

Theoretical study on the interactions between methanol and imidazolium-based ionic liquids

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Abstract To better understand the property of the binary systems composing of imidazolium salt, $[\text{emim}]^+\text{A}^-$ ($\text{A}=\text{Cl}^-$, Br^- , BF_4^- , and PF_6^-) and methanol, we have investigated in detail the interactions of methanol molecule with anions A^- , cation $[\text{emim}]^+$, and ion pair $[\text{emim}]^+\text{A}^-$ of several ionic liquids (ILs) based on 1-ethyl-3-methylimidazolium cation by performing density functional theory calculations. It is found that H-bonds are universally involved in these systems, which may play an important role for the miscibility of methanol with imidazolium-based ILs. The interaction mechanisms of methanol molecule with anion and cation are found to be different in nature: the former mainly involves $\text{LP}_\text{X}-\sigma_{\text{O}-\text{H}}^*$ interaction, while the latter relates with the decisive orbital overlap of the type of $\text{LP}_\text{O}-\sigma_{\text{C}-\text{H}}^*$. Based on the present calculations, we have provided some reasonable interpretations for properties of the binary mixtures of ILs and alcohol and revealed valuable information for the interaction details between ILs and alcohols, which is expected to be useful for the design of more efficient ILs to form superior solvent system with alcohol.

Keywords Density functional theory · H-bond · Ionic liquid

Introduction

In recent years, room temperature ionic liquids (ILs), composed exclusively of organic cations and inorganic anions, have elicited substantial interest both in academia and in industry. This is mostly because of their unique physicochemical properties [1, 2], such as low melting point, vanishing vapor pressure, powerful solvent capacity, large liquid range, excellent thermal stability, and high ionic conductivity. In particular, in light of their nonvolatile nature, ILs have been very popular as solvents in many fields of chemistry, including catalysis [3, 4], organic synthesis [5, 6], separation [7, 8], and biochemistry [9, 10]. Real IL-based solvent systems for various applications usually contain other components, for instance, water, alcohol, and ether. Therefore, it is crucial to acquire the properties of the mixtures of ILs with these other components. At present, much interest has been focused on the macroscopical properties for the mixtures, such as density, viscosity [11], conductivity and solubility [12–14], not much is known about the detailed interaction mechanism between ILs and other components at the molecular level. Thus, theoretical studies to address the microscopic structural details of the mixtures are extraordinarily expected, from which we can extract valuable information for understanding the physicochemical properties of these mixtures.

The binary systems composed of ILs and alcohols are frequently used in experimental fields, for example, as special solvents for some small molecules containing various functional groups [15], as auxiliary liquid of the catalyst for alkene hydroformylation reaction [16], and as reaction media of esterification reaction [17]. It is just their extensive application in the chemical field that results in some experimental [18–24] and dynamic simulation [25–28]

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studies on the binary mixtures. For example, Brennecke et al. [19, 20] discussed the factors governing the phase behavior of ILs with alcohols via a systematic experimental investigation. Gholami and co-workers [21] reported some solvatochromic parameters for binary solvent mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{bmim}]^+\text{BF}_4^-$) with alcohols by performing a minimum number of experiments. And Atamas [26] and Lopes [27] et al. studied the interaction between ILs and methanol using molecular dynamic simulations. Despite these efforts, our understanding for the interaction mechanism of ILs and alcohols at the molecular level is still very limited. In this work, we present a systematic theoretical study on the binary mixtures of 1-ethyl-3-methylimidazolium-based ILs (denoted as $[\text{emim}]^+\text{A}^-$, $\text{A}=\text{Cl}^-$, Br^- , BF_4^- , and PF_6^-) with methanol. By performing density functional theory (DFT) calculations, we obtain a better understanding about the preferential localizations of methanol around anions, cation, and ion pair, as well as the nature of interaction between them. The calculated results are expected to provide information for understanding the physicochemical property of the binary mixtures.

Computational details

Throughout this work, we used the popular B3LYP functional, which has been confirmed to give results for both geometries and energies of many systems as good as more expensive methods [28], such as MP methods [29, 30] and coupled-cluster methods [31, 32]. The standard 6-31++G(d,p) basis

set [33–35] was adopted in the calculations. No symmetry constraints were imposed on any initial structures. All the optimized structures were characterized as minima by frequency analysis, through which the zero-point vibrational energy (ZPE) corrections were obtained. The basis set superposition errors (BSSE) for the interaction energies has been corrected using the counterpoise method [36]. The interactions of methanol molecule with anions, cation, and ion pair of the ILs were understood based on natural bond orbital (NBO) analysis [37, 38] and the frontier molecular theory [39, 40]. All calculations were completed using Gaussian 03 program package [41].

Results and discussion

The interaction of methanol with anions

The anions of ILs have been proved to have a significant influence on the solubility of alcohol in ILs [19, 23]. In experiments, the Cl^- , Br^- , BF_4^- and PF_6^- are the most common anions involved in imidazolium salts. Therefore, we first study the interactions of methanol with Cl^- , Br^- , BF_4^- and PF_6^- anions. The optimized lowest-energy geometries are shown in Fig. 1, and the calculated interaction energies are summarized in Table 1.

The common geometrical feature in the four methanol-anion complexes (M-A^-) is that anions prefer to occur near the hydroxyl H atom of methanol. This can be attributed to the more positive charge on the hydroxyl H atom. The O-H bonds of methanol in M-Cl^- , M-Br^- , M-

Fig. 1 The most stable geometries for the methanol-anion complexes (M-A^- , $\text{A}=\text{Cl}^-$, Br^- , BF_4^- , and PF_6^-), optimized at the B3LYP/6-31++G (d,p) level of theory. Bond lengths are in Å, and bond angles are in degrees

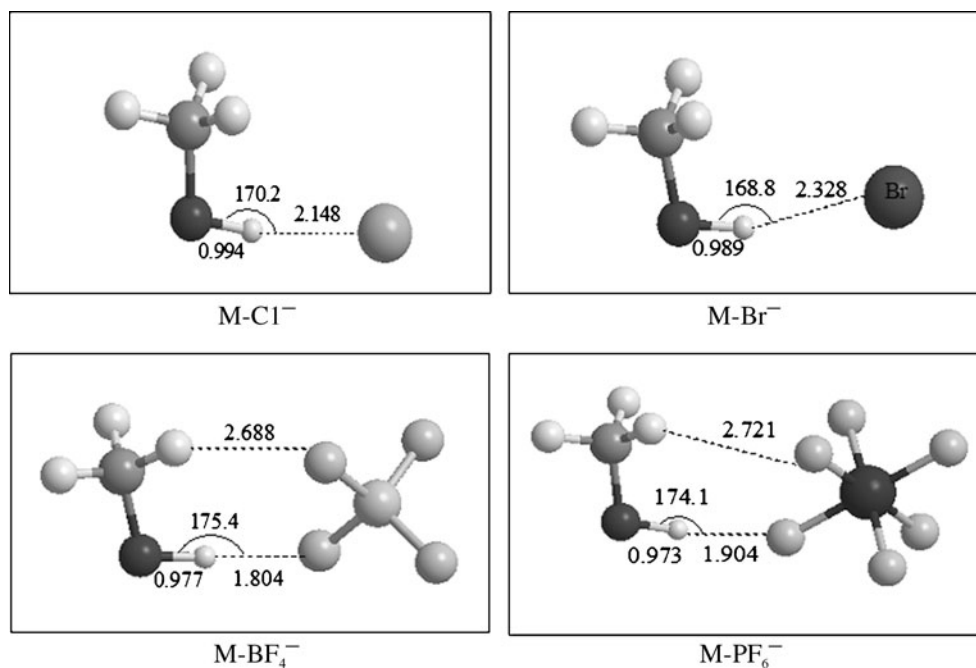
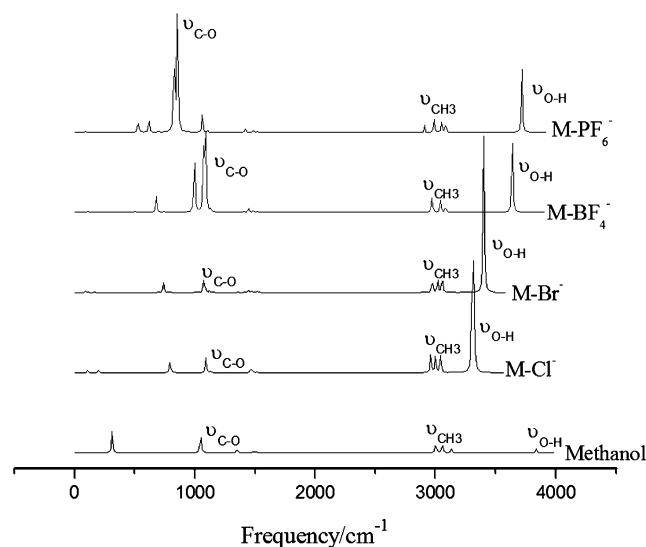


Table 1 The BSSE-corrected interaction energies (kcal mol⁻¹) for the complexes of methanol-anion (M-A⁻), methanol-[emim]⁺ (M-E⁺), and methanol-[emim]⁺Cl⁻ (M-[emim]⁺Cl⁻)

Complex	ΔE	
M-A ⁻	M-Cl ⁻	14.34
	M-Br ⁻	12.16
	M-BF ₄ ⁻	9.77
	M-PF ₆ ⁻	7.57
M-E ⁺	I _a	9.43
	I _b	7.84
	I _c	7.64
	I _d	6.90
M-[emim] ⁺ Cl ⁻	III _a	12.04
	III _b	11.80
	III _c	10.18
	III _d	9.09

$$\Delta E = E_{\text{complex}} - E_{\text{cation/anion/ion pair}} - E_{\text{methanol}} - \text{BSSE}$$

BF₄⁻ and M-PF₆⁻ complexes are 0.994, 0.989, 0.977, and 0.973 Å, which are larger by 0.029, 0.024, 0.012 and 0.008 Å than that in free methanol molecule (0.965 Å), respectively. The calculated O-H···X angles are in the range of 168.8–175.4°, and H···X distances vary from 1.804 to 2.328 Å, which are longer than the corresponding covalent bond distance but shorter than the sum of the van der Waals radii of H and X atoms [42, 43]. These facts imply that H-bonds between methanol and anions have been formed in these complexes, as confirmed by the substantial red shifts of the O-H stretch vibrational frequencies. Figure 2 compares the calculated IR spectrum of the free methanol molecule with ones of four M-A⁻ complexes. The O-H normal mode occurs at 3838.65 cm⁻¹ in free methanol molecule, however, it shifts to 3305.6 cm⁻¹ in M-Cl⁻, 3401.62 cm⁻¹ in M-Br⁻, 3586.97 cm⁻¹ in M-BF₄⁻, and 3720.11 cm⁻¹ in M-PF₆⁻. This observation indicates the O-H bond is becoming weaker due to the formation of H-O···X H-bonds. The red shift decreases with increasing the anion size, indicating the H-O···X H-bond strength in the complexes decreases in the order of M-Cl⁻ > M-Br⁻ > M-BF₄⁻ > M-PF₆⁻. Furthermore, as seen in Fig. 1, for complexes M-BF₄⁻ and M-PF₆⁻, there also exist C-H···F H-bond interactions. However, calculated C-H···F H-bonds are much longer than O-H···X H-bonds, suggesting the C-H···F H-bonds play a less important role for stabilizing the methanol-anion complexes than the O-H···X H-bonds. It is worth noting that in an early study, Wang et al. [44] found that the stable structure of PF₆⁻ with H₂O molecule cannot be obtained due to the weak interaction between them. In contrast, our calculations confirm that methanol-PF₆⁻ complex is a stationary point without any imaginary

**Fig. 2** Calculated infrared spectra for methanol and methanol-anion complexes at the B3LYP/6-31++G (d,p) level of theory

frequency. This explains why methanol has a good solubility for the hydrophobic hexafluorophosphate-based ionic liquids.

To better understand the methanol-anion interaction, we examine the second-order perturbation stabilization energy, $E(2)$, of the interaction between donor orbital (i) and acceptor orbital (j) using the perturbation theory [45, 46], which is defined as

$$E(2) = q_i \cdot \frac{F(i,j)^2}{E(j) - E(i)},$$

Where q_i is the donor orbital occupation, $E(i)$, $E(j)$ are the diagonal elements (orbital energies), and $F(i,j)$ is the off-diagonal NBO Fock matrix element. The larger the $E(2)$ value is, the stronger the orbital interaction is. The calculated results show that the interaction between the lone pair of the X atom in anions (LP_X) and the antibonding orbital of the O-H bond in methanol (σ_{O-H}^*) dominates over the interaction of methanol and anions. Such $LP_X - \sigma_{O-H}^*$ interaction results in the electron transfer from the proton acceptor (LP_X) to the donor (σ_{O-H}^*) and the O-H···X H-bond formation and hence stabilizing the M-A⁻ complexes. The $E(2)$ values for the $LP_X - \sigma_{O-H}^*$ interaction in the M-Cl⁻, M-Br⁻, M-BF₄⁻ and M-PF₆⁻ complexes are 24.24, 18.88, 15.21 and 10.04 kcal mol⁻¹, and the occupancy on the σ_{O-H}^* orbital in these four complexes increase by 0.0656, 0.0558, 0.0246 and 0.0163e compared to that in the isolate methanol molecule (0.0056e). In contrast, indicating the electron transfer occurs from the proton acceptor (LP_X) to the donor (σ_{O-H}^*). These results confirm again that the H-bond strength in the methanol-anion complexes follows the order: M-Cl⁻ > M-Br⁻ > M-BF₄⁻ > M-PF₆⁻. This order is in agreement with the observed solubility of alcohol in ILs

based on Cl^- , Br^- , BF_4^- and PF_6^- anions [47–51], suggesting that the $\text{O-H}\cdots\text{X}$ H-bond plays a predominant factor for the miscibility between ILs and alcohols.

For a binary system, the interaction energy between two components is an important index for evaluating the stability of a complex. As shown in Table 1, the BSSE-corrected interaction energies are 14.34, 12.16, 9.77 and 7.57 kcal mol^{-1} for the M-Cl^- , M-Br^- , M-BF_4^- and M-PF_6^- complexes, respectively, which are within the range of the moderate H-bond energies (4–15 kcal mol^{-1}) [52]. As expected, the interaction energy decreases with increasing the anion size or the decreasing $\text{O-H}\cdots\text{X}$ H-bond strength. The relative stability of these M-A^- complexes can also be understood by performing the frontier molecular orbital (FMO) analysis. In the framework of the FMO theory, the stability of a binary complex is inversely proportional to the HOMO-LUMO difference between the highest occupied molecular orbital (HOMO) of one molecule and the lowest unoccupied molecular orbital (LUMO) of another molecule. A small HOMO-LUMO difference implies a large orbital overlap between two molecules, and thus leads to a strong interaction between them and hence a stable structure. Calculated data for the HOMO and LUMO energies of methanol and anions are shown in Table 2. The negative eigenvalues of the HOMO energy levels for these species are attributed to their high chemical stabilities. Clearly, the energy differences between the HOMOs of anions and the LUMO of methanol are smaller than those between the LUMOs of anions and the HOMO of methanol. According to the FOM theory, the smaller one will determine the reactivities of methanol with anions. So the main FMO interaction may occur between the HOMO of anions and the LUMO of methanol. The $\text{HOMO}_A\text{-LUMO}_M$ difference decreases with the increasing anion size, indicating a decreasing interaction between methanol and anions and hence the reducing stabilities of the M-A^- complexes, i.e. $\text{M-Cl}^- > \text{M-Br}^- > \text{M-BF}_4^- > \text{M-PF}_6^-$.

The interaction of methanol with $[\text{emim}]^+$ cation

Experimental results¹⁹ show that solubility of alcohols in ILs also remarkably depends on the choice of cation in ILs. To ascertain the role of cation in the solubility of alcohol in

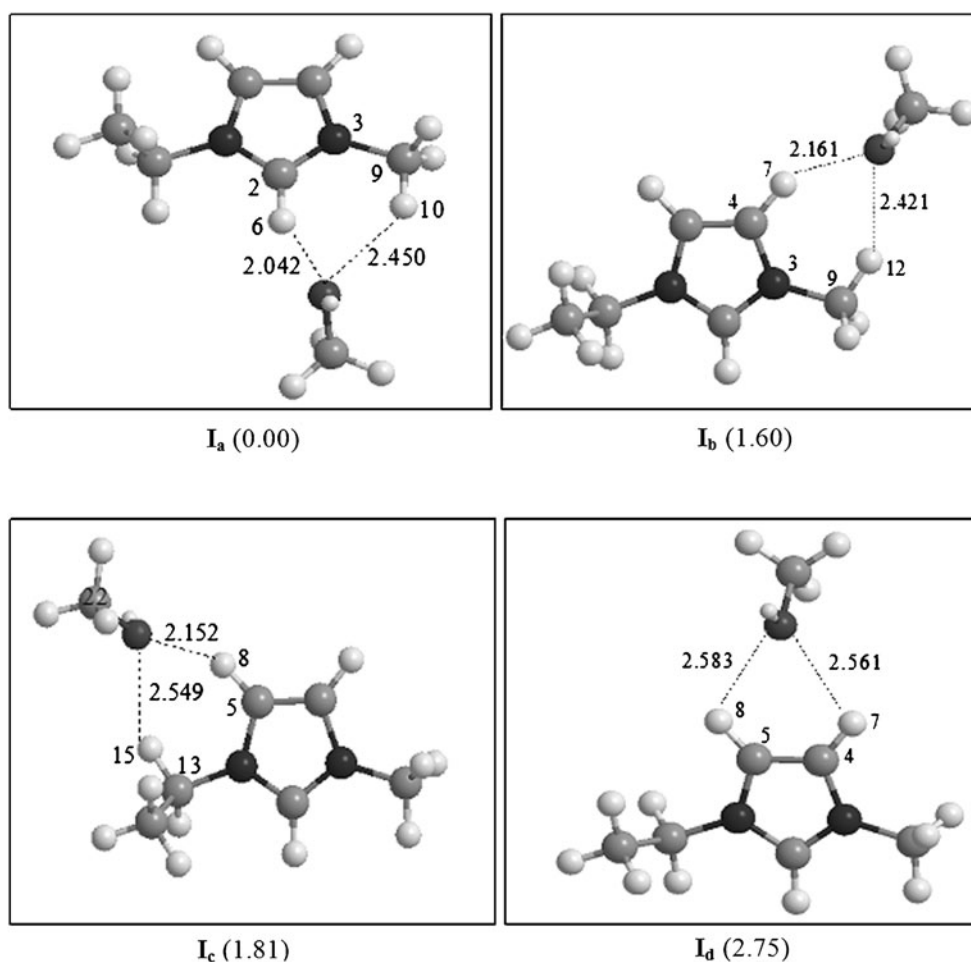
ILs, as a example, we study the methanol- $[\text{emim}]^+$ (M-E^+) interaction. Figure 3 shows the four most stable geometries for the methanol- $[\text{emim}]^+$ complex ($\mathbf{I}_a\text{-I}_d$). Clearly, the $\text{C-H}\cdots\text{O}$ H-bonds between methanol and $[\text{emim}]^+$ exist universally in all four M-E^+ geometries. In contrast to the normal or classical H-bond in methanol-anion systems, the H-bond in the methanol-cation system involves the furcate H-bonds. In these geometries, the hydroxyl O atom of methanol is almost coplanar with the imidazolium ring. Structure \mathbf{I}_a is the most stable, where methanol is located in front of $[\text{emim}]^+$ and near the methyl group, forming $\text{C2-H6}\cdots\text{O}$ and $\text{C9-H10}\cdots\text{O}$ H-bonds. Two $\text{O}\cdots\text{H}$ distances $\text{C2-H6}\cdots\text{O}$ and $\text{C9-H10}\cdots\text{O}$ in the furcated H-bond are 2.042 and 2.450 Å, respectively, indicating that the former is dominant. This can be attributed to the strongest acidity of H6 atom [53]. Structures \mathbf{I}_b and \mathbf{I}_c are less stable in energy than \mathbf{I}_a by 1.60 and 1.81 kcal mol^{-1} , where the methanol is located on the methyl side (\mathbf{I}_b) and the ethyl side (\mathbf{I}_c) at the rear of the imidazolium ring, respectively. Structure \mathbf{I}_d lies above \mathbf{I}_a in energy by 2.75 kcal mol^{-1} , where the hydroxyl O atom interactions with two H atoms on imidazolium ring to form a relatively weaker furcated H-bond, as indicated by the $\text{O}\cdots\text{H7}$ and $\text{O}\cdots\text{H8}$ distances (2.561 and 2.583 Å). The largest energy difference for the four structures shown in Fig. 2 is less than 3 kcal mol^{-1} , indicating that they may co-exist in a state of thermal equilibrium at room temperature. The calculated interaction energies of methanol with $[\text{emim}]^+$ in all four geometries are shown in Table 1 again. These values are smaller than those of methanol with mono-atomic anion systems, M-Cl^- , and M-Br^- , but comparable with ones with multy-atomic anion systems, M-BF_4^- and M-PF_6^- .

The calculated stabilization energies $E(2)$ of the orbital interactions between methanol and $[\text{emim}]^+$ show that the $\text{LP}_O\text{-}\sigma_{\text{C-H}}^*$ interactions are decisive for the methanol-cation system. The $E(2)$ values are 10.57 and 0.90 kcal mol^{-1} for the $\text{LP}_O\text{-}\sigma_{\text{C2-H6}}^*$ and $\text{LP}_O\text{-}\sigma_{\text{C9-H10}}^*$ interactions for structure \mathbf{I}_a , 6.38 and 2.29 kcal mol^{-1} for the $\text{LP}_O\text{-}\sigma_{\text{C4-H7}}^*$ and $\text{LP}_O\text{-}\sigma_{\text{C9-H12}}^*$ interactions for structure \mathbf{I}_b , 6.98 and 1.39 kcal mol^{-1} for the $\text{LP}_O\text{-}\sigma_{\text{C5-H8}}^*$ and $\text{LP}_O\text{-}\sigma_{\text{C13-H15}}^*$ interactions for structure \mathbf{I}_c , as well as 0.7 and 0.62 kcal mol^{-1} for the $\text{LP}_O\text{-}\sigma_{\text{C4-H7}}^*$ and $\text{LP}_O\text{-}\sigma_{\text{C5-H8}}^*$ interactions for structure \mathbf{I}_d , respectively. Clearly, the H-

Table 2 Energy eigenvalues of the HOMOs and LUMOs of methanol (M) and various anions ($\text{A}=\text{Cl}^-$, Br^- , BF_4^- , and PF_6^-) calculated at the B3LYP/6-31++G(d,p) level of theory (in eV)

Species	E_{HOMO}	E_{LUMO}	$E_{\text{HOMO}_A} - E_{\text{LUMO}_M}$	$E_{\text{HOMO}_M} - E_{\text{LUMO}_A}$
Methanol	-7.687	-3.646	—	—
Cl^-	-0.769	5.893	2.877	13.580
Br^-	-0.860	4.815	2.786	12.502
BF_4^-	-4.526	4.394	-0.88	12.081
PF_6^-	-5.400	4.076	-1.754	11.763

Fig. 3 The optimized geometries for the methanol-[emim]⁺ complexes at the B3LYP/6-31++G (d,p) level of theory. Bond lengths are in Å. The values in parentheses are the relative energies (kcal mol⁻¹)



bonds of the hydroxyl O atom in methanol with the H atoms on the imidazolium ring are generally stronger than those with the H atoms on the alkyl chain, implying that the C^{ring}-H...O H-bonds play a more important role for stabilizing the M-E⁺ complex. Furthermore, we find that the C^{ring}-H...O H-bond between methanol and [emim]⁺ is weaker than those of methanol with anions Cl⁻, Br⁻, but similar to that of methanol with BF₄⁻ and PF₆⁻ anion.

Interactions of methanol with [emim]⁺Cl⁻ ion pair

In fact, there exist no isolate anions and cations in the realistic ILs, where the anions and cations connect each other by H-bonds to form an extended network. In order to obtain more valuable information for the interaction of alcohol with ILs, we further study the interaction between methanol and ion pair. Imidazolium chloride is the most widely used ionic liquid in experiments, so we chose [emim]⁺Cl⁻ as a representative of the ion pairs for study. Figure 4 shows the five most stable ion-pair conformers (**II_a**-**II_e**) with their relative energies. In these ion pair structures, Cl⁻ anion is generally located on the same plane with the imidazolium ring, except structure **II_c**,

with Cl⁻ anion positioned above the imidazolium ring, and forms stronger H-bonds with the H atoms on imidazolium ring and weaker H-bonds with H atoms on the alkyl groups. Similar to the methanol-cation system, the H-bonds in the ion pair are also furcate in form. Structures **II_a**, **II_b** and **II_c**, (where Cl⁻ anion is near the H6 atom having the strongest acidity) are more stable in energy by ~7 kcal mol⁻¹ than structures **II_d** and **II_e**, where Cl⁻ is far from the H6 atom. These results are in good agreement with the previous reports [54–56].

To obtain stable geometries of the methanol-[emim]⁺Cl⁻ system, methanol was initially put at all possible sites around these [emim]⁺Cl⁻ ion pairs. In Fig. 5, we show a dozen low-energy structures with their relative energies. These structures can be divided into two catalogues: structures **III_a**-**III_e** and structures **III_f**-**III_m**. In the former, where the O atom of methanol and Cl⁻ anion remain almost coplanar with the imidazolium ring, and appear simultaneously near the C2-H6 fragment, generally contain the interactions among methanol, anion and cation three species. Thus structures are energetically more favorable since they involve more H-bonds. While in the latter,

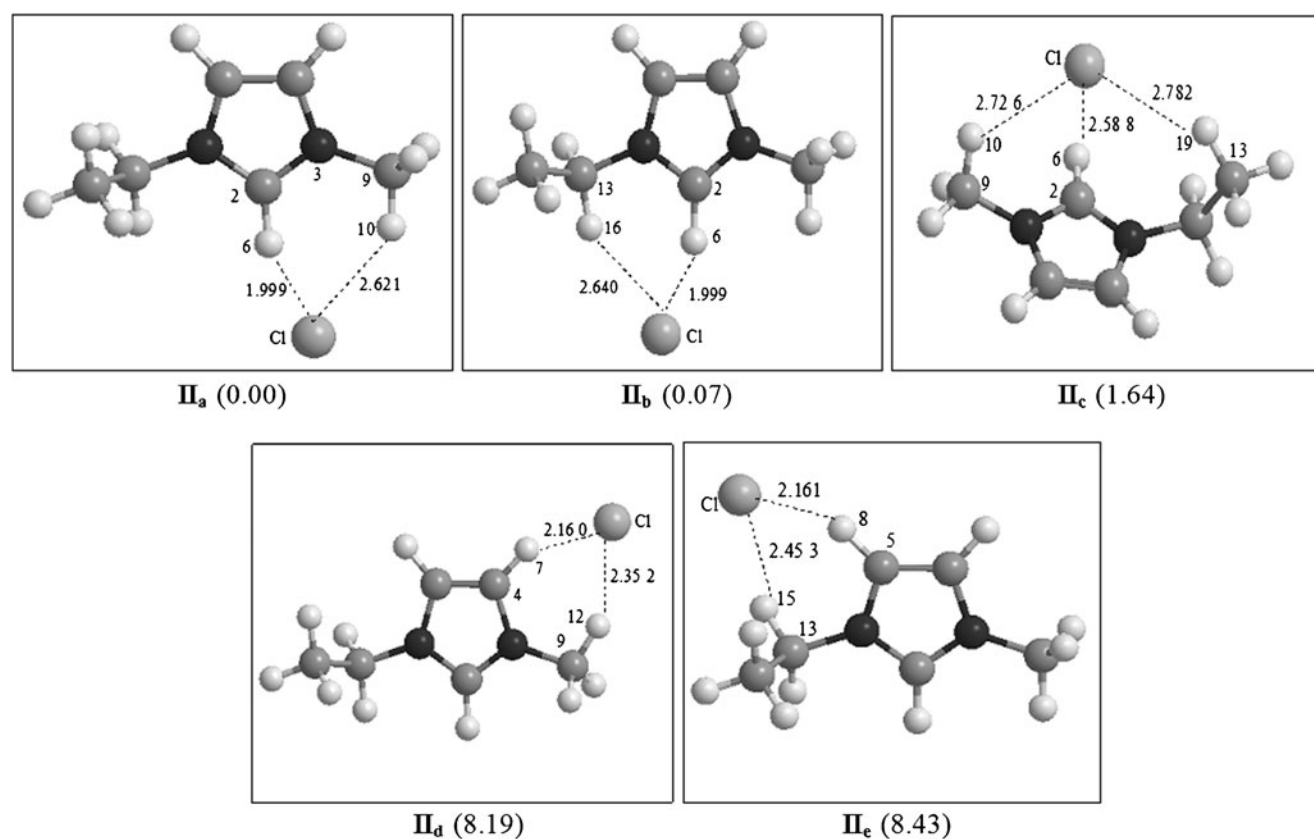


Fig. 4 The optimized geometries of the $[\text{emim}]^+\text{Cl}^-$ ion pair at the B3LYP/6-31++G(d,p) level of theory. Bond lengths are in Å. The values in parentheses are the relative energies (kcal mol^{-1})

structures **III_f**–**III_m**, there is no interaction between methanol and Cl^- anion, so they are less favorable in energy by 7–9 kcal mol^{-1} .

As observed from all these stable geometries of the M- $[\text{emim}]^+\text{Cl}^-$ complexes, the addition of methanol notably disturbs the H-bond interactions between cation and anion. In comparison with the isolated ion pair structures, most of C–H... Cl^- distances between cation and anion in structures **III_a**–**III_m** are obviously lengthened, indicating that the addition of methanol in ILs reduces the H-bond interactions of anion with cation, and thus may lead to the decrease of density and viscosity of ILs. In fact, such phenomenon has been observed by some experiments [57, 58]. The calculated interaction energies between methanol and $[\text{emim}]^+\text{Cl}^-$ ion pair for the four most stable geometries (**III_a**–**III_e**) are shown in Table 1, which are in a range of 9.09–12.04 kcal mol^{-1} .

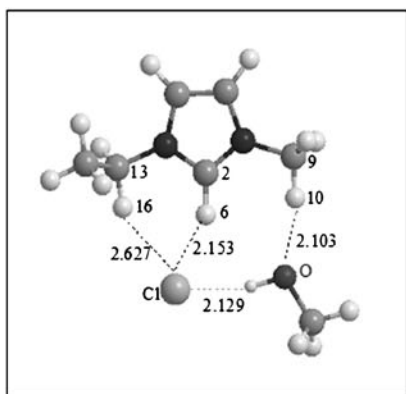
We now see the geometry of the energetically most favorable structure, **III_a**, in detail. This structure can be regarded as a result of attaching the methanol molecule to the ion pair **II_b**. The methanol molecule in **III_a** interacts with both the Cl^- anion and $[\text{emim}]^+$ cation via a $\text{Cl}\cdots\text{H}-\text{O}$ H-bond and a $\text{H}\cdots\text{O}-\text{H}$ H-bond, respectively. The formation of these two new H-bonds may be mainly responsible for the miscibility of imidazolium-based ILs with methanol,

which reduces the strong electrostatic force between the cation and anion, making good miscibility between imidazolium chlorine IL and methanol.

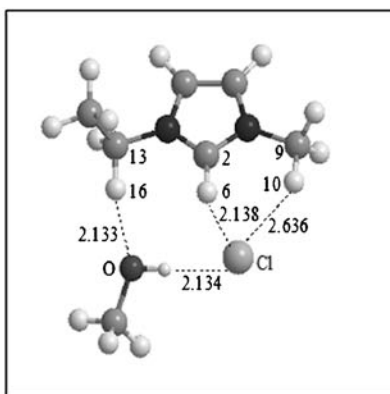
Conclusions

In this paper, we have carried out a DFT study on the interactions of methanol with the anions, cation, and ion pair of several methylimidazolium salt ILs, $[\text{emim}]^+\text{A}^-$ ($\text{A}=\text{Cl}^-$, Br^- , BF_4^- , and PF_6^-). It is found that H-bonds universally exist in these systems, which may play a decisive role for the stability and miscibility of the IL-methanol binary systems. The molecule-anion interaction mainly works via the electron transfer from the lone pair of the halogen atom in anions to the antibonding orbital of the O–H bond in methanol, and this interaction weakens with increasing anion size. In contrast, the molecule- $[\text{emim}]^+$ contact dominantly occurs by the orbital interaction

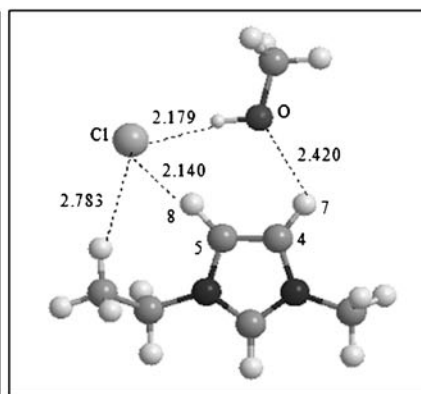
Fig. 5 The optimized geometries for the complexes of the $[\text{emim}]^+\text{Cl}^-$ ion pair with methanol at the B3LYP/6-31++G(d,p) level of theory. Bond lengths are in Å. The values in parentheses are the relative energies (kcal mol^{-1})



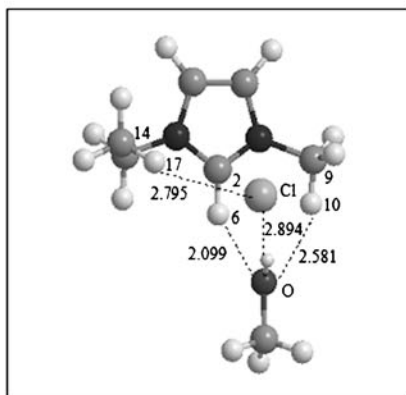
III_a (0.00)



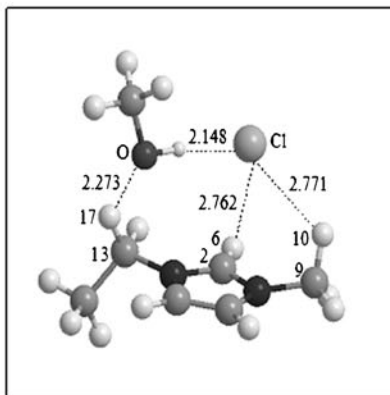
III_b (0.24)



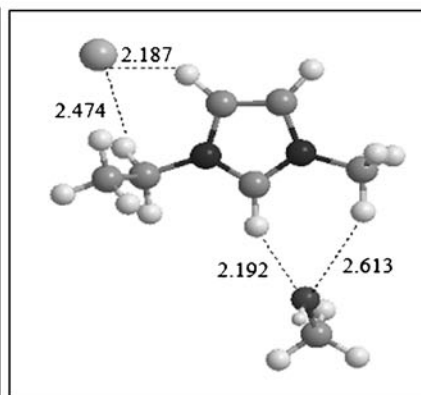
III_c (1.86)



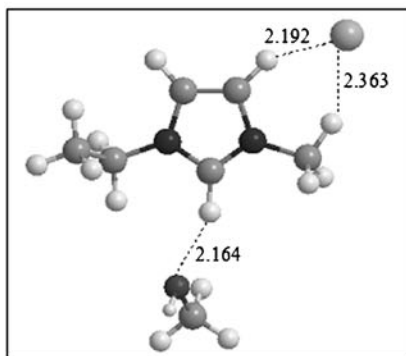
III_d (1.95)



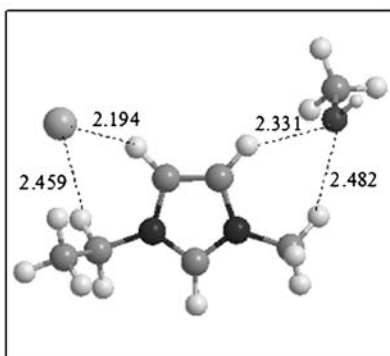
III_e (3.58)



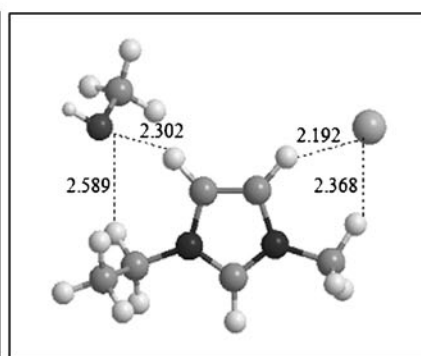
III_f (7.06)



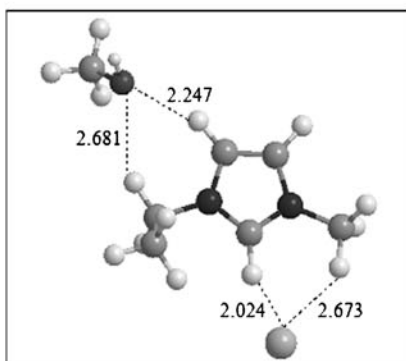
III_h (7.17)



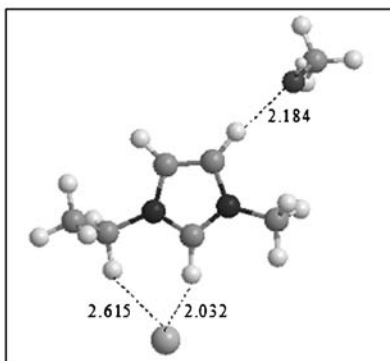
III_i (8.14)



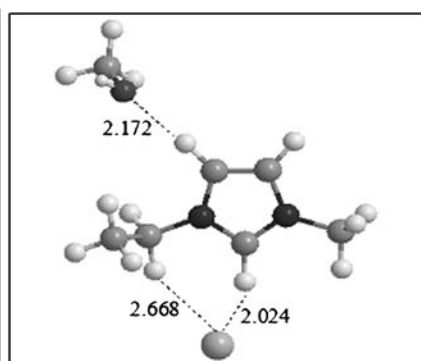
III_j (8.23)



III_k (8.63)



III_l (8.74)



III_m (8.82)

between the lone pair of the hydroxyl oxygen in methanol and the antibonding orbital of the C2-H6 on the cationic imidazolium ring. Cl^- and Br^- anions present slightly stronger interaction with the methanol molecule than $[\text{emim}]^+$ cation, while the interactions of BF_4^- and PF_6^- anions with the methanol molecule are comparable to that of the cation. The present results support and rationalize the fact that solubility of alcohol in ILs di-alkylimidazolium-based ion liquids follows the order: $[\text{emim}]^+\text{Cl}^- > [\text{emim}]^+\text{Br}^- > [\text{emim}]^+\text{BF}_4^- > [\text{emim}]^+\text{PF}_6^-$. The calculated data also show that addition of methanol into the ILs notably disturbs the H-bond interactions between cation and anion, which would affect the physicochemical properties of ILs.

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