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Characterization of lyotropic liquid crystals formed in the mixtures of 1-alkyl-3-methylimidazolium bromide/p-xylene/water

Xin-Wei Li^a, Jin Zhang^a, Bin Dong^a, Li-Qiang Zheng^{a,*}, Chen-Ho Tung^b^a Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan 250100, China^b Technical Institute of Physics and Chemistry, The Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

1-Alkyl-3-methylimidazolium bromide ($C_n\text{mimBr}$), are substituted for surfactants and formed lyotropic liquid crystalline phases with p-xylene and water. Small angle X-ray scattering (SAXS), polarized optical microscopy (POM), ²H nuclear magnetic resonance (²H NMR) and rheological measurement were performed to investigate the lyotropic liquid crystalline phases. A lyotropic bicontinuous cubic phase formed in imidazolium-type ionic liquid (IL) system was found for the first time. Moreover, the effect of chain length of $C_n\text{mimBr}$ on the phase behavior, structural parameters and rheological properties was studied. The strong “ π - π stacking” of imidazolium based ILs and their “ π -cation” interactions with p-xylene molecules have unique effect on the structural parameters, especially the thickness of the water channel (d_w).

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1. Introduction

Green chemistry strategies to avoid using hazardous solvents have attracted great attention. Most of these beneficial alterations have relied mainly on finding new environmentally benign solvents, but recent studies have demonstrated that ionic liquids (ILs) can replace conventional organic solvents. A variety of ILs based on imidazolium, pyridinium, and ammonium cations have been prepared. They are fluid around or below 100 °C, have no significant vapor pressure, are non-flammable, have outstanding catalytic properties, and are stable at temperatures up to 300 °C or more [1–4]. Previous studies have shown excellent applications of ILs as environmentally benign solvents in organic synthesis [1], as electrolytes [5], and in extraction [6].

As an important series of ionic liquids 1-alkyl-3-methylimidazolium salts, $C_n\text{mimX}$, where n is the carbon number in the alkyl group, are intensively investigated because they are easy to prepare and relatively inexpensive to manufacture. Initially, $C_n\text{mimX}$ ILs with short alkyl chain length were investigated, and of those, $C_n\text{mimX}$ ILs with various anions were used as replacements of conventional solvents or water. The aggregation behaviors of traditional surfactants, such as SDS [7], Brij 76 [8], and Tween

20, Triton X-100 [9] in ILs were reported. Novel self-assembly schemes have been presented, for example, the solvophobic interactions between ILs and the hydrocarbon portion of surfactants are worth noting [9]. In order to obtain special functions, the long-chained $C_n\text{mimX}$ ILs were synthesized recently [9]. These ILs have amphiphilicity like traditional cationic surfactants because of their hydrophobic chains and polar imidazolium group, and have been called “surface active” [10] or “surfactant-like” ionic liquids [11]. There are several reports on the aggregation behavior of such long-chained imidazolium ILs in aqueous solutions [10–12] and in another IL, such as ethylammonium nitrate (EAN) [13].

Combining the unique properties and novel applications by using $C_n\text{mimX}$ salts to form ordered molecular assemblies such as micelles, microemulsions, vesicles, liquid crystals and so forth is obviously attractive and has been realized. Recently, $C_n\text{mimX}$ ILs with short alkyl chain lengths have been used to substitute for traditional organic solvents or water to create novel IL microemulsions. Han and coworkers first reported that BmimBF_4 disperses as polar nanosized droplets in continuous cyclohexane solvent with the aid of the nonionic surfactant Triton X-100 [14]. Moreover, several studies have been carried out by our group to demonstrate the microstructure of IL microemulsions and the polarity of their micro-regions [15–18], and the results indicated that the positively charged imidazolium cation of $C_n\text{mimX}$ plays an important role in constructing those novel microemulsions. In addition, lyotropic liquid crystalline phases formed in a binary system of amphiphilic

* Corresponding author. Tel.: +86 531 88366062; fax: +86 531 88564750.
E-mail address: lqzheng@sdu.edu.cn (L.-Q. Zheng).

block copolymer (P123)/BmimPF₆ [19], and ternary systems of Brij 97/water/BmimBF₄ and BmimPF₆ [20] were also reported.

Previous studies have shown that imidazolium ILs with sufficiently long alkyl chains ($n \geq 12$) display liquid-crystalline behavior in the molten state [21,22]. The thermotropic phase behavior of dry C₁₂mimBr has already been studied by Bradley et al. [23]. In addition, lyotropic liquid crystalline gels have been reported in the binary system of long-chained C_nmimX ILs and water, such as C₁₀mimBr/H₂O [24], C₁₀mimNO₃/H₂O [25], C₁₂mimCl/H₂O [26], and C₁₆mimBr/H₂O [27] binary systems. As expected, the aggregation behaviors of these surface active C_nmimX salts in ternary systems with water and oil have also been observed [28], and comparison to conventional systems indicated that both disk-like imidazolium rings and an H-bonded network play important roles in the phase behavior, which suggests that a suitable molecule design could subtly tune the phase behavior of such a system. The lyotropic liquid crystalline phases formed from C₁₆mimBr/p-xylene/water have been studied by our group [29]. Hexagonal phase and lamellar phase were found in this ternary system. Because of the difference of the head groups between C₁₆mimBr and cetyltrimethylammonium bromide (CTAB), the structural parameters of the C₁₆mimBr system are much lower. Based on our previous studies, in the present work, lyotropic liquid crystalline phases were constructed by imidazolium ILs with different carbon chains, C₁₂mimBr, C₁₄mimBr and C₁₆mimBr, with p-xylene and water. The cubic lyotropic liquid crystalline phase was found in C₁₂mimBr/p-xylene/water mixtures. To the best of our knowledge, such a reverse bicontinuous cubic phase formed in imidazolium-type ILs systems has not been reported before. Interestingly, when using SAXS and ²H NMR to characterize the liquid crystalline phases, the structural parameters were influenced by the molecular structure of C_nmimBr, illustrating a typical case of the strong “ π - π stacking” of imidazolium based ILs and its “ π -cation” interactions with the p-xylene molecules. The rheological properties of the liquid crystalline phase were also studied. The obtained results provide fundamental and useful data for a better understanding of imidazolium-type ILs.

2. Experimental

2.1. Materials

C_nmimBr ($n = 12, 14, 16$) was synthesized according to the previous work [30]. In brief, 1-methylimidazole and an excess molar amount of C_nH_{2n+1}Br ($n = 12, 14, 16$) were dissolved in dichloromethane, and the mixture was stirred at 75–80 °C for 48 h. The excess dichloromethane was then removed under reduced pressure. The product was purified by recrystallization from ethyl acetate at least four times, and then dried under a vacuum. The purity of the product was ascertained by ¹H NMR spectrum in CDCl₃. p-Xylene was purchased from Sigma (St. Louis, USA), purity approximately 99%, and used without further purification. Water was purified by double distillation.

2.2. Phase diagram

The ternary phase diagram was constructed by titrating a series of C_nmimBr/p-xylene mixtures with water at room temperature. Appropriate amounts of C_nmimBr and p-xylene were weighed. Samples were shaken for sufficient time to reach equilibrium and then progressively enriched with water (added drop by drop). The amounts of added water at which transitions occurred were derived from the mass of the mixture. By repeating this experimental procedure for other C_nmimBr to p-xylene mass ratios, the

phase boundaries were determined. The microemulsion domain was determined by visual observation for transparency; the presence of liquid crystalline mesophase structures was determined by using cross polarizers. Furthermore, the boundaries were finally determined by SAXS measurements.

2.3. Small angle X-ray scattering (SAXS)

SAXS measurements were performed using a Kratky Compact Camera (HMBG, Austria) with Ni and W filtered Cu K α radiation (wavelength $\lambda = 0.15418$ nm) generated by a PW3830 X-ray generator (5 kV \times 40 mA). Scattering intensities were plotted versus reciprocal spacing ($q = 4\pi \sin \theta / \lambda$), where θ was the scattering angle. A 600 s exposure time was used for all the samples.

2.4. Polarized optical microscopy (POM)

The textures of the samples were obtained by the POM (Olympus BX51p) with a cooled CCD (Evolution MP5.1RTV, Q-imaging, Canada) for image capture, and the temperature was kept at 25 °C with a Linkam THSME600 liquid crystal freezing and heating stage system with a TP94 temperature controller (Linkam Scientific Instrument Ltd., UK).

2.5. Quadrupolar ²H NMR

Samples selected in the phase diagrams were prepared using deuterium replaced water in a flame sealed NMR tube, and thermally equilibrated for at least 30 days at 25 °C. ²H NMR quadrupole spectra were measured with a FX-90Q NMR Spectrometer (JEOL, Japan).

2.6. Rheology measurements

Rheology measurements were performed with a Haake RS 75 apparatus. A cone-plate sensor with 20 mm diameter and 1° cone angle was used. The measuring temperature was maintained at 25 \pm 0.1 °C. Steady-shear measurements were performed on all samples in which the stress (σ) was varied while the frequency was kept at 1.0 Hz. Once the linear viscoelastic region was determined, measurements were carried out as a function of frequency at constant stress.

3. Results and discussion

3.1. Phase behaviors of C_nmimBr/p-xylene/water systems

The ternary phase diagrams of C_nmimBr/p-xylene/water system were constructed and are presented in Fig. 1. The region marked in shadow is the two phase region. Lamellar liquid crystal (L α), hexagonal liquid crystal (H₁), and microemulsion (L) phases can also be seen in these phase diagrams. It is obvious that there are large regions of liquid crystalline phase in all three phase diagrams, which are above the C_nmimBr–H₂O axis. As the carbon chain increases in length, the liquid crystalline region moves closer to the water corner. The explanation for the differences in the phase diagrams might be ascribed to the decreased hydrophobicity of the C_nmimBr, resulting in weaker hydration ability, which is consistent with traditional surfactant systems [31,32]. Particularly, there is a cubic phase region in the C₁₂mimBr/p-xylene/water system marked as C. In the cubic phase, the concentration of H₂O is between 20 and 35 wt% and solubilized p-xylene is up to 12 wt%. Recently, Wang et al. have reported that C_nmimX ILs with short alkyl chain length could form the cubic *Im3m* liquid crystalline phases in ternary systems, such as BmimPF₆/C_{18:1}E₂₀/water and

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