Journal of Molecular Liquids 219 (2016) 637–642

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Effect of 1-ethyl-3-methylimidazolium bromide on interfacial and aggregation behavior of mixed cationic and anionic surfactants

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ARTICLE INFO

Article history:
Received 22 December 2015
Received in revised form 3 February 2016
Accepted 12 March 2016
Available online xxxx

Keywords:
Mixed surfactants
EMIm Br
Nano-aggregate
Interaction parameter
Synergism

ABSTRACT

Aggregation behavior and interaction of sodium dodecyl sulfate (SDS), tetradecyl trimethyl ammonium bromide (TTAB) and their mixtures with an excess of anionic surfactant in the presence of imidazolium-based ionic liquid, 1-ethyl-3-methylimidazolium bromide (EMIm Br) were investigated using surface tension, electrical conductivity, dynamic light scattering (DLS), transmission electron microscopy (TEM) and cyclic voltammetry measurements. Different physicochemical properties such as critical micelle concentration (CMC), degree of counterion dissociation (α_{diss}), interfacial properties, the standard Gibbs energy of adsorption and the size of aggregates were determined. The effects of ionic liquid (IL) as additive on the interactions between the surfactants; TTAB, SDS and their mixtures were analyzed on the basis of regular solution theory, both for mixed monolayers at the air/liquid interface (β^{δ}) and for mixed micelles (β^{M}). Interaction parameter values suggested that the formation of aggregates is due to the synergistic interactions in the case of SDS/TTAB systems and becomes more affected by adding IL. It was shown that an excess of cationic surfactant and IL resulted in an increase in the nano-aggregate sizes. The synergism observed for three component systems (surfactant–water–IL) revealed the effect of attractive electrostatic interaction, formation of a three-dimensional hydrogen bond network and hydrophobic forces on mixed micelle formation.

1. Introduction

Ionic liquids (ILs) are usually composed of a bulky organic cation and inorganic or organic appropriate anion which are in molten state at temperature lower than 100 °C because of their low melting points [1,2]. ILs have attracted significant attention in recent years [3,4]. Both industrial and academic interest in ILs stems from their potential as green solvents as a result of chemical and nonflammability thermal stability, wide liquid range, solvent transport, low vapor pressure, and high ionic conductivity [5–8]. Another advantage of ILs is that their physical and chemical properties can be readily affected by suitable selection of anion, cation, and counter-ion [9]. So, the self-assembly of amphiphilic molecules in ILs have gained much attention due to several distinctive properties of ILs as an additive [9,10]. Surfactants and their mixtures are widely used as solubilizers, emulsifiers, and detergents in industrial processes [5,11]. These mixtures represent attractive systems for applications as they exhibit strongly synergistic interactions, for instance have superior performance to those of individual components and lead to a large reduction in the critical micelle concentration (CMC) [8,12]. The three component systems (surfactant–water–IL) are chiefly interesting because ILs can behave as co-solvents, co-surfactants and as background electrolytes [1,13,14]. This gives the chance of tuning the physicochemical properties of the surfactant aggregates formed in water–IL binary mixtures, which is of interest for potential applications [1]. Some reports have been published regarding the surfactant aggregate formation in ILs. The effect of ethylammonium nitrate (EAN, as ILs) on aggregation behavior of alkyltrimethylammonium bromide (C_nTAB), alkylpyridinium bromide (C_nPB), and nonionic Triton X-100 has been studied by Evans et al. [15,16]. Their results showed that the CMC values in EAN are larger compared to water. It was found that the mixtures are stable at temperatures up to 250 °C. In another pioneering work for surfactant self-assembly in ILs, surface and thermodynamic properties of tetraethyl ammonium tetrafluoroborate [TEA(BF_4)] and numerous ethylene oxide based non-ionic surfactants in aqueous media have been reported using surface tension, viscosity and dynamic light scattering measurements [5]. According to their results, surface tension increased with increases in IL concentration and opposite trend was monitored when surfactant concentration was increased. Also, it was supposed that the micellization power and adsorption ability were decreased at high IL concentrations. In a similar work, Mahajan et al. [6] studied the aggregation and interfacial behavior of aqueous mixtures of anionic surfactant; sodium dodecylbenzenesulfonate (SDBS) and

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http://dx.doi.org/10.1016/j.molliq.2016.03.076

imidazolium based surface active ionic liquids. The consequences revealed the presence of strong synergistic interactions prevailing between the oppositely charged SDBS and ionic liquids. The interaction causes to form micelles, vesicles or micelles and vesicles together at different mixing ratios of the components. The knowledge of surface active properties, physicochemical and thermodynamic behavior of imidazolium-based ILs in surfactant media is of great interest in colloid and interface science. It also helps to evaluate and scrutinize the role and prominence of such ILs in various applications. Most of these ILs influence surfactant self-assembly systems through the formation of a three-dimensional hydrogen bond network along with electrostatic and hydrophobic interactions. In brief, the aim of the present work is to study the effect of imidazolium-based ILs; 1-Ethyl-3-methylimidazolium bromide (EMIm Br) as additive on aggregation and surface behavior of anionic surfactant (SDS) and its mixtures with cationic surfactant (TTAB). Up to now, different properties of alone surfactants and ILs have been studied. However, few studies have been devoted to mixed surfactants in the presence of imidazolium-based ILs as additive. We also characterized the physicochemical properties and the morphology of these mixtures by performing surface tension, electrical conductivity, cyclic voltammetry (CV), dynamic light scattering (DLS) and transmission electron microscopy (TEM).

2. Experimental section

2.1. Materials and sample preparation

Sodium dodecyl sulfate (SDS), tetradecyl trimethyl ammonium bromide (TTAB) and the electroactive probe 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were purchased from Merck Company and were used for preparation of stock solutions in IL-water. 1-Ethyl-3-methylimidazolium bromide (EMIm Br) was synthesized (supporting file). Aqueous solutions of individual surfactants and SDS/TTAB mixture at different ratios of SDS to TTAB were prepared at two different percentages of EMIm Br. We weighed accurately using a digital balance with a sensitivity of ±0.1 mg. Water used in all the experiments was double distilled, with a specific conductivity of <5 μS/cm and was tested for the absence of organics using surface tension measurements. All samples were equilibrated at 25 °C in a thermostated bath.

2.2. Methods

2.2.1. Surface tensions measurements

The surface tensions of surfactant solutions along with IL at various concentrations were determined with a surface tensiometer (Jencon, India) using a platinum ring by the ring detachment technique. The tensiometer was calibrated against distilled water. Our analysis showed that the mean value of surface tension for distilled water was 71.29 mN m^{-1} at room temperature. On the basis of literatures, 72.75 mN m^{-1} is the surface tension of water at 20 °C as a reference value. The platinum ring was cleaned and dried before each measurement. A burner was employed to remove all organic materials on the platinum ring. The measurements were done in such a way that the vertically hung ring was dipped into the liquid to measure its surface tension. It was then pulled out. The maximum force needed to pull the ring through the interface was then expressed as the surface tension. The uncertainty of the measurements was ±0.5 mN/m. In all cases, more than three successive measurements were carried out.

2.2.2. Conductivity measurements

Conductivity measurements were carried out with a conductometer, Crison micro CM 2201. The conductivity cell was calibrated with KCl solutions in an appropriate concentration range. Accuracy of measured conductance was within ±0.5%. The CMC values of single and mixed surfactants in the presence of IL were determined by conductivity measurements at 298 K. The pure surfactant solutions were prepared by diluting the concentrated stock solution. The mixed solutions were prepared by mixing two pure solutions and were kept for at least 2 h to reach equilibrium. The conductivity at each mole fraction was measured by successive addition of concentrated solution of surfactant mixture in IL-water solution. The uncertainty of the measurements was ±0.2 μS.

2.2.3. Cyclic voltammetry (CV) measurements

Cyclic voltammetry measurements were performed at 298 K using a SAMA 500 model, with electro-active probes of TEMPO, an Ag/AgCl reference electrode, and platinum counter- and working electrodes. The solutions were prepared in the presence of electroactive probe TEMPO (3 mM) and supporting electrolyte KCl (0.1 M) in order to keep the ionic strength constant. Reversible scans were obtained for stock solutions of pure components and a complete range of mole fractions of their mixtures.

2.2.4. Dynamic light scattering (DLS) measurements

A Zetasizer Nano (Malvern, MRK825–02, UK) was used for DLS measurements. The refraction index and viscosity of the solutions were measured before each experiment.

2.2.5. Transmission electron microscopy (TEM)

Transmission electron micrographs were recorded on a Zeisselectron microscope (EM-10C) operated at 100 kV. Solution of definite concentration was prepared and then a drop of IL/surfactant mixture was dispersed on the surface of a TEM copper grid covered by a holey carbon film. The solution should be dried before data acquisition. The magnification can be done up to 5×10^5 times at high resolution mode.

3. Results and discussion

3.1. Determination of CMC and phase transition

The surface tension and conductivity measurements of IL/surfactant mixtures have been investigated in aqueous media. Fig. 1 shows the CMC values of pure TTAB, SDS and the mixed surfactants (SDS/TTAB) in water-IL mixture in the rich regions of anionic surfactant.

The values of surface tension and conductivity measurements are collected in Table 1. One can see in Table 1 that the mole fraction increases of TTAB and IL percents causes to decrease in CMC values and also makes two breaks in the value of surface tension. In the 90:10 SDS/TTAB systems, tensiometry plot showed two breaks. These breaks may be due to the formation of different aggregates, which occur because of a change in the shape and the size of the micelles. The conductometry plot did show a break at around the same value where there was the second break in the surface tension plot. With further increases in the IL concentration and cationic surfactant mole fraction, phase transition is easier. In general, the effect on surfactants is a combination of some factors such as electrostatic and hydrophobic interaction, electrolyte effect and hydrogen bonding with solvent, IL, and surfactants. In pure and mixed systems, the increase in IL concentration leads to reduction in CMC values due to two factors including the solvency effect and the electrostatic effect. The addition of IL and increasing the mole fraction of TTAB, effects both the interactions between hydrophobic groups and the interactions between hydrophilic groups in mixed systems. Ionic liquid can also effect on surfactant self-assembly systems through the formation of a three-dimensional hydrogen bond network along with electrostatic and hydrophobic interactions. The addition of IL strengthens the attractive electrostatic interaction between their two oppositely charged polar groups, and consequently is an advantage for micelle formation. The increase in values of IL concentration can be mainly attributed to the increase in electrostatic attraction between the two oppositely charged, polar, ionic head groups of SDS and TTAB upon mixing.