



A FT-IR spectroscopic study of ultrasound effect on aqueous imidazole based ionic liquids having different counter ions



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ABSTRACT

Ultrasound (US) effect on 1-butyl-3-methyl-imidazolium (BMI) ionic liquids having different counter anions, BF_4^- , PF_6^- and Cl^- in aqueous medium was studied by FT-IR spectroscopy. Their deconvolution spectra were used to analyze the change of hydrogen bond in the absence and presence of US exposure to the ionic liquid. The FT-IR spectra were measured in different water contents without and with US at 23 kHz. These results indicated that the counter anion species in the imidazole based the ionic liquids played an important role for water solvation, when the US was exposed. The US hardly changed hydrogen bonding in the aqueous BMI- PF_6^- , while the BMI- BF_4^- and BMI- Cl^- showed obvious change in their FT-IR spectra. Especially for the BMI- Cl^- , significant change was observed by the US exposure in the range of 2.6 wt% to 20 wt% of water contents. The results showed that the US could break the hydrogen bond in the BMI- Cl^- ionic liquids. In the case of BMI- BF_4^- , the FT-IR band at $950\text{--}1152\text{ cm}^{-1}$ was significantly intensified under US exposure, due to that the US influenced BF_4^- -water interaction. But, it was observed that the ionic liquid having PF_6^- was very less changed in the US system.

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1. Introduction

Ionic liquid has characters of both organic salt and liquid, when the temperature is below $100\text{ }^\circ\text{C}$. Such material attracts numerous attention of researchers, because ionic liquid possesses some unique properties of negligible volatility, flammability, and compatibility with designable structures in different materials [1]. Also, more recently, ionic liquids are treated as “green solvent” and “designable solvent”. Thus, it has been used as catalyst in chemical reaction [2], reaction media [3] and absorbent for metal extraction [4]. Despite exploring the new application of ionic liquids, researches on the interaction between ionic liquids and other organic substance such as water [5], acetonitrile [6], methanol [7] and polymer [8] are seen. In the point of view of interaction between ionic liquids and water, importance issue is included, because the presence of water in ionic liquids system strongly influences their physical and chemical properties, for instance, in viscosity, electrical conductivity, and reactivity [9–12].

It was known that hydrogen bond between water and imidazole-based ionic liquid (Fig. 1) exists in the bonding interaction concerning three hydrogen atoms, which is signed as: $\text{C}_2\text{-H}$, $\text{C}_4\text{-H}$ and $\text{C}_5\text{-H}$ in imidazole ring carbon hydrogen atoms [5,13].

Thus, water formed hydrogen bond with these three hydrogen atoms as investigated by Cammarata et al. [14]. For the interaction between water and ionic liquids, counter anion played an important role in the formation of the hydrogen bond. Here, the anion formed hydrogen bonds via water molecular as a form of anion... H_2O ...anion, when the water concentration was low. López-Pastor et al. [7] discovered that water could interact with BF_4^- contained ionic liquids in the forms of $\text{BF}_4^- \dots \text{H}_2\text{O} \dots \text{BF}_4^-$, and $\text{BF}_4^- \dots \text{H}_2\text{O} \dots \text{H}_2\text{O} \dots \text{BF}_4^-$, when the BF_4^- was counter anion of the ionic liquid. In addition, water-ionic liquid systems showed that both anion and cation could form hydrogen bond with water. In this case, the interaction of ionic liquids and water was studied with FT-IR spectroscopy [11]. It was proved that OH stretching band of water appeared at $3000\text{--}3800\text{ cm}^{-1}$ was sensitive to the environmental change in ionic liquids [15].

On the other hand, ultrasound (US) was used as tools of environmental change in organic synthesis [16], materials science [17], medical treatment [18] and food industry [19]. Therefore, US could strongly affect the chemical and physical processes in the US frequency beyond the hearing ability of human beings [20]. Our group has investigated the effect of US on hydrogen bonds in slurring [21] and aqueous polymers as environmental stimulates [22]. In our previous work, it was reported that US stimulate the polymer solution through breaking the hydrogen bond between polymer and water [15,22]. It was also illustrated that

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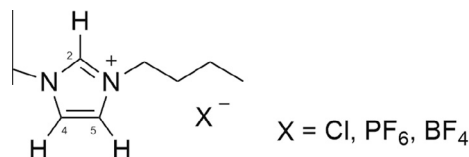


Fig. 1. Chemical structure of imidazole based ionic liquids having different counter ions.

the US stimulation induced water–polymer interaction and enhanced the polymer size domain by changing hydrogen-bonded solvation of water. The US behavior on the breakage of hydrogen bonding was examined by FT-IR spectroscopy for the characteristic hydrogen bonds. Similar work [23] was reported that US could induce the gelation of the solution by switching the intramolecular hydrogen bond to intermolecular hydrogen bond in Fmoc–OG/cyclohexane solution. However, there was no research on investigation of US effect on the interaction of water and ionic liquids. Therefore, it is challengeable to study the US effect on water-ionic liquids via hydrogen bonds under operation of US. In the present study, the influence of US on the interaction of water and three kind of imidazole-based ionic liquids (Fig. 1) was studied. Here, the ionic liquids (ILs) contained different counter anions of Cl^- , BF_4^- and PF_6^- . Evidence was found that US effect on the hydrogen bonds of the imidazole based ILs exhibited dependence of the counter anions.

2. Material and methods

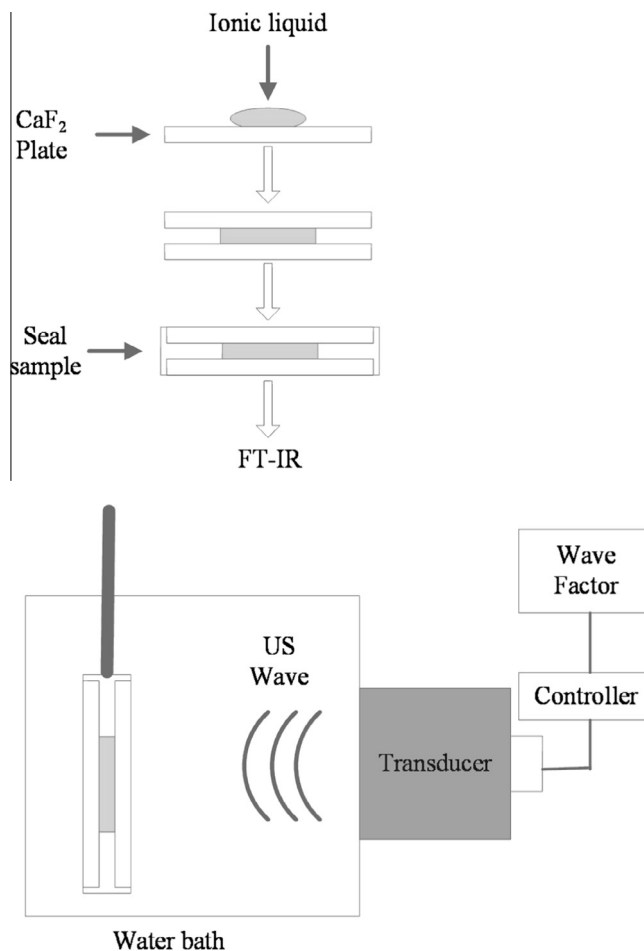
2.1. Materials

Fig. 1 shows chemical structures of ionic liquids of 1-butyl-3-methyl-imidazolium tetrafluoroborate (BMI– BF_4), and 1-butyl-3-methylimidazolium hexafluorophosphate (BMI– PF_6). These were purchased from TCI Co., Ltd. (Japan). Another 1-butyl-3-methylimidazolium containing chloride ion (BMI–Cl) was prepared according to prior report using 1-methylimidazole and 1-chlorobutane system [24]. Both of 1-methylimidazole and 1-chlorobutane were purchased from TCI Co., Ltd. (Japan).

Water solutions of three kinds of ILs were made as followed. For the BMI– PF_6 , the water saturated solution was made by putting sample in a humid atmosphere with relative humidity of 70–75% until the weight of the ILs was constant. As a result, the water content was 2.6 wt% at the constant condition. For the BMI– BF_4 , the aqueous solutions were made with water contents of 2.6 wt% and 5 wt%, 12 wt%. For the solid BMI–Cl, firstly, it was melted at 350 K in the oil bath, and it remained in the supercool liquid at room temperature [25]. Then, the aqueous solution was prepared with different water contents of 2.6 wt%, 5 wt%, 10 wt%, 15 wt% and 20 wt%.

2.2. Determination of FT-IR spectra effecting with US exposure to BMI–ILs

FT-IR spectra were measured by using JASCO FT-IR/4100 spectrometer before and after the US exposure for their aqueous ILs containing different counter anions. In the experiments, each solution was dropped on CaF_2 plate with diameter of 30 mm and thickness of 2 mm (Pier Optics Co. Ltd.). Then another CaF_2 plate was covered on the solution (Scheme 1). The illustration of the US experiment is presented in the Scheme 1 with similar setup in our previous report [15]. Because of the penetration of water into the IL sites, the CaF_2 plates with sample were sealed with Teflon tape (0.1 mm \times 13 mm, Sanyo, Japan). The sample– CaF_2 window was immersed in the US water bath and exposed by 50 W US for



Scheme 1. Processes of making samples (upper) and experimental set (bottom) for US experiment.

1, 3, 5 and 10 min with the frequency of 23 kHz. The temperature of water bath was 25 °C and controlled by using flowing water with thermostat (Lauda ecoline E100). Then, FT-IR spectra were recorded with a 4 cm^{-1} spectral resolution. For peak deconvolution, the FT-IR spectra were fitted with Voigt function using Origin. In these cases, the chi-squared value for each fitting curve was more than 0.99 in the deconvolution.

3. Results and discussion

3.1. US effect on the change of FT-IR spectra of ILs solution

As shown in Fig. 1, three ionic liquids having imidazole framework were chosen in the present work for the investigation of US effect determined by FT-IR spectra.

Fig. 2 shows FT-IR spectra of three ionic liquids before and after the 23 kHz US exposure at the different time. Here, the concentrations of water in the imidazole ionic liquids were adjusted to 2.6 wt% for each sample. As a comparison, FT-IR spectra of three ionic liquids in the dry condition were also recorded and illustrated as dotted line in the spectra. It could be seen that in the BMI– PF_6 almost no change of their peaks was observed at different US exposure system and the dry system. However, BMI–Cl (Fig. 2b) and BMI– BF_4 (Fig. 2c) ILs showed the apparent change in their spectra at different time of exposure to US. In the case of the BMI–Cl, the broad peak assigned to OH stretching band at $3100\text{--}3700\text{ cm}^{-1}$, was changed by the US exposure. In the assignments for each IR

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