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Morphological transformations in Triton X-100 micelles modulated by imidazolium and pyridinium type Ionic Liquids: Investigations by scattering techniques

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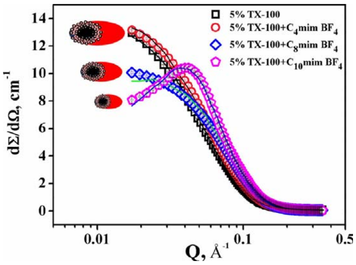
GRAPHICAL ABSTRACT



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ABSTRACT

The phase behaviour and aggregation characteristics of aqueous solution of Triton X-100 in the presence of several 1-alkyl-3-methylimidazolium salts, $[C_n\text{mim}^+]X^-$ and 1-alkylpyridinium salts $[C_n\text{Py}^+]X^-$, where n is the alkyl chain length (4,6,8.10) and X^- is the anion $CF_3SO_3^-$ and BF_4^- has been explored. The effect of nonpolar alkyl chain length, cation and anion of these ionic liquids was investigated from cloud point (CP), dynamic light scattering (DLS) and small angle neutron scattering (SANS). ILs with longer alkyl chain on cation drastically increased CP and decreased micelle size. The size, hydrophobicity and polarity of anions also showed marked effect on solution behavior of Triton X-100. The results indicate opposite effect on CP and hydrodynamic diameter (D_h) on addition of ionic salts. SANS results demonstrate that added ILs modulated the size of TX-100 micelle, which is further discussed in terms of penetration of cation and anion into TX-100 micelle depending on the nature of alkyl chain attached to the cation/anion and varying size, hydrophobicity, surface activity of anion.

1. Introduction

Ionic liquids (ILs) are defined as molten organic salts having melting point below 100 °C and have attracted much attention in recent years due to their unique physical properties, which include low volatility, non-flammability, high thermal stability, high ionic conductivity, among other [1–3]. ILs are applied as solvents in many applications, e.g., organic synthesis, electrochemistry, catalysis, separation and as alternatives to conventional organic solvents [3–5]. Most extensively used ILs have been quaternary ammonium salts based on imidazolium

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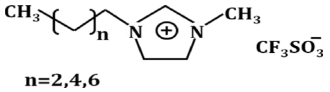
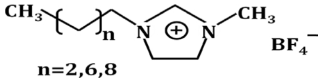
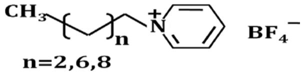
and pyridinium cation structure. These can be non-amphiphilic, amphiphilic or biamphiphilic depending on alkyl chain substitution in heterocyclic cation and/or inorganic/organic anions.

Several reports in literature investigate on amphiphilic ionic liquid aggregation in water [6–11] as well as in other ionic liquids as solvents [12–14]. Ionic liquids, both amphiphilic and non-amphiphilic are examined as additives to investigate their effect on aqueous micellar behaviour of ionic [15–18] and nonionic [19–27] surfactants. Usually, non-amphiphilic ILs behave as co-solvent/salt, while amphiphilic ILs have shown to form mixed micelles.

Triton X-100 is extensively used polyoxyethylene based non-ionic surfactant with application in various industies including biology and biotechnology [28,29]. The solution behavior of Triton X-100 in aqueous media, saline media and various additives/surfactants is well documented in our previous studies [30–34]. Few reports on aqueous TX–100 + ILs system investigate on aggregation of TX-100 in ILs [35–37],while others examined the effect of ionic liquids on the aggregation behavior in aqueous TX-100 solutions [25,26,38–41]. Behera et al. [25,26] have reported that 1-butyl-3-methylimidazolium ILs with hydrophilic tetrafluoroborate (C_4mim BF_4) and hydrophobic hexafluorophosphate (C_4mim PF_6) induced remarkable changes in micellar characteristics of TX-100. In these studies, author concluded that C_4mimPF_6 partitions into the TX-100 micellar phase and resides both close to the core as well as in the palisade layer of TX-100 micelles, which has been accounted for favorable interactions between C_4mimPF_6 and TX-100. Zhang et al. [38] have observed higher CMC value of TX-100 in presence of long chain IL 1-dodecyl-3-methylimidazolium tetrafluoroborate (C_{12}mim BF_4) and formation of mixed micelles as influenced by different interaction forces. Sun et al. [39] have studied interactions of aqueous Triton X-114 solutions and 1-alkyl-3-methylimidazolium based ILs with different anions, namely bromide (Br^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-) and bis (trifluoromethylsulfonyl)imide (NTf_2^-). It was concluded that both hydrophilic ILs with long alkyl chain (e.g., C_{12}mimBr) and hydrophobic ILs with short alkyl chain (e.g., $C_4mimNTf_2$), significantly influenced the aggregate size and increased zeta potential. The authors also reported CMCs and CPs of surfactants and also confirmed the exact localization of IL in micelles. Luo and coworker have examined micellization and surface properties of mixed system comprising Triton X-100 and 1-alkyl-3-methylimidazolium bromide (C_{12}, C_{14}), which indicate synergistic interaction driving to formation of mixed micelle and the spontaneity of micellization and adsorption [40]. Microfluidity in the palisade layer of the TX-100 micelle on the addition of C_4mim BF_4 was studied by Sarkar and coworkers [42]. Our group has also studied the effect of various types of imidazolium based room temperature ionic liquids (RTILs), surface active ionic liquids (SAILs) and biamphiphilic ionic liquids (BAILs) on solution behavior of TX-100 [27,43]. We have reported that morphology of TX-100 micelle is governed by concentration of ILs, alkyl substitution on IL cation and suitable combination of cation with anion structure.

The study on phase behavior and micellar characteristics of TX-100 in presence of ILs can be of sustained interest for the designing of chemical formulations for various applications. The current literature reveals the phase behavior changes on addition of ILs to aqueous TX-100 micelles, but the morphological transformation driven by these molecular interactions are not explained in considerable detail. We plan to address these molecular level interactions using detailed scattering analysis. The change on micellar size and aggregation characteristics of the mixed micelles are investigated by small angle neutron scattering and explained in terms of relative changes in aggregation number and micellar core dimensions. The small angle neutron scattering (SANS) and dynamic light scattering (DLS) are correlated to understand the mixed micelle characteristics as function of type of cations and the anion structures bearing different size and polarity.

Table 1
Structure of ionic liquids used in present study.

Ionic liquids	Structure
$C_4mimCF_3SO_3$ $C_6mimCF_3SO_3$ $C_8mimCF_3SO_3$	
C_4mim BF_4 C_8mim BF_4 C_{10}mim BF_4	
C_4Py BF_4 C_8Py BF_4 C_{10}Py BF_4	

2. Experimental

2.1. Materials

TX-100, sodium dodecyl sulphate (SDS), pyridine and ILs namely1-alkyl-3-methylimidazolium trifluoromethanesulfonate ($C_n$mim CF_3SO_3), 1-alkyl-3-methylimidazolium tetrafluoroborate ($C_n$mim BF_4), were purchased from sigma-aldrich and used as received. ILs 1-alkyl-pyridinium tetrafluoroborate (C_nPy BF_4) was synthesized and characterized using NMR. The structures of all the ILs used in this study are listed in Table 1.

2.1.1. Synthesis of 1-alkyl pyridinium tetrafluoroborate (C_nPy BF_4)

1-Alkyl pyridinium tetrafluoroborate ionic liquids were synthesized in two steps [44]. In step-1, alkyl pyridinium chlorides were prepared by mixing pyridine and excess amount of 1-chloroalkane for 12 h. The reaction was carried out in a three necked round bottom flask equipped with a nitrogen gas inlet adapter, thermometer pocket, magnetic stirrer and reflux condenser with a guard tube filled with fused calcium chloride. The obtained products were purified by repeated washing with ethyl acetate at 0–5 °C over a period of 2 h and dried under vacuum at 70 °C. 1-Alkyl pyridinium tetrafluoroborate were synthesized in step-2 with the substitution of the chloride ion by the BF_4^- ion. In this process, 1-alkyl pyridinium chloride was mixed with excess ammonium tetrafluoroborate and kept stirring for 8–10 h. The products were filtrated to remove NH_4Cl and kept in oven for overnight to remove water at 90 °C. The obtained products were dissolved in dichloromethane in separating funnel and the organic phase was separated. The obtained C_nPy BF_4 dried in oven at 80 °C for about 24 h. The synthesized ionic liquids were characterized by NMR spectroscopy. ^{1}H NMR and ^{13}C NMR spectra of C_4Py BF_4 shown in below Fig. 1.

2.2. Methods

2.2.1. Cloud point (CP)

The cloud points of mixed aqueous solutions comprising TX-100-ILs surfactant system were determined at fixed concentration of 5% TX-100 (w/v) and addition of different concentration of ILs, followed by gently heating. Cloud points of surfactant solutions were determined visually by noting the turbid solution at certain temperature. The measured values were reproducible up to 0.5 °C.

2.2.2. Dynamic light scattering (DLS)

The average size of the micelle was measured using dynamic light scattering (DLS) experiments using Malvern Zetasizer Instrument (Nano-ZS 4800,UK) equipped with He–Ne laser operating at a wavelength of 633 nm at 25 °C. Each measurement system was repeated 3 times and average values were considered. The micellar hydrodynamic diameter (D_h) was obtained using the Stokes-Einstein equation[32].