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Synergistic interactions in W/O microemulsions containing imidazolium based C_{12}mimBr and sodium lauryl sulfate

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The physicochemical properties and synergistic effects of W/O microemulsion systems containing imidazolium based surfactant, 1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr)-sodium lauryl sulfate (SLS)/ alcohol/alkane/ 5% NaCl solution at different molar ratios of water-to-surfactant (ω_0) are studied. The W/O microemulsions are formed at the molar fractions of SLS-to-C_{12}mimBr+SLS (X_{SLS}) ranges of 0.0-0.3 and 0.7-1.0. The synergism between C_{12}mimBr and SLS can be seen from the values of X_a^o (mole fraction of alcohol in the oil phase), X_a^i (mole fraction of alcohol in the interfacial layer) and $-G^o_{o\rightarrow i}$ (the standard free energy change of transferring alcohol from the continuous oil phase to the interfacial layer). The increase in the values of X_a^o and X_a^i, and the decrease in $-G^o_{o\rightarrow i}$ values with ω_0 is attributed to the increasing hydrophilicity of the microemulsions. By increasing the carbon chain lengths of the alcohol molecules, or by increasing the salt concentrations, the values of X_a^o and X_a^i decrease, whereas that of $-G^o_{o\rightarrow i}$ increases for the W/O microemulsions containing the mixed surfactants. On the other hand, the effect of the alkane carbon chain lengths is exactly the opposite of the effect of the alcohol carbon chain lengths on the these parameters.

Keywords: Solution chemistry, Synergistic interactions, Microemulsions, W/O microemulsions, Surfactants, Imidazolium surfactants, Sodium lauryl sulfate

Ionic liquids are ionic, salt-like materials that are liquid at or near room temperatures, composed of organic cations and organic or inorganic anions. Ionic liquids have good physicochemical properties including low vapor pressure and freezing point, wide liquid regions and excellent thermal stability, etc.[1,2]. They are the green alternatives for organic solvents[3-5]. The most widely used ionic liquids is imidazolium[6,7]. The imidazolium based ionic liquids with long carbon chain can be used as surfactants. These surface active ionic liquids (SAILs) have obvious advantages over traditional surfactants[8-11].

The interactions of SAILs with traditional surfactants or additives in aqueous solutions have been widely investigated. Studies on micellar solutions containing $C_n$mimCl (n = 8, 10, 12) and anionic surfactant, SDBS, showed that the mixed catanionic systems possess superior surface activity as compared to the pure components. These results showed the existence of synergistic interactions between the oppositely charged SAILs and SDBS due to the strong electrostatic and hydrophobic interactions[12]. In addition, mixed micellar solutions have been utilized as templates for the preparation of Ag nanoparticles. The morphology of Ag nanoparticles was found to be controlled by the molar ratio of SDBS-to-SAIL in the mixture. The mixed SDBS-SAIL systems showed improved physicochemical properties and therefore are potentially applicable for synthesis of nanoparticles with different morphologies[12].

The interactions between the hydrophobic IL anions (NTf_2^- and PF_6^-) and Triton X-114 (TX-114) micelles[13], and between aromatic counterions (*m*-HB and *p*-HB) and C_{12}mimBr[14] have been examined. The hydrophobic IL anions barely affected the CMC value and the aggregation number of TX-114 micelles, and the hydrophobic interaction is the main interactions between TX-114 and the IL anions[13]. The introduction of these aromatic counterions effectively screens electrostatic repulsion and favors the micellization[14].

Herein, the synergistic effect of the mixed cationic C_{12}mimBr and anionic SLS surfactants[15-20] on the thermodynamic and structural properties of the W/O microemulsion systems has been studied. The effects of alcohols, oils and salinities on the physicochemical parameters of the microemulsions are discussed.

Experimental

Imidazolium based surfactant, 1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr), was synthesized by the literature method[21] and characterized by IR, MS and ^{1}H NMR. The changes in surface tension were measured with varying C_{12}mimBr concentrations, and no minimum points were found on the surface tension curve, indicating that no surfactive impurities exist. Sodium lauryl sulfate (SLS), heptane, octane, decane, butan-1-ol, pentan-1-ol, hexan-1-ol and NaCl are of AR grade. Milli-Q water was used in all the experiments.

A DF-101S constant temperature magnetic mixer (with accuracy up to +0.1 K, Jiangsu, China) and FA1104 analytical balance (with accuracy up to +0.0001 g, Shanghai, China) were used in this study.

With the total number of moles of C_{12}mimBr and SLS fixed at 0.5 mmol, and at a specified molar fraction of C_{12}mimBr-to-SLS+C_{12}mimBr (X_{SLS}), the two surfactants were weighed and placed in a series of Teflon-sealed glass tubes. Then, 2 mL of oil and water (The volume of water was determined by the molar ratios (ω_0) of water-to-surfactant) was added into the tubes. The test tubes were sealed and placed in the thermostatic water bath at 313 K. Under stirring using a magnetic mixer, the alcohol was added drop by drop into the tubes until the system become clear. The volume of alcohol added was recorded. After that, a small amount of oil was added into the system, and then the alcohol was slowly added again until the system changed from turbid to clear. The volumes of the added oil and alcohol were recorded again. The above mentioned procedure was repeated five times, and the volumes of oil and alcohol added each time were recorded. The above process was repeated at different X_{SLS} values.

Results and discussion

Figure 1 shows the dilution curves of W/O microemulsions, viz., C_{12}mimBr/SLS/butan-1-ol/octane/5% NaCl solution at different molar ratios of water-to-surfactant, w_0 (= n_w/ n_s, where n_w and n_s are the moles of water and surfactant, respectively). The molar fractions of SLS-to-C_{12}mimBr+SLS (X_{SLS}) were fixed at different values at the same interval (0.0, 0.1, 0.2 ···1.0). It was found that the W/O microemulsions are formed at the X_{SLS} ranges of 0.0-0.3 and 0.7-1.0. When the X_{SLS} values are in the range of 0.4–0.6, precipitation occured in the systems. The dilution curves of the W/O microemulsions in Fig. 1 obey the dilution equation[22].

$$\frac{n_a}{n_s}=\frac{n_a^i}{n_s}+\frac{n_a^o}{n_s}=\frac{n_a^i}{n_s}+\frac{n_a^o}{n_o}\frac{n_o}{n_s}=I+k\left(\frac{n_o}{n_s}\right) \qquad \ldots(1)$$

In Eq. 1, n_a, n_a^i, and n_a^o are the moles of the alcohol, in the entire system, in the interfacial layer (i) and in the oil phase, respectively.

The slope (k) and intercept (I) in dilution equation (1) can be obtained from Fig. 1. Therefore, The physicochemical parameters X_a^o (the mole fraction of the n-alkyl alcohol in the oil phase), X_a^i (the mole fraction of the n-alkyl alcohol in the interfacial layer) and $-G_{o\rightarrow i}^o$ (the standard free energy change of transferring n-alkyl alcohol from the continuous oil phase to the interfacial layer) can be calculated from Eqs (2), (3) and (4), respectively.

$$X_a^i=\frac{n_a^i}{n_s+n_a^i}=\frac{I}{1+I} \qquad \ldots(2)$$

$$X_a^o=\frac{n_a^o}{n_o+n_a^o}=\frac{k}{1+k} \qquad \ldots(3)$$

$$\Delta G_{o\rightarrow i}^o=-RT\ln K \qquad [K=\frac{X_a^i}{X_a^o}=\frac{I(k+1)}{k(I+1)}] \qquad \ldots(4)$$

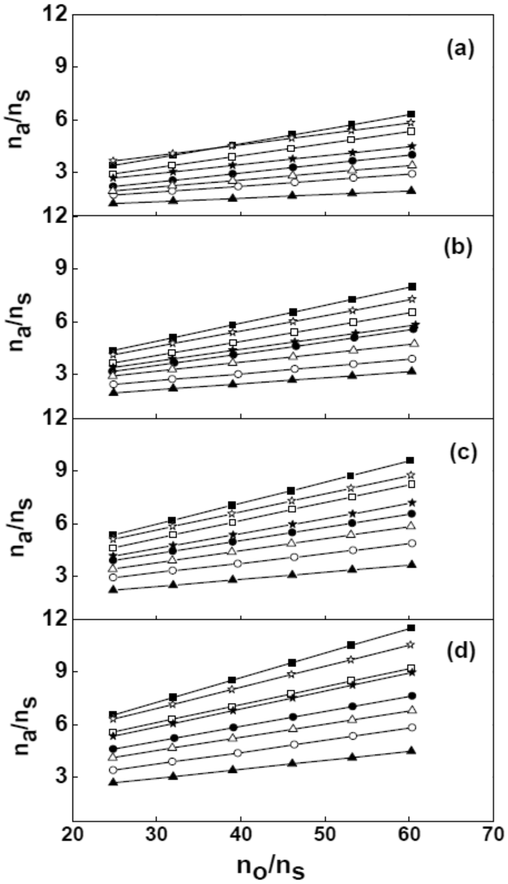

Fig. 1 — Dilution curves of microemulsions, C_{12}mimBr/SLS/butan-1-ol/octane/5%NaCl solution at different ω_0 values. [X_{SLS} = 0.0 (■), 0.1 (□), 0.2 (●), 0.3 (○), 0.7 (▲), 0.8 (△), 0.9 (★), 1.0 (☆). a: ω_0 = 10; b: ω_0 = 20; c: ω_0 = 30; d: ω_0 = 40].

The changes in X_a^i, X_a^o and $-G^o_{o\to i}$ values at different ω_0 values with X_{SLS} plotted in Fig. 2 shows that the values of both X_a^i, X_a^o were smaller, whereas the $-G^o_{o\to i}$ values were larger in the W/O microemulsions containing both the mixed surfactants C_{12}mimBr+SLS compared to that in the systems containing the single surfactant, C_{12}mimBr or SLS. This indicates the existence of synergism between C_{12}mimBr and SLS.

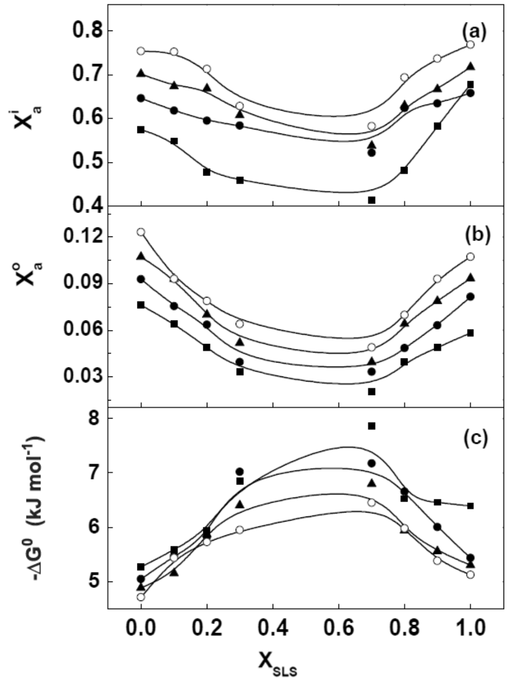

Fig. 2– The changes in X_a^i, X_a^o and $-G^o_{o\to i}$ values at different ω_0 values with X_{SLS} of W/O microemulsions C_{12}mimBr/SLS/butan-1-ol/octane/5% NaCl solution. [ω_0 = 10 (■); 20 (▲); 30 (●); 40 (○)].

The electrostatic interaction exists between cationic C_{12}mimBr and anionic SLS, enabling the surfactant molecules to arrange more closely in the interfacial layer[23,24]. Thus, the amount of alcohol needed to balance the interfacial layer (X_a^i), and therefore the amount of alcohol dissolved in oil phase would decrease. This implies the improved ability for alcohols to transfer from oil phase to the interfacial layer, resulting in the increase in the $-G^o_{o\to i}$ values.

The values of X_a^o and X_a^i increases with increasing ω_0 value (Fig. 2). This is due to the increasing hydrophilicity of the microemulsions as ω_0 increases. Therefore, the amount of alcohol needed to balance the interfacial layer increases. On the other hand, the $-G^o_{o\to i}$ value decreases with an increasing ω_0 value, indicating the low ability of the alcohol to transfer from the oil phase to the interfacial layer.

The effects of alkanes (A), alcohols (B) and salt concentrations (C) on the dilution curves of the W/O microemulsions containing mixed surfactants C_{12}mimBr and SLS are shown in Fig. 3. According to Eqs (2), (3) and (4) and from Fig. 3, the values of X_a^i, X_a^o and $-G^o_{o\to i}$ can be obtained.

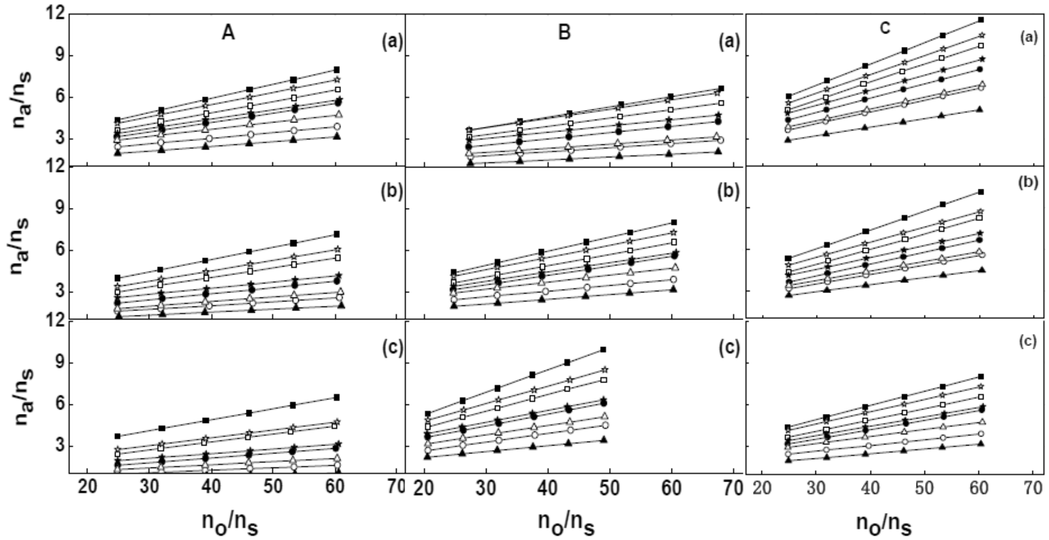

Fig. 3 – Effect of alkanes (A), alcohols (B) and salt concentrations (C) on the dilution curves of the W/O microemulsions containing C_{12}mimBr/SLS/alcohol/alkane/NaCl solution. [X_{SLS} = 0.0 (■), 0.1 (□), 0.2 (●), 0.3 (○), 0.7 (▲), 0.8 (△), 0.9 (★), 1.0 (☆). A: Butan-1-ol/5% NaCl solution. (a) heptane, (b) octane, (c) decane; (B) Octane/5% NaCl solution. (a) butan-1-ol, (b) pentan-1-ol, (c) hexan-1-ol; (C) Butan-1-ol/octane/NaCl solution. NaCl conc.: (a) 0%, (b) 2.5%, (c) 5.0%, (d) 7.5%].

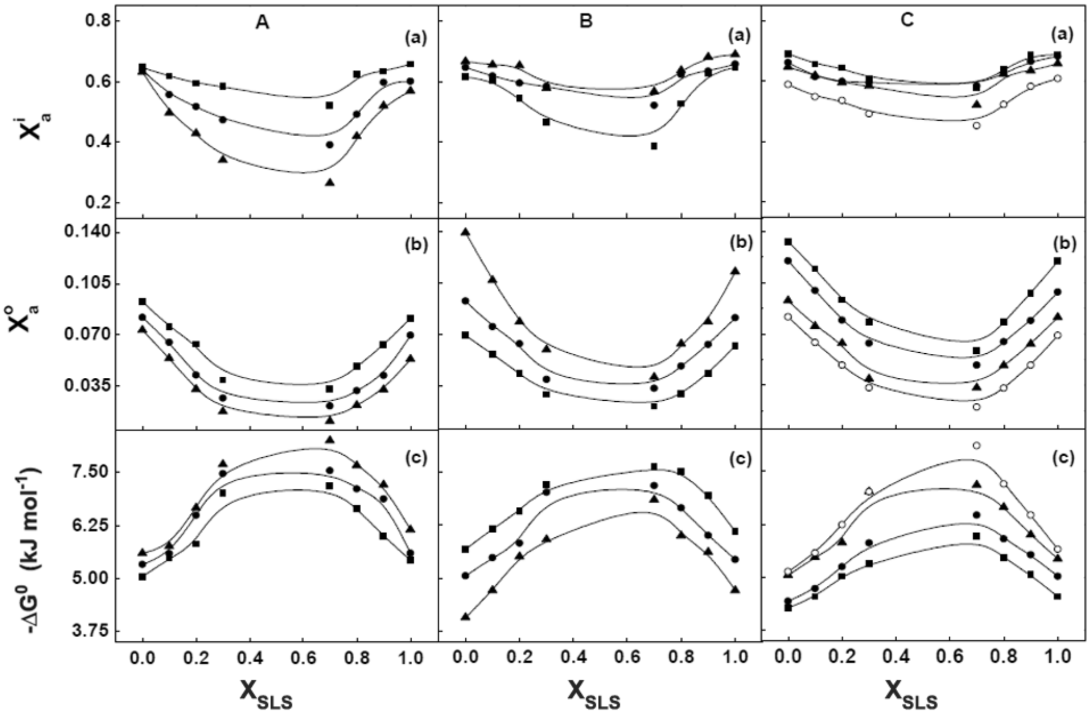

Fig. 4 − Effect of alkanes (A), alcohols (B) and salt concentrations (C) on X_a^i (a), X_a^o (b) and $-G_{o\rightarrow i}^o$ (c) values of C_{12}mimBr/SLS/butan-1-ol/octane/5%NaCl solution. A: Butan-1-ol/5% NaCl solution. heptane (■), octane (●), decane (▲); (B) Octane/5% NaCl solution. butan-1-ol (■); pentan-1-ol (●); hexan-1-ol (▲); (C) Butan-1-ol/octane/5%NaCl solution. NaCl conc.: 0% (■), 2.5% (●), 5.0% (▲),7.5% (○)].

The changes in X_a^i, X_a^o and $-G_{o\rightarrow i}^o$ with X_{SLS} are shown in Fig. 4. Figure 4(A) shows the effect of alkanes with different carbon chain lengths on the values of X_a^i, X_a^o and $-G_{o\rightarrow i}^o$. By increasing the carbon chain lengths of the alkane molecules, X_a^i and X_a^o increases, whereas $-G_{o\rightarrow i}^o$ decreases. It is not easy for alkane molecules with longer carbon chain lengths to penetrate into the interfacial layer to increase the hydrophobicity of the W/O microemulsions. Therefore, a larger amount of alcohol is needed to balance the interfacial layer of the W/O microemulsions. Hence, the spontaneous transfer ability of the alcohol from oil phase to the interfacial layer ($-G_{o\rightarrow i}^o$) would decrease.

The effect of the alcohol carbon chain length is exactly opposite of the effect of alkane carbon chain length on these parameters, i. e., both X_a^i and X_a^o decreases, while $-G_{o\rightarrow i}^o$ increases for the W/O microemulsions as the carbon chain length of the alcohol molecules increases (Fig. 4B). This can be explained as due to the alcohols with longer chain lengths having higher efficiency in changing the curvature of the interfacial layer. Therefore, the amount of the alcohol required to balance the interfacial layer as well as the amount of the alcohol dissolved in the oil phase would decrease. As a result, the transferring ability of the alcohol from oil to the interfacial layer $-G_{o\rightarrow i}^o$ would increase.

The values of both X_a^i and X_a^o decreases, whereas $-G_{o\rightarrow i}^o$ increases, when there is an increase in the salt concentrations (Fig. 4C). This pattern of change is similar to increase in the carbon chain lengths of the alcohol molecules. This may be interpreted as due to the compression of the hydrophilic group of the surfactants. The increase in the salt concentrations suppresses the hydrophilic head of C_{12}mimBr and SLS molecules, weakening the hydrophilic property, thus promoting the formation of the W/O microemulsions.

In the present study, dilution experiments of the W/O microemulsions, C_{12}mimBr-SLS/butan-1-ol/octane/5% NaCl solution, were carried out at different molar ratios of water-to-surfactant. It was found that the W/O microemulsions are formed at the molar fraction ranges (X_{SLS}) of 0.0–0.3 and 0.7–1.0. In the X_{SLS} range of 0.4–0.6, precipitation occurred in the systems. Synergism between C_{12}mimBr and SLS was found to exist in the W/O microemulsions containing these two surfactants. The synergistic effect results in the decrease in both X_a^i and X_a^o values and increase in $-G^o_{o\to i}$ values. As ω_0 increases, the hydrophilicity of the systems increases. Thus, the values of X_a^i and X_a^o increase, whereas $-G^o_{o\to i}$ values decrease. The increase in ω_0 values is not conducive to the formation of W/O microemulsions. As a result of either an increase the carbon chain lengths of the alcohol molecules, or a decrease in carbon chain lengths of the alkane molecules, or an increase in the salt concentration increases, both X_a^i and X_a^o would decrease, while $-G^o_{o\to i}$ would increase.

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