

Effect of temperature and salt on the phase behavior of nonionic and mixed nonionic–ionic microemulsions with fish-tail diagrams

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Abstract

The phase behavior of Brij-56/1-butanol/*n*-heptane/water is investigated at 30 °C with α [weight fraction of oil in (oil + water)] = 0.5, wherein a $2 \rightarrow 3 \rightarrow \bar{2}$ phase transition occurs with increasing W_1 (weight fraction of 1-butanol in total amphiphile) at low X (weight fraction of both the amphiphiles in the mixture) and a $2 \rightarrow 1 \rightarrow \bar{2}$ phase transition occurs at higher X . Addition of an ionic surfactant, sodium dodecylbenzene sulfonate, destroys the three-phase body and decreases the solubilization capacity of the system at different δ (weight fraction of ionic surfactant in total surfactant). A three-phase body appears at $\alpha = 0.25$, but not at $\alpha = 0.75$ for the single system. No three-phase body appears with the mixed system at either α value. Increased temperature increases the solubilization capacity of the Brij-56 system; on the other hand, a negligible effect of temperature on the Brij-56/SDBS mixed system has been observed. Addition of salt (NaCl) produces a three-phase body for both single and mixed systems and increases their solubilization capacities. The monomeric solubility of 1-butanol in oil (S_1) and at the interface (S_1^s) has been calculated using the equation hydrophile–lipophile balance plane for both singles- and mixed-surfactant systems. These parameters have been utilized to explain the increase in solubilization capacity of these systems in the presence of NaCl.

Keywords: Phase transitions; Fish-tail diagram; Mixed surfactants; SDBS; Brij-56; Hydrophile–lipophile balance

1. Introduction

Substantial amounts of oil and water can be solubilized in the form of homogeneous, isotropic thermodynamically stable solutions with the help of surfactants, called microemulsions. Their structures, dynamics, and transport properties have been well reported because of numerous scientific and technological applications, starting from tertiary oil recovery to nanoparticle synthesis [1,2]. Owing to their diphilic nature, surfactants can form monolayers between oil and water and the curvature of the monolayers plays a key role in determining the microstructure of the dispersion [3]. The curvature of the interfacial film depends upon the nature of the amphiphile, the composition of the oil and aqueous phases, and the temperature and additives. Amphiphiles with a small

hydrophobic moiety and a large hydrophilic group (generally single-chain ionic and hydrophilic nonionic surfactants) tend to form films curving around the oil, which results in the formation of surfactant solutions of oil droplets in aqueous phase in equilibrium with excess oil phase (Winsor I system). On the other hand, amphiphiles with large hydrophobic moiety and small polar group curve around the aqueous phase to produce water droplets in oil medium in equilibrium with excess water (Winsor II system). When the hydrophile–lipophile balance (HLB) is established, a middle-phase microemulsion is formed in equilibrium with excess oil and water phases [4,5]. The middle-phase microemulsion has a bicontinuous structure with oil and water microdomains separated by a microinterface [6]. For nonionic surfactants, especially polyoxyethylene glycol-type nonionic surfactants, the hydrophile–lipophile balance can be achieved by tuning the temperature, whereupon a middle-phase microemulsion can be obtained at the HLB temperature [7]. Addition

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of electrolyte is needed to attain a balance in ionic surfactants [8]. For hydrophilic nonionic surfactants, addition of short-chain alcohols (as cosurfactants) is needed to achieve the balance [9–12]. Short-chain alcohols distribute between the bulk oil phase and the interface, thereby tuning the interfacial curvature and attaining the HLB composition. But, if the solubility of alcohols is high in the oil phase, the solubilization capacity of the surfactant + cosurfactant system decreases [13].

The solubilization capacity of nonionic surfactants can be improved by blending it with other surfactants. Addition of a second nonionic surfactant has been reported to enhance the solubilization capacity of nonionic surfactants [14]. Blending of nonionic surfactants with ionic surfactant can also improve their solubilization capacity [15–18]. Addition of ionic surfactant reduced the temperature sensitivity of nonionic surfactant [19] and also influenced the phase behavior [20–22]. Mixing of surfactants can often be proved to be advantageous over use of a single surfactant, since they can extract properties superior than the individual ones. But such studies involving mixed hydrophilic surfactants in the presence of lipophilic alcohol are rather scarce [23–26]. We report a preliminary study on the investigation of the phase behavior of nonionic (Brij-56) and mixed surfactants (Brij-56 and SDBS)/lipophilic cosurfactant (1-butanol)/*n*-heptane/water using fish-tail diagrams. The effect of temperature and salt (NaCl) on the phase behavior has been studied in order to understand the relationship between the maximum solubilization capacity of microemulsions and distribution of surfactant(s) and cosurfactant at the water–oil interface inside the microemulsion.

2. Experimental

2.1. Materials

Polyoxyethylene(10) cetyl ether (Brij-56), cetyltrimethylammonium bromide (CTAB), and sodium dodecyl sulfate (SDS) are products of Fluka, Switzerland and E. Merck, Germany respectively. Sodium bis-(2-ethylhexyl)sulfosuccinate (AOT, 99%) and sodium dodecylbenzene sulfonate (SDBS) are obtained from Sigma, USA and Alcolac, USA (under the tradename Siponate DS-10) respectively. *n*-heptane, 1-butanol, and sodium chloride (NaCl) are products of SRL, India and are of extrapure AR grade. SDBS was purified by successive extraction and recrystallization from isopropyl and methyl alcohols and then dried over vacuum. The purity was improved to about 99.5% as reported [27]. All other chemicals were used without further purification. Double distilled water of conductance less than $2 \mu\text{S cm}^{-1}$ was used.

2.2. Procedure to determine phase diagrams

Calculated amounts of surfactant(s), alcohol, oil, and water (or aqueous NaCl) were taken in sealed test tubes and

shaken vigorously in a vortex shaker for 5–10 min to ensure proper mixing and then kept in a thermostatic water bath ($\pm 0.1^\circ\text{C}$) at desired temperatures. The samples were checked after ensuring complete phase separation and the phase change was detected by direct visual inspection.

3. Results and discussion

3.1. Construction of phase diagram

In the absence of any external field and at constant pressure, for a five-component system comprising water (A), oil (B), nonionic surfactant (C), ionic surfactant (D), and cosurfactant (E), there can at most be five independent variables [16,26,28,29], such as temperature (T) and four composition variables. To construct the phase diagram in two dimensions, three out of these five variables need to be kept constant. In the present study, temperature, weight fraction of the ionic surfactant in the total surfactant ($\delta = D/(C + D)$), and weight fraction of oil in the mixture of oil and water ($\alpha = B/(A + B)$) are kept constant. The phase diagrams are presented in the following way. The weight fraction of both the amphiphiles [surfactant(s) plus cosurfactant] in the mixture, $X = (C + D + E)/(A + B + C + D + E)$, is plotted horizontally and the weight fraction of the cosurfactant in the total amphiphile, $W_1 = E/(C + D + E)$, is plotted vertically at constant α , δ , and T . When electrolytes (NaCl) of different concentrations (ϵ in mol dm^{-3}) are used, the aqueous NaCl phase is treated as a pseudo-one-component system [26,30].

3.2. Phase behavior of Brij-56 (and SDBS)/1-butanol/water (or aqueous NaCl) system

In order to underline the solubilization behavior of 1-butanol in aqueous medium in presence of surfactants, the phase behavior of the ternary system Brij-56 (and SDBS)/1-butanol/water (or aqueous NaCl) at 30°C has been studied. The result is depicted in Fig. 1. The lower part of the phase boundary represents a single-phase region, whereas the upper part is a two-phase region. It is found that 1-butanol is sparingly soluble in water in absence of any surfactant, but the presence of a nonionic surfactant (Brij-56) increases its solubility in water. It can be assumed that at a concentration of Brij-56 higher than its critical micellization concentration (cmc), 1-butanol is solubilized in the interface and/or the interior of the aqueous Brij-56 micellar aggregates. All the Brij-56 and 1-butanol molecules form mixed micelles, since the monomeric solubilities of both are negligibly small in the aqueous medium. With increase in the content of 1-butanol, the surfactant system becomes lipophilic and is eventually separated from water. Therefore, it is considered that the phase boundary corresponds to a cloud point curve in a binary water–nonionic

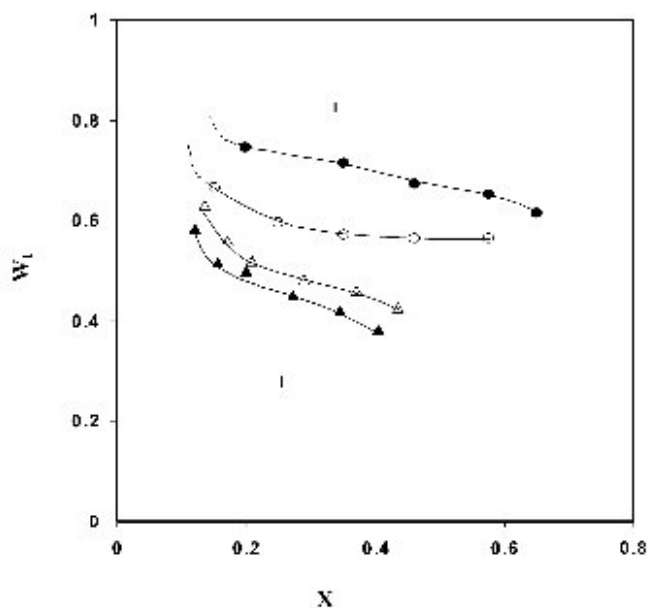


Fig. 1. Phase behavior of Brij-56/SDBS/1-butanol/water (aqueous NaCl) at 30 °C, where X and W_1 represent weight fraction of amphiphile (surfactant plus cosurfactant) in the total system and weight fraction of 1-butanol in the total amphiphile, respectively. Hollow symbols represent single-surfactant system (δ , mole fraction of ionic surfactant in total surfactant mixture = 0) and solid symbols represent mixed-surfactant system ($\delta = 0.1$) with ϵ (concentration of NaCl in mol dm⁻³) = 0 (○) and $\epsilon = 0.2$ (△). I and II represents single- and biphasic systems, respectively.

surfactant system [12]. When SDBS is blended with Brij-56 ($\delta = 0.1$), the 1-butanol solubility in the aqueous phase is increased. Addition of SDBS increases the hydrophilicity of the mixed surfactant system, which in turn makes the phase separation to occur at a higher W_1 . Addition of 0.2 mol dm⁻³ NaCl lowers the mixing fraction of 1-butanol in both Brij-56 and mixed Brij-56/SDBS ($\delta = 0.1$) systems. It has been reported earlier that the cloud point temperature of nonionic surfactant is affected by the addition of electrolyte. Small and strongly polarizable anion (Cl⁻) tends to promote the water structure and dehydrate the ether oxygen of poly(oxyethylene)-type nonionic surfactant. This consequently decreases the cloud point temperature by making the surfactant less hydrophilic (salting-out effect) [31,32]. It can be observed from Fig. 1 that solubility of 1-butanol is further lowered in the Brij-56/SDBS system as compared to the Brij-56 system in presence of NaCl. Addition of electrolyte shields the head group of the anionic surfactant and thus makes the system less hydrophilic. No phase separation is noticed in Brij-56/1-butanol/*n*-heptane system both in absence and presence of SDBS.

3.3. Phase behavior of Brij-56/1-butanol/*n*-heptane/water system

The phase behavior of Brij-56/1-butanol/*n*-heptane/water at 30 °C with $\alpha = 0.5$ is represented in Fig. 2. Single (I)-, two (II)-, and three (III)-phase regions appear in the phase diagram and are duly noted in the figure. Appearance of vis-

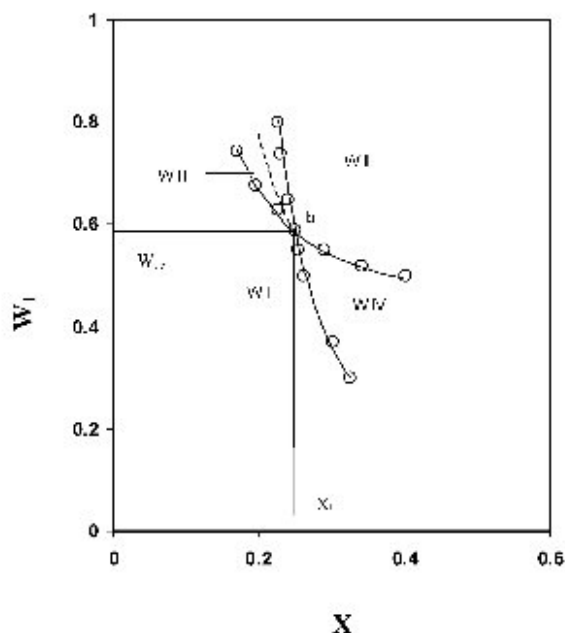


Fig. 2. Phase behavior of Brij-56/1-butanol/*n*-heptane/water at 30 °C with α (weight fraction oil in oil and water mixture) = 0.5, where X and W_1 represent weight fraction of amphiphile (surfactant plus cosurfactant) in the total system and weight fraction of 1-butanol in the total amphiphile, respectively. W I, W II, W III, and W IV represents o/w microemulsion in equilibrium with excess oil (Winsor I), w/o microemulsion in equilibrium with excess water (Winsor II), and triphasic (Winsor III) and monophasic (Winsor IV), systems respectively. The dotted line along the three-phase body has been used to calculate interfacial parameters (Eq. (1)).

cous and gel phases in the high- X and low- W_1 region has not been shown in the figure. The o/w type microemulsion phase coexists with the excess oil phase (Winsor I, denoted as $\underline{2}$) at low W_1 , whereas the w/o type microemulsion phase coexists with the excess water phase (Winsor II, denoted as $\bar{2}$) at higher W_1 . A $\underline{2} \rightarrow 3 \rightarrow \bar{2}$ transition occurs with increasing W_1 at low X and a $\underline{2} \rightarrow 1 \rightarrow \bar{2}$ transition occurs at higher X , where 3 and 1 represent three-phase (Winsor III) and single-phase (Winsor IV) systems respectively. At low W_1 , the hydrophilic amphiphile monolayer bends itself around oil in order to produce o/w droplets (Winsor I system). With increasing W_1 , the radius of curvature increases and droplet nature of the microemulsion is converted into a bicontinuous one and a Winsor III system is formed. On further increase of W_1 , the high lipophilicity of the amphiphile mixture tunes the monolayer to bend around water in order to produce w/o droplets in oil continuous medium (Winsor II system). Single-phase microemulsion forms upon the addition of sufficient quantity of amphiphiles (surfactant plus alcohol). The point at which the three-phase body meets the one-phase body (denoted by b in the figure) corresponds to the maximum solubilization capacity of the system, and the corresponding amphiphile concentration is denoted by X_b and that of alcohol is denoted by W_{1b} (Fig. 2). X_b indicates the minimum concentration of amphiphile required for the formation of single-phase microemulsion with equal amount of water and heptane. The lower the value of

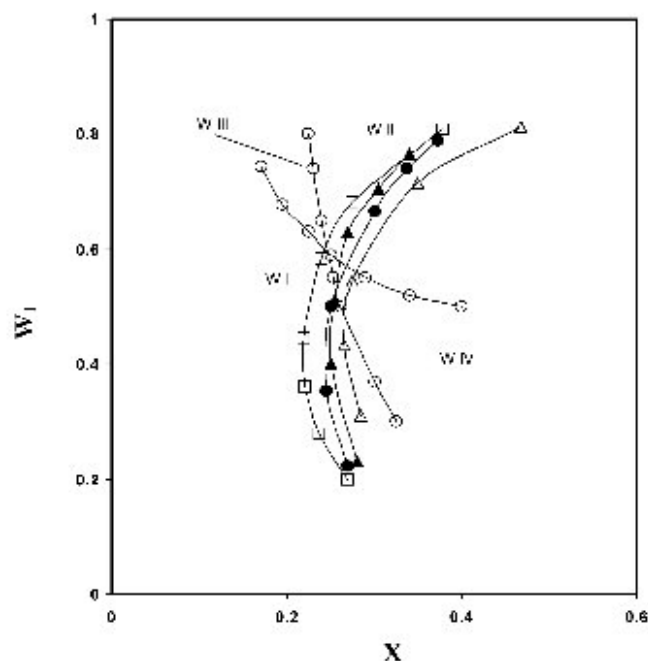


Fig. 3. Phase behavior of Brij-56/ionic surfactant/1-butanol/*n*-heptane/water at 30 °C with $\alpha = 0.5$ (weight fraction oil in oil-and-water mixture), where X and W_1 represent weight fraction of amphiphile (surfactant plus cosurfactant) in the total system and weight fraction of 1-butanol in the total amphiphile respectively. The ionic surfactants used are (●) SDBS; (Δ) CTAB; (□) SDS; (▲) AOT.

X_b , the higher is the solubilization capacity of the surfactant system. For the present system, the obtained values of X_b and W_{1b} are obtained at 0.248 and 0.593, respectively. However, these values are higher than those obtained for $C_{12}EO_8$ /hexanol/heptane/water system (X_b , 0.113 and W_{1b} , 0.505) by Kunieda et al. [33]. It may be due to the lower lipophilicity of both Brij-56 (HLB, 12.9) and 1-butanol used in the present study compared to the amphiphiles used by them.

3.4. Effect of ionic surfactant

Effect of the addition of ionic surfactant (SDBS, SDS, AOT, and CTAB) on the phase behavior of Brij-56/1-butanol/*n*-heptane/water has been shown in Fig. 3. δ is fixed at 0.1 for all the mixed systems. It is observed that a three-phase body does not appear for any of the studied mixed systems; instead a wide channel of single-phase region appears in each mixed system. Addition of small amount of ionic surfactant destroys the hydrophile–lipophile balance of the Brij-56 system and hence no three-phase body is formed. The effect of the extent of ionic surfactant on the phase behavior of mixed Brij-56/SDBS/1-butanol/*n*-heptane/water system at three different weight fractions of SDBS ($\delta = 0.05, 0.1$, and 0.2) at 30 °C has been exemplified in Fig. 4. It has been found that no three-phase body is formed for any of these three compositions, and almost identical large single-phase regions are obtained for $\delta = 0.1$

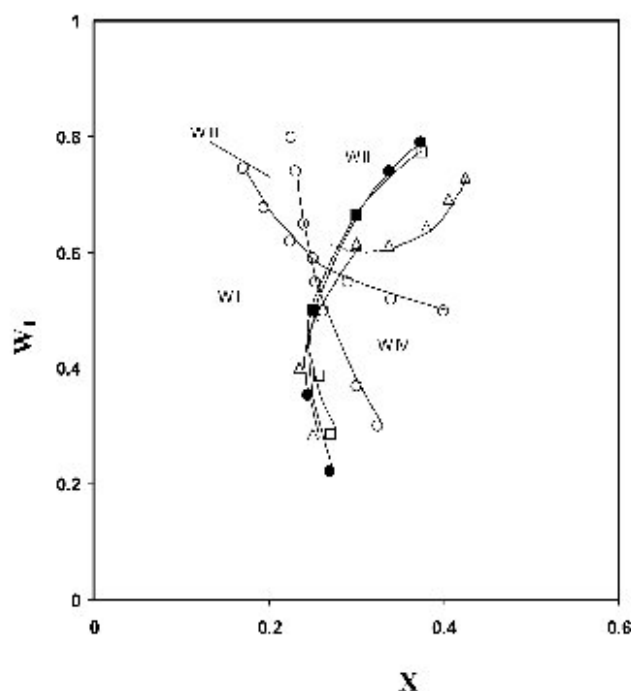


Fig. 4. Phase behavior of Brij-56/SDBS/1-butanol/*n*-heptane/water at 30 °C, where X and W_1 represent weight fraction of amphiphile (surfactant plus cosurfactant) in the total system and weight fraction of 1-butanol in the total amphiphile, respectively, with α (weight fraction oil in oil and water mixture) = 0.5 and δ (mole fraction of ionic surfactant in total surfactant mixture) = 0 (○); 0.05 (Δ); 0.1 (●), and 0.2 (□).

and 0.2. No $1 \rightarrow \bar{2}$ transition occurs at these compositions, except at high X for the $\delta = 0.05$ system.

In the present study, it has been observed that addition of SDBS increases the solubilization of Brij-56/1-butanol in water (Fig. 1). The effect may be due to the electrical repulsion among the Brij-56/SDBS mixed micelles in aqueous medium, which lowers their tendency to phase separate with increasing 1-butanol weight fraction. The solubility of the anionic surfactant SDBS in the Brij-56/*n*-heptane/1-butanol mixture is negligibly small. Thus it increases the stability of the Brij-56/1-butanol/water system, but leaves that of the oil continuous system unaltered. The disappearance of the three-phase body may be attributed to this effect. The present observation on the destruction of three-phase body upon the addition of ionic surfactant is similar to that reported by Kahlweit et al. [34]. They obtained three-phase body in C_6E_2 /octane/water system in the amphiphile concentration vs temperature profile, but when C_6E_2 was mixed with an anionic surfactant, sodium decyl sulfate ($NaC_{10}SO_4$), the three-phase body disappeared in order to form a wide single channel. It was argued that the addition of ionic amphiphile raises the upper loop in the binary water– C_6E_2 mixture as it makes the nonionic surfactant more hydrophobic. Kunieda and co-workers [19,21] also reported earlier that no three-phase microemulsion was produced in SDS/ $C_{12}EO_2$ /decane/water/ $NaCl$ system due to the large hydrophilicity of SDS. On the other hand, a single-phase microemulsion was formed along with a liquid crys-

talline phase for the system. In the present study destruction of the hydrophile–lipophile balance of the Brij-56 system upon the addition of a small quantity of ionic surfactant (SDBS) establishes the pronounced effect of the hydrophilic ionic surfactant on the hydrophile–lipophile balance of the mixed surfactant system. It can also be observed from Fig. 3 that the $\bar{2} \rightarrow 1$ transition is not significantly affected in Brij-56/ionic mixed systems in comparison to the Brij-56 system, but no $1 \rightarrow \bar{2}$ transition is obtained within the experimental range for any of the studied mixed surfactant systems. Addition of ionic surfactant makes the mixed system hydrophilic and thus the aqueous phase does not separate out even at high 1-butanol weight fraction.

3.5. Effect of α

The effect of α on the phase behaviors of Brij-56 (and SDBS)/1-butanol/*n*-heptane/water systems at two different α values, 0.25 and 0.75, at 30 °C has been depicted in Figs. 5A and 5B along with $\alpha = 0.5$ (in dotted lines). It has been found that with $\alpha = 0.25$, the three-phase body is formed for the single-surfactant system at a relatively lower X_b (0.174) but slightly higher W_{1b} value (0.627) in comparison with the same system at $\alpha = 0.5$ with X_b (0.253) and W_{1b} (0.593) (Fig. 5A). The mixed-surfactant system, however, produces wide single-phase channel formation similar to that obtained with $\alpha = 0.5$. Fig. 5B depicts the phase diagram of the same systems at $\alpha = 0.75$. It has been found that both the single- and mixed-surfactant systems exhibit identical trends to form wide single-phase channels at this composition. No three-phase body is formed for the Brij-56 system. It is evidenced from Figs. 5A and 5B that Brij-56/1-butanol is an efficient solubilizer of *n*-heptane/water at a lower weight fraction of the oil ($\alpha = 0.25$). At a higher weight fraction of the oil ($\alpha = 0.75$), the hydrophile–lipophile balance of this system gets disturbed and the solubilization capacity is reduced significantly. Brij-56 is a hydrophilic surfactant (HLB = 12.9) at the experimental temperature and thus can act as a good solubilizer at a higher weight fraction of water. However, the extent of oil weight fraction (α) has a negligibly small effect on the phase behavior of the Brij-56/SDBS mixed system as shown in Figs. 5A and 5B, which indicates the hydrophilic nature of the mixed system.

3.6. Effect of temperature

The phase diagrams of Brij-56 (and SDBS)/1-butanol/*n*-heptane/water have been constructed at four different temperatures, 20, 30, 40, and 50 °C at $\alpha = 0.5$ (fixed), to underline the effect of temperature on the phase behaviors of these systems (at $\delta = 0$ and 0.1 for single and mixed systems, respectively). The results are represented in Figs. 6A and 6B. It has been found that no three-phase body is formed at 20 °C for the single-surfactant system; instead a single-phase channel is obtained (Fig. 6A). However, three-phase bodies are formed at elevated temperatures

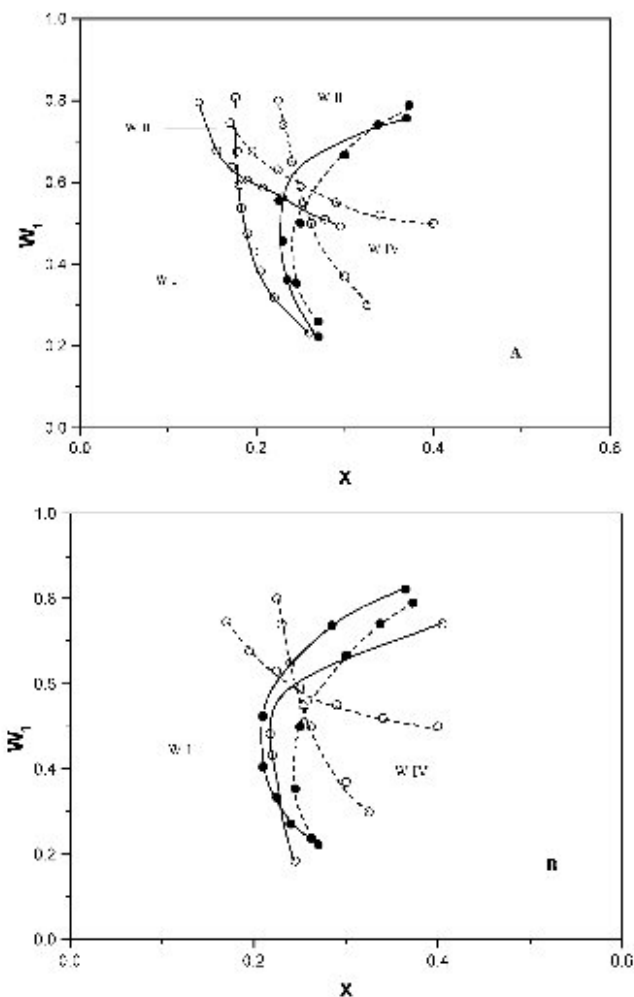


Fig. 5. Phase behavior of Brij-56/SDBS/1-butanol/*n*-heptane/water at 30 °C with (A) α (weight fraction oil in oil-and-water mixture) = 0.25 and (B) $\alpha = 0.75$, where X and W_1 represent weight fraction of amphiphile (surfactant plus cosurfactant) in the total system and weight fraction of 1-butanol in the total amphiphile, respectively. Hollow and solid circles represent single (δ , mole fraction of ionic surfactant in total surfactant mixture = 0) and mixed ($\delta = 0.1$) surfactant systems, respectively. The dotted phase diagrams are of the respective systems with $\alpha = 0.5$.

(40 and 50 °C) and both X_b (0.22 and 0.175, respectively) and W_{1b} (0.5347 and 0.421, respectively) decreases with increased temperature. It has been reported earlier that non-ionic surfactants become lipophilic at elevated temperatures due to the dehydration of the oxyethylene group [33,35]. Therefore, Brij-56 can be assumed to be substantially hydrophilic at 20 °C, and no hydrophile–lipophile balance is produced at this temperature within the experimental range and hence no three-phase body is formed. On the other hand, with increasing temperature up to 40 and 50 °C, the Brij-56/1-butanol system reaches the hydrophile–lipophile balance at a lower amphiphile weight fraction and the capacity to solubilize equal amounts of oil and water increases with increase in temperature. However, Kunieda et al. [10], reported that X_b increased with increase in temperature with a subsequent decrease in W_{1b} for sucrose monolaurate

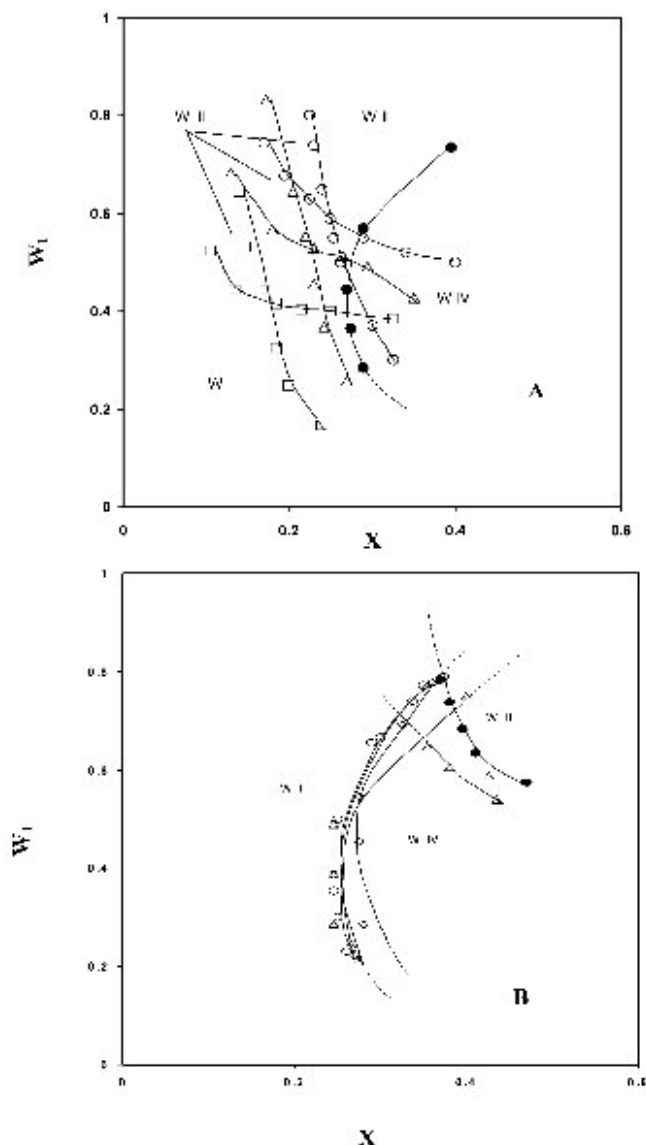


Fig. 6. Phase behavior of Brij-56/SDBS/1-butanol/*n*-heptane/water, where X and W_1 represent weight fraction of amphiphile (surfactant plus cosurfactant) in the total system and weight fraction of 1-butanol in the total amphiphile, respectively, with α (weight fraction oil in oil-and-water mixture) = 0.5 and δ (mole fraction of ionic surfactant in total surfactant mixture) = 0 (A) and $\delta = 0.1$ (B) at 20 (●), 30 (○), 40 (△), and 50 °C (□).

(L-1695)/tetraethylene glycol ether ($R_{12}EO_4$)/heptane/water system. It was argued that the increased oil solubility of $R_{12}EO_4$ with increase in temperature is responsible this observation. In the present study, Brij-56 becomes less hydrophilic with rise in temperature and hence less amount of lipophilic 1-butanol is required to form the balance. This in turn increases the solubilization capacity of the surfactant system.

Fig. 6B depicts the phase behavior of the mixed system Brij-56/SDBS/1-butanol/*n*-heptane/water at different temperatures (20, 30, 40, and 50 °C) at $\alpha = 0.5$ (fixed) with $\delta = 0.1$. It has been observed that no three-phase body is formed at the studied temperature range. However, at higher temper-

atures (40 and 50 °C) $1 \rightarrow \bar{2}$ transition is registered at higher X values. The phenomenon can be explained as follows. The effect of temperature on the solubility and hydration of ionic surfactant is opposite to that of nonionic surfactant. With rising temperature, dissociation of the ionic head group increases and the ionic surfactant becomes more hydrophilic at higher temperatures [36,37]. It was further reported that temperature has a negligible effect on the hydrophile–lipophile balance of SDS [19]. In the present study, SDBS can also be assumed to be highly hydrophilic and its hydrophile–lipophile balance is almost unchanged at higher temperatures. As a result, the increased lipophilicity of Brij-56 at elevated temperatures is suppressed and no three-phase body is formed even at 50 °C.

3.7. Effect of salt (NaCl)

The phase behavior of Brij-56/1-butanol/*n*-heptane/water system has been studied at 30 °C with $\alpha = 0.5$ as a function of NaCl of different concentrations ($\varepsilon = 0.025, 0.05, 0.075, 0.125, \text{ and } 0.2 \text{ mol dm}^{-3}$). Some representative phase diagrams are shown in Fig. 7A. It has been found that three-phase body appears in all these systems, and their solubilization capacities increase with increasing ε . It is evident from this figure that the point of HLB composition (the point of maximum solubility) moves toward lower values of X_b and W_{1b} with increasing NaCl concentration. A similar trend was reported earlier by Kunieda et al. [12] that addition of NaCl shifted the three-phase body to lower cosurfactant mixing ratios for a water/octaethylene glycol dodecyl ether ($C_{12}EO_8$)/hexanol/decane system at 25 °C. However, it has been observed earlier in Fig. 1 that the addition of NaCl decreases the hydrophilicity of Brij-56, and hence a lower weight fraction of 1-butanol is required to establish the hydrophile–lipophile balance. The X_b and W_{1b} values obtained from Fig. 7A are presented in Table 1. It is found that with increasing salinity, the Brij-56/1-butanol system becomes more efficient in solubilizing equal amounts of oil and water (w/w).

Fig. 7B depicts the phase behavior of mixed Brij-56/SDBS/1-butanol/*n*-heptane/water system at different NaCl concentrations (as mentioned earlier) with $\delta = 0.1$ (fixed) and $\alpha = 0.5$ (fixed). It has been observed that no three-phase body appears at $\varepsilon = 0.025$. However, both $\bar{2} \rightarrow 1$ and $1 \rightarrow \bar{2}$ transitions are observed under this experimental condition. On further increase of salinity to $\varepsilon = 0.05$, a three-phase body appears, but the values of X_b (0.228) and W_{1b} (0.621) are relatively higher than that of the Brij-56 stabilized system (Table 1). It has been reported earlier that three-phase body appears for ionic surfactants only upon the addition of electrolytes [38]. Addition of electrolyte suppresses the dissociation of SDBS headgroups [39]. This makes the SDBS molecules less hydrophilic and a smaller amount of 1-butanol is required to form a three-phase microemulsion to keep the same hydrophile–lipophile property of mixed surfactant at the interface. The apparent increase in the solubilizing power

Table 1

X_b , W_{1b} , S_1 , S_1^s , C_1 , and C_2 values for the system Brij-56/SDBS/1-butanol/heptane/water at 30 °C in the presence of NaCl of different concentrations (ε , mol dm⁻³)

| ε | X_b | W_{1b} | S_1 | S_1^s | C_1 | C_2 | $C_1 + C_2$ | $C_1/(C_1 + C_2)$ |
|---------------|-------|----------|--------|----------------|--------|--------|-------------|-------------------|
| | | | | $\delta = 0$ | | | | |
| 0 | 0.253 | 0.593 | 0.2849 | 0.0125 | 0.0012 | 0.1029 | 0.1041 | 0.0117 |
| 0.025 | 0.233 | 0.575 | 0.2554 | 0.022 | 0.0025 | 0.0990 | 0.1015 | 0.0246 |
| 0.05 | 0.219 | 0.569 | 0.2342 | 0.0548 | 0.0050 | 0.0944 | 0.0995 | 0.0512 |
| 0.075 | 0.198 | 0.507 | 0.1885 | 0.0678 | 0.0071 | 0.0975 | 0.1047 | 0.0685 |
| 0.125 | 0.182 | 0.494 | 0.1648 | 0.09 | 0.0092 | 0.0920 | 0.1012 | 0.0908 |
| 0.2 | 0.175 | 0.491 | 0.1571 | 0.1004 | 0.0082 | 0.0890 | 0.0973 | 0.0922 |
| | | | | $\delta = 0.1$ | | | | |
| 0.05 | 0.228 | 0.621 | 0.2637 | 0.0355 | 0.0033 | 0.0864 | 0.0897 | 0.0372 |
| 0.075 | 0.219 | 0.605 | 0.2475 | 0.0432 | 0.0040 | 0.0865 | 0.0905 | 0.0448 |
| 0.125 | 0.201 | 0.524 | 0.1818 | 0.1512 | 0.0165 | 0.0956 | 0.1122 | 0.1475 |
| 0.2 | 0.180 | 0.442 | 0.1191 | 0.2003 | 0.0241 | 0.1004 | 0.1245 | 0.1936 |

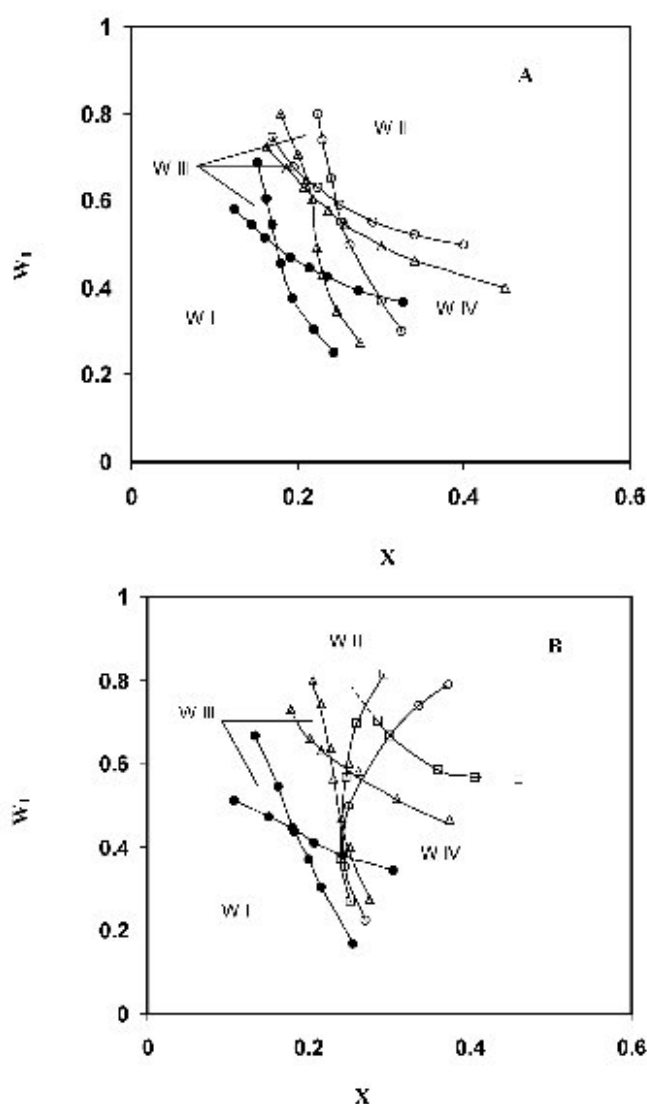


Fig. 7. Phase behavior of Brij-56/SDBS/1-butanol/*n*-heptane/water, where X and W_1 represent weight fraction of amphiphile (surfactant plus cosurfactant) in the total system and weight fraction of 1-butanol in the total amphiphile, respectively, with α (weight fraction oil in oil and water mixture) = 0.5 and δ (mole fraction of ionic surfactant in total surfactant mixture) = 0 (A) and $\delta = 0.1$ (B) at 30 °C in presence of NaCl of varying concentrations (ε , mol dm⁻³): 0 (○); 0.025 (□); 0.05 (△); 0.2 (●).

at higher salinity is mainly attributed to the decrease in solubility of the cosurfactant in the microoil domain [30].

3.8. Calculation of interfacial composition inside the bicontinuous microemulsion

The three-phase region is a nonvariant region as all the intensive variables (T , P , α , and δ) are fixed for the five-component system. The composition and structure of the microemulsion phase along the midst curve in the three-phase body (as shown in Fig. 2 by the dotted line) is also fixed and is equal to the single-phase at the three-phase point [6,9,10,26,33]. The three-phase region consists of microoil and microwater domains separated by a microoil–water interface [6]. The surfactant molecules are adsorbed at the microoil–water interface and form an interfacial layer. The Brij-56 and SDBS molecules can be assumed to be solubilized in the microoil and microwater domains to a negligible extent. Also, the monomeric solubility of 1-butanol is very small in water and can be neglected.

Since the whole phase behavior of the five-component system can be represented by a composition tetrahedron at constant T , P , and δ , the hydrophile–lipophile balance plane [4] (the HLB balance plane is defined as the condition of equal mass fractions of oil and water solubilized in the same surfactant phase, called the optimum middle phase) must include the particular three-phase tie-triangle including the microemulsion in the middle curve of the Winsor III region [26,39–41]. The HLB plane equation can be expressed as [4, 6,10,33,40]

$$W_1 = S_1^s \left\{ S_1 (1 - S_1^s) \alpha / [(1 - S_1)(1/X - 1)] \right\}, \quad (1)$$

where S_1^s represents the 1-butanol solubility in the total amphiphilic mixture ($C + D + E$) at the water–oil interface inside the microemulsion phase. S_1 is the monomeric solubility of 1-butanol in the microoil domain and is equal to the 1-butanol fraction in the excess oil phase. S_1^s is obtained as the intercept of the linear plot of $(1/X - 1)$ against W_1 , and S_1 can be calculated from the slope of the straight line.

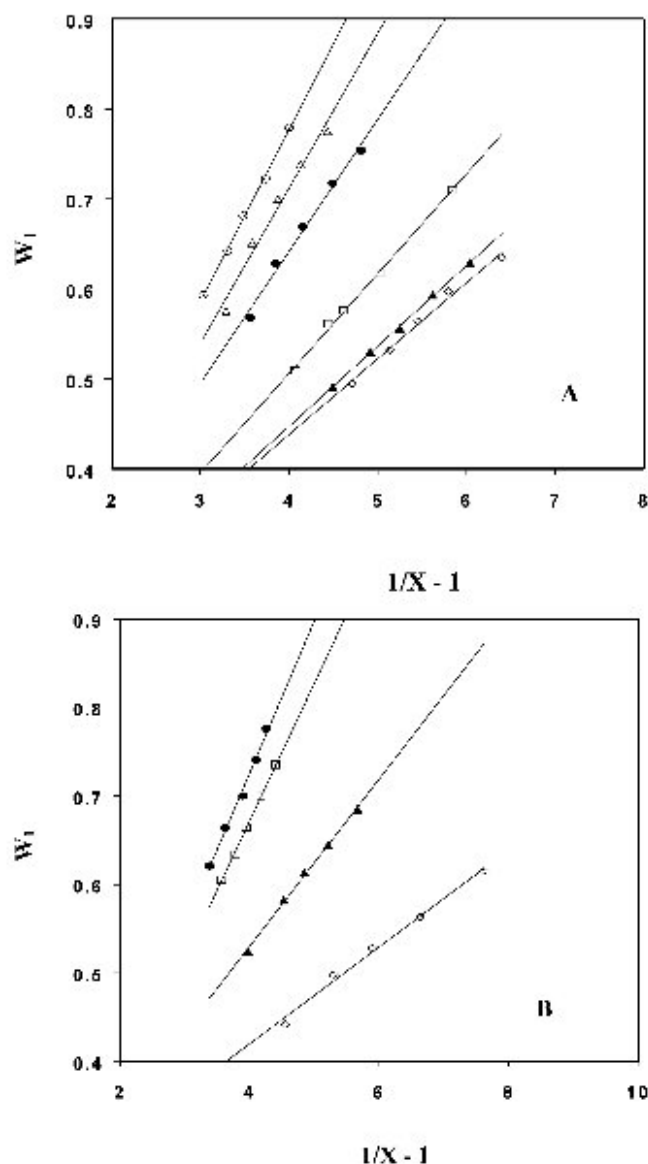


Fig. 8. Plot of $1/X - 1$ against W_1 (fraction of 1-butanol in total amphiphile) for the system Brij-56/SDBS/1-butanol/*n*-heptane/water with α (weight fraction oil in oil-and-water mixture) = 0.5 and δ (mole fraction of ionic surfactant in total surfactant mixture) = 0 (A) and $\delta = 0.1$ (B) at 30 °C in presence of NaCl of varying concentrations (ϵ , mol dm⁻³), 0 (O); 0.025 (Δ); 0.05 (\bullet); 0.075 (\square); 0.125 (\blacktriangle); 0.2 (\diamond).

The surfactant and cosurfactant concentration at the microinterface can be obtained as [12,26,30,33]

$$C_1 = X_b W_{1b} - \left\{ \frac{\alpha(1 - X_b)S_1}{(1 - S_1)} \right\}, \quad (2)$$

$$C_2 = X_b(1 - W_{1b}), \quad (3)$$

where C_1 and C_2 are the weight fractions of lipophilic 1-butanol and hydrophilic Brij-56 in the system at the water-oil interface within the single microemulsion phase at point b. The total surfactant concentration in the oil-water interface inside the microemulsion ($C_1 + C_2$) can be compared with the total surfactant concentration ($C + D + E$).

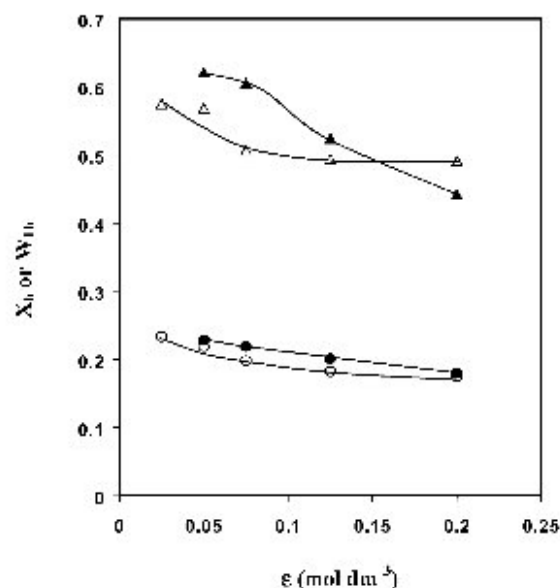


Fig. 9. Variation of X_b (\circ) and W_{1b} (Δ) as a function of salinity (ϵ , concentration of NaCl in mol dm⁻³) for the system Brij-56/SDBS/1-butanol/*n*-heptane/water at δ (mole fraction of ionic surfactant in total surfactant mixture) = 0 (hollow symbols) and $\delta = 0.1$ (solid symbols).

In the present study, $1/X - 1$ has been plotted against W_1 for Brij-56 (and SDBS)/1-butanol/*n*-heptane/aqueous NaCl system at different ϵ . The results are shown in Figs. 8A and 8B and a good linear fit is obtained. The corresponding S_1 , S_1^s , C_1 , and C_2 values are calculated utilizing Eqs. (1)–(3) and are presented in Table 1. It is evident from Table 1 that the monomeric solubility of 1-butanol in the microoil domain (S_1) decreases and the weight fraction of 1-butanol in the microinterface (S_1^s) increases with increasing salinity, which in turn increases the net solubilizing power of both single- and mixed-surfactant systems. The decreased hydrophilicity of both the nonionic and anionic surfactant perhaps decreases the monomeric solubility of 1-butanol in the oil phase. A similar observation was reported by Li et al. [26], wherein the monomeric solubility of hexanol in oil phase decreased with increasing NaBr concentration for mixed microemulsion system, CTAB/SDS/1-hexanol/dodecane/aqueous NaBr with a consequent increase of S_1^s . ($C_1 + C_2$) values do not change appreciably for the Brij-56 system, whereas that of the Brij-56/SDBS mixed system has been found to increase monotonically (Table 1). S_1^s values obtained from Eq. (1) should be equal to the $C_1/(C_1 + C_2)$ values obtained from Eqs. (2) and (3). In this report, these values are in good agreement within the experimental errors.

The X_b or W_{1b} values and S_1^s or S_1 values for the Brij-56 and mixed Brij-56/SDBS systems have been plotted as a function of salinity, ϵ , and the results are depicted in Fig. 9 and 10, respectively. It has been found that the X_b values are comparable for both the systems and decreases marginally with increasing salinity, whereas W_{1b} decreases appreciably with increasing salinity for both the systems. W_{1b} has a higher value for the mixed system in comparison to the

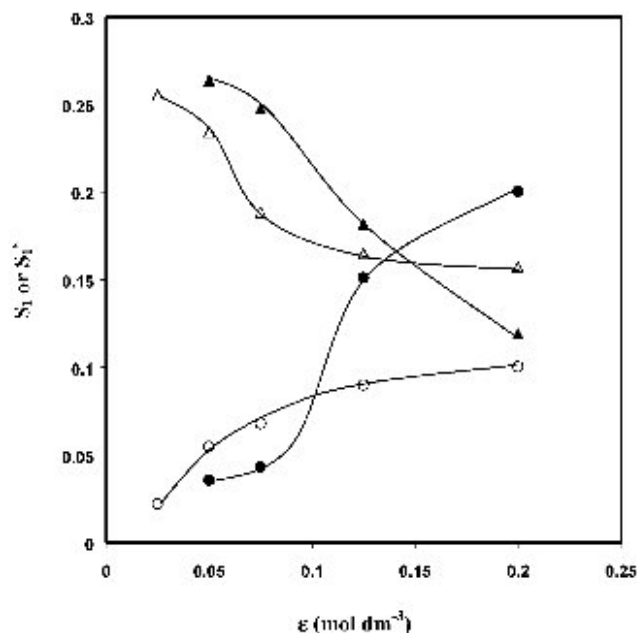


Fig. 10. Variation of S_1^s (1-butanol solubility in the total amphiphilic mixture at the water–oil interface inside the microemulsion phase) (○) and S_1 (monomeric solubility of 1-butanol in the microoil domain) (Δ) as a function of salinity (ϵ , concentration of NaCl in mol dm^{-3}) for the system Brij-56/SDBS/1-butanol/*n*-heptane/water with δ (mole fraction of ionic surfactant in total surfactant mixture) = 0 (hollow symbols) and $\delta = 0.1$ (solid symbols).

Brij-56 system at lower ϵ values, but becomes lower at a higher ϵ value (0.2) (Fig. 9). It has been further observed that S_1 decreases appreciably for the mixed system at $\epsilon = 0.2$, whereas S_1^s increases than the corresponding Brij-56 system (Fig. 10). It has been observed earlier that the miscibility gap of Brij-56/1-butanol/water increased with addition of SDBS (as evidenced from Fig. 1), which corroborates the increased S_1^s and decreased S_1 of the mixed system at $\epsilon = 0.2$. As mentioned earlier, addition of NaCl suppresses the dissociation of SDBS headgroups and makes the surfactant lipophilic. With increasing ϵ to 0.2, the lipophilicity of the Brij-56/SDBS system exceeds that of the Brij-56 system, which in turn decreases the oil solubility (S_1) and increases the interfacial concentration (S_1^s) of 1-butanol for the mixed system in respect to the single Brij-56 system. This makes the formation of three-phase body to occur at a lower W_{1b} value for the mixed system than the Brij-56 system.

4. Summary

Brij-56/1-butanol/*n*-heptane/water system forms usual fish-tail diagram at 30 °C with $\alpha = 0.5$. Addition of ionic surfactants (SDBS, SDS, CTAB, AOT) disturbs the hydrophile–lipophile balance of the system. No three-phase body is formed for Brij-56/ionic surfactant(s)/1-butanol/*n*-heptane/water system; instead a wide channel of single-phase region is formed. Increasing temperature increases the solubilization capacity of the Brij-56 system, whereas it has

negligible effect on the Brij-56/SDBS mixed system. Addition of salt (NaCl) induces three-phase body formation in the Brij-56/SDBS system, and the solubilization capacity of both single and mixed surfactant systems increases with addition of NaCl. The monomeric solubility of 1-butanol in oil phase (S_1) is decreased, whereas the interfacial concentration of 1-butanol (S_1^s) increases with the addition of NaCl, which in turn increases the solubilization capacity of these systems.

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References

- [1] B.K. Paul, S.P. Moulik, J. Dispersion Sci. Technol. 18 (1997) 301.
- [2] S.P. Moulik, B.K. Paul, Adv. Colloid Interface Sci. 78 (1998) 99.
- [3] R. Leung, D.O. Shah, J. Colloid Interface Sci. 129 (1987) 320.
- [4] H. Kunieda, K. Shinoda, J. Colloid Interface Sci. 107 (1985) 107.
- [5] H. Kunieda, N. Ishikawa, J. Colloid Interface Sci. 107 (1985) 122.
- [6] M.A. Pes, H. Kunieda, Trends Phys. Chem. 5 (1995) 75.
- [7] U. Olsson, K. Shinoda, B. Lindman, J. Phys. Chem. 90 (1986) 4083.
- [8] M. Kahlweit, R. Strey, J. Phys. Chem. 90 (1986) 5239.
- [9] M.A. Pes, K. Aramaki, N. Nakamura, H. Kunieda, J. Colloid Interface Sci. 178 (1996) 666.
- [10] H. Kunieda, N. Ushio, A. Nakano, M. Miura, J. Colloid Interface Sci. 159 (1993) 37.
- [11] Y. Sottmann, R. Strey, S.H. Chen, J. Chem. Phys. 106 (1997) 6483.
- [12] K. Aramaki, H. Kunieda, M. Ishitobi, T. Tagawa, Langmuir 8 (1997) 2266.
- [13] H. Kunieda, K. Hanno, S. Yamaguchi, K. Shinoda, J. Colloid Interface Sci. 107 (1985) 129.
- [14] H. Kunieda, M. Yamagata, Langmuir 9 (1993) 3345.
- [15] M. Kahlweit, B. Faulhaber, G. Busse, Langmuir 10 (1994) 2528.
- [16] M. Kahlweit, R. Strey, J. Phys. Chem. 91 (1987) 1553.
- [17] L.D. Ryan, E.W. Kaler, J. Phys. Chem. B 102 (1998) 7549.
- [18] J.A. Silas, E.W. Kaler, R.M. Hill, Langmuir 17 (2001) 4534.
- [19] K. Aramaki, K. Ozawa, H. Kunieda, J. Colloid Interface Sci. 196 (1997) 74.
- [20] K. Fukuda, U. Olsson, U. Würz, Langmuir 10 (1994) 3222.
- [21] H. Kunieda, K. Ozawa, K. Aramaki, A. Nakano, C. Solans, Langmuir 14 (1998) 260.
- [22] C.B. Doglus, E.W. Kaler, J. Chem. Soc. Faraday Trans. 90 (1994) 471.
- [23] X. Li, G. Zhao, E. Lin, J. Dispersion Sci. Technol. 17 (1996) 111.
- [24] X. Li, E. Liu, J. Colloid Interface Sci. 184 (1996) 20.
- [25] X. Li, J. Wang, J. Dispersion Sci. Technol. 20 (1999) 993.
- [26] X. Li, K. Ueda, H. Kunieda, Langmuir 15 (1999) 7973.
- [27] D.C.H. Cheng, E. Gulari, J. Colloid Interface Sci. 90 (1982) 410.
- [28] M. Kahlweit, R. Strey, J. Phys. Chem. 92 (1988) 1557.
- [29] H. Kunieda, A. Nakano, M. Akimaru, J. Colloid Interface Sci. 170 (1995) 78.
- [30] H. Kunieda, R. Aoki, Langmuir 12 (1996) 5796.
- [31] H. Schott, Colloid Surf. 11 (1984) 51.
- [32] A. Kabalnov, U. Olsson, H. Wennerström, J. Phys. Chem. 99 (1995) 6220.
- [33] H. Kunieda, A. Nakano, M.A. Pes, Langmuir 11 (1995) 3302.
- [34] M. Kahlweit, G. Busse, B. Faulhaber, Langmuir 10 (1994) 1134.

- [35] G. Karlstrom, *J. Phys. Chem.* 89 (1985) 4692.
- [36] H. Kunieda, C. Solans, in: C. Solans, H. Kunieda (Eds.), *Industrial Application of Microemulsions*, Dekker, New York, 1997, ch. 2.
- [37] M. Kahlweit, R. Strey, *Angew. Chem.* 97 (1985) 655.
- [38] M. Kahlweit, R. Strey, R. Schomacker, D. Haase, *Langmuir* 5 (1989) 305.
- [39] M. Bourell, R.S. Schechter, *Microemulsions and Related Systems*, Surfactant Science Series, vol. 30, Dekker, New York, 1988, ch. 5.
- [40] H. Kunieda, Y. Saito, in: B. Lindman, S.E. Friberg (Eds.), *Organized Solutions*, Dekker, New York, 1992, p. 67.
- [41] J.-L. Chai, G.-Z. Li, G.-Y. Zhang, J.-J. Lu, Z.-N. Wang, *Colloids Surf. A* 231 (2003) 173.