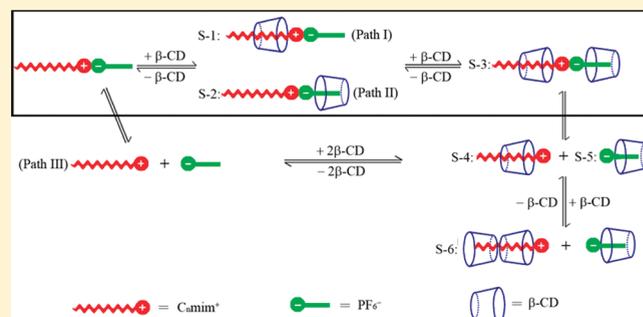


Multiple Equilibria Interaction Pattern between the Ionic Liquids $C_n\text{mimPF}_6$ and β -Cyclodextrin in Aqueous Solutions

Jingjing Zhang and Xinghai Shen*

Beijing National Laboratory for Molecular Sciences (BNLMS), Radiochemistry and Radiation Chemistry Key Laboratory of Fundamental Science, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

ABSTRACT: The interactions of ionic liquids (ILs) 1-alkyl-3-methylimidazolium hexafluorophosphate ($C_n\text{mimPF}_6$, $n = 2, 4, 6, 8$) with β -cyclodextrin (β -CD) in aqueous solutions are investigated in this article. The stoichiometry and apparent association constants were obtained by the competitive fluorescence method, NMR measurements, and isothermal titration calorimetry (ITC). The results showed that $C_2\text{mimPF}_6$, $C_4\text{mimPF}_6$, and $C_6\text{mimPF}_6$ form 1:1 (guest:host) inclusion complexes with β -CD whereas the 1:2 inclusion complex can be formed between $C_8\text{mimPF}_6$ and β -CD. We studied the existence state of the ILs and found that they exist mainly as separated ions with a minor percentage existing as associated ion pairs within the concentration studied. By ESI/HRMS, the coexistence of different complexes including $C_n\text{mim}^+ \cdot \text{PF}_6^- - \beta\text{-CD}$, $C_n\text{mim}^+ - \beta\text{-CD}$ (or $C_n\text{mim}^+ - \beta\text{-CD}_2$), and $\text{PF}_6^- - \beta\text{-CD}$ was observed. It is also deduced that the intermediate complex, $(\beta\text{-CD} - \text{cation}) \cdot (\text{anion} - \beta\text{-CD})$, may dissociate into cation- β -CD and anion- β -CD complexes. Thermodynamic parameters determined by ITC indicate that, while the inclusion process for $C_6\text{mimPF}_6/\beta\text{-CD}$ complex is entropy and enthalpy driven, the interactions of other $C_n\text{mimPF}_6$ ($n = 2, 4, 8$) with β -CD are enthalpy controlled. Based on these results, a more comprehensive pattern involving multiple equilibria on the interaction between $C_n\text{mimPF}_6$ and β -CD in aqueous solutions is presented herein.



INTRODUCTION

Cyclodextrins (CDs), a series of doughnut-shaped cyclic oligosaccharides composed of six, seven, and eight D-(+)-glucose units named α -, β -, and γ -CD, respectively, can form inclusion complexes with a number of organic and inorganic guest molecules.^{1–6} They are commercially available, nontoxic, and water soluble, which makes them suitable for numerous applications in the pharmaceutical industry, foodstuffs, and so on.^{7,8} Ionic liquids (ILs), which consist of organic cations and appropriate anions, have been regarded as a good alternative to conventional and environmentally detrimental volatile solvents. Their intriguing properties such as negligible vapor pressures, nonflammability, tunable physicochemical properties, high electrical conductivities, and wide electrochemical windows make them extensively studied in the fields of chemical reactions, separations, and electrochemistry.^{9–14} Furthermore, in the field of supramolecular chemistry, ILs are becoming more and more important. They could either directly participate in the assembly of supramolecular organizations or influence the assembly of various supramolecular structures.¹⁵ The combination of CDs and ILs is interesting and has been applied in supramolecular systems with novel structures and properties,^{16–22} in catalysis,²³ in separations,^{24–29} etc. As a result, the interaction between CD and IL is of great importance and there are some reports on this subject.^{30–35}

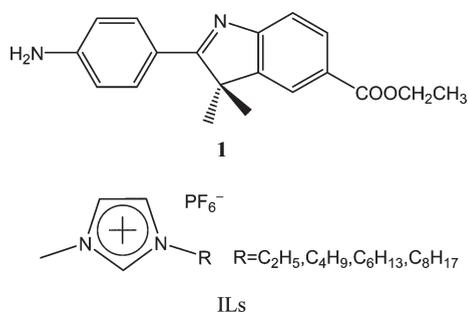
Our research group is interested in the topic and has investigated the interaction between imidazolium-based ILs and β -CD in aqueous solutions in the past several years.^{36,37} Based on the results from ourselves and others, an interaction pattern between ILs and β -CD was proposed.³⁷ That is, there are two paths of complexation: if the cation interacts with β -CD more strongly than the anion does, the cation first interacts with β -CD to form $(\beta\text{-CD} - \text{cation}) \cdot \text{anion}$ complex (path I); contrarily, if the anion interacts with β -CD more strongly than the cation does, the anion interacts with β -CD first to form $\text{cation} \cdot (\text{anion} - \beta\text{-CD})$ complex (path II). Both paths will further result in the formation of $(\beta\text{-CD} - \text{cation}) \cdot (\text{anion} - \beta\text{-CD})$ complex when the second β -CD binds the $(\beta\text{-CD} - \text{cation}) \cdot \text{anion}$ or $\text{cation} \cdot (\text{anion} - \beta\text{-CD})$.³⁷ In this pattern, ILs were considered as entire cation–anion ion pairs. Very recently, it has been noted that the existing form of ILs in hydrous circumstances depends on the water content.^{38–42} With a small amount of water, the “wet” ILs can be regarded as nanostructured supramolecular networks with polar and nonpolar regions.^{41,43} The increase of water content leads to the formation of contact ion pairs,³⁸ and when the water content is relatively high, the ion pairs mainly dissociate into separated cations and anions.⁴² Consequently, one may wonder about

Received: July 7, 2011

Revised: August 17, 2011

Published: September 07, 2011

Scheme 1. Molecular Structures of 1 and ILs ($C_n\text{mimPF}_6$, $n = 2, 4, 6, 8$)



the state of these ILs in aqueous solutions, the contact ion pairs, or the dissociated ions, and how these ILs interact with β -CD.

We also noticed in the literature that the complexation of 1-butyl-3-vinylimidazolium bis(trifluoromethylsulfonyl)imide ($C_4\text{vimTf}_2\text{N}$) by β -CD can result in the transformation from the contact ion pair $C_4\text{vim}^+ \cdot \text{Tf}_2\text{N}^-$ to the spatially separated ion pair $C_4\text{vim}^+ \cdot (\text{Tf}_2\text{N}^- - \beta\text{-CD})$.¹⁹ It is deduced that the spatially separated ion pair, (β -CD-cation)·anion or cation·(anion- β -CD), will be formed when β -CD interacts with one part of a cation·anion ion pair. According to the interaction pattern we suggested in ref 37, a 1:2 (guest:host) inclusion complex (β -CD-cation)·(anion- β -CD) might be formed when both the anion and cation can interact strongly with β -CD. If the second β -CD complexes the spatially separated ion pair (β -CD-cation)·anion or cation·(anion- β -CD), whether the 1:2 (β -CD-cation)·(anion- β -CD) complex can stably exist or not will be further examined herein. In this article, we will try to answer these questions and suggest a more comprehensive pattern on the interaction between ILs and CD in aqueous solutions by taking the ILs 1-alkyl-3-methylimidazolium hexafluorophosphate ($C_n\text{mimPF}_6$, $n = 2, 4, 6, 8$) for examples (Scheme 1).

EXPERIMENTAL SECTION

Materials. The synthesis and purification of 2-(*p*-aminophenyl)-3,3-dimethyl-5-carboethoxy-3*H*-indole **1** (Scheme 1) were done according to refs 44 and 45. β -CD (Beijing Aoboxing, China) was recrystallized twice using tridistilled water and dried under vacuum for 24 h. KPF_6 , $C_2\text{mimPF}_6$, $C_4\text{mimPF}_6$, $C_6\text{mimPF}_6$, and $C_8\text{mimPF}_6$ (>99% purity) were purchased from Lanzhou Institute of Chemical Physics, China. Analytical grade reagent urea and spectrographic grade reagent methanol were used as received. D_2O (99.9% isotopic purity, Beijing Chemical Reagents Company) was used as solvent in NMR measurements. α, α, α -Trifluorotoluene (>99% purity) purchased from ACROS was used as received. Tridistilled water was used throughout the experiments.

Instruments. Fluorescence spectra were measured on an FL-4500 (Hitachi, Japan) spectrophotometer. The temperature was controlled by placing the sample in a cell compartment whose walls were accessible to water circulation, and the final temperature (298.0 ± 0.1 K) of the sample was obtained by a thermocouple (Check-temp, Hanna, Italy). ^1H NMR and ^{19}F NMR spectra were recorded on a Bruker AV400 MHz NMR spectrometer. Isothermal titration calorimetry (ITC) was carried out on a Nano ITC 2G. A conductivity meter (FE30, Mettler Toledo) was used to measure conductivity at 298.0 ± 0.1 K.

The high-resolution mass spectrometry used with electro-spray ionization (ESI/HRMS) was done on a Fourier transform ion cyclotron resonance mass spectrometer, APEX IV (Bruker, USA).

Methods. *Competitive Fluorescence Measurement.* Stock solution of **1** was prepared in methanol, and 50 μL aliquots of this stock solution were added to 5 mL volumetric flasks to maintain a final concentration of 10^{-6} M for fluorescence measurements. 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 buffer was used.^{46,47}

Job Plot. The preferred stoichiometry of β -CD complex can be evaluated using Job's method.⁴⁸ This method was transferred to the NMR spectroscopy by Blanda et al.⁴⁹ Both are based on the so-called "continuous variation method". The solutions of host and guest are mixed in a way that the mole ratio $[\text{Host}]/[\text{Guest}]$ varies and the total concentration remains constant. The change in the chemical shift of defined guest ^1H and ^{19}F of a host-guest mixed solution relative to the guest solution ($\Delta\delta = \delta(\text{mixture}) - \delta(\text{guest})$) describes a linear function of the mole fraction (X) of each species under these conditions. A plot of the product $(\Delta\delta)X$ (guest) against X (host) yields a curve whose maximum determines the stoichiometry of the complex. 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 referenced to an external sample of α, α, α -trifluorotoluene ($\delta = -63.90$).

Isothermal Titration Calorimetry. In the experimental process of ITC, the IL solution in the syringe was injected over 28 drops with a respective volume of 8 μL into the measuring cell, which was filled with the aqueous solution of β -CD. The temperature was 298.0 K, and the stirrer rotational speed was 250 min^{-1} . The equilibrium time between two injections was long enough for the signal to return to the baseline. The dilution heat was determined in a separate measurement by injecting the corresponding IL solution into water and it was subtracted from the determined heat flow. The net reaction heat in each run was analyzed by using the "ligand binding analysis" within the software Digitam 4.1 to simultaneously compute the association constant K and molar reaction enthalpy (ΔH°), and the standard deviation from the titration curve. Other thermodynamic parameters, i.e., the standard Gibbs free energy of binding (ΔG°) and entropy change (ΔS°), can be obtained by the following equations:

$$\Delta G^\circ = -RT \ln K \quad (1)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

where R is the gas constant and T is the absolute temperature.

Computation of the Dissociation Degree. The dissociation degree (α) of $C_n\text{mimPF}_6$ can be estimated by analyzing the molar conductivity data by means of the Lee-Wheaton equation in the form suggested by Pethybridge and Taba (eqs 3–9).^{50,51}

$$\Lambda_m = \alpha \left\{ \Lambda_m^0 [1 + C_1(\beta\kappa) + C_2(\beta\kappa)^2 + C_3(\beta\kappa)^3] - \frac{\partial\kappa}{1 + \kappa R} \left[1 + C_4(\beta\kappa) + C_5(\beta\kappa)^2 + \frac{\kappa R}{12} \right] \right\} \quad (3)$$

$$K_A = \frac{1 - \alpha}{c\alpha^2 f_{\pm}^2} \quad (4)$$

$$f_{\pm}^2 = \exp \left[-\frac{\kappa\beta}{1 + \kappa R} \right] \quad (5)$$

$$\alpha = \frac{-1 + \sqrt{1 + 4K_A f_{\pm}^2}}{2K_A f_{\pm}^2} \quad (6)$$

$$\kappa = \left(\frac{8\pi N_A e^2 |z|^2 \alpha c}{1000 \epsilon k T} \right)^{1/2} \quad (7)$$

$$\vartheta = \frac{|z|Fe}{(299.79)(3\pi\eta)} \quad (8)$$

$$\beta = \frac{z^2 e^2}{\epsilon k T} \quad (9)$$

where C_i ($i = 1-5$) is a complex function of the product κR , as given in the literature.⁴⁷ f_{\pm} and R are the mean activity coefficient of the ions and the ion distance parameter, respectively, and Λ_m^0 and K_A are the limiting molar conductivity and ionic association constant of the ILs, respectively. The other parameters have the usual meanings.

The values of α , Λ_m^0 , K_A , and f_{\pm}^2 can be determined by means of nonlinear least-squares iterations. In practice, the calculations were performed by finding the values of the parameters after making the objective function eq 10 to be minimized:^{52,53}

$$S = \sum_{i=1}^n (\Lambda_{m,i}^{\text{calc}} - \Lambda_{m,i}^{\text{exp}})^2 w_i \quad (10)$$

where w_i is the weighting factor.

RESULTS AND DISCUSSION

Competitive Fluorescence Method. The competitive fluorescence method has been applied to study the interaction between host and guest successfully.^{36,37,54} Substituted 3H-indoles such as molecule **1** are sensitive to microenvironments and have been used as probes to study cyclodextrin-based supramolecular systems,^{55,56} which are especially suitable for the systems of weak interactions between hosts and guests, e.g., β -CD and 1-butyl-3-methylimidazolium chloride ($C_4\text{mimCl}$).³²

The fluorescence spectra of **1** in the $C_n\text{mimPF}_6/\beta\text{-CD}$ system were measured, and those in the $C_2\text{mimPF}_6/\beta\text{-CD}$ system are shown in Figure 1a. Within the range of the concentration studied in this paper, the ILs $C_n\text{mimPF}_6$ exhibit no obvious fluorescence emission. The fluorescence intensity of **1** in the aqueous solution of $C_n\text{mimPF}_6$ is slightly larger than that in water, which means the ILs cannot quench the fluorescence of **1**. Consequently, all the fluorescence spectra originate only from probe **1**. Similar to the previous report,⁴⁶ 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 **1** and $\beta\text{-CD}$, respectively; 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) estimated are $856 \pm 148 \text{ M}^{-1}$, $2248 \pm 158 \text{ M}^{-1}$, 5.17 ± 1.45 , and 13.9 ± 0.2 , respectively, with a correlation coefficient $r^2 = 0.999$ by nonlinear regression analysis. The values are close to those reported in the literature.^{55,56} The equilibrium concentrations of $\beta\text{-CD}$, i.e., $[\text{CD}]$, at different $[C_n\text{mimPF}_6]_0$ (the initial concentration of $C_n\text{mimPF}_6$) can be calculated using the K'_1 , K'_2 , I_1/I_0 , and I_2/I_0

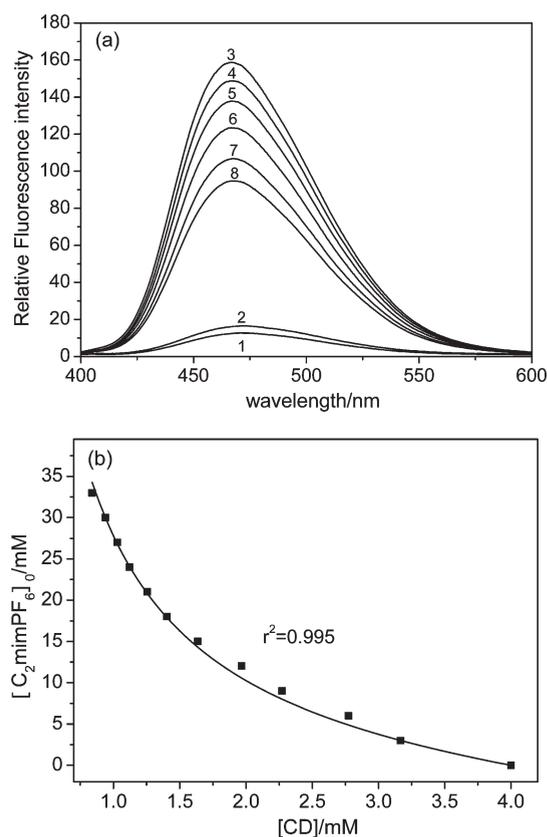


Figure 1. (a) Fluorescence spectra of **1** in water (1), in aqueous solution of 60 mM $C_2\text{mimPF}_6$ (2), and in aqueous solutions of 4 mM $\beta\text{-CD}$ at various concentrations of $C_2\text{mimPF}_6$: 0 mM (3), 6 mM (4), 12 mM (5), 18 mM (6), 27 mM (7), and 33 mM (8). (b) Initial concentration of $C_2\text{mimPF}_6$, $[C_2\text{mimPF}_6]_0$, vs equilibrium concentration of $\beta\text{-CD}$, $[\text{CD}]$. The solid line is the nonlinear regression fit to the experimental data points following the model of 1:1.

values.⁵⁵ The concentration of $\beta\text{-CD}$ binding with $C_n\text{mimPF}_6$ can be obtained from $[\text{CD}]_0 - [\text{CD}]$. Figure 1b shows the variation of $[C_n\text{mimPF}_6]_0$ as a function of $[\text{CD}]$. For the 1:1 inclusion complex, $[C_n\text{mimPF}_6]_0$ is related to $[\text{CD}]$ by the following equation:

$$[C_n\text{mimPF}_6]_0 = \frac{([\text{CD}]_0 - [\text{CD}])(1 + K_1[\text{CD}])}{K_1[\text{CD}]} \quad (11)$$

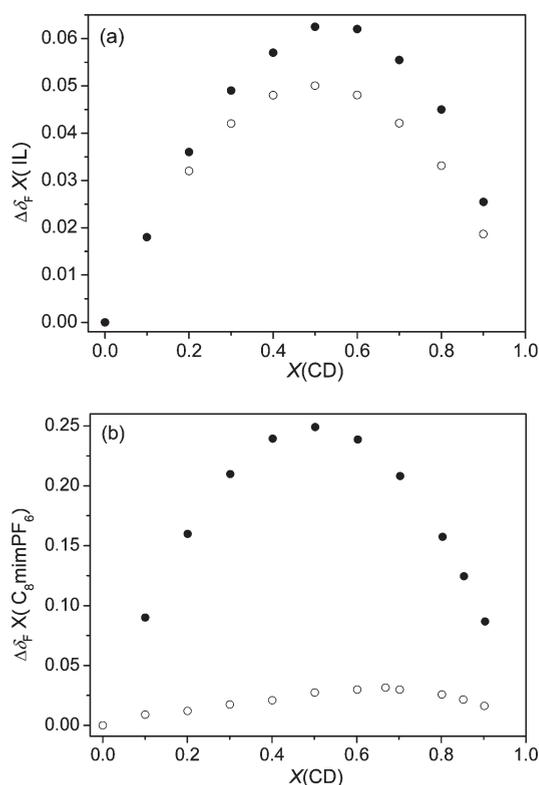
For the coexistence of 1:1 and 1:2 inclusion complexes, K_1 and K_2 can be obtained by the following equation:

$$[C_n\text{mimPF}_6]_0 = \frac{([\text{CD}]_0 - [\text{CD}])(1 + K_1[\text{CD}] + K_1K_2[\text{CD}]^2)}{K_1[\text{CD}] + 2K_1K_2[\text{CD}]^2} \quad (12)$$

The results of the interaction between $\beta\text{-CD}$ and $C_n\text{mimPF}_6$ are shown in Table 1. Both $C_2\text{mimPF}_6$ and $C_4\text{mimPF}_6$ form 1:1 inclusion complexes with $\beta\text{-CD}$, whose association constants are slightly larger than that of KPF_6 with $\beta\text{-CD}$. $C_6\text{mimPF}_6$ also forms the 1:1 complex with $\beta\text{-CD}$, and the association constant is obviously larger than that of KPF_6 with $\beta\text{-CD}$. For the $C_8\text{mimPF}_6/\beta\text{-CD}$ system, 1:1 and 1:2 complexes coexist. On the addition of 3 M urea, K_1 decreases a little and K_2 decreases

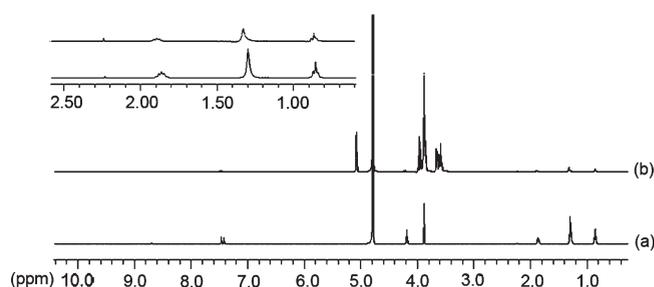
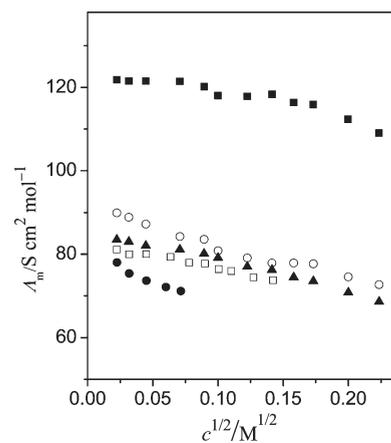
Table 1. Stoichiometry and Association Constants of KPF₆ and C_nmimPF₆ (n = 2, 4, 6, 8) with β-CD in Water and of C₈mimPF₆ with β-CD in the Aqueous Solution of Urea by Competitive Fluorescence Method

	KPF ₆	C ₂ mimPF ₆	C ₄ mimPF ₆	C ₆ mimPF ₆	C ₈ mimPF ₆		
					[urea] = 0	[urea] = 3 M	[urea] = 5 M
stoichiometry	1:1	1:1	1:1	1:1	1:1 and 1:2	1:1 and 1:2	1:1
K ₁ /M ⁻¹	100 ± 1	121 ± 2	159 ± 3	371 ± 15	1177 ± 95	1086 ± 85	888 ± 49
K ₂ /M ⁻¹	—	—	—	—	259 ± 39	46 ± 15	—

**Figure 2.** Job plots derived from the chemical shift of fluorine atoms in PF₆⁻ for β-CD solutions mixed with (a) KPF₆ (○) and C₆mimPF₆ (●), and (b) C₈mimPF₆ in the absence (○) and presence (●) of 5 M urea.

remarkably. After 5 M urea is added, only the 1:1 complex is formed.

NMR Measurements. The established method of continuous component variations according to Job and Blanda was used to confirm the complex stoichiometry,^{19,57} which is especially proper to strengthen the conclusion that only one kind of complex is present.⁴⁸ As for the interaction between ILs and CDs, the method has been applied for the complexation between Tf₂N⁻ and β-CD.¹⁹ Job plots of KPF₆ or C_nmimPF₆ with β-CD are shown in Figure 2. In Figure 2a, the maximum value for KPF₆ corresponds to 0.5. When the influence of β-CD on the ¹⁹F signal of C₂mimPF₆ and C₄mimPF₆ was tested, a maximum at 0.5, similar to that of KPF₆, was found (data not shown), certifying that KPF₆, C₂mimPF₆, and C₄mimPF₆ form 1:1 inclusion complexes with β-CD. No obvious shift of the ¹H signals of C₂mimPF₆ and C₄mimPF₆ was observed in the presence of β-CD. For C₆mimPF₆ and C₈mimPF₆, a significant influence of β-CD on both the ¹H and ¹⁹F signals of the ILs was found. As is shown in Figure 3, the ¹H signal of CH₂ groups in the alkyl side

**Figure 3.** ¹H NMR spectra of (a) free C₆mimPF₆, and (b) mixture of C₆mimPF₆ and β-CD in D₂O. The inset is the magnifying plot from 0.6 to 2.6 ppm.**Figure 4.** Molar conductivity vs the concentration of C_nmimPF₆ and KPF₆ in water. From bottom to top: C₈mimPF₆ (●), C₆mimPF₆ (□), C₄mimPF₆ (▲), C₂mimPF₆ (○), and KPF₆ (■).

chain is widened upon the addition of β-CD and shifted down-field from 1.30 ppm (Figure 3a) to 1.31 ppm (Figure 3b), indicating that the long alkyl chains of C₆mimPF₆ and C₈mimPF₆ have close contact with β-CD.³² The maximum of the ¹⁹F signal at 0.5 in Figure 2a for the C₆mimPF₆/β-CD system ensures the formation of only the 1:1 inclusion complex. In Figure 2b, a maximum of ¹⁹F deviating from 0.5 suggests the existence of a second complex between C₈mimPF₆ and β-CD. Upon the addition of 5 M urea, the maximum of ¹⁹F signals returning to 0.5 indicates the formation of only the 1:1 inclusion complex under this condition, in agreement with the results of the competitive fluorescence method.

Conductivity Measurements. In order to understand the state of the C_nmimPF₆ ILs in aqueous solutions, conductivity measurements were carried out. The molar conductivities of KPF₆ and C_nmimPF₆ aqueous solutions are shown in Figure 4.

Table 2. Dissociation Degree (α), Square of the Mean Activity Coefficient of the Ions (f_{\pm}^2), Limiting Molar Conductivity (Λ_m^0), and Ionic Association Constant (K_A) of the Aqueous Solutions of $C_n\text{mimPF}_6$ ($n = 2, 4, 6, 8$) at Different Concentrations

aqueous solutions of ILs		α	f_{\pm}^2	$\Lambda_m^0/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$K_A/\text{dm}^3\cdot\text{mol}^{-1}$
$C_2\text{mimPF}_6$	0.5 mM	0.98	0.95	90.6 ± 0.5	3.1 ± 0.4
	10 mM	0.76	0.85		
	50 mM	0.50	0.78		
$C_4\text{mimPF}_6$	0.5 mM	0.98	0.95	86.3 ± 0.4, 105.3 ± 0.1 ⁵²	2.8 ± 0.3, 6.3 ± 0.3, ⁵⁸ 113 ± 1 ⁵²
	10 mM	0.76	0.85		
	50 mM	0.50	0.78		
$C_6\text{mimPF}_6$	0.5 mM	0.98	0.95	83.2 ± 0.3	1.3 ± 0.5, 7.4 ± 0.4 ⁵⁸
	6 mM	0.82	0.87		
	20 mM	0.65	0.82		
$C_8\text{mimPF}_6$	0.5 mM	0.98	0.95	79.2 ± 0.7	13 ± 4, 8.2 ± 0.4 ⁵⁸
	2 mM	0.92	0.91		
	5 mM	0.84	0.88		

The molar conductivity, Λ_m , values of 0.5–50 mM $C_2\text{mimPF}_6$, 0.5–50 mM $C_4\text{mimPF}_6$, 0.5–20 mM $C_6\text{mimPF}_6$, and 0.5–5 mM $C_8\text{mimPF}_6$ aqueous solutions are 121.8–109.0, 89.9–72.7, 83.5–68.6, 81.1–73.8, and 78.0–71.1 $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, respectively.

Before the interaction pattern between $C_n\text{mimPF}_6$ and $\beta\text{-CD}$ in aqueous solutions is discussed, one should consider the state of these ILs. Significant attention has been devoted to the study of the IL-rich part of the water–IL binary phase diagram. It was suggested that, with the continuous increase in the amount of water, the network structure of pure ILs is destroyed into huge ionic clusters, which are then dissociated into water-surrounded ion pairs.⁴¹ There are also some reports on the state of dilute IL solutions. For 2 wt % $C_4\text{mimPF}_6$ aqueous solution, only around 13% of the ions exist as pairs revealed by molecular dynamics simulations.⁴² It was investigated that slight ionic association occurs for the aqueous solutions of 1-butyl-3-methylimidazolium tetrafluoroborate ($C_4\text{mimBF}_4$), $C_4\text{mimPF}_6$, and 1-alkyl-3-methylimidazolium bromine ($C_n\text{mimBr}$).⁵² In this study, as the concentrations of $C_n\text{mimPF}_6$ are close to that in the above two reports, it is supposed that the $C_n\text{mimPF}_6$ mainly dissociate into separated ions.

On the other hand, by the computation of the dissociation degree α according to the molar conductivity data in Figure 4, the values of αf_{\pm}^2 , Λ_m^0 , and K_A are obtained as shown in Table 2. As the literature values of the limiting ionic molar conductivity λ° for PF_6^- , $C_4\text{mim}^+$, $C_6\text{mim}^+$, and $C_8\text{mim}^+$ are 59.28, 31.9, 28.3, and 25.6 $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$,⁵⁸ respectively, the limiting molar conductivities (Λ_m^0) of $C_4\text{mimPF}_6$, $C_6\text{mimPF}_6$, and $C_8\text{mimPF}_6$ are accordingly 91.2, 87.6, and 84.9 $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ based on the equation $\Lambda_m^0 = \lambda_+^\circ + \lambda_-^\circ$, which are close to the Λ_m^0 values in Table 2. There is also a discrepancy between our values and the literature ones,^{52,58} as shown in Table 2, which may originate from the use of different methods, etc.⁵² The result of the dissociation degree α indicates that most of the IL ion pairs dissociate into separated ions within the concentration studied. From the results, one can infer that the free cations $C_n\text{mim}^+$, anions PF_6^- , and $C_n\text{mim}^+\cdot\text{PF}_6^-$ ion pairs may all interact with $\beta\text{-CD}$.

ESI/HRMS Method. The ESI/HRMS method is effective for studying the composition of noncovalent complexes including cyclodextrin–guest complexes;^{59,60} thus it is applied to determine

the complex compositions in the systems. From the ESI results of $C_n\text{mimPF}_6/\beta\text{-CD}$ mixtures (Figure 5), the signals corresponding to the complexes $C_n\text{mim}^+\cdot\text{PF}_6^- - \beta\text{-CD}$ (S-1 or S-2), $C_n\text{mim}^+ - \beta\text{-CD}$ (S-4), and $\text{PF}_6^- - \beta\text{-CD}$ (S-5) have been observed (Tables 3 and 4). For the mixtures of $C_2\text{mimPF}_6$ and $\beta\text{-CD}$ (Table 3), the signal corresponding to the 1:2 complex does not appear at various molar ratios of $C_2\text{mimPF}_6$ to $\beta\text{-CD}$, implicating the formation of the 1:1 complex in the system. The situations of the $C_4\text{mimPF}_6/\beta\text{-CD}$ and $C_6\text{mimPF}_6/\beta\text{-CD}$ systems are similar to that of the $C_2\text{mimPF}_6/\beta\text{-CD}$ system.

When equal moles of $C_8\text{mimPF}_6$ and $\beta\text{-CD}$ are mixed (Table 4), the signals corresponding to the $C_8\text{mim}^+\cdot\text{PF}_6^- - \beta\text{-CD}$ (S-1), $C_8\text{mim}^+ - \beta\text{-CD}$ (S-4), and $\text{PF}_6^- - \beta\text{-CD}$ (S-5) complexes can be observed. When the molar ratio of $C_8\text{mimPF}_6$ to $\beta\text{-CD}$ is 0.5, the signals corresponding to the $C_8\text{mim}^+ - \beta\text{-CD}_2$ (S-6) complex, as the major component, can be detected. According to the interaction pattern in ref 37, the interaction between the $C_8\text{mim}^+\cdot\text{PF}_6^-$ ion pair and $\beta\text{-CD}$ follows path I as the cation moiety interacts with $\beta\text{-CD}$ more strongly than the anion does. Besides, PF_6^- can also strongly interact with $\beta\text{-CD}$ and the 1:2 ($\beta\text{-CD} - C_8\text{mim}^+$)·($\text{PF}_6^- - \beta\text{-CD}$) (S-3) complex should be formed as long as $\beta\text{-CD}$ is sufficient in the system.³⁷ Nevertheless, the signal corresponding to ($\beta\text{-CD} - C_8\text{mim}^+$)·($\text{PF}_6^- - \beta\text{-CD}$) (S-3) was not observed at any molar ratio of $C_8\text{mimPF}_6$ to $\beta\text{-CD}$. As seen in Figure 5, the signals of 1157.356 31, 1133.360 50, 1179.369 55, 1135.374 36, 1133.357 42, 1179.370 13, 1133.360 46, and 1179.360 71 correspond to ($\beta\text{-CD} + \text{Na}$)⁺, ($\beta\text{-CD} - \text{H}$)⁻, ($\beta\text{-CD} + \text{HCOO}$)⁻, ($\beta\text{-CD} + \text{H}$)⁺, ($\beta\text{-CD} - \text{H}$)⁻, ($\beta\text{-CD} + \text{HCOO}$)⁻, ($\beta\text{-CD} - \text{H}$)⁻, and ($\beta\text{-CD} + \text{HCOO}$)⁻, respectively.

Isothermal Titration Calorimetry (ITC). Isothermal titration calorimetry, which is accurate for the determination of thermodynamic parameters, i.e., ΔG , ΔH , and ΔS , has been extensively applied in the study of host–guest complexes.^{19,61–63} Herein, we use the method to study the thermodynamic parameters of the interaction between $C_n\text{mimPF}_6$ and $\beta\text{-CD}$ in aqueous solutions.

The calorimetric titration curves of $\text{KPF}_6 - \beta\text{-CD}$ and $C_n\text{mimPF}_6 - \beta\text{-CD}$ systems are shown in Figure 6. Figure 7 shows the fitting curves to obtain the thermodynamic parameters of the formation of $\text{KPF}_6/\beta\text{-CD}$ and $C_n\text{mimPF}_6/\beta\text{-CD}$ complexes. The results of the complexation of $C_n\text{mimPF}_6$ by $\beta\text{-CD}$ in

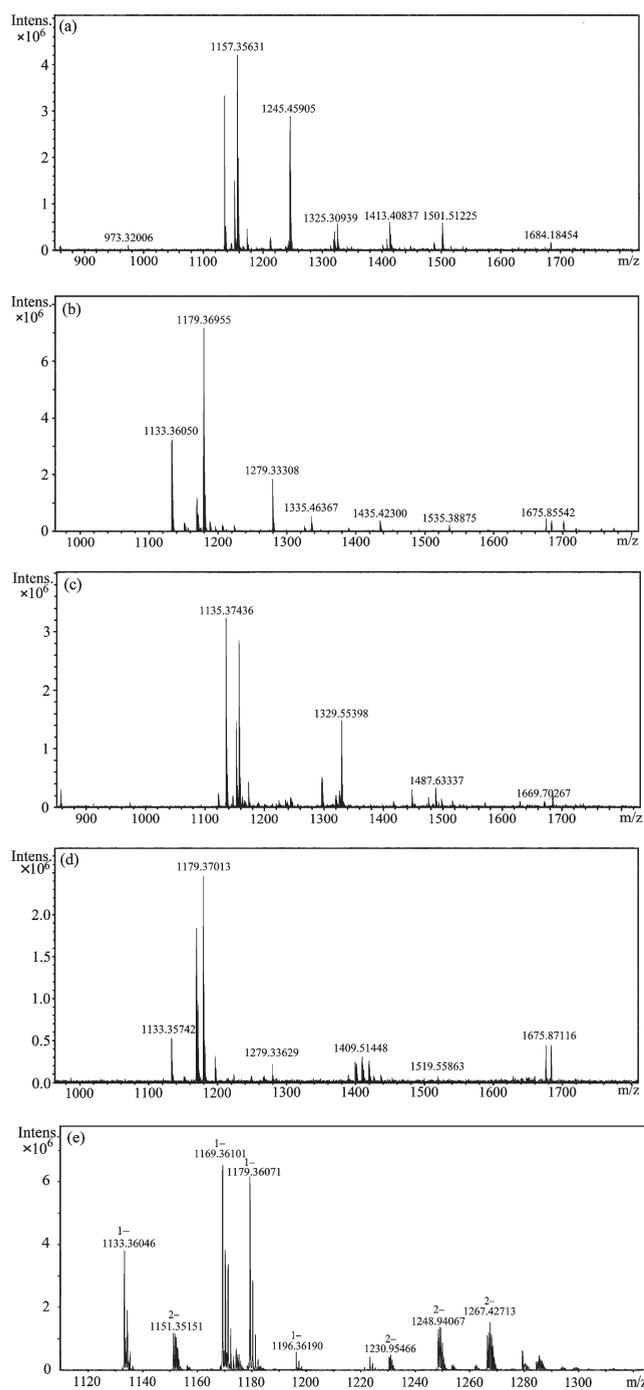


Figure 5. ESI spectra of C_n mimPF₆ and β -CD. (a) Positive and (b) negative ESI spectra of equal moles of C_2 mimPF₆ and β -CD. (c) Positive and (d) negative ESI spectra of equal moles of C_8 mimPF₆ and β -CD. (e) Negative ESI spectra of C_8 mimPF₆ and β -CD mixture solution with molar ratio of 1:2.

aqueous solution are shown in Table 5. Negative ΔG values show that the inclusion processes proceed spontaneously. In the case of KPF₆, C_2 mimPF₆, and C_4 mimPF₆, negative ΔH and ΔS 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. Though the negative ΔS values are unfavorable for the formation of the inclusion

complexes, the unfavorable effect can be overcome by the more negative values of ΔH leading to energetically favorable values. For the C_6 mimPF₆/ β -CD system, the ΔS value of the inclusion complexation becomes positive; that is, the process is entropy and enthalpy driven. The ΔS value of complexation for the C_8 mimPF₆/ β -CD system is negative, indicating that the process is enthalpy-controlled again.

Comparison of the Stoichiometry and the Association Constant by Different Methods. The stoichiometry and the association constant have been obtained by different methods. All the results showed that 1:1 complexes are formed between KPF₆, C_n mimPF₆ ($n = 2, 4, 6$), and β -CD. C_8 mimPF₆ and β -CD form the 1:2 inclusion complex as determined by the method of ITC, but not the coexisting 1:1 and 1:2 ones demonstrated by the competitive fluorescence method. This is reasonable since the amount of β -CD is much larger than that of C_8 mimPF₆ in the cell during the experiment of ITC. From the results of conductivity measurements and ESI/HRMS, it can be established that most of the C_n mimPF₆ ion pairs dissociate into separated ions within the concentration we studied and both the dissociated ions, PF₆⁻ and C_n mim⁺, and the ion pair C_n mim⁺·PF₆⁻ can interact with β -CD randomly. Consequently, the association constants K_1 of C_n mimPF₆/ β -CD inclusion complexes are attributed to the weighting average of the association constants of 1:1 C_n mim⁺·PF₆⁻- β -CD (S-1 or S-2), 1:1 C_n mim⁺- β -CD (S-4), and 1:1 PF₆⁻- β -CD (S-5) complexes, while the association constant K_2 of the 1:2 C_8 mimPF₆/ β -CD inclusion complex originates from that of the C_8 mim⁺- β -CD₂ (S-6) complex.

Interaction Pattern Involving Multiple Equilibria. On the basis of the above results, when the interaction pattern between C_n mimPF₆ and β -CD in aqueous solutions is discussed, both the dissociation equilibrium of C_n mim⁺·PF₆⁻ ion pairs and the complexation of the dissociated ions by β -CD should be considered.

For C_2 mimPF₆ and C_4 mimPF₆, the ¹H signals are hardly changed on the addition of β -CD and the association constants are slightly larger than that of KPF₆ with β -CD, which suggests that the complexation processes of C_2 mim⁺·PF₆⁻ and C_4 mim⁺·PF₆⁻ ion pairs comply with path II since the anion moiety interacts with β -CD more strongly than the cation one.³⁷ Among separated ions C_2 mim⁺, C_4 mim⁺, and PF₆⁻, PF₆⁻ plays a leading role in the interaction with β -CD. As for C_6 mim⁺·PF₆⁻ and C_8 mim⁺·PF₆⁻ ion pairs, an obvious shift on both the ¹H and ¹⁹F signals indicates the complexation of the cation moiety and the anion one by β -CD, which is further certified by a much larger association constant of the C_6 mimPF₆/ β -CD complex than that of the KPF₆/ β -CD complex. According to the pattern in ref 37, 1:2 (β -CD C_6 mim⁺)·(PF₆⁻- β -CD) and (β -CD- C_8 mim⁺)·(PF₆⁻- β -CD) (S-3) complexes should be formed. However, only the 1:1 complex was actually formed between C_6 mimPF₆ and β -CD, and the signals corresponding to the (β -CD- C_6 mim⁺)·(PF₆⁻- β -CD) and (β -CD- C_8 mim⁺)·(PF₆⁻- β -CD) (S-3) complexes cannot be detected by ESI/HRMS, indicating that the amount of (β -CD- C_n mim⁺)·(PF₆⁻- β -CD) (S-3) is very small if there is any or the complex is not stable. It has been reported that the complexation of the contact ion pair of ionic liquids by β -CD will result in a spatial separation of the ion pair.^{19,32} The possible reason is that after β -CD interacts with the cation moiety or the anion moiety of the C_n mim⁺·PF₆⁻ ion pair, the contact ion pair becomes the spatially separated ion pair (β -CD- C_n mim⁺)·PF₆⁻ (S-1) or C_n mim⁺·(PF₆⁻- β -CD) (S-2), which is similar to the interaction of C_4 mimTf₂N or C_{16} mimPF₆ with

Table 3. Comparison between Observed m/z Values (m/z_{obs}) and Calculated m/z Values (m/z_{calc}) for Equal Moles of C_2mimPF_6 and $\beta\text{-CD}$ (Obtained by ESI/HRMS)

corresponding complex	attributed species	m/z_{calc}	m/z_{obs}	intensity ^a
S-4	$(\text{C}_2\text{mim}-\beta\text{-CD})^+$	1245.461 44	1245.459 05	++
S-2	$(\text{C}_2\text{mim}\cdot\text{PF}_6-\beta\text{-CD} + \text{Na})^+$	1413.415 39	1413.408 37	+
S-5	$(\text{PF}_6-\beta\text{-CD})^-$	1279.333 40	1279.333 08	++
S-2	$(\text{C}_2\text{mim}\cdot\text{PF}_6-\beta\text{-CD} + \text{HCOO})^-$	1435.423 27	1435.423 00	+
S-2	$(\text{C}_2\text{mim}\cdot\text{PF}_6-\beta\text{-CD} + \text{PF}_6)^-$	1535.389 80	1535.388 75	+

^aThe observed intensity is reported in the following relative convention: +, species detected (relative intensity <45%); ++, major species (relative intensity >45%).

Table 4. Comparison between Observed m/z Values (m/z_{obs}) and Calculated m/z Values (m/z_{calc}) for Different Molar Ratios of $\text{C}_8\text{mimPF}_6/\beta\text{-CD}$ (Obtained by ESI/HRMS)

corresponding complexes	attributed species	m/z_{calc}	m/z_{obs}	intensity ^a
$[\text{C}_8\text{mimPF}_6]/[\beta\text{-CD}] = 1$				
S-4	$(\text{C}_8\text{mim}-\beta\text{-CD})^+$	1329.555 34	1329.553 98	++
S-1	$(\text{C}_8\text{mim}\cdot\text{PF}_6-\beta\text{-CD} + \text{C}_8\text{mim})^+$	1669.705 64	1669.702 67	+
S-5	$(\text{PF}_6-\beta\text{-CD})^-$	1279.333 40	1279.336 29	++
$[\text{C}_8\text{mimPF}_6]/[\beta\text{-CD}] = 0.5$				
S-6	$(\text{C}_8\text{mim}-\beta\text{-CD}_2 + \text{Cl} - 2\text{H})^{2-}$	1248.940 57	1248.940 67	+
S-6	$(\text{C}_8\text{mim}-\beta\text{-CD}_2 + 2\text{Cl} - \text{H})^{2-}$	1267.428 21	1267.427 13	+

^aThe observed intensity is reported in the following relative convention: +, species detected (relative intensity <45%); ++, major species (relative intensity >45%).

$\beta\text{-CD}$.^{19,32} It is implicated that when the second $\beta\text{-CD}$ interacts with the anion moiety or the cation one of the spatially separated ion pair S-1 or S-2, because the lattices are destroyed, and the electrostatic forces between the cation moiety C_nmim^+ and the anion one PF_6^- decrease, the intermediate complex $(\beta\text{-CD}-\text{C}_n\text{mim}^+)\cdot(\text{PF}_6-\beta\text{-CD})$ (S-3) dissociates into $\text{C}_n\text{mim}^+-\beta\text{-CD}$ (S-4) and $\text{PF}_6-\beta\text{-CD}$ (S-5). The dissociated C_nmim^+ forms 1:1 inclusion complex with $\beta\text{-CD}$, and the formation of the 1:2 $\text{C}_8\text{mim}^+-\beta\text{-CD}_2$ (S-6) inclusion complex, is related to the molar ratio of C_8mim^+ to $\beta\text{-CD}$. For C_nmim^+ , it is deduced that the hydrophobic alkyl side chain interacts with $\beta\text{-CD}$ by NMR measurement. Amajjahe et al.¹⁹ reported that Tf_2N^- and PF_6^- are accommodated by $\beta\text{-CD}$ while the atoms with negative charge prefer to be out of the cavity. In our previous work, we also found that Tf_2N^- , PF_6^- , and BF_4^- could interact with $\beta\text{-CD}$ to a great extent, and atoms with negative charge such as N^- , P^- , and B^- are out of $\beta\text{-CD}$.^{36,37} By the measurement of ^{19}F NMR, it is found that the fluorine signals of PF_6^- are shifted greatly on the addition of $\beta\text{-CD}$ (Figure 2). Combining the results in the references, we suggest that the fluorine atoms of the anion enter the cavity of $\beta\text{-CD}$ while the atom with negative charge P^- is out of $\beta\text{-CD}$. Consequently, the driving force is mainly the hydrophobic interaction. The results agree with those of other anions such as BF_4^- .

As a result, a multiple equilibria interaction pattern between C_nmimPF_6 and $\beta\text{-CD}$ in aqueous solutions is suggested as shown in Scheme 2. The interaction of the $\text{C}_n\text{mim}^+\cdot\text{PF}_6^-$ ion pair with $\beta\text{-CD}$ as in the frame generally complies with the previous pattern.³⁷ However, when the second $\beta\text{-CD}$ interacts with the spatially separated ion pair, $(\beta\text{-CD}-\text{cation})\cdot\text{anion}$ (S-1) or $\text{cation}\cdot(\text{anion}-\beta\text{-CD})$ (S-2), the formed complex $(\beta\text{-CD}-\text{cation})\cdot(\text{anion}-\beta\text{-CD})$ (S-3) may dissociate into $\text{cation}-\beta\text{-CD}$ (S-4) and $\text{anion}-\beta\text{-CD}$ (S-5) complexes. Moreover, the dissociation equilibrium of the ion pair is included in the pattern. The dissociated

cations and anions interact with $\beta\text{-CD}$ randomly. For the anion PF_6^- , it interacts with $\beta\text{-CD}$ and forms the 1:1 $\text{PF}_6^- - \beta\text{-CD}$ (S-5) complex. C_nmim^+ and $\beta\text{-CD}$ form the 1:1 $\text{C}_n\text{mim}^+ - \beta\text{-CD}$ (S-4) complex first, which then binds another $\beta\text{-CD}$ to form the 1:2 $\text{C}_n\text{mim}^+ - \beta\text{-CD}_2$ (S-6) complex if the alkyl chain of the IL is long enough (e.g., C_8mim^+).

As is shown in Scheme 2, for the interaction between C_6mimPF_6 and $\beta\text{-CD}$, the compositions of 1:1 species S-1 or S-2, S-4, and S-5 can be detected. S-3 will dissociate into S-4 and S-5 complexes. The 1:1 inclusion complex between C_6mimPF_6 and $\beta\text{-CD}$ is the weighting average of S-1 or S-2, S-4, and S-5. For the interaction between C_8mimPF_6 and $\beta\text{-CD}$, the compositions of S-1, S-4, and S-5 can also be detected and S-3 will dissociate into S-4 and S-5. Besides, S-4 will bind another $\beta\text{-CD}$ to form S-6. The 1:1 inclusion complex between C_8mimPF_6 and $\beta\text{-CD}$ is the weighting average of S-1, S-4, and S-5, while the 1:2 inclusion complex originates from S-6. Therefore, the coexisting 1:1 and 1:2 inclusion complexes can be formed between C_8mimPF_6 and $\beta\text{-CD}$.

Thermodynamic Parameters of the Inclusion Complexes. When the ILs are C_2mimPF_6 and C_4mimPF_6 , the interaction of the ion pairs with $\beta\text{-CD}$ follows path II. For the dissociated ions, they interact with $\beta\text{-CD}$ and form 1:1 complexes. No matter the dissociated ions and ion pairs, the interaction is mainly that of PF_6^- with $\beta\text{-CD}$. Consequently, both the association constants and thermodynamic parameters are close to those of $\text{KPF}_6-\beta\text{-CD}$ (Tables 1 and 5). It has been certified that the strength order of C_2mim^+ , C_4mim^+ , and PF_6^- interacting with $\beta\text{-CD}$ is $\text{PF}_6^- > \text{C}_4\text{mim}^+ > \text{C}_2\text{mim}^+$.³⁷

For C_6mimPF_6 , an interesting phenomenon is that the ΔS value for the inclusion complexation is positive, which is strikingly different from that of C_2mimPF_6 and C_4mimPF_6 (Table 5). The phenomenon of positive ΔS for the host-guest association

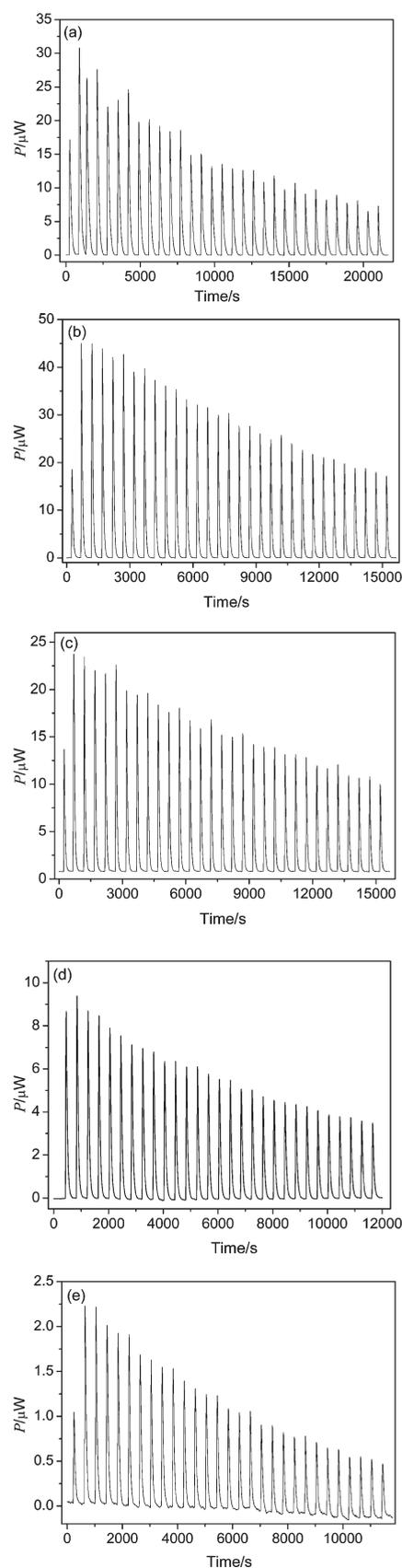


Figure 6. Variation of heat flow P as a function of time. From the top to the bottom, the titrants are KPF_6 (a), C_2mimPF_6 (b), C_4mimPF_6 (c), C_6mimPF_6 (d), and C_8mimPF_6 (e), respectively.

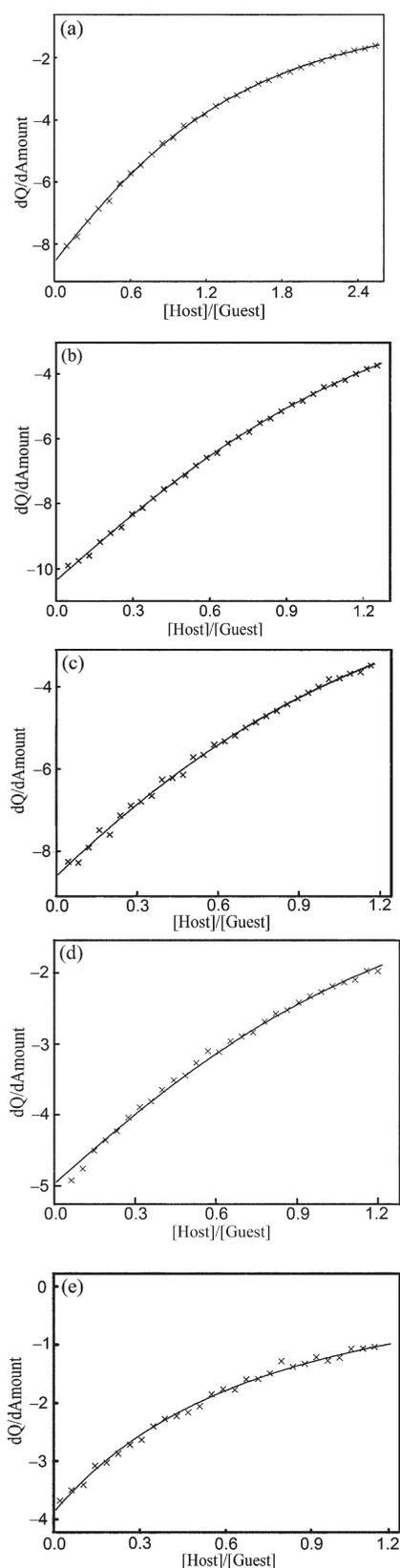
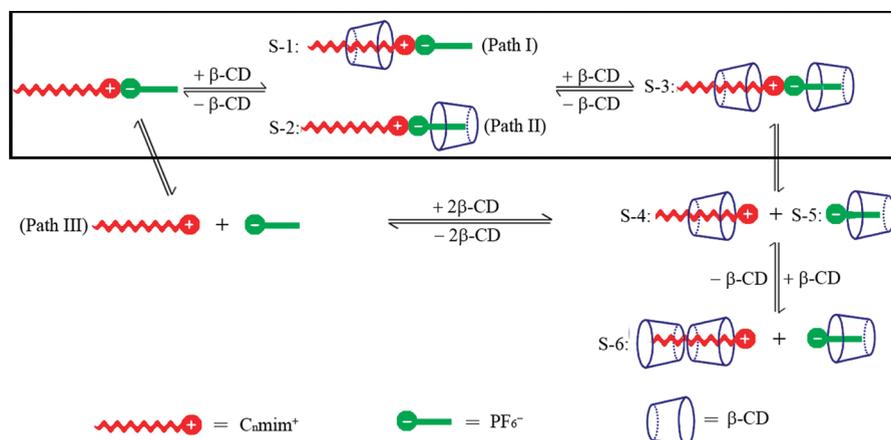


Figure 7. Rate of change in heat caused by the host–guest interaction vs concentration ratio of host to guest, $[\text{Host}]/[\text{Guest}]$. Host represents $\beta\text{-CD}$. Guests represent KPF_6 (a), C_2mimPF_6 (b), C_4mimPF_6 (c), C_6mimPF_6 (d), and C_8mimPF_6 (e), respectively. The points are obtained from experiment, and the line is the result of regression analysis.

Table 5. Thermodynamic Parameters ΔG , ΔH , and ΔS and Association Constant K for the Complex Formed by KPF_6 , C_nmimPF_6 , and $\beta\text{-CD}$ in Aqueous Solution

	K	stoichiometry	$\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta G/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
KPF_6	$163 \pm 2 \text{ M}^{-1}$	1:1	-17.3 ± 0.1	-12.6	-15.8
C_2mimPF_6	$170 \pm 5 \text{ M}^{-1}$	1:1	-18.0 ± 0.2	-12.7	-17.8
C_4mimPF_6	$189 \pm 5 \text{ M}^{-1}$	1:1	-17.7 ± 0.5	-13.0	-15.8
C_6mimPF_6	$401 \pm 3 \text{ M}^{-1}$	1:1	-9.1 ± 0.3	-14.8	19.1
C_8mimPF_6	$119\,936 \pm 7340 \text{ M}^{-2}$	1:2	-36.4 ± 1.7	-29.0	-24.8

Scheme 2. Multiple Equilibria Interaction Pattern between C_nmimPF_6 and $\beta\text{-CD}$ in Aqueous Solutions

has been observed before.⁶⁴ In the process, the loss of conformational freedom is inherently accompanied by a decrease in entropy. On the other hand, before association, both the host CD and guest are highly solvated, and the solvent molecules around the host and the guest are highly ordered. During the association, the solvation shells of both the host and the guest undergo reorganization accompanied by the loss of some solvent molecules. This process creates disorder in the system and thus leads to a favorable entropic gain. The ΔS is the combined result of these factors.

Different from C_nmimPF_6 ($n = 2, 4, 6$), C_8mimPF_6 can form a 1:2 inclusion complex with $\beta\text{-CD}$. The process is greatly exothermic and the ΔS becomes negative again. In order to understand the driving force of the complexation, urea is added to the system since the urea effect study is an effective method of characterizing the hydrophobic nature of the interaction between CDs and guest molecules.^{55,56} In agreement with the report in the literature,^{55,56} urea gives rise to a much greater decrease in K_2 as shown in Table 1. When 5 M urea is added to the system, only the 1:1 complex is formed, which is also certified by the Job plot of C_8mimPF_6 with $\beta\text{-CD}$ in the presence of 5 M urea (Figure 2b). As a result, one can see that the main driving force for the formation of inclusion complexes between C_nmimPF_6 and $\beta\text{-CD}$ is the hydrophobic interaction. Combining all the results, one can see that the strength of the interaction of C_nmim^+ and PF_6^- with $\beta\text{-CD}$ follows the order $\text{C}_8\text{mim}^+ > \text{C}_6\text{mim}^+ \sim \text{PF}_6^- > \text{C}_4\text{mim}^+ > \text{C}_2\text{mim}^+$, which is in accordance with the conclusion before.³⁷

CONCLUSIONS

We have investigated the interactions between 1-alkyl-3-methylimidazolium hexafluorophosphate C_nmimPF_6 ($n = 2, 4, 6, 8$) and $\beta\text{-CD}$ in aqueous solutions. The following conclusions are obtained:

1. By conductivity measurement and the computation of dissociation degree, we have studied the state of the ILs C_nmimPF_6 in aqueous solutions. It can be concluded that the ILs mainly exist as dissociated ions with a minor percentage of ion pairs within the concentration studied.
2. C_2mimPF_6 , C_4mimPF_6 , and C_6mimPF_6 form 1:1 inclusion complexes with $\beta\text{-CD}$, and C_8mimPF_6 can form a 1:2 complex with $\beta\text{-CD}$. The inclusion complexation of C_2mimPF_6 , C_4mimPF_6 , and C_8mimPF_6 by $\beta\text{-CD}$ is enthalpy driven, and that of C_6mimPF_6 by $\beta\text{-CD}$ is entropy and enthalpy driven.
3. By ESI/HRMS, the coexistence of signals corresponding to $(\beta\text{-CD}-\text{C}_n\text{mim}^+) \cdot \text{PF}_6^-$ (S-1) or $\text{C}_n\text{mim}^+ \cdot (\text{PF}_6^- - \beta\text{-CD})$ (S-2), $\text{C}_n\text{mim}^+ - \beta\text{-CD}$ (S-4) or $\text{C}_n\text{mim}^+ - \beta\text{-CD}_2$ (S-6), and $\text{PF}_6^- - \beta\text{-CD}$ (S-5) complexes is observed, indicating that both the ion pairs and dissociated ions interact with $\beta\text{-CD}$, and that $(\beta\text{-CD}-\text{C}_n\text{mim}^+) \cdot (\text{PF}_6^- - \beta\text{-CD})$ (S-3) dissociates into $\text{C}_n\text{mim}^+ - \beta\text{-CD}$ (S-4) and $\text{PF}_6^- - \beta\text{-CD}$ (S-5) complexes. On the basis of the results, a more comprehensive interaction pattern involving multiple equilibria between C_nmimPF_6 and $\beta\text{-CD}$ in aqueous solutions is presented. The complexation of $\text{C}_n\text{mim}^+ \cdot \text{PF}_6^-$ ion pairs by $\beta\text{-CD}$ generally complies with the pattern we suggested before; that is, the cation (path I) or the anion (path II) first interacts with $\beta\text{-CD}$ depending on which part of the ion pair interacts more strongly with $\beta\text{-CD}$. When both the cation and the anion can interact strongly with $\beta\text{-CD}$, the formed 1:2 $(\beta\text{-CD}-\text{cation}) \cdot (\text{anion}-\beta\text{-CD})$ inclusion complex dissociates into the $\beta\text{-CD}-\text{cation}$ and $\text{anion}-\beta\text{-CD}$ complexes, of which the cation with long chain further interacts with $\beta\text{-CD}$. The dissociated cations and anions of the ILs interact with $\beta\text{-CD}$ randomly to form

two kinds of 1:1 inclusion complexes (path III), of which the cation with long chain also complexes another β -CD.

AUTHOR INFORMATION

Corresponding Author

*Tel.: 86-10-62765915. Fax: 86-10-62759191. E-mail: xshen@pku.edu.cn.

ACKNOWLEDGMENT

The authors are grateful to Prof. Xiangyun Wang for his help in the computation of the dissociation degree, Mr. Jiang Zhou and Ms. Xiaoran He (Analytical Instrument Center of Peking University) for their help in ESI/HRMS measurements, and Mr. Jingxin Yang (Beijing NMR Center) for his help in NMR measurements. This work was financially supported by the National Natural Science Foundation of China (Grant 20871009).

REFERENCES

- (1) Harada, A.; Takashima, Y.; Yamaguchi, H. *Chem. Soc. Rev.* **2009**, *38*, 875–882.
- (2) Song, L. X.; Bai, L.; Xu, X. M.; He, J.; Pan, S. Z. *Coord. Chem. Rev.* **2009**, *253*, 1276–1284.
- (3) Szejtli, J. *Chem. Rev.* **1998**, *98*, 1743–1753.
- (4) Liu, Y.; Chen, Y. *Acc. Chem. Res.* **2006**, *39*, 681–691.
- (5) Rekharsky, M. V.; Inoue, Y. *Chem. Rev.* **1998**, *98*, 1875–1918.
- (6) Connors, K. A. *Chem. Rev.* **1997**, *97*, 1325–1357.
- (7) Astray, G.; Gonzalez-Barreiro, C.; Mejuto, J. C.; Rial-Otero, R.; Simal-Gandara, J. *Food Hydrocolloids* **2009**, *23*, 1631–1640.
- (8) Del Valle, E. M. M. *Process Biochem.* **2004**, *39*, 1033–1046.
- (9) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083.
- (10) Zhao, D. B.; Wu, M.; Kou, Y.; Min, E. *Catal. Today* **2002**, *74*, 157–189.
- (11) Dupont, J. J. *Braz. Chem. Soc.* **2004**, *15*, 341–350.
- (12) Chiappe, C.; Pieraccini, D. J. *Phys. Org. Chem.* **2005**, *18*, 275–297.
- (13) Weingaertner, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 654–670.
- (14) Leclercq, L.; Schmitzer, A. *Supramol. Chem.* **2009**, *21*, 245–263.
- (15) Shen, X.; Chen, Q.; Zhang, J.; Fu, P. *Supramolecular Structures in the Presence of Ionic Liquids*; InTech: Rijeka, Croatia, 2011.
- (16) Amajjahe, S.; Choi, S.; Munteanu, M.; Ritter, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 3435–3437.
- (17) Amajjahe, S.; Munteanu, M.; Ritter, H. *Macromol. Rapid Commun.* **2009**, *30*, 904–908.
- (18) Amajjahe, S.; Ritter, H. *Macromolecules* **2008**, *41*, 3250–3253.
- (19) Amajjahe, S.; Ritter, H. *Macromolecules* **2008**, *41*, 716–718.
- (20) Leclercq, L.; Schmitzer, A. R. *J. Phys. Org. Chem.* **2009**, *22*, 91–95.
- (21) Leclercq, L.; Lacour, M.; Sanon, S. H.; Schmitzer, A. R. *Chem.—Eur. J.* **2009**, *15*, 6327–6331.
- (22) Gonsior, N.; Hetzer, M.; Kulicke, W. M.; Ritter, H. *J. Phys. Chem. B* **2010**, *114*, 12468–12472.
- (23) Maksimov, A. L.; Sakharov, D. A.; Filippova, T. Y.; Zhuchkova, A. Y.; Karakhanov, E. A. *Ind. Eng. Chem. Res.* **2005**, *44*, 8644–8653.
- (24) Qin, W. D.; Wei, H. P.; Li, S. F. Y. *Analyst* **2002**, *127*, 490–493.
- (25) Wang, B.; He, J.; Bianchi, V.; Shamsi, S. A. *Electrophoresis* **2009**, *30*, 2812–2819.
- (26) Wang, B.; He, J.; Bianchi, V.; Shamsi, S. A. *Electrophoresis* **2009**, *30*, 2820–2828.
- (27) Huang, K.; Zhang, X. T.; Armstrong, D. W. *J. Chromatogr. A* **2010**, *1217*, 5261–5273.
- (28) Zhou, Z. M.; Li, X.; Chen, X. P.; Hao, X. Y. *Anal. Chim. Acta* **2010**, *678*, 208–214.
- (29) Zhang, J. J.; Shen, X. H.; Chen, Q. D. *Curr. Org. Chem.* **2010**, *15*, 74–85.
- (30) Zheng, Y.; Xuan, X. P.; Wang, J. J.; Fan, M. H. *J. Phys. Chem. A* **2010**, *114*, 3926–3931.
- (31) Subramaniam, P.; Mohamad, S.; Alias, Y. *Int. J. Mol. Sci.* **2010**, *11*, 3675–3685.
- (32) Gao, Y.; Zhao, X.; Dong, B.; Zheng, L.; Li, N.; Zhang, S. J. *Phys. Chem. B* **2006**, *110*, 8576–8581.
- (33) Gao, Y. A.; Li, Z. H.; Du, J. M.; Han, B. X.; Li, G. Z.; Hou, W. G.; Shen, D.; Zheng, L. Q.; Zhang, G. Y. *Chem.—Eur. J.* **2005**, *11*, 5875–5880.
- (34) Li, N.; Liu, J.; Zhao, X. Y.; Gao, Y. A.; Zheng, L. Q.; Zhang, J.; Yu, L. *Colloids Surf., A: Physicochem. Eng. Aspects* **2007**, *292*, 196–201.
- (35) Francois, Y.; Varenne, A.; Sirieix-Plenet, J.; Gareil, P. *J. Sep. Sci.* **2007**, *30*, 751–760.
- (36) He, Y. F.; Shen, X. H. *J. Photochem. Photobiol., A: Chem.* **2008**, *197*, 253–259.
- (37) He, Y. F.; Chen, Q. D.; Xu, C.; Zhang, J. J.; Shen, X. H. *J. Phys. Chem. B* **2009**, *113*, 231–238.
- (38) Schroder, C.; Hunger, J.; Stoppa, A.; Buchner, R.; Steinhauser, O. *J. Chem. Phys.* **2008**, *129*, 10.
- (39) Schroder, C.; Neumayr, G.; Steinhauser, O. *J. Chem. Phys.* **2009**, *130*, 11.
- (40) Schroder, C.; Rudas, T.; Neumayr, G.; Benkner, S.; Steinhauser, O. *J. Chem. Phys.* **2007**, *127*, 9.
- (41) Zhang, L. Q.; Xu, Z.; Wang, Y.; Li, H. R. *J. Phys. Chem. B* **2008**, *112*, 6411–6419.
- (42) Raju, S. G.; Balasubramanian, S. *J. Phys. Chem. B* **2009**, *113*, 4799–4806.
- (43) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192–5200.
- (44) Skrabal, P.; Steiger, J.; Zollinger, H. *Helv. Chim. Acta* **1975**, *58*, 800–814.
- (45) Popowycz, A. M.S. Thesis, University of Montreal, 1991.
- (46) Shen, X. H.; Belletete, M.; Durocher, G. *J. Phys. Chem. B* **1998**, *102*, 1877–1883.
- (47) Shen, X. H.; Belletete, M.; Durocher, G. *Chem. Phys. Lett.* **1999**, *301*, 193–199.
- (48) Connors, K. A. *Binding Constants*; John Wiley & Sons, Inc.: New York, 1987.
- (49) Blanda, M. T.; Horner, J. H.; Newcomb, M. *J. Org. Chem.* **1989**, *54*, 4626–4636.
- (50) Lee, W. H.; Wheaton, R. J. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1128–1145.
- (51) Pethybridge, A. D.; Taba, S. S. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 368–376.
- (52) Wang, H. Y.; Wang, J. J.; Zhang, S. L.; Pei, Y. C.; Zhuo, K. L. *ChemPhysChem* **2009**, *10*, 2516–2523.
- (53) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103–6110.
- (54) He, Y. F.; Shen, X. H.; Gao, H. C.; He, Y. K. *J. Photochem. Photobiol., A: Chem.* **2008**, *193*, 178–186.
- (55) Shen, X. H.; Belletete, M.; Durocher, G. *J. Phys. Chem. B* **1997**, *101*, 8212–8220.
- (56) Shen, X. H.; Belletete, M.; Durocher, G. *Langmuir* **1997**, *13*, 5830–5836.
- (57) Loftsson, T.; Magnusdottir, A.; Masson, M.; Sigurjonsdottir, J. F. *J. Pharm. Sci.* **2002**, *91*, 2307–2316.
- (58) Katsuta, S.; Ogawa, R.; Yamaguchi, N.; Ishitani, T.; Takeda, Y. *J. Chem. Eng. Data* **2007**, *52*, 248–251.
- (59) Mohamed, M. H.; Wilson, L. D.; Headley, J. V.; Peru, K. M. *Rapid Commun. Mass Spectrom.* **2009**, *23*, 3703–3712.
- (60) Kralj, B.; Smidovnik, A.; Kobe, J. *Rapid Commun. Mass Spectrom.* **2009**, *23*, 171–180.
- (61) Bouchemal, K. *Drug Discovery Today* **2008**, *13*, 960–972.
- (62) Nielsen, A. L.; Andersen, M. B. O.; Bugge, T. V.; Nielsen, C. F.; Nielsen, T. B.; Wimmer, R.; Yu, D.; Larsen, K. L. *J. Polym. Sci., Polym. Chem.* **2009**, *47*, 6619–6629.
- (63) Nielsen, T. T.; Wintgens, V.; Amiel, C.; Wimmer, R.; Larsen, K. L. *Biomacromolecules* **2010**, *11*, 1710–1715.
- (64) Liu, Y.; Cao, R.; Chen, Y.; He, J. Y. *J. Phys. Chem. B* **2008**, *112*, 1445–1450.