

Comparison of the Composition and Structural Parameters of W/O Microemulsions Containing Gemini Imidazoliums with Those Containing Monomeric Analogues

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Abstract The composition and structural parameters of W/O microemulsions containing the gemini surfactant 1,4-bis(3-alkylimidazolium-1-yl) butane bromide $[(C_n-4-C_n)Br_2, n = 12, 14, 16]$ + pentan-1-ol + octane + water and W/O microemulsions containing the ionic liquid surfactant 1-alkyl-3-methylimidazolium ($C_n\text{mimBr}, n = 12, 14, 16$) + pentan-1-ol + octane + water were studied and compared. The mole fractions of the n -alkyl alcohol at the interfacial layer X_a^i in $(C_n-4-C_n)Br_2$ based microemulsion systems are always larger than those in $C_n\text{mimBr}$ based microemulsion systems. However, the mole fractions of the n -alkyl alcohol in the oil phase X_a^o are nearly the same for both the microemulsion systems. The $(C_n-4-C_n)Br_2$ based microemulsion systems have greater absolute values of the free enthalpy values $-\Delta G_{o \rightarrow i}^o$ than that for $C_n\text{mimBr}$ based systems. In the $(C_n-4-C_n)Br_2$ based microemulsion systems, a large number of cosurfactants at the interfacial layer is conducive to the formation of a smaller droplet W/O microemulsion. The effects of n -alkyl alcohols, alkanes, salinity and temperature on the composition and structural parameters of the $(C_n-4-C_n)Br_2$ based and $C_n\text{mimBr}$ based microemulsion systems were also investigated and discussed.

Keywords Interfacial composition · Structural parameter · Microemulsion · Dilution method · Gemini imidazolium

Introduction

Gemini surfactants (GS) contain two hydrophilic groups and two hydrophobic groups. The two head groups of GS are connected by a spacer group. Compared to conventional surfactants containing a similar single hydrophilic group and a single hydrophobic group, the properties of interest of GS include their lower-than-usual critical micelle concentration (CMC) values and high efficiency in decreasing the surface tension of water [1–7]. GS have been attracting considerable interest in the academic and industrial fields. Their behavior at the air/solution interface, the thermodynamics of micellization, the mixed micellization with various conventional surfactants, and the phase behavior of GS have been widely studied and reviewed [8–13]. Recently, a micellization study on aqueous solutions of a series of symmetrical cationic GS with different spacer lengths was systematically conducted, and the effect of spacer length on the micellization of the synthesized GS was investigated [14]. The values of CMC suggest that the shorter the spacer length, the higher the surface activity of the ionic liquid-type gemini imidazolium surfactants [15]. Ethylene glycol, ionic liquids and organic hydrotropes have often been used to modify the properties of aqueous solutions of GS. The addition of ethylene glycol to aqueous gemini micellar solutions causes the sphere-to-rod transition to occur at high surfactant concentrations [16]. The effect of ionic liquids on cationic gemini solutions could be regarded as the comprehensive effects of inorganic salt, cosurfactant, and cosolvent on the surfactant solution [17].

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The properties of aqueous solutions of cationic GS can be efficiently modified by the addition of organic hydrotropes. When the volume fraction of hydrotrope increases, the value of CMC of GS in water + hydrotrope media increases [18]. The interactions between the surfactants and the hydrotropes are synergistic in nature, greatly reducing the CMC values [19–21]. Mixed micellization properties of the cationic [22] and anionic [23] monomeric surfactants with GS have been studied. The mixed system in water exhibits synergism in the formation of mixed micelles. In addition, GS had more influence on the TCP (temperature of cloud point) of the nonionic polymer cellulose ether. This might be due to the stronger interactions of GS as compared to their single-chain counterparts [24]. Recently, researchers showed that GS had more influence on the cloud point of amphiphilic drugs, and could serve as a better drug carriers [25–27]. In the presence of GS, the thermodynamic parameters were also evaluated at TCP [28–30].

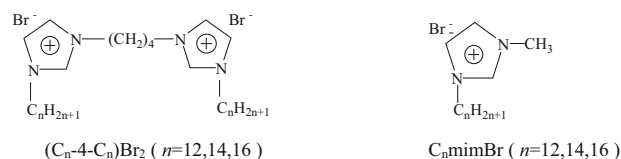
In comparison to the micellization study in aqueous solutions of GS mentioned above, there have been fewer research studies done on the microemulsions formed by GS. The middle-phase microemulsions of GS were investigated by salinity scan [31]. It was shown that the oil-in-water single phase could form a Winsor III type microemulsion over a wide salt concentration range. The oil in water (O/W) microemulsion of GS could be used in the polymerization of styrene [32, 33].

A dilution method of W/O microemulsions was commonly used to determine the composition and structural parameters of W/O microemulsions [34, 35]. In this paper, the composition and structural parameters of the W/O microemulsion systems containing 1,4-bis(3-alkylimidazolium-1-yl) butane bromide $[(C_n-4-C_n)Br_2]$ was investigated using the above-mentioned dilution method, and a comparison with the microemulsion system containing their monomeric analogues was also made.

Experimental

Materials and Apparatus

Gemini imidazolium surfactants with a four-methylene spacer group $(C_n-4-C_n)Br_2$ ($n = 12, 14, 16$) [1,4-bis(3-dodecylimidazolium-1-yl) butane bromide, 1,4-bis(3-tetradecyl imidazolium-1-yl) butane bromide, 1,4-bis(3-cetyl imidazolium-1-yl) butane bromide], and their corresponding monomers $C_n\text{mimBr}$ ($n = 12, 14, 16$) [1-dodecyl-3-methylimidazolium, 1-tetradecyl-3-methylimidazolium, 1-cetyl-3-methylimidazolium] (Scheme 1) were synthesized and purified according to literatures [6, 36–40]. The purities of the surfactants synthesized were checked using



Scheme 1 Chemical structures of gemini imidazolium (left) and their monomeric analogues (right)

$^1\text{H-NMR}$ spectroscopy in DMSO and LC-MS. The purities were also examined by observing the curves of surface tension and no minimum points were found from the curves. The surfactants were left to dry in vacuum for 2 days prior to use.

Heptane, octane, decane, dodecane, butan-1-ol, pentan-1-ol and heptan-1-ol (with mass fraction purity >0.99) were all of A. R. grade and purchased from Alfa Aesar Johnson Matthey, USA. All these chemicals were used without further purification. NaCl (with mass fraction purity >0.99) was A.R. grade and purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Doubly distilled water of conductivity less than $3 \mu\text{S} \cdot \text{cm}^{-1}$ at 298 K was used in the experiments.

Methods

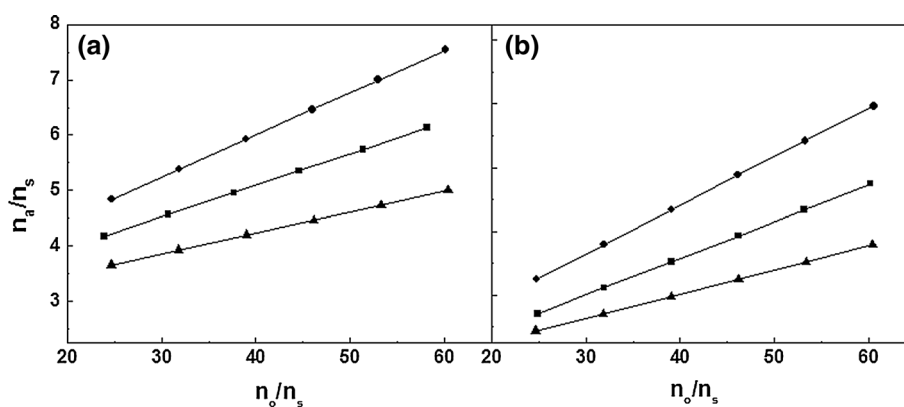
A fixed amount of surfactant (0.5 mmol) was placed in a dry test tube, and was mixed with fixed amounts of oil and water. The molar ratio of water to surfactant (ω_w) was kept constant. The tube was then placed in a thermostatted water bath. *N*-alkyl alcohol was added slowly using a burette under stirring using a magnetic mixer at constant temperature until the original turbid system became just clear. Then a small predetermined amount of oil was added into the tube and the system turned cloudy. The *n*-alkyl alcohol was added again until the system became clear. The procedure was repeated several times. The volumes of *n*-alkyl alcohol and alkane required were recorded. Each experiment was repeated two times, and the average values were used for data processing. Except for the experiments on the effects of temperatures, all the other experiments were performed at 313.15 K (uncertainty ± 0.1 K). The error limit of the dilution method was ca. $\pm 3\%$ [41, 42].

Results and Discussion

Composition and Structural Parameters of the W/O Microemulsions

Figure 1 shows the W/O microemulsion dilution curves for the microemulsion systems $(C_n-4-C_n)Br_2$ (a), $C_n\text{mimBr}$ (b) + pentan-1-ol + octane + 5 % NaCl solution.

Fig. 1 Plots of n_a/n_s vs n_o/n_s for $(C_n-4-C_n)Br_2$ (a), C_nmimBr (b) + pentan-1-ol + octane + 5 % NaCl solution W/O microemulsions with different surfactants at $\omega_0 = 20$. **a** Filled circles $(C_{12}-4-C_{12})Br_2$, filled squares $(C_{14}-4-C_{14})Br_2$, filled triangles $(C_{16}-4-C_{16})Br_2$. **b** Filled circles $C_{12}mimBr$, filled squares $C_{14}mimBr$, filled triangles $C_{16}mimBr$



From the slopes (I) and intercepts (k) of the straight lines in Fig. 1, the composition and structural parameters for the microemulsion systems, i.e. n_s (the number of moles of the surfactant), n_a^o (the moles of the n -alkyl alcohol in the oil phase), n_a^i (the number of moles of the n -alkyl alcohol in the interfacial layer), R_e (the effective radius of the water pool), N_d (the total number of the droplets), \bar{N}_s (the average aggregation number of the surfactant), and \bar{N}_a (the average aggregation number of n -alkyl alcohols) were calculated [43] according to the S1 section of the Supporting Material and listed in Table 1.

For the two types of microemulsion systems containing $(C_n-4-C_n)Br_2$ and C_nmimBr as surfactants, respectively, the mole fraction of the n -alkyl alcohol in the oil phase X_a^o , the mole fraction of the n -alkyl alcohol in the interfacial layer X_a^i , and the standard free energy change of transferring n -alkyl alcohol from the continuous oil phase to the interfacial layer $-\Delta G_{o \rightarrow i}^o$ were calculated according to Eqs. 1–3 from Table 1.

$$X_a^o = \frac{n_a^o}{n_o + n_a^o} \tag{1}$$

$$X_a^i = \frac{n_a^i}{n_s + n_a^i} \tag{2}$$

$$-\Delta G_{o \rightarrow i}^o = -RT \ln K = -RT \ln \frac{X_a^i}{X_a^o} \tag{3}$$

X_a^o , X_a^i , $-\Delta G_{o \rightarrow i}^o$ and the radius of the water pool R_w (refer to Ref. [34]) for $(C_n-4-C_n)Br_2$ based and C_nmimBr based microemulsion systems were plotted and compared in Fig. 2. The related theoretical considerations were presented in the S1 section of the Supplementary Material.

Figure 2 indicates that the pattern of change of four parameters of X_a^o , X_a^i , $-\Delta G_{o \rightarrow i}^o$ and R_w are similar to the chain lengths ($n_{c,s}$) of $(C_n-4-C_n)Br_2$ and C_nmimBr molecules increase in $(C_n-4-C_n)Br_2$ based and C_nmimBr based W/O microemulsion systems. That is, as $n_{c,s}$ increases, X_a^o and X_a^i values would decrease, whereas $-\Delta G_{o \rightarrow i}^o$ would increase. R_w would decrease gradually as $n_{c,s}$ increases.

For all the W/O microemulsion systems in Fig. 2, the comparison of parameters (X_a^o , X_a^i , $-\Delta G_{o \rightarrow i}^o$ and R_w) between surfactants $(C_n-4-C_n)Br_2$ and C_nmimBr are shown as follows. X_a^o : $(C_n-4-C_n)Br_2 \approx C_nmimBr$; X_a^i and $-\Delta G_{o \rightarrow i}^o$: $(C_n-4-C_n)Br_2 > C_nmimBr$; R_w : $(C_n-4-C_n)Br_2 < C_nmimBr$.

It can be explained that as the carbon chain lengths ($n_{c,s}$) of $(C_n-4-C_n)Br_2$ and C_nmimBr molecules increase, the hydrophobicity of the surfactants increases. Therefore the amount of the n -alkyl alcohol required to reach the

Table 1 Composition and structural parameters for $(C_n-4-C_n)Br_2$, C_nmimBr + pentan-1-ol + octane + 5 % NaCl solution W/O microemulsions with different surfactants at $\omega_0 = 20$

	n_a^o/n_o	n_a^i/n_s	$10^4 n_s/mol$	$10^4 n_a^i/mol$	R_e (nm)	$N_d \times 10^{-18}$	\bar{N}_s	\bar{N}_a
$(C_n-4-C_n)Br_2$ + pentan-1-ol + octane + 5 % NaCl solution								
$(C_{12}-4-C_{12})Br_2$	0.076	2.95	5.02	14.8	1.62	52.2	5.81	17.1
$(C_{14}-4-C_{14})Br_2$	0.057	2.81	5.02	14.1	1.35	113	2.75	7.74
$(C_{16}-4-C_{16})Br_2$	0.038	2.72	5.00	13.6	1.19	183	1.65	4.48
C_nmimBr + pentan-1-ol + octane + 5 % NaCl solution								
$C_{12}mimBr$	0.076	1.64	5.01	8.22	3.25	2.86	105	172
$C_{14}mimBr$	0.057	1.55	5.01	7.77	3.22	3.03	100	154
$sC_{16}mimBr$	0.038	1.50	5.00	7.50	3.04	3.75	80	121

Error limits $n_a^o/n_o \pm 0.002$, $n_a^i/n_s \pm 0.04$, $n_a^i \pm 2\%$, $R_e \pm 3\%$, N_d , \bar{N}_s , and $\bar{N}_a \pm 5\%$

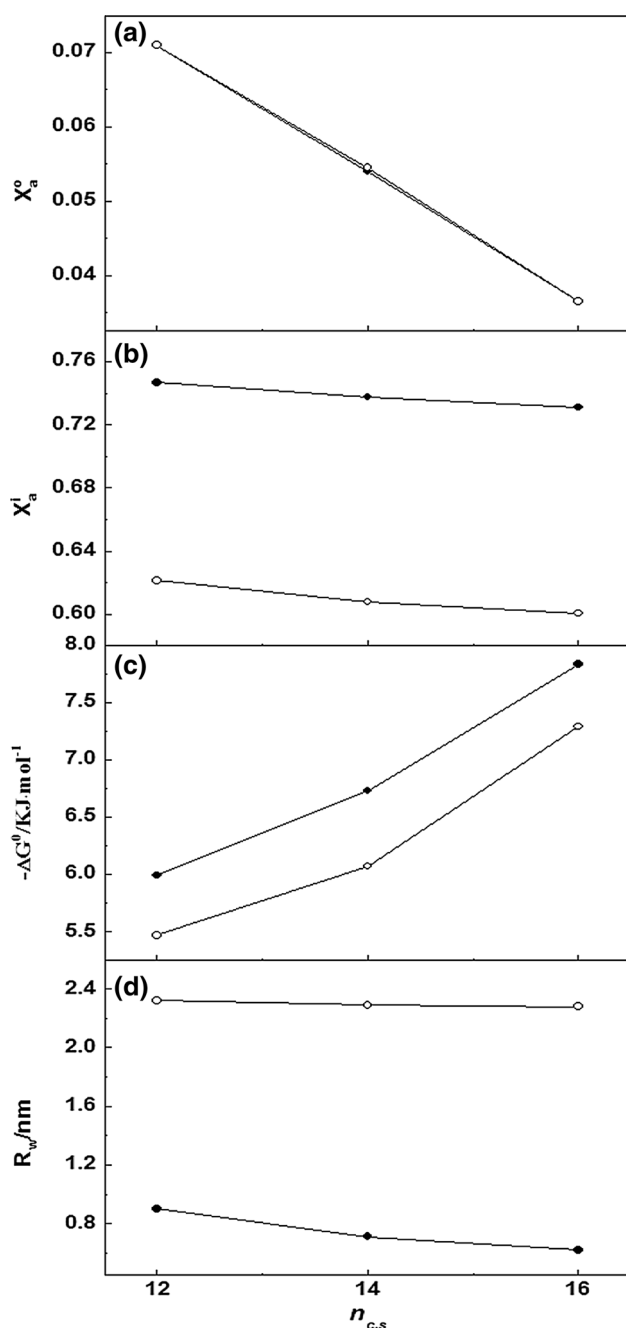


Fig. 2 Comparison of X_a^o (a), X_a^i (b), $-\Delta G_{0 \rightarrow i}^o$ (c) and R_w (d) for the two surfactants based microemulsions $(C_n-4-C_n)Br_2$ (filled circles), C_nmimBr (open circles) + pentan-1-ol + octane + 5 % NaCl solution

balanced interfacial layer would decrease, resulting in the decrease in X_a^o and X_a^i values. The strengthened hydrophobic property of the surfactant as its carbon chain length increases enables the formation of the stable microemulsion to be more spontaneous [44] (Fig. 2c).

Compared with the corresponding mono-chain analogues C_nmimBr , the gemini surfactants are more tightly packed in the interfacial layer because the two hydrocarbon

chains are bridged by a short spacer chain ($-\text{CH}_2\text{CH}_2-\text{CH}_2\text{CH}_2-$) [45]. This bridge effect implies a somewhat greater spontaneous curvature of the interfacial layer of $(C_n-4-C_n)Br_2$, and thus more n -alkyl alcohol molecules must be incorporated into the interfacial layer of $(C_n-4-C_n)Br_2$, in comparison to C_nmimBr (Fig. 2b). This phenomenon results in the greater $-\Delta G_{0 \rightarrow i}^o$ values for $(C_n-4-C_n)Br_2$ based microemulsion systems than that for C_nmimBr based systems (Fig. 2c). This was also explained by the differences in size and shape of the surfactants $(C_n-4-C_n)Br_2$ and C_nmimBr in the two microemulsion systems [46].

Figure 2d shows that the size of the water pool R_w for the $(C_n-4-C_n)Br_2$ based microemulsion systems are smaller than that for their monomeric analogues C_nmimBr systems. The GS-based microemulsion systems can have potential application in the synthesis of nanoparticles of smaller size. As the total number of the droplets N_d increases, there would be a decrease in both the average aggregation number of the surfactant \bar{N}_s and the n -alkyl alcohols \bar{N}_a .

Effects of N -Alkyl Alcohols and Alkanes

Figures 3, 4 show the effects of n -alkyl alcohols and alkanes on the plots of n_a/n_s vs n_o/n_s for W/O microemulsion systems $(C_{16}-4-C_{16})Br_2$ (a), $C_{16}mimBr$ (b) + n -alkyl alcohol + alkane + 5 % NaCl solution, respectively.

The n_a^o/n_o , n_a^i/n_s , n_s , n_a^i , R_e , N_d , \bar{N}_s , \bar{N}_a values were calculated and listed in S2 section of Supporting Material. The values of X_a^o , X_a^i , $-\Delta G_{0 \rightarrow i}^o$ and R_w of these W/O microemulsion systems were obtained and are compared in Fig. 5.

Figure 5 indicates that for all the W/O microemulsion systems studied with different n -alkyl alcohols or alkanes, the comparison of parameters (X_a^o , X_a^i , $-\Delta G_{0 \rightarrow i}^o$ and R_w) between surfactants $(C_n-4-C_n)Br_2$ and C_nmimBr are shown as follows. X_a^o : $(C_{16}-4-C_{16})Br_2 \approx C_{16}mimBr$; X_a^i and $-\Delta G_{0 \rightarrow i}^o$: $(C_{16}-4-C_{16})Br_2 > C_{16}mimBr$; R_w : $(C_{16}-4-C_{16})Br_2 < C_{16}mimBr$.

As the carbon chain length of the n -alkyl alcohol ($n_{c,a}$) increases, X_a^o and X_a^i would decrease, whereas $-\Delta G_{0 \rightarrow i}^o$ and R_w would increase (Fig. 5A). The n -alkyl alcohols with longer chain lengths have higher efficiency in changing the hydrophilicity, making the amphiphilic mixture more hydrophobic. Therefore, less n -alkyl alcohol is needed to balance the hydrophile-lipophile property of the interfacial layer and less n -alkyl alcohol is solubilized in the oil phase. Hence, the spontaneous transfer ability of the n -alkyl alcohol from oil to the interfacial layer ($-\Delta G_{0 \rightarrow i}^o$) would increase.

It can be seen from Fig. 5 that the trends of change for all parameters displayed by Fig. 5B are contrary to the

Fig. 3 Plots of n_a/n_s vs n_o/n_s for (C₁₆-4-C₁₆)Br₂(a), C₁₆mimBr(b) + *n*-alkyl alcohol + octane + 5 % NaCl solution W/O microemulsions with different *n*-alkyl alcohols at $\omega_0 = 20$. Filled triangles butan-1-ol, filled squares pentan-1-ol, filled circles heptan-1-ol

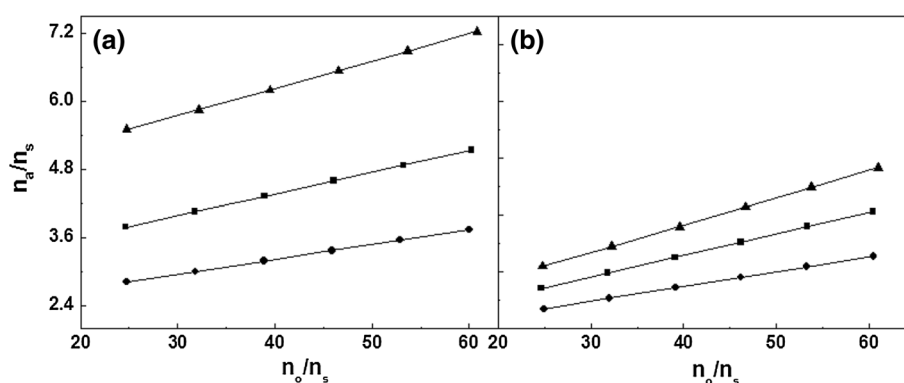
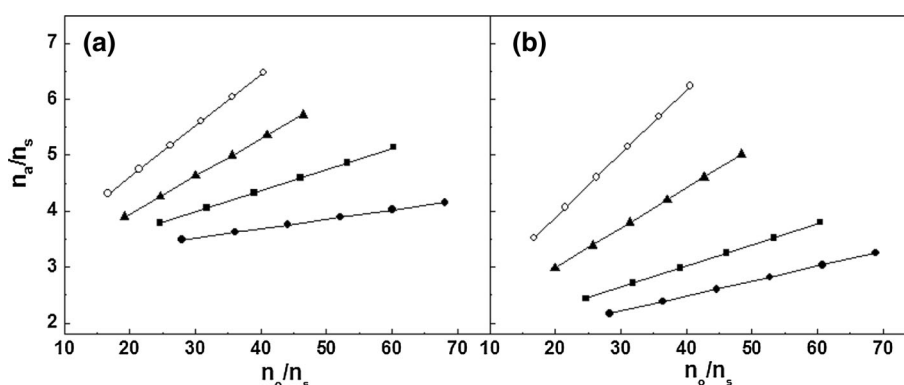


Fig. 4 Plots of n_a/n_s vs n_o/n_s for (C₁₆-4-C₁₆)Br₂(a), C₁₆mimBr(b) + pentan-1-ol + alkane + 5 % NaCl solution W/O microemulsions with different alkanes at $\omega_0 = 20$. Filled circles heptane, filled squares octane, filled triangles decane, open circles dodecane



trends of change displayed by Fig. 5A. As the carbon chain length of alkane molecules increases, the molar fraction of both the *n*-alkyl alcohols at the interfacial layer, X_a^i and the molar fraction of the *n*-alkyl alcohol in oil phase, X_a^o would increase. However, the extent of increase for the latter was more significant, leading to a decrease in the $-\Delta G_{o \rightarrow i}^o$ values. This results in the weakening of the spontaneous transfer of the *n*-alkyl alcohol from the oil to the interfacial layer. This phenomenon can be explained in terms of the penetrating ability of oil molecules into the surfactant interfacial layer [47]. As the smaller oil molecules are prone to penetrate the surfactant palisade layer, the interfacial layer tends to be convex towards oil. This facilitates the change of the curvature of the interfacial layer. Thus, less *n*-alkyl alcohol is needed to adjust the hydrophile-lipophile property of the interfacial layer [48].

Effects of Salinity and Temperature

Figures 6, 7 show the effects of salinity and temperature on the dilution curves for the W/O microemulsion systems. The composition and structural parameters (n_a^o/n_o , n_a^i/n_s , n_s , n_a^i , R_e , N_d , \bar{N}_s , \bar{N}_a) were listed in S2 section of the Supplementary Material.

The effects of NaCl concentrations (Fig. 8A) and temperatures (Fig. 8B) on the values of X_a^o , X_a^i , $-\Delta G_{o \rightarrow i}^o$ and R_w for the two W/O microemulsion systems (C₁₆-4-C₁₆)Br₂ and C₁₆mimBr + pentan-1-ol + octane + NaCl solution were calculated and compared in Fig. 8.

As NaCl concentration increases, X_a^o and X_a^i would decrease, whereas $-\Delta G_{o \rightarrow i}^o$ would increase (Fig. 8A). This phenomenon can be explained by the salting-out effect. The solubility of alcohol in oil (X_a^o) would remarkably decrease at higher salinity for ionic surfactants (C₁₆-4-C₁₆)Br₂ and C₁₆mimBr [49]. The hydrophilic group of (C₁₆-4-C₁₆)Br₂ or C₁₆mimBr was compressed upon the increase in the NaCl concentration in the microemulsion droplets. Thus, the surfactant molecules tend to be less hydrophilic and the alcohol required to form the W/O microemulsion would be reduced. Therefore, X_a^i values would decrease with increasing salt concentration for the microemulsion systems. The increase in the $-\Delta G_{o \rightarrow i}^o$ values with increasing salt concentration indicates that salt promotes the transfer of pentan-1-ol from the oil to the interfacial layer.

Figure 8B shows that as temperature increases, the mole fractions of alcohol at the interfacial layer (X_a^i) for both microemulsion systems would increase, and more alcohol would be needed to balance the interfacial layer. Also, as

Fig. 5 Comparison of the effects of *n*-alkyl alcohols (*left*) and alkanes (*right*) on the values of X_a^o (**a**), X_a^i (**b**), $-\Delta G_{o \rightarrow i}^o$ (**c**) and R_w (**d**) for the two W/O microemulsions (C₁₆-4-C₁₆)Br₂ (filled circles), C₁₆mimBr (open circles) + *n*-alkyl alcohol + alkane + 5 % NaCl solution

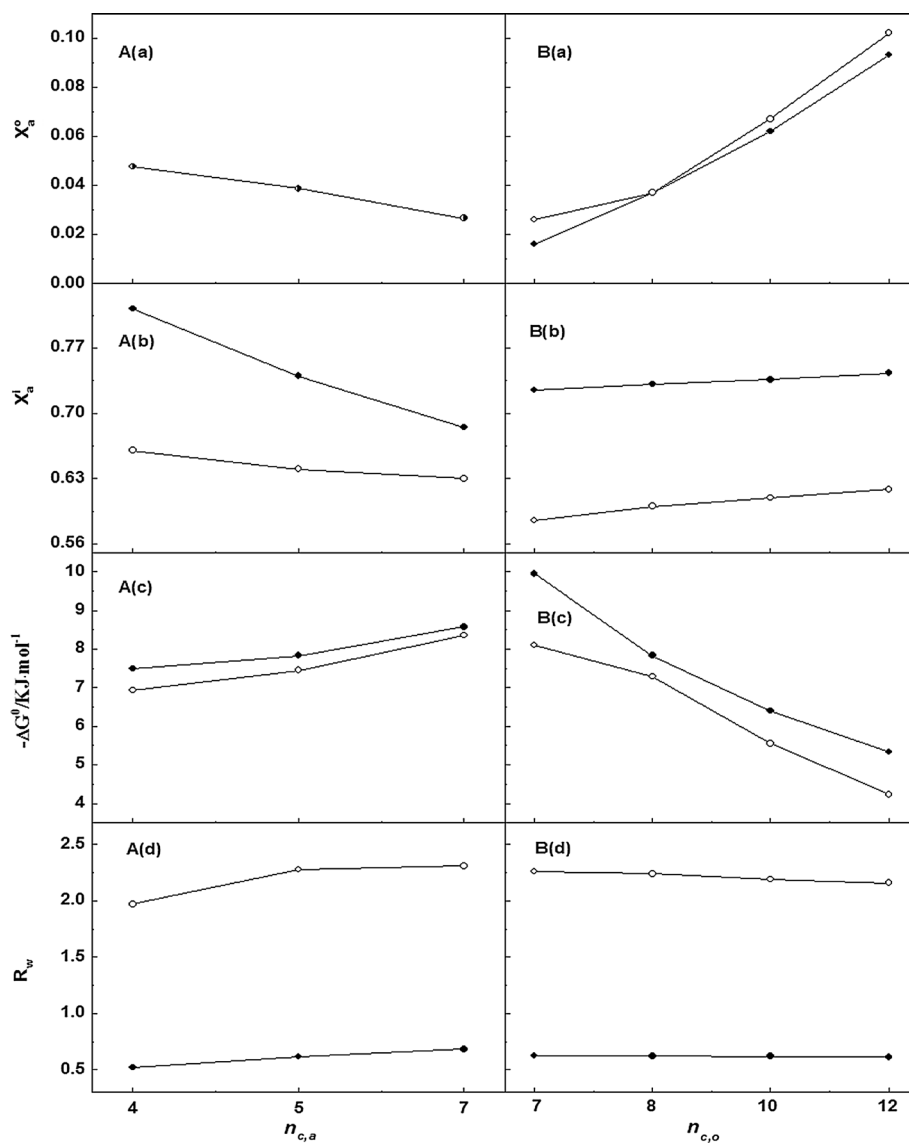


Fig. 6 Plots of n_a/n_s vs n_o/n_s for (C₁₆-4-C₁₆)Br₂(a), C₁₆mimBr(b) + pentan-1-ol + octane + NaCl solution W/O microemulsions with different salinities at $\omega_0 = 20$. NaCl concentrations: open squares 0 %, open circles 2.5 %, filled triangles 5.0 %, filled squares 7.5 %, filled circles 10 %

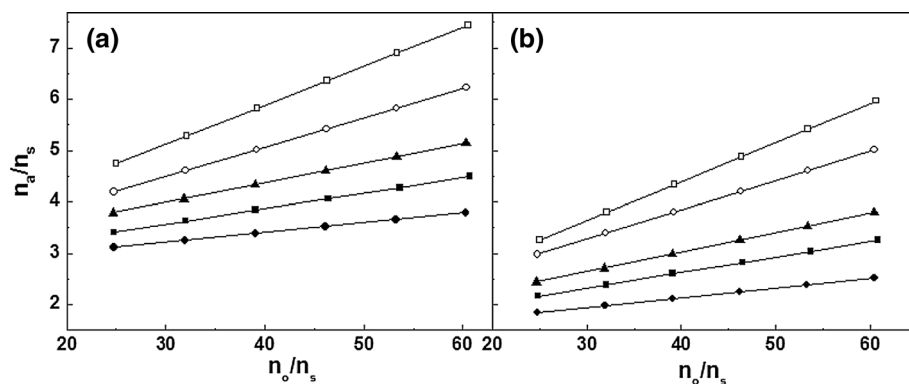


Fig. 7 Plots of n_a/n_s vs n_o/n_s for (C₁₆-4-C₁₆)Br₂(a), C₁₆mimBr(b) + pentan-1-ol + octane + 5 % NaCl solution W/O microemulsions with different temperatures at $\omega_0 = 20$. Filled circles 303 K, filled squares 313 K, filled triangles 323 K, open circles 333 K

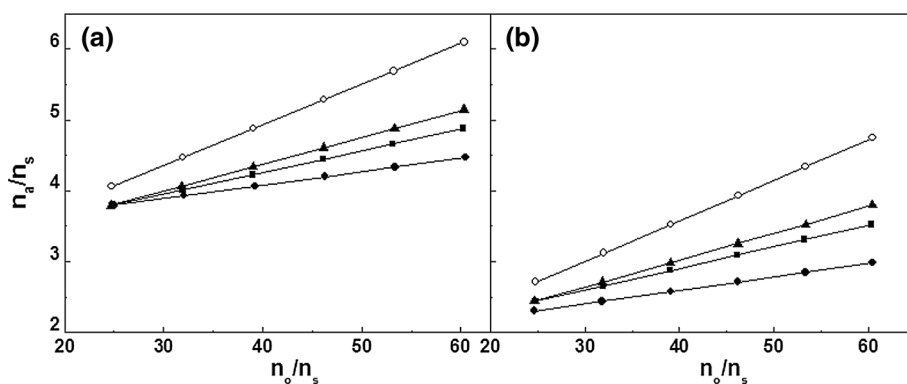
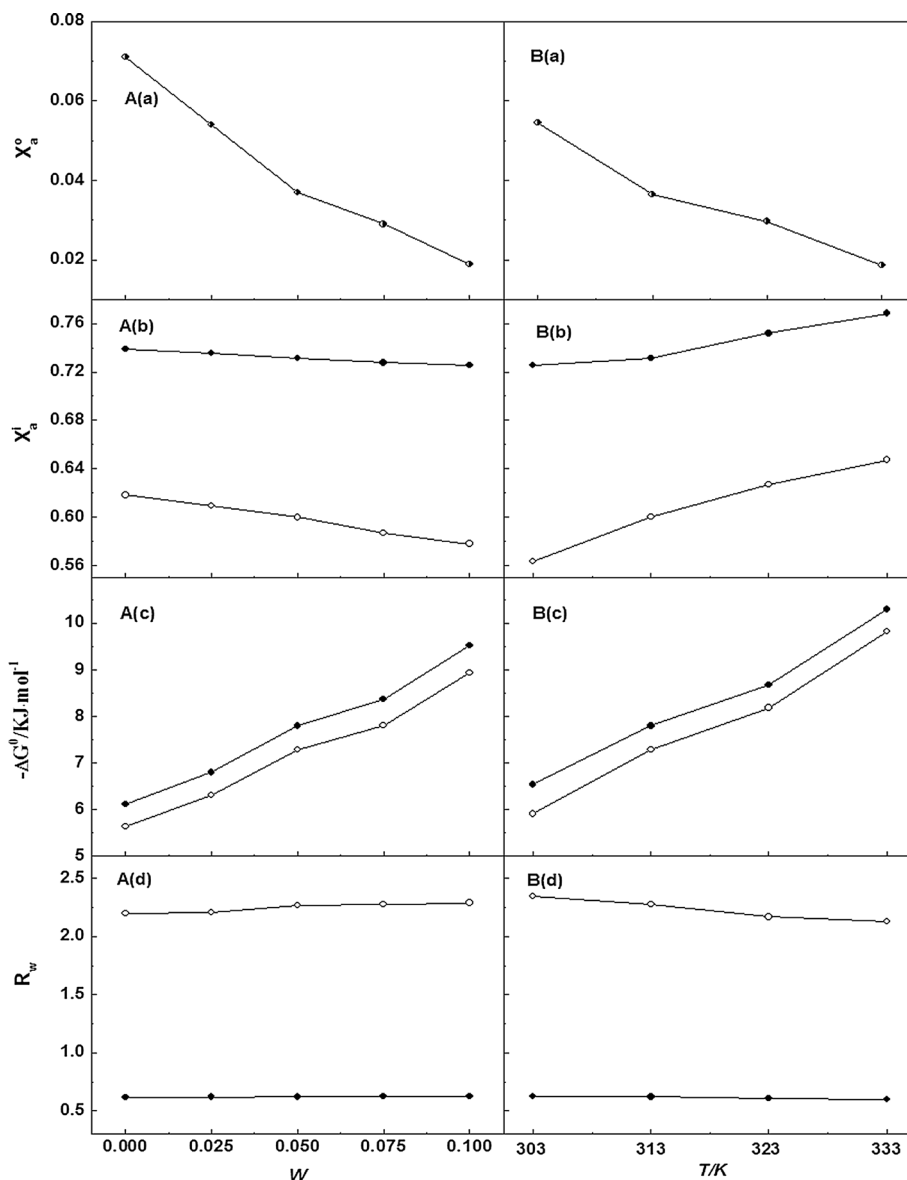


Fig. 8 Comparison of the values of X_a^o (a), X_a^i (b), $-\Delta G_{o \rightarrow i}^o$ (c) and R_w (d) between the two W/O microemulsions (C₁₆-4-C₁₆)Br₂ (filled circles), C₁₆mimBr (open circles) + pentan-1-ol + octane + NaCl solution with $\omega_0 = 20$



temperature increases, the mole fractions of the alcohol in the oil phase (X_a^o) would decrease, resulting in an increase in $-\Delta G_{o \rightarrow i}^o$ values.

Conclusions

The composition and structural parameters of W/O microemulsions containing the gemini surfactant 1,4-bis(3-alkylimidazolium-1-yl)butane bromide $[(C_n-4-C_n)Br_2]$ + pentan-1-ol + octane + water were studied and compared with that of W/O systems containing ionic liquid surfactant 1-alkyl-3-methylimidazolium ($C_n\text{mimBr}$) + pentan-1-ol + octane + water. Compared with the corresponding mono-chain analogues $C_n\text{mimBr}$, the gemini surfactants are more tightly packed in the interfacial layer in the microemulsions, and more n -alkyl alcohol molecules are incorporated into the interfacial layer of $(C_n-4-C_n)Br_2$ (X_a^i). This results in the greater $-\Delta G_{o \rightarrow i}^o$ values for $(C_n-4-C_n)Br_2$ based microemulsion systems. The size of the water pool R_w for the $(C_n-4-C_n)Br_2$ based microemulsion systems are smaller than those for their monomeric analogues $C_n\text{mimBr}$ systems.

As the carbon chain length of the n -alkyl alcohol increases, both X_a^o , the mole fraction of the n -alkyl alcohol in the oil phase, and X_a^i , the mole fraction of the n -alkyl alcohol in the interfacial layer would decrease, whereas $-\Delta G_{o \rightarrow i}^o$, the standard free energy change of transferring n -alkyl alcohol from the continuous oil phase to the interfacial layer would increase. As the carbon chain length of alkane molecules increases, both X_a^i and X_a^o would increase, while $-\Delta G_{o \rightarrow i}^o$ values would decrease.

As NaCl concentration increases, X_a^o and X_a^i would decrease, whereas $-\Delta G_{o \rightarrow i}^o$ would increase. This phenomenon can be explained by the salting-out effect.

As temperature increases, the values of X_a^i for both microemulsion systems would increase, whereas X_a^o would decrease, resulting in an increase in $-\Delta G_{o \rightarrow i}^o$ values.

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