



Liquid crystalline phases of 1,2-dimethyl-3-hexadecylimidazolium bromide and binary mixtures with water

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ABSTRACT

1,2-Dimethyl-3-hexadecylimidazolium bromide, which lacks an acidic proton at the C-2 imidazolium ring position, exhibits thermotropic SmA_2 phase behavior above its melting point of 90.3 °C and up to 232.1 °C. The corresponding layer spacing and the full width at half maximum from XRD patterns display a temperature dependence. In binary mixtures with water, over a concentration range of 40–75%, lyotropic liquid crystalline phases form between 0.5 and 25 °C. The molecules of the new ionic liquid (IL) in the binary mixtures show three different self-assembly processes, namely, formation of rod micelles, coexistence of rod micelles and a hexagonal phase, and a pure hexagonal phase. The distance between the two centers of adjacent columns of cylinder units remains nearly constant at 4.97 ± 0.04 nm when the IL content exceeds 70%, indicating that the cylinder units attain a dense and highly ordered packing.

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1. Introduction

Ionic liquids (ILs), which are composed of weakly bound anions and usually large organic cations, are a special class of salts that have melting points at or close to room temperature. Their nonvolatility, low flammability, high electrochemical and thermal stability, and high ionic and thermal conductivity have made ILs a very popular class of medium for a wide range of catalytic and synthetic reactions; biotechnological, electrochemical, and solar cell applications; ordered thin films; and other innovative uses in engineering [1–5]. Liquid crystals (LCs) offer a combination of order and mobility in one material. They can flow like liquid but are anisotropic compounds with orientational self-organization at the nanometer level. The order of these compounds can be determined or changed by temperature (thermotropic) or solvents (lyotropic). The merger of ILs and LCs has yielded a new class of materials called ionic liquid crystals (ILCs). These unique properties of ILCs have led to their widespread applications in biomaterials, nanomaterial synthesis, electro-optics, and electrobiology [6–8].

1-Alkyl-3-methylimidazolium-type ILs with long alkyl chains can exhibit thermotropic or lyotropic liquid-crystalline phases. Firestone et al. studied the organization of IL molecules and suggested the existence of a long-range structure [9]. Zhang et al. explored lyotropic liquid crystals formed by 1-cetyl-3-methylimidazolium bromide/*p*-xylene/water [10]. Trilla et al. exploited phase behavior based on bis- and trisimidazolium salts bearing hydro-

phobic hexadecyl chains and a bridging mesitylene moiety [11]. Zhou and co-workers studied hydrogen bond formation between an IL anion and the silano group of silica gel and the π - π stack interactions between neighboring imidazolium rings to form a network [12]. However, most of these studies on ILCs of imidazolium-type ILs focus on 1-alkyl-3-methylimidazolium containing an acidic proton at the C-2 imidazolium ring position, which decreases its chemical and electrochemical stability and precludes its use in anisotropic media and electrolytes [13].

Recently, we reported a method for preparing a new imidazolium-type IL lacking an acidic proton at the C-2 imidazolium ring position to improve the chemical and the electrochemical stabilities. We also studied its self-assembly behavior in solvent mixtures with 1-decanol and water [14]. The results demonstrated that the new IL exhibited two types of well-ordered lyotropic ionic liquid crystals, hexagonal and lamellar phases. Further investigation of the new ILs is necessary and of great interest. We report herein the phase transitions, self-assembly processes, and liquid crystal structures of pure 1,2-dimethyl-3-hexadecylimidazolium bromide and its binary mixtures with water by combining polarizing optical microscopy (POM), differential scanning calorimetry (DSC), small-angle X-ray scattering (SAXS), and temperature-dependent wide-angle X-ray diffraction (WXRd).

2. Materials and methods

2.1. Materials

All the following materials were used as received without further purification. 1-Hexadecyl bromide (97%) and 1,2-dimethylim-

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imidazole (98%) were of reagent grade from Alfa Aesar and Acros Organics, respectively. Ethyl acetate (99.5%) from Shanghai Chemical Reagent Co. was of analytical grade. H₂O was double distilled. The preparation of 1,2-dimethyl-3-hexadecylimidazolium bromide has been reported in an earlier publication [14]. Portions of 3.0514 g (10.0 mmol) of 1-hexadecyl bromide and 0.9609 g (10.0 mmol) of 1,2-dimethylimidazole were mixed in a flask, refluxed at 85 °C for 18 h, and then cooled to room temperature. The obtained solid was purified by recrystallization from ethyl acetate. Finally, the crystalline was dried in vacuum at 60 °C for 2 days. The IL was checked using ¹H nuclear magnetic resonance (¹H NMR), ¹³C NMR, infra-red spectroscopy (IR) and DSC. The purity of the IL was about 99.3% by Elementer (Vario EL Cube).

2.2. Self-assembly of binary mixtures and characterization

The aqueous systems were prepared by first adding appropriate weight ratios of the components in a glass tube, and then repeatedly mixing and centrifuging. The mixtures were stored at 20 °C for at least a week before further examination. Throughout the study, the components of 1,2-dimethyl-3-hexadecylimidazolium bromide were expressed as IL%.

Phase transition temperatures were examined by a NETZSCH 200F3 differential scanning calorimeter (DSC) under a nitrogen flow. The pure IL and its homogeneous mixtures with different components were added into an aluminum pan, and then the pan was sealed and set in the oven of the DSC apparatus. Samples usually weighing 2–3 mg were used for this analysis. In DSC measurements, the heating-cooling cycle was repeated twice at a scanning rate of 3 °C/min. Thermogravimetric analysis (TGA) was performed using NETZSCH 409 PC instruments. The samples were heated in steps of 10 °C/min from room temperature to 400 °C in flowing nitrogen.

A Leica DMLP polarizing optical microscope (POM) with a charged coupled device (CCD) camera and a THMS 600 hot stage was used to observe and analyze morphological changes during thermal transitions. The samples were placed between two cover slips. For thermotropic liquid crystals, the samples were preheated to the clearing point and cooled to crystallization for data collection, while for the lyotropic phase, the samples were first cooled sufficiently to a low temperature (–30 °C) and then heated for data collection. Cooling and heating were conducted at a rate of 1 °C/min.

SAXS measurements were performed with a Kratky SAXS system attached to a Rigaku Rotaflex small-angle X-ray instrument using a Cu K α X-ray source at 40 kV and He atmosphere ($\lambda = 1.54 \text{ \AA}$). The distance between the samples and the detector was 604.5 nm. The exposure time was 30 min for all samples. The average lattice spacing between two lamellar structures was estimated from the position q of the first (and the most intense)

diffraction peak using Bragg's Law, $d = 2\pi/q$, while the distance between two centers of the adjacent columns was $D = 4\pi/\sqrt{3}q$.

Temperature-dependent wide-angle X-ray diffraction (WXR) was implemented using a Philips X'pert Pro diffractometer using Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation equipped with an X'celerator in a continuous scan with a step size of 2θ equal to 0.02°. At every 10 °C WXR powder patterns were recorded with an exposure time of 6 min in the heating run from crystal to isotropic at 10 °C/min.

3. Results and discussion

3.1. Self-assembly of neat IL

The thermotropic properties of the IL were characterized by DSC, POM, TGA, and WXR. Fig. 1 is the TGA and DSC curves of the pure IL. The TGA measurement indicates a weight loss of ca. 1% below 250 °C and a heavy weight loss of about 98% between 250 and 400 °C, as shown in Fig. 1a. The initial weight loss of ca. 1% is related to desorption of moisture bonded to the hydrophilic IL. The subsequent weight loss of about 98% is due to thermal decomposition of the IL. It can be concluded that no chemical reaction of the IL occurs before 250 °C. Fig. 1b shows the DSC curves of the pure IL. Some enthalpy changes can be seen in the DSC curves, indicating the formation of different phases. When the IL is heated from 25 to 235 °C, two phase transitions are observed. The first transition, centered at 90.3 °C with a characteristic large enthalpy change, is attributed to the melting point, while the second peak, at 232.1 °C with a small enthalpy change, is associated with a mesophase-to-isotropic phase transition. Bowlas et al. [15] and Gordon et al. [1] have reported that 1-alkyl-3-methylimidazolium ILs with sufficiently long alkyl chains ($n \geq 12$) show liquid crystalline behavior at temperatures above their melting points. There is also similar thermotropic liquid crystalline behavior in our study of imidazolium-type ILs lacking an acidic proton at the C-2 imidazolium ring position.

The mesomorphic property of the IL has been confirmed by polarizing optical microscopy (Fig. 2). The textures are ascribed to intrinsic spontaneous alignment. Fan-shaped focal conic textures, a common feature of the smectic A phase, were observed when the isotropic sample was cooled [16]. The micrographs taken at 230, 200, and 42 °C show the existence of a fan-shaped focal conic texture appearing in the isotropic phase, a pure fan-shaped focal conic texture, and a mixture of a solid and a fan-shaped form, respectively, indicating the isotropic–mesophase and mesophase–solid phase transitions clearly. The IL showed a supercooled crystallization process, and it began to freeze at a lower temperature (48 °C). The SmA phase of the IL exhibits a broad temperature window and a stable state from 48 to 235 °C, which is beneficial for applications.

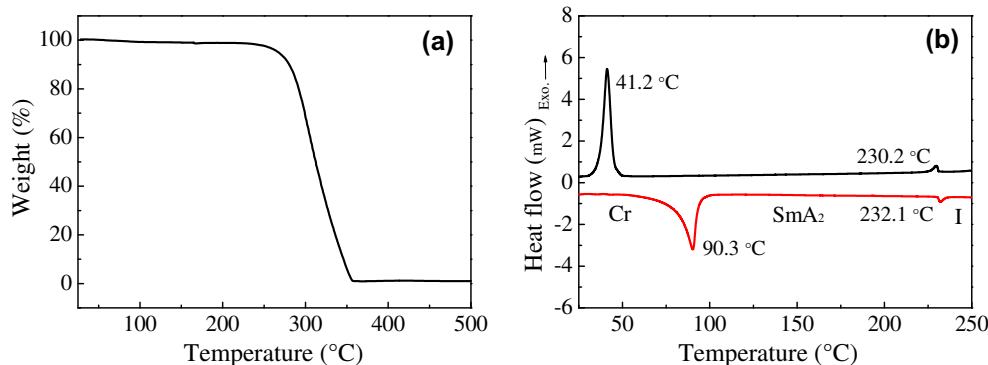


Fig. 1. TGA (a) and DSC (b) curves of pure IL.

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