



Amphiphilic copolymers and surface active ionic liquid systems in aqueous media – Surface active and aggregation characteristics



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ABSTRACT

The surface active and micellar behavior of a di- and tri-block copolymer of EB and EBE, where E is oxyethylene and B is oxybutylene moieties and surface active ionic liquids (SAILs) namely 4-dodecyl-4-methylmorpholinium chloride, $[C_{12}mmor][Cl]$ and 1-dodecyl-1-methylpyrrolidinium chloride, $[C_{12}mpyr][Cl]$ is studied in aqueous media by surface tension, steady-state fluorescence and particle size measurements. The critical micelle concentration (CMC), surface active parameters (adsorption efficiency, surface excess, surface tension reduction, minimum area per molecule at air/water interface, etc.), average translation diffusion coefficient, size parameters and aggregation numbers are calculated. The effect of both SAILs and also copolymers as additives on the surface active and micellar behavior of one another is studied. The shape and size parameters of the micelles of the pure copolymer or SAILs are determined from translational diffusion coefficients at infinite dilution. The mixed micelles of copolymer–SAIL systems are treated in terms of spheres and it is observed that their hydrodynamic radii decreased with the increase in the proportion of SAIL. The aggregation number of mixed micelles as determined from steady state fluorescence quenching method initially increased, reached a peak value and decreased drastically at high SAIL mole fractions. It is rationalized that the SAILs in general facilitate the dissolution of copolymer micelles but the mixed micelles predominantly consist of SAIL molecules or micelles over most of the mole fraction range. Regular solution theory formulations are tested on copolymer–SAIL mixture solutions and micellar mole fraction, interaction parameter (β) and activity coefficients (f_1, f_2) are calculated. The values of β ranged from -3.3 to -5.9 suggesting synergistic interactions between the two amphiphiles.

1. Introduction

Attempts have been made to invent new amphiphilic systems that possess both hydrophobic and hydrophilic moieties in the same molecule and exhibit more novel and efficient surface adsorption and bulk aggregation in aqueous solutions [1–3]. Such systems are in demand especially to replace classical ionic or nonionic surfactants that are widely studied and used in various applications of technological importance such as wetting, detergency, solubilization, emulsion formation, catalysis, foaming, corrosion inhibition, bactericides, dispersions, and antistatic agents. Other areas where surfactants form essential ingredients are membranes, microemulsions, liposomes, vesicles and gels. Even though the entire surfactants chemistry in terms of surface adsorption and micelle formation in aqueous solutions is well understood, the performance of classical surfactants in less polar or nonpolar media is limited due to the restrictions that come with the basic molecular architecture i.e. an hydrophobic alkyl chains (up to C_{18}) and small polar head groups. These structural restrictions result

into the limitations on the micelle size and aggregation number and sensitivity to a given solution conditions including temperature. These limitations led to the search of alternative amphiphilic systems. Block copolymers with amphiphilic character have emerged for improved performance both in aqueous and non-aqueous media [4]. Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) tri-block copolymers with a molar mass range of 2000–20,000 Da are made available commercially under the trade names of pluronics (BASF) [5] and polaxomers (ICI). The surfactant behavior of these block copolymers has been well studied in detail and the summary of such studies has been discussed and analyzed in excellent reviews [6–9]. One of the novelties of (PEO–PPO–PEO) copolymers is that by controlling the molecular architecture of individual block copolymers, it is possible to create micellar self assembly based nanostructures with tunable morphologies ranging from simple well defined micelles and vesicles to network structures. One of the short comings inherent in the synthesis of these block copolymers is that, purity and monodispersity of samples is not always ensured [8,10,11]. To circumvent this, PEO–PBO di-block

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and PEO–PBO–PEO tri-block copolymers, where PBO represents poly (oxybutylene) are prepared by replacing the PPO units by anionic polymerization of 1,2-butylene oxide and their surfactant properties have been studied using conventional methods [12–17]. Our own laboratory has reported detailed investigation on the surface active and association behavior of di- and tri-block copolymers of type PEO–PBO or PEO–PBO–PEO (and of commercial origin) using surface tension, dynamic light scattering and small angle neutron scattering methods [18,19]. It is concluded that the size and shape of the micelles depend on the relative proportion of hydrophobic and hydrophilic block lengths and block type.

Surface active ionic liquids (SAILs) resemble classical cationic surfactants in their molecular structure which usually consists of a hydrophobic alkyl chain and a polar head group along with a counter anion. SAILs are higher homologues of room temperature ionic liquids (RTILs). Unlike RTILs which are essentially a special class of organic molten salts that are liquids at room temperature, SAILs have melting temperatures below 100 °C and possess many unique as well as special physical and chemical properties namely negligible vapor pressure and non-inflammability, high thermal stability, capacity to dissolve organic, inorganic and even polymeric substances, wide liquidus range and tunable molecular structures. Some of these properties of the ILs or RTILs are being exploited in a wide variety of applications that include chemical synthesis and catalysis [20], biocatalytic transformations [21,22], electro chemistry [23,24], analytical and separations science [25–27] and polymer science [28], etc. Surfactant properties play a decisive role in the formation of IL based microemulsions [29], solubilization of aromatics in aqueous media [30] and catalytic action [31,32]. Self organization of alkyl imidazolium based ionic liquids is therefore recently investigated and studied by various research groups and the salient features of these studies is discussed in two recent reviews [33,34]. It is concluded that the ionic liquids with alkyl chain length longer than four carbons generally behave as amphiphilic compounds displaying interfacial interactions at air/water interface and aggregation in bulk. The aggregation behavior is however is also influenced by several factors such as structure of the cations and anions, presence of inorganic or organic additives and even surfactants in the aqueous media. Our own laboratory has reported detailed studies on the surfactant properties of series of surface active ionic liquids with variations in the alkyl chain length, different head groups and counter halide anions [35–38]. Our detailed SANS investigations have revealed that SAILs with alkyl chain lengths (< C₈ atoms) display characteristic critical aggregation concentration but do not form micelle-like aggregates. On the other hand, SAILs with alkyl chains containing more than C₈ atoms form well defined ellipsoidal shaped micelles with a hydrophobic interior surrounded by the polar head group. Our studies had clearly established that ionic liquid based surfactant like substances are easily possible and more research work on their application side is required to invent green surfactants. One of the advantages of ionic liquid design for inventing new surfactants is that SAILs with alkyl chains as short as butyl chain are possible while conventional surfactant systems need a minimum of decyl chain and above [35,37,38]. Moreover recently the synthesis and aggregation behavior of trisiloxane tailed SAILs are also reported [39,40].

A literature survey also further revealed that as compared to the studies on surfactant-like behavior of individual amphiphilic ionic liquids in aqueous media, few investigations on the interfacial and association behavior of aqueous mixtures of imidazolium based SAILs – ionic or – nonionic surfactants on one hand and association of amphiphilic copolymers in RTILs as solvents on the other hand are made. The results from such studies are highly useful in finding ways to improve the properties of one another and also help explore the RTILs as green solvents in surfactant based applications. The studies on the binary systems of RTILs and anionic surfactants namely sodium dodecyl sulfate [41,42] and sodium dodecylbenzenesulfonate [43] by a variety of sophisticated techniques revealed that the neutralization of opposite

charge on the head groups of the two components resulted in the formation of mixed micelles containing either simple micelles/vesicles or micelles and vesicles depending upon the mixing ratio. The CMCs of mixed micellar systems was found to depend highly on the nature of the alkyl groups in the RTILs [41,42]. Sharma et al. [44] have monitored the mixed micelle formation in mixtures of 1-tetradecyl-3-methylimidazolium bromide and single chain tetradecyltrimethylammonium bromide, dimethyltetradecylammonium bromide and alkane-bis (tetradecyldiethylammonium bromide) in aqueous media and reported that the interactions between SAIL and single chain cationics are antagonistic in nature and the replacement of the single chain surfactant with double chain surfactant resulted in to synergistic interactions. Nonionic surfactant triton X-100 is also reported to interact with 1-butyl-3-methylimidazolium hexafluorophosphate [45], 1-dodecyl-3-methylimidazolium tetrafluoroborate [46] and the interactions with the former led to the increase of the CMC and decrease of aggregation number of nonionic surfactant. The micelle formation of both the cationic [47] or nonionic surfactants [48–50] in ionic liquids as solvent media was also explored and it was reported that the mixed micelles are formed mainly through the interactions among the hydrophobic alkyl chains.

The exploratory studies on the utility of RTILs as a solvent media for the micelle formation of amphiphilic copolymers of type PB-PEO [51]. PEO–PPO–PEO [52–54] concluded that as compared to aqueous solutions, the RTIL solutions exhibited distinct temperature dependent micellar morphological features. Parmar et al. [55] have examined the effect of three ILs of type 1-alkyl-3-methylimidazolium tetrafluoroborates (C_nmim BF₄, n = 4,6,8) on the micellar characteristics of aqueous pluronic P103 solutions using scattering and NMR techniques. It was in general reported that ILs hinder the micelle formation of copolymer and however form the mixed micelles. A similar study by Vekariya et al. [56] investigated effect of series of RTILs (consisting alkyl chains (up to C₈ atoms) and different head groups) on the micellar behavior of pluronic F127. It was demonstrated that ILs disfavor the formation of copolymer micelles. As far as our assessment, the information about the changes in the micellar features especially of amphiphilic copolymers in RTIL solutions is limited and the complexity of these changes depends on the alkyl chain length of IL cation, nature of cationic head group, nature and type of anion, also the way in which solutions are prepared and also the nature of micelles formed by RTILs themselves. More studies are required in solution conditions where the information on the behavior of the individual components namely copolymer or RTILs is clearly known.

Keeping these things in mind, present study is planned to measure and report the surface and association features of two individual surface active ionic liquids (SAILs) of type 4-dodecyl-4-methylmorpholinium chloride, [C₁₂mMor][Cl] and 1-dodecyl-1-methylpyrrolidinium chloride [C₁₂mpyr][Cl] denoted as SAIL1 and SAIL2 and two amphiphilic copolymers of type, PEO–PBO and PEO–PBO–PEO in aqueous solutions. Both of these components individually form micelles in water. The aqueous solutions are prepared so as to consider the SAILs or copolymers as additives and also their mixture solutions in different proportions. The effect of each of the components on the surface active and association features of the other at the air/water interface and in aqueous solutions is studied by surface tension, particle size analysis and steady state fluorescence measurements. The effect of SAILs on the shape and aggregation number of the copolymer micelles in aqueous solutions is examined through the translational diffusion coefficients at infinite dilution and fluorescence quenching methods. The regular solution theory formulations are applied for the CMCs of mixture solutions to calculate the interaction parameter.

2. Materials and methods

2.1. Chemicals and reagents

The Diblock and Triblock copolymers were obtained as a gift

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