



Mixed system of ionic liquid and non-ionic surfactants in aqueous media: Surface and thermodynamic properties



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ARTICLE INFO

Article history:

Received 26 June 2013

Received in revised form 20 January 2014

Accepted 31 January 2014

Available online 11 February 2014

Keywords:

Ionic liquid

Tetraethyl ammonium tetrafluoroborate

[TEA(BF₄)]

Non-ionic surfactant

Surface tension

Thermodynamics parameters

ABSTRACT

The mixed system of ionic liquid (IL) tetraethyl ammonium tetrafluoroborate [TEA(BF₄)] and numerous ethylene oxide based non-ionic surfactants in aqueous media were studied using surface tension, viscosity and dynamic light scattering (DLS) measurements. Various surface properties like critical micelle concentration (cmc), maximum surface excess concentration (Γ_{\max}), minimum surface area per surfactant molecule (A_{\min}), surface tension at the cmc (γ_{cmc}), adsorption efficiency (pC_{20}), and effectiveness of surface tension reduction (π_{cmc}) as well as thermodynamic parameters of micellization have been determined. DLS and viscosity measurements revealed that the micellar growth was attributed to the bridged solvophilicity of the POE chain in surfactants at elevated temperatures. In most of the cases, the progression ensues from exothermic to endothermic with increase in temperature of the mixed system. Thermodynamic parameter indicates that the micelle formation process is enthalpy driven at low temperature and entropy driven at higher temperature.

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1. Introduction

Ionic liquids (ILs) are a class of organic salts commonly poised of relatively large organic cations and inorganic or organic anions that cannot form a systematic crystal structure and thus persist as liquid at or near room temperature. Unlike molecular liquids, the ionic nature of these liquids consequences in a exclusive amalgamation of inherent physical properties such as capability to dissolve organic, inorganic and polymeric materials, high thermal stability, low or no measurable vapor pressure, non-flammability, wide electrochemical window, electrical conductivity, and wide liquid range [1–4]. The physicochemical and solvation properties of ILs can be effectively “tuned” by simple altering of the substituent groups encompassing the cation and/or anion. Recently, they have been applied as novel solvents in organic synthesis [5,6], catalysis [7], electrochemistry [8] and chemical separation [9–11]. Particularly, they have an advantage as an environmentally benign solvent, i.e., “green solvent,” subsequently their non-volatile nature can prevent the environmental pollution.

Non-ionic surfactants are widely used as solubilizers, emulsifiers, and detergents in countless industrial processes [12]. The self-assembly of amphiphilic molecules in ILs have gained much

attention due to several distinctive properties of ILs as a solvent [13,14]. The behavior of amphiphilic molecules in ILs is relatively fascinating research subject from an academic point of view. When amphiphilic molecules undergo self-assembly in ILs, the molecular aggregates are expected to solubilize essentially insoluble materials in the ILs. This solubilization by molecular assemblies of amphiphiles would widen the application field of ILs [15,16].

In pioneering work for surfactant self-assembly in ILs, the aggregation behavior of alkyltrimethylammonium bromides, alkylpyridinium bromides, and non-ionic Triton X-100 in a ethylammonium nitrate (EAN) have been reported [17,18]. Later attention in this field has been rather focused on imidazolium-based ILs which are composed of 1-alkyl-3-methyl imidazolium cation and appropriate anion. It was shown that some traditional surfactants form micelles in two ILs, 1-butyl-3-methylimidazolium chloride (bmimCl) and hexafluorophosphate (bmimPF₆) [19]. The micelle formation of non-ionic surfactants, polyethyleneglycol alkyl ethers, in 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄) and (bmimPF₆) was also reported [20]. Some other reports have been published regarding the surfactant aggregate formation in ILs [21–24]. However, most of these initial reports are rather fragmented work except for the aggregation behavior of non-ionic surfactant, Tween 20 in bmimBF₄ and bmimPF₆ [25], and fluorinated cationic surfactant, FC-4 in bmimBF₄, bmimPF₆ [26] and in bis(trifluoromethylsulfonyl) imide (bmimTf₂N) [27] and surface

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adsorption and aggregation behavior of POE-type nonionic surfactants in bmimPF₆ [16].

The complete understanding about the physico-chemical properties, such as surface tension, viscosity and thermodynamic surface properties is indispensable in designing any process involving ILs on an industrial scale [28,29]. The knowledge of surface active properties, thermodynamic and thermophysical behavior of ammonium based ILs in surfactant media is of great interest in colloid and interface science. It further helps to evaluate and scrutinize the role and prominence of such ILs in various applications. For ILs to be effectively used as solvents in extraction, or other fields, knowledge of the surface tension is essential. The surface tension of an entainer is a vital property that reveals information about the surface, intermolecular interactions, and forces in the liquid and exerts a substantial impact on the transfer and energy across the interface. Thus, surface tension has a decisive effect on the separation, adsorption, and distillation, in the performance of biological membranes and many other chemical engineering processes [30]. Recently, intensive research has been done to study various properties for the popular ILs [31–34].

So far TEA(BF₄) was used as phase transfer catalyst, for electrophoresis, and as solvent in separation techniques [35]. The purpose of present work is to study the effect of temperature and composition of mixed systems on their surface properties. To the best of our knowledge, the interaction study of tetraethyl ammonium tetrafluoroborate [TEA(BF₄)] IL-surfactants mixed systems in aqueous media and its thermodynamic properties have not been reported till date. Results obtained in the present study might be useful for applications in several areas of separation, adsorption, and distillation.

2. Experimental

2.1. Materials

Nonionic surfactants namely, polyethylene glycol 4-(1,1,3,3-tetramethylbutyl) phenyl ether (Triton X-100), Polyethylene glycol hexadecyl ether polyoxyethylene (10) cetyl ether (Brij-56), polyethylene glycol hexadecyl ether polyoxyethylene (20) cetyl ether (Brij-58), polyoxyethylene (20) sorbitan monolaurate (Tween-20) and polyoxyethylene (20) sorbitan monooleate (Tween-80) were obtained from Sigma–Aldrich. All supplied materials were of reagent grade and used without further purification. The high purity grade IL [TEA(BF₄)] was received with compliments from Tatva Chintan Pharma Chem Pvt. Ltd. (India). Deionized water from Milipore Elix 3, USA and triply distilled water (surface tension $72 \pm 0.2 \text{ mN} \cdot \text{m}^{-1}$, specific conductivity order of $10^{-3} \text{ mSc} \cdot \text{m}^{-1}$) was used for all the Samples.

2.2. Methods

2.2.1. Surface tension measurements

The cmc of IL-surfactant mixed systems in aqueous media were determined by surface tension (γ) method with different compositions of mole fraction (i.e., 0.2 to 0.8). Surface tension was measured by means of a pendant drop method with a Borosil mansingh survismeter [36,37] in a temperature controlled water bath. The measurements were carried in the temperature range from (298.15 to 318.15) K and at atmospheric pressure. The mixed different mole fraction solutions were prepared by mixing two pure solutions and were kept for at least 30 min for equilibration before measuring the surface tension. Surface tension was measured as a function of surfactant concentration in wt.%, the break point in the plot corresponded to cmc value. The accuracy of surface tension was within $\pm 0.1 \text{ mN} \cdot \text{m}^{-1}$.

2.2.2. Viscosity measurements

Viscosity of mixed IL-surfactant systems in aqueous media were measured at various temperatures from (298.15 to 318.15) K by using Borosil mansingh survismeter [36,37] in temperature controlled water bath. The apparatus was calibrated using ultrapure water with known viscosity. The experiments were repeated twice to ensure good reproducibility.

2.2.3. DLS measurements

The size of micelles formed in the mixed IL-surfactant systems were measured by means of DLS method. DLS measurements were performed with a Malvern Zetasizer Nano (Malvern, UK) as a function of temperature from (293.15 to 333.15) K. The temperature of the sample was controlled within $\pm 0.1 \text{ K}$ by a Peltier-type electronic temperature controlling system attached to the apparatus. The measurements were conducted twice for each sample and a good reproducibility was obtained for particle size distribution. The values of mean hydrodynamic diameter reported in this paper are based on the volume weighted size distribution.

3. Results and discussion

3.1. Surface tension

The surface tensions of mixed IL-surfactant systems have been studied in aqueous media. Figure 1 shows the representative surface tension plot for 0.2 TEA(BF₄)-0.8 surfactant mixtures as a function of surfactant concentration (C) at $T = 308.15 \text{ K}$. The surface tensions of mixed IL-surfactant systems in aqueous media showed noteworthy decrease with an increase in the surfactant concentration up to certain concentration and subsequently stayed constant. This behavior is analogous to that observed for aqueous surfactant solutions, and advocates that the surfactants start to form molecular aggregates, i.e., micelles, at the concentration corresponding to the break point appearing in the surface tension vs $\log C$ plot. cmc was calculated from the break point, which also resembles to the surface tension at the cmc, γ_{cmc} .

The experimental data of surface tension vs mole fraction of the IL (X) [TEA(BF₄)] in the binary systems of TEA(BF₄) + Triton X-100, or Brij-56, or Brij-58, or Tween-20, or Tween-80] in aqueous media at different temperatures are shown in figure 2. For all the systems, the surface tension increases with increase in IL content and it decreases with increasing surfactant content in IL-surfactant mixture. For Triton X-100, Brij-58 and Tween-80, the surface tension

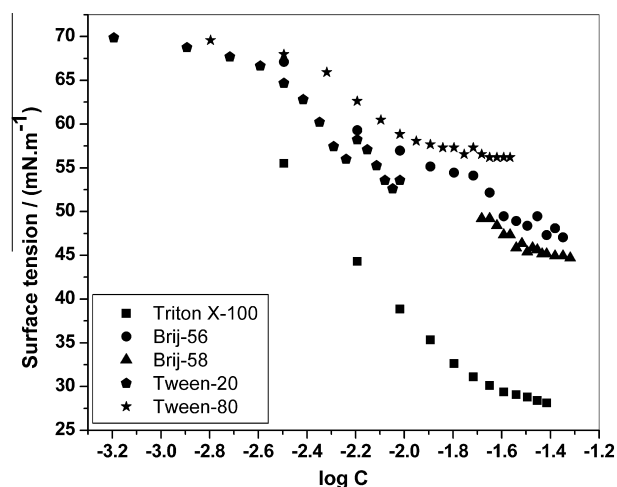


FIGURE 1. Surface tension vs $\log C$ plot for 0.2 TEA(BF₄)-0.8 surfactant mixture in aqueous media at $T = 308.15 \text{ K}$.

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