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Lyotropic liquid crystal phase behavior of various amphiphiles in ternary protic ionic liquid containing solvents

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Amphiphiles exhibiting micellar and higher order lyotropic mesophases in aqueous solvent environments have been extensively used in a broad range of applications such as detergents, sol-gel processes, biocatalysis, microencapsulation, nano-material synthesis and drug delivery [1, 2]. In recent years the use of non-aqueous solvents, or their binary/ternary mixtures, in self-assembly processes has received increasing attention due to their advantageous features, such as enhanced protection against hydrolysis of bio-active materials and hence, improved long-term stability of these compounds [3]. In particular, protic ionic liquids (PILs) are the largest and most tailorable class of non-aqueous solvents possessing the ability to support amphiphile self-assembly. In this work, lyotropic liquid crystal phase (LLCP) behavior of the various amphiphiles including cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and monopalmitolein (MP) as investigated in the ternary solvent system of water, ethylamine and nitric acid, where the stoichiometric acid-base composition corresponds to the well characterised PIL of ethylammonium nitrate (EAN). A total of 26 unique solvent environments were used, covering the pH and ionicity ranges of 0-13.5 and 0-11 M, respectively. The effect of amphiphile concentration and temperature on the formation of LLCPs was also determined. The LLCPs in these solvent environments were studied using differential scanning calorimetry, cross polarized optical microscopy and small and wide-angle X-ray scattering. Neat water and EAN were used as reference environments for comparison. Phase diagrams were separately constructed for amphiphile concentrations of 50 wt% and 70 wt% between 25 ℃ and 75 ℃, as it is given in Fig. 1 for CTAB representatively. LLCPs were identified as micellar, hexagonal and cubic phases and were present from 35 ℃ in some of the solvent composition. Thermal stability and diversity of phases were found to be greater and broader in solvent compositions with excess ethylamine present. In acid-rich solvent combinations, some structural changes were observed due to the dramatic change in solubility of amphiphiles and its effect on the phase behavior was also examined.

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