

## ARTICLE

## Interactions of 1-hexyl-3-methylimidazolium Bromide with Acetone

Cui-ping Zhai<sup>a,c</sup>, Jian-ji Wang<sup>b</sup>, Xiao-peng Xuan<sup>b</sup>, Han-qing Wang<sup>a\*</sup>, Miao Chen<sup>a\*</sup>

a. State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China b. School of Chemistry and Environmental Sciences, Henan Key Laboratory of Environmental Pollution Control, Henan Normal University, Xinxiang 453007, China; c. College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475001, China

(Dated: Received on September 28, 2005; Accepted on April 10, 2006)

<sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were determined to investigate the interactions of acetone with a room temperature ionic liquid 1-hexyl-3-methylimidazolium bromide [C<sub>6</sub>mim]Br at various mole fractions. Changes in chemical shifts of hydrogen nuclei and of carbon nuclei with the acetone concentration indicated the formation of hydrogen bond between anion of the ionic liquid and methyl protons of acetone. The NMR results were in good agreement with the *ab initio* computational results.

**Key words:** <sup>1</sup>H and <sup>13</sup>C NMR, Chemical shift, 1-hexyl-3-methylimidazolium bromide ionic liquid, Acetone, Interaction

## I. INTRODUCTION

Room temperature ionic liquid is a class of organic molten salts composed entirely of anions and cations. Room temperature ionic liquid has many potential applications because of their unique physical and chemical properties [1-7], such as negligible vapor pressure, high thermal and chemical stability, wide electrochemical windows, large liquid range and excellent solubility with many substances. Due to their good solvency and recyclability, ionic liquids have been used as organic solvents or catalysts in organic and organometallic synthesis [8-11]. Therefore, information on interactions between the ionic liquids and organic molecular solutes is very important for their application in chemical reactions and for designing of many technological processes. Some studies on the interactions between the ionic liquids and different organic compounds have been reported. These results suggested that the main interactions between them are hydrogen bond, aromatic ring current effect, van der Waals interactions and ion-dipole interactions [12-16]. In our previous works [17,18], we studied the interactions of [C<sub>4</sub>mim][PF<sub>6</sub>], [C<sub>6</sub>mim][PF<sub>6</sub>], [C<sub>6</sub>mim][BF<sub>4</sub>], [C<sub>8</sub>mim][PF<sub>6</sub>] and [C<sub>8</sub>mim][BF<sub>4</sub>] with acetone using nuclear magnetic resonance (NMR) spectroscopy and *ab initio* calculations. It was found that hydrogen bonds are formed between the ring protons of the ionic liquids and carbonyl oxygen of acetone.

Proton NMR is a well-known technique for studying hydrogen-bonded systems [19,20]. Since nuclei of the ionic liquid-acetone systems are readily observed by NMR, we attempted to study aspects of the interactions of different ionic liquids with acetone from the

<sup>1</sup>H NMR experiments. Similar experiments using <sup>13</sup>C NMR have also been carried out. The particular ionic liquid chosen for detailed study was the mixture of 1-hexyl-3-methylimidazolium bromide [C<sub>6</sub>mim]Br.

## II. EXPERIMENTS

The ionic liquid was synthesized according to the previously reported methods [21,22]. The resulting ionic liquid was washed, and dried in vacuum at 70 °C for 72 h in order to remove organic solvents and water. Mixtures of acetone and the ionic liquid were prepared by adding acetone-d<sub>6</sub> (d-99.9%) into ionic liquid to reach the specified molar ratios. Samples were placed in a 5-mm-NMR tube, capped and sealed with parafilm. Acetone-d<sub>6</sub> was used as the internal lock solvent. TMS was used as the internal reference, which was kept constant and was not affected by the change of sample concentration.

NMR experiments were performed using a Bruker AV-400 spectrometer, <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400.13 and 100.62 MHz, respectively. All experiments were performed at 25±0.1 °C.

Calculations were performed by using the Gaussian 03 program, The geometry optimizations were carried out using the DFT method at B3LYP/6-311+G\* level.

## III. RESULTS AND DISCUSSION

<sup>1</sup>H and <sup>13</sup>C NMR signals were assigned to various hydrogen and carbon atoms of the mixed systems of acetone-d<sub>6</sub> and the ionic liquid as shown in Fig.1. Tables I and II listed the <sup>1</sup>H and <sup>13</sup>C NMR data for the acetone-d<sub>6</sub> and [C<sub>6</sub>mim]Br mixtures.

Variations of <sup>1</sup>H and <sup>13</sup>C chemical shifts,

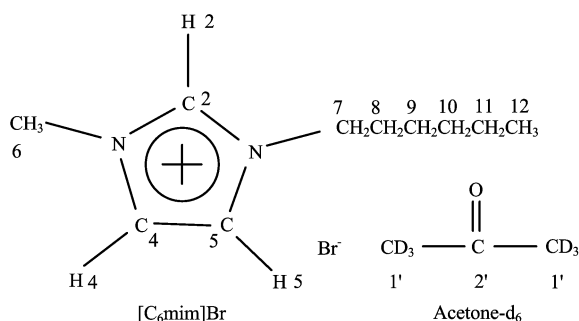
\* Author to whom correspondence should be addressed. E-mail: whqwt@yahoo.com.cn, miaochen99@yahoo.com.cn

TABLE I The  $^1\text{H}$  NMR chemical shifts (ppm) of acetone- $\text{d}_6$  and  $[\text{C}_6\text{mim}]\text{Br}$  mixtures.

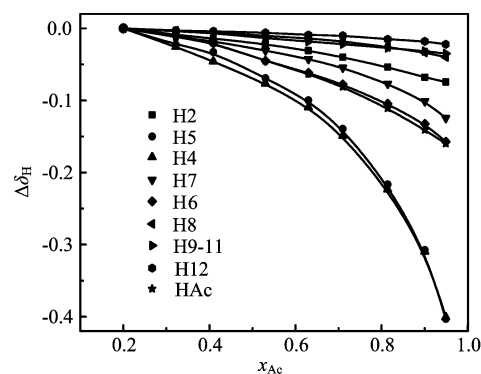
$\chi_{\text{AC}}$	H1'	H2	H4	H5	H6	H7	H8	H9-11	H12
0.200	2.242	10.389	8.536	8.633	4.326	4.643	2.012	1.277	0.837
0.322	2.230	10.380	8.510	8.610	4.316	4.631	2.009	1.274	0.834
0.409	2.222	10.375	8.490	8.600	4.305	4.625	2.007	1.271	0.833
0.530	2.197	10.367	8.459	8.564	4.281	4.612	2.002	1.266	0.831
0.630	2.179	10.358	8.426	8.533	4.264	4.600	1.998	1.264	0.828
0.710	2.161	10.349	8.387	8.493	4.248	4.588	1.994	1.260	0.825
0.814	2.131	10.335	8.312	8.416	4.221	4.566	1.986	1.256	0.821
0.900	2.101	10.321	8.226	8.325	4.193	4.542	1.979	1.255	0.820
0.949	2.082	10.314	8.135	8.230	4.169	4.518	1.973	1.251	0.817

TABLE II The  $^{13}\text{C}$  NMR chemical shifts (ppm) of acetone- $\text{d}_6$  and  $[\text{C}_6\text{mim}]\text{Br}$  mixtures.

$\chi_{\text{AC}}$	C1'	C2'	C2	C4	C5	C6	C7	C8	C9	C10	C11	C12
0.200	30.865	207.178	137.520	122.760	123.810	36.056	49.330	31.110	30.263	25.710	22.450	14.045
0.322	30.820	207.131	137.550	122.810	123.850	36.061	49.360	31.160	30.305	25.750	22.480	14.060
0.409	30.770	207.100	137.600	122.860	123.900	36.135	49.400	31.220	30.350	25.800	22.520	14.080
0.530	30.669	207.040	137.700	122.971	124.030	36.231	49.480	31.336	30.472	25.908	22.615	14.127
0.630	30.574	206.967	137.779	123.052	124.109	36.315	49.549	31.425	30.574	25.988	22.701	14.168
0.710	30.479	206.876	137.877	123.138	124.199	36.391	49.647	31.506	30.655	26.070	22.770	14.191
0.814	30.325	206.726	138.038	123.255	124.339	36.485	49.795	31.652	30.795	26.216	22.899	14.249
0.900	30.155	206.554	138.195	123.329	124.439	36.574	49.909	31.784	30.916	26.339	23.015	14.295
0.949	30.030	206.340	138.330	123.370	124.488	36.636	50.005	31.852	30.966	26.411	23.070	14.315

FIG. 1 Chemical structures of  $[\text{C}_6\text{mim}]\text{Br}$  and acetone.

$\Delta\delta = \delta_{\text{obs}} - \delta_{(\chi_{\text{AC}})_{\text{min}}}$ , for  $[\text{C}_6\text{mim}]\text{Br}$  and acetone- $\text{d}_6$  (AC) at various mole fractions of acetone- $\text{d}_6$  ( $\chi_{\text{AC}}$ ) are shown in Fig.2 and Fig.3, respectively, where  $\delta_{\text{obs}}$  is the measured chemical shifts for the ionic liquid and acetone- $\text{d}_6$  mixtures, and  $\delta_{(\chi_{\text{AC}})_{\text{min}}}$  is the measured chemical shifts for the ionic liquid and acetone- $\text{d}_6$  mixture at the minimal mole fraction of acetone- $\text{d}_6$ . As can be seen, chemical shifts of aromatic protons of the ionic liquid are generally sensitive to the changes in the concentration of acetone- $\text{d}_6$ , and H4 and H5 moved to the higher field than H2 with increasing mole fraction of acetone- $\text{d}_6$ . Alkyl protons of the ionic liquid showed little concentration dependence. However, changes of  $^{13}\text{C}$  chemical shifts of the ionic liquid have the opposite trends.

FIG. 2 Difference of the  $^1\text{H}$  chemical shifts of  $[\text{C}_6\text{mim}]\text{Br}$  and acetone- $\text{d}_6$  mixtures as a function of the mole fraction of acetone- $\text{d}_6$ .

$^1\text{H}$  chemical shifts of the methyl protons of acetone- $\text{d}_6$  moved to the same direction as that of the ring protons of the ionic liquid, and they are more sensitive to the composition of the mixtures than those of the acetone molecules mixed with other ionic liquids [17,18]. The upfield changes in the chemical shifts for the carbon of the methyl group are larger than that of the carbonyl carbon in acetone- $\text{d}_6$ .

$^1\text{H}$  and  $^{13}\text{C}$  NMR data indicated that there is not only formation of the  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bond between the carbonyl oxygen of acetone- $\text{d}_6$  and the cationic protons but also formation of the  $\text{C}-\text{H}\cdots\text{Br}$  hydrogen bond

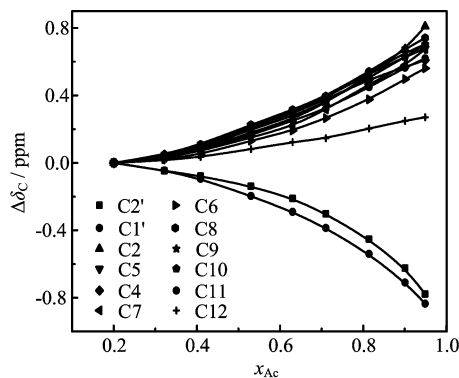


FIG. 3 Difference of the  $^{13}\text{C}$  chemical shifts of  $[\text{C}_6\text{mim}]\text{Br}$  and acetone- $\text{d}_6$  mixtures as a function of the mole fraction of acetone- $\text{d}_6$ .

between the methyl protons of acetone- $\text{d}_6$  and anion of the ionic liquid [17,18,23,24]. It is known that breaking of a hydrogen bond can cause the proton chemical shift move upfield. The strength of the  $\text{C}-\text{H}\cdots\text{Br}$  hydrogen bond decreased with increasing mole fraction of acetone- $\text{d}_6$ , thus the electron density of the methyl protons of acetone- $\text{d}_6$  also increased, and its chemical shift moved upfield.

Changes in the  $^1\text{H}$  chemical shifts of the cations can be interpreted in terms of interionic interactions of the ionic liquid. There were several reports on the study of cation-cation and cation-anion interactions of this ionic liquid [25,26]. The results indicated that there were two types of interactions, one is the  $\pi$ - $\pi$  stacking of the aromatic cations, and the other is the hydrogen bond between the protons of the cations and the anions. The hydrogen bond strength of  $\text{H}2\cdots\text{Br}$  is stronger than that of  $\text{H}4\cdots\text{Br}$  and  $\text{H}5\cdots\text{Br}$ , and they are affected by the ionic liquid concentrations. It is well-known that the intermolecular hydrogen bond is influenced by the solution concentration, while the intramolecular hydrogen bond is not. So the interaction observed here belongs to the intermolecular hydrogen bond. At higher concentrations of the ionic liquid,  $\text{H}2$ , entering the shielding cone of the neighboring cation, is influenced not only by the  $\text{H}2\cdots\text{Br}$  hydrogen bond strength but also by the aromatic current. While  $\text{H}4$  and  $\text{H}5$ , pointing outside, are only influenced by the  $\text{H}\cdots\text{Br}$  hydrogen bond strength. When adding acetone- $\text{d}_6$  into the IL, the interactions between the ionic liquid and the acetone- $\text{d}_6$  are through the formation of the  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds. With the increase of  $\chi_{\text{AC}}$ , the strength of the  $\text{H}\cdots\text{Br}$  hydrogen bond is weakened, and the signal of  $\text{H}2$  moves upfield. At the same time, the  $\pi$ - $\pi$  stacking interactions decreases while the  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bond increases, and the signal of  $\text{H}2$  moves downfield. The changes in chemical shift of  $\text{H}2$  indicated that the  $\text{H}\cdots\text{Br}$  hydrogen bond effect is stronger than that of the  $\pi$ - $\pi$  stacking and that of the  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bond. This makes the signal of  $\text{H}2$  move slightly upfield. As

for  $\text{H}4$  and  $\text{H}5$ , they are affected by the  $\text{H}\cdots\text{Br}$  and the  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds, and the former is the predominant effect. So the signals of  $\text{H}4$  and  $\text{H}5$  moved apparently upfield when the strength of  $\text{H}\cdots\text{Br}$  hydrogen bond is weakened.

Generally, the criteria for the presence of  $\text{Y}-\text{H}\cdots\text{X}$  hydrogen bond is that the  $\text{H}\cdots\text{X}$  distance must be less than the sum of the van der Waals radii of  $\text{H}$  and  $\text{X}$ , and the  $\text{Y}-\text{H}\cdots\text{X}$  angle must be greater than  $90^\circ$  [25]. In order to confirm the formation of hydrogen bond in the present systems, *ab initio* calculations on various interaction sites of acetone with  $\text{Br}^-$  have been performed. However, only one optimized structure is obtained, as shown in Fig.4. The calculated hydrogen bond length and angles are also presented in Fig.4. Obviously, only the distance of  $\text{H}2''\cdots\text{Br}$  and  $\text{H}4''\cdots\text{Br}$  are shorter than  $3.05 \text{ \AA}$ , which corresponds to the sum of the van der Waals radii of  $\text{H}$  ( $1.2 \text{ \AA}$ ) and  $\text{Br}$  ( $1.85 \text{ \AA}$ ) [27].

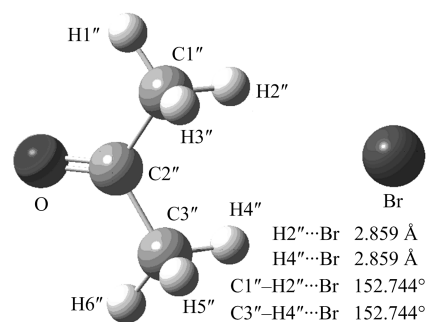


FIG. 4 Optimized structure of the acetone- $\text{Br}^-$  interactions.

Figure 4 revealed the interactions between anion of the ionic liquid and the methyl protons of acetone- $\text{d}_6$ . The computational results are consistent with the experimental data. These results are different from those reported in the previous works [17,18], in which the ionic liquids-acetone- $\text{d}_6$  systems are mainly conducted by the interactions of  $\text{H}2$ ,  $\text{H}4$ ,  $\text{H}5$ ,  $\text{H}6$  and  $\text{H}7$  of the cations with carbonyl oxygen of acetone- $\text{d}_6$ . Based on these results, we can conclude that different anions of the ionic liquids not only influence the strength of the interactions between acetone- $\text{d}_6$  and the ionic liquid, but also determine different types of interactions.

#### IV. CONCLUSION

The results indicated that the methyl protons of the acetone- $\text{d}_6$  interact with the anion of  $[\text{C}_6\text{mim}]\text{Br}$ , and they formed  $\text{C}-\text{H}\cdots\text{Br}$  hydrogen bond. The *ab initio* computational results supported the results deduced from the  $^1\text{H}$  and  $^{13}\text{C}$  NMR experimental data. Based on our previous work, these results also confirmed that the anion of ionic liquid has major effects on the interactions between ionic liquids and the organic compounds.

## V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.20273019).

- [1] P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.* **35**, 1168 (1996).
- [2] A. Noda, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B.* **105**, 4603 (2001).
- [3] P. J. Dyson, D. J. Ellis, D. G. Parker and T. Welton, *Chem. Commun.* 25 (1999).
- [4] B. M. Quinn, Z. F. Ding, R. Moulton and A. J. Bard, *Langmuir* **18**, 1734 (2002).
- [5] B. Cabovska, G. P. Kreishman, D. F. Wassell and A. M. Stalcup, *J. Chromatogra. A* **1007**, 179 (2003).
- [6] C. Cadena, J. L. Anthony, J. K. Shah, T. I. Morrow, J. F. Brennecke and E. J. Maginn, *J. Am. Chem. Soc.* **126**, 5300 (2004).
- [7] H. M. Luo, S. Dai and P. V. Bonnesen, *Anal. Chem.* **76**, 2773 (2004).
- [8] P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, GmbH & Co, KgaA, Weinheim: Wiley-VCH Verlag, 174 (2002).
- [9] T. Welton, *Chem. Rev.* **99**, 2071 (1999).
- [10] P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.* **39**, 3772 (2000).
- [11] J. Dupont, R. F. Souza and P. A. Z. Suarez, *Chem. Rev.* **102**, 3667 (2002).
- [12] A. Heintz, J. K. Lehmann and C. Wertz, *J. Chem. Eng. Data.* **48**, 472 (2003).
- [13] J. M. Crosthwaite, S. N. V. K. Aki, E. J. Maginn and J. F. Brennecke, *J. Phys. Chem. B.* **108**, 5113 (2004).
- [14] C. G. Hanke, N. A. Atamas and R. M. Lynden-Bell, *Green Chem.* **4**, 107 (2002).
- [15] L. Crowhurst, P. R. Mawdsley, J. M. Perez-Arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.* **5**, 2790 (2003).
- [16] B. M. Su, S. G. Zhang and Z. C. Zhang, *J. Phys. Chem. B* **108**, 19510 (2004).
- [17] C. P. Zhai, J. J. Wang, Y. Zhao, X. P. Xuan, J. M. Tang and H. Q. Wang, *Z. Phys. Chem.* **220**, 775 (2006).
- [18] C. P. Zhai, J. J. Wang, Y. Zhao, X. P. Xuan and H. Q. Wang, *Acta Phys. Chim. Sin.* **22**, 456 (2006).
- [19] M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.* **68**, 811 (1964).
- [20] A. A. Fannin, L. A. King, J. A. Levisky and J. S. Wilkes, *J. Phys. Chem.* **88**, 2609 (1984).
- [21] J. D. Holbrey and K. R. Seddon, *J. Chem. Soc. Dalton Tran.* 2133 (1999).
- [22] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.* **3**, 156 (2001).
- [23] L. Turi, *Chem. Phys. Lett.* **275**, 35 (1997).
- [24] W. R. Fawcett, P. Brooksby, D. Verbovy, I. Bakó and G. Pálinkás, *J. Mol. Liq.* **118**, 171 (2005).
- [25] A. G. Avent, P. A. Chaloner, M. P. Day, K. R. Seddon and T. Welton, *J. Chem. Soc., Dalton Trans.* 3405 (1994).
- [26] A. Elaiwi, P. B. H. Chcock, K. R. Seddon, N. Srinivasan, Y. M. Tan, T. Welton and J. Azora, *J. Chem. Soc., Dalton Trans.* 3467 (1995).
- [27] R. Taylor and O. Kennard, *J. Am. Chem. Soc.* **104**, 5063 (1982).