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Interaction between β-cyclodextrin and ionic liquids in aqueous solutions investigated by a competitive method using a substituted 3H-indole probe

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Abstract

We report herein the interaction of three kinds of ionic liquids, i.e., 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF_6), 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF_4) and 1-butyl-3-methylimidazolium chloride (bmimCl) with β-cyclodextrin (β-CD) using 2-(*p*-aminophenyl)-3,3-dimethyl-5-carboethyoxy-3*H*-indole (**1**) as a fluorescent probe through a competitive method. The formation of the 1:1 (guest:host) inclusion complex was suggested and the association constants at different temperatures were estimated, from which the thermodynamic parameters $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ were also obtained. The negative entropy and enthalpy changes indicated that the formation of above inclusion complexes was entropically unfavorable and enthalpy-driven. Conductivity measurements were also employed to study above systems. The results showed agreement with those based on the competitive method. Furthermore, through NMR, the location of anions in the system of ILs and β-CD was investigated. We suggested that the anion was accommodated to a great extent by the cavity forming ion pair with imidazolium cation which was totally in the cavity of β-CD. The above work demonstrated that molecule **1** is a very sensitive fluorescence probe for studying the interaction of a non-fluorescent guest with cyclodextrins.

Keywords: Inclusion complex; Ionic liquid; β-Cyclodextrin; Steady-state fluorescence; ^{19}F NMR; Conductivity

1. Introduction

Ionic liquids (ILs), organic salts, as a "green" alternative to the conventional and environmentally detrimental volatile solvents, have negligible vapor pressure, excellent thermal stability, strong ability to dissolve many chemicals, high electrical conductivity, wide electrochemical window, and ability of repetitive utilization [1–3]. All the unusual properties help ILs to be widely applied in material syntheses [4–6], chemical reactions [7–9], separations [10–12], electrochemistry [13,14] and formation of ordered molecular assembly [15]. Among various ILs, the alkylimidazolium salts, 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF_6), 1-butyl-3-methyl imidazolium tetrafluoroborate (bmimBF_4) and 1-butyl-3-methylimidazolium chloride (bmimCl) (see Scheme 1) are widely investigated.

Cyclodextrins (CDs) are a series of doughnut-shaped cyclic oligosaccharides, mostly composed of 6, 7, and 8 D-(+)-glucose units named α-, β-, and γ-CD, respectively. Their hydrophobic cavity can accommodate various guest molecules to form inclusion complexes. This leads to widespread applications in pharmaceutical chemistry, food technology, analytical chemistry, chemical synthesis, and catalysis [16,17].

Understanding the interaction between IL and CD is important to analytical chemistry and material synthesis [18–20]. The effect of ILs as solvents on CDs has been first studied. It was found that the presence of ethylammonium nitrate involves a decrease in the solubility of β-CD in water. With further addition of this IL, the solubility increases anew. The solubility of β-CD in this IL is about 20 times the value in pure water [21]. Also, Liu et al. have reported that β-CD is only sparingly soluble in weakly coordinating ionic liquids such as bmimBF_4. However, the ionic liquids which contain the dicyanamide anion can dissolve 750 g L^{-1} of β-CD at 75 °C [22]. CDs or their derivatives dissolved in ILs can be used to prepare stationary phases

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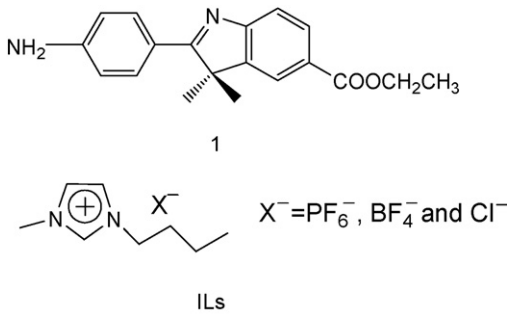

Scheme 1. Molecular structures of **1** and ILs ($bmimPF_6$, $bmimBF_4$ and bmimCl).

in gas chromatography [23]. Moreover, Qi et al. have used ILs as running electrolytes in capillary zone electrophoresis and β-CD as a modifier for the separation of anthraquinones extract of Chinese herb [18]. The inclusion complexation of methyl orange or phenol with CDs in bmimCl has been studied using near-infrared spectrometry [24,25]. Sueishi and Ide have also investigated the inclusion complexation of methyl orange with β-CD in $bmimBF_4$ [26].

Later, through the results of solubility and conductivity, Gao et al. suggested that the inclusion complex in 1:1 (guest:host) stoichiometry between β-CD and $bmimPF_6$ was formed [27]. Using surface tension measurements, they further found that another three kinds of surface-active ionic liquids, i.e., 1-dodecyl-3-methylimidazolium hexafluorophosphate ($C_{12}mimPF_6$), 1-tetradecyl-3-methylimidazolium hexafluorophosphate ($C_{14}mimPF_6$) and 1-hexadecyl-3-methylimidazolium hexafluorophosphate ($C_{16}mimPF_6$) could form 1:1 or both 1:1 and 2:1 inclusion complexes with β-CD [3]. The formation of 1:1 and 2:1 inclusion complexes between $C_{12}mimPF_6$ and β-CD was also reported by Li et al. [28]. However, the association constants have not been reported in the above studies.

Very recently, affinity capillary electrophoresis method was employed to obtain the stoichiometry and association constants of the inclusion complexes between the alkylimidazolium cations in ILs and CDs. However, owing to the limitation by the accuracy of methods, the weak interaction between β-CD and the ILs with short alkyl chains such as $bmimBF_4$ was not detected [29]. Therefore, it is important to employ a reliable method to study the interaction between CDs and such kinds of ILs.

The competitive method with fluorescent and UV–visible probes has been employed to investigate the inclusion complexes between CDs and guest molecules, especially non-fluorescent or non-UV guests [30–33]. Using the competitive method with fluorescent probe, the interaction between β-CD and several surfactants has been successfully investigated [30–32]. Very recently, using the same method, we have studied the interaction between β-CD and Triton X-100. The formation of 1:1 and 1:2 inclusion complexes was confirmed and the association constants were estimated [34]. Therefore, the competitive method with a fluorescent probe is worth studying further to obtain reasonable association types and constants between ILs and CDs.

For substituted 3*H*-indoles have great sensitivity to microenvironments [35], their use as probes has been highlighted in reverse micelles [36], micelles [37–39], surfactant vesicles [40] and cyclodextrins [41,42]. We have studied the locations of different groups of a cationic surface-active 3*H*-indole probe molecule in the AOT (sodium bis-(2-ethylhexyl) sulfosuccinate)-based water-in-oil microemulsion [43,44]. Especially, we synthesized a 3*H*-indole-β-CD, which showed novel recognition behavior and photoinduced energy transfer with naphthalene and its derivatives [45,46]. Other investigation has been also performed with 3*H*-indoles, including **1** (see Scheme 1) [32,39,42,47,48], which can form two types of inclusion complexes, i.e., 1:1 and 1:2 types [32], with β-CD in aqueous solutions.

In this work, we have used **1** as a fluorescent probe to investigate the inclusion complexes of β-CD with $bmimPF_6$, $bmimBF_4$ and bmimCl, respectively. The types of the inclusion complexation between ILs and β-CD were obtained. Moreover, the association constants of the inclusion complexes at different temperatures were also estimated, from which the thermodynamic parameters were obtained. In addition, the conductivity measurement was employed to investigate the IL/β-CD systems. The results showed agreement with those based on the competitive method.

Finally, to get deep insight into the location of anions of ILs in inclusion complexes [3,27,28], the ^{19}F NMR measurements have been carried out.

2. Experimental

2.1. Materials

The synthesis and purification of **1** were done according to the literature [49,50]. β-CD (AP, Fine Chemical Products of Nankai University) was recrystallized twice using tridistilled water and dried under vacuum for 24 h. $BmimPF_6$, $bmimBF_4$, bmimCl and α,α,α-trifluorotoluene purchased from Acors 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 Company) was used as solvent in NMR measurements.

2.2. Instruments

Fluorescence spectra were measured on a FL-4500 (Hitachi, Japan) spectrophotometer. Each solution was excited near its maximum absorption wavelength (356 nm for **1**). Both the excitation and emission band passes were 5 nm throughout. The scan speed was 240 nm min^{-1}. The temperature was controlled by placing the sample in a cell compartment whose walls were accessible to water circulation. The final temperature of the sample was measured by means of a thermocouple (Checktemp, Hanna, Italy) immersed in the solution (±0.1 K). A low-frequency conductivity meter (Model DDS-307, Shanghai Cany Precision Instrument Co., Ltd.) was used to measure conductivity at 298.0 ± 0.1 K. At the same temperature, the ^{19}F

NMR was recorded on Bruker AV400 MHz NMR spectrometer.

2.3. Methods

Fresh sample solutions were used in the absorption and fluorescence measurements. Stock solution of **1** 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 samples for the competitive method were prepared by adding ILs to the β-CD-**1** systems. We also tried another procedure for preparing above samples, i.e., adding **1** to the β-CD-IL system. It was found that the sequence of addition of reagents did not affect the results in this case (see the Supplement Information, Part I). The pH values of all the solutions with **1** as a probe in this study were adjusted to 9.5 by adding NaOH, and no buffers were used [47,48]. The external reference α,α,α-trifluorotoluene was applied for ^{19}F NMR. The chemical shift was given on the δ scale (ppm) and reference to an external sample of α,α,α-trifluorotoluene ($\delta = -63.90$).

3. Results and discussion

3.1. Investigation on the IL/β-CD systems using fluorescence competitive method

The fluorescence intensity of **1** in the aqueous solution of ILs such as $bmimPF_6$ is slightly larger than that of **1** in water (Fig. 1), although **1** may enter into the self-aggregation of ILs [1,51]. The red edge effect (REE) happened to the fluorescence spectra of pure ILs [52,53], however, the aqueous solution of each IL ($bmimPF_6$, $bmimBF_4$ and bmimCl) in the investigated range of concentration showed no obvious fluorescence emission. Thus, the fluorescent spectra in Fig. 1 originated only from probe **1**.

The fluorescence spectra of **1** in the $bmimPF_6$/β-CD system are also shown in Fig. 1. The concentration of $bmimPF_6$ is in the range from 0 to 36 mM, whereas the concentration of β-CD is fixed at 4 mM. According to the literature, the fluorescence intensity of **1** at 4 mM of β-CD reaches a plateau showing that most molecules of **1** exist in 1:2 complexes, and thus the 1:1:1 (guest A:guest B:host) ternary complex between **1**, $bmimPF_6$ and β-CD can be assumed not to form [32]. 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, respectively, while I_0, I_1 and I_2 stand for the fluorescence intensity of **1** in pure water, in the 1:1 complex and in the 1:2 complex, respectively) were estimated at various temperatures [47], by NLR analysis with a correlation coefficient $r^2 = 0.999$ (see the Supplement Information, Part II). The equilibrium concentration of β-CD, i.e., [CD], at different $[bmimPF_6]_0$ (the initial concentration of $bmimPF_6$) can be calculated, using the corresponding K'_1, K'_2, I_1/I_0, and I_2/I_0 values [32,47]. If only 1:1 inclusion complex is formed between $bmimPF_6$ and β-CD, one can consider the following equilibrium:

$$bmimPF_6 + CD \overset{K_1}{\rightleftharpoons} bmimPF_6\text{-}CD \quad (1)$$

where $bmimPF_6$-CD represents the 1:1 complex, the association constant of which is K_1. Considering Eq. (1) and the mass balances of $bmimPF_6$ and β-CD, $[bmimPF_6]_0$ is related to [CD] by the following equation [30–32,34]:

$$[bmimPF_6]_0 = \frac{([CD]_0 - [CD])(1 + K_1[CD])}{K_1[CD]} \quad (2)$$

According to Eq. (2), it was estimated that the K_1 value at 291.2 K was $198 \pm 3\ M^{-1}$ (see Table 1). Fig. 2 shows the nonlinear regression fits to the experimental data points following Eq. (2) at different temperatures with the correlation coefficient $r^2 = 0.999$. We have also tried to consider the other models describing the interaction of $bmimPF_6$ with β-CD, but no reasonable results were obtained. Using the same method, the interaction of $bmimBF_4$ and bmimCl with β-CD, respectively, was also studied. These two ILs also formed 1:1 inclusion complexes with β-CD, the association constants of which were summarized in Table 1.

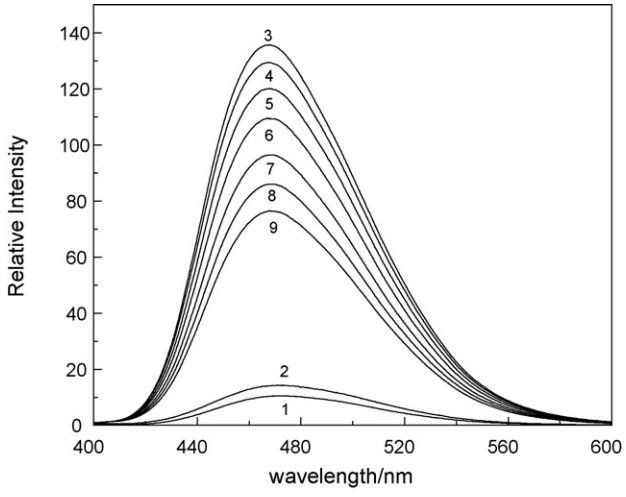

Fig. 1. Fluorescence spectra of **1** in water (1), in 36 mM $bmimPF_6$ (2), and in 4 mM β-CD with various concentrations of $bmimPF_6$: 0 (3); 6 mM (4); 12 mM (5); 18 mM (6); 24 mM (7); 30 mM (8) and 36 mM (9). $T = 291.2$ K.

Table 1
Association constants of $bmimPF_6$, $bmimBF_4$ and bmimCl with β-CD at various temperatures

T (K)	K_1 (M^{-1})			Method
	$bmimPF_6$	$bmimBF_4$	bmimCl	
276.2	333 ± 4	60.2 ± 0.8	10.5 ± 0.1	Fluorescence
284.0	256 ± 2	50.2 ± 0.6	9.2 ± 0.1	
291.2	198 ± 3	39.4 ± 0.3	8.8 ± 0.1	
299.0	145 ± 1	30.6 ± 0.3	8.0 ± 0.1	
306.8	112 ± 2	24.4 ± 0.2	7.4 ± 0.1	
316.0	84 ± 1	19.4 ± 0.1	6.9 ± 0.1	
298.0	110 ± 10	–	–	Conductivity
	99 ± 6	–	–	NMR (Peak 1)
	129 ± 7	–	–	NMR (Peak 2)

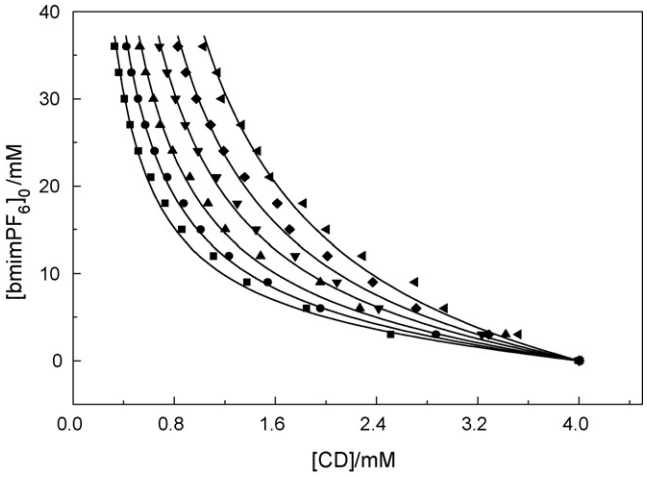

Fig. 2. Initial concentration of $bmimPF_6$ vs. the equilibrium concentration of β-CD. The lines are the nonlinear regression fits to the experimental data points following Eq. (2) at different temperatures: 276.2 K (■); 284.0 K (●); 291.2 K (▲); 299.0 K (▼); 306.8 K (♦); 316.0 K (◄).

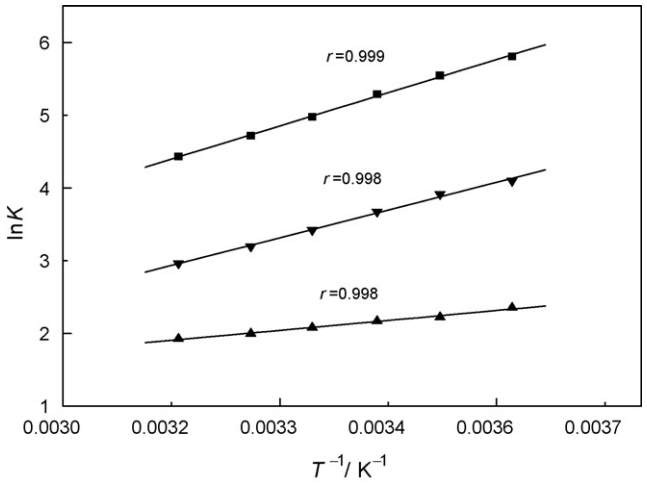

Fig. 3. The linear relationship of $\ln K$ vs. $1/T$ for the interaction between $bmimPF_6$ (■), $bmimBF_4$ (▼) and bmimCl (▲) with β-CD.

On the basis of the association constants obtained with the above method (Table 1), according to the van't Hoff equation:

$$\ln K = -\frac{\Delta H^{\Theta}}{\mathrm{RT}} + \frac{\Delta S^{\Theta}}{R} \quad (3)$$

One can easily find that linear relationships between $\ln K$ and $1/T$ exist (Fig. 3). Thermodynamic parameters ΔH^{Θ}, ΔS^{Θ} for the formation of the inclusion complexation have been obtained (see Table 2).

Table 2
Thermodynamic parameters ΔG^{Θ} (298 K), ΔH^{Θ} and ΔS^{Θ} for the inclusion complexation of $bmimPF_6$, $bmimBF_4$ and bmimCl with β-CD

	ΔG^{Θ} (KJ mol^{-1})	ΔH^{Θ} (KJ mol^{-1})	ΔS^{Θ} (J mol^{-1}K^{-1})
$bmimPF_6$	−12.5	−25.3	−43.0
$bmimBF_4$	−8.6	−21.1	−42.0
bmimCl	−5.2	−7.6	−8.2

Negative ΔG^{Θ} values show that the inclusion processes proceed spontaneously, while negative ΔH^{Θ} and ΔS^{Θ} values mean that the inclusion complexation is exothermic and enthalpy-controlled, but not entropy driven. This is the common situation concerning the formation of inclusion complexes between CDs and various guest molecules. In this case, the negative ΔS^{Θ} values are unfavorable to the formation of the inclusion complexes. However, this unfavorable effect is overcome by the more negative values of ΔH^{Θ} leading to energetically favorable values, i.e., negative values of ΔG^{Θ}.

3.2. Investigation on the IL/β-CD systems using conductivity

The conductivity measurement is commonly employed to investigate the inclusion phenomenon. Through this method, the stoichiometries of the inclusion complexes can be deduced from the breaks in the curves of the molar conductivity versus the concentration of β-CD [54]. In our case, the conductivity of the aqueous solution including an IL (5.0 mM) and different quantities of β-CD were measured at 298.0 K (Fig. 4A). For $bmimPF_6$, the conductivity decreases remarkably with increasing β-CD concentration, indicating the formation of inclusion complex between β-CD and the IL. The inflection point appears at a concentration of about 5.0 mM, showing that the stoichiometry of the compound between $bmimPF_6$ and β-CD is equimolar, which is in agreement with the result reported in literature [27]. 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 [54–56]:

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

where $\Delta\Lambda$ is the decrease in molar conductivity of the $bmimPF_6$ occasioned by adding β-CD, $\Delta\lambda$ the difference in the ionic conductivities of the unassociated and associated ions of $bmimPF_6$, C_s same as $[bmimPF_6]_0$, and C_c the initial concentration of β-CD. According to Eq. (4), it was estimated that the K_1 and $\Delta\lambda$ values at 298.0 K were $110 \pm 10\ \mathrm{M}^{-1}$ and $55 \pm 2\ \mathrm{S\,cm^2\,mol^{-1}}$, respectively. Fig. 4B shows the well fit with a correlation coefficient $r^2 = 0.998$. The K_1 value obtained with conductivity measurement was very close to the value based on the fluorescence competitive 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.

For $bmimBF_4$ and bmimCl, the addition of β-CD induces a slight decrease of the conductivity. Unlike the situation of $bmimPF_6$, it is difficult to observe an obvious break in the conductivity curves of these two ILs, indicating their weak interaction with β-CD.

3.3. Investigation on the IL/β-CD systems using ^{19}F NMR

NMR spectroscopy is the most widely used technique to study cyclodextrin complexes. For the IL/β-CD systems, the ^1H NMR

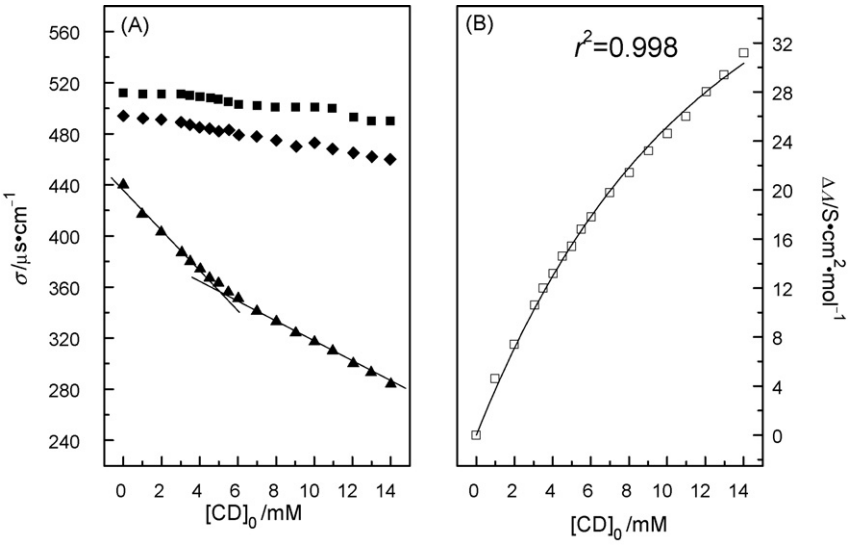

Fig. 4. (A) Dependence of the conductivity on the concentration of β-CD at 298.0 K for the aqueous solutions of bmimPF$_6$ (▲), bmimBF$_4$ (♦) and bmimCl (■). (B) Plot of $\Delta\Lambda$ vs. the concentration of β-CD for bmimPF$_6$ at 298.0 K.

measurement has been carried out [3,27,28], however, the ^{19}F NMR study has been seldom reported.

Fig. 5 shows the spectra of ^{19}F NMR of bmimPF$_6$ (4×10^{-5} M) at various concentrations of β-CD. It was found that both of the fluorin signals (−72.82 and −74.70) were shifted upfield by adding β-CD. The maximum difference of the chemical shift at 12 mM of β-CD was about 0.38.

It is known that the Benesi–Hildebrand equation for a complex of 1:1 stoichiometry is [57,58]:

$$\frac{1}{\Delta\delta_{ob}} = \frac{1}{\Delta\delta_c K_1}\frac{1}{[CD]} + \frac{1}{\Delta\delta_c} \quad (5)$$

where the equilibrium [CD] can be replaced by the total molar concentration of CD in the case of a large excess of host, $\Delta\delta_{ob}$ is the chemical shift difference observed in a guest for a given [CD], $\Delta\delta_c$ 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 bmimPF$_6$ showed in Fig. 5, according to Eq. (5), it was estimated that the K_1 and $\Delta\delta_c$ values at 298.0 K were $99 \pm 6\ M^{-1}$ and 0.70 ± 0.05 ppm (Peak 1), $129 \pm 7\ M^{-1}$ and 0.61 ± 0.04 ppm (Peak 2), respectively. Fig. 6 shows the well fit with a correlation coefficient $r = 0.999$. The K_1 values obtained with NMR measurement of PF_6^- anion were very close to those based on the fluorescence competitive method and conductivity method (see Table 1). The interaction between bmimBF$_4$ (5×10^{-5} M) and β-CD was also investigated by ^{19}F NMR. It was found that the fluorin signals (−152.12 and −152.07) of bmimBF$_4$ were also shifted upfield by adding β-CD, however, the maximum dif-

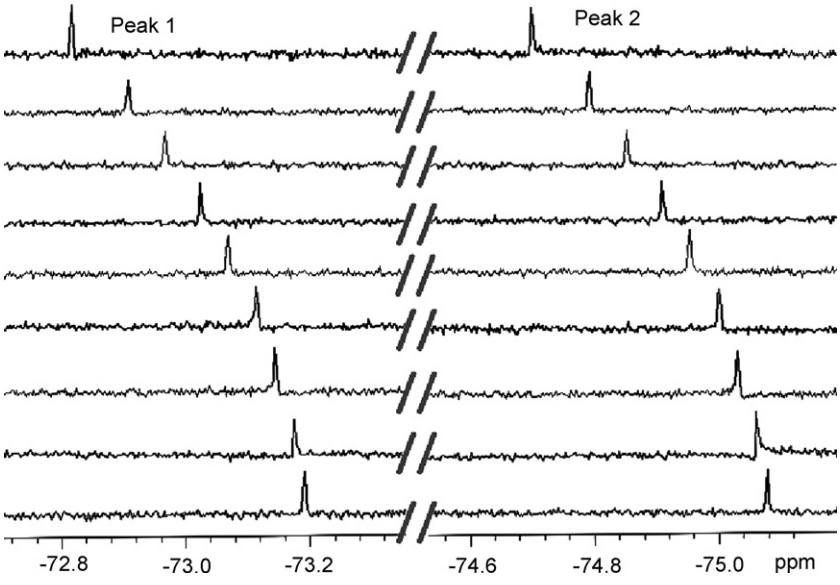

Fig. 5. ^{19}F NMR spectra of 4×10^{-5} M bmimPF$_6$ in D$_2$O with different concentrations of β-CD (mM, up to down): 0; 1.50; 3.00; 4.50; 6.00; 7.50; 9.00; 10.5; 12.0. T = 298.0 K.

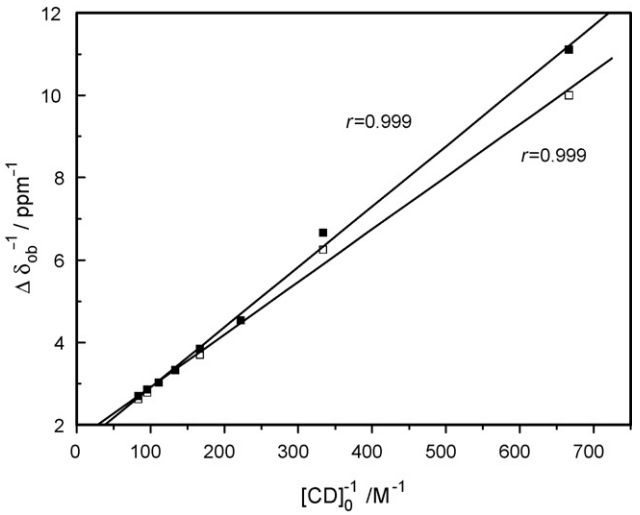

Fig. 6. Benesi–Hildebrand plots for fluorin signal Peak 1 (■) and Peak 2 (□) of $bmimPF_6$/β-CD system at 298.0 K.

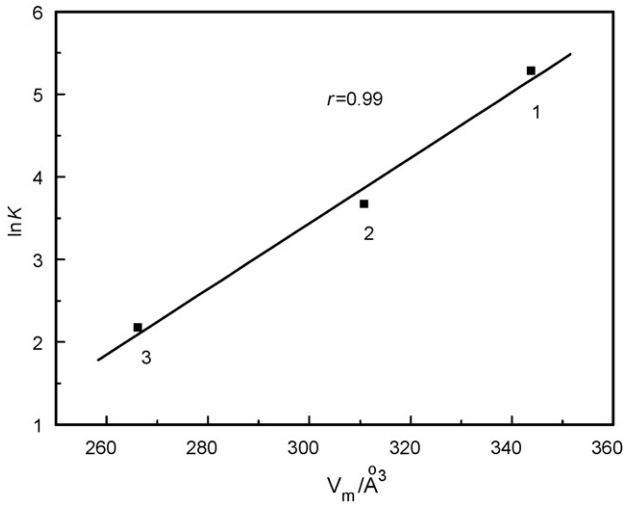

Fig. 7. Plot of ln K as a function of the molecular volume of IL. (1) $bmimPF_6$; (2) $bmimBF_4$; (3) bmimCl. T = 291 K.

ference in the observed chemical shift was only 0.02 in the presence of 12.0 mM β-CD. The interaction was too weak to estimate the association constant with the Benesi–Hildebrand equation.

3.4. The binding site of ILs in the β-CD cavity

Gao et al. have found that the whole imidazolium cation of $bmimPF_6$ was included by the cavity of β-CD through the solid-state ^{13}C CP/MAS NMR and ^{1}H NMR measurements [27]. Using ^{13}C CP/MAS NMR and ^{1}H–^{1}H ROESY NMR, they also studied the interaction of three surface-active ILs ($C_{12}mimPF_6$, $C_{14}mimPF_6$ and $C_{16}mimPF_6$) with β-CD. It was suggested that the long hydrocarbon chain of the ILs was inside the cavity and the imidazolium ring group protruded outside [3]. For $C_{12}mimPF_6$, using the methods of ^{13}C CP/MAS NMR and 2D ^{1}H–^{1}H COSY NMR [28], Li et al. have also reported that only the long chain tail of the imidazolium cation entered the cavity of β-CD.

It seems not difficult to understand that the cation of ILs without long hydrocarbon chain can be included into the cavity of β-CD. The key problem is the location of anion. It has been suggested that the anion perhaps dissociates near the β-CD molecules [27]. According to the results of ^{19}F NMR measurements (Section 3.3), the fact that the fluorin signals of PF_6^- were shifted upfield with the addition of β-CD suggested that the anion interacted with β-CD to a great extent and thus suffered an obvious change of environment.

It is known that the dependence of ln K (or standard free energy of transfer) on the molecular volume can be taken as a strong evidence of hydrophobic interaction [37]. Fig. 7 illustrates the plot of ln K as a function of V_m (which is estimated from the density of ILs), for the interaction between different ILs and β-CD. The plot exhibits a straight line with a correlation coefficient r = 0.99. This result suggests that the ILs as a whole entity can interact with the cavity of β-CD.

Nevertheless, the dehydration of the hydrophilic anion of an IL in water is energetically unfavorable to its entering deeply into the hydrophobic cavity of β-CD despite the static interaction. It is well known that the solvation energy of above anions of ILs is much different. Thus, the great difference of the association constants can be ascribed to the different interactions of anions with the cavity of β-CD regardless of the same cation of ILs included in the cavity of β-CD.

4. Conclusions

The interaction of the ionic liquids, i.e., $bmimPF_6$, $bmimBF_4$ and bmimCl, with β-CD was studied by steady-state fluorescence, conductivity and NMR measurements. Using molecule **1** as a fluorescence probe through a competitive method, the 1:1 inclusion complexes between ILs and β-CD were characterized. The association constants of the inclusion complexes at different temperatures were also estimated, from which the thermodynamic parameters ΔG^{Θ}, ΔH^{Θ} and ΔS^{Θ} were obtained. The negative entropy and enthalpy changes indicated that the formation of above inclusion complexes was entropically unfavorable and enthalpy-driven. The ability for ILs to associate with β-CD followed the order: $bmimPF_6 \gg bmimBF_4 > bmimCl$. Furthermore, we thought that the anion was accommodated to a great extent by the cavity forming ion pair with imidazolium cation which was totally in the cavity of β-CD. Our work demonstrates that molecule **1** is a very sensitive fluorescence probe for studying the interaction of a non-fluorescent guest with cyclodextrin.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.jphotochem.2008.01.001.

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