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Self-assembled catanionic surfactant mixtures in aqueous/ionic liquid systems

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ABSTRACT

Aggregation behavior of catanionic surfactant mixtures, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) with three imidazolium-based ionic liquids, 1-butyl-3-methylimidazolium bromide (BMImBr), 1-butyl-3-methylimidazolium chloride (BMImCl), and 1-hexyl-3-methylimidazolium bromide (HMImBr) water systems has been investigated by using tensiometry, cyclic voltammetry and dynamic light scattering (DLS). Surface tension reduction effectiveness (γ_{CMC}), surface excess (Γ_{max}), and mean molecular surface area (A_{min}) have been determined by means of plots of the surface tension (γ) as a function of the total surfactant concentration. Intramicellar interaction parameter (β) and the ionic liquid effect on it have been investigated. Voltammetric measurements were carried out to calculate the micellar self-diffusion coefficient (D) and intermicellar interaction parameter (k_d) of catanionic surfactant in ionic liquid at 298.15 K. In an aqueous solution, the presence of ionic liquids causes a decrease in critical micelle concentration (CMC) of surfactants. The decrease of the CMC value is primarily due to a reduction in the electrostatic repulsions between headgroups.

1. Introduction

Aqueous mixtures of cationic and anionic surfactants exhibit many unusual properties that aren't presented by other combinations of mixed surfactants. Mixtures of cationic and anionic surfactants (catanionic mixtures) represent attractive systems for applications as they exhibit strongly synergistic interactions, which for instance lead to a large reduction in the critical micelle concentration (CMC). The strongly attractive interactions between headgroups with each other lead to a dramatic reduction in their areas, which allows the easy formation of aggregates, due to the changing packing parameter. Oppositely charged surfactants can form a wide variety of phases such as spherical micelles, rod-like micelles, disk vesicles, and lamellar liquid crystals, with the phase geometry depending on the strength of intermolecular interactions, the geometrical shape of the surfactants, the mole fraction of oppositely charged surfactants, concentration, and environmental factors (temperature, additives, etc). One of the noteworthy properties of systems of oppositely charged surfactants is their ability to spontaneously form vesicles [1,2].

Ionic liquids (ILs) are a class of organic molten electrolytes at or near room temperature. Ionic liquids are usually composed of heterocyclic organic cations and various anions and have unique properties such as non-volatility, non-flammability, non-aqueous and non-toxicity, high solubility power, and a wide temperature range for liquid phase [3]. The unusual properties of ionic liquids like non-flammability may open the possible uses of room temperature ionic liquids (RTILs) in many research areas such as electrical devices to avoid the explosion or ignition [4]. Also, their properties can be fine-tuned by varying the component ions of the ILs. Thus, ILs have attracted much attention as electrolytes and solvent media for chemical reactions and extractions, material preparation and gas absorbents. Since ionic liquids exhibit extremely low vapor pressures and long liquid ranges, and are highly polar yet non-coordinating, they are good solvents for a wide range of organic and inorganic materials. Current publications indicate that replacing an organic solvent with an ionic liquid may lead to remarkable improvement in well-known processes. For example, these amazing liquids have been utilized not only as clean solvents, but also as catalysts for green chemistry and electrolytes for batteries, photochemistry and electro-synthesis and even as advanced heat transfer fluids and lubricants [5]. Their amphiphilic characteristic has recently attracted interest in the investigation of their self-assembly process in water [6] or their effect as additives on self-assembly of amphiphiles in an aqueous medium [7,8]. Moreover, the self-assembly of other amphiphiles like surfactants, lipids, and block copolymers in ionic liquid solvents has been studied widely [9].

Recent investigations have clearly demonstrated the effectiveness of ILs in altering the key physicochemical properties of aqueous surfactant systems composed of zwitterionic [4], nonionic [10,11] and anionic [7,8] surfactants. The effectiveness of ILs in changing the properties of an aqueous surfactant system depends on the kind and extent of interaction(s) between the cation/anion of the IL and surfactant head-

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group. At lower concentrations of IL these electrostatic interactions have turned out to be of utmost importance in deciding the physicochemical properties of the aqueous surfactant system [5].

The relatively larger hydrophilic headgroup of the IL results in a larger maximum surface excess concentration (Γ_{max}) and a smaller minimum molecular cross-sectional area (A_{min}). Electrical conductivity studies show a small degree of counter ion binding to these micelles, which may increase the electrostatic repulsions between the hydrophilic heads of adjacent surfactant molecules. Both factors of the hydrophilic head-group size and electrostatic repulsion in [C_{16}hpim]Br micelles lead to a looser packing of the surfactant molecules in the micelles [12].

In this research, the aggregation behavior of catanionic surfactant mixture, n-hexadecyl-trimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) in cationic-rich region and in three imidazolium based ionic liquids, 1-butyl-3-methylimidazolium bromide (BMImBr), 1-buthyl-3-methylimidazolium chloride (BMImCl), and 1-hexyl-3-methylimidazolium bromide (HMImBr)/water systems, which differ in tail length of cation and anion type, was investigated using tensiometry, dynamic light scattering (DLS), and cyclic voltammetry. We expect that the present study helps to better understand the aggregation mechanism and phase behavior of catanionic surfactant mixture in aqueous/IL systems. Also, this study helps in the investigation of various ionic liquid effects on the size of aggregates.

2. Experimental

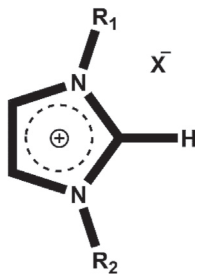
2.1. Materials

SDS (>99%), CTAB (99%), sodium bromide (NaBr, extra pure) and ferrocene (98%) were obtained from Merck. Samples were prepared by mixing the appropriate volumes of SDS and CTAB stock solutions. Since, preparing pure SDS solutions is complicated by the fact that some hydrolysis to dodecyl alcohol takes place, fresh SDS solutions were therefore used for experiments. 1-Butyl-3-methylimidazolium bromide, 1-buthyl-3-methylimidazolium chloride, and 1-hexyl-3-methylimidazolium bromide were synthesized by Dr. Sharifi in Chemistry and Chemical Engineering Research Center of Iran (Fig. 1) [13]. All samples were equilibrated at 298.15 K in a thermostated bath.

2.2. Methods

2.2.1. Surface tension measurements

Surface tension measurements were carried out at 298.15 K by the ring method using a Sigma 700 tensiometer under an atmospheric pressure. The platinum ring was thoroughly cleaned and flame-dried before each measurement. Measurements of the surface tension of distilled water at 298.15 K were used to calibrate the tensiometer and to check the cleanliness of the glassware. In all cases, more than three successive measurements were carried out, and the standard deviation did not exceed ±0.1 m Nm^1. The temperature was controlled to within ±0.1 °C by circulating thermostated water through the jacketed glass cell.



BMImCl	R1= Butyl	R2= Methyl	X= Cl
BMImBr	R1= Butyl	R2= Methyl	X= Br
HMImBr	R1= Hexyl	R2= Methyl	X= Br

Fig. 1. The molecular structure of ILs.

2.2.2. Cyclic voltammetry measurements

Cyclic voltammetry measurements were performed at 298.15 K using a SAMA 500 model, with electro-active probes of ferrocene, an Ag/AgCl reference electrode, and platinum counter- and working electrodes. All solutions were prepared to a final volume of 25 ml, containing 0.001 mol lit^{-1} ferrocene, and different concentrations of surfactants. Due to the insolubility of ferrocene in water, ferrocene was first dissolved in ethanol.

2.2.3. Dynamic light scattering

The foundation of DLS is based on the scattering of light by moving particles. The dynamic light scattering experiments were performed on a particle size analyzer, model (9.PLUS). All the measurements were done at a scattering angle of 90° and a temperature of 298.15 K, which was controlled by means of a thermostat.

3. Results and discussion

3.1. Determination of the CMC

The CMC of the surfactants was determined above the Krafft temperature, T_k. In general, the T_k values for surfactant–water solutions are below room temperature. The CMC is only a weak function of temperature. However, to achieve greater accuracy, the temperature was constant (298.15 K) during all experiments by using a circulating bath. Table 1 shows the CMC values for different compositions of the binary CTAB/SDS mixtures (in the cationic-rich region). These values were determined from surface tension plots.

The plots of surface tension vs log [surfactant] in the presence of various ionic liquid concentrations have been shown in the Supporting file (S1, S2, and S3). As seen, CMC decreases with an increase in ionic liquid concentration. This can be mainly attributed to the fact that, under these conditions, the repulsion forces between the headgroups decrease.

Table 1
Critical micelle concentration (CMC) in mM for cationic-rich mixtures at various ionic liquid concentrations and NaBr as inorganic salt.[a]

Molar ratio	Ionic liquid concentration (mol/l)			
	0	0.008	0.02	0.05
BMImCl				
CTAB	0.910*	0.067	0.053	0.048
0.98	0.763	0.100	0.067	0.062
0.96	0.811	0.062	0.057	0.043
BMImBr				
CTAB	0.910	0.119	0.084	0.048
0.98	0.763	0.091	0.057	0.043
0.96	0.811	0.053	0.029	0.028
HMImBr				
CTAB	0.910	0.090	0.057	0.038
0.98	0.763	0.062	0.053	0.036
0.96	0.811	0.048	0.043	0.038
NaBr				
CTAB	0.910	0.474	0.369	0.130
0.98	0.763	0.388	0.278	0.129
0.96	0.811	0.453	0.280	0.136

* The CMC of pure CTAB.

[a] Standard uncertainty U is U(CMC) = ±0.06.