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Influence of head group on the interactional behavior of cationic surface active ionic liquids with pluronic F108 in aqueous medium

Shruti Chabba, Rajni Vashishat, Rakesh Kumar Mahajan *

Department of Chemistry, UGC - Centre for Advanced Studies, Guru Nanak Dev University, Amritsar 143005, India

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ABSTRACT

The present work aims at studying the interactions between surface active ionic liquids (SAILs) 1-dodecyl-3-methylimidazolium bromide [C_{12}mim][Br]; *N*-dodecyl-*N*-methylpiperidinium bromide, [C_{12}mpip][Br]; *N*-dodecyl-*N*-methylpyrrolidinium bromide, [C_{12}mpyr][Br] and pluronic F108 in aqueous medium and to draw the comparison between the effect of different SAILs with respect to head group present in them. The binding of SAILs with pluronic F108 below as well as above the critical micelle temperature (*cmt*) of the pluronic has been studied by isothermal titration calorimetry (ITC), dynamic light scattering (DLS) and zeta (ζ) potential measurements. A combined analysis of these techniques revealed that SAILs can bind to monomeric as well micellar pluronic F108 with [C_{12}mim][Br] showing a higher binding affinity in comparison to the other SAILs. Further, the interactions between SAILs and pluronic F108 in mixed micelles have been studied employing surface tension and fluorescence measurements, Various micellar, interfacial and thermodynamic parameters have being obtained for mixed systems of SAILs with pluronic F108. The interactions between F108-SAIL binary mixtures have been found to be non-ideal and strongly synergistic. The modifications in the physicochemical properties of pluronic F108 upon addition of SAILs are expected to enhance and expand the industrial and pharmaceutical applications of pluronics.

1. Introduction

Pluronics, the triblock copolymers, are a class of water soluble non-ionic polymers consisting of poly(ethyleneoxide) and poly(propyleneoxide) blocks with general formula $(PEO)_n$-$(PPO)_m$-$(PEO)_n$. They self assemble to form micelles in aqueous solutions above a certain concentration called critical micelle concentration (*cmc*) and a temperature called critical micelle temperature (*cmt*). The micelles formed by these polymers have a core-shell structure with the hydrophobic PPO blocks constituting the micellar core and hydrophobic PEO blocks occupying corona [1–3]. These non-ionic polymers have unique solution behavior and thus, found extensive applications in emulsification, detergency, preparation of mesoporous and nanostructure materials, as polymer gel electrolyte and drug delivery systems [4–7]. One of the interesting properties of these polymers is their ability to serve as model systems to mimic the hydrophilic/hydrophobic interface in cellular membranes [8]. Hence they act as promising candidates as vehicles for drug delivery applications being biocompatible and non-toxic. Usually, in most of the drug delivery formulations pluronics are used in the presence of surfactants hence a detailed knowledge about the physical properties of mixtures of surfactants and polymers is of fundamental importance. The interactions between surfactants and triblock polymers have been extensively studied by many research groups including ours [9–15]. Hecht and Hoffman studied the effect of sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide (CTAB) on pluronic F127 using multiple techniques [16]. They reported that SDS leads to complete destruction of F127 micelles and also inhibits the copolymer micelle formation. Schillen and co-workers studied the interactions between triblock copolymers (L121, P123, F127) and ionic surfactants, SDS and hexadecyltrimethylammonium chloride (CTAC) using differential scanning calorimetry (DSC) and isothermal titration calorimetry (ITC) [17].

Ionic liquids, a class of molten electrolytes with melting point below 100 °C, are gaining considerable technological, industrial and academic importance in recent years. Most of their utility stems from their unique properties such as high thermal and electrochemical stability, extremely low vapor pressure, large liquid range, nonflammability and strong solvation abilities [18–21]. Another interesting aspect of IL is their amphiphilicity which can be imparted to them by attaching a long chain either with cation or anion. These types of ILs are known as surface active ionic liquids (SAILs). The surface activity of these SAILs has been found to be dependent upon various factors such as nature of counter-ion, nature of cation and alkyl chain length. The aggregation behavior SAILs based on imidazolium cation has been extensively explored by many researchers [22–27]. In addition to imidazolium based ILs, new ILs based on different hydrophilic head groups have also been

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* Corresponding author.
E-mail address: rakesh_chem@yahoo.com (R.K. Mahajan).

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synthesized and characterized [28–32]. Zhao and Zheng synthesized and investigated the self assembling behavior of *N*-alkyl-*N*-methylpyrrolidinium bromide (C_nMPB n = 12, 14 and16) in aqueous solutions [33].

Thus it is indispensable to study the interactional behavior of different SAILs with pluronics because of the interesting inherent properties and the potential practical applications of such mixtures. There are only few reports where effect of ILs on aggregation behavior of triblock copolymers has been studied. Most of these reports focus on the effect of short chain ILs ($<C_8$) on the aggregation behavior of the polymer. Zheng et al. studied the effect of 1-butyl-3-methylimidazolium bromide (BmimBr) on aggregation behavior of pluronic P104 [34]. At low concentrations, BmimBr penetrated in the core of P104 micelles while at higher concentrations BmimBr and P104 clusters were found to coexist. Soni and co-workers observed the effect of pyridinium based short chain ILs on the aggregation behavior of pluronic P123 and found that the aggregation number of P123 was found to decrease with the addition of ILs [35]. To the best of our knowledge, there is no report in literature comprising the detailed study of interactional behavior of SAILs with pluronic F108 in aqueous solution.

Herein, we investigated the interactions of SAILs viz. 1-dodecyl-3-methylimidazolium bromide [C_{12}mim][Br]; *N*-dodecyl-*N*-methylpiperidinium bromide, [C_{12}mpip][Br]; *N*-dodecyl-*N*-methylpyrrolidinium bromide, [C_{12}mpyr][Br] with pluronic F108 ($PEO_{129}PPO_{50}PEO_{129}$) in aqueous medium using various techniques. The work described in the paper has been carried out in two parts. Firstly employing the isothermal titration calorimetry (ITC), dynamic light scattering (DLS) and zeta potential measurements, the binding of different SAILs with pluronic F108 has been studied below (25 °C) as well as above (45 °C) its *cmt*. Then in second part, using the tensiometric and fluorescence measurements, the characterization of micellar and interfacial behavior of binary mixtures of SAILs with pluronic F108 has been made. The aggregation behavior has been evaluated in terms of micellar parameters like critical micelle concentration (*cmc*), micellar mole fraction in mixed state (X_1^m) and interaction parameter (β). Surface parameters such as surface tension at *cmc* (γ_{cmc}), surface excess concentration (Γ_{max}), minimum area per molecule (A_{min}) have been obtained from surface tension data. The investigation is expected to develop basic information on the interactional behavior of SAILs with pluronics.

2. Materials and methods

2.1. Chemicals and reagents

The SAILs; [C_{12}mim][Br], [C_{12}mpip][Br] and [C_{12}mpyr][Br] were synthesized according to the procedure mentioned elsewhere [33,36,37]. The synthesized compounds were characterized using ^{1}H NMR. Pluronic F108, 1-methylimidazole (99%), *N*-methylpiperidine (99%), *N*-methylpyrrolidine (99%), 1-bromododecane (99%) were procured from Sigma Aldrich and used as received. The molecular structures of the SAILs and Pluronic F108 have been given in Scheme 1.

2.2. Surface tension measurements

Surface tension measurements were made using a KRUSS (Hamburg, Germany) Easy Dyne tensiometer by Wilhelmy plate technique. The plate was flame dried before taking each measurement. The temperature of the instrument was controlled using an Orbit thermostat with the accuracy of ±0.1 °C.

2.3. Fluorescence measurements

Steady-state fluorescence measurements were carried out using a Hitachi F-4600 fluorometer at 25 °C. The data acquisition was made using a quartz cuvette of path length 1 cm. The emission and excitation slit width were fixed at 2.5 nm. The concentration of Pyrene used as the fluorescent probe was 1 μM. The excitation wavelength was fixed at 334 nm and the emission spectra were scanned in the range of 350–550 nm.

2.4. Dynamic light scattering measurements

Dynamic light scattering measurements (DLS) were carried out using a zetasizer Nano ZS light scattering apparatus (Malvern Instruments, UK) equipped with a He-Ne laser in backscattering mode at a scattering angle of 173° at 25 °C and 45 °C. The solutions were filtered through a membrane filter with pore size 0.45 μm before measurements. The samples were thermally equilibrated before each measurement and data was analyzed using standard algorithms. The temperature of the instrument was controlled with an accuracy of ±0.1 °C.

2.5. Zeta potential (ζ) measurements

Zeta potential experiments were measured using a Zetasizer Nano ZS Malvern Instrument Ltd. (UK). The electrophoretic mobility of the sample was measured from the velocity of the particles using a Laser Doppler Velocimeter (LDV) and then converted to zeta potential. All the measurements were conducted at 25 °C ± 0.1 °C and 45 °C ± 0.1 °C. The temperature of the measurements was controlled with an accuracy of ±0.1 °C. All the experiments were carried out in triplicate.

2.6. Isothermal Titration Calorimetry (ITC) measurements

The calorimetric measurements were carried out using a MicoCal ITC200 from GE Healthcare Life Sciences at 25 ± 0.1 °C and 45 ± 0.1 °C. Amounts of 40 μL of known concentrated stock solution of SAILs were taken in instrument controlled Hamilton syringe and 2 μL aliquots of stock solution of SAILs were added into the sample cell filled with 200 μL of a solution containing distilled water or 0.1 wt% F108 solution. All the measurements were repeated in triplicate.

3. Results and discussion

3.1. Binding of SAILs with monomeric pluronic F108 at 25 °C

3.1.1. Isothermal titration calorimetry (ITC) measurements

Isothermal titration calorimetry has been extensively used to study the interaction of surfactants with polymers and it is described as a vital and direct method to monitor the energy changes taking place during the interaction processes [38–40]. Therefore, ITC measurements were performed to obtain an insight into the interaction mechanism of the SAILs having different cationic head groups with pluronic F108. First of all, the micellization of three SAILs in water was studied by isothermal titration calorimetry. The calorimetric titration curves of observed enthalpy changes (ΔH_{obs}) as a function of concentration of respective SAILs are presented in Fig. 1 and S1 of Supplementary information. In a typical ITC experiment, when the concentration of titrated micellar solution is below *cmc*, the ΔH_{obs} is mainly due to break up of added micelles into the monomers and further dilution of monomers. On the other hand, when final concentration reaches above *cmc,* only the dilution of added micelles takes place and ΔH_{obs} ultimately decreases. The observed changes in enthalpy of dilution as a function of concentration of [C_{12}mim][Br] has been shown in Fig. 1a. Since the dilution process is endothermic, the enthalpy of micellization process is exothermic for pure SAILs. The *cmc* values of pure SAILs can be obtained from the break point in the curve or by plotting the first order differential curve of ITC thermogram (as shown in Fig. S2) in case the break point is not clear visually. The values of enthalpy of micellization (ΔH°_m) are calculated from enthalpy difference between two linear