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The Enhanced Dissolution of β -Cyclodextrin in Some Hydrophilic Ionic Liquids[†]

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β -Cyclodextrin (β -CD) is difficult to dissolve in water and in many common solvents and searching for the proper solvents is the key step to expand its application. In this work, six kinds of hydrophilic ionic liquids 1-*n*-butyl-3-methylimidazolium chloride, 1-(2-hydroxyethyl)-3-methylimidazolium chloride, 1-allyl-3-methylimidazolium chloride, 1-*n*-butyl-3-methylimidazolium dicyanamide, 1-(2-hydroxyethyl)-3-methylimidazolium dicyanamide and 1-allyl-3-methylimidazolium dicyanamide have been prepared. The solubilities of β -cyclodextrin in these ionic liquids have been determined in the temperature range from 333.2 to 363.2 K with 5 K intervals. The solution thermodynamic parameters of β -cyclodextrin have been calculated from the solubility data. It was shown that solubility of β -cyclodextrin was remarkable in ionic liquids, it was as high as 125.0 g in 100 g of [Amim][N(CN)₂] at 348.2 K. The dissolution process was unfavorable thermodynamically and controlled by the enthalpic term. ¹H NMR and IR spectroscopic measurements were used to study the enhanced dissolution of β -cyclodextrin in the ionic liquids. The results indicated that 1:1 inclusion complexes were formed between β -cyclodextrin and imidazolium cations of the ionic liquids. The differences in the solubility of β -cyclodextrin have been discussed from the interionic interaction between cation and anion of the ionic liquids and the inclusion interaction of the cations of the ionic liquids into the cavities of β -cyclodextrin. The strength of the interionic interactions was found to be predominant for the dissolution of β -cyclodextrin. It is expected that such information may find application in the molecular design of the stationary phases in gas chromatography.

1. Introduction

Cyclodextrins (CDs) are a series of cyclic oligosaccharides, which are usually composed of more than 5 α -D-glucopyranoside units linked by α -1,4 glycosidic bonds. The structures of cyclodextrins are alike in that each of them contains a molecular cavity. The hydroxyl groups are on the outside of the cavity so that the outside surface is hydrophilic, while the inner cavity is hydrophobic. Owing to their unique structure, cyclodextrins are able to accommodate a lot of guest molecules and have been widely applied in pharmaceutical chemistry, food industry, and other fields.^{1–3} Among them, β -cyclodextrin (β -CD) which contains 7 glucose units (Figure 1) is insoluble in water and in many common solvents.⁴ Therefore, searching for proper solvents and increasing its solubility is the key step to expand the application of β -cyclodextrin.

As a new kind of green solvents, ionic liquids (ILs) have a variety of excellent properties, such as negligible vapor pressure, nonflammability, thermal and chemical stability, chemical tunabilities, and recyclability.^{5–9} This makes ILs attractive as the potential novel materials in catalysis, organic synthesis, separation, and electrochemistry.^{9–11} Recent studies demonstrate that ILs are capable of dissolving a number of carbohydrates including glucose, sucrose, starch, and cellulose among others.^{12–14}

In recent years, although investigations on the interactions between β -CD and ILs have been reported in literature,^{15–22}

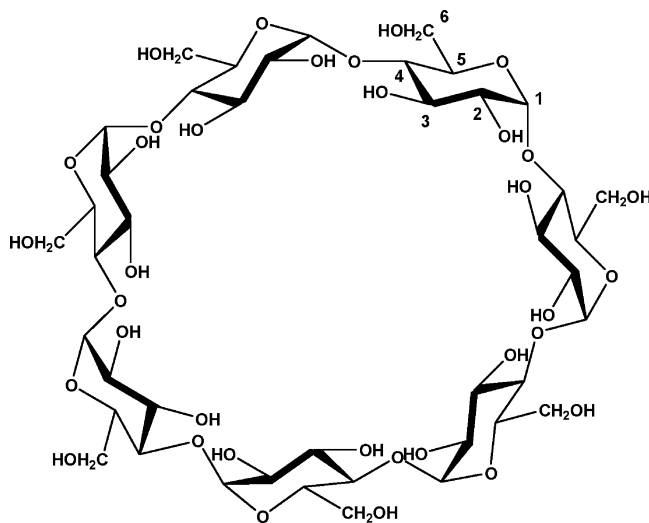


Figure 1. The structure of β -CD.

most of the studies are focused on the interactions between β -CD and ILs in aqueous solutions. Gao et al.¹⁶ reported that β -CD and [Bmim][PF₆] could form 1:1 inclusion complexes in water with the whole imidazolium cation entering the cavity of β -CD. Further study showed that [C₁₂mim][PF₆], [C₁₄mim][PF₆], and [C₁₆mim][PF₆] could also form 1:1 or 2:1 inclusion complexes with β -CD in water.^{17,18} For these three ionic liquids, it was the alkyl chain of imidazolium ring that entered into the cavity of β -CD. He et al.^{19,20} determined the association constants of β -CD with [Bmim]Cl, [Bmim][PF₆], and [C₁₂mim][BF₄] in aqueous solutions at 298 K. It was also reported that the anions of some

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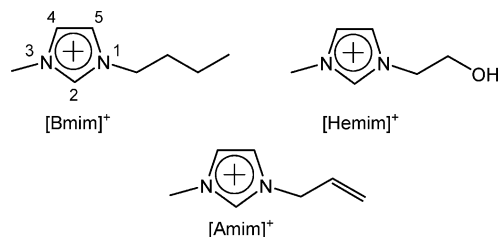


Figure 2. The structures of imidazolium cations studied in this work.

ILs, such as $[\text{Tf}_2\text{N}]^-$ and $[\text{NfO}]^-$, could form inclusion complexes with β -CD in water as well.²¹ Literature survey reveals that only one report¹⁵ deals with the direct interaction between β -CD and ILs in the absence of any molecular solvent. Actually, only one solubility datum point was reported at 348 K¹⁵ for β -CD in the ionic liquid $[\text{Bmim}][\text{N}(\text{CN})_2]$, although β -CD derivatives dissolved in ILs have been used as the stationary phases in gas chromatography.²²

In this paper, we present our solubility data of β -CD in the hydrophilic ILs (their cationic structures were shown in Figure 2): 1-*n*-butyl-3-methylimidazolium chloride ($[\text{Bmim}]\text{Cl}$), 1-(2-hydroxyethyl)-3-methylimidazolium chloride ($[\text{Hemim}]\text{Cl}$), 1-allyl-3-methylimidazolium chloride ($[\text{Amim}]\text{Cl}$), 1-*n*-butyl-3-methylimidazolium dicyanamide ($[\text{Bmim}][\text{N}(\text{CN})_2]$), 1-(2-hydroxyethyl)-3-methylimidazolium dicyanamide ($[\text{Hemim}][\text{N}(\text{CN})_2]$) and 1-allyl-3-methylimidazolium dicyanamide ($[\text{Amim}][\text{N}(\text{CN})_2]$) in the temperature range from 333.2 to 363.2 K with 5 K intervals. On the basis of these data, the standard solution Gibbs energy ΔG_s° , standard solution enthalpy ΔH_s° , and standard solution entropy ΔS_s° have been calculated for the dissolution of β -CD. Thermodynamic analysis has been performed to understand the controlling factor for the dissolution. The enhanced solubility of β -CD in these ionic liquids was studied through ^1H NMR and IR spectra. It was found that 1:1 inclusion complexes were formed between β -CD and cations of the ILs. The results have been discussed from the disruption of the attractive interactions in the ionic liquids and the formation of the inclusion complexes.

2. Experimental Section

2.1. Materials. All the chemicals used in this work were purchased commercially with purity higher than 99.5%. β -CD, 1-methylimidazolium, acetone, and methylene chloride were obtained from Shanghai Chem. Co., Ltd. 1-Chlorobutane, 2-chloroethanol, and sodium dicyanamide were purchased by Beijing Chem. Co., Ltd., and allyl chloride was from Alfa Aesar. The liquid solvents were distilled twice before use. Sodium dicyanamide and β -CD were recrystallized twice in distilled water and dried under vacuum for 24 h at 333 K.

2.2. Synthesis of the ILs. $[\text{Bmim}]\text{Cl}$. The IL was synthesized according to the procedure described in literature.²³ The final

product was obtained as a white waxlike solid at room-temperature. Yield: 87.4%. ^1H NMR: δ = 9.446 (s, 1H), 7.840 (d, 1H), 7.765 (d, 1H), 4.177 (t, 2H), 3.856 (s, 3H), 1.747 (m, 2H), 1.233 (m, 2H), and 0.873 (m, 3H) ppm.

$[\text{Bmim}][\text{N}(\text{CN})_2]$. For the synthesis of $[\text{Bmim}][\text{N}(\text{CN})_2]$, the procedure reported by Liu and co-workers¹⁵ was followed. The final product was obtained as a colorless liquid. Yield: 89.4%. ^1H NMR: δ = 9.099 (s, 1H), 7.758 (d, 1H), 7.694 (d, 1H), 4.162 (t, 2H), 3.849 (s, 3H), 1.769 (m, 2H), 1.265 (m, 2H), and 0.902 (m, 3H) ppm. ^{13}C NMR: δ = 135.79, 122.77, 121.50, 118.37, 48.38, 35.08, 30.90, 18.35, and 12.30 ppm.

$[\text{Amim}]\text{Cl}$. This IL was synthesized according to the literature.²⁴ The final product was obtained as a yellow viscous liquid. Yield: 96.3%. ^1H NMR: δ = 9.434 (s, 1H), 7.786 (d, 1H), 7.769 (d, 1H), 6.005 (m, 1H), 5.282 (m, 2H), 4.865 (d, 2H), and 3.853 (s, 3H) ppm.

$[\text{Amim}][\text{N}(\text{CN})_2]$. The IL was synthesized according to the procedure described in literature.²⁵ The final product was obtained as a pale yellow liquid. Yield: 92.2%. ^1H NMR: δ = 9.287 (s, 1H), 7.792 (d, 1H), 7.750 (d, 1H), 5.491 (t, 1H), 4.241 (t, 2H), 3.873 (s, 3H), and 3.695 (m, 2H) ppm. ^{13}C NMR: δ = 135.89, 130.34, 123.13, 121.58, 120.23, 118.49, 50.66, and 35.39 ppm.

$[\text{Hemim}]\text{Cl}$. This IL was synthesized based on the procedure reported in literature.²⁶ The final product was obtained as a white wax-like solid at room temperature. Yield: 80.7%. ^1H NMR: δ = 9.287 (s, 1H), 7.792 (d, 1H), 7.750 (d, 1H), 5.491 (t, 1H), 4.241 (t, 2H), 3.873 (s, 3H), and 3.695 (m, 2H) ppm.

$[\text{Hemim}][\text{N}(\text{CN})_2]$. A 10 g portion of $[\text{Hemim}]\text{Cl}$ and 5.6 g of $\text{NaN}(\text{CN})_2$ were added into 20 mL of acetone. The suspension was stirred at room temperature for 48 h and then filtered through G4 glass frit. After the solvent was removed by rotary evaporation, the residual liquid was diluted with methylene chloride and filtered again. The filtrate was concentrated by rotary evaporation and dried under vacuum at 343 K for 48 h. The final product was obtained as a colorless liquid. Yield: 76.6%. ^1H NMR: δ = 9.060 (s, 1H), 7.699 (d, 1H), 7.666 (d, 1H), 5.147 (t, 1H), 4.204 (t, 2H), 3.863 (s, 3H), and 3.718 (m, 2H) ppm. ^{13}C NMR: δ = 137.20, 123.74, 123.05, 119.47, 59.72, 52.07, and 36.07 ppm.

2.3. Determination of Solubilities. The procedure used for the determination of β -CD solubilities was similar to that reported in literature.²⁷ For this purpose, β -CD (1.00 wt % of the IL) was added into a 20 mL colorimetric tube which contained 2–3 g of the dried IL, and the tube was sealed with parafilm. The colorimetric tube was immersed in an oil bath (DF-101S, Gongyi Yingyu Instrument Factory, China), and the bath temperature was controlled to be $T \pm 0.5$ K. The mixture was heated at a given temperature and stirred under argon atmosphere. Additional β -CD (1.00 wt % of the IL) was added until the solution became completely clear under polarization

TABLE 1: Solubilities of β -CD in the ILs at Different Temperatures

<i>T</i> (K)	solubility (gram per 100 g of the IL)					
	$[\text{Bmim}]\text{Cl}$	$[\text{Hemim}]\text{Cl}$	$[\text{Amim}]\text{Cl}$	$[\text{Bmim}][\text{N}(\text{CN})_2]$	$[\text{Hemim}][\text{N}(\text{CN})_2]$	$[\text{Amim}][\text{N}(\text{CN})_2]$
333.2	^a		79.4	73.0	90.5	102.3
338.2		78.4	87.8	81.1	98.4	109.8
343.2	69.7	86.1	97.3	89.5	106.2	117.4
348.2	79.4	94.5	105.9	97.4	114.0	125.0
353.2	90.6	102.5	112.3	105.1	121.5	132.2
358.2	99.3	110.4				
363.2	106.7					

^a The solubility was not measured at the given temperature because of the high viscosities of the system.

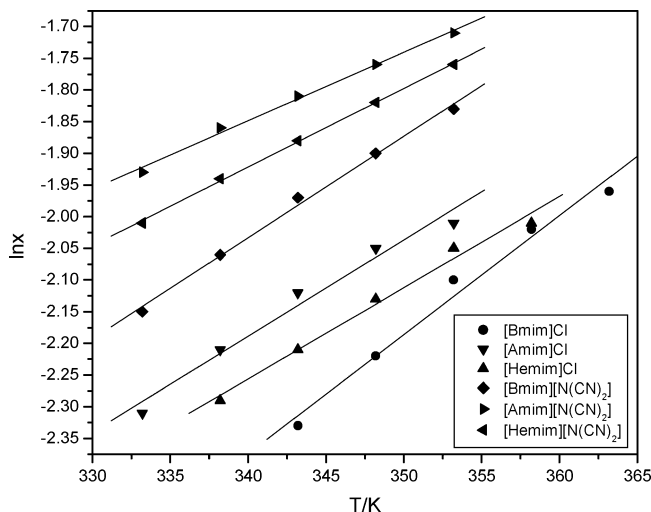


Figure 3. Plots of $\ln x$ versus T for β -CD in the ILs.

microscope (Nanjing Jiangnan Novel Optics Co. Ltd., China). When β -CD became saturated, judged by the fact that β -CD could not be dissolved further within 1 h, its solubility (expressed by gram per 100 g of ionic liquid) at the given temperature could be calculated from the amounts of the IL and β -CD added. For each IL, the solubility values of β -CD were measured at five temperatures with 5 K intervals. The initial temperature for the dissolution was set at 333.2, 338.2, and 343.2 K according to the melting points of different ILs. The maximal error in the solubility measurements was in the range from 0.75 to 1.4% depending on the solubility magnitudes.

2.4. Measurements of NMR and IR Spectra. The ^1H NMR and ^{13}C NMR experiments of the ILs were performed on a Bruker AV-400 MHz spectrometer in DMSO and D_2O , respectively, at 298 K. In the measurements of ^1H NMR for the samples of β -CD in ILs, acetone was used as an external to suppress the interference from other solvents. It should be pointed out that for the ^1H NMR investigation of the interaction between β -CD and the ILs, only the dicyanamide-based ILs + β -CD systems were studied since their low viscosity facilitated the ^1H NMR measurements.

IR spectra of ILs with and without β -CD were recorded on a Nicolet Nexus IR/Raman spectroscopy at 298 K with a resolution of 2 cm^{-1} . To reduce the error in the calculation of vibrational intensity, the β -CD + IL samples with the highest concentration of β -CD were used to study the interaction between β -CD and the ILs. The molar ratio of β -CD to the ILs was in the range from 0.15 to 0.22.

3. Results and Discussions

3.1. Solubilities and the Standard Solution Thermodynamic Parameters of β -CD in the ILs. Data in Table 1 show some interesting features for the dissolution of β -CD in the ILs under the same experimental conditions: (i) Compared with the [Bmim][N(CN) $_2$] used in literature,¹⁵ much higher solubilities of β -CD have been observed in [Amim]Cl, [Hemim][N(CN) $_2$], and [Amim][N(CN) $_2$]. For example, solubility of β -CD in [Amim][N(CN) $_2$] is about 32% higher than that in [Bmim][N(CN) $_2$] at the temperature range investigated. (ii) Solubilities of β -CD in the ILs decrease in the order, [Amim][N(CN) $_2$] > [Hemim][N(CN) $_2$] > [Bmim][N(CN) $_2$], and [Amim]Cl > [Hemim]Cl > [Bmim]Cl; (iii) solubilities of β -CD in dicyanamide-based ILs are much higher than those in chloride-based ones; and (iv) solubilities of β -CD increase with

TABLE 2: Solution Thermodynamic Parameters of β -CD in the ILs at Different Temperatures

T (K)	ΔH_S^θ (kJ mol $^{-1}$)	ΔG_S^θ (kJ mol $^{-1}$)	$T\Delta S_S^\theta$ (kJ mol $^{-1}$)
[Bmim]Cl			
343.2	18.4	6.7	11.7
348.2	19.0	6.4	12.6
353.2	19.5	6.2	13.3
358.2	20.1	6.0	14.1
363.2	20.6	5.9	14.7
[Hemim]Cl			
338.2	13.7	6.4	7.3
343.2	14.1	6.3	7.8
348.2	14.5	6.2	8.3
353.2	14.9	6.0	8.9
358.2	15.4	5.9	9.5
[Amim]Cl			
333.2	14.0	6.4	7.6
338.2	14.5	6.2	8.3
343.2	14.9	6.1	8.8
348.2	15.3	6.0	9.3
353.2	15.8	5.9	9.9
[Bmim][N(CN) $_2$]			
333.2	14.8	6.0	8.8
338.2	15.2	5.8	9.4
343.2	15.7	5.6	10.1
348.2	16.1	5.5	10.6
353.2	16.6	5.4	11.2
[Hemim][N(CN) $_2$]			
333.2	11.4	5.6	5.8
338.2	11.8	5.5	6.3
343.2	12.1	5.4	6.7
348.2	12.5	5.3	7.2
353.2	12.9	5.2	7.7
[Amim][N(CN) $_2$]			
333.2	10.0	5.4	4.6
338.2	10.3	5.3	5.0
343.2	10.6	5.2	5.4
348.2	10.9	5.1	5.8
353.2	11.2	5.0	6.2

increasing temperature. These results indicate that structure of the cation, nature of the anion, interactions between cations and anions of the ionic liquids, and the temperature affect the solubility of β -CD significantly.

On the basis of the solubility data, the standard solution Gibbs energy, ΔG_S^θ , for β -CD in the ILs can be calculated by the following equation:

$$\Delta G_S^\theta = -RT \ln x \quad (1)$$

where x stands for the solubility expressed by the mole fraction of β -CD, while R and T have their usual meanings. According to the Gibbs–Helmholtz equation and eq 1, we can obtain the following equation:

$$\Delta H_S^\theta = RT^2 \left(\frac{d \ln x}{dT} \right) \quad (2)$$

By plotting $\ln x$ versus T , good straight lines are observed in all the cases as shown in Figure 3. Values of ΔH_S^θ have been calculated from the slopes of the resulting straight lines and eq 2.²⁸ The remaining $T\Delta S_S^\theta$ can be obtained by

$$T\Delta S_S^\theta = \Delta H_S^\theta - \Delta G_S^\theta \quad (3)$$

TABLE 3: ^1H NMR Chemical Shifts of β -CD in [Bmim][N(CN) $_2$]

proton	δ (ppm)			$\Delta\delta$ (ppm)	
	$w = 10\%^a$	$w = 15\%$	$w = 20\%$	$\Delta\delta_1^b$	$\Delta\delta_2^c$
H-1 (outer)	4.072	4.051	4.037	-0.021	-0.014
H-2 and H-4 (outer)	2.598	2.574	2.570	-0.024	-0.004
H-3 (inner)	2.863	2.841	2.823	-0.022	-0.018
H-5 (inner)	not observed	not observed	appear		
H-6 (inner)	2.807	2.789	2.771	-0.018	-0.018
OH-2 and OH-3 (outer)	4.842	4.802	4.755	-0.040	-0.047
OH-6 (outer)	3.507	3.483	3.428	-0.024	-0.055

^a w stands for the mass fraction of β -CD in [Bmim][N(CN) $_2$]. ^b $\Delta\delta_1 = \delta(w = 15\%) - \delta(w = 10\%)$. ^c $\Delta\delta_2 = \delta(w = 20\%) - \delta(w = 15\%)$.

The results have been listed in Table 2. It can be seen that values of ΔG_s^θ , ΔH_s^θ and ΔS_s^θ are positive for all the systems studied. The positive ΔG_s^θ values suggest that interactions between the ILs are stronger than those between β -CD and ILs. The dissolution of β -CD in the ILs is unfavorable thermodynamically. In addition, the positive entropy changes and the relation $|\Delta H_s^\theta| > |T\Delta S_s^\theta|$ are always found for the dissolution process, which indicates that the dissolution processes in the ILs are entropically favorable and controlled by the enthalpy term. To enhance the solubility, the increase of temperature is necessary.

3.2. The Interactions between β -CD and the ILs. The excellent dissolution capabilities of β -CD in the ILs inspired us to study the interactions between them. As stated in the introduction, the formation of inclusion complexes between β -CD and ILs has been reported in aqueous solutions. To examine if the inclusion complexes were also formed in the dissolution process, the interaction of β -CD with [Bmim][N(CN) $_2$] was studied by ^1H NMR as an example.

The ^1H NMR chemical shifts for β -CD in [Bmim][N(CN) $_2$] + β -CD were listed in Table 3. Owing to the high viscosity of the mixture, the peaks of H-2 and H-4 as well as OH-2 and OH-3 protons turned into one broad peak, respectively. With the increase of the mass fraction of β -CD in [Bmim][N(CN) $_2$], these protons shifted upfield, and the H-5 peak was observed in the mixture of 20% β -CD + 80% [Bmim][N(CN) $_2$] (see Figure 4). This suggests that inclusion complexes between β -CD and [Bmim][N(CN) $_2$] were really formed in such a case.¹⁶ The ^1H chemical shift of the protons (H-3, H-5, and H-6) in the inner cavity of β -CD was attributed to the shielding effect of cations of the ILs, which is an indication for the entry of cation of the ILs into the cavity of β -CD. Also, the signals of the hydroxyl protons

(OH-2, OH-3, and OH-6) outside the cavity of β -CD were found to shift upfield because of the interactions of these β -CD protons with anions of the ILs. On the other hand, it can be seen from Table 4 that all the protons of [Bmim] $^+$ shift upfield as the mass fraction of β -CD increases. Compared to the protons of the butyl chain, those of the imidazolium cation have larger chemical shifts under the same conditions. This supports the conclusion that some imidazolium cations have entered into the cavities of β -CD and have stronger interaction with β -CD than the protons of butyl chain. At the same time, the electron densities of protons of the imidazolium cations decrease due to the partial disruption of the interionic interactions between cation and anion of [Bmim][N(CN) $_2$] by the inclusion of some imidazolium cations into the cavity of β -CD. This also makes the chemical shifts to change toward upfield.

The dissolution of β -CD in the ILs was further investigated by IR spectra. It is known that infrared absorbance ratio reflects the relative content of different chemical groups. If the inclusion complexes between β -CD and cation of the ILs could be formed, the relative absorbance of imidazolium ring would decrease compared with the anion. Additionally, since the absorbance of the [N(CN) $_2$] $^-$ anion is intensive and can be easily distinguished, IR spectra of [Bmim][N(CN) $_2$] and [Bmim][N(CN) $_2$] + β -CD (molar ratio of β -CD to the IL = 0.19) have been selected for the study (see Figure 5).

If the infrared intensity of imidazolium cation and dicyanamide anion of the [Bmim][N(CN) $_2$] is I_1 and I_2 , respectively. According to Lambert–Beer's law, they can be written as

$$I_1 = A_1 b_1 c_1 \quad (4)$$

$$I_2 = A_2 b_2 c_2 \quad (5)$$

where c_1 and c_2 stand for the concentrations of free imidazolium cation and dicyanamide anion, respectively. It is known that under the same experimental conditions, the values of A_1 and b_1 are approximately equal to those of A_2 and b_2 , respectively,²⁹ for the identical molecules, and the ratio a ($= I_1/I_2$) can be expressed by

$$a = I_1/I_2 = c_1/c_2 \quad (6)$$

On the basis of the IR spectra of [Bmim][N(CN) $_2$] and β -CD + [Bmim][N(CN) $_2$] mixture, the vibrational intensities of C=N group of imidazolium ring ($\nu_{\text{C=N}}$) and C \equiv N group of dicyanamide anion ($\nu_{\text{C=N}}$) have been calculated and given in Table 5. According to the data in Table 5, it could be concluded that the

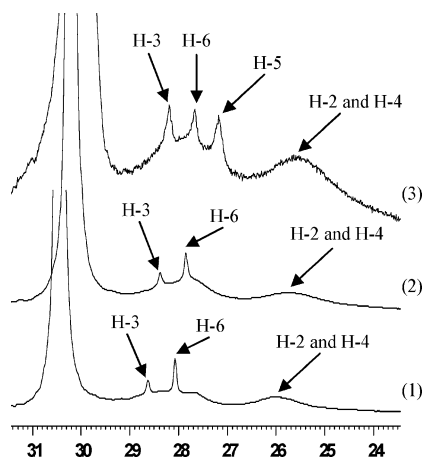


Figure 4. ^1H NMR spectra of β -CD in [Bmim][N(CN) $_2$] at different mass fractions of β -CD: (1) 10%, (2) 15%, (3) 20%.

TABLE 4: ^1H NMR Chemical Shifts of $[\text{Bmim}]^+$ in $\beta\text{-CD} + [\text{Bmim}][\text{N}(\text{CN})_2]$ Mixture

proton	δ (ppm)			$\Delta\delta$ (ppm)	
	$w = 10\%^a$	$w = 15\%$	$w = 20\%$	$\Delta\delta_1^b$	$\Delta\delta_2^c$
H-2	8.099	8.066	8.041	-0.033	-0.025
H-4 and H-5	6.787, 6.723	6.759, 6.696	6.736, 6.675	-0.028, -0.027	-0.023, -0.021
N-CH ₂ -	3.328	3.306	3.287	-0.022	-0.019
N-CH ₃	3.045	3.023	3.004	-0.022	-0.019
C-CH ₂ -C	0.936	0.917	0.900	-0.019	-0.017
CH ₂ -Me	0.404	0.388	0.371	-0.016	-0.017
C-CH ₃	-0.028	-0.044	-0.061	-0.016	-0.017

^a w stands for the mass fraction of $\beta\text{-CD}$ in $[\text{Bmim}][\text{N}(\text{CN})_2]$. ^b $\Delta\delta_1 = \delta(w = 15\%) - \delta(w = 10\%)$. ^c $\Delta\delta_2 = \delta(w = 20\%) - \delta(w = 15\%)$.

ratio of cation to anion in the pure IL (a_0) and IL + $\beta\text{-CD}$ mixture (a_m)

$$a_0 = v_{\text{C}=\text{N}}/v_{\text{C}\equiv\text{N}} = 0.11 \quad (7)$$

$$a_m = v_{\text{C}=\text{N}}/v_{\text{C}\equiv\text{N}} = 0.09 \quad (8)$$

Therefore, the following equations could be obtained:

$$a_m/a_0 \approx 0.82 \quad (9)$$

$$1 - \frac{a_m}{a_0} \approx 0.18 \quad (10)$$

It is evident that the $(1 - a_m/a_0)$ value of 0.18 is very close to the molar ratio of $\beta\text{-CD}$ (0.19) in $[\text{Bmim}][\text{N}(\text{CN})_2]$. This indicates that some cations of $[\text{Bmim}][\text{N}(\text{CN})_2]$ have entered into the cavities of $\beta\text{-CD}$ completely to form 1:1 inclusion complexes so that the relative infrared absorbance decreases for the imidazole rings. Similar conclusions can be obtained for the other $\beta\text{-CD} +$ dicyanamide-based ionic liquids systems. Considering the fact that the chloride-based ILs used in the present work have the same cations as the corresponding dicyanamide-based ILs, it can be inferred that $\beta\text{-CD}$ can form inclusion complexes with all cations of the studied ILs in the dissolution process.

3.3. The Effects of the Inclusion Complex Formation and the Interactions between Cation and Anion of the ILs on the Solubility of $\beta\text{-CD}$. From the viewpoint of chemical thermodynamics, the dissolution process of $\beta\text{-CD}$ can be divided

into two main steps: (i) partial destruction of the attractive interactions between cation and anion of the ILs; and (ii) formation of the inclusion complexes between $\beta\text{-CD}$ and cation of the ILs. Therefore, the standard dissolution enthalpies of $\beta\text{-CD}$ may be expressed as the sum of two contributions:

$$\Delta H_S^\theta = \Delta H_{\text{C-A}}^\theta + \Delta H_{\text{C-CD}}^\theta \quad (11)$$

where $\Delta H_{\text{C-A}}^\theta$ represents the enthalpy change for the breaking of the attractive interactions between cations and anions in the ILs, and $\Delta H_{\text{C-CD}}^\theta$ stands for the enthalpy change caused by formation of the inclusion complexes between cations of the ILs and $\beta\text{-CD}$, that is, the enthalpy of inclusion. It is expected that the first term is positive, whereas the second term is negative. Because the ΔH_S^θ values determined experimentally are positive, the $\Delta H_{\text{C-A}}^\theta$ term would be predominant. This suggests that the enthalpies of inclusion are not negative enough to overcome the positive contribution from the destruction of the attractive interaction in the ILs.

To form inclusion complex, the geometric compatibility of $\beta\text{-CD}$ with the imidazolium cations is a key factor. It has been reported that volumes of the $[\text{Bmim}]^+$ and the cavity of $\beta\text{-CD}$ are about 0.196 and 0.262 nm³, respectively.^{1,30} The cavity diameter of $\beta\text{-CD}$ is between 0.6 and 0.65 nm, and the width of $[\text{Bmim}]^+$ is about 0.58 nm.³¹ That is to say that the size of $[\text{Bmim}]^+$ and cavity of $\beta\text{-CD}$ is close to each other, $[\text{Bmim}]^+$ can be included into the cavity of $\beta\text{-CD}$ to form the complexes. To the best of our knowledge, no size data for $[\text{Hemim}]^+$ and $[\text{Amim}]^+$ cations have been reported in literature. However, it can be inferred from their structures that $[\text{Hemim}]^+$ and $[\text{Amim}]^+$ should have similar diameters as $[\text{Bmim}]^+$. Therefore, it is appropriate to state that no significant differences would be found in the inclusion enthalpies and entropies for the ILs investigated, and the main difference in the dissolution of $\beta\text{-CD}$ is attributed to the difference in the destruction of the attractive interactions in these ILs.

It has been reported from density function theory calculations that the absolute values of interaction energies in some studied ILs follow the order³²⁻³⁴ $[\text{Bmim}]\text{Cl} > [\text{Bmim}][\text{N}(\text{CN})_2]$ and $[\text{Amim}]\text{Cl} > [\text{Amim}][\text{N}(\text{CN})_2]$, so that $[\text{Bmim}]\text{Cl}$ and $[\text{Amim}]\text{Cl}$ are solid, but $[\text{Bmim}][\text{N}(\text{CN})_2]$ and $[\text{Amim}][\text{N}(\text{CN})_2]$ are liquid at room temperature. This indicates that the attractive interactions in the chloride-based ILs are stronger than those in the dicyanamide-based ILs. Accordingly, more energies are needed to break those interactions in the chloride-based ILs so that the dissolution of $\beta\text{-CD}$ can be successfully processed. This is a possible reason why the solubilities of $\beta\text{-CD}$ in the dicyanamide-based ILs are higher than in the chloride-based ILs at the same temperature.

As an approximation, melting points of ionic liquids can be used for the rough estimation of the relative order of the

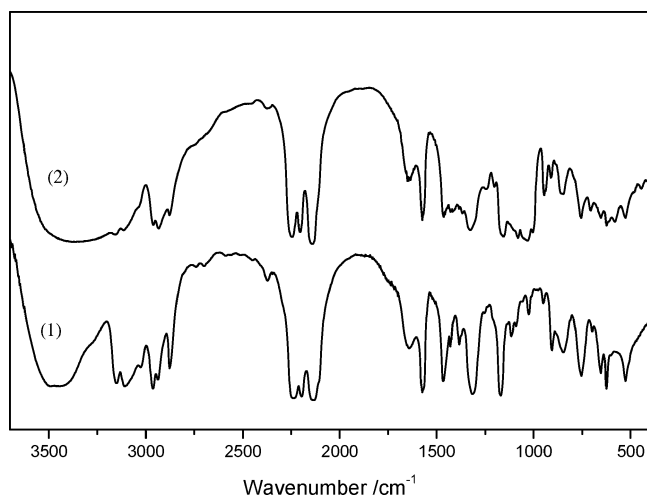


Figure 5. Infrared spectra of $[\text{Bmim}][\text{N}(\text{CN})_2]$ and $\beta\text{-CD} + [\text{Bmim}][\text{N}(\text{CN})_2]$: (1) $[\text{Bmim}][\text{N}(\text{CN})_2]$; (2) $\beta\text{-CD} + [\text{Bmim}][\text{N}(\text{CN})_2]$.

TABLE 5: Infrared Intensity of the $\nu_{C=N}$ and $\nu_{C\equiv N}$ Vibrational Modes

vibrational modes and their ratio	intensity	
	[Bmim][N(CN) ₂]	β -CD + [Bmim][N(CN) ₂]
$\nu_{C=N}^a$	15.1	11.1
$\nu_{C\equiv N}^b$	134.4	119.9
$\nu_{C=N}/\nu_{C\equiv N}$	0.11	0.09

^a The peak of $\nu_{C=N}$ is at around 1570 cm⁻¹. ^b The peak of $\nu_{C\equiv N}$ is at around 2200 cm⁻¹.

interaction energies in the ILs when such data are not available. The higher the melting points, the greater the interaction energies of the ILs are. It was found that melting points of ionic liquids increase in the order^{26,35,36} [Amim]Cl (~290 K) < [Hemim]Cl (~333 K) < [Bmim]Cl (~343 K). The reverse order would be approximated for the interaction energies. This information makes it possible to interpret the increased solubilities of β -CD in the ILs from [Bmim]Cl, [Hemim]Cl to [Amim]Cl, and from [Bmim][N(CN)₂], [Hemim][N(CN)₂] to [Amim][N(CN)₂] mentioned as one of the interesting features observed from the solubility data in Table 1.

Similar to eq 11, the standard solution entropy can be expressed by

$$\Delta S_s^\theta = \Delta S_{C-A}^\theta + \Delta S_{C-D}^\theta \quad (12)$$

where ΔS_{C-A}^θ and ΔS_{C-D}^θ represent the entropy change for the disruption of the ordered structures of ILs (positive) and for the formation of the inclusion complexes (negative), respectively. Therefore, the positive ΔS_s^θ values observed experimentally imply that structure change of the ILs is greater than that caused by formation of the inclusion complexes.

4. Conclusions

In this work, the solubilities, standard solution Gibbs energies, solution enthalpies, and solution entropies have been determined for β -CD in six kinds of hydrophilic ionic liquids. It is shown that the solubilities of β -CD were remarkable in these ionic liquids and followed the order [Amim][N(CN)₂] > [Hemim][N(CN)₂] > [Amim]Cl > [Bmim][N(CN)₂] > [Hemim]Cl > [Bmim]Cl, and the dissolution process was unfavorable thermodynamically and controlled by enthalpic term. ¹H NMR and IR spectra measurements indicated that 1:1 inclusion complexes were formed between β -cyclodextrin and imidazolium cations of the ionic liquids. However, the disruption of the attractive interactions and the ordered structures of the ILs predominates the dissolution process. This is quite different from the dissolution of β -CD in aqueous IL solutions, in which the process was driven by the inclusion of cations of the ILs into the cavity of β -CD. In addition, the effect of the ILs structure on the solubilities of β -CD was examined. The result indicated that, for the same cation, the solubilities of β -CD were much higher in the dicyanamide-based ILs than in the chloride-based ILs because of the weaker interactions in the former systems. Therefore, in order to design effective ILs for the dissolution of β -CD, interactions in ionic liquids need to be studied extensively. Considering the fact that cyclodextrins and their derivatives dissolved in ILs can be used to prepare the stationary

phases in gas chromatography, the above findings may be useful for the molecular design of such stationary phases.

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References and Notes

- (1) Szejtli, J. *Chem. Rev.* **1998**, 98, 1743.
- (2) Engeldinger, E.; Armspach, D.; Matt, D. *Chem. Rev.* **2003**, 103, 4147.
- (3) Martin Del Valle, E. M. *Proc. Biochem.* **2004**, 39, 1033.
- (4) Sabadini, E.; Cosgrove, T.; Egídio, F. D. C. *Carbohydr. Res.* **2006**, 341, 270.
- (5) Maginn, E. J. *Acc. Chem. Res.* **2007**, 40, 1200.
- (6) Greaves, T. L.; Drummond, C. J. *Chem. Rev.* **2008**, 108, 206.
- (7) Hardacre, C.; Holbrey, J. D.; Nieuwenhuyzen, M.; Youngs, T. G. A. *Acc. Chem. Res.* **2007**, 40, 1146.
- (8) Castner, E. W.; Wishart, J. F.; Shirota, H. *Acc. Chem. Res.* **2007**, 40, 1217.
- (9) Han, X. X.; Armstrong, D. W. *Acc. Chem. Res.* **2007**, 40, 1079.
- (10) Hapiot, P.; Lagrost, C. *Chem. Rev.* **2008**, 108, 2238.
- (11) Pârvolescu, V. I.; Hardacre, C. *Chem. Rev.* **2007**, 107, 2615.
- (12) El Seoud, O. A.; Koschella, A.; Fidale, L. C.; Dorn, S.; Heinze, T. *Biomacromolecules* **2007**, 8, 2629.
- (13) Murugesan, S.; Linhardt, R. J. *Curr. Org. Synth.* **2005**, 2, 437.
- (14) Zhu, S. D.; Wu, Y. X.; Chen, Q. M.; Yu, Z. N.; Wang, C. W.; Jin, S. W.; Ding, Y. G.; Wu, G. *Green Chem.* **2006**, 8, 325.
- (15) Liu, Q. B.; Janssen, M. H. A.; Rantwijk, F. V.; Sheldon, R. A. *Green Chem.* **2005**, 7, 39.
- (16) 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.
- (17) Gao, Y. A.; Zhao, X. Y.; Dong, B.; Zheng, L. Q.; Li, N.; Zhang, S. H. *J. Phys. Chem. B* **2006**, 110, 8576.
- (18) Li, N.; Liu, J.; Zhao, X. Y.; Gao, Y. A.; Zheng, L. Q.; Zhang, J.; Yu, L. *Colloids Surf. A* **2007**, 292, 196.
- (19) He, Y. F.; Shen, X. H. *J. Photochem. Photobiol. A* **2008**, 197, 253.
- (20) He, Y. F.; Chen, Q. D.; Xu, C.; Zhang, J. J.; Shen, X. H. *J. Phys. Chem. B* **2009**, 113, 231.
- (21) Amajjahe, S.; Ritter, H. *Macromolecules* **2008**, 41, 716.
- (22) Berthod, A.; He, L.; Armstrong, D. W. *Chromatographia* **2001**, 53, 63.
- (23) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, 3, 156.
- (24) Zhang, H.; Wu, J.; Zhang, J.; He, J. S. *Macromolecules* **2005**, 38, 8272.
- (25) Laus, G.; Bentivoglio, G.; Schottenberger, H.; Kahlenberg, V.; Kopacka, H.; Röder, T.; Sixta, H. *Langmuir* **2005**, 21, 84, 71.
- (26) Branco, L. C.; Rosa, J. N.; Ramos, J. J. M.; Afonso, C. A. M. *Chem.—Eur. J.* **2002**, 8, 3671.
- (27) Fukaya, Y.; Sugimoto, A.; Ohno, H. *Biomacromolecules* **2006**, 7, 3295.
- (28) Queimada, A. J.; Mota, F. L.; Pinho, S. P.; Macedo, E. A. *J. Phys. Chem. B* **2009**, 113, 3469.
- (29) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1958.
- (30) Krossing, I.; Slattery, J. M.; Daguene, C.; Dyson, P. J.; Oleinikova, A.; Weingartner, H. *J. Am. Chem. Soc.* **2006**, 128, 13427.
- (31) Berthod, A.; Kozak, J. J.; Anderson, J. L.; Ding, J.; Armstrong, D. W. *Theor. Chem. Acc.* **2007**, 117, 127.
- (32) Turner, E. A.; Pye, C. C.; Singer, R. D. *J. Phys. Chem. A* **2003**, 107, 2277.
- (33) Emel'yanenko, V. N.; Verevkin, S. P.; Heintz, A. *J. Am. Chem. Soc.* **2007**, 129, 3930.
- (34) Guo, M. Master Dissertation. Henan Normal University, China, 2009.
- (35) Zhao, H.; Baker, G. A.; Song, Z. Y.; Olubajo, O.; Crittle, T.; Peters, D. *Green Chem.* **2008**, 10, 696.
- (36) Yeon, S. H.; Kim, K. S.; Choi, S.; Lee, H.; Kim, H. S.; Kim, H. *Electrochim. Acta* **2005**, 50, 5399.