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Supramolecular Structures in the Presence of Ionic Liquids

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1. Introduction

Supramolecular chemistry is defined as “chemistry beyond the molecule”, bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces (Lehn, 1988, 1995). Supramolecular chemistry may be divided into two broad and partially overlapping areas concerning: (1) *supermolecules*, well-defined and discrete oligomolecular species that result from the intermolecular association of a few components (a receptor and its substrate(s)) following a built-in scheme based on the principles of molecular recognition; (2) *supramolecular assemblies*, polymolecular entities that result from the spontaneous association of a large undefined number of components into a specific phase having more or less well-defined microscopic organization and macroscopic characteristics depending on its nature (such as micelles, microemulsions, vesicles, films, layers, membranes, mesomorphic phase and so on) (Lehn, 1995). Investigation on supramolecular systems is receiving more and more attention (Beletskaya et al., 2009; Constable, 2008; Descalzo et al., 2006; He et al., 2008b; Metrangolo et al., 2008; Oshovsky et al., 2007).

Different from simple inorganic salts (such as NaCl) who often melt at very high temperature, ionic liquids (ILs) are a kind of organic salts that are liquid at or near room temperature, always taking 100 °C as an upper limit. Figure 1 shows the structures of some typical cations and anions of ILs. The imidazolium, especially 1-alkyl-3-methylimidazolium ($C_n\text{mim}^+$), is one of the most popular cations. So far, ILs have attracted much attention and been widely used as an attractive class of green solvents in the fields of chemical reactions, organic and material syntheses, solvent extraction, and electrochemistry because of their negligible vapor pressure, nonflammability, high thermal and chemical stability, high polarity, wide electrochemical window and tunable physicochemical properties (Chiappe & Pieraccini, 2005; Dupont, 2004; Leclercq & Schmitzer, 2009a; Weingartner, 2008; Welton, 1999; Zhao et al., 2002).

In the field of supramolecular chemistry, ILs could either participate directly in the assembly of supramolecular organizations, or influence the assembly of various supramolecular structures in a certain way, leading to the appearance of many novel and interesting phenomena. In addition, there exist three-dimensional supramolecular networks with polar and non-polar regions in imidazolium ILs, which can be used as powerful supramolecular receptors (Dupont, 2004; Leclercq & Schmitzer, 2009a). Therefore, this review will summarize the work in the literature, concerning the above novel and

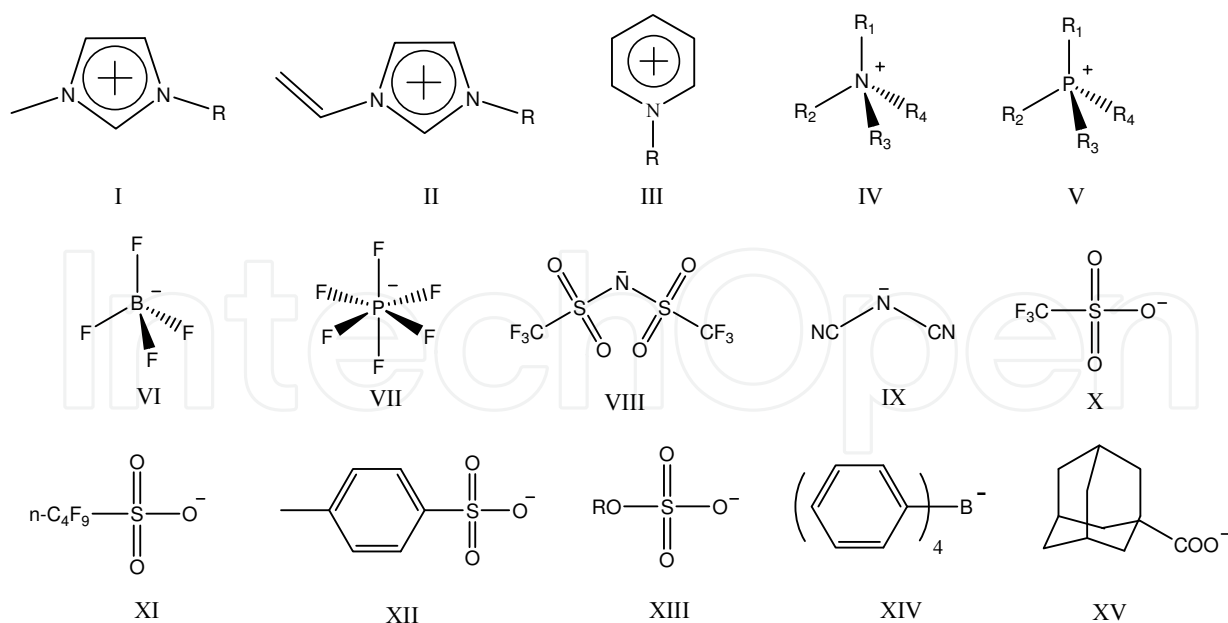


Fig. 1. Structures of some typical cations and anions of ionic liquids: I: 1-alkyl-3-methylimidazolium ($C_n\text{mim}^+$); II: 1-alkyl-3-vinylimidazolium ($C_n\text{vim}^+$); III: 1-alkylpyridinium ($C_n\text{Py}^+$); IV: tetraalkylammonium; V: tetraalkylphosphonium; VI: tetrafluoroborate (BF_4^-); VII: hexafluorophosphate (PF_6^-); VIII: bis(trifluoromethylsulfonyl)imide (Tf_2N^-); IX: dicyanimide ($(\text{CN})_2\text{N}^-$); X: trifluoromethanesulfonate (TfO^-); XI: nonafluorobutanesulfonate (NfO^-); XII: tosylate (OTos^-); XIII: alkylsulfate ($C_n\text{OSO}_3^-$); XIV: tetraphenylborate (TPhB^-); XV: adamantylcarboxylate (AdCO_2^-).

interesting phenomena. The IL-relevant supramolecular systems include not only inclusion complexes with cyclodextrins (CDs), cucurbit[n]urils, calixarenes as host molecules, but also micelles, microemulsions, liquid crystals (LCs), gels. Supramolecular structures based on the host network of ILs themselves will also be presented. Furthermore, the effects of ILs on the assembly of supramolecular systems (such as rotaxanes and polyrotaxanes, etc.) will be discussed.

2. Supramolecules systems formed by ionic liquids with different host molecules

2.1 Ionic liquids as guests for native and modified cyclodextrins

2.1.1 New structures and properties

Supramolecular systems formed by ILs with CDs demonstrate new structures and properties. ILs can affect the lower critical solution temperature (LCST) of polymers consisted of CDs (Amajjahe et al., 2008; Amajjahe & Ritter, 2008a). Amajjahe et al. (Amajjahe et al., 2008) investigated the influence of three different 1-butyl-3-vinylimidazolium ILs [$C_4\text{vim}$][Tf_2N], [$C_4\text{vim}$][NfO] and [$C_4\text{vim}$][AdCO_2] as guests on the LCST values of poly(NIPAAM-co- β -CD Methacrylate) (PNCM). The copolymer PNCM can form supramolecular polyelectrolyte-type structures, so-called pseudopolyanions through host-guest interactions with suitable ionic guests. This increased hydrophilicity of pseudopolyanions results from the free carboxylate (AdCO_2^-) and sulfonate (NfO^-) groups, which are preferentially located in the aqueous phase and therefore responsible for the

increased LCST values. However, the complexation of Tf_2N^- leads to a decreased LCST value because the hydrophobic Tf_2N^- is preferentially located in the centre of the CD-cavity. With the increasing hydrophobicity of ILs, the cloud point of PNCM is reduced. Besides, the shrinkage and expansion behavior of pseudopolyanions could be controlled by supramolecular interaction of the CD components with three different ILs.

ILs can influence the properties of CDs and vice versa. The poly($[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$) showed a pseudo-LCST effect in the presence of CD (Amajjahe & Ritter, 2008a). It was found that the CD ring complexes only the polymer anion and slips off at higher temperature when the poly(IL) becomes insoluble in water. The polymerization of ILs can be controlled by CDs (Amajjahe & Ritter, 2008b). The monomer $[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$ cannot polymerize in water in the presence of β -CD by radical mechanism, which is the result of the complex formation and the spatial ion pair separation leading to quasi “naked vinylimidazolium cations” (Figure 2). This effect should be compensated with the addition of a foreign salt because of cation-cation repulsion and then polymerization occurs. As a result, the controllable polymerization is realized.

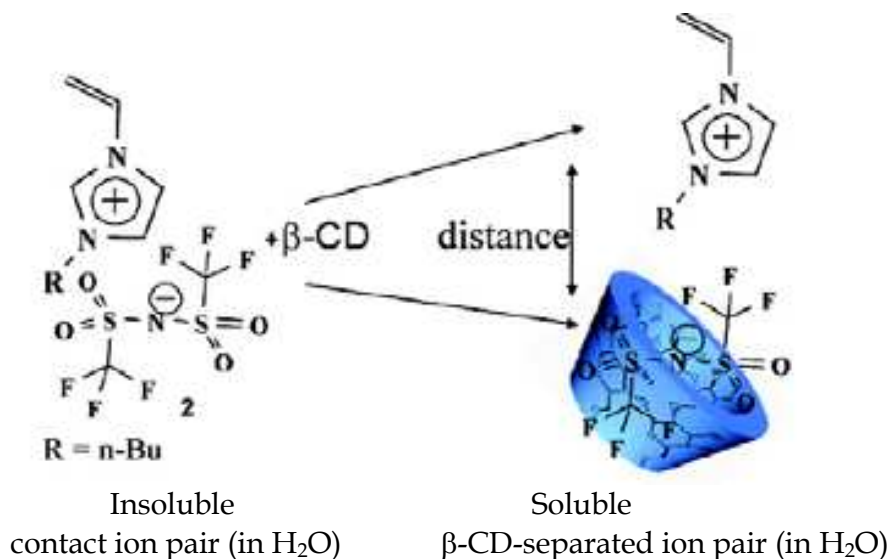


Fig. 2. Host-guest complex formation of $[\text{C}_4\text{vim}][\text{Tf}_2\text{N}]$ with β -CD at 298K in water. Reprinted from Amajjahe & Ritter (2008b).

Besides, imidazolium salts can also be employed as carbene precursor for organometallic catalysis, where hydrogen/deuterium exchange reaction of the C(2)-proton occurs. Formation of the inclusion complexes (ICs) of imidazolium salts with the native β -CD and the heptakis-(2,6-di-O-methyl)- β -CD (DM- β -CD) is a simple and efficient method to modify the acidity of the imidazolium H(2) and its environment (Leclercq & Schmitzer, 2009b). Encapsulation of 1, 3-disubstituted imidazolium chloride by β -CDs results in the inhibition of the H(2)/D exchange in the complex.

Recently, Leclercq et al. (Leclercq et al., 2009a) discovered that the imidazolium surfactants $[\text{C}_{12}\text{mim}]$ and $[\text{C}_{16}\text{mim}]$ can be used as “micellar promoters” in catalyzing hydroformylation reactions. Because of the inclusion of surfactants in the CDs, the addition of α -CD can modulate the aggregation properties of the surfactants. At high temperature, the supramolecular interactions of the imidazolium surfactants favor the micellization process. And by decreasing the temperature, CDs complex the surfactant monomers and destabilize the micelles.

2.1.2 Interaction between ionic liquids and cyclodextrins

The new properties of ILs on the addition of CDs originate from the interaction between ILs and CDs, mostly the inclusion complexation between them. Thus, the study on this topic is important. Various methods have been applied to investigate the interaction between ILs and CDs, such as the solubility (Gao et al., 2005a), infrared spectroscopy (Li et al., 2007c), ultra-violet spectroscopy, XRD (Gao et al., 2006c; Gao et al., 2005a; Li et al., 2007c), conductivity (Amajjahe & Ritter, 2008b; He et al., 2009), TGA (Gao et al., 2006c; Gao et al., 2005a; Li et al., 2007c), affinity CE (ACE) (Francois et al., 2007), NMR (Amajjahe & Ritter, 2008b; Gao et al., 2006c; He et al., 2009; Li et al., 2007c), fluorescence competition (He & Shen, 2008; He et al., 2009), microcalorimetry (Amajjahe et al., 2008; Amajjahe & Ritter, 2008b; Li et al.), surface tension measurements (Gao et al., 2006c) and so on. By these methods, the formation constants of ICs, the stoichiometry for ILs and CDs can be obtained.

Gao et al. (Gao et al., 2005a) investigated the system of $[C_4mim][PF_6]$ and β -CD using NMR and suggested that the whole imidazolium cation (C_4mim^+) was probably included into the cavity of β -CD, while the PF_6^- ion dissociated near the β -CD. They also studied ICs formation of β -CD with three kinds of IL surfactants, $[C_{12}mim][PF_6]$, $[C_{14}mim][PF_6]$, and $[C_{16}mim][PF_6]$ (Gao et al., 2006c). There were two kinds of inclusion complexations, *i.e.*, 1:1 and 1:2 (β -CD/IL) stoichiometries for β -CD- $[C_{12}mim][PF_6]$ and β -CD- $[C_{14}mim][PF_6]$ ICs, and only 1:1 stoichiometry for β -CD- $[C_{16}mim][PF_6]$ ICs due to the strong steric inhibition of $[C_{16}mim][PF_6]$. Unlike the possible structure suggested for the $[C_4mim][PF_6]/\beta$ -CD inclusion complex, only the alkyl side chain on the imidazolium ring of these three ILs entered into the cavity of β -CD. The similar result was obtained by Li et al. (Li et al., 2007c), which indicated that only the alkyl side chain of the $[C_{12}mim][PF_6]$ was included into the cavity of β -CD. Francois et al. (Francois et al., 2007) developed ACE method to characterize the complex formation between seven cations of various imidazolium-based ILs ($[C_2mim][Tf_2N]$, $[C_4mim][Tf_2N]$, $[C_4mim][BF_4]$, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ($[C_4dmim][BF_4]$), $[C_8mim]Br$, $[C_{10}mim][BF_4]$ and $[C_{12}mim][BF_4]$) and eight neutral CDs (α -CD, β -CD, γ -CD, hydroxypropyl- α -CD (HP- α -CD), hydroxypropyl- β -CD (HP- β -CD), hydroxypropyl- γ -CD (HP- γ -CD), heptakis-(2,6-di-O-methyl)- β -CD (DM- β -CD) and heptakis-(2,3,6-tri-O-methyl)- β -CD (TM- β -CD)). According to classical nonlinear and linear treatments, they obtained the complex stoichiometry and formation constant K . The majority of systems followed a 1:1 complexation stoichiometry model but in four cases ($[C_{10}mim][BF_4]$, $[C_{12}mim][BF_4]$ and α -CD, DM- β -CD) a 1:2 stoichiometry was better satisfied. It was established that the main factor influencing the strength of the inclusion complexation was the length of alkyl side chain on the imidazolium ring. The presence of a methyl group at the C(2) position and the nature of anion associated to the imidazolium cation in the IL did not show significant influence on the complexation constant obtained. Also, the size of the CD cavity noticeably impacts the stability of the 1:1 complexes, with stronger complexes being given by β -CD. Furthermore, it was shown that two CD molecules can likely be threaded along C_{10} and C_{12} alkyl side chains and there was no inclusion of the imidazolium ring into the cavity of β -CD. Mostly, the interaction of CDs and ILs are studied in aqueous solution. Recently, it was investigated that the dissolution of β -CD could be enhanced in some hydrophilic ILs and 1:1 inclusion complexes were formed between β -CD and imidazolium cations of the ILs (Zheng et al.).

Differently, several inclusion complexes of β -CD with anion of ILs were also reported. As mentioned in Section 2.1.1, the anion Tf_2N^- of $[C_4vim][Tf_2N]$ formed exclusively host-guest

complex with β -CD (Amajjahe et al., 2008; Amajjahe & Ritter, 2008b). Similarly, the anion PF_6^- but not the cation C_4vim^+ was found to be accommodated by β -CD. We reported that $[\text{C}_4\text{mim}][\text{PF}_6]$, $[\text{C}_4\text{mim}][\text{BF}_4]$, and $[\text{C}_4\text{mim}]\text{Cl}$ formed 1:1 inclusion complexes with β -CD, respectively (He & Shen, 2008). Through ^{19}F NMR, we also found that PF_6^- and BF_4^- could interact with β -CD but the latter interaction was relatively weak.

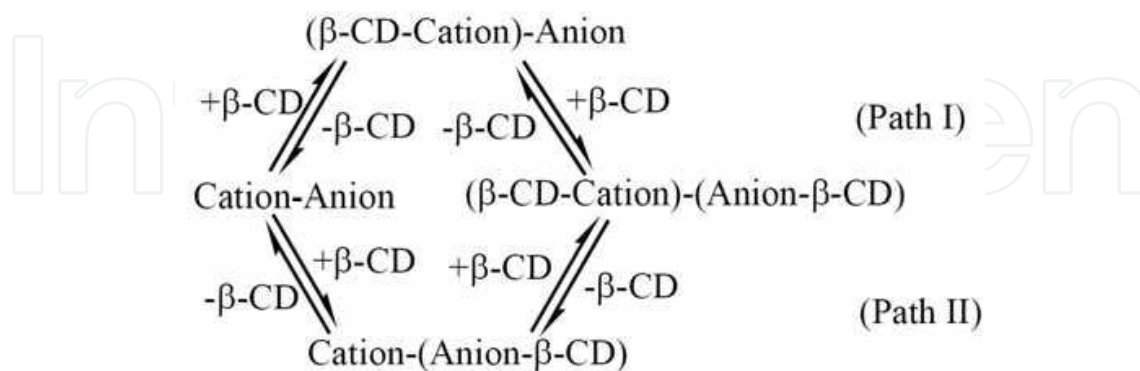


Fig. 3. Two-Step Equilibrium in an IL/ β -CD System (Path I: the cation interacts with β -CD more strongly than the anion does, Path II: the anion interacts with β -CD more strongly than the cation does). Reprinted from He et al. (2009).

Considering the above studies, a general pattern in the IL/ β -CD system and a two-step equilibrium was brought forward as shown in Figure 3. It was confirmed that the alkyl side chain on the imidazolium ring but not the imidazolium ring itself entered into the cavity of β -CD. As for the IL $[\text{C}_{12}\text{mim}][\text{Tf}_2\text{N}]$, the cation and the anion both exhibited strong interactions with β -CD simultaneously (He et al., 2009). It was suggested that the strength of the interaction of various cations and anions in ILs with β -CD follows the following order: $\text{NfO}^- > \text{C}_{12}\text{mim}^+ > \text{Tf}_2\text{N}^- \sim \text{AdCO}_2^- \sim \text{C}_{10}\text{mim}^+ > \text{C}_8\text{mim}^+ > 1\text{-hexyl-2,3-dimethylimidazolium cation (C}_6\text{dmim}^+) \sim \text{PF}_6^- > \text{BF}_4^- > 1\text{-butyl-2,3-dimethylimidazolium cation (C}_4\text{dmim}^+) \sim \text{C}_4\text{vim}^+ \sim \text{C}_4\text{mim}^+ > \text{Cl}^-$.

Leclercq et al. (Leclercq & Schmitzer, 2008) discovered multiple equilibria in the complexation of dibenzylimidazolium bromide by CDs. In aqueous solution, dibenzylimidazolium bromide forms dimeric assemblies by T-stacking between an acidic proton of the imidazolium and the benzyl aromatic ring of another cation (Figure 4). This dimeric association can be disturbed by the addition of native CDs. The control of the majority species in solution can be made by the judicious choice of CD concentration and its

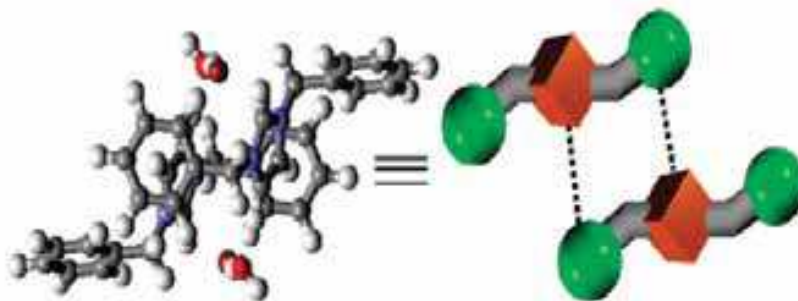


Fig. 4. Structure of the dibenzylimidazolium bromide water dimer obtained by PM3 in accordance with the crystalline structure and the conventional representation adopted in this study. Reprinted from Leclercq & Schmitzer (2008).

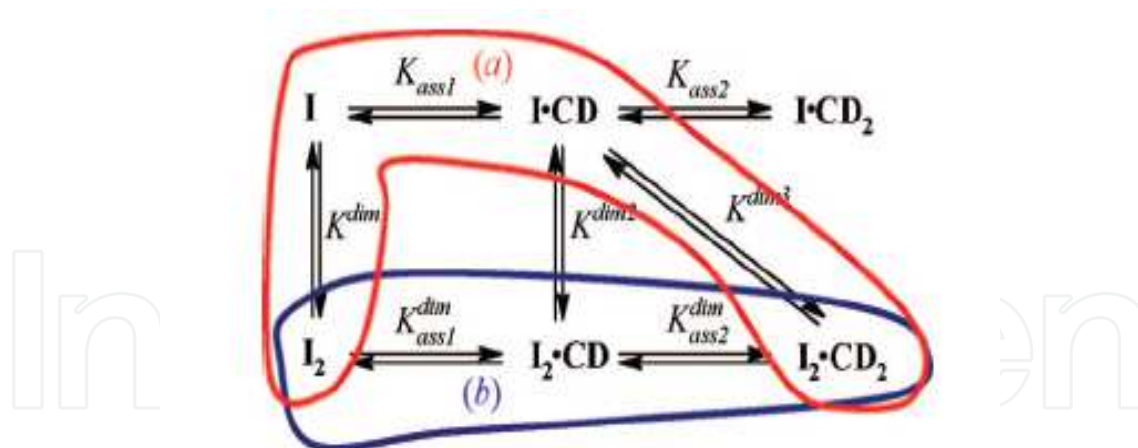


Fig. 5. Equilibrium distributions for the formation of $I_2 \cdot CD_2$ from I_2 in the presence of (a) α -CD and (b) β -CD. I and I_2 represent the dibenzylimidazolium bromide salt and the dimer, respectively. Reprinted from Leclercq & Schmitzer (2008).

macrocycle size. The dimer is complexed directly by β -CD, whereas in the presence of α -CD, the dimer is dissociated to form a 1:1 IC; at higher concentration, this 1:1 complex can dimerize (Figure 5).

2.2 Ionic liquids as guests for Cucurbit[n]uril system

Cucurbit[n]uril (CBn) is another important host molecule in supramolecular chemistry. The complex formation of ILs and CBns is not all the same with CDs because of the different structure between them (Montes-Navajas et al., 2008). C_1mim^+ forms a fairly stable complex with Cucurbit[7]uril (CB7), similarly, as the numbers of carbon atoms in the aliphatic chain grows, from C_1mim^+ to C_6mim^+ , the binding constant between ILs and CB7 increases (Miskolczy et al., 2009). However, further lengthening of the alkyl group destabilizes the complex, because a growing segment of the carbon chain cannot be confined in CB7. When inclusion complexes between 1,1'-dialky-3,3'-(1,4-phenylene)bisimidazolium dibromide salts and CB7 were studied, the stoichiometry of the complexes not only depends on the alkyl chains, but also lies on the relative concentration of the imidazolium salt and CB7 (Noujeim et al., 2009). Unlike β -CD, the fact that the anion barely influences the binding constant of IL-CB7 complexes is probably due to the significant negative charge density of the carbonyl-lined portals of CB7, which hinders the interaction with anions. Moreover, CB7 has a less polar cavity than β -CD, which disfavors the ion pairing. St-Jacques et al. (St-Jacques et al., 2008) studied the position of charge-diffuse peralkylated onium cations, NR_4^+ , PR_4^+ and SR_3^+ ($R=Me$, Et , nPr , nBu), which could be the cations of ILs, in the cavity of CB7. With cationic guests, the stability constants of the CB are larger than those of the corresponding CDs and can be several orders of magnitude larger when the guest is a dication. Different cations prefer to locate in different positions of CB. With simple hydrophilic cations, such as protons, alkali metal and alkali earth cations and transition metal ions, the preferred binding location(s) on CB are the carbonyl-lined portals, to take advantage of the ion-dipole interactions. With cationic organic or organometallic guests, very strong binding is achieved when the cationic portion(s) of the guest can be positioned near the portals. However, as these charge-diffuse peralkylated onium cations, when considering size selectivity, with the smaller guests inside its cavity, rather than at the carbonyl-lined portals by the study of NMR. At the same time, they discovered that the stability constants are dependent on the size and coordination number of the central atom and

the size and hydrophobicity of the alkyl group. The CB7 has a preference for Et over Me for NR_4^+ and SR_3^+ and the opposite for PR_4^+ , with trends of $\text{PMe}_4^+ > \text{NMe}_4^+ > \text{SMe}_3^+$ and $\text{SEt}_3^+ > \text{NEt}_4^+ > \text{PEt}_4^+$ in binding constants with CB7.

Cucurbit[6]uril (CB6) is poorly soluble in water and insoluble in organic solvents. The interaction of CB6 and $[\text{C}_n\text{mim}]\text{Br}$ was found to significantly increase the solubility of CB6 in neutral water (Zhao et al., 2010). CB6 was pulled into neutral water through encapsulation of an imidazolium-based IL (Liu et al., 2008). According to ^1H NMR titration experiments, C_2mim^+ and C_4mim^+ demonstrated different binding modes with CB6. The small changes in alkyl chain length can dramatically increase the solubility of CB6. Besides, 2:1 stoichiometry between C_2mim^+ and CB6 provides opportunities for a new type of self-assembly with CB6. However, the formation of 1:1 complex between C_2mim^+ and CB6 was found recently (Kolman et al., 2009). The supramolecular interaction between series of 1-alkyl-3-methylimidazolium guests with variable alkyl substituent lengths and CB6 in the solution and the solid state was studied. All imidazolium guests form 1:1 complexes with CB6. However, the mode of inclusion binding depends on the length of the alkyl substituent (Figure 6). The imidazolium aromatic ring is polarized upon complexation with CB6 and the electron density shifts from the nitrogen located in the proximity of the carbonyl portal of CB6 toward the opposite nitrogen atom.

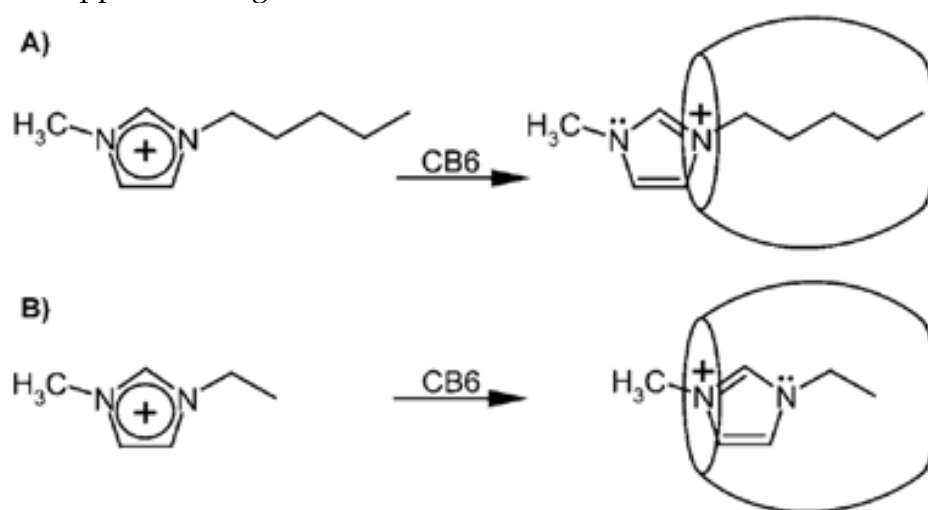


Fig. 6. Two different modes of inclusion binding between 1-alkyl-3-methylimidazolium guests and CB6. Reprinted from Kolman et al. (2009).

Commonly, inclusion complex formation with CB7 can be applied to enhance the fluorescence response of guest (Megyesi et al., 2008), for example berberine, a clinically important natural alkaloid. When using CB7 as macrocyclic host compound, a very stable 1:1 inclusion complex formed and led to about 500-fold fluorescence intensity enhancement, which can facilitate the detection of berberine even below nanomolar concentration. The change of association constant and the fluorescence quantum yield of the complex can be accomplished by the addition of NaCl. Interestingly, 1-alkyl-3-methylimidazolium type ILs can modify the fluorescent properties of the complex much more efficiently than NaCl. It is the result that the formation of ternary complex by time-resolved fluorescence studies. The results can be applied in enzyme assays, because berberine fluorescence is insensitive to the environment, such as pH and the other compounds. On the other hand, inclusion complex formation can be used to separation processes. Because $[\text{C}_n\text{mim}]\text{Br}$ is only capable of

binding with CB7 in a CB5/CB7 mixture, CB7- $[C_n\text{mim}][\text{Br}]$ can be removed from the mixture and realize the isolation of CB7 (Jiao et al., 2010). Besides, it is also a green process since imidazolium ILs can be reused.

2.3 Ionic liquids as guests for Calixarene system

Inazumi et al. (Inazumi et al., 2007) studied the inclusion complexation of *p*-sulfonatocalix[6]arene (Calix-S6) with three kinds of phenothiazine dyes in a mixture of $[C_4\text{mim}][\text{BF}_4]$ and ethanol. It was found that a competing complexation happened between the included dye and the IL molecules and that the 1:1 inclusion complex was formed by $C_4\text{mim}^+$ and Calix-S6. Very recently, the inclusion complex formation of $C_n\text{mim}^+$ type ILs with Calix-S6 and *p*-sulfonatocalix[4]arene (Calix-S4) was verified by the fluorescence competition method with berberine alkaloid as fluorescent probe (Miskolczy & Biczok, 2009). The stability of $C_n\text{mim}^+$ -Calix-S4 complex was significantly larger than that of $C_n\text{mim}^+$ -Calix-S6 supramolecules due to better size match in the former case. The influence of the length of the aliphatic side chain was opposite for Calix-S4 and Calix-S6. The lengthening of the aliphatic side chain of the imidazolium moiety diminished the equilibrium constant of the complexation with Calix-S4, but enhanced the stability of Calix-S6 complexes. The larger conformational mobility of Calix-S6 compared to that of Calix-S4 rendered the larger macrocycle more adaptable to the geometrical features of $C_n\text{mim}^+$ permitting stronger host-guest interaction when the aliphatic chain of $C_n\text{mim}^+$ is longer. They demonstrated that the electrostatic attraction between $C_n\text{mim}^+$ ion and the sulfonato groups at the upper rim of calixarene macrocycle was not the dominant driving force of complexation. As for the anions, the strength of $C_n\text{mim}^+$ inclusion in Calix-S6 was anion independent. It was different from the characteristics of ILs in β -CD because of ion pair formation within the β -CD cavity. In the case of $C_n\text{mim}^+$ -Calix-S6 complex, such an interaction is not feasible because the negative charge of the macrocycle prevents anion ingress into the cavity of the host. Ling et al. reported the multicomponent materials containing Calix-S4, imidazolium or bis-imidazolium cations, phosphonium cations and different lanthanide ions (Ling et al., 2009, 2010a, b). It was investigated that the imidazolium head group resided in the calixarene cavity and the terminus of alkyl chain penetrated the adjacent hydrophobic bi-layer, comprising of the calixarenes and phosphonium ions.

3. Supramolecular assemblies based on ionic liquids

Generally, amphiphilic molecules self-assemble to form micelle, microemulsion, lyotropic liquid crystal and vesicle. Moreover, long-chain ILs can act as ionic surfactants and form similar self-assembly in water or oil. Qiu et al. summarized the studies of IL based microemulsions from the perspective of the role of ILs (Qiu & Texter, 2008). ILs participated in the formation of the microemulsions, in which ILs replaced oil, water or surfactants. Hao et al. reviewed the self-assembled structures (such as micelles, microemulsions, liquid crystals and vesicle) in ILs, which acted as the solvent (Hao & Zemb, 2007). In this part, we summarized the IL based organized assemblies, in which IL participated in the formation of micelles, microemulsions, vesicles and liquid crystals rather than acted as solvents.

3.1 IL based micelles (ionic liquid as surfactant)

Micelles generally form in water and the hydrophobic effect is the main driving force. Recently, micelles formed in nonaqueous polar solvents (including ILs) have been reported.

Because of the existence of electrostatic repulsion among the hydrophilic groups, surfactant molecules are kept apart and loosely arranged, which may result in the larger size of the aggregates in ILs than that in aqueous systems (Figure 7) (Li et al., 2008a). In addition, the aggregation of amphiphilic copolymers and surfactant-like ILs in ILs was reported.

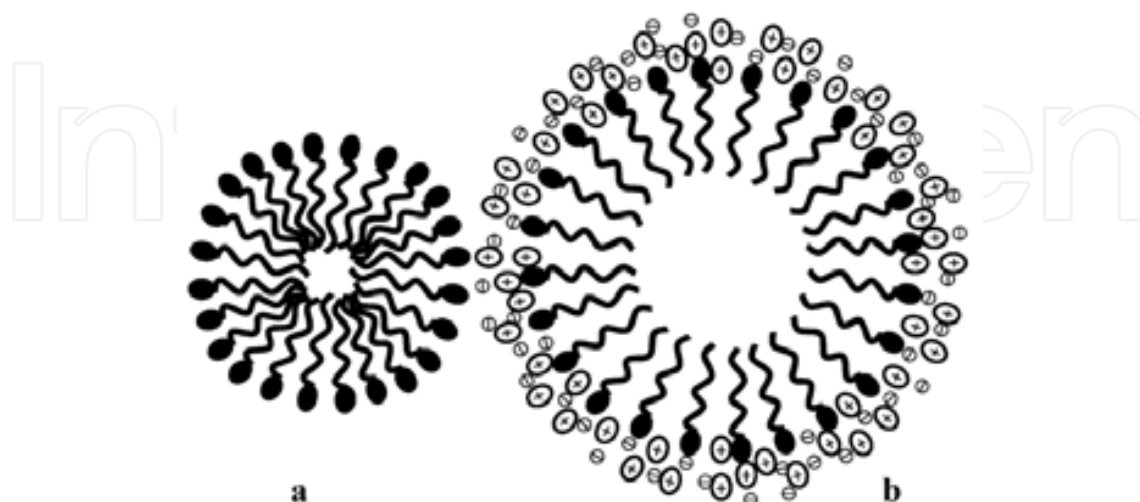


Fig. 7. Schematic representation of long-chain IL aggregates in water (a) and in $[C_4mim][BF_4]$ (b). Hollow ellipses and hollow circles represent the cations and anions in ILs, respectively. Reprinted from Li et al. (2008a).

ILs based on the 1-alkyl-3-methylimidazolium cation (C_nmim^+) possess an inherent amphiphilicity. In recent years, surfactant behaviors of such ILs received much attention. Miskolczy and his coworkers (Miskolczy et al., 2004) investigated the association of ILs possessing n-octyl moiety either in the cation or in the anion in aqueous solution. It was found that 1-butyl-3-methylimidazolium octyl sulfate acted as a surfactant above cmc (0.031 M). Whereas, 1-methyl-3-octylimidazolium chloride produced inhomogeneous solution of larger aggregates, which were dissolved on the addition of more than 2:1 molar excess of sodium dodecylsulfate (SDS) due to the formation of mixed micelle. The aggregation behavior of 1-alkyl-3-methylimidazolium ILs in aqueous solutions has been investigated (Bowers et al., 2004). It was proposed that the short-chain $[C_4mim][BF_4]$ formed polydisperse spherical aggregates, whereas the $[C_8mim]I$ formed regularly sized micelles above the cmc. The micelle formation of surface active $[C_{2n}mim]^+$ ($n = 4\sim 8$) in aqueous solution was investigated by several methods, such as surface tension, electrical conductivity measurements and fluorescence techniques et al. (Blesic et al., 2007; Blesic et al., 2008; Dong et al., 2007; Dong et al., 2008a; Dong et al., 2008b; El Seoud et al., 2007; Inoue et al., 2007; Jungnickel et al., 2008; Luczak et al., 2008; Luczak et al., 2009; Modaressi et al., 2007b; Singh & Kumar, 2007, 2008; Vanyur et al., 2007; Wang et al., 2008; Wang et al., 2007; Zhang et al., 2008b; Zhao et al., 2008a). Results showed that the long chain imidazolium ILs acted as ionic surfactants and stronger aggregation tendency of the ILs might be attributed to characteristic nature of imidazolium head group such as potency of H-bond formation, which is lacking in common ionic surfactants. The aggregation number of the ILs was found to increase with the increasing length of the alkyl chain and a possible microscopic aggregation structure such as stairs has been proposed (Zhao et al., 2008a). Aggregation-induced conformational changes in different ILs were shown to depend on the aromatic ring, alkyl chain, counterions, and their interactions with water. Fluorescence quenching

method in which pyridinium ILs acted as quenchers was firstly used to detect the aggregation behavior of surfactant ILs (Blesic et al., 2008).

The influence of the anions on the aggregation of ILs was first reported by Wang et al., and explained by the hydrated radius or Gibbs energy of hydration of the anions (Wang et al., 2008). The ring type of the cations also had significant effect on the aggregation behavior of the ILs, which was controlled mainly by the balance among the factors of hydrophobicity of the cations, binding strength of the cations with a given anion, and the steric repulsion between the head groups of the cations. The former two factors promote but the latter factor weakens the aggregates formation. Zheng and his coworkers (Dong et al., 2008a) studied the aggregation of surface active $[C_{16}mim]Br$ and reported the formation of wormlike micelles in the presence of salts, similar to the situation of some traditional ionic surfactants in aqueous solution. Also, $[C_{16}mim]Br$ was used as a new cationic surfactant for separation of phenolic compounds by MEKC (Niu et al., 2009).

ILs based on imidazolium and ammonium salts with longer-substituent cations self-assemble on negatively charged polyimide substrates via electrostatic force. Whereas for shorter-substituent cations, no aggregates formed due to the less hydrophobic interaction than the electrostatic repulsive interaction between the cations and the counter anions (Zhao et al., 2008b). Dorbritz et al. (Dorbritz et al., 2005) found that the formation of aggregates of $[C_4mim][BF_4]$ and $[C_4mim][Tf_2N]$ in aqueous solution depended on the solvent, the IL concentration and the anion structure of the ILs. They also mentioned that ILs can be used to improve the solubility of hydrophobic compounds.

Anderson's group (Pino et al., 2009) studied the micellar properties of aqueous solutions of two ILs, 1-hexadecyl-3-butyylimidazolium bromide and 1,3-didodecylimidazolium bromide, in the presence of several organic solvents (methanol, 1-propanol, 1-butanol, 1-pentanol, and acetonitrile) by surface tensiometry. For both ILs, increases in the cmc values and minimum surface area per surfactant molecule, decreases in the maximum surface excess concentration, adsorption efficiency and effectiveness of surface tension reduction were obtained when increasing the organic solvent content.

The aggregation behavior and thermodynamic properties of micellization for the IL-type Gemini imidazolium surfactants with different spacer length ($[C_{12-s}-C_{12}im]Br_2$, $s = 2, 4, 6$) have been investigated. Results showed that the surface activity of $[C_{12-s}-C_{12}im]Br_2$ decreased with increasing spacer length, and the micellization was entropy-driven when $s=2$ and 4, whereas aggregation of $[C_{12-6}-C_{12}im]Br_2$ is enthalpy-driven at lower temperature but entropy-driven at higher temperature (Ao et al., 2009).

Compound	n	m	$n+m$
1	8	1	9
2	10	1	11
3	12	1	13
4	4	4	8
5	4	8	12
6	8	4	12
7	8	8	16

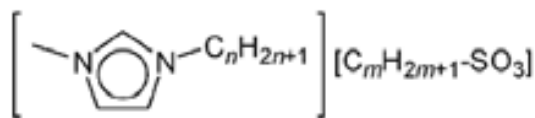


Fig. 8. General structure of 1-alkyl-3-methylimidazolium alkylsulfonate ILs ($[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$); $m+n$ is the sum of the number of carbon atoms in the two alkyl-substituents. Reprinted from Blesic et al. (2009b).

Anionic and cationic alkyl-chain effects on the self-aggregation of both neat and aqueous solutions of 1-alkyl-3-methylimidazolium alkylsulfonate salts, $[\text{C}_n\text{H}_{2n+1}\text{mim}][\text{C}_m\text{H}_{2m+1}\text{SO}_3]$ (Figure 8), have been investigated for the first time by Blesic et al. (Blesic et al., 2009b). They compared the effects of the alkyl-substitution patterns in both the cation and anion on the surfactant properties of these salts. It was found that the ILs with methylsulfonate anions ($n = 8, 10$, and 12) behaved as conventional cationic surfactants, showing a decrease of the cmc with the increase of the alkyl chain length in the cation. When the amphiphilic character is present in both the cation and anion ($n = 4$ and 8 , $m = 4$ and 8), a synergistic packing effect appears to lead to the formation of novel catanionic surfactants with both cmc values lower than anticipated, and enhanced surface activity. Bhargava and his coworkers (Bhargava & Klein, 2009) applied molecular dynamics (MD) to study the cation aggregation of $[\text{C}_{10}\text{mim}]\text{Br}$ in aqueous solution and found that the chains were buried inside the micelle to avoid unfavorable interactions with water, leaving the polar headgroups exposed to water. Recently, Kunz et al. (Thomaier & Kunz, 2007) have reported the aggregation behavior of surfactant-like ILs, $[\text{C}_{16}\text{mim}]\text{Cl}$ and $[\text{C}_{16}\text{mim}][\text{BF}_4]$, in another IL ethylammonium nitrate (EAN), where the structures due to electrostatic interactions can persist at such high temperatures. The aggregation behavior of a series of long-chain ILs, $[\text{C}_{2n}\text{mim}]\text{Br}$ ($n = 5\sim 8$), in $[\text{C}_4\text{mim}][\text{BF}_4]$ was studied by Li et al. (Li et al., 2008a) for the first time. The results indicated that the cmc for the long-chain ILs in $[\text{C}_4\text{mim}][\text{BF}_4]$ are much larger than that in water and diameters of the spherical aggregates obtained by freeze-fracturing electron microscopy (FFEM) and dynamic light scattering (DLS) measurements were $70\sim 100$ nm. Davis and his coworkers (Merrigan et al., 2000) synthesized four new surfactant fluorinated ILs (Figure 9) and reported the formation and stabilization of dispersions of perfluorocarbons in $[\text{C}_6\text{mim}][\text{PF}_6]$ for the first time.

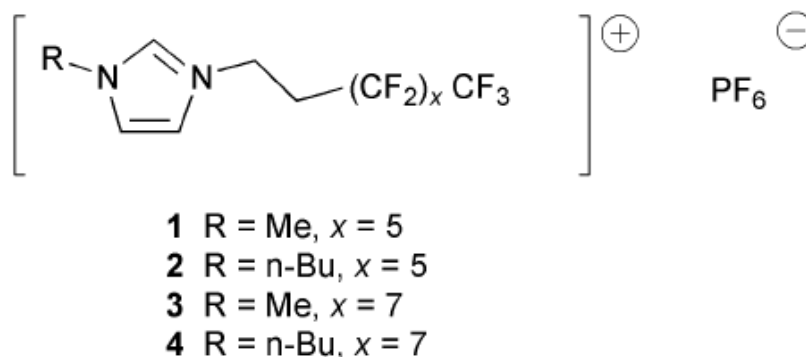


Fig. 9. General structures of the new fluorous ILs. Reprinted from Merrigan et al. (2000).

3.2 Ionic liquid based microemulsions

IL based microemulsions, which utilize ILs to replace one or more components of classical microemulsions, are so attractive that lots of papers have been published to characterize these kinds of IL based microemulsions.

First of all, IL based microemulsions, in which ILs replaced water of traditional microemulsions, have been extensively characterized by a number of techniques. Microregion of phase diagram of IL based microemulsions was detected by cyclic voltammetric technique (Gao et al., 2006a), electrical conductivity (Gao et al., 2004; Gao et al., 2006b; Gao et al., 2007b; Gao et al., 2006d; Li et al., 2007b), and direct observation, where the phase boundaries were determined by observing the transition from transparency to

turbidity (Cheng et al., 2007a; Cheng et al., 2007b; Cheng et al., 2008; Gao et al., 2005b; Li et al., 2005a). Based on the phase diagram, DLS (Cheng et al., 2007a; Gao et al., 2004; Gao et al., 2006b; Gao et al., 2008b; Gao et al., 2005b; Li et al., 2007b), FFEM (Cheng et al., 2007a; Gao et al., 2004; Gao et al., 2008b), small-angle X-ray scattering (SAXS) (Li et al., 2005a) and small-angle neutron scattering (SANS) (Eastoe et al., 2005) have been applied to characterize the microemulsions with polar IL cores. These techniques proved the swollen of reversed micelle with the addition of IL, which indicated the formation of reversed microemulsion. More detailed information was gained through FTIR (Gao et al., 2006b), ^1H NMR (Gao et al., 2006b; Gao et al., 2008b), UV-vis spectroscopy (Gao et al., 2006b; Gao et al., 2008b; Gao et al., 2005b; Li et al., 2007b) and conductivity measurements (Gao et al., 2006b; Gao et al., 2008b; Li et al., 2005a). Sarkar and his coworkers (Adhikari et al., 2007; Chakrabarty et al., 2005; Seth et al., 2006, 2007a; Seth et al., 2007b) initiated the work of applying steady-state and time-resolved fluorescence spectroscopy to investigate IL based microemulsions. Coumarin 151, 153 and 490 were adopted as the probes. The results showed the solvation time inside the polar cores of the microemulsions was retarded compared to that in neat IL because of restrictions in the ionic motions imposed by the microemulsions. Li et al. (Li et al., 2007b) studied the reversed microemulsion of TX-100 in toluene with $[\text{C}_4\text{mim}][\text{BF}_4]$ cores, using methyl orange and methylene blue as probes. With the addition of $[\text{C}_4\text{mim}][\text{BF}_4]$ into TX-100/toluene micelle, the polarity of the microemulsion increased firstly, and then became constant, indicating the formation of "IL pool". $[\text{C}_4\text{mim}][\text{BF}_4]/\text{TX-100}/p\text{-xylene}$ reversed microemulsion was investigated and a plausible structure with "IL pool" was presented (Gao et al., 2006b). It was proposed that the electropositive imidazolium ring of IL destroyed the hydrogen-bonding between TX-100 molecules. Successive addition of $[\text{C}_4\text{mim}][\text{BF}_4]$ led to the appearance of large-sized microemulsion droplet clusters (Gao et al., 2008b).

Additionally, ILs may also replace the other components of traditional microemulsions. In this field, Cheng et al. (Cheng et al., 2007b) reported the first microemulsion formed by two ILs, i.e., hydrophobic $[\text{C}_4\text{mim}][\text{PF}_6]$ and hydrophilic propylammonium formate (PAF). The formation of IL based microemulsion in supercritical carbon dioxide with N-ethyl perfluorooctylsulfonamide was reported (Liu et al., 2007). The first microemulsion comprising an IL ($[\text{C}_{16}\text{mim}]\text{Cl}$) as surfactant and another IL (EAN and $[\text{C}_4\text{mim}][\text{BF}_4]$, respectively) as polar pseudo-phase was presented (Zech et al., 2009). Zheng and his coworkers (Li et al., 2009c) reported the phase diagram of $p\text{-xylene}-[\text{C}_{14}\text{mim}]\text{Br}$ -water ternary system, where hexagonal, lamellar lyotropic liquid crystals or microemulsions formed depending on the composition. They confirmed the formation of oil-in-water (O/W) microemulsion through the linear increasing volume of the droplets with added $p\text{-xylene}$. Gao et al. (Gao et al., 2009a) considered the hydrophobic interaction between the added organic solvents and hydrophobic groups of surfactant molecules to be the driving force in the formation of oil-in-IL (O/IL) microemulsions (Figure 10). They observed a bicontinuous microstructure by FFEM for the first time with successive addition of organic solvents.

The effect of additional water on the microstructure and properties of IL based microemulsions has been studied. In the $[\text{C}_4\text{mim}][\text{BF}_4]/\text{TX-100}/\text{triethylamine}$ microemulsion, water located in the palisade layers and made a base environment which might be used to prepare metal hydroxides and metal oxides (Li et al., 2007a). For the $[\text{C}_4\text{mim}][\text{BF}_4]/\text{TX-100}/\text{benzene}$ microemulsion, water molecules interacted with oxyethylene (OE) units of TX-100 through hydrogen-bonding and attracted electropositive imidazolium ring of IL with electronegative oxygen (Gao et al., 2007a; Gao et al., 2007b). Hence, the amount of solubilized $[\text{C}_4\text{mim}][\text{BF}_4]$ enhanced with the increase of water content

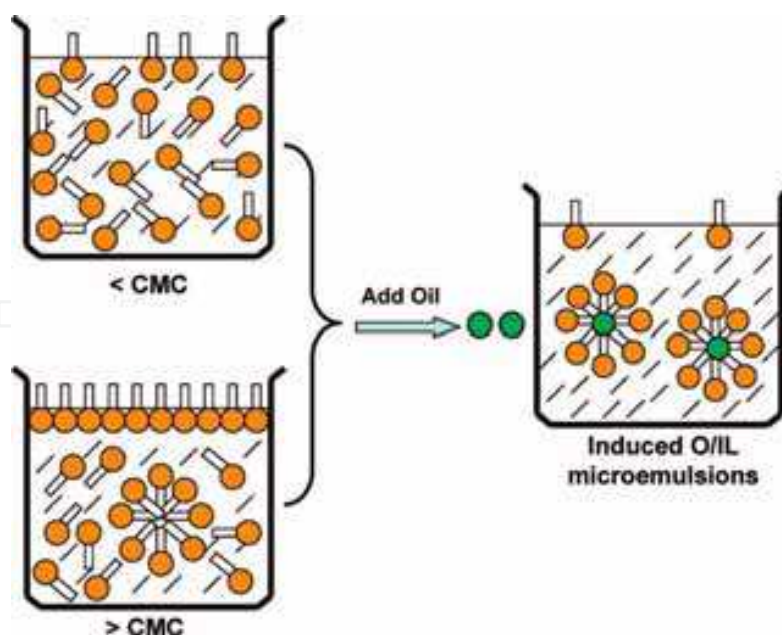


Fig. 10. Schematic diagrams of solution environments before (left) and after (right) adding organic solvents to the mixture of TX-100 and $[C_4mim][BF_4]$. Reprinted from Gao et al. (2009a).

because the water molecules were like “glue” that stuck the IL and OE units more tightly together. However, an increase in the amount of water in $[C_4mim][BF_4]$ /TX-100/cyclohexane microemulsions led to the phase separation and a remarkable decrease in the size of droplets (Gao et al., 2008a). Therefore, the number of droplets increased, which was further confirmed by conductivity measurements. The opposite effects caused by the water added on IL based microemulsions with same composition except continuous oil attracted us to study the role of the water.

3.3 Ionic liquid based lyotropic liquid crystal systems

Liquid crystals are liquid anisotropic compounds, whose properties are intermediate between that of the crystalline solid state and that of the liquid state. The refractive index, the electric permittivity, the magnetic susceptibility, and the mechanical properties of a liquid crystal depend on the direction in which these quantities are measured (Binnemans, 2005). The investigations of the lyotropic liquid crystalline phase formation containing ILs are also of great interest.

Davis and his coworkers (Davis et al., 1998) obtained a novel IL by anion metathesis with $NaPF_6$ after the imidazole-ring miconazole reacting with alkyl iodides to form imidazolium cations, which exhibited lyotropic liquid crystalline behavior while inducing the gelation of benzene. Firestone’s group reported that lyotropic liquid crystalline formed in $[C_{10}mim]Br$ -water (5-40% wt%) system (Firestone et al., 2002). They also obtained anisotropic gold nanoparticles with a variety of sizes and morphologies in the nanostructured $[C_{10}mim]Cl$ -water ionogel template by photochemical reduction of $HAuCl_4$ (Firestone et al., 2005).

Chen and his coworkers (Zhang et al., 2007) reported the formation of two lyotropic liquid crystals formed in a ternary system of $[C_{16}mim]Cl$, 1-decanol, and water at 298 K, where one was the hexagonal phase connected to the $[C_{16}mim]Cl$ -water axis and the other was the lamellar phase in the center in the phase diagram (Figure 11). The formation of liquid

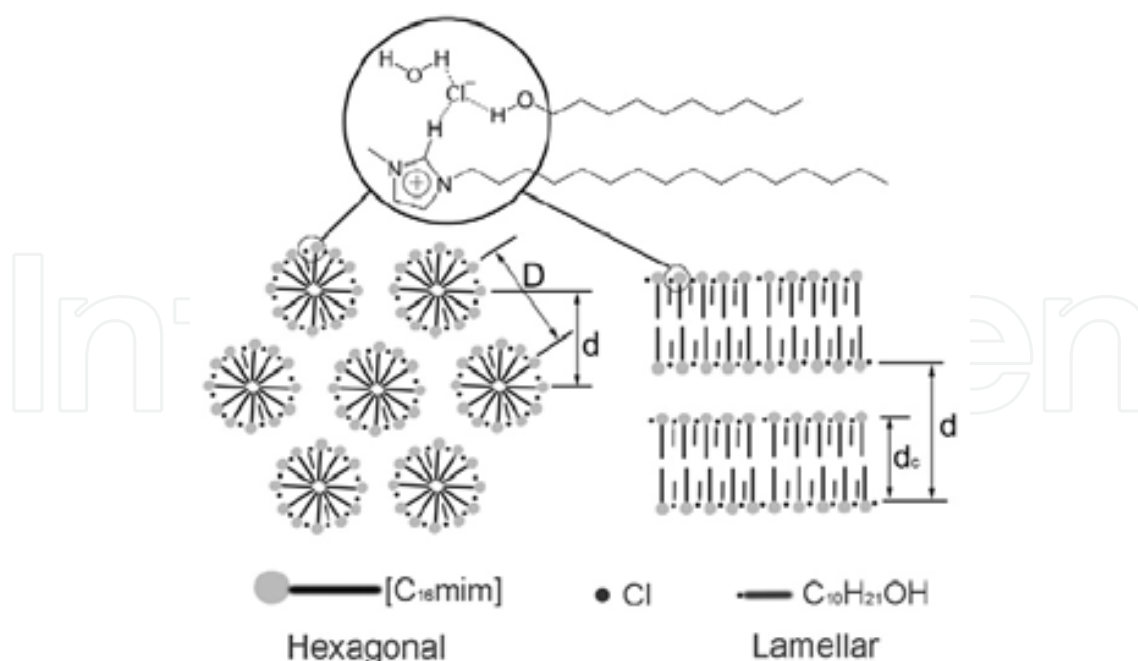


Fig. 11. Sectional schematic graph of possible structures formed in the hexagonal and lamellar phases. H-bonded network comprising H₂O, Cl⁻, the imidazolium cation, and C₁₀H₂₁OH (top). Reprinted from Zhang et al. (2007).

crystalline phases is believed to arise from a hydrogen-bonded network comprised of an imidazolium ring, anion, 1-decanol, and water. Two types of lyotropic liquid crystalline phases, hexagonal and lamellar, formed in the ternary mixtures of [C₁₆mim]Br/*p*-xylene/water, where the lattice parameters depended on the content of surfactant and water (Zhang et al., 2007). Phase behaviors of three long-chained imidazolium ILs, i.e., [C₁₂mim]Br, [C₁₄mim]Br and [C₁₆mim]Br, with *p*-xylene and water were studied by Li et al. For the first time, the formation of a lyotropic bicontinuous cubic phase in imidazolium-type IL system was reported (Li et al., 2009b). The hexagonal lyotropic liquid crystalline phase formed in the ternary system of the [C₁₂mim]Br in aqueous solution of [C₄mim][BF₄] (Wu et al., 2009b). In addition, it was found that the cylindrical units compacted much denser for the hexagonal phases formed by [C₁₂mim]Br in comparison with that formed by dodecyltrimethylammonium bromide (DTAB).

It was reported that a lamellar phase could be formed in aqueous solutions of Brij-97 by solubilizing [C₄mim][PF₆] and [C₄mim][BF₄] (Wang & Zhou, 2009). [C₄mim][PF₆] was dominantly penetrated between the OE chains of surfactant molecules, whereas [C₄mim][BF₄] was mainly located in the water layer of hexagonal phases and therefore, the strength of the network of hexagonal phase formed in the Brij-97/water/[C₄mim][BF₄] system was stronger than that of the Brij-97/water/[C₄mim][PF₆] system.

However, the reports on the molecular aggregations using IL as co-surfactants are still scarce in the literature. As a kind of co-surfactant, ILs are superior to alcohol because of its negligible vapor pressure, high stability and viscosity. Friberg et al. (Friberg et al., 2000) studied the solubilization of [C₄mim][PF₆] in the lamellar phase of Brij-30/water system, and the results showed that IL can be solubilized into the lamellar phase without changing the dimensions of the amphiphilic layer. Wang et al. (Wang et al., 2005) determined the phase diagram of ternary system of Brij-97/IL ([C₄mim][PF₆] or [C₄mim][BF₄])/water and investigated the location of IL in the hexagonal liquid crystal. Ge et al. (Ge et al., 2007)

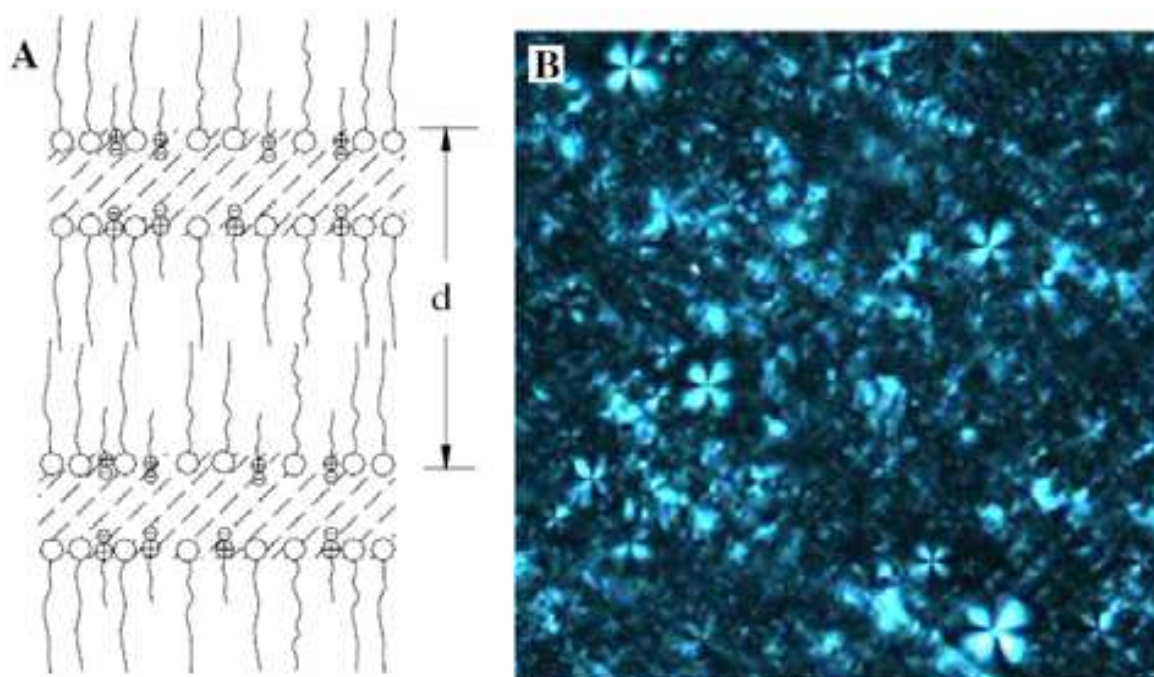


Fig. 12. Structure illustration (A) and typical micrograph (B) of lamellar phase in Brij-30/[C₄mim][PF₆]/H₂O system. The weight ratio of B is Brij-30: [C₄mim][PF₆]: H₂O = 54:6:40. Reprinted from Ge et al. (2007).

reported the microstructure of lamellar liquid crystal composed of Brij-30, [C₄mim][PF₆] and water (Figure 12), where the structure strength was enhanced by increasing the amount of Brij-30 and [C₄mim][PF₆] and impaired with the increase of water content. The lubrication properties of the ternary system were investigated and the effect of IL on the lubrication properties of traditional lamellar phase was confirmed.

Su et al. (Xiao et al., 2008) fabricated a new type of thermotropic liquid-crystalline photosensitive supramolecular ionic self-assembly of polyelectrolyte and functional unit azobenzene IL crystal (azo-ILC), where the thermal and phase behaviors can be modulated by changing the spacer length (methylene units in azo). Ma et al. (Ma et al., 2008) found that the addition of very small amounts of an alcohol or water into tri-n-decylmethylphosphonium chloride and bromide salts (1P10X) induced the formation of liquid crystalline, where strong association between the hydroxyl groups of alcohol or water and the head groups of 1P10X is indicated.

However, little attention has been given to the protein crystallization system where IL is added. Li et al. found that the addition of [C₄mim][BF₄] could promote the crystallization of lysozyme, which was probably resulted from the influence of the ionic polarization and kinetics in the lysozyme crystallization (Li et al., 2008c).

3.4 Ionic liquid based Vesicles and gels

Vesicles represent one class of self-assembly formed by phospholipids and synthetic surfactants. Generation of vesicles from single surfactants or from mixtures of anionic and cationic surfactants has been reported over the last several years.

Diakylidimethylammonium bromide formed bilayer membranes in the designed IL systems and ionophilic ether groups of ILs were found to be indispensable for the stable solvation of ammonium bilayers (Nakashima & Kimizuka, 2002). This is the first report which supported

that IL is in favor of the formation of surfactant vesicle phase. Kimizuka and his coworkers (Kimizuka & Nakashima, 2001) reported that stable bilayer membranes formed when glycolipids were dispersed in sugar-philic ether-containing ILs, which displayed reversible thermal transformation from fibrous assemblies to vesicles. Marangoni and his coworkers (Singh et al., 2009) reported the formation of spontaneous vesicle in the binary mixture of SDS and an IL amphiphile, hexylpyridinium tetrafluoroborate. Strong electrostatic interactions between bulky organic ions are the main force of the formation of vesicle aggregates.

Tang et al. (Tang et al., 2006) reported that Brij-76 were temperature dependant on the self-assembly processes in $[\text{C}_4\text{mim}][\text{BF}_4]$, where passed gel, clear solution, vesicles and emulsion transformations at 30, 85, 90 and 110 °C, respectively. Zhao et al. (Zhao et al., 2009a) investigated the phase behavior of ternary system which was composed of $[\text{C}_{16}\text{mim}]\text{Cl}$, SDS and water. It was found that a novel gel phase with quite high water content could be fabricated and the lamellar structure was obtained in SDS-rich region. Both the hydrophobic interaction of alkyl chains and interactions between oppositely charged head groups played important roles for the gel formation.

The self-assembled surfactant vesicles formed by the fluorosurfactant $\text{Zn}(\text{OOCCH}_2\text{C}_6\text{F}_{13})_2$ or by mixtures of tetradecyldimethylamine oxide (C_{14}DMAO) and $\text{Zn}(\text{OOCCH}_2\text{C}_6\text{F}_{13})_2$ were reported by Hao's group (Hao et al., 2005). Tan et al. (Tan et al., 2009) reported that the gelation of $[\text{C}_4\text{mim}][\text{PF}_6]$ were induced by the self-assembly of gelators, where the mean minimum concentrations were found to be less than 2 wt% (Figure 13). The similar ion conductivities of $[\text{C}_4\text{mim}][\text{PF}_6]$ gels to those of the pure $[\text{C}_4\text{mim}][\text{PF}_6]$ indicated that the supramolecular structures in the $[\text{C}_4\text{mim}][\text{PF}_6]$ gels had apparently no effect on the mobility of the ions. Thus, the $[\text{C}_4\text{mim}][\text{PF}_6]$ gels formed by the gelators may be used as electrolytes in electrochemical devices.

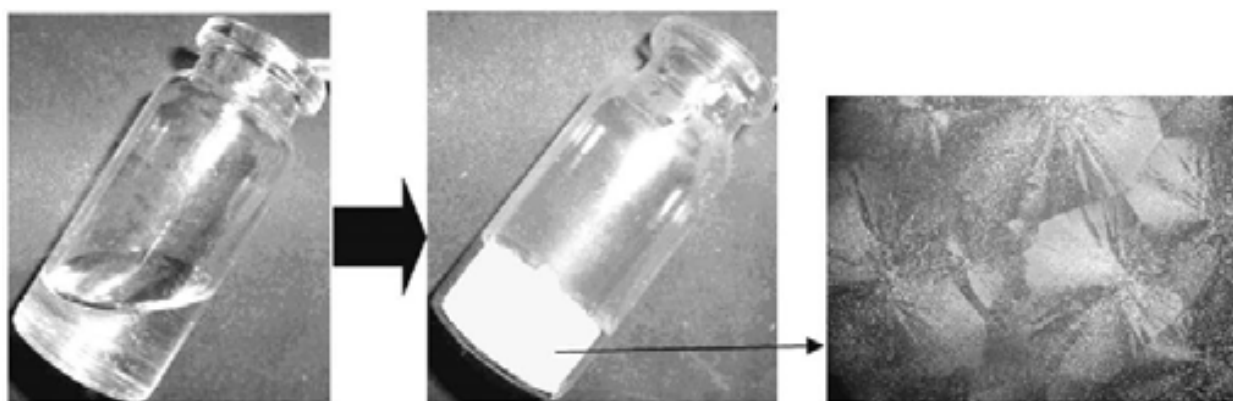


Fig. 13. Schematic illustration of gelation of $[\text{C}_4\text{mim}][\text{PF}_6]$ and the POM image of a $[\text{C}_4\text{mim}][\text{PF}_6]$ gel formed in the presence of 2 wt% of BODM (magnification: 1000). Reprinted from Tan et al. (2009).

4. Supramolecular structures based on the host networks in ionic liquids

Generally, ILs are considered as homogeneous solvents, similar to the normal molecular solvents. However, it has been found that supramolecular networks exist in pure ILs, especially in imidazolium ILs, which have already been extensively reviewed in the literature (Dupont, 2004; Leclercq & Schmitzer, 2009a). Here, we illustrate the self-

organisation of ILs and some of the organisations observed in pure ILs in order to raise the interesting in exploring how the supramolecular structure of ILs affect the formation of supermolecules and supramolecular assemblies.

4.1 Supramolecular networks in ionic liquids

4.1.1 Supramolecular structures in solid state

A typical supramolecular model for imidazolium ILs in solid state (Dupont, 2004; Leclercq & Schmitzer, 2009a), suitable to small and spherical anions with symmetric cations, came from an overview of X-ray analyses results (Choudhury et al., 2005, 2006; Dupont et al., 2000; Fuller et al., 1994; Golovanov et al., 2005; Gordon et al., 1998; Holbrey et al., 2004; Saha et al., 2003), which indicates the existence of an extended network of cations and anions connected together by hydrogen bonding (Figure 14A) (Dupont, 2004; Leclercq & Schmitzer, 2009a). The unimeric unit is always constituted by one imidazolium cation surrounded by at least three anions and each anion is surrounded by at least three imidazolium cations. With respect to the specific number of anions/cations that surround the cation/anion, it depends on the geometry of anion and the nature of the imidazolium residues. The strongest hydrogen bond always involves the most acidic H(2) of imidazolium ring, followed by H(4) and H(5) of the imidazolium cation and sometimes by the proton of the α -carbon on nitrogen. These hydrogen bonds, which are mostly electrostatic in nature, are weak to moderate ($H \cdots X$ bond lengths > 2.2 angstrom, $C-H \cdots X$ bond angles between 100° and 180°). Besides hydrogen bonding, other interactions (such as electrostatic interactions, π - π stacking, $C-H \cdots \pi$ interactions and combination of these interactions) between the cations and the anions can also lead to the formation of the supramolecular network. For example, anions with phenyl residues (such as $TPhB^-$) can interact with imidazolium cations via $C-H \cdots \pi$ interactions and form a supramolecular framework (Dupont et al., 2000). Recently, Leclercq et al. (Leclercq et al., 2009b) synthesized N,N' -diaromatic diimidazolium cations, which include electron-rich (aromatic) and electron-poor (imidazolium) rings, and found that a perfect alternation of electron-rich and electron-poor ring can maximize the π - π stacking.

Furthermore, the above two-dimensional organization may evolve to three-dimensional structures through the chains of imidazolium rings (Figure 14B). In some cases, π - π stacking interactions among imidazolium rings, and a relatively weak $C-H \cdots \pi$ interactions through the methyl group and the π system of the imidazolium ring can also be found in 1-alkyl-3-

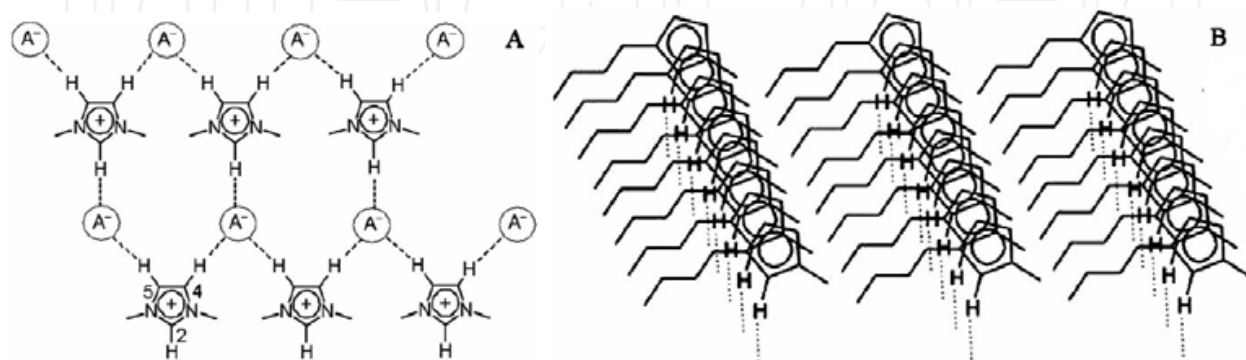


Fig. 14. Simplified two- (A) and three-dimensional (B) supramolecular structures of imidazolium ILs. Reprinted from Leclercq & Schmitzer (2009a).

methylimidazolium salts. Particularly, in some special confined circumstances, such as the hollow interiors in multi-walled carbon nanotubs and the nanospace between graphite walls, these weak interactions may be strengthened, resulting in high-melting-point crystals of imidazolium ILs (Chen et al., 2007; Sha et al., 2009). This molecular arrangement can form channels, where the spherical anions are accommodated as one-dimensional chains. This structural pattern also rests with the geometry of anion and the nature of the imidazolium residues.

Therefore, Dupont (Dupont, 2004) proposed that the best description for the imidazolium salts in the solid state is $[I_xX_{x-n}]^{n+}[I_{x-n}X_x]^{n-}$, where I represents the imidazolium cation and X represents anion.

As for other ILs, such as tetrabutylammonium trifluoromethanesulfonate, who is short of hydrogen band, π - π stacking interactions and C-H $\cdots\pi$ interactions, electrostatic interactions are important in the construction of the extended networks (Leclercq et al., 2008). Recently,

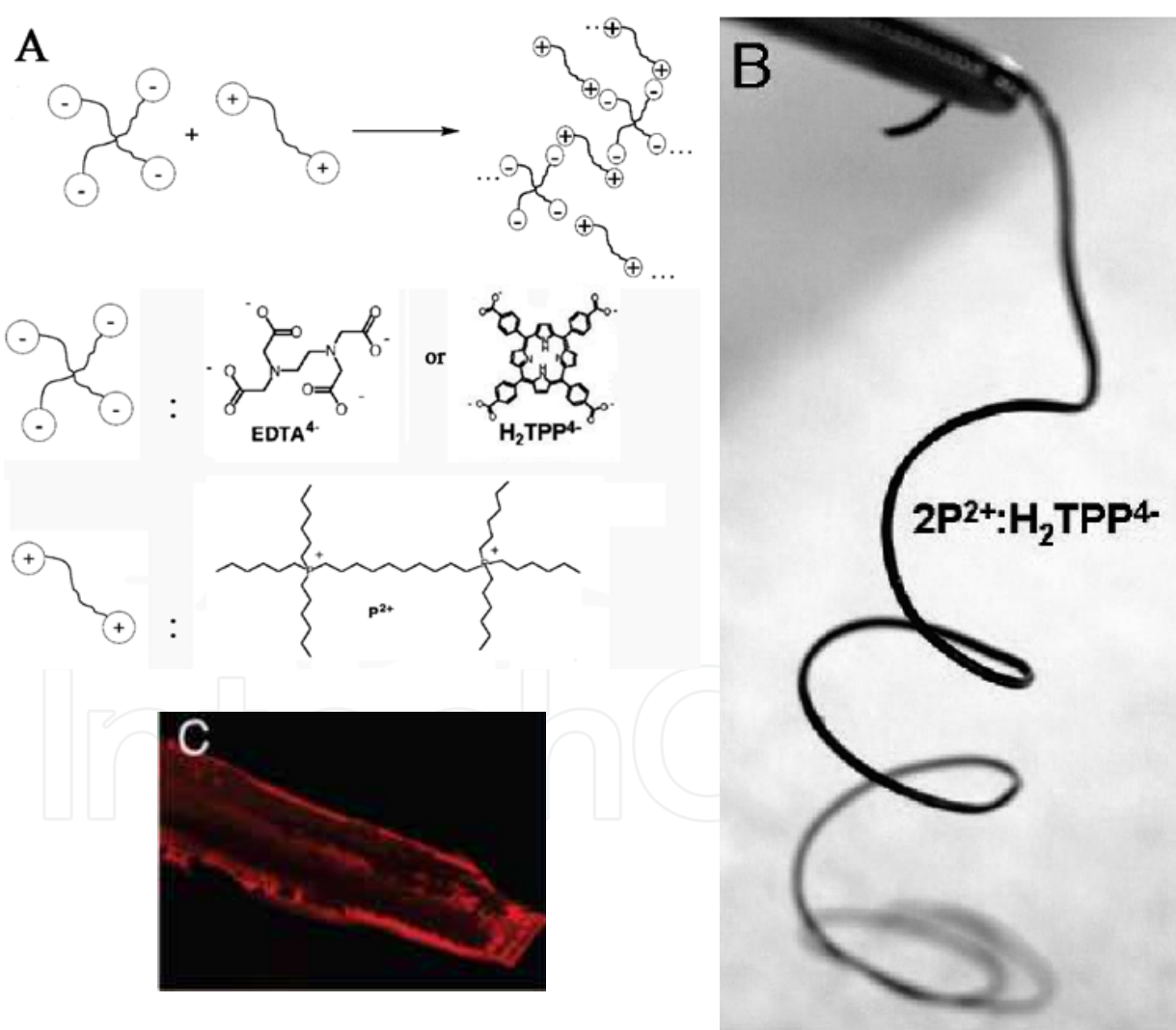


Fig. 15. (A) Schematic diagram of the formation of a supramolecular ionic network and the molecular structures of the corresponding units. (B) Photograph and (C) fluorescent micrograph ($\lambda_{\text{ex}} = 514 \text{ nm}$) of an ionic network fiber prepared from $2P^{2+}:H_2TPP^{4-}$. Reprinted from Wathier & Grinstaff (2008) and Craig (2009).

Wathier and Grinstaff (Wathier & Grinstaff, 2008) prepared an IL with ionic networks using a phosphonium dication (P^{2+}) and a tetraanion, ethylenediaminetetraacetate ($EDTA^{4-}$) (Figure 15A), which has a viscosity of about 1.2×10^4 Pa s. When $EDTA^{4-}$ was replaced by *para*-tetracarboxy-5,10,15,20-tetraphenyl-21H,23H-porphine, H_2TPP^{4-} (Figure 15A), an IL with a viscosity of ca. 10^6 Pa s at 25 °C was obtained. While the $2P^{2+}:H_2TPP^{4-}$ IL was heated to 160 °C, a fiber could be hand-pulled from the liquid (Figure 15B). Within the fiber, the porphyrins retained their fluorescence properties (Figure 15C), thus suggesting the potential utility in sensors, etc. Furthermore, the above work suggests that ionic networks formed from effective noncoordinating ionic pairs, in particular those found in ILs, might provide an interesting, useful, and complementary strategy for the formation of supramolecular structures (Craig, 2009).

4.1.2 Supramolecular structures in liquid phase

When ILs are transformed from crystal to liquid state, the long-range order is lost, but long-range Coulomb interactions between cations and anions in ILs are maintained (Dupont, 2004; Leclercq & Schmitzer, 2009a). This concept is supported by the results of IR (Dieter et al., 1988; Ozawa et al., 2003; Talaty et al., 2004), Raman (Katayanagi et al., 2004; Talaty et al., 2004), neutron diffraction analysis (Deetlefs et al., 2006; Hardacre et al., 2003), X-ray reflectivity experiment (Carmichael et al., 2001), small-angle X-ray diffraction analysis (Bradley et al., 2002) and large-angle X-ray scattering experiment (Kanzaki et al., 2009), indicating that 1,3-dialkylimidazolium ILs have analogous structural patterns in the solid and liquid phases. It is the long-range Coulomb interactions in ILs that can lead to longer spatial correlations than those in comparable classic van der Waals organic liquids (Cang et al., 2003). In other words, the supramolecular structures observed in crystal are reserved in liquid state (Dupont, 2004; Leclercq & Schmitzer, 2009a). Although Fujii et al. (Fujii et al., 2008b) found that the liquid structure of $[C_2mim][Tf_2N]$ IL is significantly different from its layered crystal structure, the ordered structure still exists, where the charge-charge interaction rather than the hydrogen bonding plays an essential role. Besides imidazolium ILs, other ILs (such as N-alkyl-N-methylpyrrolidinium ILs (Fujii et al., 2008a; Fukuda et al., 2008)) have also order structures in liquid state.

Several MD simulations (Lopes & Padua, 2006; Urahata & Ribeiro, 2004; Wang & Voth, 2005), especially the work of Lopes and Padua (Lopes & Padua, 2006), suggested the presence of polar domains that are formed by the head groups of the cations and anions, and of nonpolar domains that are formed by the alkyl groups in 1-alkyl-3-methylimidazolium ILs ($C_n \geq C_4$). As the length of the alkyl chain increases, the nonpolar domains become larger and more connected, and cause swelling of the ionic network, in a manner analogous to microphase separation (Lopes & Padua, 2006). Recently, the results of X-ray diffraction (XRD) experiment (Triolo et al., 2007), fluorescent spectra (Hu & Margulis, 2006), Raman spectra (Iwata et al., 2007; Shigeto & Hamaguchi, 2006), NMR (Mele et al., 2006), femtosecond solvation dynamics study (Adhikari et al., 2007) and optical Kerr Effect spectra (Xiao et al., 2007) of 1-alkyl-3-methylimidazolium ILs also suggested the presence of heterogeneous structures. Furthermore, the result of the XRD experiment also reflected that the size of the inhomogeneous structures is proportional to the length of the alkyl chain (Triolo et al., 2007). Thus, this suggests that the above-mentioned nanodomains are built up by the aggregation of neutral alkyl chains surrounded by charges, whose uniform spatial distribution is determined by the strong electrostatic interactions (Triolo et al., 2007). Thus,

there will be a competition between the interactions of a given solute with those two regions (Blesic et al., 2009a). Rebelo et al. (Rebelo et al., 2007) suggested that a nonpolar solute (e.g., n-hexane) will interact preferentially with the nonpolar domains, while a dipolar or associative solutes (e.g., water) will interact with the polar domains. Therefore, this kind of heterogeneous structure of ILs will make the solubility and reactivity of solutes in ILs obviously different from those in the normal molecular solvents.

4.1.3 Thermotropic liquid crystal phase of ionic liquids

As for imidazolium ILs with long alkyl chains ($C_n \geq C_{12}$), liquid crystal (LC) phase often appears in the course of increasing temperature (Bowlas et al., 1996; Bradley et al., 2002; De Roche et al., 2003; Getsis & Mudring, 2008; Holbrey & Seddon, 1999; Lee et al., 2000; Lee et al., 1997; Li et al., 2005b; Zhou & Antonietti, 2004). If an anion has a long alkyl chain, the long alkyl chains on the imidazolium ring are not necessary for the formation of LC (Mukai et al., 2004). In addition, some metal complex anion, such as $PdCl_4^-$ and $CuCl_4^-$, can be applied (Bowlas et al., 1996; Hardacre et al., 2001; Lee et al., 2004; Lin & Vasam, 2005). Generally, the temperature range for LCs can be adjusted by altering counter anion and the length of alkyl chain.

Up to now, most of the found LC structures of imidazolium ILs are smectic A phase, consisting of interdigitated bilayers. This supramolecular structure can be considered as the result of the alternate assembling of ionic layers and van der Waals layers. In the former, the ionic head groups interact with the counterions through Coulomb force, while the latter build from (anti)parallel stacking of the alkyl chains through van der Waals force. Moreover, the

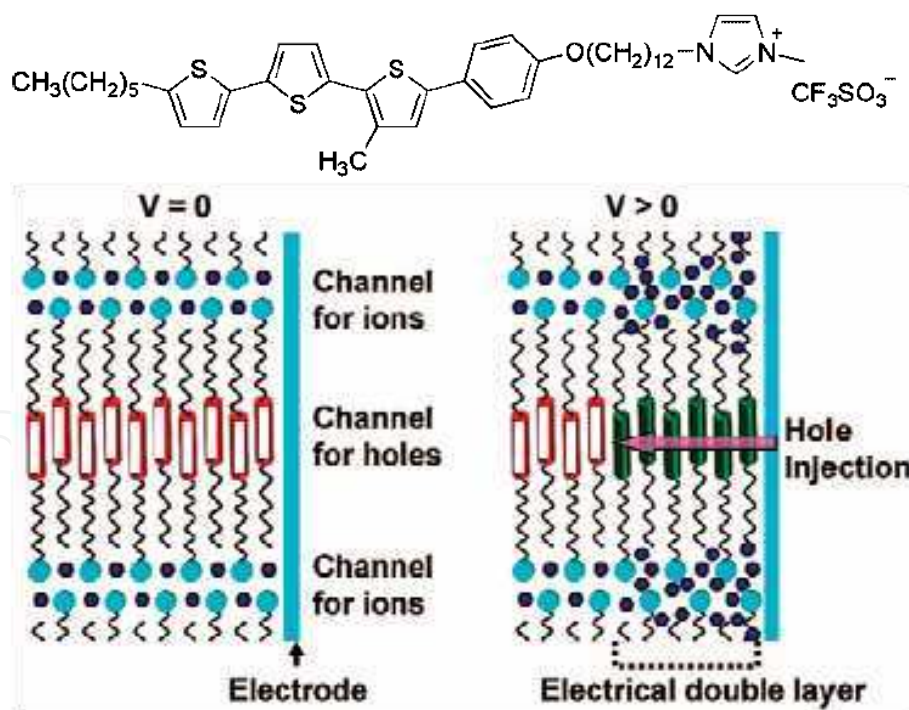


Fig. 16. Molecular structure of 1-methylimidazolium ILs containing phenylterthiophene moiety (up), and schematic image of a nanostructured liquid crystal consisting of ionic and π -conjugated moieties (bottom): blank cylinders are neutral phenylterthiophene moieties; dark cylinders are the oxidized ones; smaller spheres and larger plates are triflate anions and imidazolium moieties, respectively. Reprinted from Yazaki et al. (2008a).

hydrogen bonds between the H-atoms of imidazolium cations and anions are important in the formation and stabilization of ionic layers (Lee et al., 2000; Lee et al., 2004; Lee et al., 1997).

The functionalization of imidazolium is a useful method for the application of imidazolium ionic LCs. Recently, Kato and collaborators (Yazaki et al., 2008a) synthesized a new ILs with a 1-methylimidazolium group as an ion-conductive part and π -conjugated phenylterthiophene moiety related to the electronic charge transport (Figure 16). In its smectic A phase, the ionic and the π -conjugated moieties were nanosegregated, leading to the formation of two-dimensional ion-conductive channels between hole transport layers (Figure 16) (Yazaki et al., 2008a). Consequently, the holes were injected from the anode and transported into the hole transport layers consisting of phenylterthiophene moieties (Figure 16), resulting in the oxidation of the π -conjugated moieties (Yazaki et al., 2008a). In experiment, the IL exhibited electrochromism in the LC state without a liquid electrolyte layer, unlike conventional redox-active conjugated polymers and liquid crystals (Yazaki et al., 2008a). This LC would be applied to various electronic devices such as light-emitting electrochemical cells as well as the electrochromic devices.

The structure of imidazolium ionic LCs is much simplex, which makes its application in many fields confined. In order to resolve this problem, much effective effort has been made (Goossens et al., 2008; Kumar & Pal, 2005; Pal & Kumar, 2006; Seo et al., 2007; Yasuda et al., 2010; Yazaki et al., 2008b; Yazaki et al., 2010; Yoshio et al., 2004; Yoshio et al., 2006; Yoshio et al., 2007; Yoshizawa et al., 2004; Zhang et al., 2008d), especially the work of Kato and collaborators (Yasuda et al., 2010; Yazaki et al., 2008b; Yazaki et al., 2010; Yoshio et al., 2004; Yoshio et al., 2006; Yoshio et al., 2007). They observed the appearance of a hexagonal columnar LC structure in 1-methylimidazolium ILs with tri-alkoxy substituted phenyl groups, a class of LC mesogens, attached to the nitrogen atom (Yoshio et al., 2004; Yoshio et al., 2006; Yoshio et al., 2007). Besides a wide temperature range of LC phase (Yoshio et al., 2004; Yoshio et al., 2006; Yoshio et al., 2007) and tunable feasible adjustment of LC properties by altering counter anions (Yoshio et al., 2007), the synthesized compounds in columnar LC state were highly anisotropic ion-conductive in one-dimension (Yoshio et al., 2004; Yoshio et al., 2006; Yoshio et al., 2007), which would be useful for transportation of ions, energy, and information at the nanometer level. Recently, Kato et al. (Yazaki et al., 2008b) prepared two new 1-methylimidazolium-based ionic LCs, containing an L-glutamic acid moiety and bis(alkyloxy)phenyl groups (Figure 17). The ionic conductivities and LC structures of the obtained 1-methylimidazolium ILs could be conveniently adjusted by anions, which would potentially be used as an on-off switch of ions (Figure 17) (Yazaki et al., 2008b).

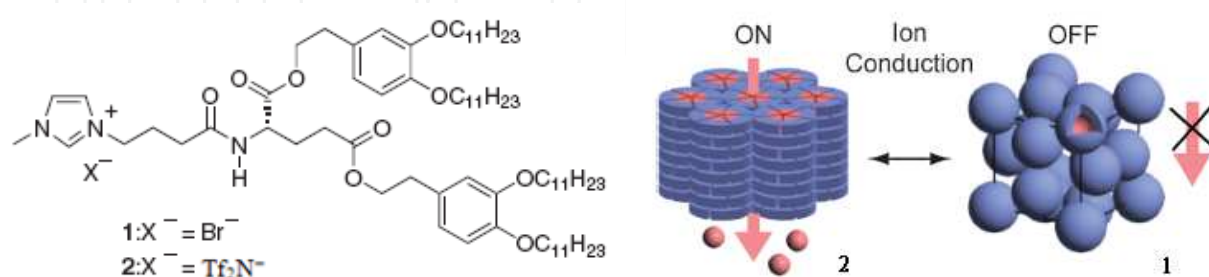


Fig. 17. Molecular structures of 1-methylimidazolium ILs containing an L-glutamic acid moiety and bis(alkyloxy)phenyl groups (left), and schematic illustration of an ideal on-off switch of ion conduction using the structural change from columnar to micellar cubic LC structures (right). Reprinted from Yazaki et al. (2008b).

Besides imidazolium ionic LCs, other thermotropic ionic LCs based on pyridinium (Bowlas et al., 1996; Cruz et al., 2000; Cui et al., 2002; Gordon et al., 1998; Neve et al., 2000; Neve et al., 2001; Taubert, 2004), quaternary ammonium (Alami et al., 1993; Arkas et al., 1999; Lu et al., 1997; Pott & Meleard, 2009; Tittarelli et al., 1997), quaternary phosphonium (Abdallah et al., 2000; Chen et al., 2002; Gowda et al., 2004), pyrrolidinium (Goossens et al., 2009), dithiolium (Artzner et al., 1997) and guanidinium ILs (Kim et al., 2005; Mathevet et al., 2005; Sauer et al., 2008) have also been explored. Two important phenomena should be especially noticed. Firstly, some of them have several kinds of liquid-crystalline structures. For example, with the change of alkyl chain length and counter anions, highly ordered smectic phases (the smectic E phase and the uncommon smectic T phase), smectic A phases, and hexagonal columnar phases were observed in the pyrrolidinium ILs (Goossens et al., 2009). Secondly, the behaviors of tri-alkyl-methyl-ammonium ionic LCs may be fine-tuned further to well defined hydrophobic thickness corresponding to uneven numbers of mean alkyl carbons, by the use of simple binary liquid mixtures (Pott & Meleard, 2009).

4.2 Inclusion phenomenon of guest compounds in the ionic liquid network

As the above description, neat imidazolium ILs have supramolecular framework. Furthermore, up to now, much evidence indicated that some of the supramolecular networks can be reserved when ILs are mixed with other materials and inclusion-type structures are formed.

4.2.1 Inclusion of water in ionic liquids

Because ILs can absorb significant amount of water from the atmosphere and trivial water is difficult to be removed, water becomes the most common impurity in ILs (Huddleston et al., 2001; Seddon et al., 2000; Takamuku et al., 2009). The existence of water in ILs may affect many of their physical and chemical properties, such as polarity, viscosity, conductivity, and reactivity as well as solvation and solubility properties (Brown et al., 2001; Cammarata et al., 2001; Najdanovic-Visak et al., 2003; Schroder et al., 2000; Widegren et al., 2005).

In order to explain the large differences in the effect of water on the diffusion coefficient for neutral and for ionic species in imidazolium IL media, Compton et al. (Schroder et al., 2000) postulated that “wet” ILs may not be regarded as homogeneous solvents, but have to be considered as “nano-structured” with polar and non-polar regions.

Through the research based on attenuated total reflectance IR spectroscopy, Cammarata et al. (Cammarata et al., 2001) considered that water molecules absorbed from the air by 1-alkyl-3-methylimidazolium ILs are mostly in the “free” (not self-associated) state, most of which act as bridge between anions (X^-), such as BF_4^- and PF_6^- , via hydrogen bond of type $X^- \cdots HOH \cdots X^-$. Later, Mele et al. (Mele et al., 2003) found that the H(2), H(4) and H(5) within the imidazolium ring could interact with water molecules via hydrogen bond of type $C-H \cdots O$ at very low water content by NMR spectroscopy through intermolecular nuclear Overhauser enhancements on $[C_4mim][BF_4]$ IL. Based on the MD simulations and NMR experiment, Mele et al. (Moreno et al., 2008) further indicated that the ions of $[C_4mim][BF_4]$ IL are selectively coordinated by individual water molecules, but the ionic network is largely unperturbed at low water content. Recently, Zhang et al. (Zhang et al., 2008c) found that water molecules tend to interact with the anion moiety of ILs first, via hydrogen bond, rather than with hydrogen atoms within the imidazolium, which is further confirmed by the most recent work of Takamuku et al. (Takamuku et al., 2009). It is also found that water is not homogeneously mixed with $[C_2mim][BF_4]$ IL at low water content (Zhang et al., 2008c).

In addition, no direct hydrogen bonds between cations and anions were observed in the crystal structure of [1,3-dibenzylimidazolium]Br·H₂O, but water molecules connected anions and cations in the supramolecular framework (Leclercq et al., 2009c). In other words, water molecules were included in the crystal lattice.

Thus, the existing states of water molecules in the liquid and crystal phases support the hypothesis of polar and non-polar regions of the supramolecular network. From another point of view, at low water content, the water could be regarded as guest included in the supramolecular framework of imidazolium ILs.

4.2.2 Inclusion of aromatic compounds in ionic liquids

After mixing of some imidazolium ILs with excess of aromatic hydrocarbons, biphasic mixtures are obtained. The lower layer is IL-rich phase, which exhibits the characteristics of typical liquid clathrates, i.e., low viscosity (relative to the initial neat ILs), immiscibility with excess aromatic solvents, and non-stoichiometric (but reproducible) compositions, while the concentration of IL is too low to be detected in the upper layer. Recently, it was found that the immiscibility gap became smaller when the polarity of substituted benzenes increased and their molecular size decreased (Shiflett & Yokozeki, 2008; Shiflett et al., 2009; Shiflett & Niehaus, 2010). However, when both dipole and quadrupole moments are present in an aromatic compound, they have an antagonistic effect, reducing the solubility in the IL (Shimizu et al., 2009). Up to now, such liquid clathrates or IL-biphasic systems have been used in the fields of organic syntheses (Boxwell et al., 2002; Clavier et al., 2008; DeCastro et al., 2000; Surette et al., 1996), polymerization (Csihony et al., 2002), separations of aromatics from hydrocarbons (Arce et al., 2007; Selvan et al., 2000) and so on.

Holbrey et al. (Holbrey et al., 2003) obtained crystalline [C₁mim][PF₆]·0.5C₆H₆ by cooling the lower phase of the [C₁mim][PF₆]-C₆H₆ system to room temperature. The crystal structure of the clathrate (Figure 18A) shows that there is a three-dimensional array of hydrogen-bonded cations and anions, a typical supramolecular structure for imidazolium ILs in solid state. This three-dimensional framework results in the formation of “channels” along the (001) direction of the crystal lattice in which benzene molecules are included by a staggered π - π “sandwich” between two imidazolium cations. Later, Lachwa et al. (Lachwa et al., 2006) draw the similar conclusion from the crystal structure of [C₂mim][NTf₂]·C₆H₆ (Figure 18B). However, the formed structure has to allow for a higher proportion of benzene molecules, forming a tube-like structure with a rectangular cross-section around the cations of ILs. The formation of clathrate phases could be regarded as an example of the organization of guest molecules in the pre-organised host network.

Deetlefs et al. (Deetlefs et al., 2005) further indicated that the addition of benzene to [C₁mim][PF₆] leads to an expansion of the cation-cation contacts through the neutron diffraction study on the [C₁mim][PF₆]-C₆H₆ mixtures. Moreover, around the benzene molecule, alternating cation-anion layers are observed with the first-shell anions interacting with the ring hydrogens while the cations interact with the ring electrons. The incorporation of benzene is found to displace the anions with approximate three benzenes replacing each anion, suggesting benzene intercalation into the structure as found in the solid. Benzene is also found to be homogeneously distributed throughout the IL with no evidence of micellar formation.

With respect to the inclusion crystal [C₂mim][NTf₂]·C₆H₆, through the MD study of its congruent melting, Alavi et al. (Kowsari et al., 2010) further found that the presence of a

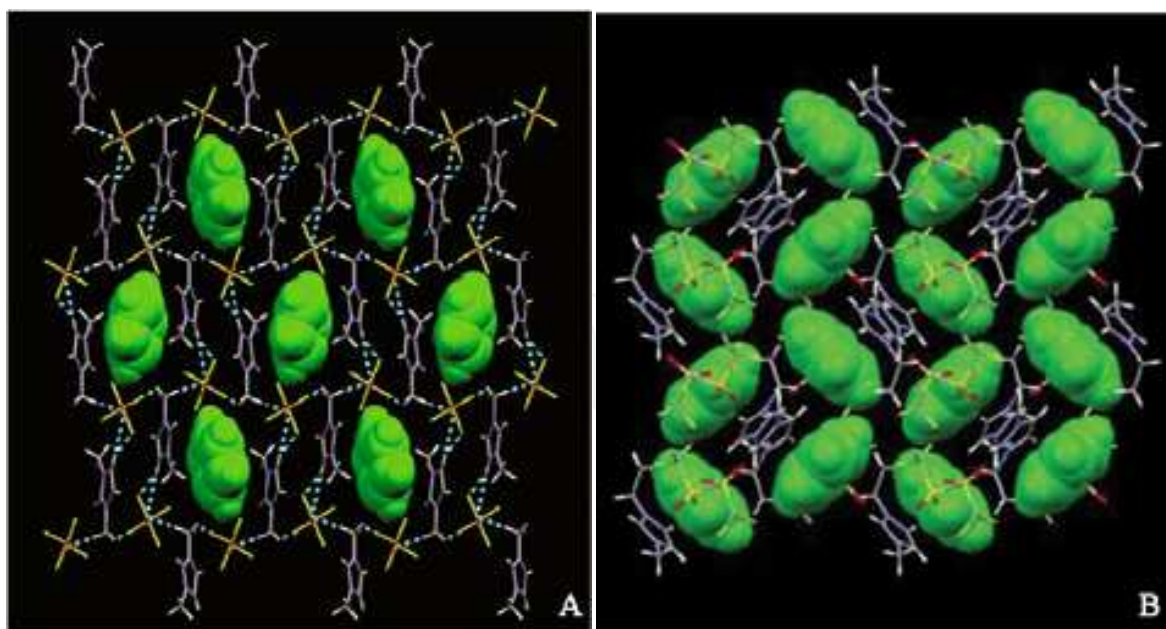


Fig. 18. Packing patterns in the crystal structures of $[\text{C}_1\text{mim}][\text{PF}_6] \cdot 0.5\text{C}_6\text{H}_6$ (A) and $[\text{C}_2\text{mim}][\text{NTf}_2] \cdot \text{C}_6\text{H}_6$ (B). Reprinted from Holbrey et al. (2003) and Lachwa et al. (2006).

stoichiometric number of benzene molecules does not affect the nearest neighbor ionic association between $[\text{C}_2\text{mim}]^+$ and $[\text{NTf}_2]^-$, but increases the mean-square displacements of both cations and anions compared to pure liquid $[\text{C}_2\text{mim}][\text{NTf}_2]$, showing that second shell ionic associations are weakened.

Besides imidazolium ILs, other ILs based on quaternary ammonium (Coleman et al., 1990; Pickett, 1985), pyridinium (Christie et al., 1991) and so forth (Gaudet et al., 1988) can also form liquid/solid clathrates with aromatic molecules, in which suitable anions are important.

4.2.3 Co-crystals of ionic liquids

It has been reported that imidazolium ILs are able to form co-crystals with quaternary ammonium ILs with same anions (Leclercq et al., 2007, 2008), *e. g.*, $[\text{C}_2\text{mim}][\text{TfO}]$ with [tetrabutylammonium][TfO] ($[\text{Bu}_4\text{N}][\text{TfO}]$) (Leclercq et al., 2008). The co-crystal structure of $[\text{C}_2\text{mim}][\text{TfO}]$ and $[\text{Bu}_4\text{N}][\text{TfO}]$ (Figure 19) could be described as a supramolecular framework formed by C_2mim^+ and TfO^- through hydrogen bonding, in which all Bu_4N^+ are trapped (Leclercq et al., 2008). This phenomenon may be considered to be another example of the inclusion of guest molecules in the supramolecular host network.

Besides the above three kinds of molecules, gas molecules (such as CO_2) (Costantini et al., 2005; Dupont, 2004; Gutowski & Maginn, 2008; Huang et al., 2006; Weingartner, 2008) and (bio)macromolecules (Dupont, 2004; Feher et al., 2007; Leclercq & Schmitzer, 2009a), even nanoparticles (Dupont, 2004; Leclercq & Schmitzer, 2009a; Lee et al., 2009), may act as guests included in the supramolecular host framework of ILs.

5. Effects of ionic liquids on the formation of supramolecular structures

ILs can not only participate directly in the formation of supramolecular systems, but also influence the formation of various supramolecular structures.

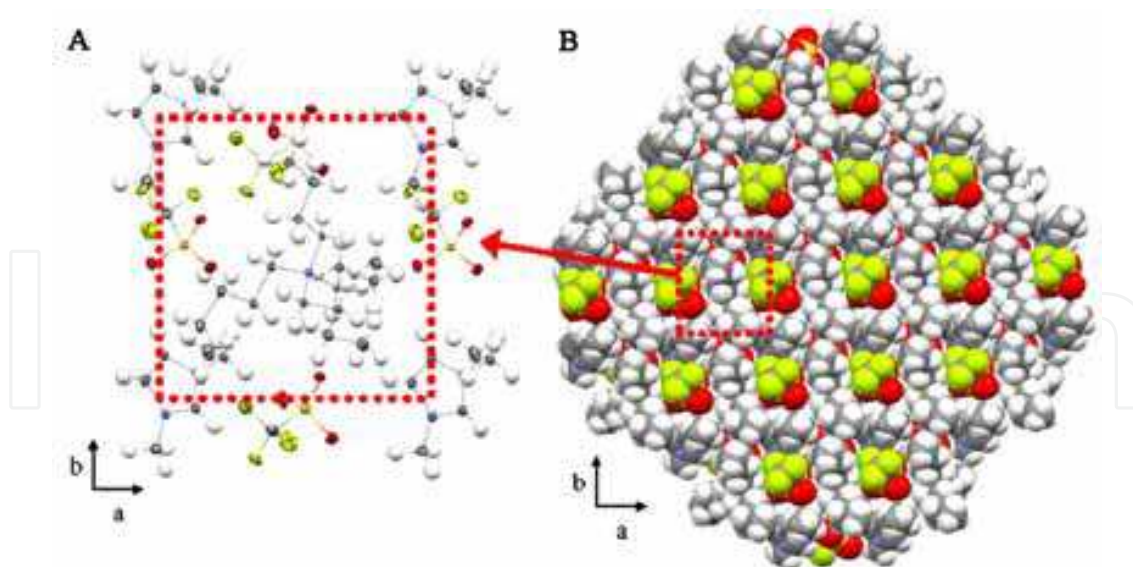


Fig. 19. (A) View of the local assembly around a tetrabutylammonium cation (Bu_4N^+) and (B) space-filled view of the co-crystal of $[\text{C}_2\text{mim}][\text{TfO}]$ and $[\text{Bu}_4\text{N}][\text{TfO}]$. Reprinted from Leclercq et al. (2008).

5.1 Effects of ionic liquids on the formation of polyrotaxanes and polypseudorotaxanes

Polyrotaxanes (PRs) and polypseudorotaxanes (PPRs) formed by CDs in the presence of ILs have been studied. Samitsu et al. (Samitsu et al., 2006) used ILs as new solvents for PR, consisting of α -CD and poly (ethylene glycol). They found that halogen-containing ILs, such as chlorides or bromides, were good solvents for PRs, regardless of their cations. This discovery was applied in the preparation of IL-containing slide-ring gels (SR gels), which are supramolecular networks of PR swollen with ILs, using a devised “non-drying” technique accompanied by solvent exchange. A kind of PPRs were prepared by supramolecular self-assembly of β -CDs threaded onto the triblock copolymers (Pluronic F127) in $[\text{C}_4\text{mim}][\text{PF}_6]$ with two different manners (Jing et al., 2007). It was found that not only the PO segments but also many EO segments are included by β -CD molecules in the PPRs. Interestingly, which one, F127 or $[\text{C}_4\text{mim}][\text{PF}_6]$, will finally be included inside β -CD, can be controlled by ethanol amount around the initially β -CD/ $[\text{C}_4\text{mim}][\text{PF}_6]$ ICs. At higher ethanol concentration, F127 may squeeze $[\text{C}_4\text{mim}][\text{PF}_6]$ molecules out from β -CD and thread themselves instead into the cavity of β -CD and finally precipitate with more CDs being stacked (Figure 20).

5.2 Effects of ionic liquids on the formation of the supramolecular structures in the extraction systems based on crown ethers

No significant close contacts are observed between ILs and crown ethers based on the study of co-crystallisation of imidazolium based salts with 18-crown-6 (18C6), though coulomb interactions between the ionic (liquid) components and hydrogen bonding are important (Gjikaj et al., 2008). However, because of the influence of ILs to the system of crown ethers, they are being used in the extraction of metal ions, amino acid and so on.

For the first time, Dai et al. (Dai et al., 1999) used the system dicyclohexano-18-crown-6 (DCH18C6) - $[\text{R}_1\text{R}_2\text{mim}][\text{NTf}_2]/[\text{PF}_6]$ to extract Sr^{2+} , obtaining the distribution coefficient as

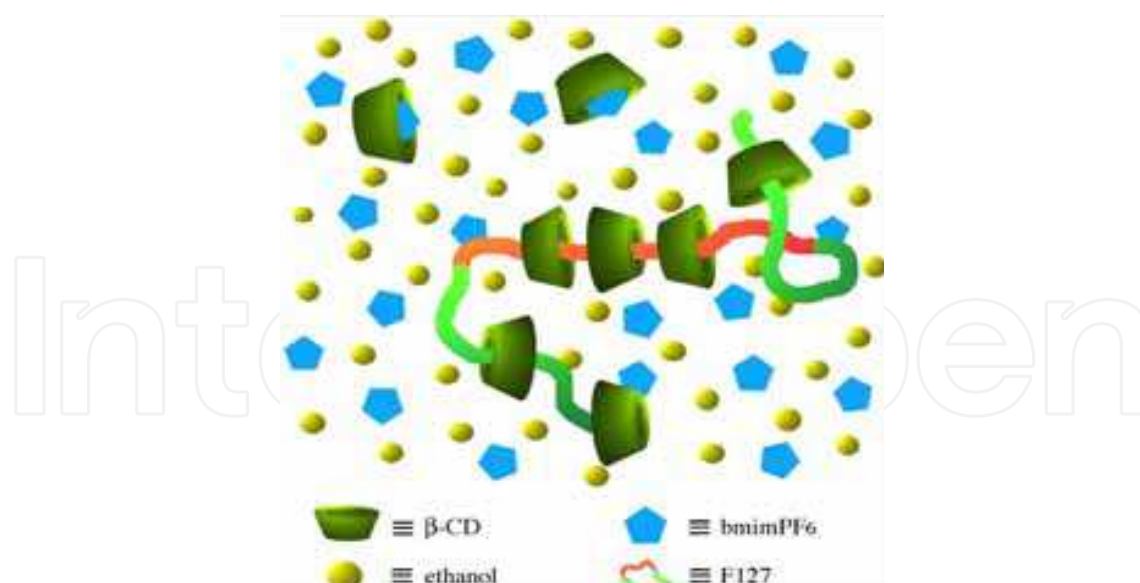


Fig. 20. Schematic representation of the inclusion choice between F127 and $[C_4mim][PF_6]$. Reprinted from Jing et al. (2007).

high as 10^4 . The extraction process can be easily tailored by varying the substituting groups in the imidazolium cation and the counter anions. In succession, more and more systems involved ILs and crown ethers were investigated (Chun et al., 2001; Langmaier et al., 2009; Nockemann et al., 2007; Okamura et al., 2010; Stepinski et al., 2010; Visser et al., 2000; Xu et al., 2009). These results discovered that as the alkyl group in the ILs was elongated, the extraction efficiency decreased, but the extraction selectivity increased. The distribution is not only related to the concentration and the hydrophobicity of crown ethers, but also to the composition of the aqueous phase. To increase the extraction efficiency of metal ions, the additives, such as TBP, were added into the system due to the formation of a synergistic adduct (Stepinski et al., 2005). The magnitude of the synergistic enhancement is shown to depend on the alkyl chain length of the ILs $[C_nmim][Tf_2N]$ cation, with the effect diminishing as the cation hydrophobicity increases until for $[C_{10}mim][Tf_2N]$.

The traditional crown ether, for example DCH18C6, can extract metal ions efficiently. However, metal ions are not easy to be stripped. In order to overcome this disadvantage, a series of *N*-alkyl aza-18-crown-6 ethers were synthesized (Luo et al., 2004a). These crown ethers in ILs were investigated as recyclable extractants for separation of Sr^{2+} and Cs^+ from aqueous solutions. They discovered a strong dependence of selectivity on the type of ILs. Recently, Shimojo et al. (Shimojo et al., 2009) reported the first study on the “intramolecular” synergistic extraction of a metal ion in an IL-based system. Sr^{2+} was extracted by a novel extractant β -diketone-substituted diaza-18-crown-6 (H2 β DA18C6). By compared with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and *N,N'*-dibenzyl-4,13-diaza-18-crown-6 (DBzDA18C6), they found that H2 β DA18C6 provides a remarkably high performance for Sr^{2+} extraction into $[C_2mim][Tf_2N]$ due to a cooperative “intramolecular” interaction when compared with the “intermolecular” synergy extraction system of the mixture of HPMBP and DBzDA18C6. The two protons from protonated H2 β DA18C6 were released to extract Sr^{2+} , the transfer of Sr^{2+} into $[C_2mim][Tf_2N]$ proceeds via the proton exchange reaction.

Because ILs are usually used in the separation of radioactive nuclides and the radiation effect on ILs for the extraction of metal ions is important. The influence of γ -radiation on the IL $[C_4mim][PF_6]$ and $[C_4mim][Tf_2N]$ during extraction of Sr^{2+} by DCH18C6 was studied

(Yuan et al., 2008, 2009). The irradiation of IL influences greatly on this system. The Sr^{2+} partitioning in irradiated $[\text{C}_4\text{mim}][\text{PF}_6]$ decreases as the absorption dose increases. This is the result of the formation of acid during the irradiation of $[\text{C}_4\text{mim}][\text{PF}_6]$. Due to the competition between H^+ and Sr^{2+} , the extraction efficiency decreased and can be recovered by simple washing the irradiated $[\text{C}_4\text{mim}][\text{PF}_6]$ with water.

Besides, stability constants of metal ion complexes with crown ethers in IL aqueous solutions were obtained (Popov et al., 2007) and the solubilization of the ILs $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$ by the presence of crown ether was studied (Rickert et al., 2007). It is also reported that the stability of cesium complexed with 18C6 in ILs is affected by the nature of both cation and anion of ILs (Vendilo et al., 2009; Vendilo et al., 2010b). Moreover, the complex stability is important for the extraction process (Vendilo et al., 2010a).

In the conventional organic solvents extractions, limited solubility of ionic species in nonionic organic solvents is the main problem and the toxicity of free crown ethers makes them unsuitable for industrial use. Task Specific ILs (Bates et al., 2002; Visser et al., 2001) (TSILs) contain specific functionality covalently incorporated within one of the ionic components of the IL, typically within the cation. Therefore, the “crowned” IL-crown ether as a functional group to functionalized IL was performed for a liquid/liquid extraction of metal ions (Park et al., 2006) and molecular-recognition ability (Ishida et al., 2004; Liu et al., 2005). The “crowned” ILs obtain their selectivity through their ability to fine-tune and reorganize their crown ether structure changing their number and type of donor atoms, appending ionizable groups, and modifying their lipophilicity. Ishida et al. (Ishida et al., 2004) designed and synthesized novel imidazolium-based ILs with a pseudo crown-ether moiety. The oxygen lone pairs had a potential as Lewis-basic and/or hydrogen-accepting functionality. Owing to the molecular-recognition ability, the enantiometric imidazolium cations could differently sense the chirality of the europium complexes. A series of novel ILs comprising crown-ether functionalities in cations or anions (crowned ILs) were prepared and characterized (Liu et al., 2005). The physical properties of different functionalized ILs were different, for example the thermal decomposition temperatures (T_{dec}) of the ILs containing crowned cations are generally 80-100 °C higher than those of the ILs having crowned anions. The ILs functionalized by the crown ether may display potential utility in catalytic application as well as in separation and electrochemical sensing. Luo et al. (Luo et al., 2006) synthesized a new class of TSILs based on the covalent attachment of imidazolium cations to a monoaza-crown ether fragment. These TSILs exhibited lower extraction efficiency than the IL extraction systems using DCH18C6 or N-octylaza-18-crown-6 as extractant. This can be attributed to the coulombic repulsion from the covalently attached imidazolium cation. The selectivity of these TSILs is dependent on the structure of substituents on the imidazolium ring.

The mechanism of ILs-crown ethers system for metal ions extraction has been studied extensively. There are several kinds of mechanisms: cation exchange (Dai et al., 1999; Dietz & Dzielawa, 2001; Dietz et al., 2003; Hirayama et al., 2008; Park et al., 2006; Popov et al., 2007), anion exchange (Jensen et al., 2003), mechanism of multiple distribution (Dietz & Stepinski, 2005). By changing the ILs, the hydrophobicity of the IL cation increase (from $n=5$ to $n=10$ in $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$), the predominant mode of partitioning changes from ion-exchange involving the cationic portion of the IL to conventional neutral nitrato complex extraction (Dietz et al., 2003). The stereochemistry of crown ethers can also affect the mechanism. Dietz et al. (Dietz et al., 2008) studied the DCH18C6 stereochemistry influence the mode of sodium ion transfer from acidic nitrate media into ILs. DCH18C6 have five

isomers, i.e., cis-syn-cis (csc), cis-anti-cis (cac), trans-syn-trans (tst), trans-anti-trans (tat) and cis-trans (ct) (Figure 21). For the cis isomers, rising nitric acid concentration is eventually accompanied by steeply falling values of the sodium distribution ratio. This was originated the crown ether-mediated exchange of a sodium ion for a hydronium ion in a DCH18C6- H_3O^+ adduct. In contrast, for the trans isomers, rising aqueous acidity is accompanied by increasing sodium extraction, consistent with partitioning of a neutral sodium nitrate-crown ether complex. A change from a cis to a trans isomer of DCH18C6 alters the predominant mode of sodium ion portioning into $[\text{C}_{10}\text{mim}][\text{Tf}_2\text{N}]$ from ion-exchange to neutral complex extraction. As a result, the process of extracting can be controlled by the isomers of extractants.

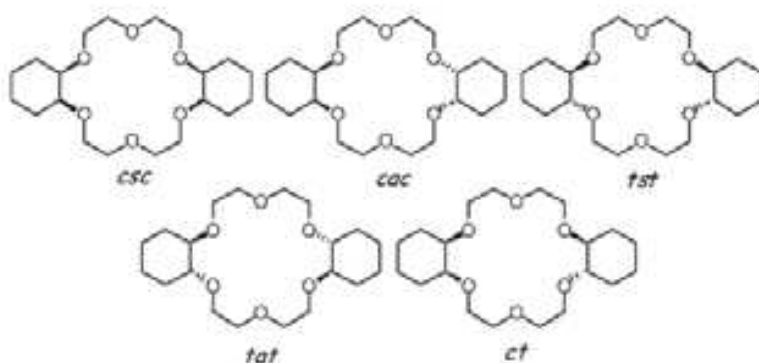


Fig. 21. Molecular structures of the cis-syn-cis (csc), cis-anti-cis (cac), trans-syn-trans (tst), trans-anti-trans (tat), and cis-trans (ct) isomers of DCH18C6. Reprinted from Dietz et al. (2008).

ILs and crown ethers used in biochemistry have also been a field of increasing interest and importance (Kragl et al., 2002; van Rantwijk et al., 2003). Amino acids are hydrophilic and therefore difficult compounds for conventional solvent extraction. Amino acids were not soluble in IL, however, by adding a crown ether to the IL phase, the positive form of amino acids is complexed by the crown ether and the complex is extracted in the IL phase (Carda-Broch et al., 2003). Amino acids Trp, Gly, Ala, Leu were efficiently extracted from aqueous solution as pH 1.5-4.0 (Lys and Arg at pH 1.5-5.5) into $[\text{C}_4\text{mim}][\text{PF}_6]$ with DCH18C6 (Smirnova et al., 2004). The most hydrophilic amino acids such as Gly were extracted as efficiently as the less hydrophilic ones. Compared to the conventional organic solvents, ILs enabled quantitative recovery of amino acids and eliminated emulsion formation, which usually occurs when cationic or anionic extractants are used.

Shimojo et al. (Shimojo et al., 2006a; Shimojo et al., 2006b) investigated a hydroxyl-group-containing IL with DCH18C6 was capable of quantitative partitioning of heme protein cytochrome c (Cyt-c) via supramolecular complexation and that the resulting Cyt-c-DCH18C6 complex acts as a homogeneous biocatalyst in ILs. While using conventional organic solvents the protein transfer was negligibly small. The partitioning of a protein into ILs is controllable on the basis of hydrophobicity and type of the functional groups of ILs. This is the first report showing protein extraction into ILs.

Extractants comprised calixarene part in IL systems were also investigated (Shimojo & Goto, 2004a; Sieffert & Wipff, 2007). Shimojo et al. (Shimojo & Goto, 2004b) studied the extraction of metal ions by a calix[4]arene-bearing pyridine in a typical IL, $[\text{C}_8\text{mim}][\text{PF}_6]$. Pyridinocalix[4]arene showed a high extraction ability and selectivity for Ag^+ in five different metal ions (Ag^+ , Cu^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+}). This compound transfers Ag^+ into IL

phases via a cation-exchange mechanism and form a stable 1:1 complex with Ag^+ . Recently, calixarene comprising crown ethers have been extensively studied in the IL-extraction system (Chen & Hussey, 2005; Chen, 2007; Luo et al., 2007; Rogers et al., 2004; Tsuda et al., 2006). Luo et al. (Luo et al., 2004b) extracted Cs^{2+} into $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$ using calix[4]arene-bis(tert-octylbenzo-crown-6) (BOBCalixC6) as an extractant by an ion-exchange mechanism. The shorter alkyl chain of the ILs, the less solubilities of BOBCalixC6 in the corresponding ILs and the higher distribution coefficients because the less hydrophobic imidazolium cations have higher ion-exchange capability. The addition of NaBPh_4 , a sacrificial cation exchanger, can decrease the loss of ILs by 24%, as a result, ion exchange take a partial role. MD study of the interfacial behavior in the Cs^+ and Na^+ extraction by a calix[4]arene-crown-6 host (L) into ILs $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$ demonstrated the IL forms a biphasic system with water (Sieffert & Wipff, 2006a, b). Compared with the classical molecular solvent (chloroform), much longer times are needed to “equilibrate” IL systems. There is more intersolvent mixing with the IL than with chloroform especially the water-in-oil content. In the aqueous phase, there is some excess of C_4mim^+ over Tf_2N^- . The LCs^+ complex and L ligand behave differently and they are better solvated by the IL than by chloroform. They are adsorbed at the chloroform interface and adopt well-defined amphiphilic orientations. At the IL interface, they are poorly attracted. The comparison of $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ and $[\text{C}_4\text{mim}][\text{PF}_6]$ of the dry versus humid form of the latter one. They discovered that the importance of humidity. In the $[\text{C}_4\text{mim}][\text{PF}_6]$ -dry as in the $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ liquid, the first solvation shell of the “naked” M^+ ions is composed of solvent anions only, while in the $[\text{C}_4\text{mim}][\text{PF}_6]$ -humid IL, it comprises from one to three solvent anions and about four H_2O molecules. In the LM^+ complexes, the cation is shielded from solvent but still somewhat interacts with a solvent anion in the dry ILs and with water in the humid IL. These results provide a number of arguments explaining the specificity and efficiency of IL based extraction systems. Very recently, Xu et al. found that the bis(2-propyloxy)calix[4]crown-6 (BPC6)/ $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$ system was highly efficient to remove Cs^+ from aqueous solution. A dual extraction mechanism, exchange of BPC6- Cs^+ complex and Cs^+ by C_nmim^+ was mentioned (shown in Figure 22) (Xu et al., 2010).

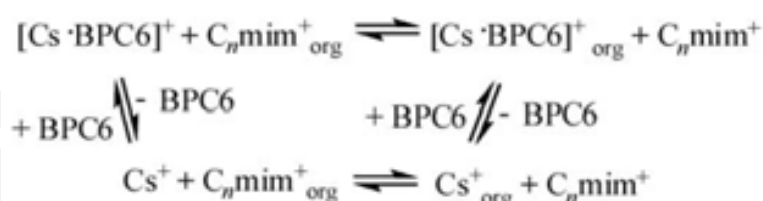


Fig. 22. A dual extraction mechanism for extraction Cs^+ by the BPC6/ $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$ system. Reprinted from Xu et al. (2010).

5.3 Effects of ionic liquids on other supermolecules

The primary role of IL is to maintain good solvent conditions over a very wide temperature range for supramolecular ion gel (Mohmeyer et al., 2006; Noro et al., 2008, 2009). Supramolecular gelation in IL could be used in many fields, such as actuators, polymer electrolytes, membranes, or gate dielectrics for organic transistors. The structures and characteristics of nanohybrids or nanocomposites or self-organized nanotubes can be changed by the assistant of ILs (Gopalan et al., 2009; Li et al., 2009a; Paramasivam et al., 2008; Park et al., 2009b; Wu et al., 2009a). There are two aspects about effects of ILs on these supermolecules,

which influence the system individually or jointly. One is that ILs affect the supermolecules because of the anions and cations of ILs and aromatic structures, which can result in electrostatic interactions, cation- π and/or π - π stacking interactions (Gopalan et al., 2009; Li et al., 2009a; Park et al., 2009a; Park et al., 2009b; Wu et al., 2009a; Zhang et al., 2009). The other is that self-assembly of ILs influence the supermolecules (Gutel et al., 2007; Ma et al., 2009; Xu et al., 2009). The sensitivity of molecularly imprinted polymers (MIPs) can be improved by IL-mediated method (Booker et al., 2006; He et al., 2008a; Wang et al., 2006; Wang et al., 2009). ILs are also used to synthesize other supramolecular host compounds (Scott et al., 2000) and can form different supramolecular networks from other solvents (Pedireddi et al., 2005).

5.4 Effects of ionic liquids on the formation of supramolecular assemblies

As mentioned above, ILs participated in the formation of micelles, microemulsions, liquid crystals and vesicles. In addition, IL also influenced the formation of the supramolecular assemblies as solvents and co-solvents.

The micelle formation of surfactants, such as SDS and Brij-35 in ILs ([C₄mim]Cl and [C₄mim][PF₆]) was first studied by Armstrong and his coworkers (Anderson et al., 2003). The micelle formation is caused by the solvophobic interactions between the hydrocarbon chains of the surfactant molecules just like hydrophobic interactions in aqueous medium. Relative studies on the aggregation of nonionic surfactants in ILs have been reported (Evans et al., 1982; Evans et al., 1983b; Fletcher & Pandey, 2004; Gao et al., 2009b; Li et al., 2008b; Patrascu et al., 2006; Wu et al., 2008). Masahiro et al. (Moniruzzaman et al., 2008) reported the formation of reverse micelles in [C₈mim][Tf₂N] comprising sodium bis(2-ethyl-1-hexyl) sulfosuccinate (AOT) as surfactant with 1-hexanol as a cosurfactant. This formation of aqueous droplets in the IL is attributed to the hydrophobic effects between the AOT tails and the long hydrocarbon chain of IL and the strong tendency of the AOT head group to interact with water. In addition, amphiphilic Pluronic polymers were found to be able to form well defined micelles in IL, the micellization was found to be entropy driving (He et al., 2006; Inoue & Misono, 2008; Ueki et al., 2009; Zhang et al., 2008e).

ILs have also been found to influence the formation of micelles as co-surfactant. Behera et al. (Behera et al., 2007a; Behera et al., 2007b) reported that [C₄mim][PF₆] and [C₄mim][BF₄] participated in the TX-100 micellar phases. It was found that the addition of 30 wt % [C₄mim][BF₄] resulted in decreased micellar size, increased cmc, and decreased N_{agg} , all of which were unchanged in aqueous [C₄mim][PF₆]-TX-100 systems because of the low solubility of [C₄mim][PF₆]. These observations implied an overall unfavorable micellization process when the IL was present. Later, the concentration-dependent dual role of the ILs in altering physicochemical properties of ionic surfactant (SDS, CTAB) was demonstrated (Behera & Pandey, 2007a, b; Beyaz et al., 2004; Lei et al., 2007; Modaressi et al., 2007a; Sifaoui et al., 2007). It is found that ILs acted as a metal salt at low concentrations and participated in the micellar phase with increasing [C₄mim][PF₆] which led to a considerable decrease in the microfluidity of SDS micelles (Behera & Pandey, 2007a, b). ILs also influence the aggregation behavior of Pluronic polymers (Dey et al., 2009; Zheng et al., 2007). Zheng et al. (Zheng et al., 2007) studied the effect of [C₄mim]Br on the aggregation behavior of PEO-PPO-PEO P104 aqueous solution. It suggested that when the concentration of [C₄mim]Br was below 1.232 mol/L, there were P104 micelles in the aqueous solution with [C₄mim]Br embedding to the micellar core, while above this concentration, P104 micelles and [C₄mim]Br clusters coexisted in the system (Figure 23).

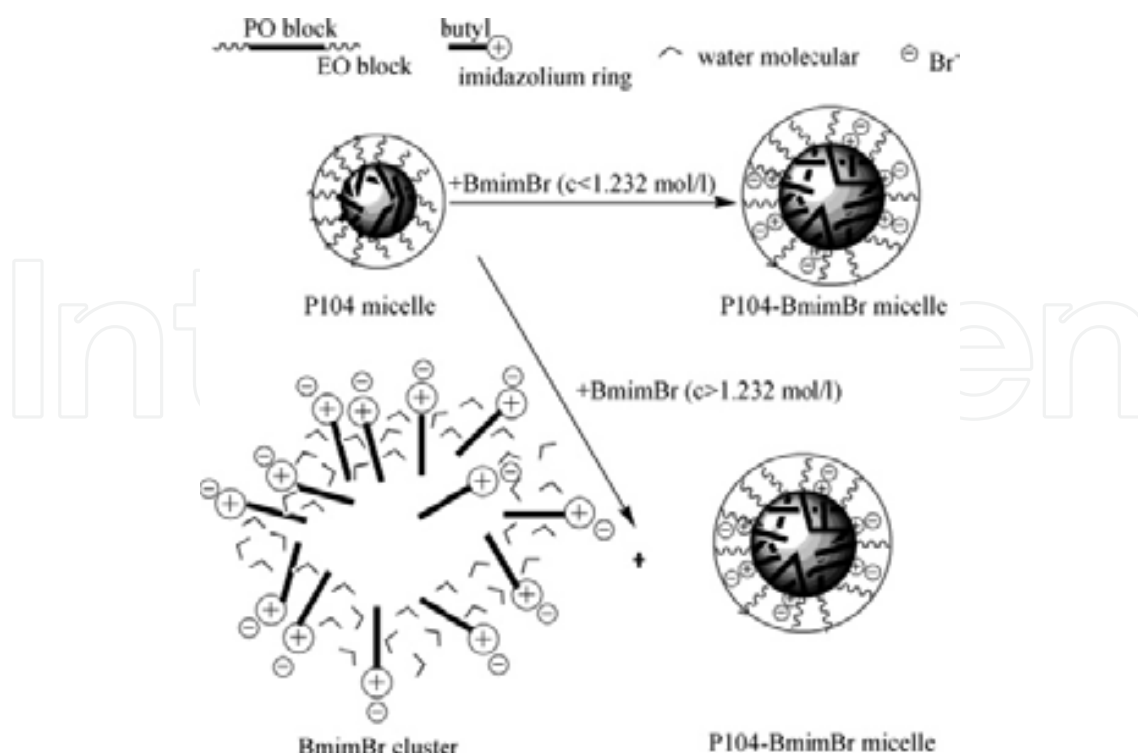


Fig. 23. Schematic illustration of the different types of complexes formed when $[C_4mim]Br$ was added to 5% Pluronic P104 aqueous solution. Reprinted from Zheng et al. (2007).

The formation of liquid crystal in ILs was firstly reported by Evans and co-workers (Evans et al., 1983a) in 1983, which was formed by β,γ -distearoylphosphatidylcholine (DSPC) in EAN. Since then, many studies on the formation of liquid crystals in ILs are reported (Araos & Warr, 2005; Atkin & Warr, 2007; Greaves et al., 2007a, b; Tamuralis et al., 1987; Wang et al., 2004; Zhang et al., 2008a; Zhao et al., 2009b). Nonionic surfactants, C_nE_m , formed lyotropic liquid crystals in EAN and it was found that longer alkyl chains were necessary to drive the formation of liquid crystalline, suggesting that a rich pattern of "solvophobic" self-assembly (Araos & Warr, 2005; Atkin & Warr, 2007). The aggregation behavior of $[C_{16}mim]Cl$ in EAN was also investigated and an additional V_2 (reverse bicontinuous cubic) phase was identified when comparing such a phase behavior with that of the $[C_{16}mim]Cl/H_2O$ binary system (Zhao et al., 2009b). Zhang et al. (Zhang et al., 2008a) reported the aggregation of Pluronic P123 in EAN, which was similar to those observed in H_2O or $[C_4mim][PF_6]$ systems. They attributed the additional V_2 phase in the P123-EAN system to the higher affinity for the hydrophobic PPO blocks to EAN than to water, which might reduce the effective area of the solvophilic headgroup and increase the volume of the solvophobic part.

6. Conclusions

In conclusion, ILs can act as guests to form supermolecules with several kinds of host molecules (i.e., cyclodextrins, cucurbit[n]urils and calixarenes), and can participate the constructing of supramolecular assemblies (i.e., micelles, microemulsions, lyotropic LCs, vesicles and gels). Besides, ILs can affect the formation of supramolecular structures, for example, the formation of polyrotaxanes and polypseudorotaxanes, the formation of the supramolecular structures in the extraction systems based on crown ethers, and so on. It is

also noticed that imidazolium ILs have a three-dimensional supramolecular network with polar and non-polar regions, which can be used as powerful supramolecular receptors. However, the host-guest interaction usually takes place in aqueous solution. In ILs, how do the host molecules interact with guest molecules, and how do ILs affect the interaction? These are two interesting and challenging subjects.

In addition, when ILs are used as solvents, how will the supramolecular structures of ILs themselves affect the formation of supramolecular assemblies. For example, when the surfactant is added into the IL/oil mixture, two cases would happen. If the hydrophobic interactions between oil and surfactant are stronger than the interactions between IL and oils, liquid clathrate can be destroyed and O/IL microemulsions form. Otherwise, a new state would exist instead of O/IL microemulsions. However, in the reference, this field has not been mentioned. Moreover, because trivial water is difficult to be removed and could be included in the supramolecular framework of imidazolium ILs, ILs are not pure, which makes the system more complicated. This supramolecular structure may also affect the formation of supramolecular assemblies. Recently, we noticed that water plays the key role in the formation of IL based microemulsions. A small quantity of water can lead to great change in the phase diagram of IL/TX-100/oil ternary systems. Therefore, the effect of the supramolecular structures of ILs on the formation of supramolecular assemblies is another valuable subject.

Now, these fields of ILs are just beginning to be noticed. With the development of the exploration in these fields, more and more interesting phenomena and important results will be obtained. Thus, the investigation of ILs will encounter a new chance and challenge.

7. Acknowledgements

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8. Abbreviations

18C6	18-crown-6
1P10X	tri-n-decylmethylphosphonium chloride and bromide
ACE	affinity capillary electrophoresis
AdCO ₂ ⁻	adamantylcarboxylate anion
AOT	sodium bis(2-ethyl-1-hexyl) sulfosuccinate
BF ₄ ⁻	tetrafluoroborate anion
BOBCalixC6	calix[4]arene-bis(tert-octylbenzo-crown-6)
BPC6	bis(2-propyloxy)calix[4]crown-6
Bu ₄ N ⁺	tetrabutylammonium cation
C ₃ Br	propyl-(2-hydroxyethyl)-dimethyl-ammonium bromide
Calix-S4	4-sulfonatocalix[4]arene
Calix-S6	4-sulfonatocalix[6]arene
CBn	cucurbit[n]uril
CD(s)	cyclodextrin(s)
cmc	critical micelle concentration
C _n dmim ⁺	1-alkyl-2,3-dimethylimidazolium cation
C _n E _m	alkyl poly-(oxyethyleneglycol) ethers

$[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$	1-alkyl-3-methylimidazolium alkylsulfonate
C_nmim^+	1-alkyl-3-methylimidazolium cation
$(CN)_2N^-$	dicyanamide anion
$C_nOSO_3^-$	alkylsulfate anion
C_nPy^+	1-alkylpyridinium cation
C_nvim^+	1-alkyl-3-vinylimidazolium cation
DBzDA18C6	N, N'-dibenzyl-4, 13-diaza-18-crown-6
DCH18C6	dicyclohexano-18-crown-6
[DDA][NO ₃]	didecyl-dimethylammonium nitrate
DLS	dynamic light scattering
DM- β -CD	heptakis-(2,6-di-O-methyl)- β -CD
DPPC	L-dipalmitoylphosphatidylcholine
DSPC	β , γ -distearoylphosphatidylcholine
DTAB	dodecyltrimethylammonium bromide
EAN	ethylammonium nitrate
FFEM	freeze-fracturing electron microscopy
H2 β DA18C6	β -diketone-substituted diaza-18-crown-6
HP- β -CD	hydroxypropyl- β -CD
HPMBP	1-phenyl-3-methyl-4-benzoyl-5-pyrazolone
HP- α -CD	hydroxypropyl- α -CD
HP- γ -CD	hydroxypropyl- γ -CD
IC	inclusion complex
IL(s)	ionic liquid(s)
ITC	isothermal titration calorimetry
LC(s)	liquid crystal(s)
LCST	lower critical solution temperature
MD	molecular dynamics
NfO ⁻	nonafluorobutanesulfonate anion
O/IL	oil-in-IL
O/W	oil-in-water
OE	oxyethylene
OTos ⁻	tosylate anion
PAF	propylammonium formate
PF ₆ ⁻	hexafluorophosphate anion
PNCM	poly(NIPAAM-co- β -CD Methacrylate)
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
SDS	sodium dodecylsulfate
tat	trans-anti-trans
TBPFO	tetrabutylammonium perfluorooctanoate
Tdec	thermal decomposition temperatures
Tf ₂ N ⁻	bis(trifluoromethylsulfonyl)imide anion
TfO ⁻	trifluoromethanesulfonate anion
TM- β -CD	heptakis-(2,3,6-tri-O-methyl)- β -CD
TPhB ⁻	tetraphenylborate anion
TSIL	task specific ionic liquid

tst	trans-syn-trans
V ₂	reverse bicontinuous cubic phase
XRD	X-ray diffraction

9. References

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