Interaction between Ionic Liquids and β-Cyclodextrin: A Discussion of Association Pattern

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We report herein the interaction of three ionic liquids, i.e., 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (**11**), 1-hexyl-2,3-dimethylimidazolium chloride (**16**), and 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (**17**), with β-cyclodextrin (β-CD). For **11** and **16**, the 1:1 inclusion complexes were determined and the association constants were estimated through a competitive fluorescence method, conductivity, and ^{19}F NMR measurements. It was confirmed that the alkyl side chain on the imidazolium ring but not the imidazolium ring itself entered into the cavity of β-CD. According to the association constants, the sequence of interaction strength of some ILs with β-CD was obtained. We also found that the cation and the anion in **17** exhibited strong interactions with β-CD simultaneously. Furthermore, a general interaction pattern of an IL with β-CD was suggested.

Introduction

Ionic liquids (ILs), organic salts, have become popular because of unusual properties such as negligible vapor pressure and their potential as attractive solvents in chemical reactions, separations, electrochemistry, and material synthesis.[1,2] Cyclodextrins (CDs) have received much attention partly because of their ability to form inclusion complexes and their wide applications.[3−6] The application of CDs in the media containing ionic liquids may produce interesting phenomena. For instance, supramolecular controlled pseudo-LCST (lower critical solution temperature) effect was observed in cyclodextrin-complexed poly(ionic liquids).[7] In an ionic liquid, i.e., 1-butyl-3-methylimidazolium hexafluorophosphate (**1**), polypseudorotaxanes have been prepared by supramolecular self-assembly of β-CD threaded onto the triblock copolymer Pluoronic F127.[8] In this system, a novel phenomenon was found; that is, not only the PO segments but also many EO segments were included by β-CD molecules in the β-CD/Pluronic F127 polypseudorotaxanes.[8] Samitsu et al. revealed the dissolution of PEG-CD polyrotaxanes in the ionic liquids composed of various alkylimidazolium cations and halogen anions.[9] It was found that these ionic liquids readily penetrated into the network of the cross-linked polyrotaxane gels, thereby yielding gels containing ionic liquids.[9] It was also expected that the dissolution of polyrotaxanes and the swelling of polyrotaxane gels in ionic liquids could lead to significant potential applications.[9]

For the wide application of ionic liquids to cyclodextrin-containing systems, it is necessary to understand how ionic liquids interact with CDs. Several research groups have reported on the inclusion complexes between CDs and ILs.[10−16] Gao et al. found the formation of the 1:1 (guest:host) inclusion complex between **1** and β-CD. Combining with NMR spectra of β-CD in the presence of **1**, they suggested that the whole imidazolium cation (C_4mim^+) was probably included by the cavity of β-CD while the PF_6^- ion dissociated near the β-CD.[10] Later, they further found that other three surface-active ionic liquids, i.e., 1-dodecyl-3-methylimidazolium hexafluorophosphate, 1-tetradecyl-3-methylimidazolium hexafluorophosphate, and 1-hexadecyl-3-methylimidazolium hexafluorophosphate could form 1:1 or both 1:1 and 2:1 inclusion complexes with β-CD.[11] Unlike the possible structure suggested for the **1**/β-CD inclusion complex, only the alkyl side chain on the imidazolium ring of these three ILs entered into the cavity of β-CD.[11] The formation of 1:1 and 2:1 inclusion complexes between 1-dodecyl-3-methylimidazolium hexafluorophosphate and β-CD was also reported by Li et al. and a similar structural pattern of the inclusion complex was suggested.[12] Francois et al. obtained the association constants between β-CD and series of alkylimidazolium cations. It was found that there was no interaction of 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium cations with β-CD. Accordingly, they suggested that there was no inclusion of the imidazolium ring into the cavity of β-CD.[13] Here, one may wonder whether or not the cationic imidazolium ring of an IL enters into the cavity of β-CD on earth.

Differently, several inclusion complexes of β-CD with anion of ILs were also reported. Amajjahe and co-workers found that the anion bis(trifluoromethylsulfonyl)imide (Tf_2N^-) of 1-butyl-3-vinylimidazolium bis(trifluoromethylsulfonyl)imide (**6**) formed exclusively host−guest complex with β-CD.[14,15] Similarly, the anion PF_6^- but not the cation C_4vim^+ in **4** (see Table 1) was found to be accommodated by β-CD.[14] In our previous work, we reported that **1**, **2**, and **3** formed 1:1 inclusion complexes with β-CD, respectively. Through ^{19}F NMR, we also found that PF_6^- and BF_4^- could interact with β-CD but the latter interaction was relatively weak.[16]

For quantitatively comparing the interaction of ILs with β-CD, we compile herein all the association constants found in the literature (see Table 1).[13,14,16] On the basis of the K_1 values in Table 1, some puzzling questions could be addressed immediately. First, it seems that the sole cation or the sole anion of an IL can interact with β-CD, depending on which interaction is predominated. Is there a possibility that the cation and the anion of an IL exhibit strong interactions with β-CD simultaneously? Second, one can see from Table 1 that large discrepancies of the association constants exist between some ILs with similar structures, e.g., **6** and **11**, **2**, and **12**. It is interesting to ascertain the reason for the discrepancy.

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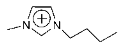
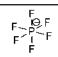
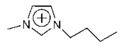
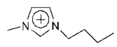
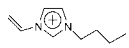
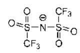
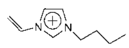
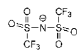
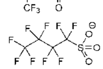
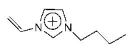
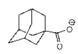
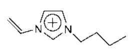
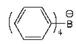
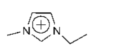
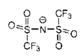
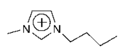
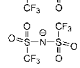
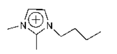
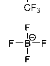
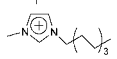
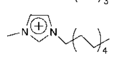
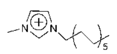
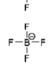
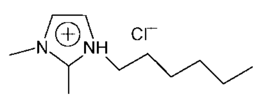
TABLE 1: Association Constants of Various ILs with β-CD at 298 K

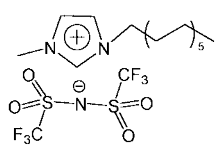
Number	ILs	Cation	Anion	K_1/ M^{-1}
1	C_4mimPF_6			156 [a]
2	C_4mimBF_4			32.2 [a], 0 [c]
3	C_4mimCl		Cl^-	8.16 [a]
4	C_4vimPF_6			289 [b]
5	C_1vimTf_2N			8190 [b]
6	C_4vimTf_2N			8100 [b]
7	$C_4vimNfO$			21000 [b]
8	$C_4vimAdCO_2$			5300 [b]
9	$C_4vimTPhB$			0 [b]
10	C_2mimTf_2N			0 [c]
11	C_4mimTf_2N			0 [c]
12	$C_4dmimBF_4$			0 [c]
13	C_8mimBr		Br^-	672 [c]
14	$C_{10}mimBF_4$			3038 [c]
15	$C_{12}mimBF_4$			10994 [c]

[a] Taken from ref 16. [b] Taken from ref 14. [c] Taken from ref 13.

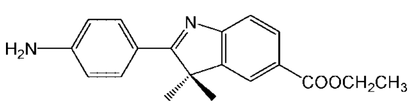
SCHEME 1: Molecular Structures of 16, 17, and 18



16



17



18

To help elucidate the above questions, we further examined the interaction of 1-hexyl-2,3-dimethylimidazolium chloride (**16**, see Scheme 1) and **11**, respectively, with β-CD. Compared with **3**, **16** has a longer alkyl side chain and **11** has a more hydrophobic anion, respectively. Moreover, we speculated that the cation and the anion of 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (**17**, see Scheme 1) might simultaneously show a strong interaction with β-CD. And then, through 2D ROESY NMR and ^{19}F NMR we examined the inclusion between **17** and β-CD. Comparing the results obtained herein with those of ILs with similar structures in the literature, and carefully analyzing all the results shown in Table 1, we would like to give a relatively clear picture regarding the interaction pattern of ILs with cyclodextrin.

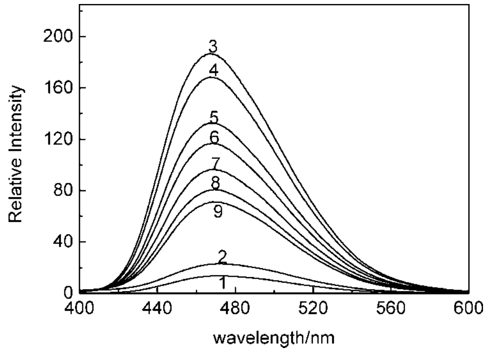


Figure 1. Fluorescence spectra of **18** in water (1), in the aqueous solution of 60.4 mM **16** (2), and in the aqueous solution of 4 mM β-CD with various concentrations of **16**: 0 (3), 10.1 mM (4), 20.1 mM (5), 30.2 mM (6), 40.3 mM (7), 50.4 mM (8), and 60.4 mM (9). T = 298.2 K.

Experimental Section

Materials. The syntheses and purifications of **11**, **17**, and 2-(*p*-aminophenyl)-3,3-dimethyl-5-carboethyoxy-3*H*-indole (**18**, see Scheme 1) were done according to refs 17 and 18, refs 19 and 20, and refs 21 and 22, respectively. β-CD (Fine Chemical Products of Nankai University, China) was recrystallized twice using tridistilled water and dried under vacuum for 24 h. **16** and α,α,α-trifluorotoluene purchased from ACROS were used as received. Methanol was redistilled after being dried with anhydrous sodium sulfate for about 24 h. Tridistilled water was used throughout the experiments. D_2O (99.9% isotopic purity, Beijing Chemical Reagents Co.) was used as solvent in NMR measurements.

Instruments. Fluorescence spectra were measured on a FL-4500 (Hitachi, Japan) spectrophotometer. A low-frequency conductivity meter (Model DDS-307, Shanghai Cany Precision Instrument Co., Ltd.) was used to measure conductivity at 298.2 ± 0.1 K. The spectra of ^{1}H NMR and ^{19}F NMR were recorded on Bruker AV400 MHz NMR spectrometer.

Methods. Fresh sample solutions were used in the fluorescence measurements. Stock solution of **18** was prepared in methanol, and 50 μL aliquots of this stock solution were added to 5 mL of volumetric flasks to maintain a final concentration of 10^{-6} M for fluorescence measurements. The pH values of all the solutions with **18** as a probe in this study were adjusted to 9.5 by adding NaOH, and no buffers were used.[23,24] The external reference α,α,α-trifluorotoluene was applied for ^{19}F NMR measurements. The chemical shift was given on the δ scale (ppm) and reference to an external sample of α,α,α-trifluorotoluene (δ = −63.90). ROESY experiments were carried out using a mixing time of 300 ms in the phase-sensitive mode.

Results and Discussion

1. Association Constants of the IL/β-CD Complexes. ***Competitive Fluorescence Method.*** The competitive method with fluorescent and UV−visible probes is very versatile and accurate to determine binding data.[16,25−29] Substituted 3*H*-indoles such as **18** have great sensitivity to microenvironments and have been widely applied as probes to study cyclodextrin-based supramolecular systems.[16,27,29,30] The fluorescence intensity of **18** in the aqueous solution of **16** is slightly larger than that of **18** in water (Figure 1), which means that **16** itself does not quench the fluorescence of **18**. The aqueous solutions of **16** in the range of concentrations investigated show no obvious fluorescence emission. Thus, the fluorescent spectra in Figure 1 originate only from probe **18**.[16]

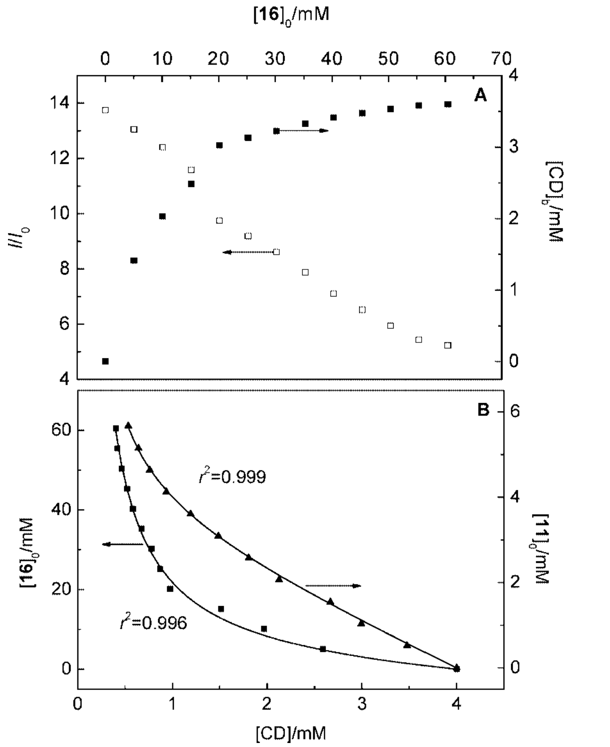


Figure 2. (A) Relative fluorescence intensity of **18** and the concentration of **16**-bound β-CD as a function of the initial concentration of **16**. (B) Initial concentration of **16** (■) and **11** (▲) vs the equilibrium concentration of β-CD, respectively. The lines are the nonlinear regression fits to the experimental data points following eq 1 at 298.2 K.

The fluorescence spectra of **18** in the **16**/β-CD systems are also shown in Figure 1. According to the previous method,[23] the K'_1, K'_2, I_1/I_0, and I_2/I_0 values (K'_1 and K'_2 are the association constants for 1:1 and 1:2 complexes between **18** and β-CD, respectively, while I_0, I_1, and I_2 stand for the fluorescence intensity of **18** in pure water, in the 1:1 complex, and in the 1:2 complex, respectively) estimated are 1060 ± 200 M^{-1}, 2770 ± 220 M^{-1}, 4.30 ± 1.60, and 14.9 ± 0.2, with a correlation coefficient $r^2 = 0.999$ by NLR analysis. The values are close to those reported in the literature.[27,30] The equilibrium concentration of β-CD, i.e., [CD], at different $[\mathbf{16}]_0$ (the initial concentration of **16**) can be calculated using the K'_1, K'_2, I_1/I_0, and I_2/I_0 values.[23,27] The concentration of β-CD binding with **16** can be obtained from the relationship $[CD]_b = [CD]_0 - [CD]$. In this study, $[CD]_b$ is always smaller than $[\mathbf{16}]_0$ indicating only the 1:1 complex between **16** and β-CD is formed (Figure 2A). For the 1:1 inclusion complex, $[\mathbf{16}]_0$ is related to [CD] by the following equation:[16,25–27,29]

$$[\mathbf{16}]_0 = \frac{([CD]_0 - [CD])(1 + K_1[CD])}{K_1[CD]} \quad (1)$$

According to eq 1, the estimated K_1 value at 298.2 K is 159 ± 2 M^{-1} (see Table 2). Figure 2B shows the nonlinear regression fits to the experimental data points with the correlation coefficient $r^2 = 0.996$. We have also tried to consider the other models describing the interaction of **16** with β-CD, but no reasonable results were obtained. Using the same method, the 1:1 inclusion complex between β-CD and **11** was also found, and the corresponding K_1 value at 298.2 K was 3000 ± 50 M^{-1} (see Figure 2B and Table 2).

TABLE 2: Association Constants of Several Guests with β-CD at 298 K

guests	K_1/M^{-1}	refs
16	159,[a] 112[b]	this work
11	3000,[a] 1500,[b] 2900[c]	this work
1-C_4H_9OH	15.8	41
1-butylimidazole	155	38

[a] Competitive fluorescence method. [b] Conductivity measurement. [c] NMR titration.

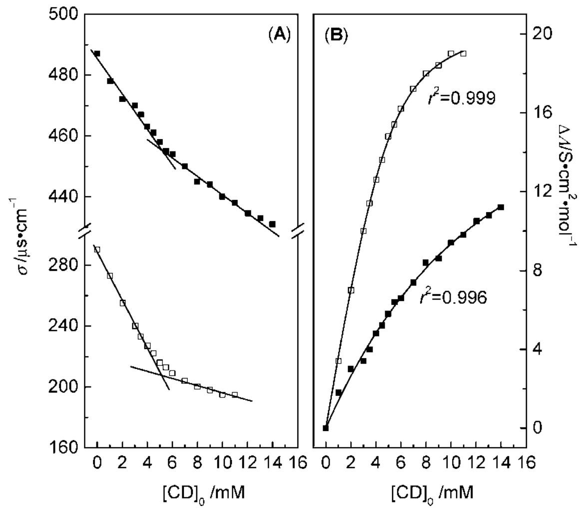


Figure 3. (A) Dependence of the conductivity on the concentration of β-CD at 298.2 K for the aqueous solutions of **16** (■) and **11** (□), respectively. (B) Plot of $\Delta\Lambda$ vs the concentration of β-CD for **16** (■) and **11** (□), respectively. T = 298.2 K.

Conductivity Measurement. The conductivity measurement is commonly employed to investigate the inclusion phenomenon and the stoichiometries of inclusion complexes.[16,31] In this study, the conductivity of the aqueous solutions including 5.00 mM of IL and different quantities of β-CD was measured at 298.2 K (Figure 3A). For both **16** and **11**, the conductivity decreases remarkably with increasing the β-CD concentration, indicating the formation of inclusion complexes between β-CD and the above two ILs. The inflection point appears at a concentration of about 5.00 mM, showing that the stoichiometry of the compound between IL and β-CD is equimolar. The association constant K_1 for 1:1 complexation was obtained by the following equation, which was first used for the interaction between ionic surfactants and CDs: [31–33]

$$\Delta\Lambda = \frac{\Delta\lambda}{2K_1C_s}[K_1(C_s + C_c) + 1 - ([K_1(C_s + C_c) + 1]^2 - 4K_1^2C_sC_c)^{1/2}] \quad (2)$$

where $\Delta\Lambda$ is the decrease in the molar conductivity of the IL occasioned by adding β-CD, $\Delta\lambda$ the difference in the ionic conductivities of the unassociated and associated ions of IL, C_s the same as $[IL]_0$, and C_c the initial concentration of β-CD. According to eq 2, it was estimated that the K_1 and $\Delta\lambda$ values for **16** at 298.2 K were 112 ± 13 M^{-1} and 20.2 ± 1.1 S•cm^2•mol^{-1}, respectively. Figure 3B shows the well fit with a correlation coefficient $r^2 = 0.996$. Also, the K_1 and $\Delta\lambda$ values for **11** were estimated to be 1500 ± 100 M^{-1} and 21.2 ± 0.2 S•cm^2•mol^{-1}, respectively, with the correlation coefficient r^2 = 0.999 (Figure 3B). The K_1 values obtained from the conductivity measurement were close to those based on

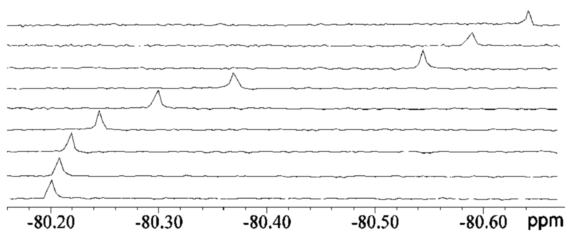


Figure 4. ^{19}F NMR spectra of 4×10^{-5} M **11** in D_2O with different concentrations of β-CD (mM, top to bottom): 0, 0.05, 0.10, 0.50, 1.00, 2.00, 4.00, 6.00, and 8.00, respectively. T = 298 K.

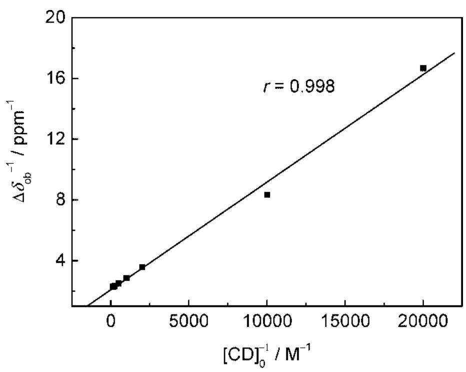


Figure 5. Benesi−Hildebrand plot of $1/\Delta\delta_{ob}$ as a function of $1/[CD]_0$ in the **11**/β-CD system at 298 K.

the competitive fluorescence method. The ionic conductivity of the cation associated with β-CD is lower than that of the unassociated ion because the mobility of the former is lower.

NMR Measurement. NMR spectroscopy is the most widely used technique to study cyclodextrin complexes. For the IL/β-CD systems, the ^{1}H NMR measurement has been carried out,[10−12] whereas the ^{19}F NMR study has been seldom reported.[14,16]

Figure 4 shows the spectra of ^{19}F NMR of **11** (4×10^{-5} M) at various concentrations of β-CD. It can be observed that the fluorine signal is shifted downfield by adding β-CD. The maximum difference of the chemical shift at 8 mM of β-CD is about 0.45 ppm.

It is well-known that the Benesi−Hildebrand equation for a complex of 1:1 stoichiometry is[34,35]

$$\frac{1}{\Delta\delta_{ob}} = \frac{1}{\Delta\delta_c K_1}\frac{1}{[CD]} + \frac{1}{\Delta\delta_c} \qquad (3)$$

where the equilibrium [CD] can be replaced by the total concentration of CD because of its large excess, $\Delta\delta_{ob}$ is the difference of the chemical shift observed for a guest in the absence and presence of CD, and $\Delta\delta_c$ is the difference in the chemical shift between the 1:1 complex and the free guest. On the basis of the chemical shift variation between free and complexed **11** shown in Figure 4, it was estimated using eq 3 that the K_1 and $\Delta\delta_c$ values at 298 K were 2900 ± 300 M^{-1} and 0.48 ± 0.04 ppm, respectively, with a correlation coefficient r = 0.998 (Figure 5). The K_1 value obtained with NMR measurement of Tf_2N^- anion was very close to those based on the competitive fluorescence method and conductivity method.

2. Interaction Pattern. In our previous work, we reported that the interaction between **3** and β-CD was very weak (K_1 = 8.16 M^{-1}).[16] The small association constant can be ascribed to the interaction between β-CD and C_4mim^+ of the ion pair C_4mim^+−Cl^-, since the inclusion of anion Cl^- with β-CD is negligible.[36,37] Unlike C_4mim^+, the neutral 1-butylimidazole molecule with similar structure interacts with β-CD much strongly (K_1 = 155 M^{-1}, see Table 2).[38] Obviously, the ionization of imidazole ring is unfavorable to its interaction with β-CD. Noticing that 1-C_4H_9OH also weakly interacts with β-CD (K_1 = 15.8 M^{-1}, see Table 2), we believe that only the butyl side chain but not the imidazolium ring enters into the cavity of β-CD. With increasing the length of alkyl side chain, the association constant of **16** with β-CD is obviously larger than that of **3**.

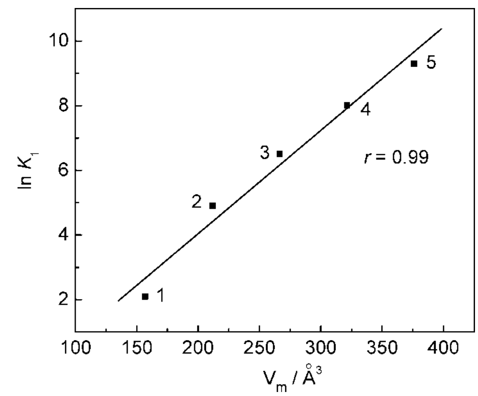


Figure 6. Plot of ln K_1 as a function of the volume of the alkyl side chain of IL: (1) **3**; (2) **16** (average value of the two association constants obtained from competitive fluorescence method and conductivity measurement in Table 2); (3) **13**; (4) **14**; (5) **15**. T = 298 K. The volume was calculated with software ChemSketch (Advanced Chemistry Development, Inc.).

It is known that a hydrophobic interaction induces a linear dependence of ln K (or standard transfer free energy) on molecular volume.[27,39] If only the alkyl side chain on the imidazolium ring of ILs interacts with β-CD, there should exist a linear relationship between ln K_1 and its volume V_m. Actually, Figure 6 exhibits such a straight line with a correlation coefficient $r \approx 0.99$. The above results further confirm that it is the alkyl side chain on the imidazolium ring that interacts with β-CD. For C_4mim^+, its interaction with β-CD is so weak that it is easily neglected. Francois et al. found that there was no inclusion between C_4mim^+ (or C_2mim^+) and β-CD (K_1 = 0).[13] Accordingly, they suggested that there was no inclusion of the imidazolium ring into the cavity of β-CD. The above analysis shows that the imidazolium ring does not interact with β-CD, however, C_4mim^+ actually interacts with β-CD to some extent through its butyl group.

It can be found that large discrepancies of the association constants exist between some ILs with similar structures, e.g., **6** and **11**, **2** and **12**, and even for the same **2** (see Table 1). This is because Francois et al. only measured the interaction between the cations of ILs with β-CD and did not examine whether the anions such as Tf_2N^- and BF_4^- interacted with β-CD through an affinity capillary electrophoresis.[13] The discrepancies just came from the interaction of their anions with β-CD. Francois et al. indicated that there was no inclusion of β-CD with the cations of **2**, **10**, **11**, and **12**, respectively.[13] For 1-butyl-3-vinylimidazolium (C_4vim^+, its structure is very similar to C_4mim^+), Amajjahe and co-workers found that it did not interact with β-CD either.[14] Thus, the observed interaction of **2** and **6** with β-CD should originate from the anions. Actually, Amajjahe and co-workers found that only anions PF_6^-, Tf_2N^-, NfO^-, and $AdCO_2^-$ but not cations C_4vim^+ or C_1vim^+ interacted with β-CD (see Table 1).[14] The estimated association constants of **11**, **1**, and **2** with β-CD obtained by our group are 3000, 156, and

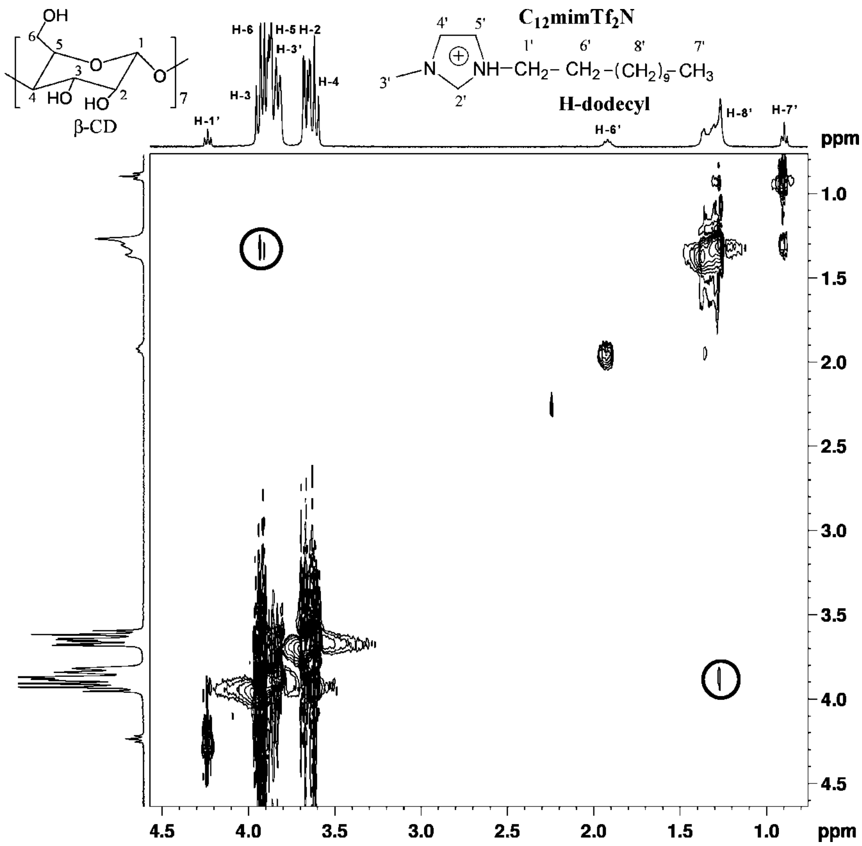


Figure 7. ^{1}H−^{1}H 2D ROESY NMR spectrum of the **17** (1.5 mM)−β-CD (2.1 mM) in D_2O at 400 MHz and T_m = 300 ms, T = 298 K.

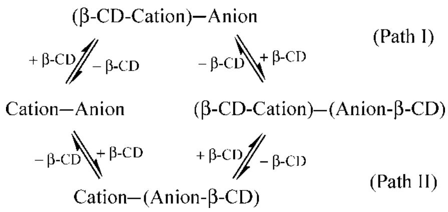
32.2 M^{-1}, respectively.[16] The different association constants originate from different anions. In fact, ^{19}F NMR measurements of **11**, **1**, and **2** in the absence and presence of β-CD showed an obvious change.[16] According to the fact that **11**, **1**, and **2** interacted with β-CD more strongly than **3**, the association constants 3000, 156, and 32.2 M^{-1} should be ascribed to the interaction of Tf_2N^-, PF_6^-, and BF_4^- anions with β-CD, respectively. This result is coincident with the reports of Amajjahe et al.[14] Because the structure of **4** is very similar to **1**, the cation C_4vim^+ does not interact with β-CD while PF_6^- does.[14] The corresponding association constant 289 M^{-1} is also close to 156 M^{-1} in our case.[14]

It was observed that both C_4mim^+ and the similar C_4vim^+ did not interact with β-CD through affinity capillary electrophoresis and microcalorimetry, respectively. In this case, we show that the interaction between C_4mim^+ and β-CD is so weak that it cannot be easily detected by other methods. For Tf_2N^- and PF_6^- interacting with β-CD, it can be seen that the association constants obtained by different methods including competitive fluorescence method, conductivity, ^{19}F NMR, and microcalorimetry show some differences. It is not unusual that different measurements induce different K values and even the different complex stoichiometries. For example, using different methods, many groups have studied the Triton X-100/β-CD system; however, the estimated association type and constants differed considerably.[29] Similar phenomena also happened to the SDS/β-CD system.[27] Using the competitive fluorescence method with **18** as a probe, we also investigated the above two systems and reasonable results were obtained.[27,29] Furthermore, using the same method, we have studied the interaction between β-CD and ILs such as **1**, **2**, and **3**.[16] In the present work, the above method, ^{19}F NMR, and conductivity are carried out. The association constants are in agreement with each other, and therefore, it is believed that the obtained results are reasonable.

According to the association constants (see Table 1), the strength of various cations (alkyl side chain) and anions (hydrophobic part) interacting with β-CD may follow the order: nonafluorobutanesulfonate (NfO^-) > 1-dodecyl-3-methylimidazolium cation ($C_{12}mim^+$) > bis(trifluoromethylsulfonyl)imide (Tf_2N^-) ∼ adamantylcarboxylate ($AdCO_2^-$) ∼ 1-decyl-3-methylimidazolium cation ($C_{10}mim^+$) > 1-octyl-3-methylimidazolium cation (C_8mim^+) > 1-hexyl-2,3-dimethylimidazolium cation (C_6dmim^+) ∼ PF_6^- > BF_4^- > 1-butyl-2,3-dimethylimidazolium cation (C_4dmim^+) ∼ 1-butyl-3-vinylimidazolium cation (C_4vim^+) ∼ 1-butyl-3-methylimidazolium cation (C_4mim^+) > Cl^-. This finding might be helpful in the fields of material synthesis and reaction control in the presence of both ILs and CDs.

On the basis of the above interaction order, both $C_{12}mim^+$ and Tf_2N^- may strongly interact with β-CD. To elucidate whether or not there exists a possibility that the cation and the anion of an IL exhibit strong interactions with β-CD simultaneously, we have investigated the interaction between **17** and β-CD. ^{1}H−^{1}H ROESY is generally employed to obtain noncovalent interaction in supramolecular systems. The 2D ROESY NMR spectra (figure not shown) show that there are no correlations observed between the protons of H-2′, H-4′, and H-5′ in **17** and the protons of H-3 and H-5 in β-CD. Thus, the imidazolium ring does not interact with β-CD, which further confirms the above conclusions. However, the resonation correlations at a center of 1.25 ppm marked with circles in Figure 7 suggest that the alkyl side chain on the imidazolium ring is inside the cavity of β-CD. These results are consistent with those for the inclusion between $C_{12}mimPF_6$ and β-CD.[11,12] At the same time, ^{19}F NMR spectra show that the signal of fluorine in anion Tf_2N^- affords a downfield shift with adding β-CD. The maximum difference of the chemical shift is about 0.45 ppm (see Supporting

SCHEME 2: Two-Step Equilibrium in an IL/β-CD System[a]



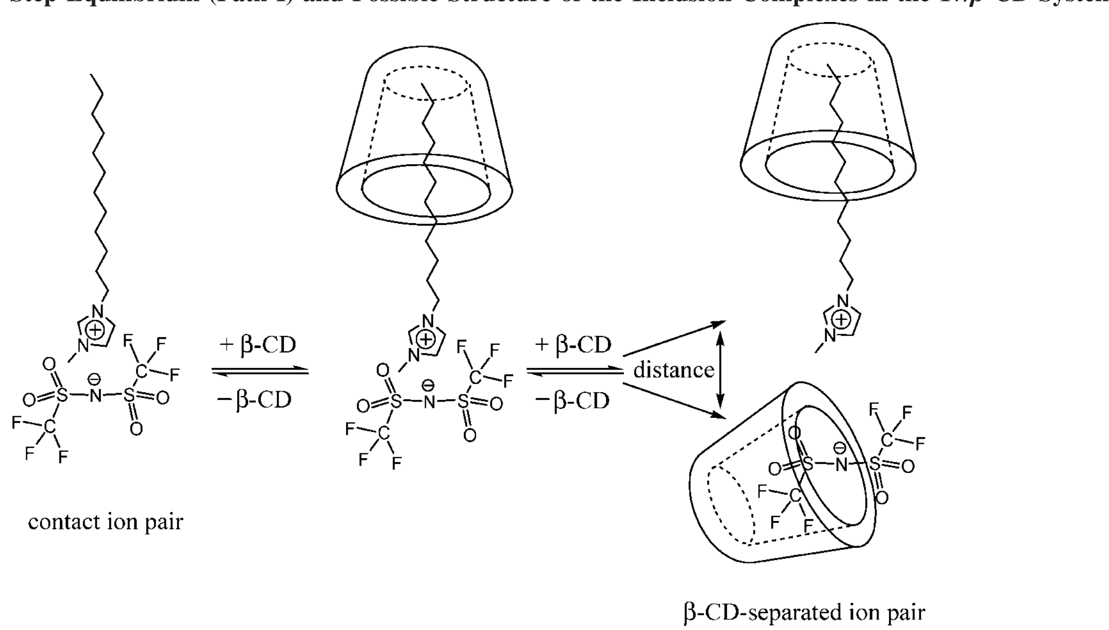
[a] Path I: the cation interacts with β-CD more strongly than the anion does. Path II: the anion interacts with β-CD more strongly than the cation does.

Information). Therefore, the simultaneous interaction of both the cation and the anion in **17** with β-CD is exhibited in this case. In the present work, through the ^{19}F NMR measurement, competitive fluorescence method and conductivity measurement, it is found that Tf_2N^- in C_4mimTf_2N formed 1:1 inclusion complexes with β-CD. This result agrees with that reported in the literature.[14] Moreover, Amajjahe and coworkers considered that the generation of 1:1 inclusion complex led to the separated ion pair from the contact ion pair.[14] For $C_{12}mim^+$, Francois et al. found that it formed 1:1 inclusion complexes with β-CD.[13] Based on the above results, it can be seen that both the cation and the anion of **17** can interact with β-CD, respectively. Obviously, there exists a 1:2 inclusion complex in the **17**/β-CD system. The dominant factor for producing the 1:2 inclusion complex is that both the cation and the anion can strongly interact with β-CD.

Combining all the above results, we suggest herein a two-step equilibrium existing in all IL/β-CD system (see Scheme 2). There are two paths (Path I and Path II) of complexation between an IL and β-CD, in which one of the cation or the anion first interacts with β-CD, respectively. If one of them interacts with β-CD very weakly, the 1:2 inclusion complex should be very few and only 1:1 inclusion complexes may be detected. However, if both the cation and the anion of an IL such as **17** can strongly interact with β-CD, the 1:2 inclusion complex is obviously shown. In fact, according to the competitive fluorescence method, we reconsider the 1:1 and 1:2 coexisting model describing interaction of **11** with β-CD. The estimated K_1 and K_2 values are 2900 ± 60 and 10 ± 5 M^{-1} with the correlation coefficient $r^2 = 0.999$ by NLR analysis (see Supporting Information). This result is also reasonable and essentially in agreement with the previous result because both the K_1 values are nearly the same. The very small K_2 value is very close to 8.16 M^{-1} and may originate from the interaction of C_4mim^+ with β-CD. This result further supports the two-step equilibrium in an IL/β-CD system.

Thus, combining the sequence of the association constants with the two-step equilibrium, we may give a clear picture of the interaction pattern at each condition. For **1**, **2**, **4**−**8**, and **10**−**12**, their interaction pattern with β-CD follows Path II. The hydrophobic part of their anions first binds β-CD to form 1:1 inclusion complexes. As the alkyl side chain of their cations is too short to obviously interact with β-CD, the 1:2 inclusion complex is difficult to be detected. For **3**, **9**, and **13**−**17**, their interaction pattern with β-CD follows Path I. As for **13**−**16**, the longer alkyl side chain of their cations first binds β-CD to form 1:1 inclusion complexes. Because of the weak interaction between their anions and β-CD, the 1:2 inclusion complex is also difficult to be detected. As to **3**, because the alkyl side chain of its cation interacts with β-CD weakly and its anion hardly interacts with β-CD, the association constant of the 1:1 inclusion complex is very small and the 1:2 inclusion complex is difficult to be found. As to **9**, we speculate that its interaction pattern with β-CD follows Path I. The alkyl side chain of its cation interacts with β-CD weakly and its anion is too large to interact with β-CD. Thus, similar to **3**, the association constant of the 1:1 inclusion complex should be very small and the 1:2 inclusion complex should be difficult to be examined. As for **17**, because the interaction between the alkyl side chain of its cation and β-CD is stronger than that of its anion, the alkyl side chain of $C_{12}mim^+$ first binds β-CD to form 1:1 inclusion complex. Then one of CF_3SO_2 groups in Tf_2N^- further interacts with β-CD, and the 1:2 inclusion complex exists to a great extent.

SCHEME 3: Two-Step Equilibrium (Path I) and Possible Structure of the Inclusion Complexes in the 17/β-CD System



The two-step equilibrium and possible structure of the inclusion complexes between **17** and β-CD are suggested as Scheme 3. It is confirmed that a Tf_2N^- interacts with only one β-CD despite two CF_3SO_2 groups existing, which may be due to the spatial hindrance coming from the ion pair. Additionally, we imagine that the 1:1 inclusion complex between the alkyl side chain of $C_{12}mim^+$ and β-CD affects the contact ion pair indistinctively because the β-CD has a distance from the charge center. However, when the CF_3SO_2 group of Tf_2N^- further interacts with β-CD, the contact ion pair becomes separated.[14]

3. Driving Forces of Complexation. It is reasonable to suggest that hydrophobic interaction is the main driving force for the formation of inclusion complexes between ILs and β-CD. Theoretically, the group with charge is energetically unfavorable to interact with β-CD because of easy hydration. For an alkylimidazolium cation, only the hydrophobic alkyl side chain interacts with β-CD while the ionized imidazole ring does not. For the hydrophobic anions such as NfO^-, Tf_2N^-, PF_6^-, and BF_4^- with many fluorine atoms, they can strongly interact with β-CD while their atoms with negative charge prefer to be out of the cavity of β-CD.[14] Similar phenomena also happen in the fluorinated surfactant/β-CD system.[40] Furthermore, there possibly exists hydrogen bonding in the complexation. For example, the oxygen of a CF_3SO_2 group in Tf_2N^- may form hydrogen bonding with the hydrogen of hydroxyl group in β-CD. In addition, the size effect is another important factor to affect inclusion process. For example, too large hydrophobic anions such as tetraphenylborate $(Ph)_4B^-$ do not form inclusion complex with β-CD because of steric hindrance effect.[14] Compared with the native β-CD, substituted β-CDs such as hydroxypropyl-β-CD, heptakis(2,6-di-*O*-methyl)-β-CD and heptakis(2,3,6-tri-*O*-methyl)-β-CD show a weakening interaction with ILs owing to the steric hindrance.[13]

According to the above results, we may further discuss how NfO^-, Tf_2N^-, PF_6^-, and BF_4^- interact with β-CD. All the above anions can form 1:1 inclusion complexes with β-CD, respectively. The hydrophobic part of each anion interacts with β-CD while the atom with negative electricity such as O^-, N^-, P^-, and B^- is out of β-CD. Scheme 3 shows the possible structure of the inclusion complex between Tf_2N^- and β-CD, in which only one CF_3SO_2 group in Tf_2N^- is involved in β-CD. For NfO^-, the highly hydrophobic perfluorobutyl group may be appropriately accommodated by β-CD and shows a very strong interaction. When the anions are PF_6^- and BF_4^-, only part of their fluorine atoms enter into the cavity of β-CD. In summary, hydrophobic interaction and size matching play dominant roles throughout the complexation.

Conclusions

We investigated the interaction of several imidazolium-based ILs with β-CD and confirmed that the imidazolium ring did not interact with β-CD while its alkyl side chain did. Hydrophobic interaction and size matching are important driving forces in the inclusion process. According to the association constants, it was found that the strength of the interaction of various cations and anions in ionic liquids with β-CD follows the following order: nonafluorobutanesulfonate (NfO^-) > 1-dodecyl-3-methylimidazolium cation ($C_{12}mim^+$) > bis(trifluoromethylsulfonyl)imide (Tf_2N^-) ~ adamantylcarboxylate ($AdCO_2^-$) ~ 1-decyl-3-methylimidazolium cation ($C_{10}mim^+$) > 1-octyl-3-methylimidazolium cation (C_8mim^+) > 1-hexyl-2,3-dimethylimidazolium cation (C_6dmim^+) ~ PF_6^- > BF_4^- > 1-butyl-2,3-dimethylimidazolium cation (C_4dmim^+) ~ 1-butyl-3-vinylimidazolium cation (C_4vim^+) ~ 1-butyl-3-methylimidazolium cation (C_4mim^+) > Cl^-. It was found that both the cation and the anion in **17** exhibited strong interactions with β-CD simultaneously. Furthermore, as a general interaction pattern of an IL with β-CD, a two-step equilibrium is suggested. There are two paths of complexation between an IL and β-CD, in which one of the cation or the anion first interacts with β-CD, respectively. This finding may be helpful in the fields of material synthesis and reaction control in the presence of both ILs and CDs.

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Supporting Information Available: Figure SI-1 shows the ^{19}F NMR spectra of 1.5 mM **17** in D_2O with different concentrations of β-CD. Figure SI-2 shows initial concentration of **11** vs the equilibrium concentration of β-CD. This material is available free of charge via the Internet at http://pubs.acs.org.

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