

## Inclusion Complexes of $\beta$ -Cyclodextrin with Ionic Liquid Surfactants

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The three kinds of ionic liquid (IL) surfactants, 1-dodecyl-3-methylimidazolium hexafluorophosphate ( $C_{12}$ -mimPF<sub>6</sub>), 1-tetradecyl-3-methylimidazolium hexafluorophosphate ( $C_{14}$ mimPF<sub>6</sub>), and 1-hexadecyl-3-methylimidazolium hexafluorophosphate ( $C_{16}$ mimPF<sub>6</sub>), were used to form the inclusion complexes (ICs) with  $\beta$ -cyclodextrin ( $\beta$ -CD). The surface tension measurements revealed that there were two kinds of inclusion formations, 1:1 and 1:2 ( $\beta$ -CD/IL) stoichiometry for  $\beta$ -CD- $C_{12}$ mimPF<sub>6</sub> and  $\beta$ -CD- $C_{14}$ mimPF<sub>6</sub> ICs, and only 1:1 stoichiometry for  $\beta$ -CD- $C_{16}$ mimPF<sub>6</sub> ICs. These inclusion compounds were further characterized by XRD, <sup>13</sup>C CP/MAS NMR, <sup>1</sup>H NMR, rotating frame nuclear Overhauser effect spectroscopy (ROESY), and thermogravimetry (TGA). The results showed that these ICs were fine crystalline powder. The host–guest system presented a channel-type structure, and each glucose unit of  $\beta$ -CD was in a similar environment. It was suggested that hydrophobicity played a crucial role in supporting the formation of ICs. The decomposition temperature of these ICs was lower than those of their precursors. Furthermore, the possible inclusion structures were also speculated. These inclusion behaviors are likely to be used to recover ILs in the process of their preparation.

### Introduction

Supramolecular self-assembly is the spontaneous association of molecules by noncovalent bonds under equilibrium conditions into stable and well-defined structures.<sup>1</sup> One typical example of supramolecular self-assembly is host–guest inclusion complexes (ICs) made of cyclodextrins (CDs) and guest molecules. It is well known that CDs are cyclic oligosaccharides of six to eight glucose units linked  $\alpha$ -1,4-linkages, which are called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CDs, respectively. They adopt a truncated conical structure, having the primary hydroxyl groups on the narrow (primary) side and the secondary hydroxyl groups on the wide (secondary) side, which results in a hydrophobic inner cavity and a hydrophilic outside surface. Such characteristic makes CDs form host–guest ICs with a number of different organic and inorganic guest molecules.<sup>2</sup> Due to this special property, CDs have been used widely in pharmaceuticals, pesticides, foodstuffs, toilet articles, and textile processing.<sup>3,4</sup> In addition to these industrial applications, they are related to many interesting topics, such as molecular recognition and self-assembly, selectivity, molecular encapsulation, chemical stabilization, and intermolecular interactions.<sup>4,5</sup>

In an aqueous solution, the slightly apolar cavity of cyclodextrin is occupied by a small quantity of water molecules that are energetically unfavored and therefore can be readily substituted by appropriate guest molecules that are less polar than water. The guest molecule prefers to penetrate the empty cavity, leading to the formation of an inclusion compound through host–guest interactions. In recent years, with increasing interest in macromolecular recognition, ICs of polymers with CDs have been investigated extensively.<sup>6–18</sup> So-called molecular necklaces may be formed through penetrating CD molecules by a polymeric chain.<sup>19</sup> Moreover, lots of organometallic

compounds also can form inclusion compounds with CDs.<sup>20</sup> Recently, the inclusion behavior of  $\beta$ -CD and hydrophobic ionic liquid (IL), 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF<sub>6</sub>) in aqueous solution has been studied.<sup>21</sup> Based on the well-known representative structure of  $\alpha$ -,  $\beta$ -, or  $\gamma$ -CDs, many different derivatives have been synthesized, which possess different inclusion capabilities.<sup>22</sup>

Ionic liquids (ILs) are nonvolatile, nonflammable and thermally stable solvents, and as such as very promising replacements for the traditional volatile organic solvents. Their quite rapid emergence as alternative solvents has involved a rapidly growing number of examples of the application such as organic synthesis, chemical reactions, chemical separations, and material preparations.<sup>23</sup> ILs are composed of sterically mismatched ions that hinder crystal formation, thus molecular structure can be used to tune physicochemical properties. The design and synthesis of functional ILs that incorporate structural or functional groups have been reported.<sup>24</sup> For example, ILs were designed as oriented solvents which could impact selectivity in reactions by ordering reactants.<sup>25</sup> Furthermore, functional ILs were also used as templates for the synthesis of mesoporous and zeolitic materials,<sup>26</sup> and in the formation of ordered thin films.<sup>27</sup> Recently, ILs having a long alkyl chain group exhibited surface active properties in their aqueous solutions. These IL surfactants have been investigated by surface tension measurements.<sup>28</sup>

There have been few reports on the combination of CDs and ILs. Qi et al. have used ILs as running electrolytes in capillary zone electrophoresis and  $\beta$ -CD as a modifier for the separation of anthraquinones extract of Chinese herb.<sup>29</sup> The inclusion complexation of methyl orange or phenol with CDs has been studied using spectral analysis in ILs.<sup>30</sup> Moreover, CDs or their derivatives dissolved in IL can be used to prepare stationary phases in gas chromatography.<sup>31</sup> However, to our knowledge, study of the inclusion interaction between CDs and IL surfac-

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tants has been not reported so far. Considering the special structures and properties of IL surfactants, it is of interest to investigate their complexation behavior using different techniques.

In this work, we investigated the inclusion interactions between  $\beta$ -CD and three IL surfactants, 1-dodecyl-3-methylimidazolium hexafluorophosphate ( $C_{12}\text{mimPF}_6$ ), 1-tetradecyl-3-methylimidazolium hexafluorophosphate ( $C_{14}\text{mimPF}_6$ ), and 1-hexadecyl-3-methylimidazolium hexafluorophosphate ( $C_{16}\text{mimPF}_6$ ). Three ICs of  $\beta$ -CD- $C_{12}\text{mimPF}_6$ ,  $\beta$ -CD- $C_{14}\text{mimPF}_6$ , and  $\beta$ -CD- $C_{16}\text{mimPF}_6$  were characterized by surface tension measurements, powder X-ray diffraction (XRD),  $^{13}\text{C}$  CP/MAS NMR,  $^1\text{H}$  NMR, rotating frame nuclear Overhauser effect spectroscopy (ROESY), and TGA analysis. Finally, their potential practical applications are also discussed in this contribution.

## Experimental Section

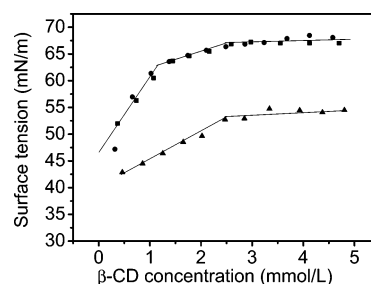
**Materials.**  $\beta$ -CD was obtained from Shanghai Chemical Reagents Company. The sample was recrystallized twice and dried at 80 °C under vacuum for at least 24 h before use. The IL surfactants  $C_{12}\text{mimBr}$ ,  $C_{14}\text{mimBr}$ ,  $C_{16}\text{mimBr}$ ,  $C_{12}\text{mimPF}_6$ ,  $C_{14}\text{mimPF}_6$ , and  $C_{16}\text{mimPF}_6$  were prepared and characterized as reported previously.<sup>32</sup> All materials used to prepare the ILs were A.R. grade. Deuterium oxide (99.9%) was purchased from Beijing Chemical Reagents Company. Water used was doubly distilled and deionized.

**Apparatus and Procedures.** Surface tension was determined on an autosurface tension instrument (type JYW-200; Chengde Material Testing Machine Factory, China). XRD patterns were taken using Cu K $\alpha$  irradiation with a Rigaku RAD-ROC X-ray diffractometer (voltage, 40 kV; current, 100 mA; scanning speed, 3°/min).  $^1\text{H}$  NMR measurements were carried out with a Varian ARX 400 NMR spectrometer at room temperature (about 25 °C). The instrument was operated at a frequency of 400.13 MHz. Calibration of proton chemical shift was achieved by using tetramethylsilane as an internal reference standard. Samples were dissolved in  $\text{D}_2\text{O}$ .  $^{13}\text{C}$  CP/MAS NMR spectra were acquired on a Bruker DRX-400NMR spectrometer with a sample spinning rate of 8.0 kHz at room temperature. ROESY experiments were carried out using a mixing time of 250 ms in the phase-sensitive mode. TGA curves were obtained by using a NETZSCH STA 409 PC/PG thermogravimetric analyzer. Samples were heated at 10 °C/min from room temperature to 700 °C in a nitrogen atmosphere.

7.5 g  $\beta$ -CD ( $6.6 \times 10^{-3}$  mol) and 0.87 g  $C_{12}\text{mimPF}_6$  ( $2.2 \times 10^{-3}$  mol) were dissolved in 50 mL of deionized water at 80 °C. The solution was maintained at 80 °C for 2 h and then allowed to cool to room temperature and deposited overnight. The resulting white suspension was obtained and collected by vacuum filtration and then washed with a large amount of hot deionized water (40 °C) to remove the free  $\beta$ -CD. The obtained inclusion complex of  $\beta$ -CD- $C_{12}\text{mimPF}_6$  was dried at 80 °C under vacuum for 2 h. Similarly, the ICs of  $\beta$ -CD- $C_{14}\text{mimPF}_6$  and  $\beta$ -CD- $C_{16}\text{mimPF}_6$  were obtained by the same procedure.

## Results and Discussion

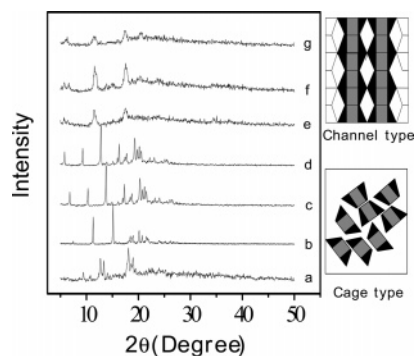
**Surface Tension Measurements.** It was reported that the ILs with a long alkyl chain were surface active in aqueous solutions.<sup>33</sup> Then, if long alkyl chain ILs,  $C_{12}\text{mimBr}$ ,  $C_{14}\text{mimBr}$ ,  $C_{16}\text{mimBr}$ ,  $C_{12}\text{mimPF}_6$ ,  $C_{14}\text{mimPF}_6$ , and  $C_{16}\text{mimPF}_6$ , can form ICs with  $\beta$ -CD, the surface tensions of their solutions would be distinctly affected by the addition of  $\beta$ -CD. Therefore, surface tension measurements can be used to elucidate not only whether



**Figure 1.** Dependence of surface tensions of 2.55 mmol/L IL surfactant aqueous solutions on the concentrations of  $\beta$ -CD. (■)  $C_{12}\text{mimPF}_6$ , (●)  $C_{14}\text{mimPF}_6$  and (▲)  $C_{16}\text{mimPF}_6$ .

inclusion can happen or not but also the stoichiometry of inclusion complexes. The surface tensions of pure water and 2.55 mmol/L IL surfactants aqueous solutions with various  $\beta$ -CD concentrations were measured respectively, and the dependence of the surface tensions on  $\beta$ -CD concentrations is shown in Figure 1. It is found that no remarkable change happens for the surface tensions of pure water when  $\beta$ -CD is added (not shown here), indicating that  $\beta$ -CD has no effect on the surface tensions of pure water. Thus, one may presume that the remarkable changes of surface tensions of IL surfactants aqueous solutions are ascribed to the formation of the inclusion complex. For  $C_{12}\text{mimPF}_6$ ,  $C_{14}\text{mimPF}_6$ , and  $C_{16}\text{mimPF}_6$  aqueous solutions, the surface tensions increase remarkably with increasing  $\beta$ -CD concentration, indicating the formation of inclusion complexes between  $\beta$ -CD and the IL surfactants. Two discernible breaks in the curves of surface tension of  $C_{12}\text{mimPF}_6$  and  $C_{14}\text{mimPF}_6$  occurs at about 1.3 and 2.6 mmol/L  $\beta$ -CD at 50 °C, respectively, suggesting that the stoichiometry of  $\beta$ -CD- $C_{12}\text{mimPF}_6$  and  $\beta$ -CD- $C_{14}\text{mimPF}_6$  is 1:2 and 1:1. However, for the surfactant  $C_{16}\text{mimPF}_6$ , the break only appears at 2.6 mmol/L  $\beta$ -CD at 60 °C (a higher temperature needed for  $C_{16}\text{mimPF}_6$  dissolved), showing a 1:1 inclusion complex. The reason perhaps is that  $C_{16}\text{mimPF}_6$  has a longer hydrophobic tail than  $C_{12}\text{mimPF}_6$  and  $C_{14}\text{mimPF}_6$ , thus a larger steric inhibition for penetrating the cavity of  $\beta$ -CD. So, only one  $C_{16}\text{mimPF}_6$  molecule is included in the  $\beta$ -CD molecule. Therefore, the  $\beta$ -CD- $C_{16}\text{mimPF}_6$  has a smaller stability constant than those of  $\beta$ -CD- $C_{12}\text{mimPF}_6$  and  $\beta$ -CD- $C_{14}\text{mimPF}_6$ . Accordingly, in their aqueous solutions, the equilibrium concentration of  $C_{16}\text{mimPF}_6$  is higher than  $C_{12}\text{mimPF}_6$  and  $C_{14}\text{mimPF}_6$ . As a result, the surface tension curve of  $C_{16}\text{mimPF}_6$  is lower than those of  $C_{12}\text{mimPF}_6$  and  $C_{14}\text{mimPF}_6$ . Thus, the surface tension measurements indicated that the long chain tails of  $C_{12}\text{mimPF}_6$ ,  $C_{14}\text{mimPF}_6$ , and  $C_{16}\text{mimPF}_6$  were included in the  $\beta$ -CD molecules. However, compared to  $C_{12}\text{mimPF}_6$ ,  $C_{14}\text{mimPF}_6$ , and  $C_{16}\text{mimPF}_6$ , IL surfactants  $C_{12}\text{mimBr}$ ,  $C_{14}\text{mimBr}$ , and  $C_{16}\text{mimBr}$  are more hydrophilic and the surface tensions of their aqueous solutions did not change with the addition of  $\beta$ -CD (not shown here), indicating that no inclusion complexes formed. The same result was also observed for hydrophilic IL  $\text{bmimBF}_4$ , whereas at the same condition, hydrophobic IL  $\text{bmimPF}_6$  could be included by  $\beta$ -CD. Therefore, it can be deduced that hydrophobicity plays an important role in the formation of inclusion complexes. It has been reported that the choice of anion determines water miscibility and has the most dramatic effect on the properties of ILs.<sup>24</sup> ILs containing the  $\text{PF}_6^-$  anion are sparingly water soluble, exhibiting a hydrophobic character, whereas  $\text{Br}^-$ -based ILs are very soluble in water. Considering that these two series of IL surfactants have the same cation, it is suggested that the nature of the anion has the most significant influence on the inclusion complexes.

**Powder X-ray Diffraction (XRD).** XRD is a widely used technique in the study of inclusion complexes for assessing the

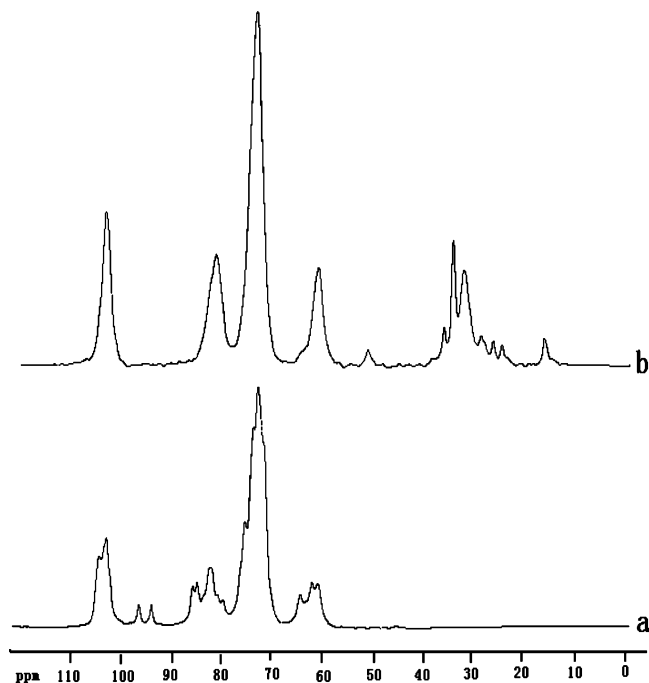


**Figure 2.** XRD patterns of (a)  $\beta$ -CD, (b)  $C_{12}$ mimPF<sub>6</sub>, (c)  $C_{14}$ mimPF<sub>6</sub>, (d)  $C_{16}$ mimPF<sub>6</sub>, (e)  $\beta$ -CD- $C_{12}$ mimPF<sub>6</sub>, (f)  $\beta$ -CD- $C_{14}$ mimPF<sub>6</sub>, and (g)  $\beta$ -CD- $C_{16}$ mimPF<sub>6</sub>.

structure and to check whether a new compound has been produced from the parent molecules.<sup>9</sup> Harada and co-workers<sup>8</sup> reported that the crystal structures of CD complexes were classified mainly into three types: channel-type, cage-type, and layer-type. Figure 2 shows the XRD patterns of  $\beta$ -CD, IL surfactants, and their respective ICs. The results suggest that the obtained ICs are fine crystalline powder. In Figure 2a, major peaks at 9.5°, 12.8°, 13.3°, and 18.1° are observed, indicating that  $\beta$ -CD represents a typical cage structure.<sup>8,14,16,18</sup> Figures 2b, 2c, and 2d show that the IL surfactants  $C_{12}$ mimPF<sub>6</sub>,  $C_{14}$ mimPF<sub>6</sub>, and  $C_{16}$ mimPF<sub>6</sub> have a similar XRD patterns, indicating the same crystal structure. However, their ICs,  $\beta$ -CD- $C_{12}$ mimPF<sub>6</sub>,  $\beta$ -CD- $C_{14}$ mimPF<sub>6</sub>, and  $\beta$ -CD- $C_{16}$ mimPF<sub>6</sub> (Figures 2e, 2f, and 2g) produce different patterns relative to their parents, with main signals at 11.6° and 17.6°, indicating a head-to-head channel-type structure,<sup>8</sup> which is different from that of  $\beta$ -CD.<sup>8,14,16,18</sup> The result is similar to that of bmimPF<sub>6</sub>, revealing that the inclusion complex is isomorphous with channel-type structure rather than the so-called “cage” type structure.<sup>21</sup>

The formation mechanism of such a channel-type structure has been widely investigated.<sup>14,15,17,34</sup> Generally, for a long-chain guest molecule, the inclusion complexes adopt a head-to-head channel-type structure in which CD molecules are stacked along an axis to form a cylinder. The hydrogen bonds between hydroxyl groups of neighboring CD molecules are mediated by water molecules.<sup>34</sup> In many cases, the hydrogen bonds between CDs play an important role in stabilizing the complexes.<sup>8</sup> Furthermore, van der Waals interactions and release of cyclodextrin strain energy upon complexation are considered to contribute to the formation of ICs.<sup>35</sup> It was also reported that the geometric compatibility or fit was thought to be a significant factor.<sup>18</sup> For the current investigated systems, it seemed that hydrophobic interaction was a crucial factor through surface tension measurements, although the IL surfactants  $C_{12}$ mimPF<sub>6</sub>,  $C_{14}$ mimPF<sub>6</sub>,  $C_{16}$ mimPF<sub>6</sub>, and  $\beta$ -CD can form a fine crystalline powder with a channel-type structure.

**Solid-State  $^{13}\text{C}$  CP/MAS NMR Spectroscopy.** High-resolution NMR spectroscopy is another technique to analyze the structure and molecular dynamics of ICs either in aqueous solution or in the solid state. It is known that the formation of the ICs should change the conformation and the electromagnetic environment of both the host CDs and the guest molecules, which should be reflected in the  $^{13}\text{C}$  CP/MAS NMR spectra of the host and guest molecules in their ICs.<sup>8,13,16,17</sup> As an example, Figure 3 shows the  $^{13}\text{C}$  CP/MAS NMR spectra of the free  $\beta$ -CD and  $\beta$ -CD- $C_{14}$ mimPF<sub>6</sub>. The  $\beta$ -CD molecules are known to have less symmetrical conformation in the crystalline state.<sup>14,16,17</sup> In this case, the spectrum of  $\beta$ -CD (Figure 3a) shows resolved carbon resonances from each of the glucose units, reflected by



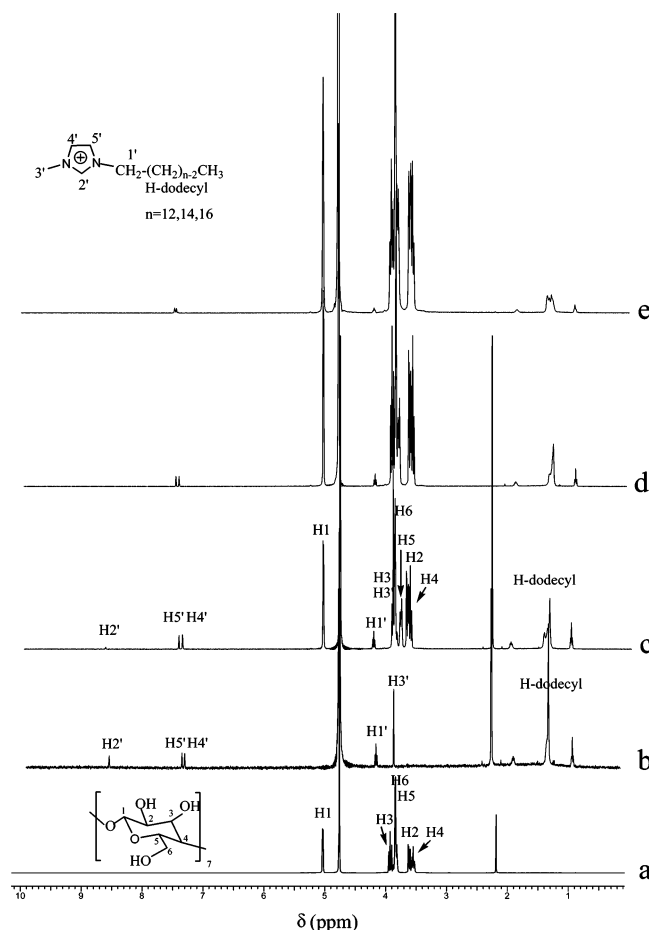
**Figure 3.**  $^{13}\text{C}$  CP/MAS NMR spectra of (a)  $\beta$ -CD and (b)  $\beta$ -CD- $C_{14}$ mimPF<sub>6</sub>.

strong splitting for all C1–C6 resonances. However, the resolved resonances disappear for the  $\beta$ -CD- $C_{14}$ mimPF<sub>6</sub>, and the  $^{13}\text{C}$  signals of the ICs give sharp singlets (Figure 3b). The results show that the  $\beta$ -CD molecules in the ICs adopt a more symmetrical conformation. That is, each glucose units of  $\beta$ -CD are in a similar environment.<sup>6,11,16</sup> The same results have also been observed for many other inclusion complex systems,<sup>8,16,17</sup> further indicating that the inclusion complex formed. In the Figure 3b, small resonance peaks in the solid-state  $^{13}\text{C}$  NMR spectrum of the  $\beta$ -CD- $C_{14}$ mimPF<sub>6</sub> IC at about 14, 23, 25, 28, 31, 33, 35, and 50 ppm are presumably due to the  $C_{14}$ mimPF<sub>6</sub> guest molecule, which indicates the presence of the  $C_{14}$ mimPF<sub>6</sub> guest molecule in the channel structure crystalline  $\beta$ -CD- $C_{14}$ mimPF<sub>6</sub> IC. The same results have also been observed for  $\beta$ -CD- $C_{12}$ mimPF<sub>6</sub> and  $\beta$ -CD- $C_{16}$ mimPF<sub>6</sub>. Accordingly, the formation of channel structure of ICs in the present study is further supported by the  $^{13}\text{C}$  CP/MAS NMR measurements.

**$^1\text{H}$  NMR Spectra.**  $^1\text{H}$  NMR is the most widely used technique to obtain information about inclusion modes and geometries.<sup>36</sup> It is very helpful to provide evidence for the information of ICs in solution, since the proton environments in both the host and guest molecules will be affected by their interaction and will hence be reflected by chemical shift variations of protons from both species.

The structures of the ICs between  $\beta$ -CD and  $C_{12}$ mimPF<sub>6</sub>,  $C_{14}$ mimPF<sub>6</sub>, and  $C_{16}$ mimPF<sub>6</sub> were further investigated using  $^1\text{H}$  NMR at room temperature. It is well known that  $\beta$ -CD molecules adopt the conformation of a torus where H-3 and H-5 protons are located inside the cavity, whereas H-2 and H-4 are outside the torus. Figure 4 shows the  $^1\text{H}$  NMR spectra in D<sub>2</sub>O of  $\beta$ -CD,  $C_{12}$ mimPF<sub>6</sub>,  $\beta$ -CD- $C_{12}$ mimPF<sub>6</sub>,  $\beta$ -CD- $C_{14}$ mimPF<sub>6</sub>, and  $\beta$ -CD- $C_{16}$ mimPF<sub>6</sub> solutions. In brief, only  $\beta$ -CD- $C_{12}$ mimPF<sub>6</sub> as a typical example was discussed here. It is obvious from Figure 4a that the expected H-5 signal of free  $\beta$ -CD cannot be clearly observed due to the overlapping with the H-6 signal and all resonances appearing as a strong and unresolved broad peak.<sup>37</sup> However, after adding  $C_{12}$ mimPF<sub>6</sub> to the  $\beta$ -CD solution, the shift of H-5 becomes obvious and has moved upfield from 3.82 to 3.75 and 3.72 ppm, as is shown in

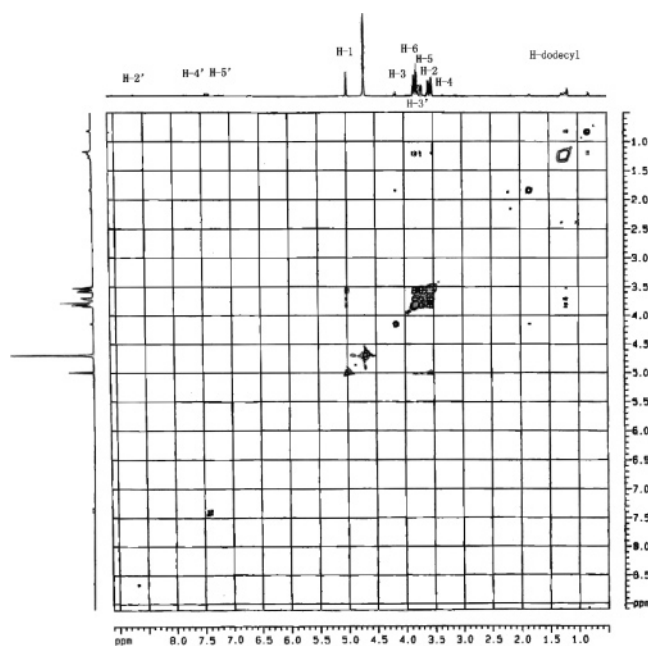




**Figure 4.**  $^1\text{H}$  NMR spectra of (a) free  $\beta$ -CD, (b)  $\text{C}_{12}\text{mimPF}_6$ , (c)  $\beta$ -CD- $\text{C}_{12}\text{mimPF}_6$ , (d)  $\beta$ -CD- $\text{C}_{14}\text{mimPF}_6$ , and (e)  $\beta$ -CD- $\text{C}_{16}\text{mimPF}_6$  in  $\text{D}_2\text{O}$ .

Figure 4c. A similar phenomenon was observed for sodium diclofenac (DCF), (+)-catechin (CA), (–)-epicatechin (EC), and undec-10-en-1-ol complexes with  $\beta$ -CD.<sup>36–38</sup> In addition to the upfield shift of H-5, we can observe that H-3 protons, appearing at 3.93 ppm, have shifted upfield to 3.84 ppm and the H-6 signal of  $\beta$ -CD has slightly shifted from 3.81 to 3.82 ppm to 3.79–3.75 ppm. Though the H-6 protons of the primary alcohol group are on the narrow side, the upfield shift is not as obvious as that of H-5 of the  $\beta$ -CD. The H-2 and H-4 of  $\beta$ -CD are located outside the cavity, and their signals remain unchanged upon the addition of  $\text{C}_{12}\text{mimPF}_6$ . These results indicate that the  $\text{C}_{12}\text{mimPF}_6$  molecules were included into the cavity of  $\beta$ -CD and no interaction existed between the outside of  $\beta$ -CD and  $\text{C}_{12}\text{mimPF}_6$ .

Moreover, the signals of  $\text{C}_{12}\text{mimPF}_6$  have changed in the presence of  $\beta$ -CD. The main peaks of long alkyl chain of  $\text{C}_{12}\text{mimPF}_6$  appearing at 2.19, 1.82, 1.22, and 0.82 ppm have moved to 2.20, 1.88, 1.23, and 0.86 ppm, respectively. Especially, the signals of most  $\text{CH}_2$  groups in the long chain, appearing at a center of 1.22 ppm, were greatly widened, indicating that the long alkyl tail of  $\text{C}_{12}\text{mimPF}_6$  had close contact with  $\beta$ -CD molecules. However, no changes happened for the other proton signals of the imidazolium ring, showing the imidazolium ring is still free. Therefore, we can conclude that only the long chain tail of  $\text{C}_{12}\text{mimPF}_6$  was included into the cavity of  $\beta$ -CD. The result is different from that of  $\text{bmimPF}_6$ , which has only a short butyl tail. In that case, the imidazolium ring was tightly included and its butyl tail was located freely near the center of the cavity along the molecular axis of  $\beta$ -CD. This result, together with the surface tension measurements, further shows that the tail



**Figure 5.**  $^1\text{H}$ - $^1\text{H}$  2D ROESY spectrum of the  $\beta$ -CD- $\text{C}_{12}\text{mimPF}_6$  in  $\text{D}_2\text{O}$  at 400 MHz and  $T_m = 300\text{ms}$ , at  $25.0^\circ\text{C}$ .

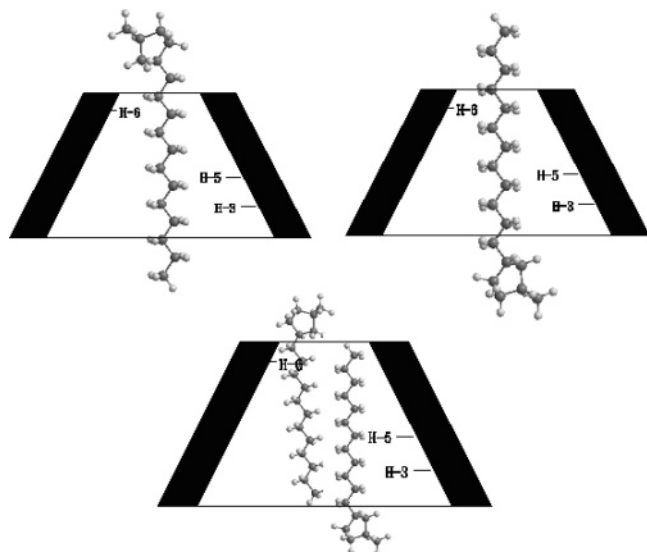
of  $\text{C}_{12}\text{mimPF}_6$  is included into the cavity of  $\beta$ -CD. A similar result was also obtained for the  $\beta$ -CD- $\text{C}_{14}\text{mimPF}_6$  and  $\beta$ -CD- $\text{C}_{16}\text{mimPF}_6$  (Figure 4d and 4e).

In addition, according to the  $^1\text{H}$  NMR spectra in Figure 4, the area ratio of the H-2' signal of  $\text{C}_{12}\text{mimPF}_6$  versus the H-1 signal of  $\beta$ -CD is 6:77 (area is not shown here), and there are seven H atoms in one  $\beta$ -CD molecule. Therefore, it can be calculated that every  $\beta$ -CD molecule includes 1.8  $\text{C}_{12}\text{mimPF}_6$  molecules. This means that there are two kinds of inclusion complexes with molecular ratios of 1:1 and 1:2 between  $\beta$ -CD and  $\text{C}_{12}\text{mimPF}_6$ , which was also concluded by the surface tension measurements above.

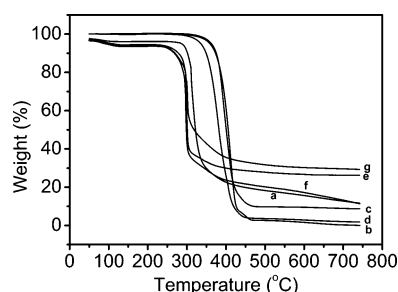
#### ROESY Spectra and Structure of Inclusion Complexes.

$^1\text{H}$ - $^1\text{H}$  ROESY is useful for determining which signals arise from protons that are close to each other in space, even if they are not bonded. A ROESY spectrum yields through-space correlations via spin–spin relaxation. So,  $^1\text{H}$ - $^1\text{H}$  ROESY spectra can further confirm the inclusion structure of ICs. Figure 5 shows the 2D ROESY spectra of  $\beta$ -CD- $\text{C}_{12}\text{mimPF}_6$ . There were no correlations observed between the protons of H-2', H-4', and H-5' of  $\text{C}_{12}\text{mimPF}_6$  and the protons of  $\beta$ -CD. The result is the same with that of the  $^1\text{H}$  NMR, showing that no interaction existed between the ring of imidazolium and  $\beta$ -CD. However, an obvious correlation was observed for the protons of H-1 and H-2 of  $\beta$ -CD. This is an inevitable phenomenon since H-1 and H-2 protons locate an adjacent position in the  $\beta$ -CD molecule. The similar correlations were also observed for the protons of H-2 and H-3, H-3 and H-4 as well as H-4 and H-5. On the 2D ROESY spectra, the interactions between H-3, H-6, H-5 of  $\beta$ -CD and the methylene groups in the hydrocarbon chain of the guest molecule, which resonate at a center of 1.25 ppm, could be identified, suggesting that the hydrocarbon chain of the guest molecule was inside the cavity and the imidazolium ring group protrudes outside. Furthermore, the 2D ROESY spectra also reveal that there are correlations among the methylene groups of IL surfactants resonating at 1.2–1.4 ppm. In this case, we cannot exclude the possibility that the included two long chains of IL molecules have close contact.

ROESY experiments along with  $^1\text{H}$  NMR spectra indicate spatial proximity for ten of the eleven methylene groups of the



**Figure 6.** Possible three inclusion structures of the  $\beta$ -CD- $C_{12}$ mimPF<sub>6</sub> in aqueous solution: (a) 1:1 stoichiometry and (b) 1:2 stoichiometry.



**Figure 7.** TGA curves obtained at a heating rate of 10 °C/min under nitrogen atmosphere for (a)  $\beta$ -CD, (b)  $C_{12}$ mimPF<sub>6</sub>, (c)  $C_{14}$ mimPF<sub>6</sub>, (d)  $C_{16}$ mimPF<sub>6</sub>, (e)  $\beta$ -CD- $C_{12}$ mimPF<sub>6</sub>, (f)  $\beta$ -CD- $C_{14}$ mimPF<sub>6</sub>, and (g)  $\beta$ -CD- $C_{16}$ mimPF<sub>6</sub>.

chain with the  $\beta$ -CD protons located in the cavity. If the chain adopts a zigzag conformation in the complex, that is, with the hydrocarbon chain completely extended, its calculated length is 12.6 Å. The height of  $\beta$ -CD is, however, about 7.9 Å. So the guest molecule should be in permanent motion in the  $\beta$ -CD cavity and adopts a conformation which tends to occupy the whole space of the cavity.<sup>36</sup> Due to the conical shape of the CD, two opposite orientations for the guest molecule in the ICs with 1:1 inclusion ratio are possible (Figure 6a). For the 1:2 stoichiometry, due to the electrostatic repulsion of positive charged imidazolium ring, we think that two IL molecules should be in a reverse orientation and thus only one inclusion formation appears (Figure 6b).

**TGA Analysis.** The thermal stabilities of the  $\beta$ -CD- $C_{12}$ mimPF<sub>6</sub>,  $\beta$ -CD- $C_{14}$ mimPF<sub>6</sub>, and  $\beta$ -CD- $C_{16}$ mimPF<sub>6</sub> were evaluated using TGA analysis and compared with pure  $\beta$ -CD,  $C_{12}$ mimPF<sub>6</sub>,  $C_{14}$ mimPF<sub>6</sub>, and  $C_{16}$ mimPF<sub>6</sub>. Figure 7 shows the weight loss curves for ICs of  $\beta$ -CD and their precursors. It is unexpected that three ICs have lower initial decomposition temperature than both IL surfactants and  $\beta$ -CD. Normally, the initial decomposition temperatures of ICs are higher than those of CDs and guest molecules, and the inclusion complexation is believed to contribute to the better stability of CDs.<sup>10,17</sup> Thus, the present TGA results are somewhat unusual. This phenomenon perhaps results from the unique molecular structures and properties of  $C_{12}$ mimPF<sub>6</sub>,  $C_{14}$ mimPF<sub>6</sub>, and  $C_{16}$ mimPF<sub>6</sub> compared with organic compounds and polymers. The current result implies that the hydrogen bond is a secondary factor to support the formation of ICs since a lot of hydrogen bonds would

increase the stability of precursors. Even so, it can be estimated that a few hydrogen bonds are only necessary to support the channel-type structure. Furthermore, the <sup>1</sup>H NMR spectra and 2D ROESY spectra show that no intensive interactions occur between the guest and host molecules. From these results, it is supposed that weak hydrophobicity plays a crucial role in the formation of ICs. The steric congestion<sup>14</sup> and the geometry distortion of the components may make these ICs unstable. Moreover, when the tails of  $[C_{12}\text{mim}]^+$ ,  $[C_{14}\text{mim}]^+$ , or  $[C_{16}\text{mim}]^+$  are included into the cavities of  $\beta$ -CD, the distance between the cations and PF<sub>6</sub><sup>-</sup> may be longer than that of their ion pairs. The quantum chemical calculation results show that the total energies of the detached cation and anion are higher than that of their ion pairs,<sup>39</sup> which may lead to lower decomposition temperature of these ICs.

The assumption that weak hydrophobicity plays a crucial role was also proved by the fact that if some organic solvents such as acetonitrile that are favorable solvents for  $C_{12}$ mimPF<sub>6</sub>,  $C_{14}$ mimPF<sub>6</sub>, and  $C_{16}$ mimPF<sub>6</sub> were added to the ICs, the ILs may be released from these ICs. However, if some intensive interactions such as hydrogen bonds contribute to the stability of ICs, the guest molecules included by CDs would not be easily recovered by this process. Based on this speciality, our future work focuses on the recovery of these surface-active ILs. It is well known that, in the process of preparation of ILs, some ILs will be wasted when rude products are salted out.<sup>32</sup> The recovery is intractable from a large amount of solid salt, especially for some surface-active compounds.

## Conclusions

The inclusion behaviors of  $\beta$ -CD and three IL surfactants,  $C_{12}$ mimPF<sub>6</sub>,  $C_{14}$ mimPF<sub>6</sub>, and  $C_{16}$ mimPF<sub>6</sub>, have been studied by various techniques. The results indicated that  $\beta$ -CD and  $C_{12}$ mimPF<sub>6</sub> or  $C_{14}$ mimPF<sub>6</sub> can form ICs with molecular ratio of 1:1 and 1:2. Only a 1:1 inclusion ratio was observed for the  $\beta$ -CD- $C_{16}$ mimPF<sub>6</sub> due to the strong steric inhibition of  $C_{16}$ mimPF<sub>6</sub>. XRD and <sup>13</sup>C CP/MAS NMR indicated that these ICs were isomorphous with a channel-type structure, and  $\beta$ -CD molecules in the ICs adopted a symmetrical conformation, each glucose unit of  $\beta$ -CD was in a similar environment. Based on the spectra of <sup>1</sup>H NMR and 2D ROESY, possible inclusion structures were speculated. TGA studies illustrated that the thermal stabilities of these ICs were lower than their two precursors. The possible reason was that weak hydrophobicity played a crucial role in the formation of ICs. The steric congestion and the geometry distortion of the  $\beta$ -CD in their ICs may reduce the thermal stability of the  $\beta$ -CD. When the tails of ILs are included into the cavities of  $\beta$ -CD, the distance between cations and PF<sub>6</sub><sup>-</sup> may be longer than that of their ion pairs, which may reduce the decomposition temperature of the ILs.

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