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Various Self-Assembly Behaviors of Amphiphilic Molecules in Ionic Liquids

Bin Dong and Yanan Gao

Additional information is available at the end of the chapter

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1. Introduction

Surfactants can self-assemble into various ordered structures, involving micelles (spherical, rod-like, worm-like, bilayer, and cylindrical), microemulsions (water-in-oil, bicontinuous, oil-in-water), liquid crystals (lamellar, hexagonal and cubic), vesicles (unilamellar, multilamellar, and oligovesicular), gel and so on. These self-assemblies can be demonstrated as a powerful route towards supramolecular objects with novel architectures, functions and properties. Over the recent years, self-assemblies of amphiphilic molecules in ionic liquids (ILs), a class of novel environmentally benign solvents, have attracted much interest and have been intensively investigated. In this chapter, we summarize the known various self-assembled structures of surfactants in ILs, involving micelles, microemulsions, liquid crystals, vesicles and gel. With a rapid growth in the number of publications on these self-assemblies, it appears that in the near future these neoteric self-assemblies are definitely going to be a versatile media in chemical reaction engineering and material chemistry.

It is known that surfactants are amphiphilic molecules with a hydrophilic headgroup and a hydrophobic chain. The dual character of surfactants makes them self-assemble into various aggregations in order to avoid contact between the water and the hydrophobic tail. The hydrophobic tails of surfactants are inclined to point towards the oil phase or hydrophobic domain. The hydrophilic polar headgroups prefer to contact with water. The self-assembly is highly cooperative and is driven by the hydrophobic effect, because the system is inclined to decrease the amount of unfavorable interactions between the hydrophobic tails and water [1]. The surfactant aggregates have different shapes depending on molecular parameters (such as curvature of aggregate surface and the packing parameter) of the surfactant and system variable such as concentration and temperature. Micelles, microemulsions, liquid crystals, vesicles and gel are most common surfactant aggregates in traditional solvents. The driving

force for the structural aggregation is the minimization of the contact of the hydrophobic groups of the surfactants with water. The curvature of aggregate surface and the packing parameter of the surfactant molecule are two important concepts when discussing aggregate shape. The molecular geometry of the surfactant gives rise to a preferred and spontaneous curvature of the aggregate surface [2,3].

The mean aggregate curvature, H , is described as:

$$H = 0.5 \left(1/R_1 + 1/R_2 \right) \tag{1}$$

where R_1 and R_2 are the radii of curvature for a surface in two perpendicular directions. The curvature is 1 when aggregates are sphere. When H is less than 1, ($R_1=\infty, R_2=R$), a cylinder self-assembled structure prefers to form. For a planar bilayer structure, H is 0. Figure 1 shows the mean curvature, H , for three common surfactant self-assembled shapes.

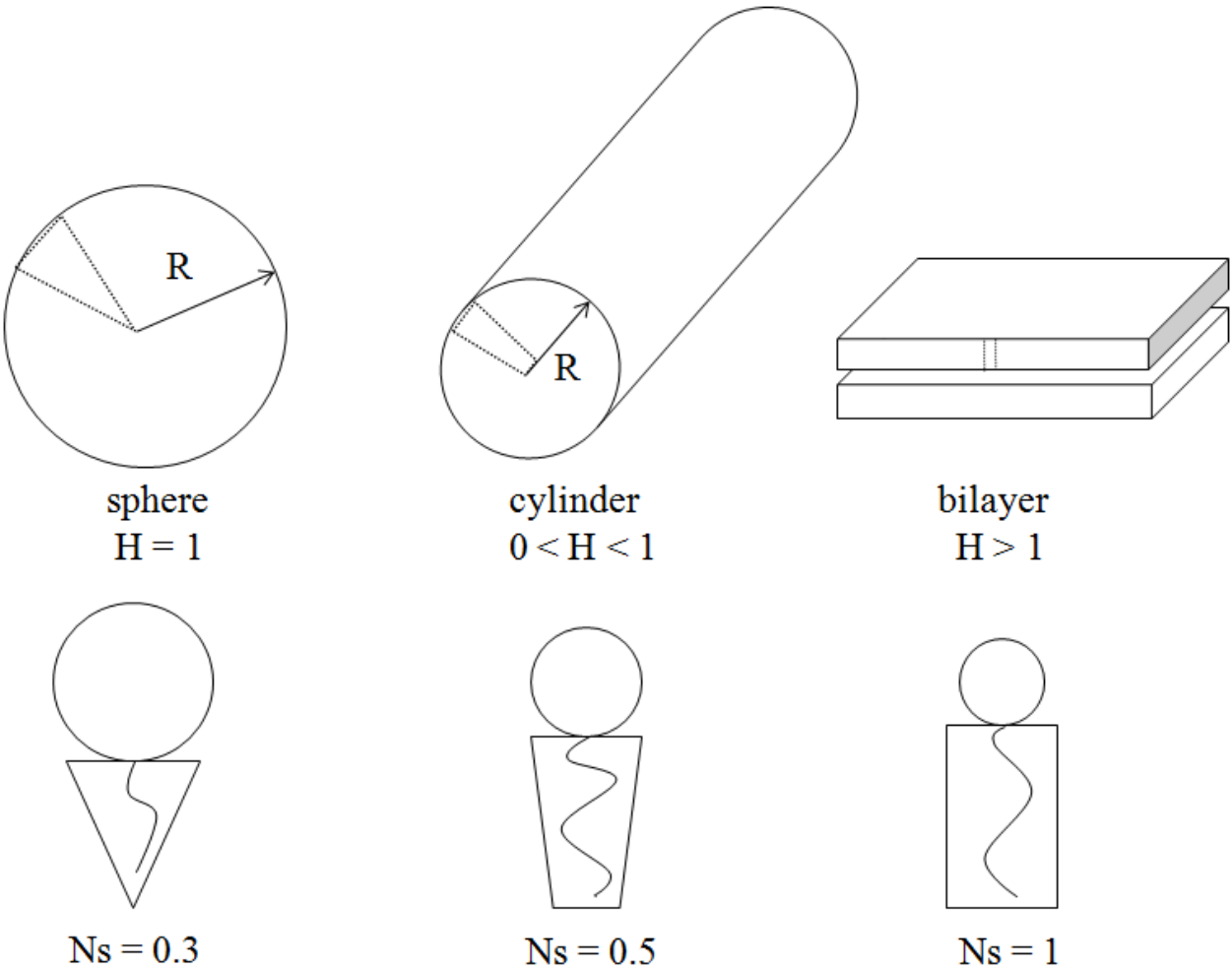


Figure 1. Schematic representation of the mean curvature, H , and the surfactant parameter, N_s , for three common surfactant aggregation shapes: sphere, cylinder and bilayer.

The surfactant parameter, N_s , another important parameter, is relative with the properties of the molecule with the preferred curvature of the aggregates.

$$N_s = v / la_0 \quad (2)$$

where v is the volume of the hydrocarbon chain, l is the length of fully stretched hydrocarbon chain and a_0 is the area per headgroup. The volume of one hydrocarbon chain is evaluated as:

$$v = 0.027 (n_c + n_{Mc}) \quad (3)$$

where n_c is the number of carbon atoms in the hydrocarbon chain, n_{Mc} is the number of methyl groups and l is evaluated as:

$$l = 0.15 + 0.127n_c \quad (4)$$

N_s can reveal the balance between the hydrophobic and hydrophilic parts of the molecules. The relationship between the aggregate shape and surfactant parameter is also shown in Figure 1. If the headgroup of a surfactant is large, this surfactant has a small N_s value and the curvature will be high. In this case, a spherical structure prefers to form. Reversely, a larger N_s value will be obtained if the headgroup of a surfactant is small. Large N_s means a low curvature and cylinders or planar layers are inclined to form.

Ionic liquids (ILs) are a special class of molten salts composed of organic cations and inorganic or organic anions. The melting points of these molten salts are generally below 100°C owing to the large bulk of organic cation that leads to the small lattice energy [4]. ILs have many useful qualities, such as a negligible vapor pressure, nonflammability, high ionic conductivity, wide electrochemical window, and thermal stability [5]. Because of their ultralow vapor pressure, ILs are considered as a possible environmentally acceptable replacements for many volatile organic solvents in chemical reactions [6], separation [7], electrochemical applications [8], and supramolecular self-assembly [9,10]. Of particular recent interest is the combination of self-assembly behaviors of surfactants and ILs. These aggregations can not only overcome the solubility limitations of ILs in immiscible solvents but also provide hydrophobic or hydrophilic nanodomains, thereby expanding potential uses of ILs in microheterogeneous systems as reaction and separation or extraction media [11]. Also, these self-assemblies may have some unknown properties and some potential applications owing to the unique features of ILs and ordered microstructures [12]. ILs as chemical reaction media have been summarized and aggregation behavior has been mentioned [5,13]. In addition, the spatial structure of ILs in itself has been recently reviewed [14]. In this chapter, we present detailed work on various self-assemblies of amphiphilic molecules in ILs for the purpose of informing the readers of the major development in this interesting area. Furthermore, we also have to mention, all self-assembled structures supported by long-chain amphiphilic ILs in non-ILs solvents were not

summarized here, as these amphiphilic ILs only behave in a manner analogous to traditional amphiphilic molecules.

2. Self-assembled micelles in ILs

A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic groups in contact with surrounding water, sequestering the hydrophobic tails in the micelle centre. Micelles only appear when the concentration of surfactant reaches a critical micelle concentration (CMC). That is to say, CMC is the minimum concentration of surfactant molecules required for the formation of micelles at a given temperature. In addition, CMC is also an important parameter to characterize the formation of micelles. When the concentration of surfactants is below the CMC, the surfactant molecules exist as free monomers in solution. The formation of micelles is a spontaneous process. Micelles can be classified into normal micelles and inverse micelles. Normal micelles have a continuous polar phase (mostly water phase) with the polar headgroups of the surfactants pointing towards the bulk solvent and the hydrocarbon groups pointing towards the micelle interior, while for inverse micelles the surfactants have the polar headgroup towards the micelle interior with the hydrocarbon groups pointing towards the continuous oil phase.

Evans et al. first reported the aggregation behavior of alkyltrimethylammonium bromides, alkyipyridinium bromides and nonionic Triton X-100 in a low melting fused salt, ethylammonium nitrate (EAN) over 30 years ago [15,16]. Critical micelle concentrations (CMCs) are determined from surface tension measurements and the aggregation behavior was investigated by classical and quasi-elastic light scattering. The solvophobic behavior of EAN shows a number of similarities with that of water. The results of CMCs, micellar aggregation numbers, second virial coefficients, and hydrodynamic radii are consistent with either a small classical spherical micelle containing only surfactant or a spherical mixed micelle containing surfactant and ethylammonium ions as a cosurfactant. The measured second virial coefficients are almost equal to those calculated for hard spheres and reflect highly screened electrostatic interactions in the totally ionized solvent [16].

However, the study of such self-assembly in ILs did not attract much attention until ILs received more and more interest in recent years. Afterwards, the formation of micelles in ILs, 1-butyl-3-methylimidazolium chloride (bmimCl) and hexafluorophosphate (bmimPF₆) were explored by Armstrong et al [17]. The solvation behavior of the micellar-IL solutions was examined using inverse gas chromatography. They found that the dissolution of many different surfactants in ILs also depressed the surface tension in a manner analogous to aqueous solutions, indicating that there are IL solvatophobic interactions with the hydrocarbon portion of the surfactants. High hydrogen bond basicity was detected for the micelles of Brij 35 and Brij 700 in bmimPF₆. They ascribed this phenomenon to the existence of hydrophilic polyoxyethylene (POE) groups of surfactants, as oxygen atoms of each individual subunit have lone pair electrons that are capable of accepting a hydrogen bond,

therefore enhancing hydrogen bond basicity [17]. The acidity of imidazolium cations of ILs has been raised, C-2 proton of bmimPF₆ is bonded to a carbon that is located between two positively charged nitrogen atoms, and hence C-2 proton is relatively acidic, as a result C-2 proton can accept electronegative oxygen atoms [18]. Therefore, it is deduced that there exist hydrogen bonds between nonionic surfactants and 1-alkyl-3-methylimidazolium cation of ILs. Merrigan et al. have demonstrated that 1-alkyl-3-methylimidazolium cations with attached long fluoros tails act as surfactants and appear to self-aggregate within 1-alkyl-3-methylimidazolium-based ILs [19].

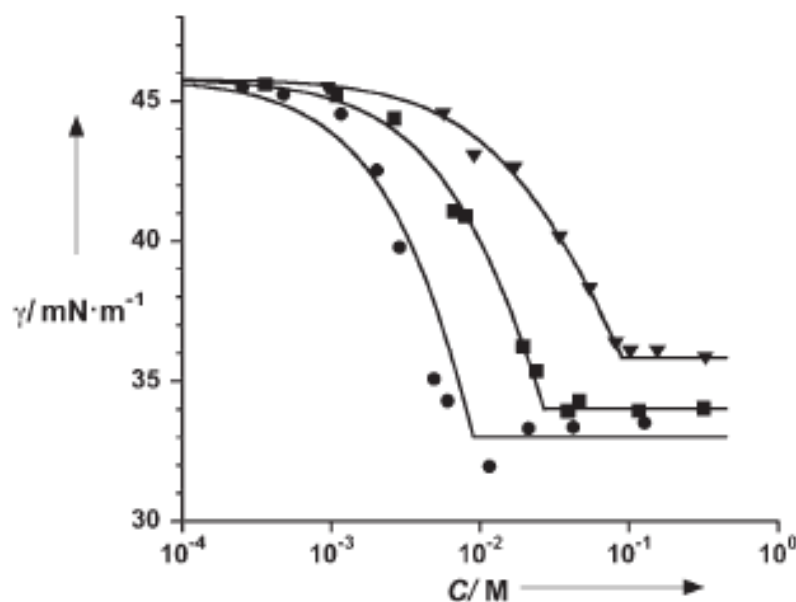


Figure 2. Surface tension (γ) of solutions of C₁₂E₈ (▼), C₁₄E₈ (■) and C₁₆E₈ (●) in bmimBF₄ at 25°C. (Reproduced from Ref.[20], with permission).

Aggregation behavior of a series of alkyl poly-(oxyethyleneglycol) ethers, a class of nonionic surfactants, denoted C_nE_m (n=12-16; m=4-8) in 1-butyl-3-methylimidazolium type ILs with various counter ions [BF₄⁻, PF₆⁻, and bis(trifluoromethylsulfonyl)amide (Tf₂N)⁻] has been investigated [20]. The surface tension of the C_nE_m/bmimBF₄ solution decreased as the surfactant concentration increased, indicating their adsorption at the air/solution interface. Figure 2 shows the changes of surface tension of C_nE_m/bmimBF₄ solution with C_nE_m concentration, a similar phenomenon as in water was observed. It was estimated that the molecular area of the surfactant decreased with increasing hydrophobicity of surfactants. The CMCs were two to four orders of magnitude higher than those in aqueous systems. Dynamic light scattering (DLS) measurements have suggested the presence of molecular aggregates. The hydrodynamic radii in bmimBF₄ were smaller than that in water and close to that in formamide. The anions of ILs were found to have a remarkable effect on the nature of micelles, however the formation mechanism was not discussed in this research [20].

Self-assembly processes of nonionic Brij 76 in bmimBF₄ with changing temperature have been detected by Li et al [21]. Under 30°C, Brij 76 self-assembled as nanofibers and a gel formed; as

temperature increased until 85°C, the mixture was clear solution; at about 90°C, Brij 76 self-assembled as vesicles; at even higher temperature of 110°C, a clouding phenomenon was observed. The Dark-field optical micrographs showing the change of aggregations with temperature are shown in Figure 3. The authors proposed that at room temperature, the 1-alkyl-3-methylimidazolium cation and the anion adsorbed to the POE chain of the Brij 76 via the Coulombic force. The cation was adjacent to the oxygen which had a high electron density and the BF_4^- stacked among the cations. The long alkyl chains interacted with each other through the hydrophobic interaction to make the Brij 76 molecule and bmimBF_4 connect like a “rod”.

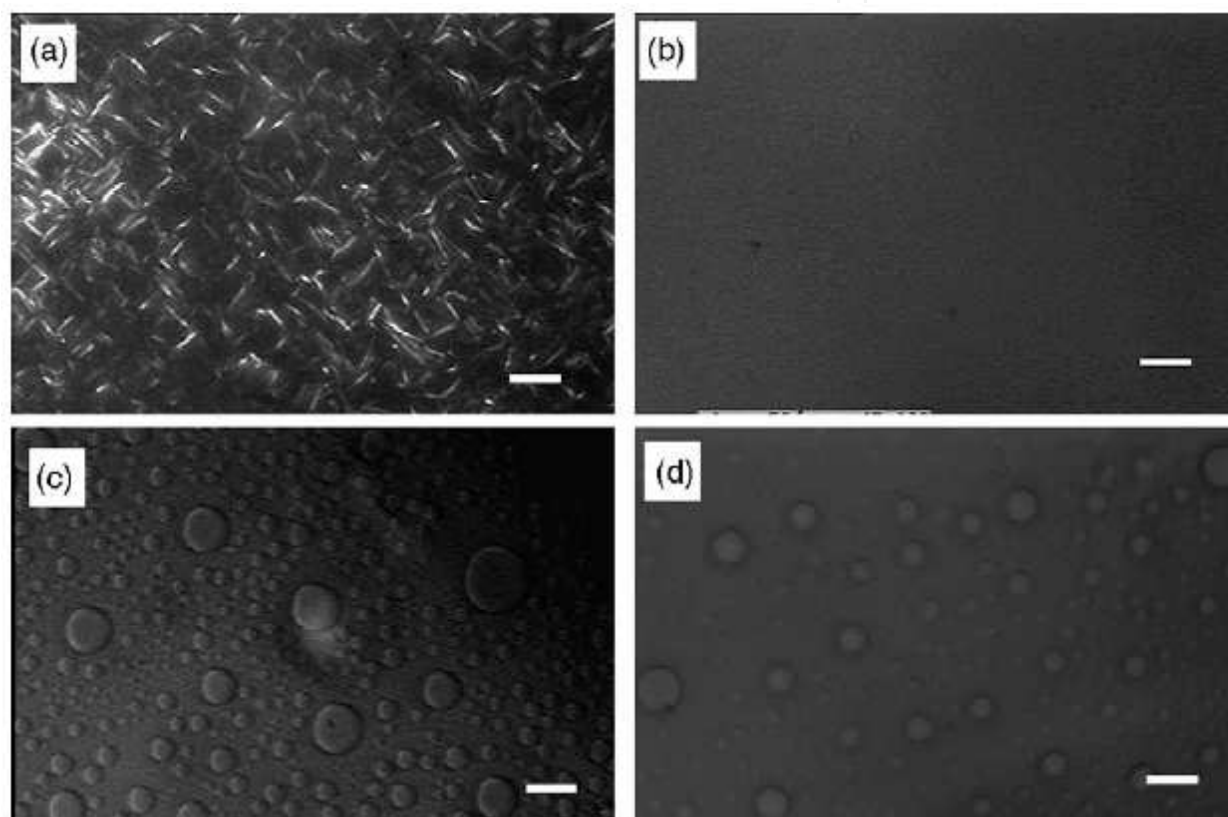


Figure 3. The Dark-field optical micrographs of the surfactant 100 mg Brij 76 dispersed in 1ml bmimBF_4 : (a) 30°C, (b) 60°C, (c) 90°C and (d) 110°C. The scale bar in each image is 10 μm . (Reproduced from Ref.[21], with permission).

Aggregation behaviors of four different alkyl-ammonium nitrates in EAN have been determined by surface tension measurements. The micelles are formed without the increase of molar partial volume meaning that the carbon chain does not perturb the spatial arrangement of the solvent. A theoretical model capable of predicting the CMCs of four alkyl ammonium nitrates in EAN has also been proposed [22]. Moreover, Kunz and coworkers reported that a mixture of two surfactant-like ILs 1-hexadecyl-3-methyl-imidazolium chloride ($\text{C}_{16}\text{mimCl}$) and 1-hexadecyl-3-methyl-imidazolium tetrafluoroborate ($\text{C}_{16}\text{mimBF}_4$) aggregated in EAN. The investigated mixtures are stable up to more than 200°C. The authors attributed this to the electrostatic interactions that do not show a pronounced temperature dependence [23]. This

investigation is much different from the result reported by Li et al [21]. From these results, it can be deduced that in addition to electrostatic interaction, there may be some other interactions between the nonionic surfactants and the 1-alkyl-3-methylimidazolium cation of ILs, such as hydrogen bonds, dipole-induced dipole type of interaction. Among them, one of the forces may dominate in competition under certain condition.

In addition, on the base of the response of solvatochromic probes, the aggregation behavior of few common anionic, cationic, and nonionic surfactants within 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (emimTf₂N) was also investigated. The possible aggregates were formed by all nonionic surfactants (Brij-35, Brij-700, Tween-20, and Triton X-100), while no aggregation was observed for the cationic surfactant cetyltrimethylammonium bromide (CTAB). The anionic surfactant sodium dodecylsulfate (SDS) does not appear to be solubilized within emimTf₂N at ambient conditions [24]. Moreover, Tran and Yu have reported that nonionic surfactants *N*-dodecylsultaine (SB-12), caprylyl sulfobetaine (SB3-10) formed micelles in bmimPF₆ and emimTf₂N [25]. So far, it seems that nonionic surfactants are more inclined to support the micellar aggregations in ILs.

The interaction between the 1-alkyl-3-methylimidazolium type ILs and nonionic surfactants was further proposed by Pandey group. The addition of bmimPF₆ to aqueous nonionic Triton X-100 solutions can alter/modify physicochemical properties of such systems in favorable manner. BmimPF₆ can partition into the Triton X-100 micellar phase both close to the core as well as in the palisade layer of Triton X-100. They suggested the presence of favorable interactions such as hydrogen bonding between C-2 proton of imidazolium cation and ethoxy/hydroxyl, between PF₆⁻ and H of the Triton X-100 hydroxyl terminal, and dipole-induced dipole type of interaction between Triton X-100 phenyl π -cloud and 1-alkyl-3-methylimidazolium cation between bmimPF₆ and Triton X-100 [26]. In addition to emimTf₂N, Triton X-100 was shown to aggregate and form micellar aggregation in bmimBF₄ and bmimPF₆, respectively [27].

Freeze-fracture transmission electron microscopy (FFTEM) showed that the micelles have an irregular droplet shape and they preferred to assemble into larger clusters. ¹H NMR and two-dimensional rotating frame nuclear Overhauser effect (NOE) experiments (2D ROESY) showed that the addition of Triton X-100 destroyed the ion pairs of pure ILs due to the electrostatic interaction between the positively charged 1-alkyl-3-methylimidazolium cation of ILs and the electronegative oxygen atoms of oxyethylene (OE) units of Triton X-100. The electrostatic interaction behaves similar to hydrogen bond that occurred between the OE units of nonionic surfactants and water molecules in aqueous micelles and cooperates with solvophobicity, leading to the formation of IL micelles [27]. The 2D ROESY analysis revealed that the microstructure of Triton X-100-based micelles in ILs is not regular spherical, which accords with the FFTEM image. Similar to the aqueous micellar systems, the hydrophobic interaction or solvophobicity was found to drive the formation of micelles [27].

Moreover, Lodge et al. first studied the self-assembly of block copolymers in ILs [28]. It was shown that four amphiphilic poly((1,2-butadiene)-block-ethylene oxide) (PB-PEO) diblock copolymers, another kinds of nonionic surfactants, aggregated strongly and formed micelles in bmimPF₆. The universal micellar structures (spherical micelle, wormlike micelle, and

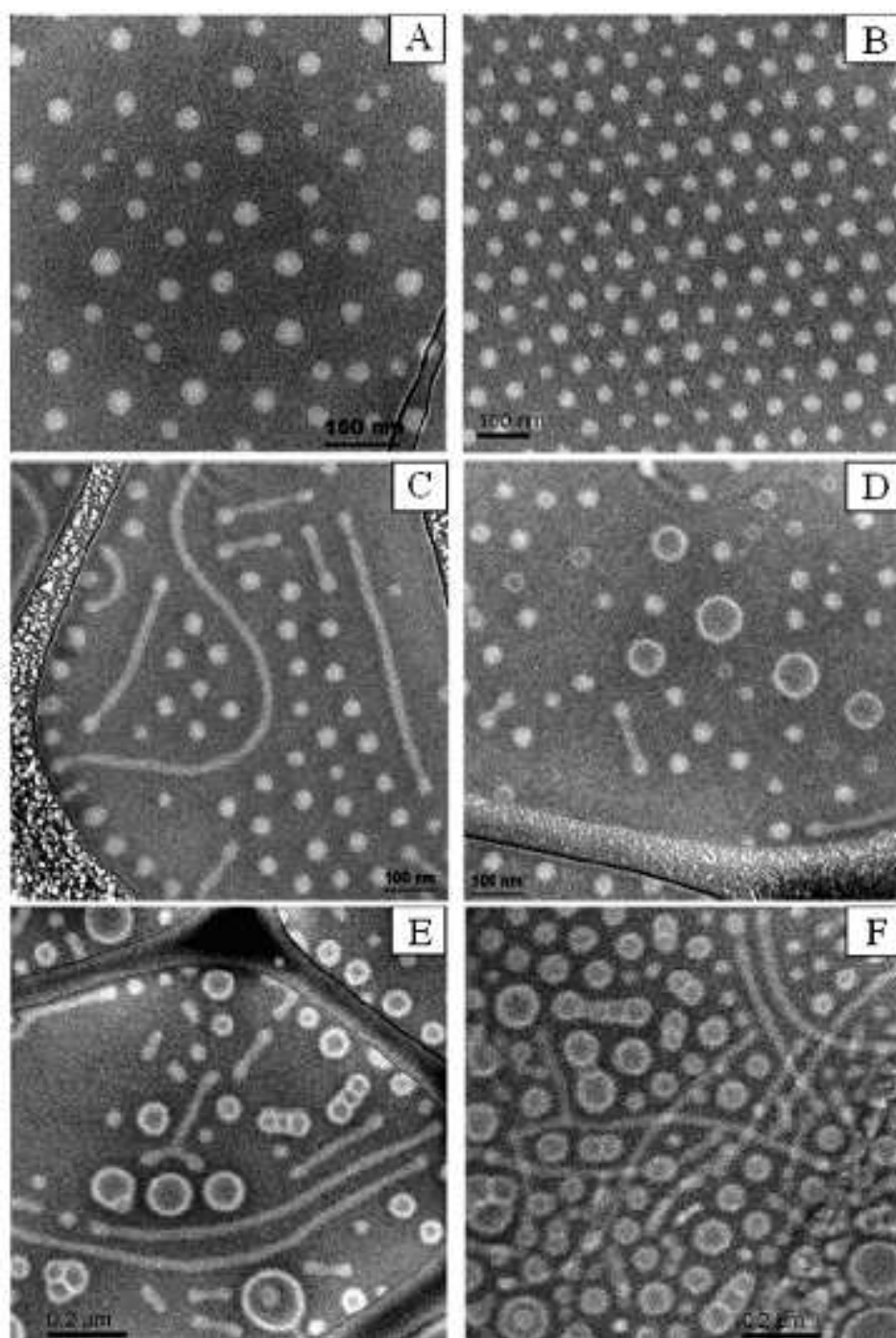


Figure 4. Cryo-TEM images of 1 wt % bmimPF₆ solutions: (A) spherical micelle, BO(9-20) ($f_{\text{PEO}}=0.64$); (B) spherical micelle, BO(9-10) ($f_{\text{PEO}}=0.45$); (C) a coexistence of spherical and wormlike micelles, BO(9-7) ($f_{\text{PEO}}=0.38$); (D) a coexistence of spherical and some vesicles, BO(9-7) ($f_{\text{PEO}}=0.38$); (E) and (F) a coexistence of wormlike micelles and vesicles, BO(9-4) ($f_{\text{PEO}}=0.25$). (Reproduced from Ref.[28], with permission).

vesicle) were all accessed by varying the length of the corona block while holding the core block constant. The nanostructural changes were directly visualized through cryogenic transmission electron microscopy (cryo-TEM) (Figure 4). Compared to aqueous solutions of the same copolymers, bmimPF₆ solutions exhibit some distinct features, such as temperature-

independent micellar morphologies between 25 and 100°C [28]. This is in accordance with the reported aggregation behavior of $C_{16}mimCl$ and $C_{16}mimBF_4$ in EAN by Kunz group [23]. They also found that three polystyrene-block-poly(methyl methacrylate) (PS-PMMA) block copolymers with varying molecular content have been shown to form micelles when dissolved in $bmimPF_6$. A morphological transition from spherical to cylindrical micelles was observed upon reduction of the PMMA volume fraction [29]. The transfer of aggregation structure by changing the surfactant molecular parameters or system variable such as concentration and temperature has been realized in traditional solvents [1].

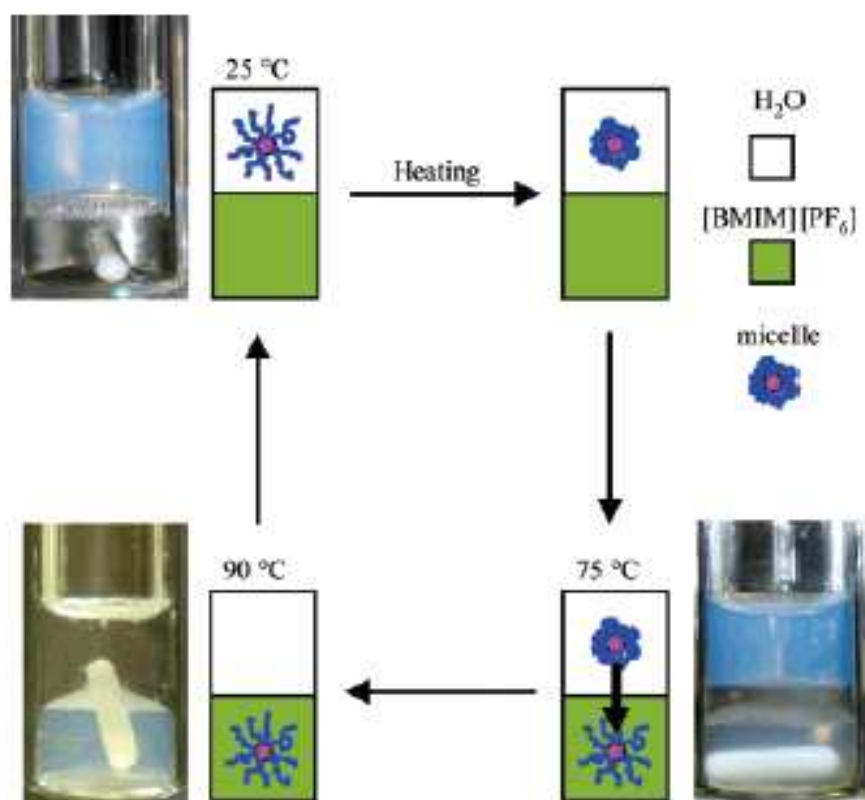


Figure 5. Schematic illustration of the round trip of PB-PEO micelles between $bmimPF_6$ (lower layer) and water (upper layer), accompanied by experimental images at each temperature. (Reproduced from Ref.[30], with permission).

Subsequently, they described an interesting and unusual round trip of the block copolymer micelles between $bmimPF_6$ and water. The reversible micelle transfer between the two media is based on the relative affinity of the two solvents to the corona chains and is triggered by temperature change. This round trip of PB-PEO micelles between $bmimPF_6$ and water with temperature was schematically illustrated in Figure 5. The micelle size and structure are preserved during the reversible transfer process. This phenomenon relies on finding a polymer (PEO in this case) that is nearly equally soluble in two otherwise immiscible solvents. Such a system could find application in transporting hydrophobic reactants/products to/from an IL reaction medium, with only the aqueous phase to handle in the ultimate recovery and purification steps [30]. Subsequently, they reported the reversible micelle transfer between

another hydrophobic ionic liquid, emimTf₂N and water [31]. The transfer was shown to be driven by the deteriorating solvent quality of water for PEO at high temperature, while the ionic liquid remains a good solvent. The transfer temperature could be tuned by adding ionic or nonionic additives to the aqueous phase to change the solvent quality of water for PEO, and by using ILs with different polarities. Moreover, Zheng and his coworkers studied the micellization of three commercially available amphiphilic poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) ethers triblock copolymers, denoted Pluronic L61 (PEO₃PPO₃₀PEO₃), Pluronic L64 (PEO₁₃PPO₃₀PEO₁₃), and Pluronic F68 (PEO₇₉PPO₃₀PEO₇₉) [32]. The three copolymers were found to aggregate and form micelles in either bmimBF₄ or bmimPF₆. The surface tension measurements revealed that the dissolution of the copolymers in ILs depressed the surface tension in a manner analogous to aqueous solutions. The CMCs of three triblock copolymers increase following the order of L61, L64, F68, suggesting that micellar formation was driven by solvatophobic effect. CMC and γ_{cmc} decrease with increasing temperature because hydrogen bonds between ILs and hydrophilic group of copolymers decrease and accordingly enhance the solvatophobic interaction. The thermodynamic parameters ΔG_{m}^0 , ΔH_{m}^0 , ΔS_{m}^0 of the micellization of block copolymers in bmimBF₄ and bmimPF₆ were also calculated. The result revealed that the micellization is a process of entropy driving [32]. From these results, it was proposed that micelles formed in ILs follow the traditional self-assembly rules such as the curvature of aggregate surface and the packing parameter of the surfactant molecule.

The properties of self-assembled micelles in ILs have been investigated by Sarkar and his coworkers [33]. The solvent relaxation dynamics is slower in bmimPF₆-Brij micelles as compared to neat bmimPF₆. The steady increase in the solvent relaxation time with addition of the surfactant is ascribed to increase in viscosity of the solution. However, the slowing down in the solvation time on going from neat IL to IL confined micelles is much smaller compared to that on going from water to water confined micellar aggregates. The fast component originates from the translational motion of the anions and does not depend on viscosity. The magnitude of the fast component increases due to the hydrogen bonds between the -OH group of the surfactant and the PF₆⁻ ions. The increase in the rotational relaxation time of the probe after formation of the micelles in bmimPF₆ is significantly smaller than the increase in aqueous micelles. The higher rotational relaxation time in the IL-surfactant mixture is attributed to the increase in the viscosity of the solution [33]. They also studied the solvent and rotational relaxation of coumarin 153 (C-153) in bmimBF₄ and bmimBF₄ confined in C₁₂E₈ and C₁₄E₈ formed micelles, respectively. In the bmimBF₄-C₁₄E₈ micelle, they have observed only a 22% increase in solvation time compared to neat bmimBF₄, whereas in the bmimBF₄-C₁₂E₈ system, about 57% increase was observed in average solvation time due to micelle formation. However, the slowing down in solvation time on going from neat IL to IL-confined micelles is much smaller compared to that on going from water to water confined micellar aggregates. The 22-57% increase in solvation time is attributed to the slowing down of collective motions of cations and anions in micelles. The rotational relaxation times becomes faster in both the micelles compared to neat bmimBF₄ [34].

3. Self-assembled microemulsions in ILs

Microemulsions are the thermodynamic stable colloid mixtures consisting of at least two immiscible solvents stabilized by an adsorbed surfactant film at the liquid-liquid interface and have a tendency to solubilize chemical species in their core and thus have the potential to function as microreactors. Recently, ILs have been used to substitute for traditional organic solvents or water to create a novel IL microemulsion. Han and coworkers first reported that bmimBF_4 can act as polar nanosized droplets dispersed in a continuous cyclohexane with the aid of nonionic surfactant Triton X-100 [12]. The microstructure and morphology of the microemulsion droplets were detected by DLS and freeze-fracture electron microscopy (FFEM). The diameters of the aggregates increase from about 15 nm to 1 μm as $[\text{bmimBF}_4]/[\text{Triton X-100}]$ molar ratio, R , varies from 0.2 to 1.5. The regular swell behavior of the bmimBF_4 -in-cyclohexane IL reverse microemulsion is in accordance with the traditional water-in-oil (W/O) microemulsions, indicating that these unusual systems behave akin to common W/O microemulsions. FFEM revealed that a droplet structure of the bmimBF_4 -in-cyclohexane microemulsion which takes the same shape as "classic" water-in-oil (W/O) microemulsions. Eastoe et al. have also investigated the same microemulsion system by small-angle neutron scattering (SANS) [11]. The result showed a regular increase in droplet volume as micelles were progressively swollen by the added bmimBF_4 , which is in consistent with the measurements of DLS and FFEM reported by Han et al. The SANS data have been treated in accordance with an ellipsoid form factor, and the ellipsoid model gave the best statistical fits, even compared to polydisperse spherical particles. The predicted ellipsoid structure is in accordance with the FFEM images to a large extent.

Recently, the formation mechanism of the bmimBF_4 -in-*p*-xylene reverse IL microemulsion has been also proposed by Zheng's group [35]. The authors discovered that the terminal hydroxyl stretching of Triton X-100 gradually shifts to a high-frequency region of the FTIR spectrum with increasing bmimBF_4 content because the hydrogen bonds between hydroxyl and oxyethylene (OE) units of Triton X-100 were weakened by the formation of electrostatic attraction between the electronegative oxygen atoms of the OE units and the positively charged imidazolium cation of bmimBF_4 . The conclusion was further confirmed by simulating the hydrophilic OE units of Triton X-100 using polyethylene glycols-(PEGs)-600 and polyethylene glycols-(PEGs)-1000 as substitutes. This electrostatic interaction has caused the proton signals of H-2, H-4, and H-5 of bmimBF_4 shift downfield. The downfield shift experienced by these protons is because, with increasing bmimBF_4 content to the microemulsion, the fraction of Triton X-100 in the system is decreased, the number of oxygen atoms attracting imidazolium ring is accordingly decreased. The electropositivity of the imidazolium cation is relatively enhanced, as a consequence the hydrogen atoms on the imidazolium ring are deshielded and resonate in a downfield position [35].

The effect of polyvinylpyrrolidone (PVP) on the microstructure of IL microemulsion has also been investigated [36]. It was found that small amounts of bmimBF_4 solution containing PVP destroyed the initial Triton X-100/cyclohexane micellar structure, while successive addition of the solution again leads to the IL microemulsion formation [36]. The similar result was also

observed for the Triton X-100/benzene/bmimBF₄, Triton X-100/toluene/bmimBF₄ systems [37, 38]. This phenomenon suggests that the IL microemulsion formation cannot be simply regarded as the swelling of initial micelle by bmimBF₄. The major driving force for the IL microemulsion formation may be the weak electrostatic attraction between the electronegative oxygen atoms of OE units of nonionic surfactants and positively charged imidazolium cation. Just due to the weak electrostatic interaction, the required amount of nonionic surfactants to support the microemulsion formation is relatively large compared to traditional microemulsions, as has been mentioned by Eastoe and Atkin [11,39]. This conclusion has been further confirmed by the recent observation that only C-2 proton, C-4 proton, and C-5 proton of bmimBF₄ and protons of all OE units of nonionic surfactant remarkably shift in ¹H NMR spectroscopy [40].

Moreover, it was reported that water has a great effect on the IL-in-benzene microemulsions. The added water molecules mainly behaved as bound water and trapped water in the palisade layers of the bmimBF₄-in-benzene microemulsion. A hydrogen binding network consisting of imidazolium cations and H₂O, BF₄⁻ anion and H₂O, H₂O and H₂O, as well as the electronegative oxygen atoms of the OE units of Triton X-100 and H₂O was bridged in the palisade layers. The hydrogen binding network is much stronger than the weak electrostatic attraction between the positively charged imidazolium cation and the electronegative oxygen atoms of OE units, which was considered as the driving force of IL microemulsion formation. The palisade layers of the IL microemulsion therefore become more firm and thus increase the stability of the microemulsion [37,41]; whereas for the bmimBF₄-in-cyclohexane IL microemulsion system, DLS revealed that the size of microemulsion droplets decreased remarkably with increasing water content although water is often used as a polar component to swell reverse microemulsions [42]. It was deduced that the number of microemulsion droplets was increased which was confirmed by conductivity measurements. ¹H NMR along with two-dimensional rotating frame NOE experiments (2D ROESY) further revealed that water molecules were mainly located in the periphery of the polar core of the microemulsion droplets and behave like a chock to be inserted in the palisade layer of the droplet. This increased the curvature of the surfactant film at the IL/cyclohexane interface and thus led to the decrease of the microemulsion droplet size. A schematic diagram illustrating the microstructural change of the bmimBF₄-in-cyclohexane microemulsion before and after adding water was shown in Figure 6. The order of surfactant molecules arranged in the interface film was increased and thus induced a loss of entropy. Isothermal titration calorimetry (ITC) indicated that an enthalpy increase compensates for the loss of entropy during the process of microstructural transition. Water decreasing the size of IL microemulsion droplets has also been found by DLS measurements when Bhattacharyya and coworkers studied the solvation dynamics of Triton X-100/1-pentyl-3-methylimidazolium tetrafluoroborate (pmimBF₄)/benzene ternary IL microemulsion system [43]. In the IL microemulsion, the surfactant Triton X-100 molecules aggregate in form of a nonpolar peripheral shell around the polar pool of IL. The microenvironment in such an assembly varies drastically over a short distance. They found that the solvation dynamics is slower than that in the IL microemulsion without water, which is ascribed to the smaller size of the water-containing microemulsion [43].

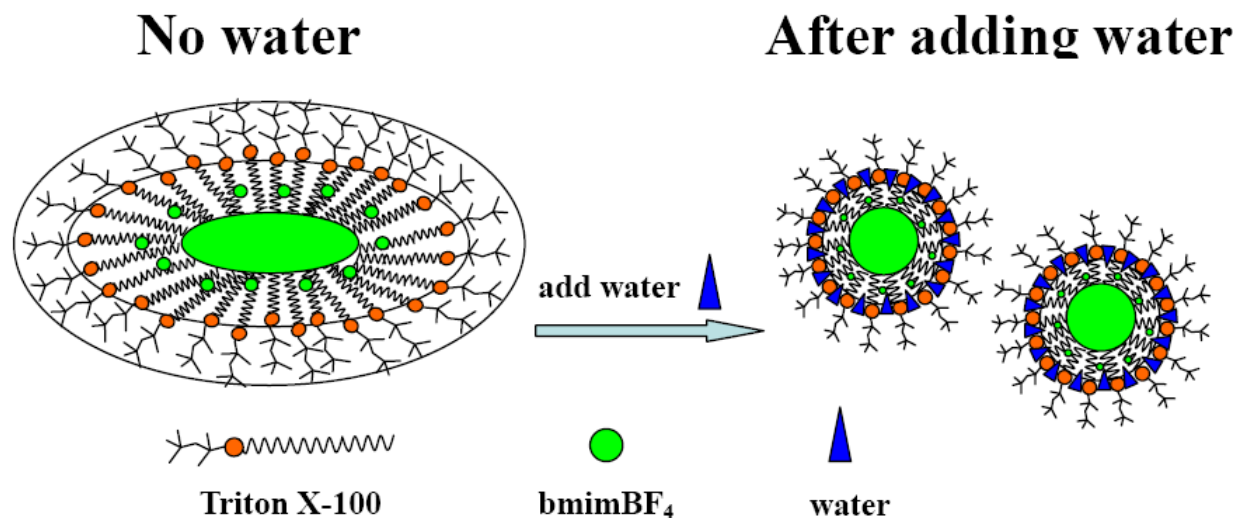


Figure 6. A schematic diagram of the bmimBF_4 -in-cyclohexane microemulsion. A large elliptical droplet structure was presumed in the absence of water and the addition of water may result in the appearance of more small-size spherical microemulsion droplets. (Reproduced from Ref.[42], with permission).

In addition, Zheng and his coworkers found an interesting IL-in-base microemulsion, in which triethylamine acts as either organic solvent or Lewis base. The added water molecules mainly bond the continuous triethylamine to form a surrounding OH^- basis environment [44]. Some of OH^- ions may enter the palisade layers of the IL microemulsions and a continuous basic interface was created. The unique solubilization behavior of water makes it possible to use the IL microemulsion as a template to prepare metal hydroxides and their corresponding oxides materials. Furthermore, the micropolarities of bmimBF_4 /Triton X-100/toluene IL microemulsions were also studied by Zheng's group by UV-Vis spectroscopic analyses [38]. The results showed that the IL pools of the microemulsion possessed a relatively fixed polar microenvironment. In the pools, metal salts $\text{Ni}(\text{NO}_3)_2$, CoCl_2 , CuCl_2 , and biochemical reagent riboflavin could be solubilized, indicating that the IL/O microemulsions have potential application in the production of metallic or semiconductor nanomaterials, and in biological extractions or as solvents for enzymatic reactions. Also, Zheng et al. investigated the phase behavior of the bmimBF_4 /Triton X-100/toluene ternary system [45]. Three different microstructures: the bmimBF_4 -in-toluene, bicontinuous, and toluene-in- bmimBF_4 microemulsion were successfully identified on the basis of the percolation theory by using toluene as the titration phase. The feasibility of the conductivity method was further proved by cyclic voltammetry experiments. In addition, an environmentally friendly IL microemulsion has also been prepared by using a common hydrophobic IL, bmimPF_6 as a replacement of organic solvents [46,47]. Both Triton X-100 and nonionic surfactant Tween-20 support the formation of such IL microemulsion. The hydrodynamic diameter (D_h) of the Triton X-100 based bmimPF_6 -in-water microemulsions is nearly independent of the water content but increases with increasing bmimPF_6 content due to the swelling of the micelles, which accords with the traditional microemulsions. The UV-Vis spectroscopy further confirmed the existence of water domains in the water-in- bmimPF_6 microemulsions [47]. It was revealed that this environmental friendly microemulsion can

solubilized both metal salts and biological molecules, also showing its potential application in nanomaterial, biological extraction or enzymatic reaction fields [46].

Han and coworkers also discovered that bmimPF_6 can also be used as polar nanosized droplets dispersed in toluene [48]. Electrical conductivities of the system with different R ($[\text{bmimPF}_6]/[\text{Triton X-100}]$ molar ratio) values were determined, and the results were used to locate the sub-regions of the single-phase microemulsion. The aggregate size of the reverse microemulsion of bmimPF_6 -in-toluene was determined using small-angle X-ray scattering (SAXS). The results showed that the size depended markedly on the R values. The effect of a compressed CO_2 gas on the properties of reverse micellar solutions with IL polar cores was also studied. It was revealed that compressed CO_2 could enhance solubilization of bmimBF_4 in the reverse micelles considerably at suitable pressures, and formation of the reverse micelles could be controlled easily by pressure. Increase of CO_2 pressure resulted in the decrease of the micellar sizes at fixed R values. Phase behavior study, UV-vis and SAXS techniques were used to investigate the effect of bmimBF_4 on the size and micropolarity of the reverse microemulsions formed by nonionic surfactant Surfynol-2502 (SF) in SC CO_2 [49]. The effect of a compressed CO_2 gas on the properties of reverse microemulsion solutions with bmimBF_4 as polar cores has been investigated. It was found that compressed CO_2 could enhance solubilization of the IL in the reverse microemulsions considerably at suitable pressures, and formation of the reverse microemulsions could be controlled easily by pressure [50].

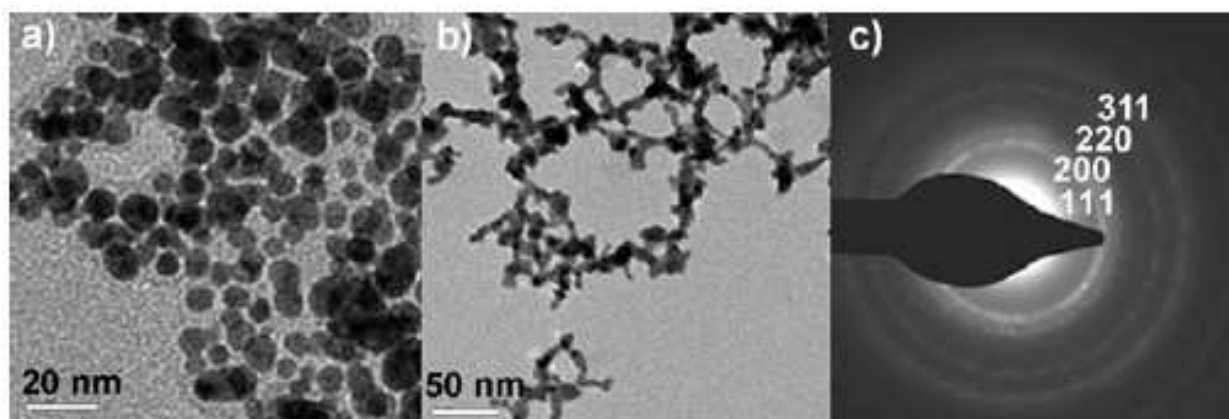


Figure 7. TEM images and electron-diffraction pattern of Au nanoparticles prepared by the RESOLV method at 308.2 K and 20.00 MPa; $[\text{N-EtFOSA}] = 0.060 \text{ g mL}^{-1}$, $[\text{TMGA}]/[\text{N-EtFOSA}]$ molar ratio, $w = 0.41$. a) Weight ratio of HAuCl_4 to TMGT, i.e., $W_{\text{HAuCl}_4}/W_{\text{TMGT}} = 0.01$; b) $W_{\text{HAuCl}_4}/W_{\text{TMGT}} = 0.04$; c) electron-diffraction pattern of the Au particles in (b). (Reproduced from Ref.[53], with permission).

Besides, Han et al. also reported that bmimPF_6 and immiscible ethylene glycol can form droplet and bicontinuous microemulsions in the presence of Triton X-100 [51]. The vapor pressures of ethylene glycol, bmimPF_6 , Triton X-100 are all very low at ambient temperature. Thus, a nonvolatile IL microemulsions was created. Subsequently, they found that bmimPF_6 can be dispersed in another hydrophilic IL propylammonium formate (PAF) with the aid of surfactant AOT. A nonvolatile IL-in-IL (bmimPF_6 -in-PAF) microemulsions is formed [52]. This kind of microemulsions may have potential applications with some advantages due to the water-free

and nonvolatile natures. Very recently, they also discovered that N-ethyl perfluorooctylsulfonamide ($\text{C}_2\text{H}_5\text{NH}\text{SO}_2\text{C}_8\text{F}_{17}$; N-EtFOSA) can form reverse microemulsions in supercritical CO_2 with 1,1,3,3-tetramethylguanidinium ($[(\text{CH}_3)_2\text{N}]_2\text{C}=\text{NH}_2^+$) acetate (TMGA), 1,1,3,3-tetramethylguanidinium lactate (TMGL), and 1,1,3,3-tetramethylguanidinium trifluoroacetate (TMGT) domains [53]. The combination of supercritical CO_2 and ILs is interesting from academic, environmental and practical points of view as the systems may combine some advantages of the two fluids. The reverse microemulsion can solubilize salts, such as methyl orange, CoCl_2 , and HAuCl_4 . To demonstrate the application of reverse micelles with IL domains, they prepared gold particles by a process known as rapid expansion of a supercritical solution into a liquid solvent (RESOLV). A CO_2 /N-EtFOSA/TMGT reverse micellar solution containing HAuCl_4 was expanded into a solution of NaBH_4 in ethanol. Spherical Au nanoparticles were formed at a low concentration and an Au network was obtained at a higher concentration of HAuCl_4 . The electron-diffraction pattern of the Au networks shows that the polycrystalline material corresponds to standard face-centered-cubic Au. TEM images and electron-diffraction pattern of Au nanoparticles prepared by the RESOLV method at 308.2 K and 20.00 MPa are shown in Figure 7.

The properties of the IL microemulsions have been intensively studied by Sarkar and coworkers. For instance, the interaction of water with bmimPF₆ in water-in-bmimPF₆ microemulsion has been probed by solvent and rotational relaxation of C-153 and coumarin 490 (C-490) as probes [54]. The rotational relaxation and average solvation time of C-153 and C-490 gradually decrease with increasing water content of the microemulsions as the size of the microemulsion increases and consequently the mobility of the water molecules also increases. Moreover, the interaction of bmimPF₆ with water in the bmimPF₆-in-water microregions of the microemulsions, has also been studied by the dynamics of solvent and rotational relaxation of C-153 and coumarin 151 (C-151) [55]. In the case of C-153 with an increase in the bmimPF₆ content in the microemulsions the change in the solvent relaxation time is small. The rotational relaxation time of C-153 also remains the same with an increase in the bmimPF₆/Triton X-100 ratios. This means that the position of C-153 remains the same, and C-153 may reside at the interface of these microemulsions. However, in the case of C-151, with an increase in bmimPF₆/Triton X-100 ratios, it was shown that the slow component of the solvation time gradually decreases, the fast component gradually increases, and the rotational relaxation time gradually increases. Therefore, the C-151 molecules gradually shifted to the core of the microemulsions.

Microemulsions consisting of nonionic C_nE_m surfactants, alkanes, and EAN have been prepared and characterized [39]. Studies of phase behavior reveal that EAN microemulsions have many features in common with corresponding aqueous systems, the primary difference being that higher surfactant concentrations and longer surfactant chains are required to offset the decreased solvophobicity of the surfactant molecules in EAN compared with water. The response of the EAN microemulsions to variation in the length of the alkane, surfactant headgroup, and surfactant chain has been found to parallel that observed in aqueous systems in most instances. EAN microemulsions exhibit a single broad SAXS peak, like aqueous systems. These are well described by the Teubner-Strey model. A lamellar phase was also

observed for surfactants with longer chains at lower temperatures. The scattering peaks of both microemulsion and lamellar phases move to lower wave vector on increasing temperature. This is ascribed to a decrease in the interfacial area of the surfactant layer. Phase behavior, SAXS, and conductivity experiments have allowed the weakly to strongly structured transition to be identified for EAN systems [39].

4. Self-assembled liquid crystals in ILs

In 1983, Evans et al. investigated that β,γ -distearoylphosphatidylcholine (DSPC) can form liquid crystals in EAN by polarized microscopy and SAXS [56]. The $L_{\beta'} \rightarrow P_{\beta'} \rightarrow L_{\alpha}$ transitions with increasing temperature are present in analogy with the behavior of DSPC in water. For a 1:1 (by weight) mixture the d spacing for the L_{α} phase is 63 Å, and the surfactant headgroup area is 76 Å². A transition involving a subgel to liquid crystalline transition was observed for L-dipalmitoylphosphatidylcholine (DPPC) bilayers in EAN. This type of transition has not been previously observed for DPPC multilamellar arrays in water [57]. Also, the phase transitions for dipalmitoylphosphatidylethanolamine (DPPE) dispersed in EAN were examined using differential scanning calorimetry (DSC) and time-resolved x-ray diffraction. Lamellar (L_{α}) to hexagonal (H_1) phase transition was observed when using time-resolved x-ray diffraction but not when using calorimetry. The presence of EAN stabilizes the existence of the H_1 phase in DPPE by its influence on the bilayer interfacial properties, primarily on the area per lipid headgroup [58].

The stability of a variety of lyotropic liquid crystals formed by a number of POE nonionic surfactants in EAN was also surveyed and reported. The pattern of self-assembly behavior and mesophase formation is strikingly similar to that observed in water, even including the existence of a lower consolute boundary or cloud point. The only quantitative difference from water is that longer alkyl chains are necessary to drive the formation of liquid crystalline mesophases in EAN, suggesting that a rich pattern of "solvophobic" self-assembly should exist in this solvent [59].

Besides, Chen and coworkers reported that nonaqueous lyotropic liquid crystalline phases of an amphiphilic triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$) formed in $bmimPF_6$ [60]. A hexagonal liquid crystal phase (H_1) formed at 38-52% of P123 in $bmimPF_6$, while at 65-87% of P123, the SAXS peak positions accord with the ratio 1:2:3, indicating a lamellar phase (L_{α}). A schematic diagram of formation mechanism of the liquid crystal was shown in Figure 8. They proposed that the strong solvophobic interaction between IL and hydrophobic parts of surfactant; hydrogen bonds between the end group of EO block and PF_6^- anion; hydrogen bonds between the cation moiety ($-N^+$) of IL and the lone pairs on oxygen atoms of EO groups may favor the appearance of long-range ordered structures. Therefore, the possible structural model of organized P123 assembly in $bmimPF_6$ should be similar to that of aqueous systems, that is, polar domains are formed with PEO blocks extending into the IL and PPO blocks form apolar or solvophobic domains [60].

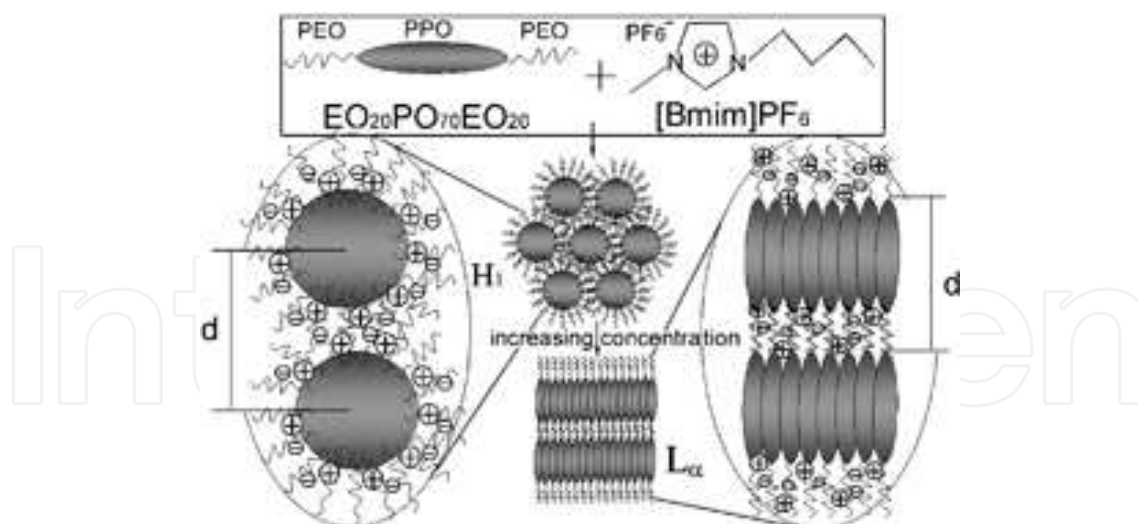


Figure 8. Schematic diagram of formation mechanism of the liquid crystal consisting of P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) in bmimPF_6 . (Reproduced from Ref.[60], with permission).

Recently, Drummond group investigated forty new surfactant-protic ionic liquids (PIL) systems. On the basis of high throughput surfactant-PIL penetration scans, they found that lamellar, inverse hexagonal, and bicontinuous cubic phases can exist as thermodynamically stable phases in excess PIL in select surfactant-PIL systems. Changes to the cation and anion can be used to modify the liquid crystalline phases [61]. They also discovered that PILs can mediate solvent hydrocarbon interactions and promote amphiphile self-assembly. The main lyotropic liquid crystal phases including hexagonal, cubic, and lamellar phases are observed in the CTAB-PIL systems, Amphiphile self-assembly in PILs has been interpreted in terms of a solvophobic driving force (analogous to the hydrophobic effect in water), with the formed aggregate structures being the result of both local molecular and global aggregate packing constraints [62].

The local sites of two different ILs: hydrophobic bmimPF_6 and relatively hydrophilic bmimBF_4 in nonionic Brij 97 formed hexagonal liquid crystalline were analyzed by SAXS, rheological techniques and polarizing optical microscopy [63]. Hydrophobic bmimPF_6 is dominantly penetrated between the OE chains of surfactant molecules, whereas hydrophilic bmimBF_4 is mainly located in the water layer of hexagonal phases. The strength of the network of hexagonal phase formed in the Brij 97/water/ bmimBF_4 system is appreciably stronger than that of the Brij 97/water/ bmimPF_6 system, indicated by the smaller area of the surfactant molecule at the interface and the higher moduli (G' , G''). Temperature has a converse effect on the lattice parameters of the two hexagonal phases. Decrease in temperature results in a decrease in lattice spacing for the bmimBF_4 system but an increase in lattice spacing for the bmimPF_6 system [63].

Very recently, the aggregation behaviors of a Gemini surfactant $[\text{C}_{12}\text{H}_{25}(\text{CH}_3)_2\text{N}^+(\text{CH}_2)_2\text{N}^+(\text{CH}_3)_2\text{C}_{12}\text{H}_{25}]\text{Br}^-_2$ (12-2-12) in two protic ionic liquids (PILs), propylammonium nitrate (PAN) and butylammonium nitrate (BAN), were investigated by Chen et al [64]. Compared to those in EAN, the minor structural changes with only one or two methylene units ($-\text{CH}_2-$) increase

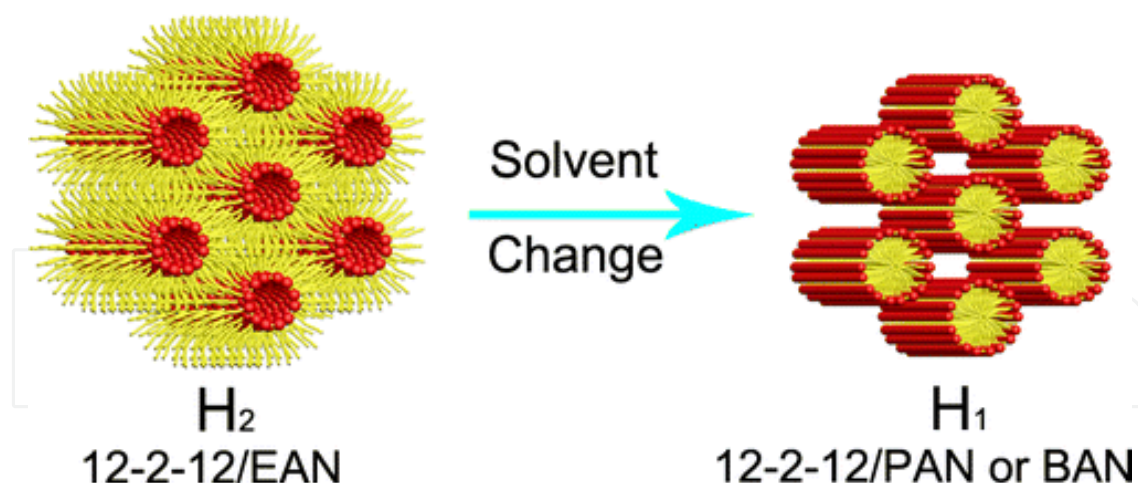


Figure 9. Phase transition of a quaternary ammonium gemini surfactant induced by minor structural changes of protic ionic liquids. (Reproduced from Ref.[64], with permission).

in cationic chain length of PIL, result in a dramatic phase transition of formed aggregates (Figure 9). The critical micellization concentration was increased in PAN, while no micelle formation was detected in BAN. A normal hexagonal phase was observed in the 12-2-12/PAN system, while the normal hexagonal, bicontinuous cubic, and lamellar phases were mapped in the 12-2-12/BAN system. Such aggregation behavior changes can be ascribed to the weaker solvophobic interactions of 12-2-12 in PAN and BAN.

5. Self-assembled vesicles and gels in ILs

Hao and coworkers reported the self-assembled surfactant vesicles formed by $Zn(OOCCH_2C_6F_{13})_2$ in $bmimBF_4$ or by mixtures of $C_{14}DMAO$ and $Zn(OOCCH_2C_6F_{13})_2$ with a $\chi_{C_6F_{13}CH_2COO^-} = 0.18$ in $bmimPF_6$ [65]. Well-defined self-assembled surfactant bilayer vesicles of $Zn(OOCCH_2C_6F_{13})_2$ in $bmimBF_4$ were identified by negative-staining TEM.

As shown in Figure 10A, the well-defined bilayer vesicles are clearly visible and the diameters of the nanospheres range from about 30 to more than 90 nm. Negative-staining TEM and FFEM (Figure 10B,C) also revealed that the mixed solutions of $C_{14}DMAO$ and $Zn(OOCCH_2C_6F_{13})_2$ in $bmimPF_6$ displayed the same self-assembled aggregation behavior as $Zn(OOCCH_2C_6F_{13})_2$ in $bmimBF_4$. The diameters of the aggregation were about 20 to 150 nm, and multilamellar vesicles were visible in the FFEM image. Also, clusters of nanospheres could be seen in the negative-staining TEM image.

Kimizuka developed the ether-containing ILs which are capable of dissolving carbohydrates such as β -D-glucose, α -cyclodextrin, amylose, agarose, and a glycosylated protein, glucose oxidase. Stable bilayer membranes are formed when glycolipids are dispersed in these sugar-philic ILs. Reversible thermal transformation from fibrous assemblies to vesicles was also displayed in Figure 11. Physical gelation of ILs occurs by dissolving amide-group-enriched glycolipids, providing a first example of self-assembling ionogels [66].

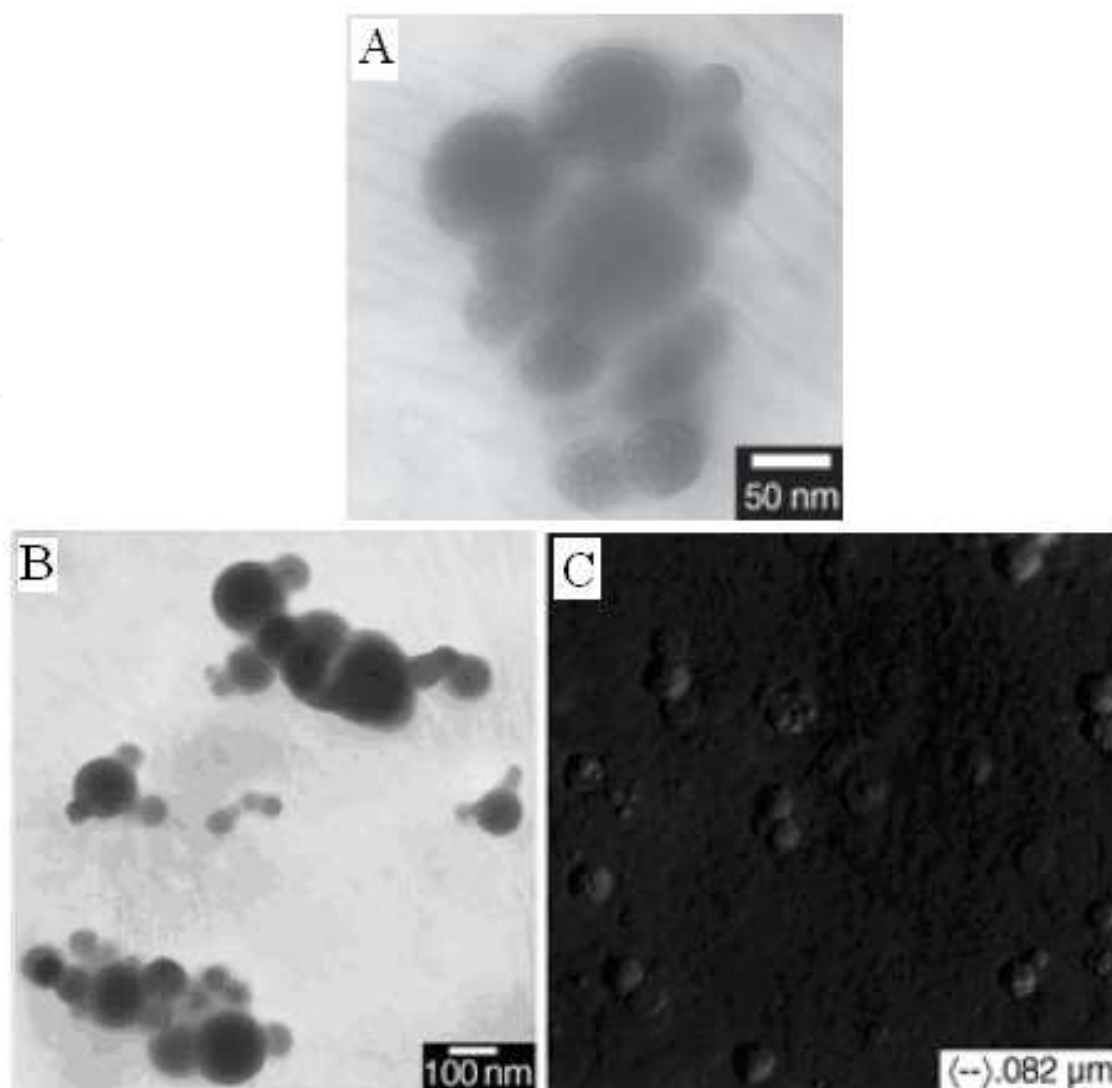


Figure 10. Negative-staining and FFTEM images of self-assembled surfactants in ILs. (A) a typical negative-staining TEM image of the self-assembled $\text{Zn}(\text{OOCCH}_2\text{C}_6\text{F}_{13})_2$ bilayer vesicles in bmimBF_4 ; (B) Negative-staining and (C) FFTEM images of self-assembled surfactant nanospheres of C_{14}DMAO and $\text{Zn}(\text{OOCCH}_2\text{C}_6\text{F}_{13})_2$ in bmimPF_6 . (Reproduced from Ref.[65], with permission).

A thermoreversible ion gel by triblock copolymer, poly(N-isopropyl acrylamide-*b*-ethylene oxide-*b*-N-isopropyl acrylamide) (PNIPAm-PEO-PNIPAm) self-assembly in IL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide (emimTFSI) has been recently reported by Lodge group [67]. The ion gel is highly conductive and possesses sufficient mechanical strength even under large strains. This thermoreversible ion gel offers the advantage of solvent-free processing in practical applications. They also found that ion gel electrolyte can be formed by gelation of poly(styrene-*block*-ethylene oxide-*block*-styrene) (SOS) triblock copolymer in bmimPF_6 . The gelation behavior, ionic conductivity, rheological properties, and microstructure of the ion gels were investigated. The ionic conductivity of the ion gels is only modestly affected by the triblock copolymer network. Its temperature dependence nearly tracks that of the bulk IL viscosity. The ion gels are

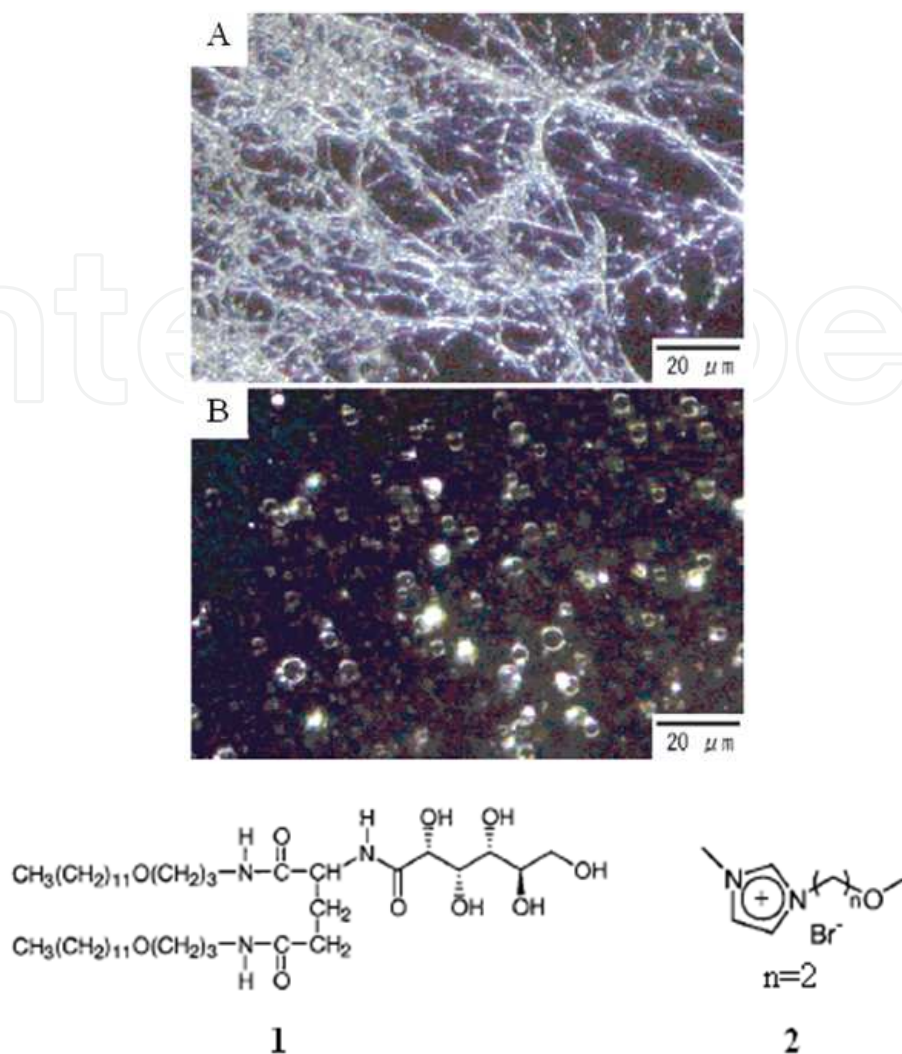


Figure 11. Dark-field optical micrographs of glycolipids dispersed in ILs: (A) fibrous nanostructures composed of **1** in **2** at 20°C; (B) vesicles composed of **1** in **2** at 50°C. (Reproduced from Ref.[66], with permission).

thermally stable up to at least 100°C and possess significant mechanical strength [68]. Moreover, they also fabricated polymer semiconductor thin film transistors using the ion gel as the gate dielectric layer. The gate capacitance of the ion gel can be as large as 40 μF/cm² at 10 Hz and 2 μF/cm² at 1 kHz. The polarization response time of the ion gel is much faster than previously tested solid polymer electrolytes, allowing the ion gel gated transistors to operate at higher frequencies and establishing ion gels as an attractive new class of solution processible gate dielectric materials for organic electronics [69].

6. Conclusion

Due to their unique characteristics and potential environmentally friendly behavior, ILs are finding more and more applications in a variety of research fields, such as extraction, separation, chemical reactions, material preparations, and chromatography, among others. It can be

said that once the physicochemical properties and microstructure of these neoteric self-assembly in ILs are well established and understood, number of their applications of the self-assemblies will increase dramatically as researchers are discovering more and more about these exciting media. There is no doubt that, in the near future, self-assemblies in ILs will establish themselves as important media in many research fields.

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Author details

Bin Dong and Yanan Gao*

*Address all correspondence to: ygao@dicp.ac.cn

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China

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