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Study On The Structures And Interactions Binary System Composed By The Ionic Liquids [Bmim][Ala] and Water /Methanol Using The Vibrational Spectra

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Abstract

The molecular geometry and vibrational frequencies of the Amino acid ILs 1-butyl-3-methylimidazolium α-aminopropionic acid salt ([bmim][Ala]), [bmim][Ala] and water /Methanol were investigated by the density functional theory (DFT) at the hybrid Becke 3-Lee-Yang-Parr (B3LYP)/6-311++G** level. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) of the [bmim][Ala], [bmim][Ala] and water /Methanol have been recorded at different concentrations. The observed vibrational spectra have been resolved and assigned in detail by comparison to the calculated results. The results indicate that the vibrational frequencies obtained by DFT (B3LYP) are in good agreement with the experiment results. The forms and the effect of the hydrogen bond that exist between [bmim][Ala] and water/Methanol have been investigated from the point view of the interaction.

Keywords: 1-butyl-3-methylimidazolium α-aminopropionic acid salt; Density functional theory; Water; Methanol; Vibrational Spectra

Introduction

In 2005, Hiroyuki Ohno and his coworkers developed a series of novel amino acid ionic liquids (AAILs) coupling the imidazolium cation with 20 different natural amino acids [1,2]. So that the AAILs become one of the most rapidly growing new research areas of ionic liquids (ILs) [3-5]. Its known that ionic liquids have some unique physical and chemical properties which including the negligibly small vapor pressure, high thermal stability, high ionic conductivity, and wide range of solubility [6-10]. As a kind of "green" solvent,the ILs have the potential to replace the traditional industrial molecular solvents [11-13].

Except that the unique physical and chemical properties that mentioned above, AAILs also possess the great merit of low costs, biodegradable, and a variety of sources from nature [14,15]. Further functional design for AAILs is also expected carboxyl group or various functional groups on the side chain of the amino acids. Extensive experimental studies have been performed on ILs and AAILs [16-18]. However, it is far from enough to summarize a general rule that can predict the physicochemical properties of the ILs for a specific application [19]. Because the features that control the physicochemical properties of ILs remain poorly understood. Thus, it is essential to understand the intermolecular forces and the IL's structure for the development of special and tunable properties of ILs. A set of theoretical methods have now been used to study ILs. Traditional molecular dynamics simulations, first-principles molecular dynamics simulations and electronic structure methods have been applied to ILs to obtain useful information on ILs [19,20].

The presence of water or Methanol in ionic liquids has a large effect on physical properties. There are a number of papers, which have studied the physical properties of binary systems of ionic liquids [21,22]. However, few reports related to the structures and the AAILs mixtures interactions of AAILs at theoretical level have been found, the mechanism of the cation–anion interaction for AAILs has not been fully understood. It is necessary to investigate these interaction systems systematically by theoretical or experimental methods. Among

various experimental techniques, infrared spectroscopy is a convenient and effective approach for the study of H-bonding interactions at the molecular level. In this paper, the structures and interactions of the [bmim][Ala], [bmim][Ala] and water /Methanol have been systematically studied by density functional theory, the ATR-IR spectra of the [bmim][Ala], [bmim][Ala] and water /Methanol were investigated. The results will be helpful for understanding of these AAILs from the perspective of structure and the AAILs mixtures interactions, and it could provide some important information for the continuous exploitation and application of AAILs.

Experimental Section

Sample preparation

The Amino acid ILs [bmim][Ala] was purchased from Sigma Co.Ltd, which was used after drying under vacuum at 323 K. The samples were analyzed by Karl Fisher titration and showed a mass% of water lower than 1×10^{-4} for [bmim][Ala]. Samples of [bmim][Ala]-Water /[bmim][Ala]-Methanol solutions for ATR-IR, measurements were prepared by weighing dried ionic liquid and doubly distilled water ,Methanol (AR, mass fraction>0.99)

The ATR-IR spectroscopy

ATR-IR measurements with a single reflectance on [bmim][Ala]-H_2O solutions at x_w = 0.29, 0.45,0.56, 0.63, and 0.68 were made at a room temperature by using a PerkinElmer Spectrum 100 FT-IR spectrometer equipped with an attenuated total reflectance

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(ATR) cell with 16 scans at 2 cm^{-1} resolution. The mole fractions of Methanol in [bmim][Ala]-Methanol mixtures are 0.16, 0.28,0.36, 0.42, and 0.49.

Calculations

DFT [23-25] calculations were carried out using Gaussian 03 [26] program package. Natural bond orbital (NBO) [27,28] analysis and atoms in molecules (AIM) [29] analysis were both used to analyze the nature of the [bmim][Ala], [bmim][Ala] and water /Methanol interactions at the B3LYP/6-311++G** level [30-32]. All calculations were performed using Gaussian 03 program , except that AIM calculation was performed by AIM 2000 package [33] and used the B3LYP/6-311++G** results as input. To confirm that full geometry optimizations and normal frequency analyses were carried out at each optimized geometry. The normal mode animations were visualized using the Gauss-view program. Normal coordinate analysis was performed to obtain a detailed assignment of the normal vibrational modes.

Results and Discussion

Geometrical structure

A series of stable ion pairs had been optimized. These ion pairs are used to detect the interaction between the ion pairs and the water molecule, the ion pairs and the Methanol molecule.

The [bmim][Ala]-Methanol binary system was optimized, and six stable configurations obtained with no imaginary frequencies are presented in Figure1 The selected geometrical parameters of these configurations are showed in Figure 1.

Most of the early investigations suggested that the miscibility of an ionic liquid with water is mostly determined by the associated anion. The [bmim][Ala]-H$_2$O binary system was optimized, and seven stable configurations obtained with no imaginary frequencies are presented in Figure 2. The selected geometrical parameters of these configurations are showed in Figure 2.

The intermolecular and intramolecular H bonds were both characterized by the bond length and bond angle   in Figure 1 and Figure 2, where a H bond will be indicated if the C–H···O distance is less than the van der Waals H···O distance of 2.72 Å and the C–H···O angle is greater than 90° [34].

Further comparison in configurations **a1–a6** found that there are three main types of structures. Methanol molecule only has interaction with the anion of ionic liquid, as **a6**. Methanol molecule only has interaction with the cation of ionic liquid, as **a4**. Methanol molecule has interaction with the cation–anion of ionic liquid, as **a1, a2, a3, a5**. Similarly, [bmim][Ala]-H$_2$O also has three main types of structures, Water molecule only has interaction with the anion of ionic liquid , like **b2,b7**. Water molecule only has interaction with the cation of ionic liquid, as **b4, b6**. Water molecule has interaction with the cation–anion of ionic liquid, as **b1, b3, b5**.

Generally, the total energy will decrease when two molecules interact. The decreased energy is called interaction energy, or binding energy. The stability of complex is related to interaction energy tightly. The basis set superposition error (BSSE) is calculated with the counterpoise procedure method advanced by Boys and Bernardi [35]. Table 1 shows the interaction energies for [bmim]

[Ala]-Methanol/[bmim][Ala]-H$_2$O complexes, ΔE_{AAIL}, including the BSSE energy [36], ΔEcp, and the interaction energy corrected by BSSE ΔE_M.

[a] The interaction energies of the ion pairs, [b]The interaction energies of the ion pairs corrected by BSSE $\Delta E_M =\Delta E$cp $-\Delta E_{AAIL}$

Configuration **a1** and **a3**, **b1** and **b5** with the interaction energy of -450.52 and -452.14 kJ/mol, -451.27 and -452.19 kJ/mol (BSSE corrected) were predicted to be the more stable configurations. The intensity orders of the interactions for the configurations are **a3 = a1 > a2 = a5 = a6> a4, b5= b1 =b3>b2 = b7> b4=b6**.

Table 1 lists the interaction energies of these complexes. Compared with the interaction energies of the anion-cation, water complexes, the interaction energies of these ion pair-water complexes are smaller. The interaction energies of the complexes **a1**, **a3**, **b1**, **b5** are 53.62, 56.79, 54.35 and 57.77 kJ/mol (Table 1), respectively. Addition of water or Methanol have a strong impact on the structure and interaction of cation-anion of [bmim][Ala] . The smaller the interaction energies are, the lower the effect on the structure.

Natural bond orbital analysis. The electronic population was studied by NBO analysis, which transforms the canonical delocalized Hartree-Fock molecular orbital into, localized orbital that are closely tied to chemical bonding concepts. Table 2 shows the delocalization energies corresponding to the most important orbital interactions together with the occupancy of the acceptor orbital and the orbital energy differences.

BD*, antibonding orbital; LP, lone pair; RY* empty atomic orbital out of valance orbital

It can be seen that there are some main orbital interactions LP(O)→BD*(O–H) , LP(O)→BD*(C–H) in these complexes. The NBO analysis has revealed that the LP(O)→BD*(C–H) interactions give the strongest stabilization to these complexes and strengthen the intermolecular H···O interactions.

AIM analysis: The bond properties between each pair of atoms were systemically analyzed using atoms in molecules (AIM) theory. To gain a deeper insight into the nature of interactions, AIM calculations were undertaken at the B3LYP/6-311++G** level of theory. It is used to analyze the bonding characteristic, which is based on a topological analysis of electron density (ρ_c) and Laplacian ($\nabla^2\rho_c$) [37]. ρ_c is used to describe the strength of a bond, with stronger bond associated with larger ρ_c value. $\nabla^2\rho_c$ describes the characteristic of the bond. As $\nabla^2\rho_c < 0$, it is named as the covalent bond. As $\nabla 2\rho c >0$, it refers to a closed-shell interaction and characteristic of ionic bond, hydrogen bond or van der Waals interaction. As $\nabla 2\rho c\approx 0$, it forms faintish chemical bond.

From the values listed in Table 3, it can be concluded that the interactions between the cation and the anion, AAIL and Methanol/ Water, which were marked by the dot line were all close shell systems (H bonding interaction), for their values of the $\nabla^2\rho_c$ all fall in the range of normal H-bond (0.020~0.139 au), and ρc is no more than 0.20 au. While for the H38-O39 in **a**, O38-H39 in **b** etc were all $\nabla^2\rho_c < 0$, and the corresponding ρc were all is greater than 0.20 au, they were characterized by covalent bonds.

On the basis of the AIM topological analysis, the H··O and H···N interactions occupy bigger proportion for the complex, The H bonds were formed between the [bmim][Ala] and Methanol molecule, [bmim][Ala] and Water molecule.
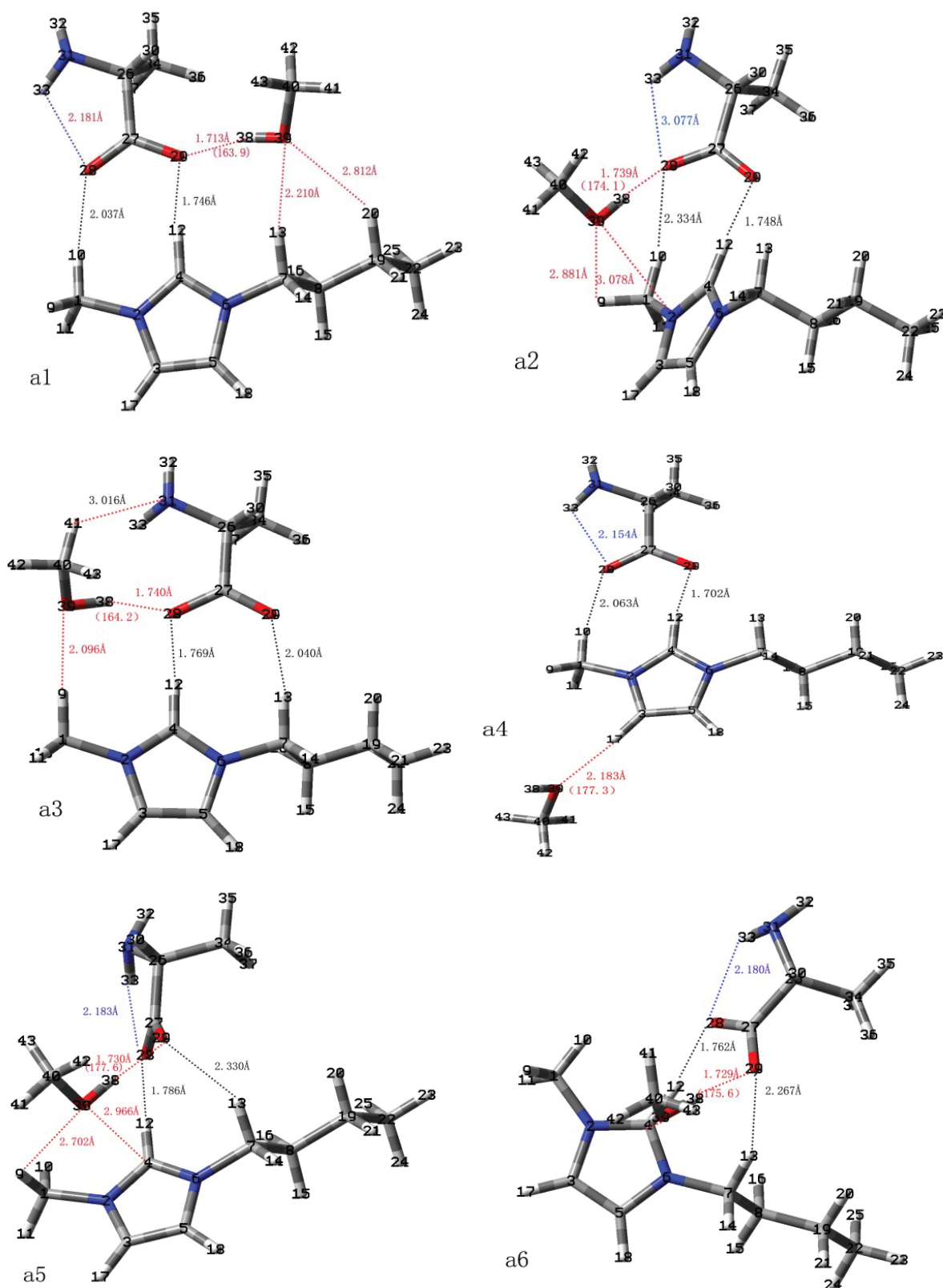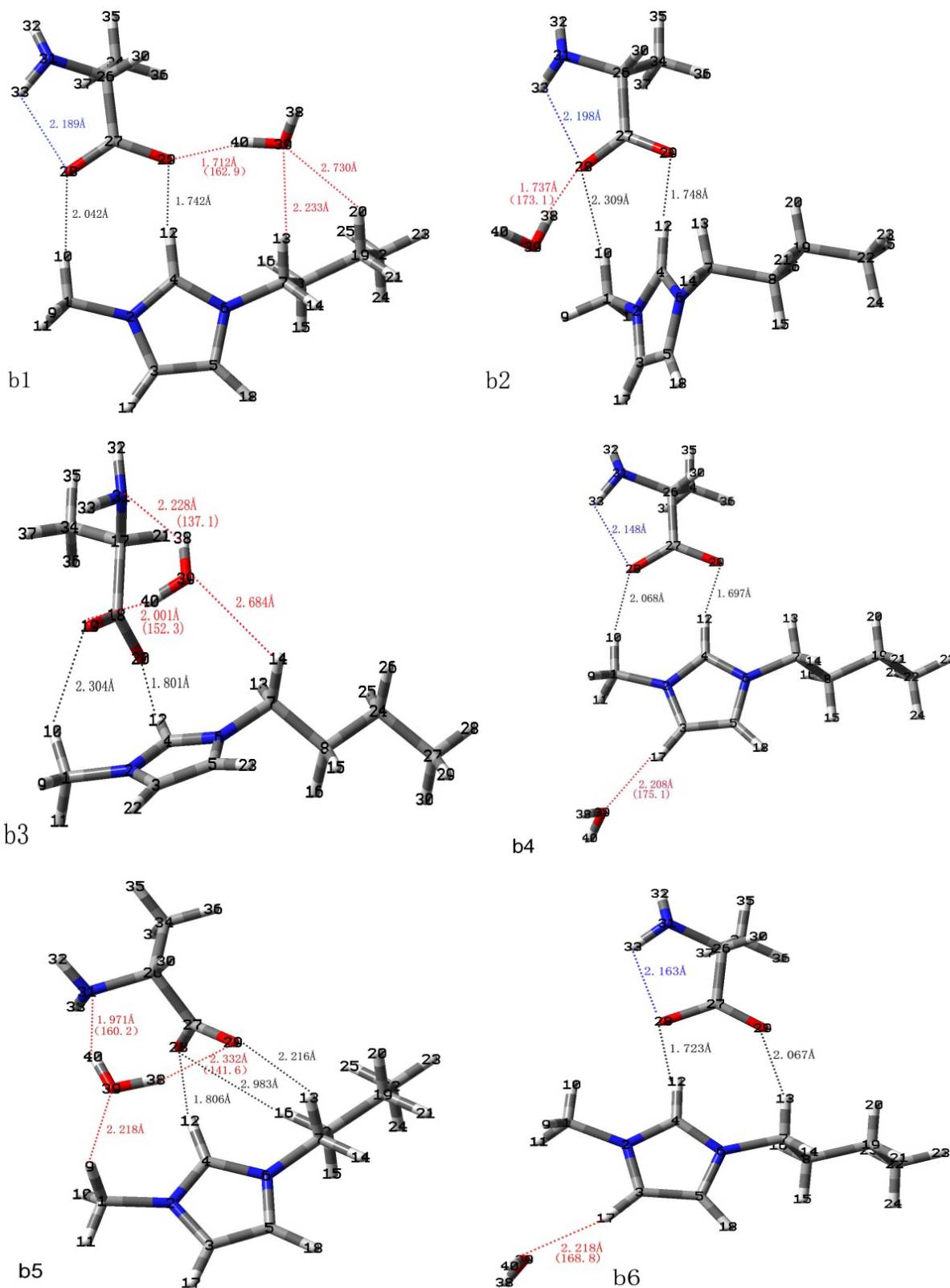
Figure 1: Optimized structures of [bmim][Ala]-Methanol (B3LYP/6-311++G**): a1, a2, a3, a4,a5,a6. Hydrogen bonds are indicated by dotted lines and the corresponding lengths (Å) and angles (deg) (in parentheses) are given.
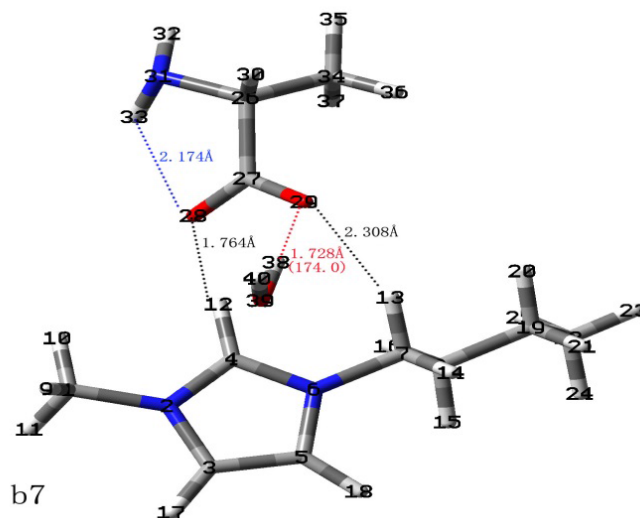
Figure 2: Optimized structures of [bmim][Ala]-H2O (B3LYP/6-311++G**): b1, b2, b3, b4,b5,b6,b7. Hydrogen bonds are indicated by dotted lines and the corresponding lengths (Å) and angles (deg) (in parentheses) are given.

	B3LYP/6-311++G** B3LYP/6-311++G**						
Complex	ΔEcp	ΔE_{AAIL}[a]	ΔE_M[b]	Complex	ΔEcp	ΔE_{AAIL}	ΔE_M
a1	-450.52	-396.90	-53.62	b1	-451.27	-396.92	-54.35
a2	-441.74	-392.42	-49.31	b2	-443.03	-392.57	-50.45
a3	-452.14	-395.35	-56.79	b3	-447.05	-396.18	-50.87
a4	-412.99	-398.93	-14.07	b4	-411.33	-398.99	-12.34
a5	-440.82	-385.99	-54.83	b5	-452.19	-394.42	-57.77
a6	-438.73	-388.84	-49.88	b6	-409.43	-396.14	-13.29
				b7	-439.79	-388.19	-51.60

Table 1: Interaction energies of complexes ΔE_{CP} (all values in kJ.mol^{-1}).

Complex	Donor	Acceptor	E(2)kJ/mol	Complex	Donor	Acceptor	E(2)kJ/mol
a1	LP (1) O29	BD*(1)O38 - H39	**58.42**	b1	LP(1) O29	BD*(1)O39 - H40	**52.98**
	LP (2) O29	BD*(1)O38 - H39	14.76		LP(2) O29	BD*(1)O39 - H40	14.55
	LP (2) O39	BD*(1)C7 - H13	9.95		LP(2) O39	BD*(1)C7 - H13	14.68
	LP (1) O39	BD*(1)C7 - H13	6.77	b2	LP(1) O28	BD*(1)O39 - H38	24.38
a2	LP (2) O28	BD*(1)O38 - H39	30.65		LP(2) O28	BD*(1)O39 - H38	30.11
	LP (3) O28	BD*(1)O38 - H39	29.90		LP(3) O28	BD*(1)O39 - H38	29.27
	LP (1) O28	BD*(1)O38 - H39	28.06	b3	LP(1) O28	BD*(1)O39 - H40	4.10
a3	LP (1) O39	BD*(1)C1 - H9	11.42		LP(3) O28	BD*(1)O39 - H40	22.08
	LP (3) O28	BD*(1)O38 - H39	26.01		LP(1) N31	BD*(1)O39 - H38	16.27
	LP (1) O28	BD*(1)O38 - H39	42.99	b4	LP(2) O39	BD*(1)C3 - H17	17.02
	LP (2) O39	BD*(1)C1 - H9	15.26	b5	LP(2) O39	BD*(1)C1 - H9	16.43
a4	LP (1) O39	BD*(1)C3 - H22	17.65		LP(1) N31	BD*(1)O39 - H38	49.55
a5	LP (3) O29	BD*(1)O38 - H39	35.59	b6	LP(2) O39	BD*(1)C3 - H17	16.73
	LP (1) O29	BD*(1)O38 - H39	27.10	b7	LP(1) O29	BD*(1)O39 - H38	23.92
	LP (2) O29	BD*(1)O38 - H39	30.82		LP(2) O29	BD*(1)O39 - H38	33.45
a6	LP (1) O29	BD*(1)O38 - H39	26.89		LP(3) O28	BD*(1)O39 - H38	31.32
	LP (2) O29	BD*(1)O38 - H39	35.75				
	LP (3) O29	BD*(1)O38 - H39	31.20				

Table 2: NBO interacting and the corresponding stable energies (kJ.mol-1).

Complex	Bond	ρ_C	$\nabla^2\rho_C$	Complex	Bond	ρ_C	$\nabla^2\rho_C$
a1	O28- H10	0.02227	0.07613	b2	O28-H10	0.013429	0.04140
	O29-H12	0.04376	0.12552		O29-H12	0.043954	0.12421
	O29-H38	0.04089	0.14173		O28-H38	0.039499	0.12972
	O39-H13	0.01561	0.05109		O28-H33	0.019211	0.08319
	O39-H25	0.00514	0.01650	b3	O28-H10	0.014167	0.04352
a2	O28-H38	0.03953	0.13009		O29-H12	0.038447	0.11815
	O39-N2	0.00731	0.02675		O28-H40	0.022751	0.07821
	O39-H9	0.00599	0.02544		N32- H38	0.015332	0.05681
a3	O28-H38	0.03876	0.13422		O28-H33	0.018268	0.05254
	O39-H19	0.00237	0.01834		O39-H14	0.00745	0.02364
	N31-H41	0.00463	0.01264	b4	O28-H10	0.020813	0.07168
	O28-H13	0.02049	0.06466		O29-H12	0.050141	0.13026
a4	O39-H22	0.01499	0.05489		O39-H17	0.013877	0.05157
	O28-H10	0.02104	0.07264		O28-H33	0.02085	0.0852
	O29-H12	0.04943	0.12960	b5	O28-H12	0.037614	0.11600
a5	O28-H12	0.04001	0.11848		O28-H16	0.004108	0.01348
	O29-H13	0.01313	0.03927		N31-H40	0.030014	0.08115
	O29-H38	0.04056	0.13045		O29-H38	0.012099	0.03807
a6	O28-H12	0.04234	0.12261		O39-H9	0.016474	0.05140
	O29-H13	0.01465	0.04493		O29-H13	0.016796	0.05283
	O29-H38	0.04077	0.13174	b6	O28-H12	0.04682	0.12726
	O39-C1	0.00843	0.03184		O29-H13	0.021097	0.07304
b1	O28- H10	0.0221	0.07526		O39-H17	0.013815	0.05061
	O29-H12	0.044143	0.12632		O28-H33	0.020236	0.08410
	O29- H40	0.040704	0.14095	b7	O28-H12	0.042071	0.12207
	O39-H13	0.014808	0.04907		O29-H13	0.013617	0.04092
	O28-H33	0.019732	0.08464		O29-H38	0.040566	0.13090
	O39-H20	0.005911	0.01889		O28-H33	0.019855	0.08444

Table 3: Calculated properties at the bond critical point for all complexes (all values in au).

Although the gas-phase calculation may be different from the liquid state, the results obtained here show us some new insights on the interaction details of the ionic liquids/water, ionic liquids/ Methanol systems. These calculations may be valuable to study to binary liquid-liquid phase systems containing amino acid ionic liquid.

Vibrational spectra

Recently, spectroscopic methods have been developed to study the structures of solutions [38,39]. Among the various spectroscopic methods, infrared spectroscopy and Raman spectroscopy play important roles in investigations on the structural properties and interactions of ionic liquids [40-43]. Exploration of hydrogen-bonding systems in which solvation, considered as a series of equilibria, can be quantified offers an interesting opportunity to explore solvent effects in recognition at a molecular level by combining experiments and theoretical calculation.

The Interaction of the ion-pairs with the water molecule: The ATR-IR spectra of the [bmim][Ala]-H$_2$O in the region 1500-1800 cm^{-1} is displayed in Figure 3. Some major peaks in the theoretical IR spectra of [bmim][Ala]-H$_2$O and H$_2$O are displayed in Figure 4. Correspondingly, assignments for the [bmim][Ala]-H$_2$O in the C-H,O-H stretching region are shown in Table 4. scaling factor 0.9890

The IR band corresponding to the bending mode (v_2) of water (either pure or dissolved in solvents) usually absorbs in the region 1595±1650 cm^{-1}. However, this band alone is seldom used to elucidate the molecular state of water. We find it with ionic liquid in IR vibrating peaks of the carboxyl group mode together research, a very good description of water in ionic liquid micro structure [44,45]. As is depicted in Figure 3. Although the positions for both vibrations observed in the present study differ from the calculated on [bmim] [Ala]-H$_2$O solutions, this tendency agrees with each other. Both from the calculated value, and the experimental data, the basic trend in the bending mode (v_2) of water of [bmim][Ala]-H$_2$O solutions was to move to higher frequencies of the vibrations spectrum. At the same time, studying on the ATR-IR spectrum found: the water content led to the increase of the maximal infrared absorption peak. The $v_{C=O}$ mode of [bmim][Ala] of [bmim][Ala]-H$_2$O solutions moved to lower frequencies and the water content led to the decrease of the maximal infrared absorption peak. All of this, indicating hydrogen bond that are the glue holding groups of water molecules and AAIL together are so plentiful in [bmim][Ala] that they play a large role in determining its properties.

The Interaction of the ion-pairs with the methanol molecule: The ATR-IR spectra of the [bmim][Ala]-CH$_3$OH in the region 950-1200 cm^{-1} and 1500-1650 cm^{-1} are displayed in Figure 5 and the C-O stretching mode of Methanol in the theoretical IR spectra is displayed in Figure 6 Correspondingly, assignments for the [bmim] [Ala]-CH$_3$OH in the C-H,O-H,C-O stretching region are shown in Table 5.

scaling factor 0.9890.

The IR band corresponding to the C-O stretching mode of Methanol (either pure or dissolved in solvents) usually absorbs in the region 980 ± 1100 cm^{-1}. Using the same method with analysis of [bmim][Ala]/
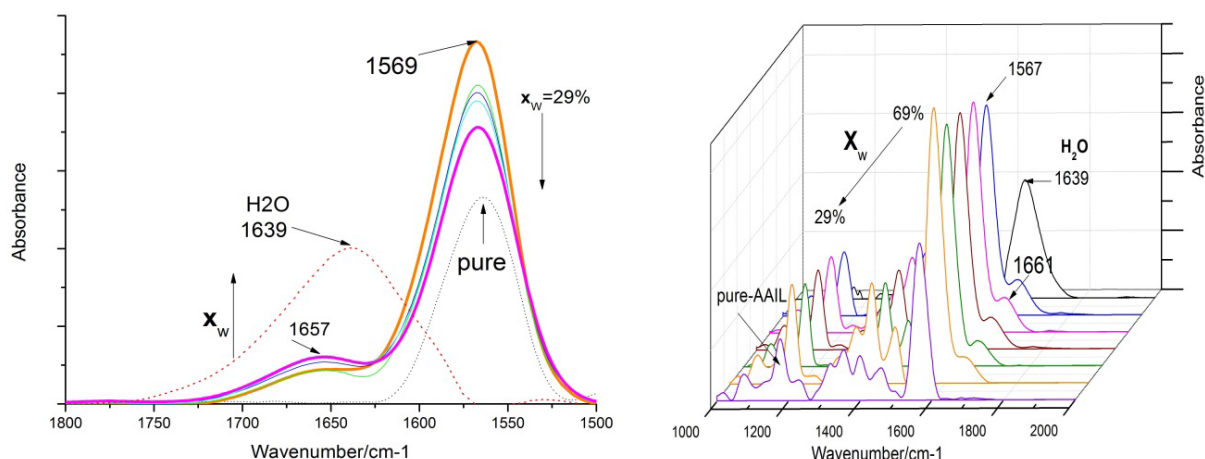
Figure 3: ATR-IR spectra of [bmim][Ala]-H_2O solutions as a function of water mole fraction. The arrows indicate the change in the mole fraction from x_w 0.29 to 0.69.
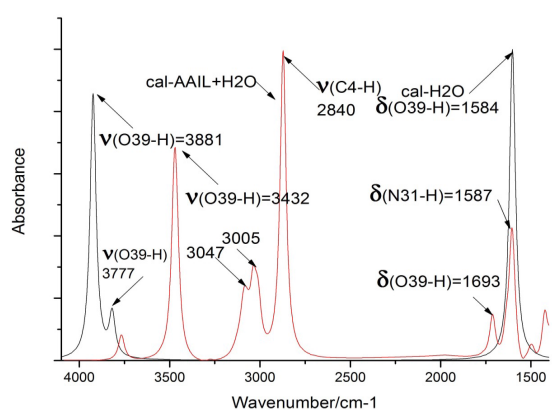

Figure 4: Some major peaks in the theoretical IR spectra of [bmim][Ala]-H_2O and H_2O.

[bmim][Ala]+H_2O				
complex	$v_{calcd(C4-H)}$	$\delta_{calcd(O38-H)}$	$\delta_{calcd(N31-H)}$	v_{obs}
b1	2692.1	1646.7	**1580.4**	
b2	2720.7	1645.7	1555.7	
b3	**2834.5**	**1691.2**	1580.4	δ_{obs} (O38-H)=1656
b4	2596.1	1609.1	1547.8	
b5	**2840.4**	**1693.2**	**1591.3**	
b6	2661.4	1610.1	1564.6	δ obs (N31-H)=1569
b7	2753.4	1642.7	1552.7	
AAIL	2739.5	---	1614.0	1659
H_2O	---	1584	---	1639

Table 4: Values of some major peaks in the theoretical and experimental IR spectra of [bmim][Ala]+H_2O.

Water, we known that the positions for both vibrations observed in the present study differ from the calculated on solutions, this tendency agrees with each other. the basic trend in the C-O stretching mode of Methanol of [bmim][Ala]-CH_3OH solution was to move to higher frequencies of the vibrations spectrum. At the same time, study on the ATR-IR spectrum found: the Methanol content led to the increase of the maximal infrared absorption peak. The $v_{C=O}$ mode of [bmim] [Ala] of [bmim][Ala]-CH_3OH solutions moved to lower frequencies

and the Methanol content led to the decrease of the maximal infrared absorption peak.

Furthermore, we have also made clear assignments of certain vibrations of AAILs in the IR region, which is also very useful for further investigations of complex systems of mixed of AAILs solution, which would be different due to the existence of various amounts of water or Methanol. This observation is very helpful for practical applications of AAILs in future. The results of experiments show the correctness of analysis.

Conclusions

The interactions of some kinds of structure of [bmim][Ala]-H_2O and [bmim][Ala]-CH_3OH were investigated using ATR-IR and DFT methods, On the basis of calculation and experiment results , the main conclusions are summarized as follows:

It was found that the interactions between [bmim]$^+$ and [Ala]$^-$ are mainly characterized by the electrostatic attractions. The intramolecular H bond system is one of the influence factors of the interactions between the cation and anion. Moreover, hydrogen bonds play a dominant role in the energy level of ionic liquids solution and the configuration characteristics.

The interactions between AAILs and H_2O or CH_3OH depended on the hydrogen bonds based on the results of AIM and NBO. Configuration of the high interaction energy is that Water or Methanol has hydrogen bonding with both cation and anion at the same time. The NBO analysis has revealed that the LP(O)→BD*(C–H) interactions give the strongest stabilization to these complexes and strengthen the intermolecular H⋯O interactions. In other words, hydrogen bonds have the greatest impact for the carbonyl and hydroxyl groups.

The addition of Water or Methanol to AAILs has a large effect on macroscopic properties, which is consistent with theoretic calculation. The change of vibration frequency of C4-H is in accordance with the previous results that the site acting was the carboxyl group mode. As a preliminary investigation on relationships between the electron density of H-bonding and stretching frequencies by IR and DFT, this work will make a contribution to the study of the microstructure for AAIL mixed solution.
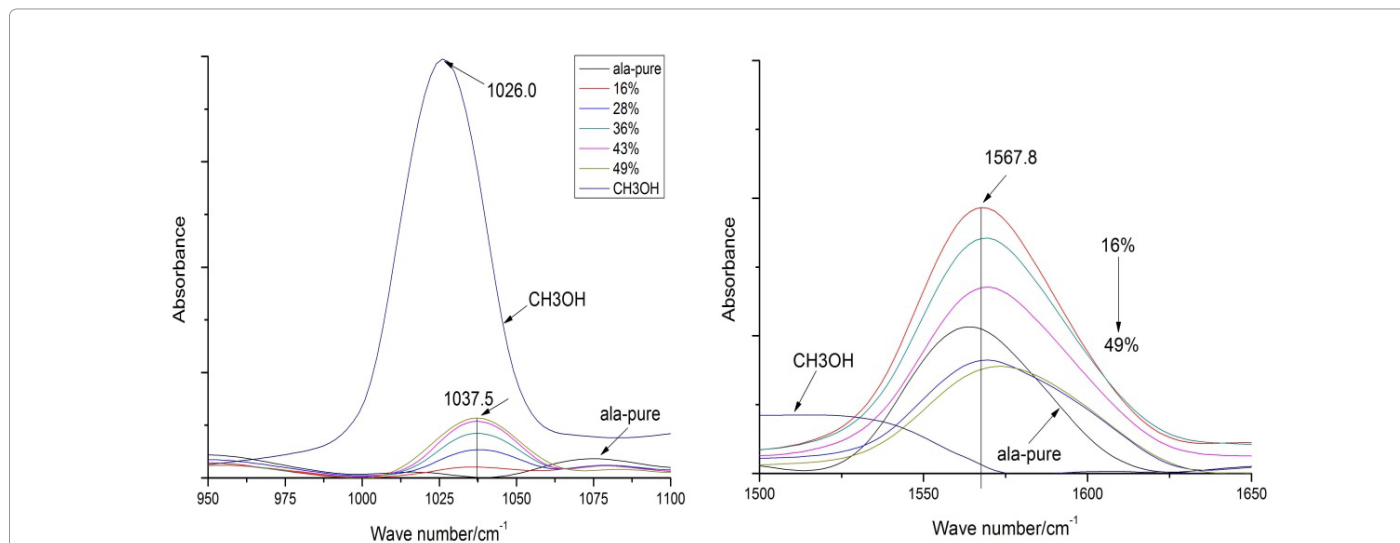
Figure 5: ATR-IR spectra of [bmim][Ala]-CH3OH solutions as a function of water mole fraction. The arrows indicate the change in the mole fraction from x M0.16 to 0.49.
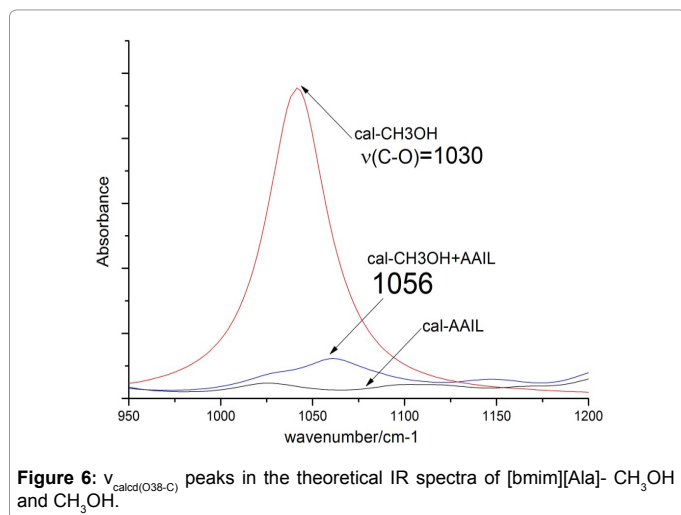

Figure 6: $v_{calcd(O38-C)}$ peaks in the theoretical IR spectra of [bmim][Ala]- CH_3OH and CH_3OH.

[bmim][Ala]+CH_3OH				
complex	$v_{calcd(C4-H)}$	$v_{calcd(O38-C)}$	$v_{calcd(O38-H)}$	v_{obs}
a1	2696.7	1057.0	3361.3	
a2	2722.3	1057.5	3361.4	v_{obs} (O38-C)=1037.5
a3	2725.3	1049.1	3396.5	
a4	2608.5	1024.5	3801.8	
a5	2784.5	1055.9	3321.7	v_{obs} (N31-H)=1569
a6	2748.6	1057.1	3338.1	
AAIL	2739.5	---	---	---
CH_3OH	---	1018.7	3803.4	1026.0

Table 5: Values of some major peaks in the theoretical and experimental IR spectra of [bmim][Ala]+ CH_3OH.

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