

Phase behavior, interfacial composition and thermodynamic properties of mixed surfactant (CTAB and Brij-58) derived w/o microemulsions with 1-butanol and 1-pentanol as cosurfactants and *n*-heptane and *n*-decane as oils

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Abstract

Phase diagrams of pseudo-quaternary systems of cetyltrimethylammonium bromide (CTAB)/polyoxyethylene(20)cetyl ether (Brij-58)/water/1-butanol (or 1-pentanol)/*n*-heptane (or *n*-decane) at fixed ω ($= [\text{water}]/[\text{surfactant}]$) of 55.6 were constructed at different temperatures (293, 303, 313, and 323 K) and different mole fraction compositions of Brij-58 ($X_{\text{Brij-58}} = 0, 0.5, \text{ and } 1.0$ in CTAB + Brij-58 mixture). Pure CTAB stabilized systems produced larger single-phase domains than pure Brij-58 stabilized systems. Increasing temperature increased the single-phase domain in the Brij-58 stabilized systems, whereas the domain decreased in the CTAB stabilized systems. For mixed surfactant systems (with $X_{\text{Brij}} = 0.5$) negligible influence of temperature in the studied range of 293 to 323 K on the phase behavior was observed. Interfacial compositions of the mixed microemulsion systems at different temperature and different compositions were evaluated by the dilution method. The n_a^i (number of moles of alcohol at the interface) and n_a^o (number of moles of alcohol in the oil phase) determined from dilution experiments were found to decrease and increase respectively for CTAB stabilized systems, whereas an opposite trend was witnessed for Brij-58 stabilized systems. The energetics of transfer of cosurfactants from oil to the interface were found to be exothermic and endothermic for CTAB and Brij-58 stabilized systems, respectively. At equimolar composition of CTAB and Brij-58, the phase diagrams were temperature insensitive, so that the enthalpy of the aforesaid transfer process was zero.

Keywords: Microemulsion; Mixed surfactant; Phase behavior; Interfacial composition; Thermodynamic properties

1. Introduction

Microemulsions are amphiphile stabilized transparent, isotropic and thermodynamically stable dispersions of otherwise immiscible water and oil [1,2]. The microheterogeneity of such dispersions make them useful in biological and technological applications [3,4]. Due to their diphilic nature, surfactants get adsorbed at the oil–water interface to render stability to the dispersion by preventing coalescence. Short chain lipophilic alcohols (called cosurfactants) blended with surfactants partition

between the coexisting aqueous and oleic phases to control the bending elasticity of the interfacial layer offering stability to the dispersion [5–8]. At a fixed ω (molar ratio of water to surfactant), a threshold amount of cosurfactant is required for a stable w/o dispersion, and droplet dimension is controlled by the cosurfactant content. An increased amount of it decreases droplet size and vice versa. Adsorption of cosurfactant at the interface essentially depends on its distribution between the oleic phase and the interface. Although direct determination of cosurfactant distribution between the interface and oil is difficult [9], reports are available in literature using techniques, like conductance, interfacial tension, small angle neutron scattering (SANS), small angle X-ray scattering (SAXS), dynamic light scattering (DLS), etc. [1,2,10,11]. Romsted [12] has de-

veloped a chemical trapping method for determining the distribution of medium chain alkanols in cationic microemulsions with different types of oils. Kunieda et al. [6,13–15] have determined the cosurfactant concentration at the interface and in the bulk oil phase in three-phase balanced microemulsions using equal amount of oil and water applying the HLB related equation developed by them [16–18]. Other group of workers [19–21] have also used this equation to determine the interfacial composition of balanced microemulsions stabilized by nonionic surfactants. We have recently used this method to determine the interfacial composition of mixed microemulsions derived from nonionic [polyoxyethylene(10)cetyl ether (Brij-56)]–anionic [sodium dodecyl benzene sulfonate (SDBS)] surfactants in presence of NaCl [22]. Recently Abuin et al. [23,24] have estimated the minimum amount of alkanol required to produce quaternary w/o microemulsion for a series of alkanols (straight chain and branched chain), hydrocarbon solvents of different size and topology, and surfactants (cationic, anionic, nonionic, zwitterionic, and natural). They concluded that the critical amount of alkanol at the interface is mainly dependent on its topology and surfactant type, and to a lesser extent on the alkanol size, ω and the solvent topology. In the above respect, the dilution experiment accomplished by adding oil at a constant water and surfactant level to destabilize an otherwise stable w/o microemulsion and then restabilizing it by adding a requisite amount of alcohol has been found to be simple, elegant and convenient. The dilution method was used by Birdi [25] and Singh et al. [26,27]. Gu et al. [28] used a calorimetric method to estimate the energetic and distribution parameters of w/o microemulsion system. The dilution method has been also used by Moulik et al. [29–31] to determine the interfacial composition, and energetics and structural parameters of different w/o microemulsion forming systems stabilized by ionic surfactants. Bayrak [32] has used the method on nonionic surfactant stabilized systems. Recently, Palazzo et al. [33,34] have determined the interfacial compositions of CTAB/*n*-hexane/1-pentanol/water w/o microemulsion system using the dilution method and found satisfactory agreement with those obtained by using the pulsed gradient spin-echo NMR (PGSE-NMR) technique.

Microemulsion systems formed with mixed surfactants are known to offer properties superior than the pure components [35–37]. It is known that ionic and nonionic surfactants physicochemically behave in opposite manner with change in temperature [38]. The formation of temperature insensitive microemulsions using ionic–nonionic blended surfactant systems has been reported [6,39,40]. But studies on interfacial composition of mixed surfactant derived microemulsion systems are rare [15,22,41]. We have recently initiated systematic physicochemical studies on w/o microemulsion systems stabilized by anionic–nonionic and cationic–nonionic blended surfactants using oils of different types [22,42–45]. In continuation of such studies, the phase behavior and interfacial composition of CTAB + Brij-58 derived w/o microemulsion systems in presence of 1-butanol or 1-pentanol as cosurfactant and *n*-heptane or *n*-decane as oil have been studied under the conditions of varied temperature and mixing ratios of the surfactants. The

distributions of cosurfactants between the interface and the oil phase at the threshold level of stability, and the transfer energetics of the process have been evaluated. According to our knowledge, such a study on mixed surfactant microemulsion systems was not done in the past.

2. Materials and methods

2.1. Materials

Cetyltrimethylammonium bromide (CTAB) and polyoxyethylene(20)cetyl ether (Brij-58) were purchased from Merck, Germany and Sigma Aldrich, USA, respectively. The oils, *n*-heptane (Hp) and *n*-decane (Dc), and the alkanols, 1-butanol (Bu) and 1-pentanol (Pn) were products of Fluka, Switzerland. All these chemicals were used without further purification. Doubly distilled water of conductivity less than $3 \mu\text{S cm}^{-1}$ was used in the experiments.

2.2. Methods

2.2.1. Construction of phase diagram

Calculated amounts of water and surfactant (at a fixed $\omega = 55.6$) with different amounts of oil were taken in sealed test tubes. The mixtures were then shaken vigorously in a vortex mixer and kept in a thermostatic water bath (accuracy, ± 0.1 K) at the desired temperature. The cosurfactant alkanol was then added to the mixtures from a microsyringe. The initially viscous mixture produced a biphasic solution after addition of a certain amount of alkanol. With gradual addition of alkanol, the upper phase of the biphasic mixture shrunk and finally disappeared upon addition of a certain volume of it. This point indicated the formation of a single-phase solution. The same procedure was repeated for 2–3 times and an average of these results was taken for the construction of phase diagrams.

2.2.2. Dilution experiments

We have used the method described by Moulik et al. [29] to perform the dilution experiment. Fixed amounts of surfactant(s) (0.5 mmol), water (27.8 mmol), and oil (14.0 mmol) were mixed in a sealed test tube, shaken vigorously in a vortex mixer for at least 5 min and then kept in a thermostated water bath (accuracy, ± 0.1 K) at the desired temperature to attain equilibrium. The composition of this mixture for the CTAB/Bu/Hp/water quaternary system is denoted by point P_0^T in the phase diagram (Fig. 1). Alkanol was then added gradually in small intervals into it from a microsyringe until a clear single-phase solution appeared (point P_0^C in the phase diagram). A calculated small amount of oil was then added into it and the formulation reverted back to the biphasic form (point P_1^T in the diagram). This biphasic mixture was again titrated with Bu until single-phase appeared (point P_1^C). This procedure was repeated noting the volumes of alkanol necessary at each step for obtaining a clear and stable w/o microemulsion. The entire procedure was followed at 293, 303, 313, and 323 K with Bu and Pn as cosurfactants and, Hp and Dc as oils, with varying $X_{\text{Brij-58}}$. Each

experiment was repeated twice or thrice and the average values were used for data processing and analysis.

3. Results and discussion

3.1. Phase behavior

Phase diagrams of pseudo-quaternary systems composed of surfactant(s), cosurfactant, oil and water at a constant temperature and pressure can be best represented with the help of three-dimensional Gibbs tetrahedron with four components as the four apexes. In the present study, the phase diagrams are constructed in a simple two-dimensional Gibbs triangles after cutting the Gibbs tetrahedron along a constant ω ($= 55.6$) plane. The compositions in the phase diagrams are represented in weight fraction.

Fig. 1 depicts the phase behavior of CTAB/water/Hp/Bu system at 303 K. Bu is soluble in Hp and hence no solubility gap appeared along the Bu–Hp axis. Bu is only partially soluble in water and it formed clear solution in presence of surfactant [22]. A thin miscibility gap appeared in the (CTAB/water) rich region of the Bu–(CTAB/water) axis. CTAB itself cannot solubilize oil and water and no miscibility region appeared along the (CTAB/water)–Hp axis. The formulations along this axis were viscous, specially in the CTAB/water rich region (denoted by a darker shade in Fig. 1). With the addition of alkanol, the viscosity of the formulation decreased and fluid biphasic region appeared (denoted by a lighter shade in Fig. 1). When an oil soluble dye Sudan IV was added into it, both the phases turned red (the intensity in the upper phase was more than the lower), whereas addition of a water-soluble dye, Eosine Blue turned the lower phase violet keeping the upper phase colorless. This indicated that the lower phase was a w/o microemulsion in equilibrium with an upper oleic phase, which might contain Bu solubilized in it. Earlier Palazzo et al. [34] identified a biphasic region at a low cosurfactant content in CTAB/*n*-hexane/*l*-pentanol/water microemulsion system. Diffusion coefficient study with the aid of ^1H NMR studies revealed that the upper phase was the oil phase with trace amount of Pn dissolved in it and the lower phase was a oil swollen normal micellar solution. The dye solubilization experiment in the present study corroborated the results. Upon further addition of Bu, the positive curvature of the interfacial film reverted and water swollen reverse micelles were formed, and the biphasic system turned monophasic (denoted by the clear region in Fig. 1). The clear region next to the biphasic region with all probability did contain w/o droplet structure. This view might not hold in the alkanol rich region; there other structures might have been developed as a function of alkanol content in the region. The elucidation of the detailed structure of the total single-phase region was beyond the scope of the present work and might be taken up in a future study. Fig. 2 represents the phase diagram of CTAB and Brij-58 stabilized systems in Hp and Dc with Bu as the cosurfactant. It was observed that under identical compositions for single-phase microemulsion formation, larger amount of Bu was required for Brij-58 stabilized systems than CTAB. On the other hand, Dc containing system required larger Bu

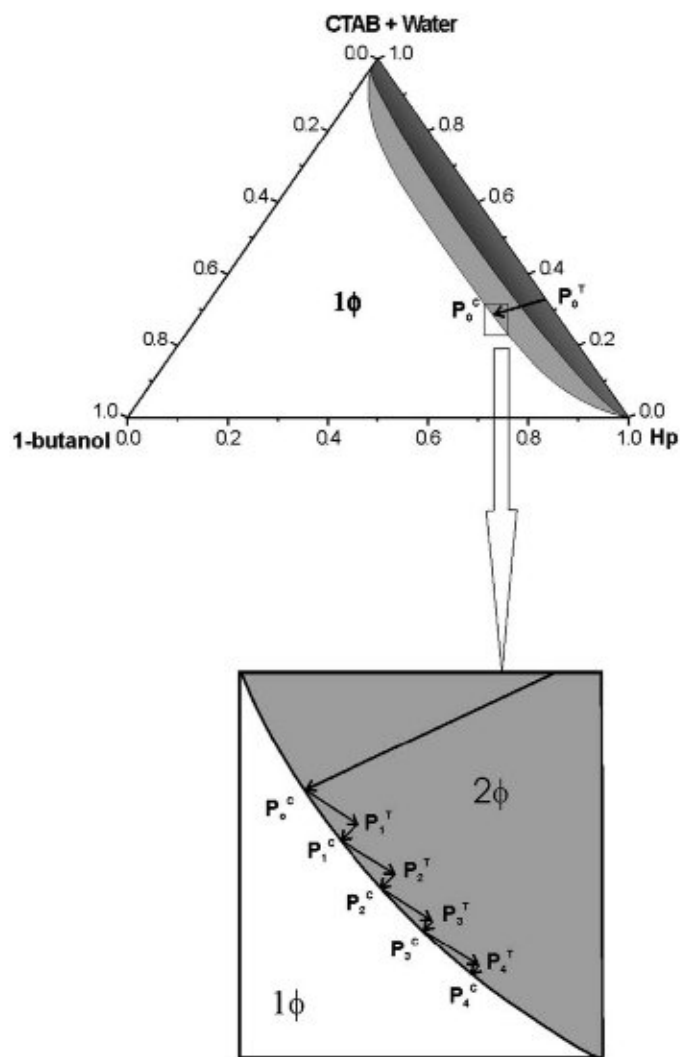


Fig. 1. Triangular phase diagram of the quaternary system, CTAB/water/1-butanol/*n*-heptane at fixed $\omega = 55.6$ at 303 K. Dark shaded area represents viscous region, lighter shaded area represents two-phase region, and clear region represents single-phase microemulsion (1ϕ). The point P_0^T denotes the start of the dilution experiment. A typical pathway of dilution experiment has been presented in the inset (see text).

than Hp stabilized system to form single-phase microemulsion. Fig. 3 represents the phase diagram of CTAB/Pn/Hp/water under identical compositions at 303 K wherein lesser amount of alkanol was required to form single-phase microemulsion than Bu. At higher weight fraction of Pn, a second biphasic region appeared [denoted by EF (emulsification failure [34]) in the phase diagram]. Such EF did not occur with Bu in the system. Higher lipophilicity of Pn than Bu might be the reason for this difference. For Brij-58 stabilized system in Pn, higher amount of alkanol was required to form single-phase microemulsion than CTAB stabilized system (figure not shown). Both single phase and EF boundary shifted toward higher weight fraction of Pn for Dc containing systems than those with Hp (also not exemplified).

The effect of temperature on the phase behavior of CTAB (or Brij-58)/water/Hp/Bu systems is depicted in Fig. 4. There, with temperature change from 293 to 323 K, the single-phase

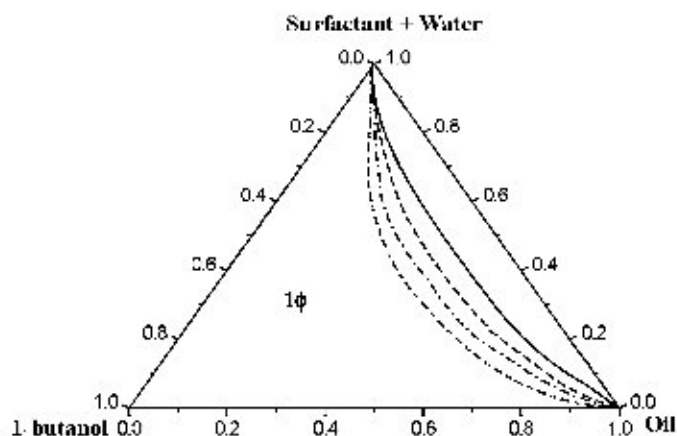


Fig. 2. Triangular phase diagram of the quaternary systems, CTAB/water/1-butanol/*n*-heptane (—); Brij-58/water/1-butanol/*n*-heptane (---); CTAB/water/1-butanol/*n*-decane (---); Brij-58/water/1-butanol/*n*-decane (---) at fixed $\omega = 55.6$ at 303 K. 1ϕ indicates single-phase microemulsion. Areas under the curves are biphasic. Appearances of viscous phases along the (surfactant + water)–oil axis have not been shown for simplicity.

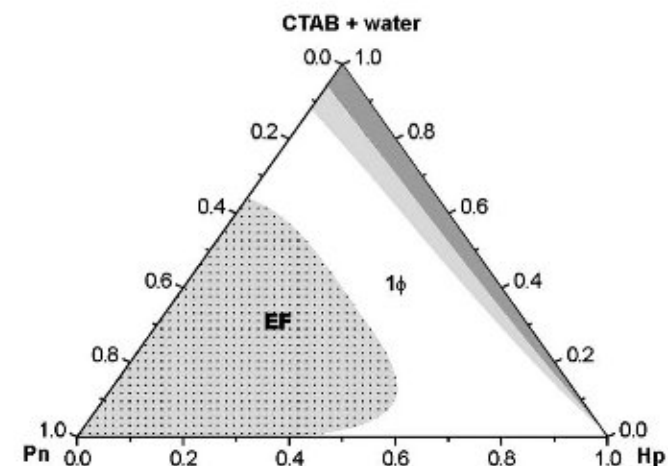


Fig. 3. Triangular phase diagram of the quaternary system, CTAB/water/1-pentanol/*n*-heptane at $\omega = 55.6$ at 303 K. The clear region represents single-phase microemulsion (1ϕ). The light and dark shaded regions along the surfactant–oil axis represent viscous and biphasic regions, respectively. The shaded region in the pentanol corner is the emulsification failure (EF) region.

domain decreased and increased for CTAB and Brij-58 stabilized systems, respectively. The hydrophilicity of ionic surfactants increases at elevated temperature due to increased head group dissociation [40], whereas nonionic surfactants become lipophilic due to dehydration of the oxyethylene head groups [14]. Thus, for CTAB stabilized systems, the requirement of lipophilic cosurfactant (herein Bu) would be more to maintain the required hydrophile–lipophile balance (HLB) [16,46]. The requirement would be opposite for systems with Brij-58.

Equimolar (CTAB + Brij-58) blended systems produced monophasic regions that were more or less average of the single components (not exemplified). We have earlier reported such averaging of microemulsion regions in (anionic + nonionic) blended systems [43,45]. The effect of temperature on the behavior of these equimolar mixed systems was herein examined.

A representative diagram for (CTAB + Brij-58)/water/Dc/Bu and (CTAB + Brij-58)/water/Hp/Bu systems is shown in Fig. 5. It was observed that increase in temperature from 293 to 323 K had negligible effect on the phase behavior of all the mixed systems in agreement with earlier studies on ionic–nonionic mixed microemulsion systems [43,45].

3.2. Interfacial composition and thermodynamics of the process

Alkanol molecules in quaternary water/surfactant/alkanol/oil w/o microemulsion systems essentially remain distributed between the oleic phase and the interface. A small amount may remain solubilized in the aqueous phase depending on its lipophilicity. Bu has small and Pn has negligible aqueous solubility. In order to stabilize a water-in-oil dispersion, a threshold amount of cosurfactant (alkanol) is required in the oil and at the interface. The distribution of cosurfactant between the interfacial region (consisting of surfactant molecules) and the oleic phase is governed by a distribution constant, which is a function of temperature. With increase in oil content, the equilibrium of a stable w/o microemulsion gets disrupted and the system splits up into two distinct phases. This destabilization may be compensated for by the addition of a threshold amount of alkanol to restore the prevailing equilibrium. This process is repeatedly followed in a dilution method.

To estimate the concentrations of alkanol at the interface and in bulk oil to get the distribution constant (K_d) by the dilution method, the physicochemical rationale elaborated by Moulik et al. [29–31] and Bayrak [32] was considered. Thus,

$$K_d = X_a^i / X_a^o \quad (1)$$

where X_a^i and X_a^o are the mole fractions of alkanol at the interface and in the oleic phase, respectively.

At the critical condition of stability under a nonvariable environment, the alkanol content of the oil is given by a constant k as shown below.

Thus,

$$k = n_a^o / n_o \quad (2)$$

where n_a^o and n_o are the number of moles of alkanol in oil and the total number of moles of oil, respectively.

The total number of moles of alkanol (n_a^i) can be written as

$$n_a^i = n_a^w + n_a^i + n_a^o \quad (3)$$

where n_a^w and n_a^i are the number of moles of alcohol in the aqueous phase and at the interface, respectively. By Eqs. (2) and (3) we may write

$$n_a^i = n_a^w + n_a^i + k n_o \quad (4)$$

For changing concentration of surfactant (n_s) the equation can be normalized as

$$n_a^i / n_s = (n_a^w + n_a^i) / n_s + k n_o / n_s \quad (5)$$

From the linear plot between n_a^i / n_s and n_o / n_s , n_a^o can be

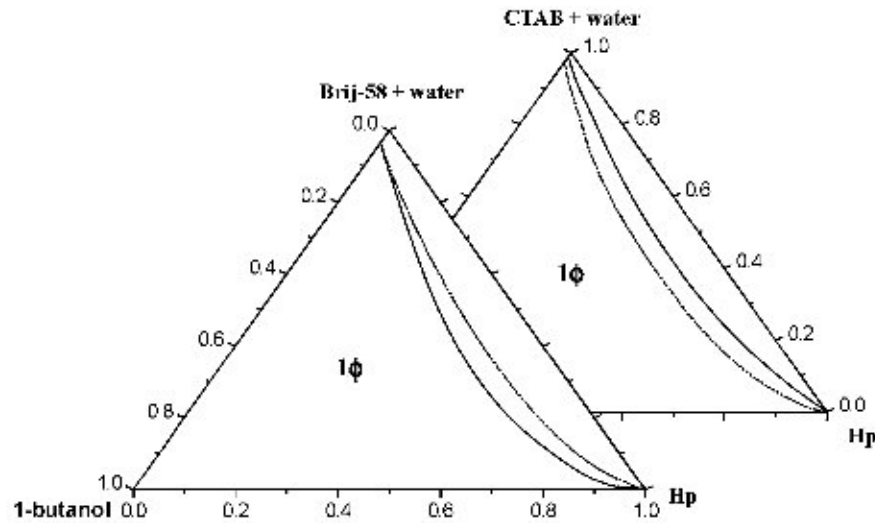


Fig. 4. Triangular phase diagrams of the quaternary systems, CTAB (or Brij-58)/water/1-butanol/n-heptane at $\omega = 55.6$ at 293 K (—) and 323 K (---). 1ϕ indicates single-phase microemulsion system. Appearance of viscous region along the (surfactant + water)–oil axis has not been shown for simplicity.

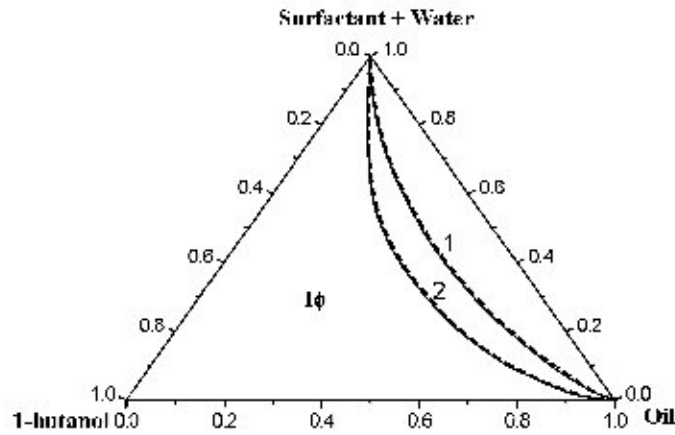


Fig. 5. Phase diagram of CTAB/Brij-58/water/1-butanol/oil systems at 293 K (solid line) and 323 K (broken line) at $\omega = 55.6$, and $X_{\text{Brij-58}} = 0.5$; (1) with Hp, and (2) with Dc. 1ϕ indicates single-phase microemulsion system. Appearance of viscous region along the (surfactant + water)–oil axis has not been shown for simplicity.

obtained from the slope (S) and n_a^i can be obtained from the intercept (I) with the knowledge of n_a^w at that temperature.

Equation (1) can be then written as

$$\begin{aligned} K_d &= X_a^i / X_a^o = \{n_a^i / (n_a^i + n_s)\} / \{n_a^o / (n_a^o + n_o)\} \\ &= \{n_a^i (n_o + n_a^o) / n_a^o (n_a^i + n_s)\} \\ &= \{n_a^i (1 + n_a^o / n_o)\} / \{n_a^o (n_a^i + n_s) / n_o\}. \end{aligned} \quad (6)$$

On simplification, Eq. (6) reduces to

$$K_d = \{\alpha(1 + S)\} / \{S(1 + \alpha)\}, \quad (7)$$

where $\alpha = (I - n_a^w / n_s) = n_a^i / n_s$.

For Pn, $n_a^w \approx 0$ and Eq. (7) takes the form

$$K_d = I(1 + S) / S(1 + I). \quad (8)$$

For a given surfactant/alkanol w/o microemulsion system, the threshold amount of alkanol required for stabilization depends on the n_a^i / n_s and n_a^o / n_o ratios. The evaluation of K_d

leads to the understanding of the thermodynamics of the process.

The standard Gibbs free energy of transfer (ΔG_t°) of alcohol from oil to the interface can be obtained from

$$\Delta G_t^\circ = -RT \ln K_d.$$

The standard enthalpy of the said transfer process (ΔH_t°) can be evaluated from equation:

$$\left[\partial(\Delta G_t^\circ / T) / \partial(1/T) \right]_p = \Delta H_t^\circ. \quad (9)$$

The use of Gibbs–Helmholtz equation leads to the calculation of the corresponding entropy change (ΔS_t°). Thus,

$$\Delta S_t^\circ = (\Delta H_t^\circ - \Delta G_t^\circ) / T. \quad (10)$$

The standard state herein considered is the hypothetical ideal state of unit mole fraction.

The method of dilution was used for CTAB/Brij-58 mixed surfactant systems (with $X_{\text{Brij-58}}$ at 0, 0.2, 0.4, 0.6, 0.8, and 1.0) in Hp and Dc at constant $\omega = 55.6$ at four different temperatures 293, 303, 313, and 323 K. Bu and Pn were used as cosurfactants in these systems. From the data collected, graphs were constructed by plotting n_a^i / n_s vs n_o / n_s according to Eq. (5). Representative illustrations are shown in Figs. 6A and 6B. The calculated values of n_a^i , n_a^o , K_d , and ΔG_t° are presented in Tables 1 and 2. It is evident from the tables that for both Bu and Pn, n_a^i increased with increase in chain length of alkane from Hp to Dc for both CTAB and Brij-58 stabilized systems. This observation was consistent with that reported by Moulik et al. [29] for CPC and Bayrak [32] for TX-100 stabilized systems. The values of n_a^i did not follow any straightforward trend as a function of $X_{\text{Brij-58}}$ for any of these systems. For Bu, n_a^i values were higher for Brij-58 derived systems than CTAB for both the oils. On the other hand, for Pn these values were higher for CTAB containing systems. The distribution of alkanol was thus found to be both oil and surfactant dependent.

It was also found from the tables that with increase in temperature, n_a^i increased and decreased for Brij-58 and CTAB sta-

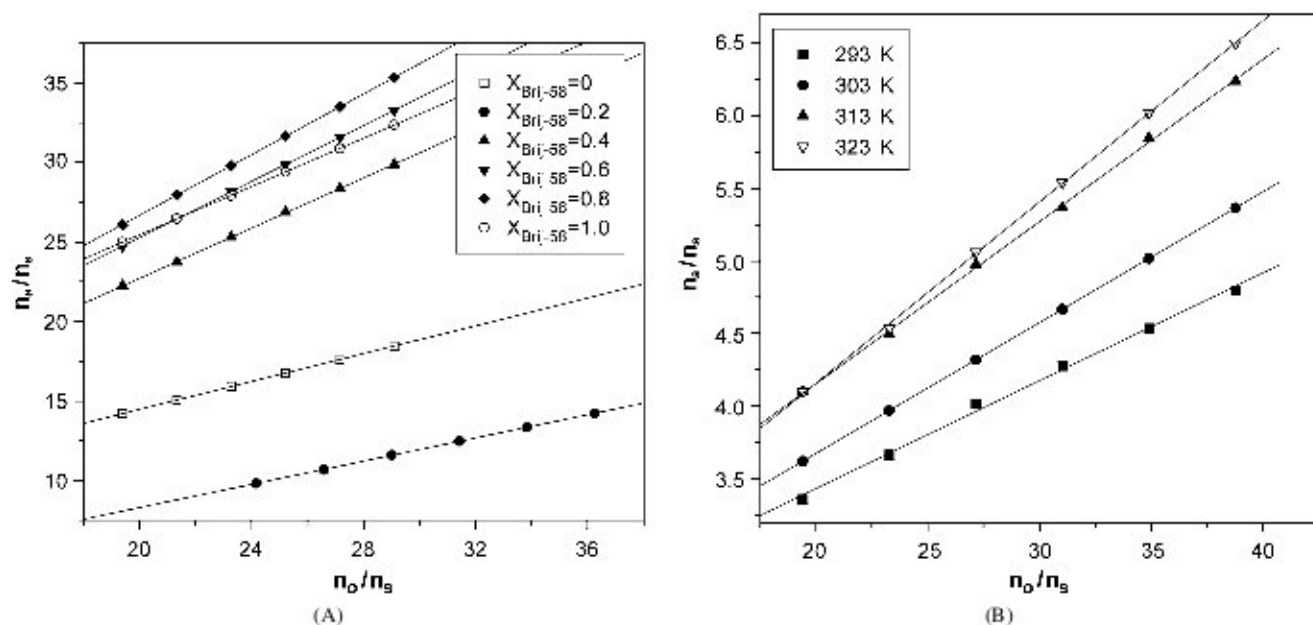


Fig. 6. (A) Plot of n_a^1/n_s vs n_o/n_s according to Eq. (5) for mixed surfactants (CTAB + Brij-58) w/o microemulsion systems comprising 0.5 mmol surfactant, 27.8 mmol water and 14.0 mmol *n*-decane stabilized by 1-pentanol at 303 K with varying $X_{\text{Brij-58}}$ of 0, 0.2, 0.4, 0.6, 0.8 and 1.0. (B) Plot of n_a^1/n_s vs n_o/n_s according to Eq. (5) for CTAB w/o microemulsion systems comprising 0.5 mmol surfactant, 27.8 mmol water and 14 mmol *n*-decane stabilized by 1-pentanol at temperatures 293, 303, 313, and 323 K.

bilized systems, respectively. At elevated temperature, the interface accommodated lesser amount of lipophilic alkanol molecules, whereas an opposite trend was followed for nonionic surfactant. Further, the n_a^0 values increased with increasing $X_{\text{Brij-58}}$ from 0 to 0.8, and then decreased for pure Brij-58 system at a constant temperature. The values with Brij-58 were higher than CTAB stabilized systems. It was also evidenced from Tables 1 and 2 that with increase in temperature, n_a^0 increased and decreased for CTAB and Brij-58 derived systems, respectively. It corroborated well with the opposite trends observed in the temperature dependent phase behavior of CTAB and Brij-58 containing systems (Fig. 4). When CTAB and Brij-58 were mixed in nearly comparable proportions ($X_{\text{Brij-58}} = 0.4$ and 0.6), the changes in both n_a^1 and n_a^0 were less than pure surfactant systems. It has corroborated well with the temperature insensitive phase behavior using mixed surfactants (Fig. 5).

The ΔG_t^0 values (Tables 1 and 2) indicated thermodynamically favorable transfer of alkanol from oil to the interface. The values evidenced a regular trend of decrease with increasing $X_{\text{Brij-58}}$ up to $X_{\text{Brij-58}} = 0.8$, where after it increased. The ΔG_t^0 values did not follow a linear course (not illustrated) with $X_{\text{Brij-58}}$ except for the Hp/Bu system at higher temperature. A comparable nonlinear behavior of mixed surfactant micellar systems was reported earlier [47]. The free energy values were more negative in Hp continuum than in Dc continuum indicating the process to be more favorable for the former than the latter. Consequently, lower volume of alcohol was required to form a stable dispersion in Hp as evidenced in the phase diagrams (Fig. 2).

The ΔG_t^0 , ΔH_t^0 , and ΔS_t^0 values at 303 K are presented in Tables 3 and 4. The magnitude of ΔG_t^0 , was found to decline with increasing proportion of Brij-58; the transfer of alkanols

from the interface to oil became less spontaneous by the presence of Brij-58. Although the Pn containing systems were more thermodynamically favored than Bu derived ones, the decline in spontaneity therein by the effect of Brij-58 was not prominent. In comparison, the transfer process in Hp was to some extent more favorable than in Dc. The process was exothermic in CTAB rich combinations ($X_{\text{Brij-58}} = 0, 0.2, \text{ and } 0.4$), and was endothermic in Brij-58 rich combinations ($X_{\text{Brij-58}} = 0.6, 0.8, \text{ and } 1.0$). The desolvation of the head group of Brij-58 during the transfer in the oil was ended up with absorption of heat. Higher ΔH_t^0 values were obtained with Pn than with Bu. The Hp delivered systems yielded much higher ΔH_t^0 than Dc delivered systems. Graphical plotting of ΔH_t^0 against $X_{\text{Brij-58}}$ with Bu and Pn produced $\Delta H_t^0 = 0$ at around equimolar mixture of CTAB and Brij-58 (Fig. 7). Thus, for nearly equimolar mixture of CTAB and Brij-58 the process of transfer became athermal. Mixed ionic–nonionic surfactant derived athermal microemulsion formulations were reported in literature [43,45]. A model calculation of ΔH_t^0 based on amphiphile composition (neglecting their mutual interaction) in terms of the relation, $\Delta H_t^0 = [(\Delta H_t^0)_{\text{Brij-58}}](X_{\text{Brij-58}}) + [(\Delta H_t^0)_{\text{CTAB}}](1 - X_{\text{Brij-58}})$ was performed. To yield $\Delta H_t^0 = 0$, the requirement of $X_{\text{Brij-58}}$ were 0.73 and 0.62 for Bu and Pn containing systems, respectively, when Hp was the oil. Similar calculation produced $X_{\text{Brij-58}} = 0.74$ and 0.48 to produce $\Delta H_t^0 = 0$ for Bu and Pn containing systems in Dc. The Bu derived values disagreed more than Pn derived values with respect to the attainment of the athermal condition. The enthalpies of transfer of alkanols in the mixed surfactant systems were not guided by the above-considered ideal additivity formula. The phenomenon needs attention through further studies. The change over of ΔH_t^0 from exothermicity to endothermicity was similarly reflected

Table 1

The temperature, cosurfactant, and surfactant composition dependent physicochemical parameters n_a^i , n_a^o , and K_d for the formation of w/o microemulsion in heptane^{a,b}

T (K)	$10^4 n_a^i$ (mol) Bu (Pn)	$10^3 n_a^o$ (mol) Bu (Pn)	K_d Bu (Pn)	$-\Delta G_i^\circ$ (kJ mol ⁻¹) Bu (Pn)
$X_{\text{Brij-58}} = 0$				
293	2.97 (8.95)	2.52 (0.68)	3.32 (19.3)	2.93 (7.21)
303	2.36 (8.16)	3.26 (0.88)	2.28 (14.6)	2.08 (6.76)
313	2.13 (7.70)	3.62 (1.28)	1.94 (10.1)	1.73 (6.02)
323	1.61 (6.51)	4.12 (1.68)	1.42 (7.32)	0.95 (5.34)
$X_{\text{Brij-58}} = 0.2$				
293	2.61 (6.98)	3.16 (1.52)	2.09 (8.20)	1.81 (5.13)
303	2.56 (6.03)	3.38 (1.70)	1.83 (6.95)	1.53 (4.89)
313	2.58 (5.13)	3.56 (2.02)	1.56 (5.51)	1.16 (4.44)
323	2.48 (4.29)	3.82 (2.71)	1.32 (3.86)	0.75 (3.63)
$X_{\text{Brij-58}} = 0.4$				
293	2.61 (8.16)	4.10 (2.98)	2.01 (4.78)	1.71 (3.81)
303	2.56 (7.32)	4.18 (3.22)	1.95 (4.27)	1.69 (3.66)
313	2.58 (7.06)	4.36 (3.48)	1.89 (3.94)	1.67 (3.57)
323	2.48 (6.91)	4.40 (3.76)	1.83 (3.66)	1.63 (3.49)
$X_{\text{Brij-58}} = 0.6$				
293	4.02 (6.99)	6.28 (5.40)	1.86 (2.74)	1.52 (2.46)
303	4.52 (6.21)	6.22 (4.72)	2.00 (2.90)	1.75 (2.68)
313	5.13 (5.89)	6.14 (4.32)	2.15 (3.04)	1.99 (2.89)
323	5.42 (5.42)	6.08 (3.84)	2.23 (3.23)	2.15 (3.15)
$X_{\text{Brij-58}} = 0.8$				
293	3.02 (3.56)	7.24 (6.36)	1.41 (1.73)	0.85 (1.32)
303	3.59 (4.14)	6.86 (5.62)	1.63 (2.06)	1.24 (1.82)
313	4.31 (4.57)	6.48 (5.01)	1.89 (2.39)	1.66 (2.26)
323	4.87 (5.34)	6.06 (3.98)	2.12 (3.12)	2.02 (3.05)
$X_{\text{Brij-58}} = 1.0$				
293	5.17 (5.97)	6.44 (5.85)	2.08 (2.40)	1.79 (2.13)
303	5.59 (6.53)	6.04 (5.01)	2.27 (2.82)	2.07 (2.61)
313	6.07 (6.81)	5.68 (3.96)	2.48 (3.49)	2.36 (3.25)
323	6.45 (7.06)	4.96 (3.04)	2.83 (4.43)	2.80 (4.00)

^a n_a^w values of 0.51, 0.477, 0.442, and 0.427 mmol for Bu per 27.8 mmol water at 293, 303, 313, and 323 K, respectively, were taken in the calculation.

^b The average errors in K_d and ΔG_i° were within ± 5 and $\pm 3\%$, respectively.

on ΔS_i° , which became positive from negative at $X_{\text{Brij-58}} \geq 0.6$. Their magnitudes in Hp delivered systems were higher than Dc delivered systems. The interface and its surroundings thus became labile (less organized) in presence of larger proportion of Brij-58. The difference in entropic behavior between Hp and Dc continuums was due to the chain length difference between the two oleic phases; the latter became less deorganized than the former.

Micellar and microemulsion systems often obey an extra thermodynamic linear correlation between the enthalpy and entropy changes [29,31,43,48–50]. Such a feature was also observed for the presently studied microemulsion systems (Fig. 8). A compensation temperature $T_{\text{comp}} = 316$ K was found from the plot vis-à-vis the experimental temperature of 303 K. Such a deviation of the compensation temperature from the experimental thermal state is not uncommon in literature [29,43, 48–50]. The linear correlation suggested mutual adjustment between the total enthalpy and its nonuseful part (i.e., the entropy) during the alkanol transfer process. However, it must be taken into account that when entropy is plotted against enthalpy, at any experimental temperature, the true functional dependence,

if any, is usually masked by a dominant statistical compensation pattern that arises solely from experimental errors. That is, the high linear correlation between these two parameters is due to the propagation of experimental error than to chemical variation. The usual source of error emanates from the fact that these thermodynamic parameters are usually derived over a very short range of $1/T$, which are far from the origin, and thus the compensation temperature usually comes out to be in close proximity of the harmonic mean ($T_{\text{hm}} = \langle 1/T_i \rangle^{-1}$) of the experimental temperatures (T_i), and the estimated correlation coefficients have values near unity. Krug et al. [51–53] proposed that such regression should be of enthalpy estimates on free energy estimates evaluated at T_{hm} instead of enthalpy–entropy estimation, since $\Delta G - \Delta H$ estimates at T_{hm} are the only estimates that are statistically independent. We have plotted ΔG_i° against ΔH_i° at T_{hm} ($= 307.6$ K) (Fig. S1 can be found in Supplementary material) and found that the plot lacks in linear correlation to a fair extent, and the data are largely scattered. It has been reported that linear compensation is rather unlikely for equilibrium processes, whereas common for chemical reactions [52]. In the present system, the enthalpy values varied over a wide

Table 2
The temperature, cosurfactant and surfactant composition dependent physicochemical parameters n_a^i , n_a^o , and K_d for the formation of w/o microemulsion in decane^{a,b}

T (K)	$10^4 n_a^i$ (mol) Bu (Pn)	$10^3 n_a^o$ (mol) Bu (Pn)	K_d Bu (Pn)	$-\Delta G_i^o$ (kJ mol ⁻¹) Bu (Pn)
$X_{\text{Brij-58}} = 0$				
293	24.5 (9.77)	5.75 (1.03)	2.87 (9.68)	2.57 (5.53)
303	23.9 (9.38)	6.15 (1.25)	2.72 (7.91)	2.52 (5.21)
313	22.9 (9.60)	6.90 (1.58)	2.50 (6.50)	2.38 (4.87)
323	21.1 (8.33)	7.39 (1.75)	2.34 (5.65)	2.29 (4.65)
$X_{\text{Brij-58}} = 0.2$				
293	24.2 (9.73)	8.75 (2.28)	2.16 (4.78)	1.88 (3.81)
303	24.5 (9.07)	9.44 (2.42)	2.07 (4.40)	1.83 (3.73)
313	23.1 (9.00)	9.82 (2.79)	2.00 (3.88)	1.81 (3.53)
323	20.8 (8.95)	10.1 (3.10)	1.93 (3.55)	1.76 (3.40)
$X_{\text{Brij-58}} = 0.4$				
293	31.5 (6.78)	10.7 (3.96)	2.01 (2.62)	1.69 (2.35)
303	29.9 (6.52)	11.1 (4.06)	1.94 (2.53)	1.67 (2.34)
313	28.5 (6.23)	11.5 (4.14)	1.89 (2.45)	1.66 (2.32)
323	25.5 (5.82)	11.9 (4.21)	1.83 (2.33)	1.62 (2.27)
$X_{\text{Brij-58}} = 0.6$				
293	32.7 (7.80)	12.5 (5.15)	1.84 (2.28)	1.49 (2.00)
303	33.7 (7.92)	12.4 (5.01)	1.86 (2.33)	1.56 (2.13)
313	34.9 (7.75)	12.2 (4.89)	1.89 (2.36)	1.65 (2.23)
323	35.8 (7.87)	12.0 (4.80)	1.90 (2.40)	1.73 (2.27)
$X_{\text{Brij-58}} = 0.8$				
293	30.4 (4.97)	13.8 (6.41)	1.73 (1.60)	1.34 (1.14)
303	33.3 (6.64)	13.4 (5.97)	1.79 (1.91)	1.46 (1.63)
313	36.8 (9.11)	12.9 (5.16)	1.84 (2.41)	1.59 (2.29)
323	40.0 (10.9)	12.4 (4.73)	1.90 (2.72)	1.72 (2.69)
$X_{\text{Brij-58}} = 1.0$				
293	45.1 (7.43)	10.9 (6.06)	2.06 (1.98)	1.76 (1.67)
303	46.6 (9.81)	10.7 (4.75)	2.09 (2.62)	1.86 (2.43)
313	49.7 (11.1)	10.2 (4.11)	2.16 (3.05)	2.01 (2.90)
323	51.2 (12.5)	9.93 (3.37)	2.20 (3.70)	2.12 (3.51)

^a n_a^w values of 0.51, 0.477, 0.442, and 0.427 mmol for Bu per 27.8 mmol water at 293, 303, 313, and 323 K, respectively, were taken in the calculation.

^b The average errors in K_d and ΔG_i^o were within ± 5 and $\pm 3\%$, respectively.

Table 3
The thermodynamic parameters for the transfer of alkanols (Bu and Pn) from heptane to the interface at varied $X_{\text{Brij-58}}$ at 303 K^a

$X_{\text{Brij-58}}$	ΔG_i^o (kJ mol ⁻¹) Bu (Pn)	ΔH_i^o (kJ mol ⁻¹) Bu (Pn)	ΔS_i^o (JK ⁻¹ mol ⁻¹) Bu (Pn)
0	-2.08 (-6.76)	-21.3 (-25.8)	-63.4 (-62.7)
0.2	-1.53 (-4.89)	-12.2 (-19.5)	-35.2 (-48.2)
0.4	-1.69 (-3.66)	-2.42 (-6.94)	-2.41 (-10.8)
0.6	-1.76 (-2.68)	4.83 (4.23)	21.7 (22.8)
0.8	-1.24 (-1.82)	10.7 (15.1)	39.3 (55.7)
1.0	-2.07 (-2.61)	7.86 (16.1)	32.8 (61.8)

^a The error limits in ΔG_i^o , ΔH_i^o , and ΔS_i^o are $\pm 3\%$, $\pm 5\%$, and $\pm 8\%$, respectively.

range, whereas such variation in free energy was rather small (between -1 to -3 kJ mol⁻¹). This might be one of the reasons for the observed nonlinearity. On the other hand, because of the small range of free energy variation a good correlation between the enthalpy and entropy changes was observed. Also, the compensation temperature (315.9 K) was found to be reasonably close to the average (308 K) of the experimental temperatures. It can also be noted that it is not possible to formulate mi-

Table 4
The thermodynamic parameters for the transfer of alkanols (Bu and Pn) from decane to the interface at varied $X_{\text{Brij-58}}$ at 303 K^a

$X_{\text{Brij-58}}$	ΔG_i^o (kJ mol ⁻¹) Bu (Pn)	ΔH_i^o (kJ mol ⁻¹) Bu (Pn)	ΔS_i^o (JK ⁻¹ mol ⁻¹) Bu (Pn)
0	-2.52 (-5.21)	-5.39 (-14.4)	-9.46 (-30.2)
0.2	-1.83 (-3.73)	-2.99 (-7.94)	-3.80 (-13.9)
0.4	-1.67 (-2.34)	-2.34 (-3.04)	-2.21 (-2.31)
0.6	-1.56 (-2.13)	0.09 (1.42)	8.11 (11.7)
0.8	-1.46 (-1.63)	2.44 (14.4)	12.9 (53.0)
1.0	-1.86 (-2.43)	1.86 (15.9)	12.3 (60.4)

^a The error limits in ΔG_i^o , ΔH_i^o , and ΔS_i^o are $\pm 3\%$, $\pm 5\%$, and $\pm 8\%$, respectively.

croemulsions over a wide range of temperature and thus the range of $1/T$ ought to be small.

4. Conclusions

The findings of the study lead to the following conclusions.

1. Both CTAB and Brij-58 (pure or mixed) could form stable w/o microemulsions with both Bu and Pn either in Hp

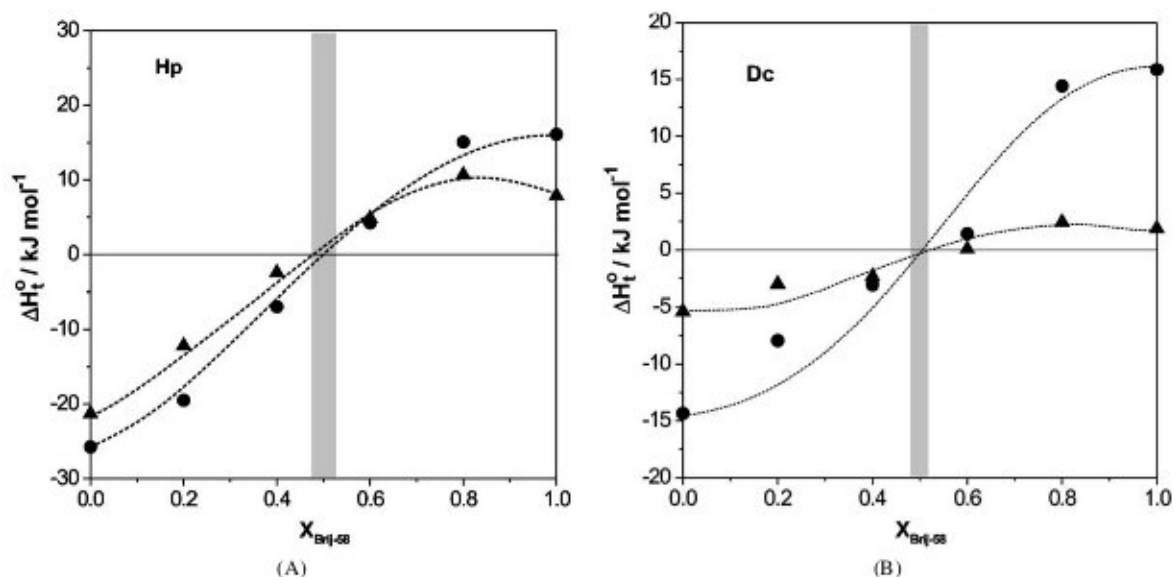


Fig. 7. Plot of ΔH_1^0 vs $X_{\text{Brij-58}}$ for CTAB/Brij-58/water/1-butanol (or 1-pentanol)/*n*-heptane (A) and CTAB/Brij-58/water/1-butanol (or 1-pentanol)/*n*-decane (B) w/o microemulsion systems comprising 0.5 mmol surfactant, 27.8 mmol water and 14 mmol oil. Triangles indicate 1-butanol and circles indicate 1-pentanol stabilized systems. The approximate equimolar region of the mixed surfactant system has been designated with a shaded vertical column.

or in Dc. At comparable conditions, CTAB produced larger monophasic zones than Brij-58. The microemulsion zone was reduced and increased with temperature for CTAB and Brij-58 stabilized systems, respectively. At equimolar CTAB and Brij-58, the temperature effect was negligible.

- The dilution method helped assessing the interfacial compositions of single (CTAB or Brij-58) and mixed (CTAB + Brij-58) surfactant microemulsion systems.
- The transfer of both Bu and Pn from oil to the interface was spontaneous but the enthalpy of the process was exothermic at lower proportion of Brij-58 in the system and at higher proportion of Brij-58 it was endothermic.
- The interface and its surroundings became labile and less organized with increasing proportion of Brij-58 in the mixed combinations with CTAB. Similar to many self-organizing systems, the ΔH_1^0 and ΔS_1^0 values fairly compensated each other.

Acknowledgments

The financial support in the form of an operating research grant to B.K.P. and a senior research fellowship to R.K.M. from the authority of Indian Statistical Institute, Kolkata, India are thankfully acknowledged. S.P.M. thanks the Indian National Science Academy for financial support with a senior scientist position.

Supplementary material

The online version of this article contains additional supplementary material.

Please visit DOI: 10.1016/j.jcis.2006.04.011.

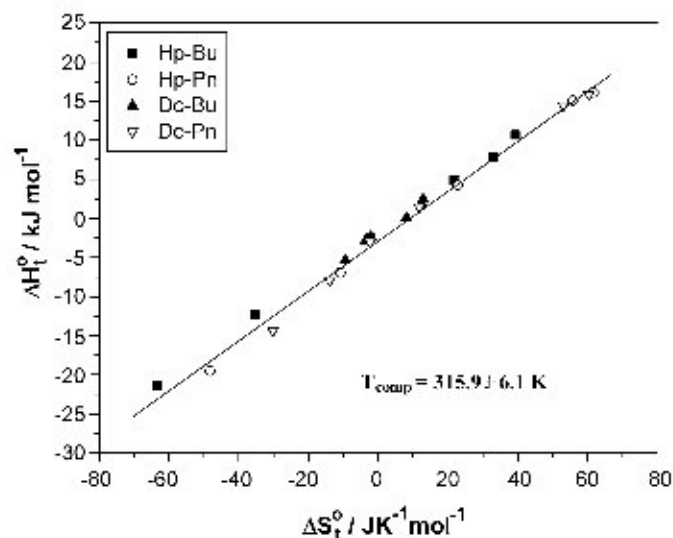


Fig. 8. Enthalpy-entropy compensation plot for CTAB/Brij-58/water/1-butanol (or 1-pentanol)/*n*-heptane (or *n*-decane) w/o microemulsion systems comprising 0.5 mmol surfactant, 27.8 mmol water and 14 mmol oil.

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