule and dimethylimidazolium (dmim) in the three-component solution of dimethylimidazolium (dmim$^+$) chloride (CL$^-$) and water amounts to – 4 kJ/mol, and the energy of the interaction between the water molecule and chlorine cations equals – 83 kJ/mol. The analysis of the mean energies of interaction between the atoms of the system and the radial distribution functions allows one to make a conclusion that chlorine cations group around the positively charged hydrogen atoms of water (Fig. 3).

The water molecule will be located in the neighborhood of one of the methyl groups of dimethylimidazolium. The obtained data correlate with those obtained in [12] with the help of the infrared spectroscopy method. In particular, the analysis of spectra of the solution of water in an ionic liquid on the basis of a 1-butyl-3-methylimidazolium cation and a BF$_4$ anion (1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM]BF$_4$) similarly to our case demonstrates the establishment of a hydrogen bond between the BF$_4$ anion and the water molecule, as well as the existence of a relatively weak interaction between the cation molecule and water due to the interaction between carbons of the methyl groups of the cation and hydrogen of the water molecule.

Thus, one can consider that the principal interaction in the system "water molecule – dimethylimidazolium (dmim$^+$) chloride (CL$^-$)" occurs between water molecules and chlorine cations. Like the two-component "water–chlorine" mixture, dimethylimidazolium molecules play no essential role in the intermolecular

between the hydrogen atoms of water and dimethylimidazolium cations. As one can see from Fig. 2, the highest probability ($\sim$6.2) is characteristic of the interaction between the positively charged hydrogen of the water molecule and chlorine cations. The position of the maximum of the first probability peak can be identified with the interatomic distance or the bond length between the atoms, for which the radial distribution function was calculated [11]. Thus, one can also see from Fig. 2 that the hydrogen bond "hydrogen – chlorine" is considerably shorter than the bond "hydrogen – nitrogen". Table 2 presents the positions of the maxima determined to an accuracy of ±0.1Å and the probabilities obtained from the ensemble of radial distribution functions for the system "dimethylimidazolium–chlorine–water".

As one can see from Table 2, the highest probability is observed for the bond between the water molecule and chlorine, namely the H^w–CL bond between the oppositely charged atoms and O^w–CL. The interaction between the water molecule and dimethylimidazolium is less probable, which must influence, in turn, the energy characteristics of intermolecular bonds in the system.

In Table 3, we present the results of calculations of the Coulomb energy and mean interaction energy in the dmim$^+$/CL$^-$ system. In order to obtain the energy properties of the "water–dmim$^+$/CL$^-$" system, we repeated the calculations five times and determined, on this basis, the averaged values of the energies and the error in their calculation.

T a b l e   2. Positions of the first maximum (r_m, Å) and probabilities (I_m, rel. un.) of the radial distribution function of water in dimethylimidazolium chloride (O^w, H^w are the oxygen and hydrogen atoms of water, respectively, CL$^-$ is the chlorine cation, CH$_3$ and H$_1$ (H$_2$) are the methyl group and hydrogen atoms of the dimethylimidazolium molecule, respectively)

atom-atom	O^w CL		O^w CH$_3$		O^w H$_1$		O^w H$_2$		H^w CL		H^w N	
	r_m	I_m	r_m	I_m	r_m	I_m	r_m	I_m	r_m	I_m	r_m	I_m
H$_2$O	3.3	4.8	3.3	2.5	2.7	2.1	2.6	2.1	2.3	6.2	4.1	1.6

T a b l e   3. Coulomb energies of the interaction between the water molecule and dimethylimidazolium (dmim$^+$) chloride (CL$^-$) (E$_{coul}$) and the mean energies of interaction (E$_{inter}$) in the system at $T = 400$ K (kJ/mol)

Energy, (kJ/mol)	E_{coul} (dmim$^+$)	E_{coul} (CL$^-$)	E_{inter} (dmim$^+$)	E_{inter} (CL$^-$)
H$_2$O	−2.0±10	−81.0±7	−5.4±0.5	14.9±0.5

interaction in the "dimethylimidazolium ($dmim^+$) chloride (CL^-)–water" system.

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ВЗАЄМОДІЯ ДІМЕТИЛІМІДАЗОЛІУМУ ХЛОРИДУ
З МОЛЕКУЛОЮ ВОДИ ПРИ $T = 400$ K

Н.О. Атамась

Р е з ю м е

У роботі подано результати розрахунків методом молекулярної динаміки структури та енергетичних характеристик при взаємодії молекули води з діметилімідазоліумом хлоридом ($dmim^+/CL^-$) при температурі $T = 400$ K. Встановлено існування водневих зв'язків між молекулою води та молекулами діметилімідазоліуму ($dmim^+$), хлору (CL^-) та визначено орієнтаційне положення молекули води відносно молекул хлору та діметилімідазоліуму.