

Preparation and Characterization of Inclusion Complexes of β -Cyclodextrin with Ionic Liquid

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Abstract: The solubilities of β -cyclodextrin (β -CD), ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆), and their mixture in water were determined, and the conductivity of these aqueous solutions was measured. It was demonstrated that β -CD and bmimPF₆ could enhance the solubility of each other, and the solubility curves of each were linear with gradients of about 1. The conductivity decreased remarkably with increasing β -CD concentration, and a dis-

cernible break in the conductivity curve could be observed when β -CD and bmimPF₆ were equimolar in the solution. The solubility and conductivity results indicated that inclusion complexes (ICs) of 1:1 stoichiometry were formed. The inclusion compounds were further characterized by using powder

X-ray diffraction (XRD) analysis, ¹³C CP/MAS (cross-polarization magic-angle spinning) NMR and ¹H NMR spectroscopy, and thermogravimetric analysis (TGA). The results showed that the ICs were a fine crystalline powder. The host-guest system exhibited a channel-type structure and each glucose unit of β -CD was in a similar environment. The decomposition temperature of the ICs was lower than that of bmimPF₆ and β -CD individually.

Keywords: cyclodextrins • host-guest systems • inclusion compounds • ionic liquids

Introduction

Cyclodextrins (CDs) as hosts can form supramolecular and host-guest inclusion compounds with a number of different organic and inorganic guest molecules.^[1] They are commercially available, nontoxic, and water soluble, which makes them suitable for numerous applications in the pharmaceutical industry, pesticides, foodstuffs, toilet articles, and textile processing.^[2-4] In addition to their industrial applications, these shallow, somewhat flexible hosts are related to many interesting topics, such as molecular recognition and self-assembly, selectivity, molecular encapsulation, chemical stabili-

zation, and intermolecular interactions.^[3,5,6] Such successful performances of CDs originate from their unique structure and properties. It is well known that CDs are a series of cyclic oligosaccharides, which are composed of six, seven, or eight glucose units connected by α -1,4-acetyl linkages, and called α -, β -, and γ -CD, respectively. They have a hollow truncated cone shape with a hydrophobic inner cavity and a hydrophilic outside surface. Based on the well-known representatives of this category, that is, α -, β -, and γ -CDs, many different derivatives have been synthesized that possess different water solubility and inclusion capabilities.^[6-8]

In aqueous solution, the slightly apolar cavity of cyclodextrin is occupied by water molecules which are energetically unfavored, and therefore can be readily substituted by appropriate guest molecules that are less polar than water. The guest penetrates the cavity, leading to the formation of an inclusion compound through several kinds of relevant interactions. Recently, with increasing interest in macromolecular recognition, the inclusion complexes of CDs and linear polymers have been extensively investigated.^[9-22] Some CDs can be penetrated by a polymeric chain, forming the so-called polypseudorotaxanes that can then be converted into molecular necklaces.^[23] Furthermore, a large number of organometallic compounds and their derivatives can form inclusion compounds with CDs, and the interaction mecha-

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nism and properties of these compounds have been discussed.^[24–26] The catalytic activities of some water-soluble metal nanoparticles modified with covalently attached CD receptors can be modulated by the inclusion interaction between organometallic compounds and CD, thus catalytic reactions can be carried out effectively.^[25,27] Matt and co-workers successfully modified CDs as ligands to form chelate complexes of CD derivatives and transition-metal ions.^[8]

In recent years, ionic liquids (ILs), which consist of organic cations and appropriate anions, have received much attention due to their potential as a green and recyclable alternative to traditional organic solvents.^[28] Compared with traditional salts, ILs have a much lower melting temperature. Their favorable properties, such as high polarity, negligible vapor pressure, high ionic conductivity, and thermal stability, make them ideal solvents in organic synthesis, chemical reactions, chemical separations, and material preparations.^[29] It has been reported that ILs can form extended hydrogen-bond systems in the liquid state and are therefore highly structured.^[30] The preorganized structure exhibits an extended network of cations–anions connected by hydrogen bonds. The solubility of cellulose in ILs was deduced to be associated with the extended hydrogen-bonded systems.^[31] The strong hydrogen-bond-driven solvent structure makes ILs potential key tools in the preparation of a new generation of chemical nanostructures.^[32] Furthermore, for imidazolium-based ILs, the interactions of the imidazolium rings result in the formation of a three-dimensional arrangement, because in some cases, typical π – π stacking interactions exist among the imidazolium rings, which result in the generation of channel-type molecular arrangements.^[33]

There have been some reports on the combination of CDs and ILs. For instance, Qi et al. used ILs as running electrolytes in capillary zone electrophoresis and β -cyclodextrin as the modifier for the separation of the anthraquinones extract of Chinese herb.^[34] The inclusion complexation of methyl orange or phenol with CDs in ILs has been studied by using spectral analyses.^[35] CDs or their derivatives dissolved in ILs can be used to prepare stationary phases in gas chromatography.^[36] Moreover, Duvivier et al. studied the solubility of β -cyclodextrin in a water–ethylammonium nitrate mixture.^[37] However, to the best of our knowledge, the study of the inclusion interaction between CDs and ILs has not been reported so far. Considering the special structure and properties of ILs, it is of interest to investigate the complexation behavior between them and CDs by using different techniques.

Results and Discussion

Solubility measurements: It is well known that β -CD has a relatively lower solubility in water compared with that of α - or γ -CD, and that the bmimPF₆ ionic liquid is hydrophobic and slightly soluble in water. The solubilities of β -CD and bmimPF₆ in water (100 mL) at 25 °C are 1.85 g and 1.88 g,

respectively,^[38] corresponding to molar concentrations of 16.3 and 66.2 mmol L⁻¹, respectively. Figure 1 shows the solubility curves of β -CD and bmimPF₆ at 25 °C. Regions **A**

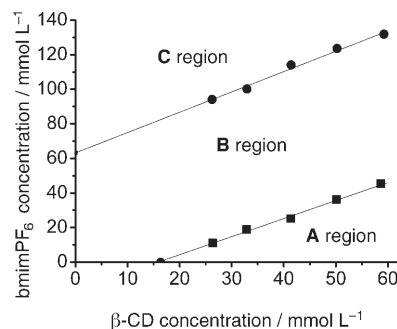


Figure 1. Solubilities of β -CD (■) and bmimPF₆ (●) in water at 25 °C.

and **C** are two-phase regions and **B** is a single-phase region. In region **A**, there exists both a water-rich phase and a β -CD-rich phase, whereas region **C** consists of a water-rich phase and a bmimPF₆-rich phase. The figure demonstrates clearly that β -CD and bmimPF₆ can enhance the solubility of each other. A reasonable explanation is that the cation of bmimPF₆ is incorporated into the cavity of β -CD. The counterions are retained outside of the β -CD torus. Ions outside the β -CD torus strongly affect the ordering of the surrounding water molecules, which is favorable for the dissolution of β -CD.^[39] It can be considered that the IL and β -CD form a more soluble inclusion compound, which consists of a cation (bmim⁺ in the β -CD torus) and an anion (PF₆⁻). The solubilities of the separate IL and β -CD are not affected considerably by the new compound. Therefore, the total solubility of the mixture is increased. The figure also shows that the two curves are linear and the gradients of the two lines are about 1, suggesting that bmimPF₆ is included by β -CD in a 1:1 molar ratio.^[4]

Conductivity study: Measurement of the conductivity is a commonly used method for studying the inclusion phenomenon, and it can be used to elucidate not only whether inclusion can occur but also the stoichiometry of the inclusion complexes (ICs) formed.^[40] As discussed above, the IL is partially soluble in water. If it forms an inclusion complex with β -CD, the solution conductivity will be distinctly affected by the addition of β -CD. The conductivity of various β -CD concentrations in aqueous IL (5.0 mmol L⁻¹) were measured at 25 °C, and the dependence of the conductivity on β -CD concentration is shown in Figure 2. The conductivity decreased remarkably with increasing β -CD concentration, indicating the inclusion-complex formation between β -CD and the hydrophobic IL. A discernible break in the conductivity curve occurred at a concentration of about 5.0 mmol L⁻¹ β -CD, suggesting that the stoichiometry of the β -CD–bmimPF₆ (**1**) ionic compound is equimolar.^[41] This conclusion is the same as that deduced from the solubility curves above. Palepu et al. determined the conductivity of solutions

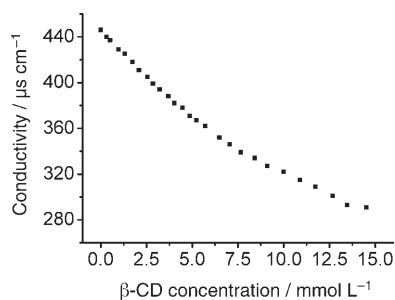


Figure 2. Dependence of conductivity of an aqueous bmimPF₆ solution (5.0 mmol L⁻¹) on the concentration of β-CD at 25.0 °C.

of sodium alkyl carboxylates in water with different alkyl groups and β-CD,^[40] and produced conductivity curves similar to that shown in Figure 2.

Powder X-ray diffraction (XRD): XRD is a widely used technique in the study of inclusion compounds for assessing the structure, and to check whether a new compound has been produced from the parent molecules.^[12] Harata and co-workers reported that the crystal structures of CD complexes are classified mainly into three types: channel, cage, and layer.^[11] Figure 3 shows the XRD patterns of β-CD and that of **1**. The results suggest that the obtained ICs between

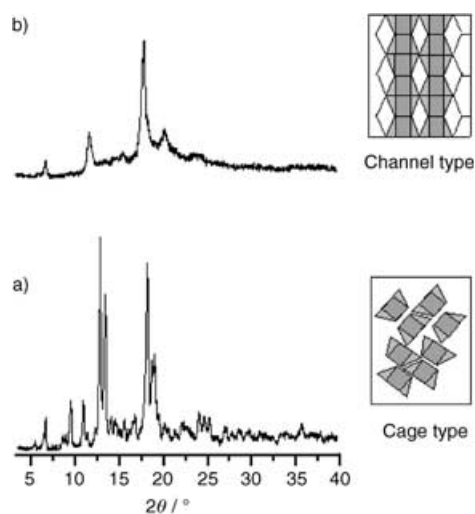


Figure 3. X-ray power diffraction patterns of a) β-CD and b) **1**.

β-CD and bmimPF₆ are fine crystalline powders, although bmimPF₆ itself is a liquid at room temperature. In Figure 3a, major peaks at 9.5, 12.8, 13.3, and 18.1° are observed, indicating that β-CD represents a typical cage structure.^[11,18,20,22] The pattern of **1** (Figure 3b) shows some sharp reflections, the main two of which at 2θ = 11.6 and 17.8° represent a head-to-head channel-type structure,^[25] which is different from that of β-CD.^[11,18,20,22] The results indicate that the inclusion complex formed from β-CD and bmimPF₆ is isomor-

phous with a channel-type structure rather than the so-called “cage” structure.

The formation mechanism of such a channel-type structure for host–guest inclusion complexes of cyclodextrins has been widely investigated.^[18,19,21,41] In general, the type of guest molecule and experimental conditions determine the packing type, described as cage or channel structures.^[42] For a long-chain molecule guest, the inclusion complexes were found to adopt a head-to-head channel-type structure in which cyclodextrin molecules are stacked along an axis to form a cylinder. In fact, the channel-type structure, without any included guests other than water of hydration, can also be obtained through an appropriate recrystallization process. Therefore, even when there are no guest molecules included other than water, the channel structure consisting of endless columns of stacked CD molecules connected to each other by hydrogen bonds has been proved to be a stable structure.^[42] The hydrogen bonds between hydroxyl groups of neighboring CD molecules were mediated by water molecules.^[41] There is credible evidence that the hydrogen bonds between CDs play an important role in stabilizing the complexes.^[11]

Solid-state ¹³C CP/MAS (cross-polarization magic-angle spinning) NMR spectroscopy: High-resolution NMR spectroscopy is another technique used to analyze the structure and molecular dynamics of ICs either in aqueous solution or in the solid state. It is known that the formation of the ICs should change the conformation and the electromagnetic environment of both the host CD and the guest molecules, which should be reflected in the ¹³C CP/MAS NMR spectra of the host and the guest molecules in the ICs.^[11,17,20,21] Figure 4 shows the ¹³C CP/MAS NMR spectra of the un-

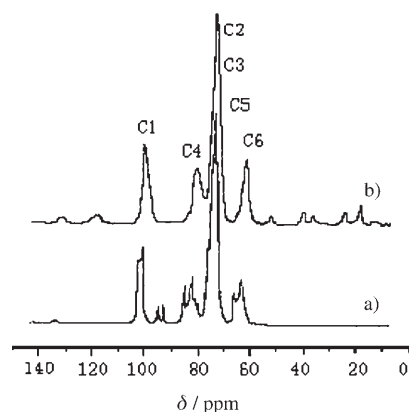


Figure 4. ¹³C CP/MAS NMR spectra of a) β-CD and b) **1**.

complexed β-CD and **1**. The β-CD molecules are known to have a less symmetrical conformation in the crystalline state.^[18,20,21] In this case, the spectrum of β-CD (Figure 4a) shows resolved carbon resonances from each of the glucose units, reflected by strong splitting for all C1–C6 resonances. However, the resolved resonances disappear for **1**, and the

^{13}C signals of **1** give sharp singlets (Figure 4b). The results show that the β -CD molecules in **1** adopt a more symmetrical conformation. That is, each glucose units of β -CD is in a similar environment.^[9,15,20] Small resonance peaks in the solid-state ^{13}C NMR spectrum of **1** at about 20, 40, 120, and 130 ppm are presumably due to the bmimPF₆ guest, which indicates its presence in the channel structure of crystalline **1**. Therefore, the formation of channel structures of ICs in the present study is further supported by these ^{13}C CP/MAS NMR measurements.

^1H NMR spectra: The solution structure of the inclusion complexes of β -CD and bmimPF₆ was further investigated by using ^1H NMR at room temperature. It is well known that β -CD molecules adopt the conformation of a torus in which the H-3 and H-5 protons are located inside the cavity, whereas H-2 and H-4 are outside the torus. The H-6 protons of the primary alcohol group are on the narrow side and H-1 is in the glycosidic bond plane of β -CD. Figure 5a shows

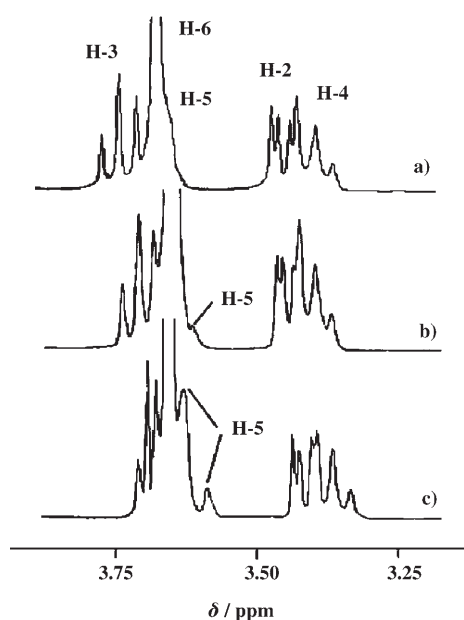


Figure 5. ^1H NMR spectra of β -CD in D_2O in the presence of bmimPF₆ at various molar ratios (bmimPF₆/ β -CD): a) 0:1; b) 0.5:1; c) 1:1.

the ^1H NMR spectrum of a solution of β -CD in D_2O ($12.0 \times 10^{-3}\text{M}$). At this stage the expected H-5 signal cannot be clearly observed, due to the overlap with the H-6 signal and the resonances appearing as a strong and unresolved broad peak.^[43] However, with the addition of bmimPF₆ the upfield shift of H-5 is quite prominent and becomes clearer as the amount of bmimPF₆ is increased, as is illustrated in Figure 5b and c. The similar phenomenon was observed for sodium diclofenac (DCF), (+)-catechin (CA), and (-)-epicatechin (EC) complexes with β -CD.^[43,44] Besides the upfield shift of H-5, we can observe that the H-6 protons, which lie on the inner surface of the primary hydroxyl group side, also shift upfield. Although H-3 lies on the inner surface of

the cavity, the upfield shift is not as obvious as that of the H-5 proton of β -CD. The main reason for this is that H-3 is located on the surface of a secondary hydroxyl group side and is a long way from the symmetrical axis of β -CD, thus no obvious interaction occurs with the included IL. Another reason is based on the assumption that the imidazolium ring entered the cavity of β -CD from the wide secondary hydroxyl group side with close contact with the atoms on the inner surface of the primary hydroxyl group side, and the butyl tail positioned near the center of the cavity along the molecular axis of β -CD did not make close contact with the H-3 protons. Moreover, H-4 and H-5 of an imidazolium ring are in similar environments and their peaks are very close together in free ILs ($\delta = 7.31$ and 7.26 ppm). However, two peaks change into one peak at $\delta = 7.32$ ppm after inclusion occurs. This indicates that H-4 and H-5 of the imidazolium ring have close contact with β -CD molecules and the interaction leads to an equivalent environment for H-4 and H-5. The upfield shifts of the H-2 and H-4 protons of β -CD are not observed due to their location outside of the torus. Upfield shift of the protons lying on the inner surface of β -CD perhaps result from shielding effects,^[44] suggesting that the IL is included into the cavity of β -CD. On the other hand, the proton signals of bmimPF₆ did not broaden clearly, indicating that bmimPF₆ fits loosely with β -CD.^[44]

Through combination of the solubility, conductivity, XRD, and NMR studies, we speculate a possible inclusion structure, illustrated in Figure 6. The PF₆⁻ ion perhaps dissociates near the β -CD molecules (not shown here).

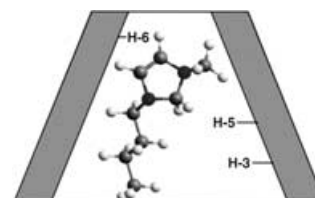


Figure 6. Plausible structure of inclusion complex **1** in aqueous solution. Molecule key: black = nitrogen, dark gray = carbon, light gray = hydrogen.

Thermogravimetric analysis (TGA): The thermal stability of **1** was evaluated by using TGA analysis, and the results were compared with pure β -CD and bmimPF₆. Figure 7 shows the weight-loss curves for **1** and its precursors. It is quite interesting that **1** has a lower initial decomposition temperature than both pure bmimPF₆ and β -CD. Normally, the initial decomposition temperatures of ICs are higher than those of CD, and the inclusion complexation is believed to contribute to the better stability of CDs.^[14,21] Thus, the present TGA results are somewhat unusual. This phenomenon results from the unique molecular structure and properties of bmimPF₆ compared with organic compounds and polymers. The steric congestion^[18] and the geometry distortion of the components may make **1** unstable. Moreover, when the

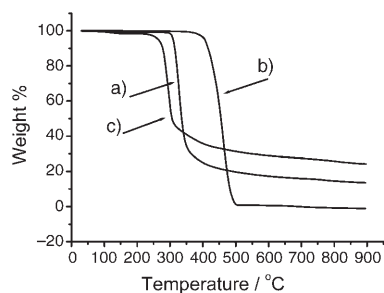


Figure 7. TGA curves obtained at a heating rate of $10^{\circ}\text{Cmin}^{-1}$ under a nitrogen atmosphere for a) β -CD, b) bmimPF_6 , and c) **1**.

cation bmim^+ is included into the cavity of β -CD, the distance between bmim^+ and PF_6^- may be longer than that in the ion pair bmimPF_6 . The quantum chemical calculation results show that the total energies of bmim^+ and PF_6^- are higher than those of the ion pair bmimPF_6 ,^[45] which may lead to lower decomposition temperature of the ICs.

The driving forces for the inclusion: We believe that the driving forces for the formation of **1** are similar to those of other β -CD-based ICs, which are related to van der Waals interactions, release of cyclodextrin strain energy upon complexation, hydrogen bonding between either the primary or secondary hydroxyl groups of the cyclodextrin and the guest, and hydrophobic interactions.^[46] Moreover, the geometric compatibility or fit is thought to be a significant factor.^[22] Recently, the theoretical calculations of ICs have revealed that van der Waals interactions are the main driving force in complexation.^[47]

Conclusion

The inclusion behavior of β -CD and bmimPF_6 in aqueous solution has been studied by solubility, conductivity, and ^1H NMR spectroscopy experiments. The results indicate that β -CD and bmimPF_6 can form ICs with a 1:1 stoichiometry. The β -CD and the IL can promote the solubility of each other due to the soluble nature of the ICs formed. XRD, ^{13}C CP/MAS NMR, and TGA studies illustrated that the ICs are isomorphous, with a channel-type structure, with the β -CD molecules adopting a symmetrical conformation, and with each glucose unit of β -CD being in a similar environment. The thermal stability of the ICs is lower than the two precursors. The possible reason for this is that the steric congestion and the geometry distortion of β -CD in **1** reduces the thermal stability of β -CD. When the cation bmim^+ is included into the cavity of β -CD, the distance between bmim^+ and PF_6^- may be longer than that in the ion pair bmimPF_6 , which may reduce the decomposition temperature of the IL.

Experimental Section

Materials: β -CD was obtained from the Chemical Factory of Nankai University and used after drying at 80°C under vacuum for at least 24 h. The bmimPF_6 ionic liquid was prepared and characterized following the procedures of other authors.^[48] All liquid reagents used to prepare the IL were AR grade. The water used was doubly distilled and deionized.

Apparatus and procedures: A low-frequency conductivity meter (Model DDS-307, Shanghai Cany Precision Instrument Co., Ltd.) with a precision of $\pm 1\%$ was used to measure solution conductivity at 25.0°C . Powder X-ray diffraction patterns were taken by using $\text{CuK}\alpha$ irradiation with a Rigaku RAD-ROC X-ray diffractometer (voltage, 40 kV; current, 100 mA; scanning speed, 3°min^{-1}). ^{13}C CP/MAS NMR spectra were acquired on a Bruker DRX-400NMR spectrometer with a sample spinning rate of 8.0 kHz at room temperature. ^1H NMR studies were carried out with a Varian ARX 400 NMR spectrometer at room temperature (ca. 25°C). The instrument was operated at a frequency of 400.13 MHz. Calibration of the proton chemical shift was achieved by using tetramethylsilane as an internal reference standard. Samples were dissolved in D_2O (99.8 atom% D, Beijing Chemical Co., Inc.). TGA curves were obtained by using a NETZSCH STA 409 PC/PG thermogravimetric analyzer. Samples were heated at $10^{\circ}\text{Cmin}^{-1}$ from room temperature to 900°C in a dynamic nitrogen atmosphere.

To prepare the powder of the inclusion compound, bmimPF_6 (1.50 g, 5.3×10^{-3} mol) and β -CD (5.99 g, 5.3×10^{-3} mol) were added to water (150 mL). The mixture was agitated for about 15 min and the solution became clear gradually. The water was removed at 65°C by using a rotary evaporator. The inclusion compounds were continuously dehydrated at 120°C until the weight was constant.

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