

Density Functional Theory Study of the Ionic Liquid [emim]OH and Complexes [emim]OH(H₂O)_n (n = 1, 2)

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Abstract In this work, the structure of the ionic liquid [emim]OH and the influence of water molecules on this ionic liquid were studied by the DFT theory at the B3LYP/6-311++G** level. The calculation results indicate that [emim]OH cannot exist in the form of ion pairs, rather it is inclined to exist the form of water and imidazole carbene. Further studies showed that water mainly influences the anion: it can disperse the negative charge of the O atom of the OH⁻ anion and form hydroxyl–water clusters with the anion. When there are two water molecules in the ionic liquid, the system is most likely to exist in the form of ion-pairs that are composed of hydroxyl–water clusters and cations. Configurations formed near the C₂-H fragment of imidazole were favored, and hydrogen bonding interaction plays an important role in the ionic liquid system.

Keywords DFT · Ionic liquid · Ion-pairs · Anionic clusters · Hydrogen bond

1 Introduction

Ionic liquids (IL) are of very important as green alternative solvents for extraction, purification, catalysis and synthesis. They possess appealing features such as low melting points, negligible vapor pressure, are nonvolatile and inflammable, and have wide electrochemical windows [1–5]. The imidazolium ionic liquids have been widely investigated over the last several years [6–8]. One of these is [emim]OH, a new novel basic ionic liquid that has been introduced as a catalyst for Michael addition, Markovnikov addition and some other reactions for which it displays fine characteristics [9, 10]. However, the structure and interaction properties of this ionic liquid are not fully understood. A theoretical investigation is necessary to ascertain the interactions that occur in this ionic liquid.

Water is the most commonly used green solvent in chemical reactions. Most of the ionic liquids can absorb water from the atmosphere, and some can even react remarkably with

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water such as the [emim]Cl/AlCl₃ ionic liquids [11, 12]. Water can significantly effect the activity of the ionic liquids, and greatly affect their physical properties [13]. Reactions catalyzed by [emim]OH can produce water, which can also influence the reaction yield and chemical selectivity of these reactions [14, 15]. Thus, it is necessary to take water into account when investigating this ionic liquid.

In this work, the structures and interionic interactions of the ionic liquid [emim]OH, including the stable configuration, hydrogen bonds, interaction energy, charge transfer, and the influence of water on this ionic liquid are studied by using DFT calculations.

2 Calculation Method

The density functional theory (DFT) provides a sound basis for the development of computational strategies for obtaining information about the energetics, structure, and electronic properties of atoms or molecules at much lower costs than the traditional ab initio wave function techniques and without losing accuracy [16–20]. Previous investigations have proven that the DFT method is suitable for calculation of the properties of ionic liquids [21–24]. The hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange-correlation function with the 6-311++G** basis set was employed to perform the geometry optimizations in this work [25, 26]. Each final optimized structure was checked to be a true minimum through a frequency calculation at the corresponding level. All calculations were performed within the framework of the Gaussian 03 program package [27].

3 Results and Discussion

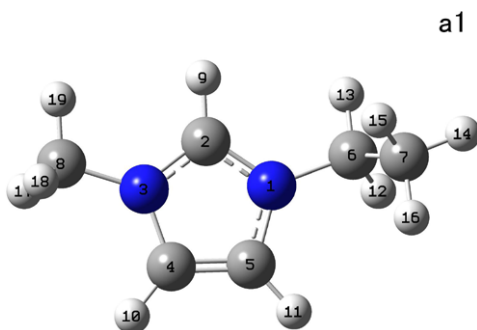
3.1 Structure of the Cation

The 1-ethyl-3-methylimidazolium cation ([emim]⁺) was fully optimized directly. The most stable geometry of [emim]⁺, named a1, was obtained at a dihedral angle *D* C₂-N₁-C₆-C₇ of 104.4°, which is consistent with the results from previous work [28]. The geometry of a1 is shown in Fig. 1 and the configuration parameters are presented in Table 1.

3.2 Structures of the Ionic Liquid [emim]OH

To obtain the most stable geometries of [emim]OH, the anion OH⁻ was located at several different positions around the cation near the C₂-H, C₄-H and C₅-H fragments [29]. The

Fig. 1 Optimized structures (B3LYP/6-311++G**) of [emim]⁺: a1



initial geometries were fully optimized. Eight stable geometries of [emim]OH, named b1 to b8, were obtained as shown in Fig. 2 and the main structural sizes and interaction energies are presented in Table 2.

In the cases of minima b1 to b4 the structure was found to have a hydroxyl covalently bound to one of the ring carbons, whereas the structures for minima b5 to b8 have a hydrogen atom removed from one of the ring carbons thus forming a water molecule and a carbene-like species (Fig. 2). The most stable predicted geometries among these (Figs. 2b5 and 2b6) possess a carbene carbon flanked by two heteroatoms bearing lone pairs of electrons.

The configurations of the imidazole rings in all of the stable geometries were changed to a certain extent. In Figs. 2b1–2b4, because of the formation of the new C-O covalent bonds, the dihedral angles D N₁-C₂-N₃-C₄, D N₁-C₂-N₃-C₄, D C₂-N₃-C₄-C₅ and D C₄-C₅-N₁-C₂ in b1–b4 changed from nearly 0° to 19.9°, -22.6°, -21.2° and 1.2°, respectively. In Figs. 2b5 to b8 the covalent bonds C₂-H, C₄-H or C₅-H are broken, and the bond angles \angle N₁-C₂-N₃, \angle N₁-C₂-N₃, \angle N₃-C₄-C₅ and \angle C₄-C₅-N₁ in structures b5 to b8 changed

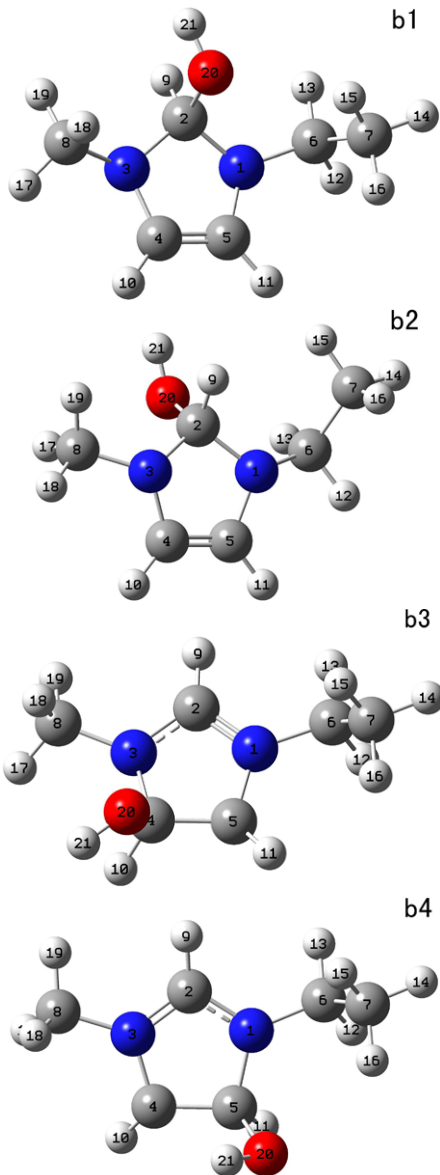
Table 1 Bond distances (Å), bond angles (degree) and dihedral angles (D , degree) of [emim]⁺

Bond distances	(Å)	Bond angles	(°)	Dihedral angles	(D , °)
N ₁ -C ₂	1.336	\angle N ₁ -C ₂ -N ₃	109.0	D N ₁ -C ₂ -N ₃ -C ₄	0.0
N ₃ -C ₄	1.382	\angle C ₂ -N ₃ -C ₄	108.4	D C ₂ -N ₃ -C ₄ -C ₅	0.1
C ₄ -C ₅	1.361	\angle N ₃ -C ₄ -C ₅	107.1	D C ₂ -N ₁ -C ₆ -C ₇	104.4
C ₂ -H ₉	1.078	\angle C ₄ -C ₅ -N ₁	107.2		
C ₄ -H ₁₀	1.077	\angle C ₅ -N ₁ -C ₂	108.3		
C ₅ -H ₁₁	1.077	\angle N ₁ -C ₆ -C ₇	112.4		

Table 2 Bond distances (Å), bond angles (degree), dihedral angles (D , degree) and interaction energies (kJ·mol⁻¹) of [emim]OH

	Bond distances	Å	Bond angles	(°)	Dihedral angles	(D , °)	Interaction energies (kJ·mol ⁻¹)
b1	C ₂ -O ₂₀	1.466	\angle N ₁ -C ₂ -N ₃	102.3	D N ₁ -C ₂ -N ₃ -C ₄	19.9	-533.49
	N ₁ -C ₂	1.433	\angle N ₁ -C ₆ -C ₇	115.7	D O ₂₀ -C ₂ -N ₃ -C ₄	-99.1	
b2	C ₂ -O ₂₀	1.459	\angle N ₁ -C ₂ -N ₃	102.3	D N ₁ -C ₂ -N ₃ -C ₄	-22.7	-534.43
	N ₁ -C ₂	1.444	\angle N ₁ -C ₆ -C ₇	112.6	D O ₂₀ -C ₂ -N ₃ -C ₄	96.0	
b3	C ₄ -O ₂₀	1.490	\angle N ₃ -C ₄ -C ₅	100.4	D C ₂ -N ₃ -C ₄ -C ₅	-21.2	-436.37
	N ₃ -C ₄	1.462	\angle N ₁ -C ₆ -C ₇	112.9	D O ₂₀ -C ₄ -C ₅ -N ₁	-98.0	
b4	C ₅ -O ₂₀	1.450	\angle C ₄ -C ₅ -N ₁	101.4	D C ₄ -C ₅ -N ₁ -C ₂	1.2	-446.77
	C ₅ -N ₁	1.473	\angle N ₁ -C ₆ -C ₇	114.1	D O ₂₀ -C ₅ -N ₁ -C ₂	-120.6	
b5	C ₂ -H ₉	1.972	\angle N ₁ -C ₂ -N ₃	103.1	D N ₁ -C ₂ -N ₃ -C ₄	0.1	-564.91
	N ₁ -C ₂	1.363	\angle N ₁ -C ₆ -C ₇	112.9	D O ₂₀ -C ₂ -N ₃ -C ₄	-175.3	
b6	C ₂ -H ₉	1.978	\angle N ₁ -C ₂ -N ₃	103.1	D N ₁ -C ₂ -N ₃ -C ₄	0.0	-565.01
	N ₁ -C ₂	1.363	\angle N ₁ -C ₆ -C ₇	112.7	D O ₂₀ -C ₂ -N ₃ -C ₄	-178.1	
b7	C ₄ -H ₁₀	1.915	\angle N ₃ -C ₄ -C ₅	101.7	D N ₁ -C ₂ -N ₃ -C ₄	-0.2	-498.24
	N ₃ -C ₄	1.407	\angle N ₁ -C ₆ -C ₇	112.8	D O ₂₀ -C ₄ -C ₅ -N ₁	-169.6	
b8	C ₅ -H ₁₁	1.913	\angle C ₄ -C ₅ -N ₁	101.8	D C ₅ -N ₁ -C ₂ -N ₃	-0.2	-500.69
	N ₁ -C ₅	1.407	\angle N ₁ -C ₆ -C ₇	112.4	D O ₂₀ -C ₅ -N ₁ -C ₂	-178.0	

Fig. 2 Optimized structures (B3LYP/6-311++G**) of [emim]OH: **b1–b8**

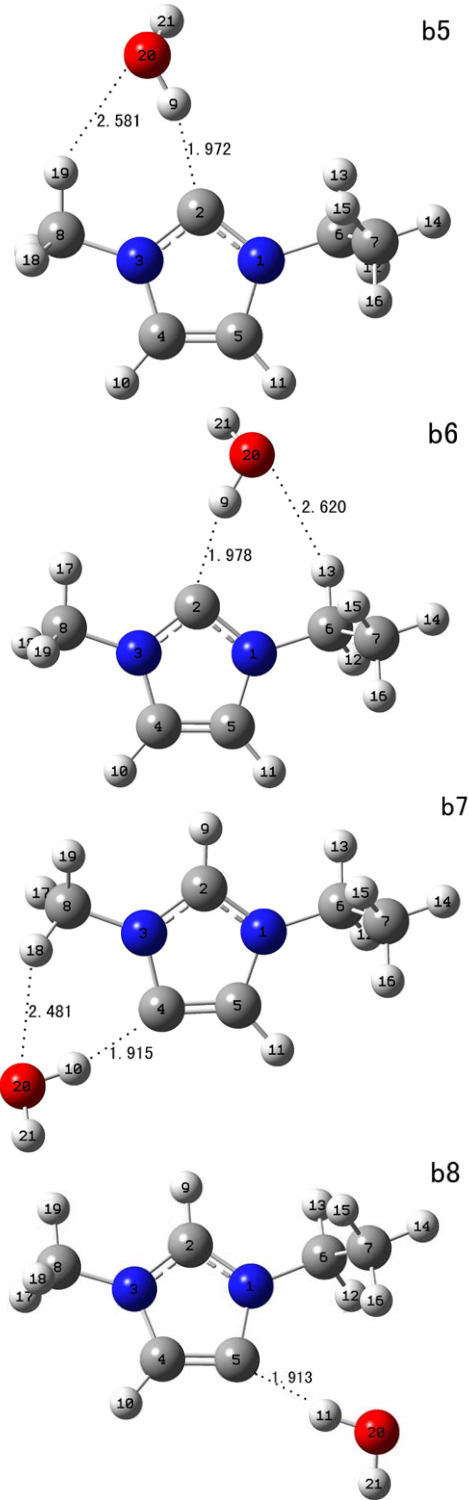


from 109.0°, 109.0°, 107.1° and 107.2° to 103.1°, 103.1°, 101.7° and 101.8°, respectively (Table 2).

The interaction energy is defined as the difference between the energy (corrected by the zero point energy, ZPE) of the system (E_{AB}) and the sum of the energies of the pure compositions ($E_A + E_B$).

$$\Delta E (\text{kJ} \cdot \text{mol}^{-1}) = 2625.5 [E_{AB}(\text{au}) - (E_A(\text{au}) + E_B(\text{au}))]$$

Fig. 2 (Continued)



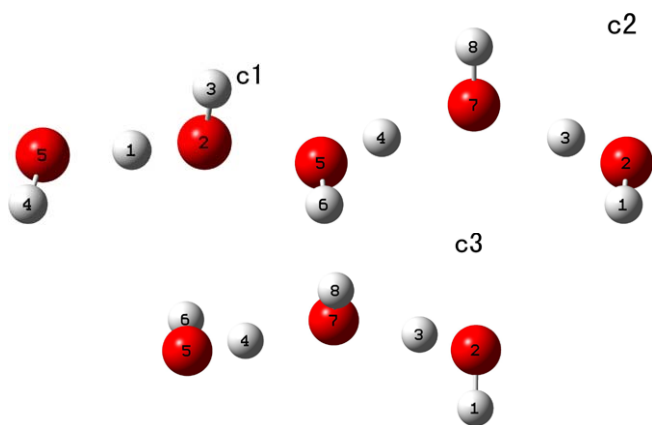


Fig. 3 Optimized structures (B3LYP/6-311++G**) of anionic clusters: **c1–c3**

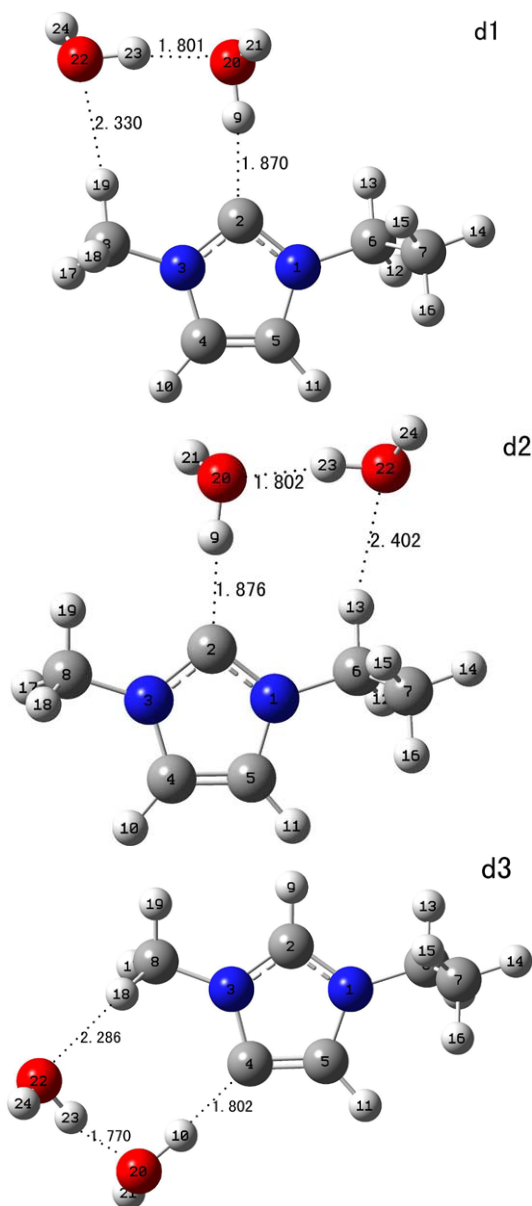
Table 3 Bond distances (Å), charge transfer (e) and interaction energies ($\text{kJ}\cdot\text{mol}^{-1}$) of anionic clusters

	Bond distances	(Å)	Charge transfer	(e)	Interaction energies ($\text{kJ}\cdot\text{mol}^{-1}$)
c1	O ₂ -H ₁	1.118	O ₅	0.159	-120.24
	H ₁ -O ₅	1.362			
c2	O ₂ -H ₃	1.034	O ₇	0.143	-203.91
	H ₃ -O ₇	1.547			
c3	O ₂ -H ₃	1.034	O ₇	0.142	-204.80
	H ₃ -O ₇	1.544			

For the ionic liquid system, E_{AB} is the energy of the ionic system and $E_A + E_B$ is the energy sum of the pure cation, anion and water. For the hydroxyl–water clusters investigated latter in this work, E_{AB} is the energy of the hydroxyl–water clusters and $E_A + E_B$ is the energy sum of the OH^- and water molecules.

The structures for minima b5 and b6 were found to be the most favored isomers of 1-ethyl-3-methylimidazolium hydroxide, and the minimum b1 and b2 structures follow (Table 2), which indicated that geometries formed near the C₂-H fragment of imidazole rings are favored. For geometries formed near a fixed C*-H fragment of the imidazole ring, the interaction energies of those that formed water (b5–b8) are significantly larger than that had hydroxyl covalently bound to the ring carbons (b1–b4), which suggested that the anion OH^- is inclined to combine with the H atoms rather than with the C atoms. The large interaction energies range in value from -436.37 to ~ -565.01 $\text{kJ}\cdot\text{mol}^{-1}$, indicating that hydrogen transfer reactions and C-O bond formation reactions are very beneficial for decreasing the energy of the [emim]OH system. In other words, the ionic liquid [emim]OH cannot exist as ion pairs. These results are consistent with several previous experimental and computational works. For examples, Formentin and coworkers used the hydrophobic ionic liquid [Bmim][PF₆] as the reaction medium to catalyze the Knoevenagel and Claisen-Schmidt reactions, and found that the ¹H NMR signal of H₉ at 8.8 ppm disappeared after NaOH was added to the system; a carbene structure was believed to have formed [30]. Turner and coworkers used ab initio calculations to investigate imidazolium-based, room-temperature

Fig. 4 Optimized structures (B3LYP/6-311++G**) of the complexes [emim]OH(H₂O): **d1–d8**



ionic liquids, and predicted that in the ionic liquid [emim]F the F⁻ anion would covalently bond to carbon or form hydrogen fluoride, with the H atoms separated from the imidazole ring to produce imidazole carbene [28, 31]. Considering anion exchange between the ionic liquid [bmim]PF₆ and NaOH, and the similar characteristics of F⁻ and OH⁻, the imidazole carbene probably forms in the ionic liquid [emim]OH.

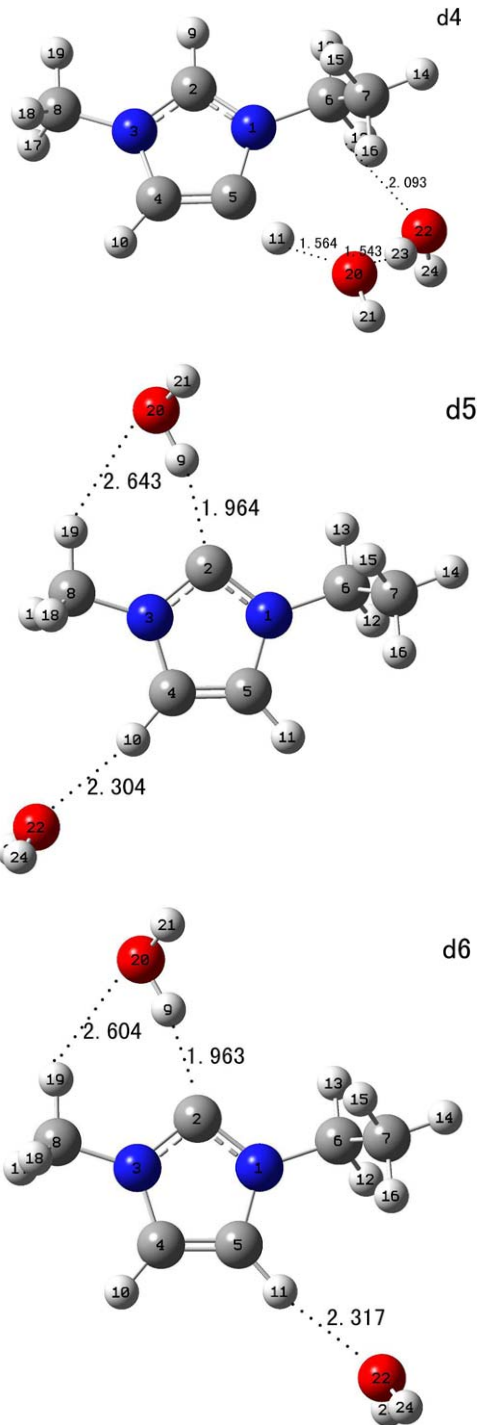
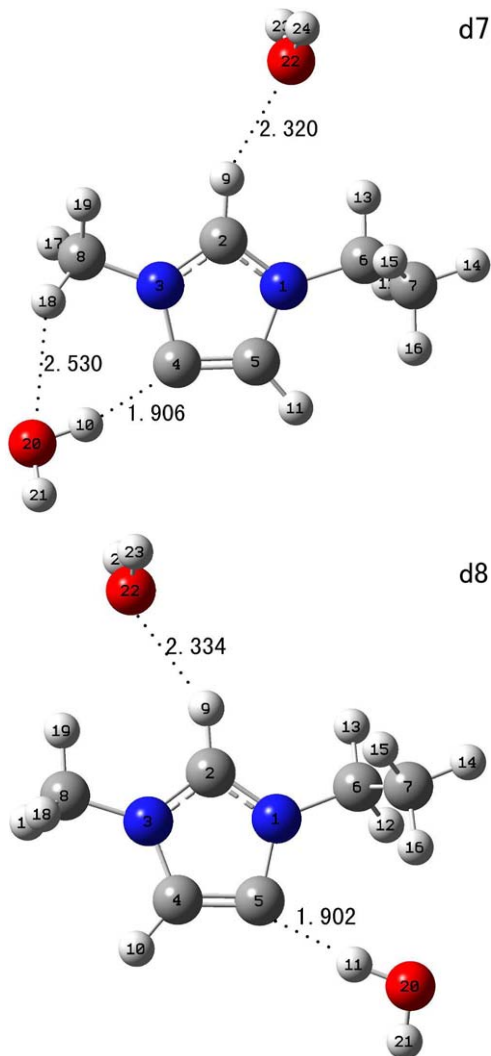
Fig. 4 (Continued)

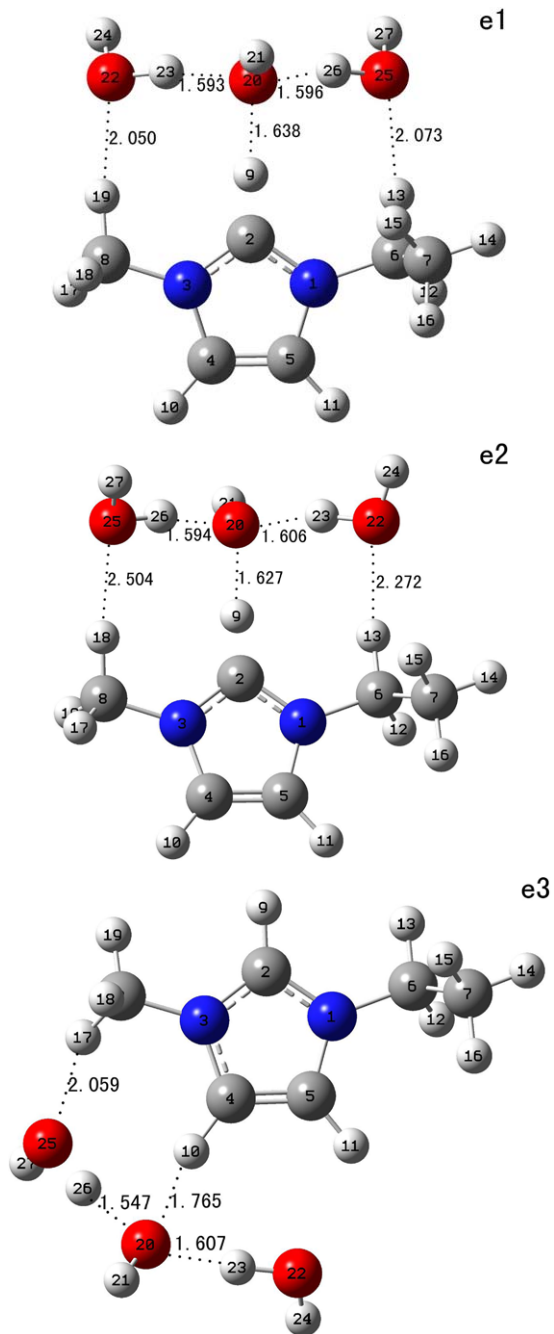
Fig. 4 (Continued)

3.3 The Influence of Water Molecules on the Anion

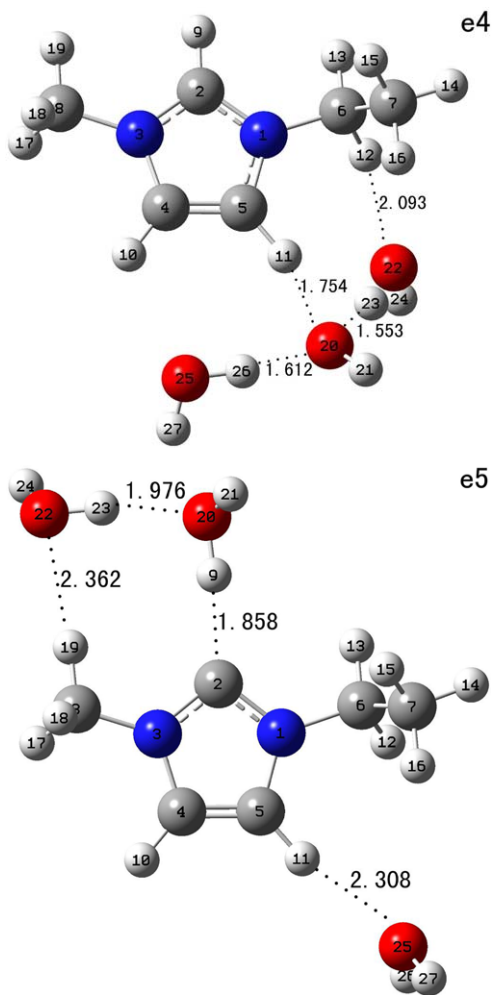
Early investigations suggested that the miscibility of an ionic liquid with water is mainly determined by the associated anion [32, 33]. Crystallographic and spectroscopic data revealed that the anion might be involved in an attractive hydrogen-bonding interaction [34, 35]. The formation of hydroxyl–water clusters was also predicted by previous calculations [36]. To investigate the influence of water on the anion OH^- in this ionic liquid, a series initial configurations of hydroxyl–water clusters $\text{OH}^-(\text{H}_2\text{O})_n$ ($n = 1, 2$) were fully optimized. Three stable geometries, named c1, c2 and c3, were obtained as shown in Fig. 3. The main structural size, charge transfer and interaction energies are presented in Table 3.

The optimization results showed that the H–O bonds in water molecules close to the O atom of OH^- are elongated. The large interaction energies also exceeded the common range of hydrogen bond energies. This showed that the water molecules had formed anionic clus-

Fig. 5 Optimized structures (B3LYP/6-311++G**) of the complexes [emim]OH(H₂O)₂: e1–e9



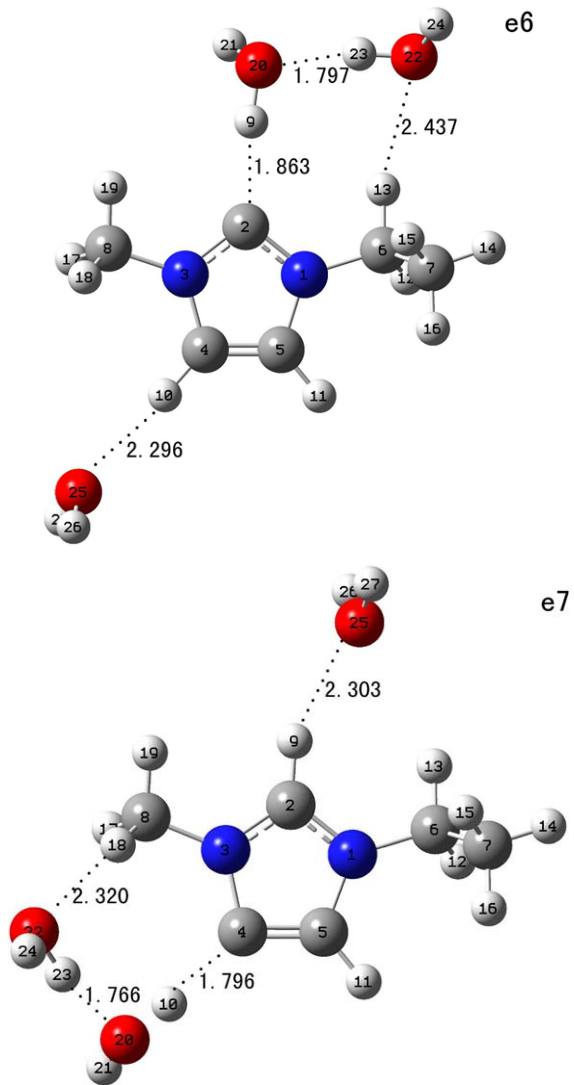
ters with OH⁻. The natural bond orbital (NBO) charge population analysis showed that, in the anionic clusters, the negative charge of the O atom of OH⁻ is dispersed. This result is basically in agreement with previous computational work: the configuration of c1 and c3,

Fig. 5 (Continued)

and the bond lengths and the hydrogen-bond distances in c1, c2 and c3, are consistent with those found in the previous work [36]. Moreover, the minimum c2 has a newly discovered geometry for the hydroxyl–water cluster, and further study showed that c2 more easily forms an ion pair with the imidazole cation than c3 because of the relatively smaller steric hindrance.

3.4 The Influence of Water Molecules on the Ionic Liquid [emim]OH

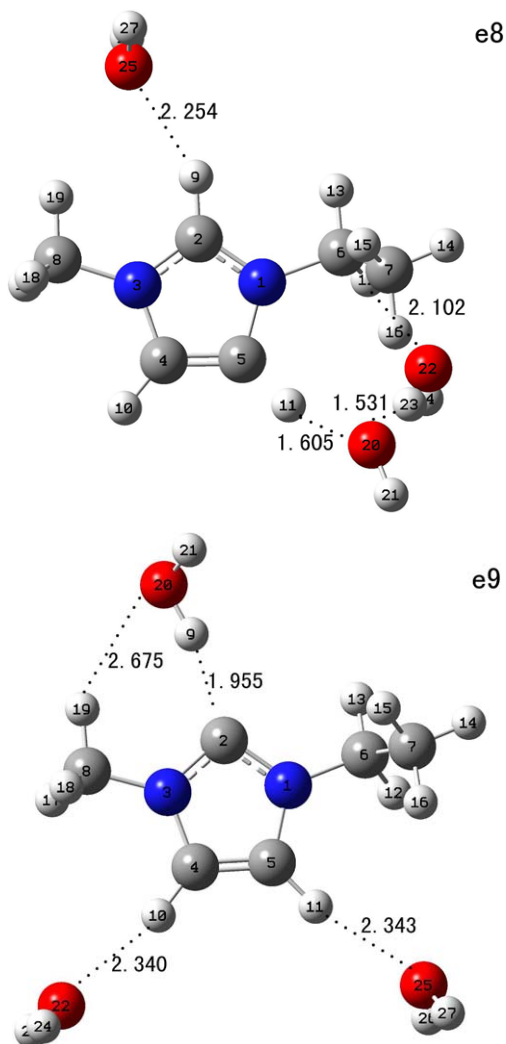
An anterior section describes how the anion OH^- mainly interacts with the H atom on the cation. The structures in which hydroxyl is covalently bound to carbon were eliminated from further investigation and only those in which OH^- interacts with H atoms are studied in this section. Although an early investigation suggested that the interaction between water molecules and the anion is primary, relatively weak interactions of the water with the cation and water with the ion pairs were also found in that the computational work [37]. Therefore, in this work, the influence of water molecules on this ionic liquid was consid-

Fig. 5 (Continued)

ered for the following two situations. One is that the $\text{OH}^-(\text{H}_2\text{O})_n$ ($n = 1, 2$) anionic cluster formed first and then is coupled with the $[\text{emim}]^+$, and the other is that one or two water molecules independently interact only with $[\text{emim}]^+$. A series of initial geometries were obtained by considering that the anion OH^- or the anionic clusters couple with $[\text{emim}]^+$ near the $\text{C}_2\text{-H}$, $\text{C}_4\text{-H}$ or $\text{C}_5\text{-H}$ fragments. The initial geometries were fully optimized. Eight stable geometries of complexes $[\text{emim}]\text{OH}(\text{H}_2\text{O})$, named d1 to d8, and nine stable geometries of complexes $[\text{emim}]\text{OH}(\text{H}_2\text{O})_2$, named e1 to e9, were obtained as shown in Fig. 4 and Fig. 5. The main structural sizes and interaction energies are presented in Tables 4 and 5.

The geometries d1 to d4 and e1 to e4 were obtained for the first case, and others were obtained for the second case. In the system with one water molecule, the structure of d4 was found to dissociate and produce the ionic emim hydroxide (Fig. 4). The remaining seven structures in the analysis were found to maintain the same carbene-like configuration.

Fig. 5 (Continued)



In d1 to d3, water molecules added to the system were found to interact with the newly formed water and the imidazole carbene by formation of simultaneous hydrogen bonds. In the systems with two water molecules, the structures of e1 to e4 were found to produce ion pairs that are composed of hydroxyl–water clusters and imidazole cations. The structures for minima e1 and e2 formed near the C₂-H fragment are found to be the most favored isomers (Table 5). The interaction between the water molecules and the cation had little influence on the ionic liquid system. Interaction energies of the minimum obtained for the second case for interaction between water and OH⁻ are significantly smaller than that obtained for the first case. For example, the relative interaction energy of e1 and b3 is 56.80 kJ·mol⁻¹, but that of e9 and b3 is only 13.42 kJ·mol⁻¹. Thus, the contribution of a single hydrogen bond between water and C₄-H or C₅-H in e9 is only about 7 kJ·mol⁻¹, which confirms that the water mainly influences the anion OH⁻ in this ionic liquid.

Table 4 Bond distances (Å), bond angles (degree), dihedral angles (*D*, degree) and interaction energies (kJ·mol⁻¹) of [emim]OH(H₂O)

	Bond distances	Å	Bond angles (°)	(°)	Dihedral angles (<i>D</i> , °)	(<i>D</i> , °)	Interaction energies (kJ·mol ⁻¹)
d1	C ₂ -H ₉	1.870	∠N ₁ -C ₂ -N ₃	103.3	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	0.3	-597.08
	N ₁ -C ₂	1.363	∠N ₁ -C ₆ -C ₇	112.9	<i>D</i> O ₂₀ -C ₂ -N ₃ -C ₄	176.8	
d2	C ₂ -H ₉	1.876	∠N ₁ -C ₂ -N ₃	103.3	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	-0.1	-597.23
	N ₁ -C ₂	1.361	∠N ₁ -C ₆ -C ₇	112.6	<i>D</i> O ₂₀ -C ₂ -N ₃ -C ₄	177.8	
d3	C ₄ -H ₁₀	1.813	∠N ₃ -C ₄ -C ₅	102.0	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	-0.1	-536.13
	N ₃ -C ₄	1.406	∠N ₁ -C ₆ -C ₇	112.8	<i>D</i> O ₂₀ -C ₄ -C ₅ -N ₁	-165.0	
d4	C ₅ -H ₁₁	1.149	∠C ₄ -C ₅ -N ₁	105.5	<i>D</i> C ₅ -N ₁ -C ₂ -N ₃	-0.0	-521.83
	N ₁ -C ₅	1.388	∠N ₁ -C ₆ -C ₇	111.7	<i>D</i> O ₂₀ -C ₅ -N ₁ -C ₂	179.3	
d5	C ₂ -H ₉	1.964	∠N ₁ -C ₂ -N ₃	103.0	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	0.0	-572.25
	N ₁ -C ₂	1.363	∠N ₁ -C ₆ -C ₇	113.0	<i>D</i> O ₂₀ -C ₂ -N ₁ -C ₃	175.7	
d6	C ₂ -H ₉	1.963	∠N ₁ -C ₂ -N ₃	103.0	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	0.0	-572.51
	N ₁ -C ₂	1.363	∠N ₁ -C ₆ -C ₇	112.8	<i>D</i> O ₂₀ -C ₂ -N ₃ -C ₄	175.6	
d7	C ₄ -H ₁₀	1.906	∠N ₃ -C ₄ -C ₅	101.6	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	-0.2	-510.10
	N ₃ -C ₄	1.408	∠N ₁ -C ₆ -C ₇	112.7	<i>D</i> O ₂₀ -C ₄ -C ₅ -N ₁	-168.9	
d8	C ₅ -H ₁₁	1.902	∠C ₄ -C ₅ -N ₁	101.7	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	0.1	-513.10
	N ₁ -C ₅	1.408	∠N ₁ -C ₆ -C ₇	112.5	<i>D</i> O ₂₀ -C ₅ -N ₁ -C ₂	-177.4	

Table 5 Bond distances (Å), bond angles (degree), dihedral angles (*D*, degree) and interaction energies (kJ·mol⁻¹) of [emim]OH(H₂O)₂

	Bond distances	Å	Bond angles (°)	(°)	Dihedral angles (<i>D</i> , °)	(<i>D</i> , °)	Interaction energies (kJ·mol ⁻¹)
e1	C ₂ -H ₉	1.135	∠N ₁ -C ₂ -N ₃	107.5	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	0.2	-621.70
	N ₁ -C ₂	1.342	∠N ₁ -C ₆ -C ₇	112.1	<i>D</i> O ₂₀ -C ₂ -N ₃ -C ₄	178.7	
e2	C ₂ -H ₉	1.138	∠N ₁ -C ₂ -N ₃	107.5	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	-0.1	-620.26
	N ₁ -C ₂	1.342	∠N ₁ -C ₆ -C ₇	112.2	<i>D</i> O ₂₀ -C ₂ -N ₃ -C ₄	-178.5	
e3	C ₄ -H ₁₀	1.107	∠N ₃ -C ₄ -C ₅	106.6	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	0.1	-579.25
	N ₃ -C ₄	1.381	∠N ₁ -C ₆ -C ₇	112.6	<i>D</i> O ₂₀ -C ₄ -C ₅ -N ₁	165.9	
e4	C ₅ -H ₁₁	1.108	∠C ₄ -C ₅ -N ₁	106.6	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	0.0	-580.12
	N ₁ -C ₅	1.382	∠N ₁ -C ₆ -C ₇	111.8	<i>D</i> O ₂₀ -C ₅ -N ₁ -C ₂	166.8	
e5	C ₂ -H ₉	1.858	∠N ₁ -C ₂ -N ₃	103.3	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	0.2	-605.45
	N ₁ -C ₂	1.363	∠N ₁ -C ₆ -C ₇	112.9	<i>D</i> O ₂₀ -C ₂ -N ₃ -C ₄	177.4	
e6	C ₂ -H ₉	1.863	∠N ₁ -C ₂ -N ₃	103.2	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	-0.1	-604.69
	N ₁ -C ₂	1.361	∠N ₁ -C ₆ -C ₇	112.6	<i>D</i> O ₂₀ -C ₂ -N ₃ -C ₄	178.5	
e7	C ₄ -H ₁₀	1.796	∠N ₃ -C ₄ -C ₅	101.9	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	-0.1	-549.06
	N ₃ -C ₄	1.407	∠N ₁ -C ₆ -C ₇	112.6	<i>D</i> O ₂₀ -C ₄ -C ₅ -N ₁	-165.5	
e8	C ₅ -H ₁₁	1.138	∠C ₄ -C ₅ -N ₁	105.6	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	0.1	-539.49
	N ₁ -C ₅	1.388	∠N ₁ -C ₆ -C ₇	111.8	<i>D</i> O ₂₀ -C ₅ -N ₁ -C ₂	178.9	
e9	C ₂ -H ₉	1.955	∠N ₁ -C ₂ -N ₃	102.9	<i>D</i> N ₁ -C ₂ -N ₃ -C ₄	0.0	-578.33
	N ₁ -C ₂	1.363	∠N ₁ -C ₆ -C ₇	112.9	<i>D</i> O ₂₀ -C ₂ -N ₃ -C ₄	176.1	

4 Conclusions

In this work, the structure of ionic liquid [emim]OH and the influence of water on it were studied by DFT theory at the B3LYP/6-311++G** level. The results of the theoretical calculations indicate that the ionic liquid [emim]OH is most likely to exist in the form of water and imidazole carbene. The water molecules mainly affect the anion and could form hydroxyl–water clusters with the anion OH⁻. When there are two water molecules in the ionic liquid system, the ion pairs of hydroxyl–water clusters and imidazole cation were connected by hydrogen-bonded networks. Configurations formed near the C₂-H fragment of imidazole are favored.

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