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Structural behavior of the lamellar mesophase formed by ternary mixtures of a two-tailed ionic liquid, 1-decanol and water

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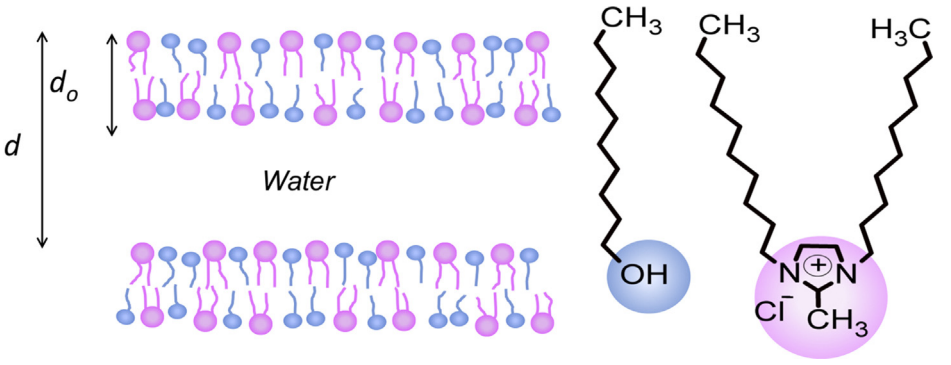
HIGHLIGHTS

- The system 1,3-didecyl-2-methyl-imidazolium chloride in decanol/water is studied.
- A single lamellar region is extended in a wide range of temperatures and compositions.
- The decanol is incorporated in the bilayer as a cosurfactant.
- The structural parameters depend on the temperature and the composition.
- Ionic liquid-alcohol interactions induce conformational changes of the IL molecule.

GRAPHICAL ABSTRACT



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ABSTRACT

The lamellar mesophase of a ternary system involving the ionic liquid 1,3-didecyl-2-methylimidazolium chloride, 1-decanol and water is studied in detail. Small and wide X-ray diffraction with synchrotron radiation, optical microscopy and differential scanning calorimetry are employed to determine the phase diagrams and the changes in the structural parameters of the lamellar structure, considering three variables: (i) the water content, (ii) the molar decanol/ionic liquid ratio and (iii) the temperature. A single lamellar L_α region is extended in a wide range of temperatures and compositions. The corresponding lamellar spacing and the cross-sectional area of the polar head group, display a temperature dependence. When the decanol/ionic liquid molar ratio is greater than 1.5, increasing temperature causes a transition from lamellar to an isotropic phase.

1. Introduction

Ionic liquids (ILs) are organic salts, which have a relatively low melting point when compared to inorganic salts. ILs are non-volatile, non-flammable and have high thermal stability. More than 10^{18} anion-cation combinations could lead to useful ionic liquids [1]. In fact, they can be considered as designer materials because their structure can be tuned by selecting an appropriate combination of ions, thereby generating specific physical and chemical

Abbreviations: IL, ionic liquid; OH, 1-decanol; $[C_nmim]^+$, 1-alkyl-3-methylimidazolium salts; DDMIC, 1, 3-didecyl-2-methylimidazolium chloride; *R*, molar ratio decanol/DDMIC; W#-R#, sample name , being W# the content of water (wt%) and R# the molar ratio decanol/DDMIC.

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properties. Consequently, ILs are ideal in terms of technical applicability, covering an expanding range of applications as replacements for organic solvents, for example in: lubricants [2], analytical applications [3], catalysis [4], electrochemistry [5], extraction processes [6], engineering liquids [7], lithium batteries [8], or biotechnology [9]. Additionally, some present self-assembling ability [10]. In these cases, they combine the unique properties of the liquid crystals with those of the ionic liquids, giving rise to specific applications, such as liquid crystal displays, dye-sensitized solar cells or electrochromic materials [11].

Quaternized imidazoles constitute an important family of ILs. Most of the studies are referred to 1-alkyl-3-methylimidazolium salts (abbreviated $[C_nmim]^+$, where n is the number of carbon atoms in the alkyl chain), which have been intensively investigated because they are easy to prepare, relatively inexpensive to manufacture [12] and can be applied in several fields. $[C_nmim]^+$ salts with short alkyl chain length are used as replacements of conventional solvents [13]. Imidazolium salts with long alkyl chains ($n \geq 12$) display thermotropic liquid-crystalline behavior in the molten state due to a microphase separation of ionic imidazolium groups from the flexible lipophilic alkyl chains [14,15]. Furthermore, $[C_nmim]^+$ are amphiphilic and possess surfactant properties, because of their hydrophobic chains and their polar imidazolium group and, like the traditional surfactants, can aggregate in water to form thermodynamically stable self-assembled structures. In short chained $[C_nmim]^+$ micellar aggregates are formed [16], and for longer chains ($n \geq 8$) lamellar or hexagonal mesophases are moreover detected [16–19]. These ordered assemblies can be employed for developing novel applications, (e.g. semi-heterogeneous catalysts [20], microreactors [21], or as templates to prepare structured materials [17,22]). The addition of a third component has been also explored, analyzing the lyotropic behavior in the presence of oils [23], or long chained alcohols [24].

Nevertheless, $[C_nmim]^+$ ILs contain an acidic proton at the C-2 imidazolium ring position, which decreases its chemical and electrochemical stability and precludes its use in some applications, e.g. electrolytes in lithium batteries. Alkylation on the C-2 position improves the chemical and electrochemical stabilities, becoming these compounds suitable for such applications [25].

Here we study a twin-tailed surfactant ionic liquid, which lacks the acidic proton at the C-2 imidazolium ring position: 1,3-didecyl-2-methylimidazolium chloride, DDMIC. It has been used as titrating agent for anionic surfactants [26], and for the preparation of ion-selective electrodes sensitive to ionic surfactants [27]. It can be also employed as pore directing agent to obtain mesoporous clays for drug delivery [28]. Nevertheless, as far as we know, there are only two studies concerning self-assembling behavior of this IL: the formation of bilayers and micelles that can be used as nanoreactors [29], and the aggregation and interaction of DDMIC with pluronics [30].

We report herein the phase behavior of the ternary DDMIC/decanol/water system. The decanol is used as cosurfactant to tune the hydrophilic lipophilic balance of the IL [31], in order to obtain a wide lamellar region in the phase diagram. This mesophase has been extensively studied because it is a simple model of the biomembranes, and because it appears in many industrial applications such as detergency or emulsification [32], and can be also used as drug vehicles [33], and nanoreactors [34]. In this work we analyze the effect of temperature, decanol/LI ratio and water concentration in the structure and stability of the lamellar mesophase, combining small and wide angle X-ray scattering with synchrotron radiation (SAXS and WAXS), polarizing optical microscopy (POM), low temperature scanning electron microscopy (CryoSEM) and differential scanning calorimetry (DSC). The aim is to obtain a system with a lamellar mesophase in a wide range of composition and temperatures that could be used to confine functional molecules or as nanoreactors.

2. Experimental part

2.1. Chemicals

1,3-didecyl-2-methyl-imidazolium chloride, ≥98% was from IoLiTec and 1-decanol 99% was from Aldrich. Deionized water (Milli-Q) was employed for the sample preparation

2.2. Density determination

The density of the components is required to determine the molar volume of the components and also the composition of the samples, expressed as volume fractions. The densities were obtained at 15, 20, 25, 30, 35 and 40 °C using an Anton Paar DMA4500 densitometer. To determine the density of DDMIC, the densities of the aqueous IL (micellar solution) were measured as a function of the IL concentration. The reciprocal density values were plotted against the DDMIC concentration and its density is obtained by extrapolating the line to the point corresponding to the pure IL.

2.3. Sample preparation

Samples were prepared by weighing the precise amounts of the three components (water, DDMIC and 1-decanol) and were homogenized mixing back and forth for several days. Afterward, they were allowed to equilibrate at 25 °C. Seven sets of samples were prepared, having each of them the same decanol/DDMIC molar ratio, $R = 0.9$, 1.0, 1.3, 1.5, 1.7, 2.0 or 2.3, and a variable water content, between 53–82 wt%. The samples are named W#-R#, being W# the content of water (wt%) and R# the molar ratio decanol/DDMIC.

2.4. Microscopy

A Nikon Labophot-2 microscope, with and without crossed polarizers, was employed. Samples where placed between a glass slide and a cover slip. In the experiments as a function on the temperature the samples were placed in a FP82 microscope hot stage, where the temperature was increased at 2 °C min^{-1} from 15 to 60 °C with a Mettler FP90 central processor, using liquid nitrogen as cooling fluid.

2.5. Differential scanning calorimetry (DSC)

The equipment was a Mettler Toledo calorimeter provided with a DSC822 oven and a sub-ambient cooling unit. Two runs were performed, in a nitrogen atmosphere, using an empty aluminum cell as a reference. The first run was scanned at 5 °C min^{-1} in the range 30–5 °C. The second run was scanned at 5 °C min^{-1} from 5 to 60 °C. Only second run results are used for calculation.

2.6. Low temperature scanning electron microscopy (CryoSEM)

Freeze fracture SEM was performed to visualize the sample morphology of selected samples. For fracturing, a portion of the samples was mounted in the sample holder and immersed in nitrogen slush for freezing. They were then transferred to the Oxford CT1500 cryotransfer chamber station unit, where, after fracturing, they were etched at −89.6 °C for 20–30 min and coated with Au for 1.5 min. For imaging, the freeze-fractured samples were transferred into the JEOL JSM-5410 SEM. The images were recorded at magnifications up to 10000×.