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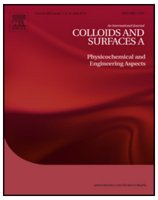

Ternary phase behavior of phytosterol ethoxylate, water, and imidazolium-based ionic liquid systems – Lyotropic liquid crystal formation over a wide range of compositions

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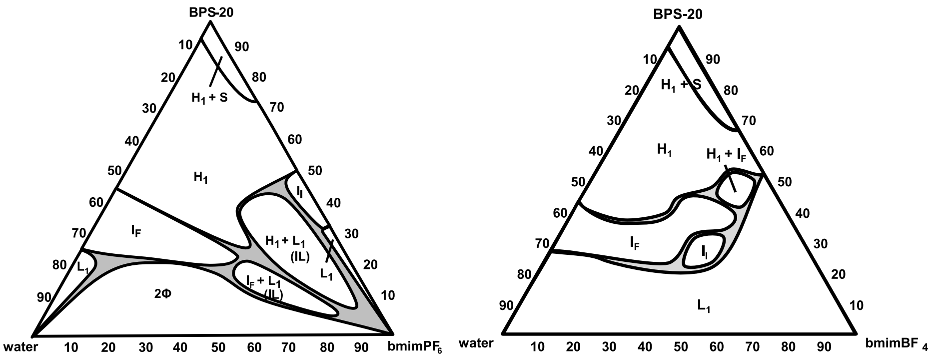
HIGHLIGHTS

- Liquid crystal formation in ternary system of nonionic surfactant, water, and ionic liquid over wide composition.
- Effect of anion species of ionic liquid on the phase behavior.
- Structural parameters calculated from SAXS measurements and the rheological properties of lyotropic liquid crystal.

GRAPHICAL ABSTRACT



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ABSTRACT

Lyotropic liquid crystal formation from ternary mixtures of nonionic surfactants [phytosterol ethoxylates (BPS-*n*)], water, and room-temperature ionic liquids [1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$)] was evaluated using optical and polarized microscopic observations, small-angle X-ray scattering (SAXS), and rheological measurements. In this study, the number of POE units was varied (BPS-*n*, n = 10, 20, 30) to form lyotropic liquid crystalline phases over a wide composition range for all of the systems. The major liquid crystalline phases formed for BPS-10, -20, and -30 were lamellar, hexagonal, and cubic phases, respectively. The differences could be explained by the size of the hydrophilic moieties (i.e., a decrease in critical packing parameters through an increase in the number of surfactant POE units). In addition, structural parameters were calculated from SAXS data for the hexagonal liquid crystalline phase with 60 wt% BPS-20. The area occupied by the hydrophilic moieties in the hexagonally packed cylinder micelle decreased with increasing ratio of water to ionic liquid, which indicated that the surfactant molecules were packed more closely in the hexagonal liquid crystalline phase at greater water concentrations. Rheology measurements indicated that ternary mixtures exhibited more elastic behavior at greater water concentrations, which also supports the change in structural parameters suggested by SAXS measurements.

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1. Introduction

Room-temperature ionic liquids (RTILs) are composed of bulky organic cations and anions, and are molten salts near room temperature. They have unique properties such as non-volatility, non-flammability, high thermal stability, and wide electrochemical potential windows [1,2]. Therefore, RTILs are of interest for various applications such as organic synthesis [1,3], electrolytes [4–6], and liquid–liquid separation [7]. They also have been investigated as new solvents that could substitute for water and oils. In colloid and interface science, many studies have investigated the interfacial chemical properties of surfactants in RTILs. Both ionic and nonionic surfactants form different types of self-assemblies (e.g., micelles and vesicles) in RTILs as well as in aqueous solution [8–12]. In addition, the phase behavior of ternary surfactants, RTILs, and water or oils have also been studied and the formation of emulsion and liquid crystalline phases has been reported [10,13–17].

The dilute solution properties and phase behavior of phytosterol ethoxylates (BPS-*n*) in aprotic RTILs have been reported [18–21]. The BPS-*n* compounds are POE-type nonionic surfactants with phytosterol as a solvophobic tail, which possess excellent surface activity such as a low critical micelle concentration (cmc) and surface tension at cmc (γ_{cmc}), and they form a liquid crystalline phase in RTIL, 1-butyl-3-methylimidazolium hexafluoroborate (bmimPF$_6$) [18]. In addition, other studies also have shown that BPS-*n* possessed excellent interfacial chemical properties in different RTILs [22–24]. A previous study reported the ternary phase behavior of BPS-20/bmimPF$_6$/oils, focusing on the effect of polar and nonpolar oils on phase behavior [21]. The present study extends this investigation by focusing on the phase behavior of a BPS-*n*/bmimPF$_6$/water ternary system. The bmimPF$_6$ is a hydrophobic RTIL with a solubility in water of ca. 2 wt% [25]. The surfactants and bmimPF$_6$ interact via hydrogen bonding between surfactant solvophilic portions and bmim cations, and surfactants form self-assemblies due to solvophobic interactions as well as interactions in the aqueous solution [8]. The solvents, bmimPF$_6$ and water, interact with solvophilic units of surfactants, but are immiscible with each other. Thus, in the surfactant/water/bmimPF$_6$ ternary system, the location of each solvent in the liquid crystalline phase is of great interest.

Few reports have examined lyotropic liquid crystalline formation in surfactant/RTIL/water ternary systems [26–29]. Wang et al. studied the ternary system of Brij 97/water/RTIL (bmimPF$_6$ and bmimBF$_4$), and investigated the effect of RTIL hydrophilicity on the hexagonal liquid crystalline phase [26]. Zhuang et al. observed the lamellar liquid crystalline phase in the Brij 30/water/RTIL system [27]. However, the nonionic surfactants used in these studies do not form a lyotropic liquid crystalline phase in the surfactant/RTIL binary system. The composition that provides the liquid crystalline phase in the ternary system is quite narrow. However, BPS-*n* forms hexagonal, cubic, and lamellar liquid crystalline phases even in a surfactant/RTIL binary system. Therefore, liquid crystal formation over a broader composition range is expected in the BPS-*n*/water/RTIL ternary system.

In the present study, the ternary phase diagrams of BPS-*n* with different numbers of POE units ($n = 10$, 20, 30), amounts of water, and RTILs (bmimPF$_6$ and bmimBF$_4$) were examined. Results showed the formation of various lyotropic liquid crystalline phases (discontinuous cubic, hexagonal, and lamellar phases) over a wide composition range. The location of each solvent (water and RTIL) in the molecular assembly also was investigated from structural parameters obtained from SAXS measurements. This information will be useful for developing approaches to the preparation of nanostructured materials using RTILs as solvents, as well as to the application of RTIL-based solid electrolytes.

2. Experimental

2.1. Materials

The room-temperature ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF$_6$) and 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$), were purchased from Sigma–Aldrich. They were dried under reduced pressure at 80 °C for 4 h before use to remove water. The nonionic surfactants, BPS-*n* (*n* denotes oxyethylene chain lengths of 10, 20, and 30), were obtained from Nikko Chemicals and used without purification. The hydrophobic portion of the BPS-*n* surfactants consisted of β-sitosterol, campesterol, and stigmasterol in a 2:1:1 ratio, and the surfactants contained less than 3 wt% polyoxyethylene as a hydrophilic impurity. The chemical structures of bmimPF$_6$ and BPS-*n* are shown in Fig. 1. The water used in this study was deionized with a Barnstead NANO Pure Diamond UV system and filtered with a Millipore membrane filter (pore size 0.22 μm).

2.2. Sample preparation

To prepare ternary mixtures of BPS-*n*, IL, and water, the three components were sealed into a 5-cm^3 test tube. The system was heated to 80 °C, and mixed at 3000 rpm using a Vortex mixer, followed by centrifugation at a constant rotation speed of 3500 rpm using a Kokusan H11-NB centrifuge. This heating-mixing-centrifugation cycle was repeated three times, after which the system was equilibrated for 2 weeks in an incubator at a constant temperature of 25 °C.

2.3. Characterization

Polarized optical microscope (POM) observations were performed at room temperature using an Olympus IMF-2 microscope.

Small-angle X-ray scattering (SAXS) measurements were performed using an Anton Paar W3830 system equipped with an *in situ* cell and humidity generator. The apparatus was operated at 40 kV and 50 mA using Cu-Kα X-rays. The X-ray irradiation time was fixed at 20 min. An imaging plate was used to collect the X-ray scattered intensities. Owing to the translucent beam stop, the raw scattering data consistently included a reduced primary intensity at a scattering vector $q = 0$. All of the data were normalized to the same incident primary-beam intensity for the transmission calibration and were corrected for background scattering from the capillary.

Rheological measurements were performed using a stress-controlled rheometer, AR-G2 (TA Instruments) with cone-plate geometries (diameter of 40 mm with cone angle of 2° 0′ 4″). The frequency was varied from 0.01 to 100 rad s^{-1} at a constant % strain of 0.1 Pa.

3. Results and discussion

3.1. Phase diagram of the BPS-*n*/water/bmimPF$_6$ ternary system: effect of POE chain length on phase behavior

The SAXS profiles and POM images obtained for the BPS-20, water, and bmimPF$_6$ system are shown in Fig. 2. The 4: 5: 1 and 4: 0: 6 (weight percentage of BPS-20: water: bmimPF$_6$) samples were isotropic and highly viscous, suggesting the formation of a cubic liquid crystalline phase. In addition, the *q* value ratios of the SAXS profiles for these samples were $\sqrt{3}:\sqrt{8}:\sqrt{11}$ and $\sqrt{2}:\sqrt{4}:\sqrt{6}$, respectively, indicating the formation of a discontinuous cubic phase of *Fd3 m* and *Im3 m* type, respectively. The POM observations of the 6: 2: 2 sample showed a fan-like texture, and the *q* value ratio from SAXS measurements was $1:\sqrt{3}:2$. These results indicate hexagonal liquid crystal formation. Both a fan-like structure and surfactant