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Fluorous protic ionic liquid exhibits a series of lyotropic liquid crystalline mesophases upon water addition

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ABSTRACT

Fluorous protic ionic liquids (FPILs) which consist of a hydrocarbon cation and fluorocarbon anion can possess a complex liquid nanostructure, consisting of segregated polar, hydrocarbon and fluorocarbon domains. FPILs are an interesting series of compounds of relevance to the fields of ionic liquids (ILs), fluorinated amphiphiles and mixed hydrocarbon/fluorocarbon amphiphile systems. Here we show the self-assembly of FPIL ethylammonium perfluorooctanoate (EOAF)–water solutions, which transitions from a low water content L₃ sponge structure in EOAF, to a L_α lamellar mesophase and then to dispersed lamellar vesicles. The robust lamellar mesophase was present between 10 and 85 wt.% EOAF, and retained up to 91 °C. This phase underwent significant swelling on addition of water. In contrast, the addition of water to the hydrocarbon analogue, ethylammonium octanoate (EO) swelled the sponge-like liquid nanostructure, with no other lyotropic liquid crystal mesophases observed.

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1. Introduction

Many ionic liquids (ILs) possess populations of cations and anions that are correlated over intermediate length scales, resulting in nano-scale heterogeneities within the bulk liquid [1–4]. The formation of this liquid nanostructure is predominantly driven by cooperative species interaction leading to species segregation. Heterogeneity formation can also be influenced by a fine balance between hydrogen bonding and electrostatic effects. The identification of the nanostructured nature of many ILs has fundamentally changed the way we think about this class of solvents. Understanding the nanostructure of ILs and its formation mechanism is critical in the development of applications for ionic liquids in overarching areas such as human health [5], materials synthesis [6–8], pharmaceuticals [9], agrochemicals [10], batteries [11] and biomaterials processing [12–14]. The interactions of solutes with ILs can be significantly influenced by whether the IL exhibits intermediate

range order, and if so, the size and persistence of the domains that are present [15,16].

Protic ionic liquids (PILs) are a class of ionic liquids formed from the stoichiometric combination of a Brønsted acid and a Brønsted base [17]. The nanostructure of two PILs, ethylammonium nitrate (EAN) and propylammonium nitrate (PAN), was first reported by two research groups in 2008 [18,19]. The experiments showed that these PILs are not homogeneous liquids, and modelling undertaken in both cases suggested a disordered locally smectic or sponge-like structure [18,19]. Further investigation into the structures by Hayes et al. using a combination of neutron diffraction and empirical potential structure refinement has suggested that PAN and EAN self-assemble into disordered L₃-sponge phases [20,21]. At low mole fractions of water a monolayer first forms in the anionic domain of the PIL, followed by the formation of water clusters, with finally the growth of discrete water pools [22,23]. It is apparent that the nanostructure of PILs may be retained even with significant proportions of water present [22]. In addition, dilution in water does not necessarily affect the correlation distance of the nonpolar domains in the PILs, which may be retained to some extent for up to 80 wt.% water present in select PIL–water systems [22].

Previously we reported a new class of protic ionic liquids, fluorous protic ionic liquids (FPILs) [24]. Members of this PIL class contain short chained alkylammonium cations and perfluorinated carboxylate anions. The chemical structure of the FPIL ethylammonium perfluorooctanoate

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(EAO) is shown in Fig. 1, along with its hydrocarbon analogue of ethylammonium octanoate (EAO), which can be considered a conventional PIL. Unlike other ILs, the interplay of homo and hetero species interaction (multiple solvophobic effects) within selected FPILs drives the segregation of the anions and cations in the liquid into three domains; a polar domain, a hydrocarbon domain and a fluorocarbon domain [24,25]. Notably, these FPILs are miscible with ethanol and butanol, and the three domains were retained on addition of the primary alcohols. It was also observed that for a wide range of alcohol concentrations there were additional nano-scaled alcohol aggregates present [26]. Similar nano-scaled aggregates have been observed on addition of alcohols to the hydrocarbon analogues [26–28].

The FPILs, such as EAOF, can be considered as an intermediate between fluorocarbon amphiphiles with small counterions (such as ammonium, chloride, etc.) and systems containing cationic hydrocarbon amphiphiles paired with anionic fluorocarbon amphiphiles. A few related systems have previously been reported. These include perfluorodecanoate paired with tetramethylammonium, butyltrimethylammonium, dibutylmethylammonium or methyltributylphosphonium [29]. For this series as the hydrophobicity of the cations increased the lyotropic liquid crystal aggregates formed had less positive curvature, going from a mesh to lamellar and then to lamellar with a reversed micelle phase. Mesh phases were present when the counterion was trimethylammonium, with a random mesh phase present for approximately 15–45 wt.% amphiphile, and a correlated mesh phase for approximately 50–85 wt.% of amphiphile, all at 25 °C [29]. The surface activity of a series of fluorinated-hydrocarbon amphiphiles have been reported for dilute aqueous concentration over a sufficient concentration range to obtain information related to the CMC [30]. Specifically these included dialkylammonium, trialkylammonium, tetraalkylammonium, ethanol-, diethanol-, and triethanolammonium cations all paired with perfluorooctanoate or perfluorooctylsulfonate anions [30]. Aqueous solutions of perfluorooctanoate amphiphiles paired with different counterions, including ammonium and ethylammonium, combined with a partially fluorinated co-surfactant of 1H,1H,3H,3H-perfluorooctan-1-ol were investigated to explore the effect of composition and temperature on the liquid crystal phases present, and it was observed that the counterion had a significant effect on the lyotropic mesophases present [31]. Though in contrast, the amphiphiles containing perfluorooctanoate paired with Li, Na or Cs showed little counterion effect on the aggregation behaviour [32]. Related amphiphiles have also been reported which contain a perfluorooctyl chain and a propyl chain in the same molecule [33, 34].

Aqueous solutions containing stoichiometric or non-stoichiometric proportions of conventional hydrocarbon amphiphiles and fluorinated amphiphiles have been reported to form lyotropic liquid crystal phases including micellar (spheroidal, rod-like or worm-like), lamellar or vesicles [29,33,35–37]. Similar mesophases have been reported for cationic fluorinated amphiphiles analogous to EAOF with different counterions [38].

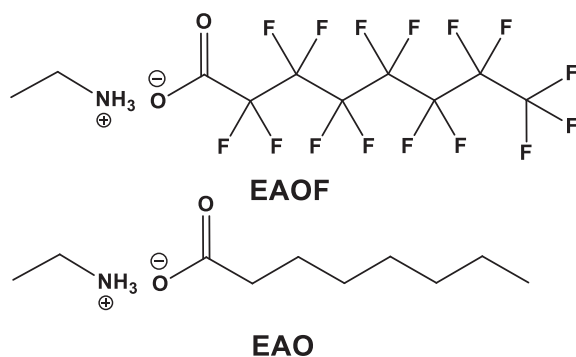


Fig. 1. Chemical structure of the FPIL ethylammonium perfluorooctanoate (EAOF) and the PIL ethyl ammonium octanoate (EAO) used in this study.

We have identified that the FPIL, ethylammonium perfluorooctanoate (EAOF), displays lyotropic liquid crystalline behaviour at room temperature on the addition of water. In this investigation we report on this lyotropic liquid crystal mesophase progression, and compared it to the behaviour of its hydrocarbon counterpart ethylammonium octanoate (EAO). The chemical structures of EAOF and EAO are provided in Fig. 1.

2. Experimental section

The fluoros protic ionic liquid (FPIL)–ethylammonium perfluorooctanoate (EAOF), and non-fluorous PIL ethylammonium octanoate (EAO) were prepared as previously reported combining equimolar quantities of Brønsted acid with Brønsted bases [39]. The molecular solvents methanol and ethanol (anhydrous, 99.5%, Sigma-Aldrich), butanol (anhydrous, 99.8%, Sigma-Aldrich), hexane (anhydrous, 95%, Sigma-Aldrich) and perfluorodecalin 95% were used as received. All FPIL/water PIL/water solutions were prepared gravimetrically using Milli-Q water. EAOF–water and EAO–water solutions were prepared which contained 10, 20, 30, 40, 50, 60, 70, 80, 90, 95 and 99 wt.% water.

Small- and wide-angle X-ray scattering (SAXS/WAXS) experiments were performed on the SAXS/WAXS beamline at the Australian Synchrotron, Clayton, Australia [40]. Samples were contained in 1.5 mm glass capillaries sealed with bees wax to prevent water absorption or loss. Samples were housed in a 60 sample capillary holder mounted on a 3-axis sample stage using a previously described method [39]. Scattering patterns for the EAOF–water samples were acquired over a SAXS q range of 0.04–1.72 Å^{−1} at temperatures of 26, 51 and 73 °C using an exposure time of 1 s. The scattering patterns for the EAO–water samples were acquired at 25 and 50 °C using a SAXS q range of 0.04–0.62 Å^{−1} and WAXS q range of 0.54–2.5 Å^{−1}. The SAXS and WAXS profiles were combined to obtain a q range from 0.04 to 2.5 Å^{−1}. The contribution from an empty capillary was subtracted from the scattering profiles which were normalised to beam stop intensity to account for variations in flux. The capillaries were nominally 1.5 mm diameter; however, there were some small deviations in size, which lead to changes in the intensities of a few percent.

Cross polarised optical microscopy experiments (CPOM) were conducted on a Nikon Eclipse Ni microscope equipped with cross-polarising lens. Samples were heated using a Mettler Toledo HS82 hot stage with a Mettler Toledo HS1 hot stage controller. Each sample was individually compressed between a microscope slide and a coverslip.

3. Results

At room temperature, EAOF forms a crystalline solid with a melting point of 58 °C [24]. On heating, or addition of a small amount of water, EAOF forms a triphasic liquid consisting of polar, hydrocarbon and fluorocarbon domains [24]. We have previously reported that it is miscible with ethanol and butanol [26], and here report that it is also miscible with water and acetone. Interestingly EAOF is insoluble in the organic solvents of chloroform, toluene and hexane, and insoluble in the fluorinated solvent perfluorodecalin. This indicates that a significant amount of hydrogen bonding, in addition to a strong dipole moment, is required to infiltrate the structure of the FPIL.

Water has led to the most unusual behaviour of the solvents described above which have been combined with EAOF. The visual appearance of a series of EAOF–water compositions, after vortexing, is shown in Fig. 2, where for many compositions there is a “gel phase” evident.

The lyotropic liquid crystal mesophases present for the EAOF–water samples were determined using SAXS and CPOM. At 25 °C the CPOM of all the 10–80 wt.% EAOF samples had distinctive birefringent texture characteristic of a lamellar phase, and images for 10, 30, 50 and 80 wt.% EAOF are provided in Fig. 3. The battonets present for 10 wt.% EAOF (Fig. 3a) were less intense compared to the phase texture present for the other samples. The samples containing 40–60 wt.% EAOF were more viscous than the other compositions, forming a stiffer gel. This is

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