

Chapter V

Physicochemical studies of mixed surfactant microemulsions with isopropyl myristate as oil

Abstract

The present study is focused on evaluation of interfacial compositions and thermodynamic properties of w/o mixed surfactant [(sodium dodecylsulfate, SDS/polyoxyethylene (23) lauryl ether, Brij-35)/1-pentanol (Pn)/isopropyl myristate (IPM)] microemulsions under various physicochemical conditions by the dilution method. The number of moles of Pn at the interface (n_a^i) and bulk oil (n_a^o), and various thermodynamic parameters [viz. standard Gibbs free energy ($\Delta G_{o \rightarrow i}^0$), standard enthalpy ($\Delta H_{o \rightarrow i}^0$) and standard entropy ($\Delta S_{o \rightarrow i}^0$) of the transfer of Pn from bulk oil to the interface] have been found to be dependent on the molar ratio of water to surfactant (ω), concentration of Brij-35 ($X_{\text{Brij-35}}$), and temperature. Temperature-insensitive microemulsions with zero specific heat capacity, (ΔC_p^0)_{o→i} have been formed at specific compositions. The intrinsic enthalpy change of the transfer process, $\Delta(H^0)^*_{o \rightarrow i}$ has been evaluated from linear correlation between $\Delta H_{o \rightarrow i}^0$ and $\Delta S_{o \rightarrow i}^0$ at different experimental temperatures. The present report also aims at a precise characterization on the basis of molecular interactions between the constituents, and provides insight into the nature of the oil/water interfaces of these systems by conductivity and dynamic light scattering studies as a function of ω and $X_{\text{Brij-35}}$. Conductivity studies reveal that incorporation of Brij-35 in non-percolating water/SDS/Pn/IPM systems makes them favorable for ω -induced percolation behavior up to $X_{\text{Brij-35}} \leq 0.5$. But further addition of Brij-35 causes a decrease in conductivity with increasing ω . Furthermore, the hydrodynamic diameters of the microemulsion droplets increase with increase in both $X_{\text{Brij-35}}$ and ω . Correlations of the results in terms of the evaluated physicochemical parameters have been attempted.

Keywords: Mixed surfactant microemulsion; Interfacial composition; Thermodynamic parameter; Antagonism; Conductance percolation; Dynamic light scattering.

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1. Introduction

Microemulsions are clear, transparent or translucent, thermodynamically stable dispersions of oil and water, stabilized by an interfacial film of surfactant(s) frequently in combination with a co-surfactant and having diameter of the droplets in the range of 10-200 nm. Typical water-in-oil (w/o) microemulsion or reverse micelles (RMs) consist of nanoscopic pools of water dispersed in nonpolar solvent stabilized by surfactant monolayer [1, 2]. The properties of confined water differ considerably from those of bulk water due to geometrical constraints of the environment and molecular interactions at the oil/water interface [3, 4]. They have been used in various fields, such as pharmaceuticals, nanoparticle synthesis, liquid-liquid extraction, cosmetic, detergency, tertiary oil recovery etc., due to their very low interfacial tension, nanometer-sized droplets, high solubilization capacity, etc [5-7]. The extensive research of microemulsions has focused on the understanding of their internal structure and dynamics. Various instrumental investigations reveal the micro-structures of microemulsion systems, such as small angle neutron scattering (SANS), small-angle x-ray scattering (SAXS), transmission electron microscopy (TEM), dynamic light scattering (DLS), nuclear magnetic resonance (NMR), conductance, viscosity, etc [8-14].

The cosurfactant (short chain lipophilic n-alkyl alcohols) plays an important role by blending with surfactant(s) and partition between the coexisting aqueous and oleic phases to control the bending elasticity of the interfacial layer offering stability to the dispersion and affect the droplet dimension of the microemulsion droplets [15]. So, to quantify the composition of the interfacial layer and the distribution of surfactant and cosurfactant between the interfacial layer and the water or oil phase, different phase diagrams were exploited, such as pseudo-ternary phase diagram, Winsor type, fishlike phase diagrams and dilution phase diagram of water-in-oil (w/o) microemulsion [16, 17]. The dilution phase diagram deals exclusively with the single phase of w/o microemulsion, and is used to determine the compositions of the interfacial layer and the bulk phase, as well as the thermodynamic parameters. Understanding the thermodynamic properties and structural characteristics of microemulsions provide an important theoretical basis for applications. In view of the above, a simple turbidimetric titration (dilution method) has been used by a number of workers [9, 18-25]. Earlier, Palazzo et al. showed that the composition of the

interface determined by a “Schulman’s cosurfactant titration” of water/cetyltrimethylammonium bromide (CTAB)/n-pentanol/n-hexane agreed well with the interfacial composition determined employing pulsed gradient spin-echo NMR (PSGE-NMR) data. The authors were also pointed out that the method has applications in scattering and diffusion studies because it provides extrapolation to single-particle properties by reducing inter-particle interactions of the microemulsion system without changing its composition [26]. Very recently, we have reported the characteristics role of cosurfactant (butanol or pentanol) on the formation and stabilization of the droplet surface, which relates to the evaluation of the interfacial composition, thermodynamic properties and structural parameters of single (CPC or SDS or Brij-35) and mixed surfactant (CPC or CTAB or SDS blend with Brij-58 or Brij-78 at different proportions) w/o microemulsions stabilized in heptane or decane or dodecane under varying physicochemical environments, by employing the dilution method [27-30]. Mixed surfactants play a promising role in surface chemical applications. Mixed surfactant systems may be less expensive and often exhibit interfacial properties more pronounced than those of the individual surface-active components of the mixture [31, 32]. The interactions between the constituent surfactants can lead to either synergism (attractive) or antagonism (repulsive) in terms of their physicochemical properties depending on the type and nature of the surfactants. The studies on mixed surfactant systems are therefore, of considerable interest from fundamental as well as applied viewpoints.

In view of these studies, the present report aims at a precise determination of the molecular interactions among the constituents, and enlighten the formation vis-à-vis nature of the oil/water interface of mixed surfactant blended w/o microemulsions [water/sodium dodecylsulfate (SDS)/polyoxyethylene (23) dodecyl ether (Brij-35)/cosurfactant (1-pentanol)/isopropyl myristate (IPM)] as function of water contents (ω), content of nonionic (X_{nonionic}), and temperature. Both of these surfactants (SDS and Brij-35) are chosen in such a way that they possess similar hydrocarbon tail (constituting 12 carbon atoms in the linear chain), but they differ in charge type and size of the polar head groups, so that the possible interactions between the hydrocarbon chains of two surfactants gets minimized. In this work, 1-pentanol is used as structure forming cosurfactant due to its versatile biological as well as technological applications [33, 34].

Also, IPM has been widely used in the formulation of biocompatible microemulsions for pharmaceutical, drug delivery and biological applications [35, 36]. However, studies on IPM (which is structurally and physicochemically different from conventional hydrocarbons [10, 37]) derived w/o mixed surfactant microemulsion is not much reported in literature using the dilution method [30]. Recently, Hait et al. [18] and Mohareb et al. [19] reported the formation characteristics of single surfactant CPC or CTAB or SDS using n-alkanol (C₅-C₉) as cosurfactant stabilized in IPM oil by dilution method. The present study sheds on the formation of w/o microemulsion, composition of mixed interfacial film, complete analysis of thermodynamic of the transfer process of cosurfactant from bulk oil to the interface, transport property and microstructure of these systems (to understand the possible interactions between the constituents of microemulsion droplets) by means of phase study, dilution method, conductivity, and dynamic light scattering (DLS) techniques. This study aims to improve the basic understanding of the formation and microstructure of mixed w/o microemulsions stabilized in polar lipophilic oil (IPM), which is not much reported in literature [30].

2. Experimental

2.1. Materials

Sodium dodecylsulfate (SDS, $\geq 99\%$) and polyoxyethylene (23) lauryl ether (Brij-35, $\geq 99\%$) were purchased from Merck, Germany and Sigma Aldrich, USA respectively. The oil, isopropyl myristate (IPM, $\geq 98\%$) and the alkanol, 1-pentanol (Pn, $\geq 98\%$) 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. Sample preparation and phase behavior

The samples comprising mixed surfactants (SDS and Brij-35) at different proportions, cosurfactant (Pn), oil (IPM) and water with constant surfactant, cosurfactant mass ratio (S : CS = 1: 2) was formulated in a screw cap glass vials. The samples were monophasic, transparent and stable. Phase behavior of chosen systems was constructed with at fixed

temperature (303K) using thermostated water bath (accuracy, ± 0.1 K). The repeat experiments were found to be reproducible with an error limit of $\pm 1\%$.

2.2.2. Method of dilution

The Schulman's method of cosurfactant titration (dilution experiment) [38] was performed to investigate the interfacial composition of w/o mixed surfactant microemulsions, as described earlier [20, 27], with necessary modification in assessment of microemulsion formation using spectrophotometric technique to measure the change in sample turbidity produced by alcohol (Pn) addition [39]. To a turbid solution comprising a blend of SDS and Brij-35 at various composition ($X_{\text{Brij-35}}$) and water in a given solvent (IPM) at 303 K, small aliquots of Pn was added. The point of single-phase microemulsion formation was evidenced by a total loss of sample turbidity, checked by the sample absorbance measured at 320 nm [39]. The sharp decrease in absorbance observed in the sample titration with alkanol (Pn) allows precise determination of the amount cosurfactant needed to stabilize the microemulsion. The absorbance measurements were carried out at 320 nm in JASCO (V-530) UV-spectrophotometer employing thermostated cell. The amount of mixed surfactant(s) and oil(s) was taken as 0.5 mmol and 14.0 mmol, respectively for each system.

2.2.3. Conductance measurement

The electrical conductivity measurements were performed using Mettler Toledo (Switzerland) Conductivity Bridge. The instrument was calibrated with standard KCl solution. The temperature was kept constant (303K) for conductivity measurement within ± 0.01 °C by circulating thermostated water, through a jacketed vessel containing the solution.

2.2.4. Dynamic light scattering (DLS) measurement

Diameter of the microemulsion droplets was determined using a Zetasizer Nano ZS90 (ZEN3690, Malvern Instruments Ltd, U.K.). A He-Ne laser of 632.8 nm wavelength was used and the measurements were made at a scattering angle of 90° . Temperature was controlled by inbuilt Peltier heating-cooling device (± 0.1 K). Refractive index of each solution was recorded with an ABBE type refractometer, as it was required as an input in determining the size of the microemulsion droplet by DLS technique. Viscosity data, as

obtained from viscosity measurements, were used in processing DLS data. Samples were filtered thrice using Millipore^(TM) hydrophobic membrane filter of 0.25 μ pore size.

3. Theoretical background of the dilution method

The w/o microemulsion consists of dispersion of water droplets in IPM continuum wherein the mixed surfactants were considered to populate at the oil/water interface in partial association with the cosurfactant (Pn), which remained distributed between the interface and the bulk oil. Thus, at a fixed [surfactant(s)], a critical concentration of Pn is required for the stabilization of the microemulsion. Addition of extra oil (IPM) extracts Pn from the interface to destabilize the system, which can be stabilized by the addition of extra cosurfactant(s) in the system. This is the fundamental basis of dilution experiment, described in Materials and Methods (Section 2). The following equations (detailed derivations are available in literatures [29, 30]) are helpful to rationalize the distribution and transfer process of Pn from the continuous oil phase to the interfacial region:

$$\frac{n_a^t}{n_s} = \frac{n_a^w + n_a^i}{n_s} + k \frac{n_o}{n_s} \quad (1)$$

$$K_d = \frac{X_a^i}{X_a^o} = \frac{n_a^i / (n_a^i + n_s)}{n_a^o / (n_a^o + n_o)} = \frac{n_a^i (n_a^o + n_o)}{n_a^o (n_a^i + n_s)} \quad (2)$$

$$\Delta G_{o \rightarrow i}^0 = -RT \ln K_d \quad (3)$$

$n_a^t, n_a^w, n_a^i, n_a^o, n_s$ denote the total number of moles of alkanol present, moles of alkanol in water, its number at the interface, in the oil phase and the total no of moles of surfactant respectively. The distribution constant of alkanol is represented by K_d where X_a^i and X_a^o are the mole fraction of alkanol in the interfacial layer and in the oil. $\Delta G_{o \rightarrow i}^0$ represents standard Gibbs free energy change of transfer of alkanol from oil to the interface.

$\Delta H_{o \rightarrow i}^0$ (enthalpy change of transfer of alkanol from oil to the interface) can be evaluated by the van't Hoff equation. Thus,

$$[\partial(\Delta G_{o \rightarrow i}^0/T)/\partial(1/T)]_p = \Delta H_{o \rightarrow i}^0 \quad (4)$$

Since the dependency of $(\Delta G_{o \rightarrow i}^0/T)$ on $(1/T)$ are nonlinear for all these systems, a two-degree polynomial equation of following form is used.

$$\left(\frac{\Delta G_{o \rightarrow i}^0}{T}\right) = A + B_1\left(\frac{1}{T}\right) + B_2\left(\frac{1}{T}\right)^2 \quad (5)$$

The differential form of the relation helps to evaluate $\Delta H_{o \rightarrow i}^0$. Thus,

$$\frac{\partial(\Delta G_{o \rightarrow i}^0/T)}{\partial(1/T)} = B_1 + 2B_2\left(\frac{1}{T}\right) = \Delta H_{o \rightarrow i}^0 \quad (6)$$

where, A, B₁ and B₂ are the polynomial coefficients.

Then the Gibbs-Helmholtz equation is used to evaluate $\Delta S_{o \rightarrow i}^0$ (entropy change of transfer of alkanol from oil to the interface),

$$\Delta S_{o \rightarrow i}^0 = \frac{\Delta H_{o \rightarrow i}^0 - \Delta G_{o \rightarrow i}^0}{T} \quad (7)$$

The evaluation of specific heat change of transfer of alkanol from oil to the interface $[(\Delta C_p^0)_{o \rightarrow i}]$ follows from the relation,

$$[(\Delta C_p^0)_{o \rightarrow i}] = (\partial \Delta H_{o \rightarrow i}^0 / \partial T)_p \quad (8)$$

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

4. Results and Discussion

4.1. Phase behavior of single and mixed surfactant microemulsion

Phase behavior actually determines the microstructure of the system [40]. Along with cosurfactant (Pn), SDS/Brij-35 (mixed surfactant) has been found to favorably augment microemulsification (1 ϕ region) of water and IPM. Phase diagram of pseudo quaternary system, water/SDS/Brij-35/Pn/IPM has been constructed in Gibb's triangle with the variation of Brij-35 ($X_{\text{Brij-35}} = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0$) in a fixed amount of mixed surfactant (SDS/Brij-35) and at a constant temperature of 303K [illustrative representation has been shown in Fig. 1 (at $X_{\text{Brij-35}} = 0, 0.5$ and 1.0), other figures are not exemplified here]. The surfactant and cosurfactant ratio used was 1:2 (w/w). Each of the phase diagrams specifically indicates the presence of two different zones i.e., clear (microemulsion; 1 ϕ region) and turbid (biphasic; 2 ϕ region). Further, the size and location of above regions (1 ϕ and 2 ϕ) have been found to be dependent on the composition of mixed surfactant (SDS and Brij-35) [41]. However, it can be argued from the overall scenario that the characteristic of the phase diagrams is the appearances of

considerable 1 ϕ region i.e. clear solution along the amphiphile-oil axis which is actually oil continuous microemulsion with isolated and aggregated w/o dispersion.

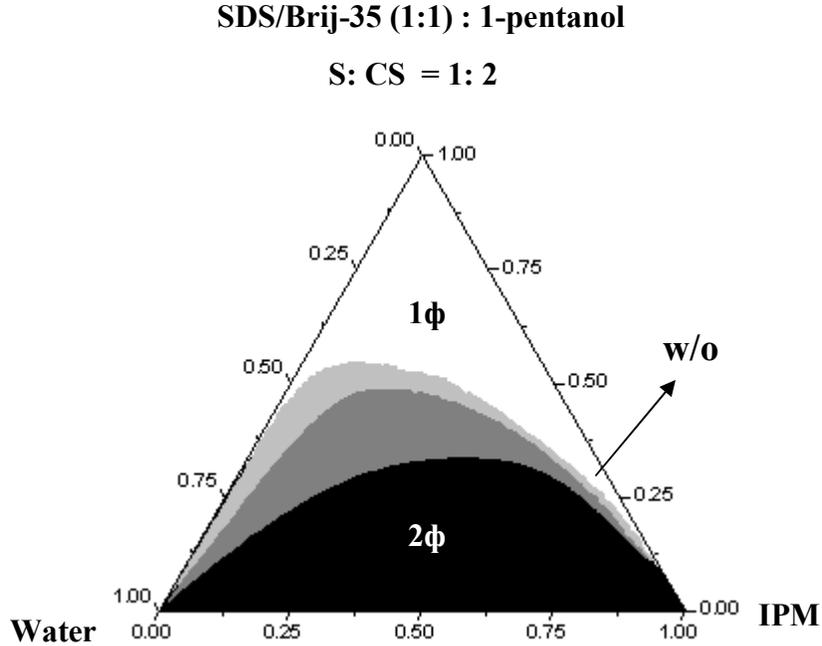


Fig. 1 Representative pseudo-ternary phase diagram of water/SDS/Brij-35/Pn/IPM w/o microemulsion at three different ratios of mixed surfactant at 303K. S/Cs mass ratio: 1:2. Area marks: unshaded, microemulsion zone (1 ϕ); shaded, turbid zone (2 ϕ) [black; $X_{\text{Brij-35}} = 0.0$, dark gray; $X_{\text{Brij-35}} = 0.5$, light gray; $X_{\text{Brij-35}} = 1.0$].

4.2. Interfacial composition of single and mixed surfactant based microemulsion by the dilution method

4.2.1. Effect of water content (ω) on compositional variations (n_a^i/n_s)

The dilution method (the Schulman's cosurfactant titration of the oil/water interface) has been used for determination of interfacial composition of SDS/Brij-35 mixed surfactant microemulsion systems at equimolar composition ($X_{\text{Brij-35}} = 0.5$) in IPM with varying ω ($= 20, 25, 30, 35$ and 40) at a constant temperature of 303K. From the data collected, graphs were constructed by plotting n_a/n_s against n_o/n_s according to Eq. (1). Representative plots are illustrated in Fig. S1 (Appendix C). The plots were strikingly linear (average R^2 was 0.9965). From Fig. S1, the values of n_a^o and n_a^i were obtained from slopes (S) and intercepts (I) respectively, and subsequently the values of K_d and $\Delta G_{o \rightarrow i}^0$ were evaluated using Eqs. (2) and (3), respectively.

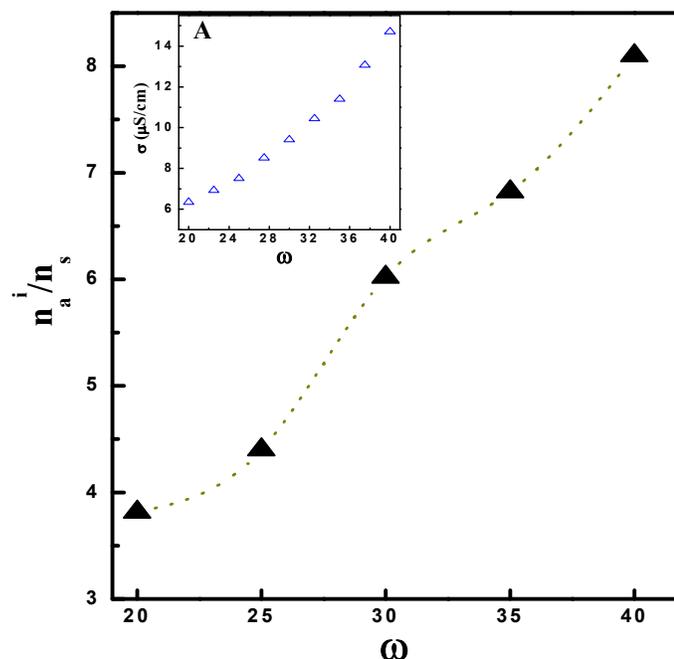


Fig. 2 Plot of n_a^i/n_s against ω for mixed surfactant (SDS and Brij-35) w/o microemulsion systems comprising total 0.5 mmol of mixed surfactant and 14.0 mmol of IPM oil stabilized by Pn at fixed $X_{\text{Brij-35}}$ ($= 0.5$) and constant temperature (303K). Inset A: Dependence of conductivity (σ) on water content (ω) for the same systems.

All these values of n_a^i , n_a^o and $\Delta G_{o \rightarrow i}^0$ are presented in Table 1. In order to understand the influence of water content (ω) on interfacial composition (n_a^i) for SDS/Brij-35 mixed systems at equimolar composition and at 303K, n_a^i/n_s values [i.e. compositional variations of amphiphiles (both surfactants and Pn) at the interface] are plotted against ω and the representative graphical plot is depicted in Fig. 2.

It is evident from Fig. 2 and Table 1 that n_a^i values increase with increase in ω . Similar trend [i.e. increase in n_a^i or (n_a^i/n_s) with increase in ω] was reported by Hait et al. [18] and Paul et al. [27] for single SDS w/o microemulsion system stabilized in IPM and Dc or Dd oils, respectively and also by Kundu et al. [30] for mixed SDS/Brij-58 or Brij-78 systems stabilized in Hp or Dc or IPM. A plausible explanation for this type of trend can be presented in the light of physicochemical (molecular) interactions among the constituents [viz. hydrophobic interaction between hydrophobic segments of the constituent

surfactants in hydrophobic domains of the aggregates; electrostatic interaction between head groups of both surfactants in hydrophilic domains; ion–dipole interaction between ionic and nonionic hydrophilic groups; and hydrogen bonding interaction among water and ionic and nonionic hydrophilic groups; interaction between alkanol and basic amphiphile (SDS) at the interface] involved in the transfer process.

Table 1. Water content (ω) dependent physicochemical parameters for the formation of w/o mixed microemulsion at fixed $X_{\text{Brij-35}}$ (0.5) and temperature (303K) ^{a, b}

System: water/SDS+Brij-35/pentanol/IPM					
ω	20	25	30	35	40
$10^4 n_a^1/\text{mol}$	19.08	22.45	30.11	34.21	40.50
$10^3 n_a^0/\text{mol}$	8.34	10.49	16.14	19.17	23.21
K_d	1.75	1.59	1.39	1.33	1.27
$-\Delta G_{o \rightarrow i}^0/\text{kJ mol}^{-1}$	1.41	1.18	0.83	0.72	0.61

^a All the mixed microemulsion systems are formed using constant amount of mixed surfactant (0.5 mmol) and oil (14.0 mmol).

^b The error limits in K_d and $\Delta G_{o \rightarrow i}^0$ were within $\pm 5\%$ and $\pm 3\%$, respectively.

Further, SDS [with DS^- as polar head group and dodecyl (C_{12}) hydrocarbon chain] and Brij-35 [23 POE chains as polar head group with similar hydrocarbon chain (C_{12}), respectively] are in the mixed state of equimolar proportion i.e. $X_{\text{Brij-35}} = 0.5$. At the threshold level of stability for the formation of w/o microemulsion, the requirement of Pn depends on its interaction with these surfactants of different characteristics at different ω 's. After addition of water to the ternary system (at $X_{\text{Brij-35}} = 0.5$), both polar head groups of SDS (DS^-) and Brij-35 (POE) surfactants have tendency to form strong hydrogen bond with water [42]. Also, a strong ion-dipole interaction between compact sulfate group in SDS and EO groups in Brij-35 exists inside the water pool. It is likely

that the origin of these interactions comes from the hydrogen bond formation between the sulfate head groups and dehydrated EO chains in the mixed corona, makes the corona more compact [43]. These types of attractive interactions between polyoxyethylene chains and anionic surfactant and hydrogen bonding interactions among surfactant head groups (DS^-) and water molecules, lead to the rigidification of the surfactant(s) monolayer [44]. Also, sulfate ions will cause dehydration of the EO chains in the mixed corona, as sulfate ions are considered as water-structure making ions, leading to an increase in hydrophobicity of the system [43]. Because of these reasons, more Pn molecules get accommodated at the droplet interface with increasing ω . Further, it is probable that the spacing between adjacent surfactant molecules at the interface increases due to decreasing surfactant concentration on the droplet surface with increase in ω . As a result, more Pn molecules are required to fill the gaps among the surfactant molecules on the droplet surface and leads to the formation of stable w/o microemulsions.

4.2.2. Effect of water content (ω) on bulk oil compositions (n_a^o)

From Table 1, it is clearly evident that n_a^o (number of moles of Pn at the bulk oil phase) increases with increasing ω in IPM. This can be argued as follows. With increasing ω , droplet is swollen and thus the interface curvature is decreased. This leads to the surfactant molecules arranging more closely at the interface and decreases the gaps resulting from the unsuitable molecular geometry of the surfactants. As a result, trend of Pn transferring from the bulk oil to the interface is weakened. So, the numbers of moles of Pn in oil phase (n_a^o) increase [21, 22]. Similar trend for n_a^o values were also reported earlier for both single and mixed surfactant microemulsions [18, 20, 29, 30].

4.2.3. Effect of $X_{Brij-35}$ and temperature on interfacial compositions (n_a^i and n_a^o)

The dilution method has also been used for the estimation of interfacial composition of water/SDS/Brij-35/Pn derived microemulsion systems (with $X_{Brij-35} = 0, 0.2, 0.4, 0.5, 0.6, 0.8$ and 1.0) stabilized in IPM at fixed $\omega = 20$ and at four different temperatures of 293, 303, 313 and 323 K. From the data collected, graphs were constructed by plotting n_a^t/n_s vs n_o/n_s according to Eq. (1). Representative illustrations are shown in Fig. S2 (Appendix C). The calculated values of n_a^i and n_a^o obtained at different mixing ratios of the surfactants ($X_{Brij-35} = 0 \rightarrow 1.0$) with varying temperatures, are presented in Table 2.

Table 2. Temperature and surfactant composition ($X_{\text{Brij-35}} = 0 \rightarrow 1.0$) dependent thermodynamic parameters for the formation of w/o microemulsion in IPM at fixed water content ($\omega = 20$)^{a, b}

$X_{\text{Brij-35}}$	T/K	$10^4 n_a^i$ (mol)	$10^3 n_a^o$ (mol)	$-\Delta G_{o \rightarrow i}^0$ (kJmol ⁻¹)	$\Delta H_{o \rightarrow i}^0$ (kJmol ⁻¹)	$\Delta S_{o \rightarrow i}^0$ (JK ⁻¹ mol ⁻¹)
0.0	293	34.47	5.91	2.28	4.89	24.53
	303	36.19	5.27	2.37	3.11	18.08
	313	37.34	4.91	2.47	1.26	11.93
	323	38.93	4.85	2.68	-0.64	6.32
0.2	293	28.40	7.17	1.74	8.65	35.48
	303	36.94	6.18	2.12	6.26	27.68
	313	40.87	5.59	2.38	3.80	19.76
	323	41.80	5.17	2.60	1.26	11.95
0.4	293	28.35	7.23	1.73	13.19	50.93
	303	38.83	5.91	2.20	11.40	44.89
	313	45.86	5.43	2.46	9.55	38.38
	323	46.19	4.78	2.80	7.64	32.34
0.5	293	14.33	9.61	1.02	8.53	32.60
	303	19.08	8.34	1.41	8.12	31.44
	313	21.20	7.71	1.62	7.68	29.74
	323	30.11	6.97	1.99	7.24	28.57
0.6	293	17.89	8.13	1.36	27.71	99.23
	303	38.63	5.59	2.29	18.17	67.54
	313	50.56	5.17	2.56	8.32	34.78
	323	51.11	4.68	2.84	-1.85	3.07
0.8	293	12.41	8.23	1.12	26.36	93.79
	303	32.95	5.32	1.99	16.82	62.10
	313	39.55	5.17	2.50	6.97	30.26
	323	40.01	4.75	2.74	-3.20	-1.42
1.0	293	17.33	5.86	1.82	0.72	8.67
	303	17.89	5.59	1.97	-5.24	-10.77
	313	26.77	5.55	2.25	-11.39	-29.23
	323	27.30	4.27	2.80	-17.76	-46.31

^a All the mixed microemulsion systems are formed using constant amount of mixed surfactant (0.5 mmol) and oil (14.0 mmol).

^b The error limits in $\Delta G_{o \rightarrow i}^0$, $\Delta H_{o \rightarrow i}^0$ and $\Delta S_{o \rightarrow i}^0$ are $\pm 3\%$, $\pm 5\%$ and $\pm 8\%$ respectively.

It is evident from Table 2 that the values of n_a^i and n_a^o did not follow any straightforward trend as a function of $X_{\text{Brij-35}}$ for any of these systems. However, the plot of interfacial composition (n_a^i) of Pn versus surfactant composition ($X_{\text{Brij-35}}$) at each temperature (Fig. 3) clearly shows a minima at $X_{\text{Brij-35}} = 0.5$ i.e., at equimolar composition of mixed surfactant (SDS/Brij-35) microemulsion.

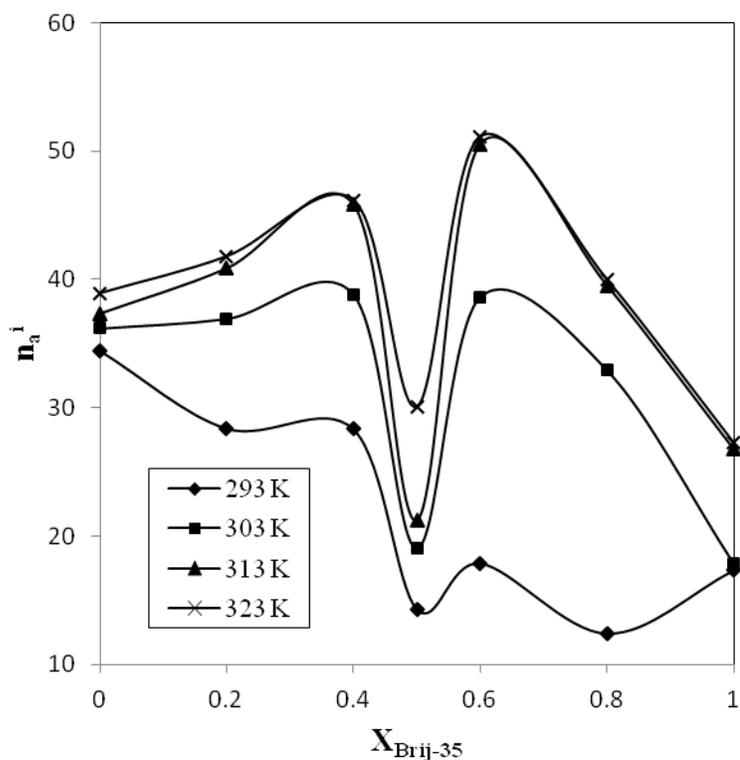


Fig. 3 Interfacial composition (n_a^i) against mol fraction of nonionic surfactant ($X_{\text{Brij-35}} = 0.0 \rightarrow 1.0$) for w/o microemulsion systems comprising 0.5 mmol of mixed surfactant and 14.0 mmol of IPM oil stabilized by Pn at fixed water content ($\omega = 20$) with different temperature (293K \rightarrow 323K).

Further, it is evident from Table 2 that with increase in temperature n_a^i increases while n_a^o decreases with increasing temperature and hence increase of temperature helps to transfer more Pn molecules (cosurfactant) from the oil to the interface. This observation is found to be consistent with that reported by Hait et al. [18] for CPC, SDS and CTAB based systems stabilized in IPM and Paul et al. [27] for CPC, SDS and Brij-35 based systems stabilized in Dc or Dd. When SDS and Brij-35 are mixed in nearly comparable

proportions ($X_{\text{Brij-35}} = 0.4 \rightarrow 0.6$), the difference between the value of parameters, e.g., n_a^i and n_a^o at lower and higher temperatures are more than the pure surfactant systems ($X_{\text{Brij-35}} = 0$ and 1.0). It indicates that interfacial arrangements or organizations of the constituents are mostly affected by increase in temperature in the vicinity of equimolar composition.

4.2.4. Thermodynamics of transfer of alkanol (Pn) from oil (IPM) to the interface

In this section, analysis of the transfer of Pn from oleic phase to the interface of mixed surfactant (ionic/nonionic) w/o microemulsions using dilution experiments from thermodynamic point of view is presented, which is seldom reported [28-30]. Such reports for w/o microemulsions stabilized in hydrocarbons and hydrophilic oil using single surfactant are available in literature [18-25]. Thermodynamic parameters ($\Delta G_{o \rightarrow i}^0$, $\Delta H_{o \rightarrow i}^0$, $\Delta S_{o \rightarrow i}^0$ and $[(\Delta C_p^0)_{o \rightarrow i}]$) for the transfer of Pn from the continuous oil phase (IPM) to the interfacial region of mixed surfactants (SDS/Brij-35) with varying ω ($= 20, 25, 30, 35$ and 40) at a fixed $X_{\text{Brij-35}} = 0.5$ and temperature (303 K) and also at a fixed ω ($= 20$) with varying $X_{\text{Brij-35}}$ ($= 0 \rightarrow 1.0$) and temperatures (293, 303, 313 and 323 K) have been evaluated according to Eqs. (3) - (8). The data are presented in Table 1 and Table 2. Representative plots of $-\Delta G_{o \rightarrow i}^0$ vs. $X_{\text{Brij-35}}$ for water/SDS/Brij-35/Pn/IPM (Fig. 4) and $\Delta H_{o \rightarrow i}^0$ or $\Delta S_{o \rightarrow i}^0$ vs. $X_{\text{Brij-35}}$ for water/SDS/Brij-35/Pn/IPM at four different temperatures are illustrated in Figs. 5A and 5B. $\Delta G_{o \rightarrow i}^0$ values are negative at all compositions ($X_{\text{Brij-35}} = 0 \rightarrow 1.0$) and temperatures in IPM, hence spontaneous formation of w/o microemulsions is suggested. Both similar and dissimilar trends in all these energetic parameters at comparable physicochemical environments are reported [18-25].

Effect of ω on $\Delta G_{o \rightarrow i}^0$ of transfer process

It is evident from Table 1 that the values of $-\Delta G_{o \rightarrow i}^0$, which is indicative of spontaneity of the alkanol transfer process ($\text{Pn}_{\text{oil}} \rightarrow \text{Pn}_{\text{int}}$), decrease with increasing ω ($= 20$ to 40) for the studied systems. With increasing ω , the droplet is swollen and thus the interfacial curvature is decreased.

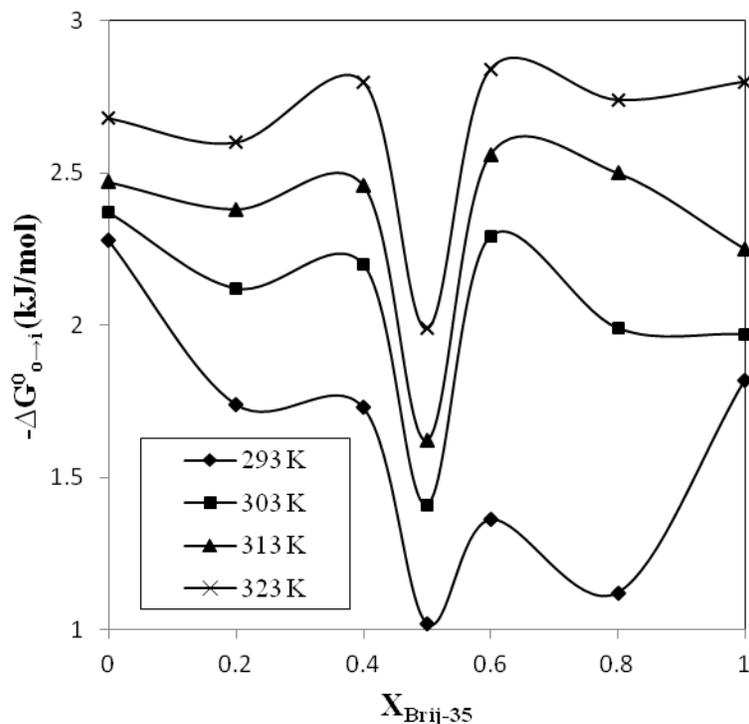


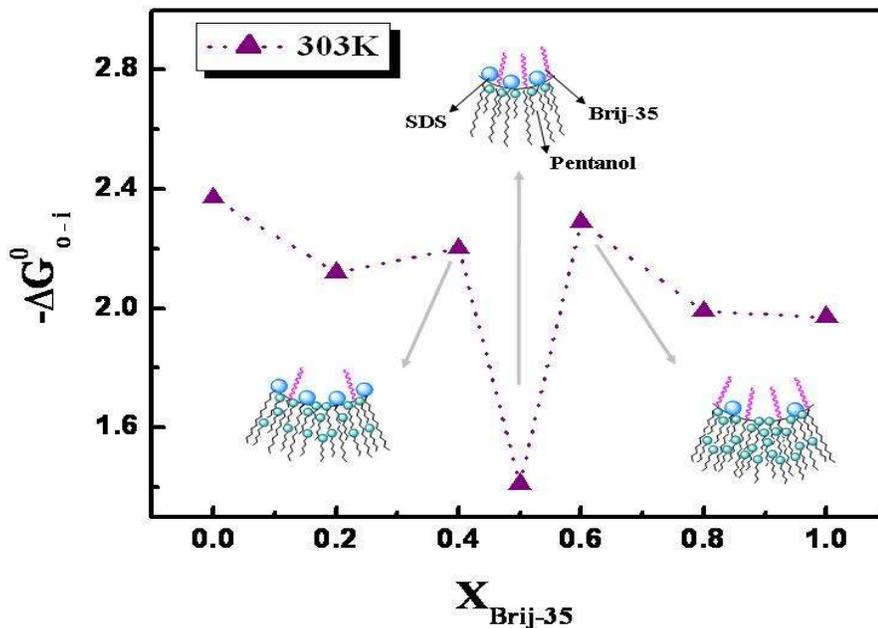
Fig. 4 Standard free energy change of transfer ($-\Delta G_{o \rightarrow i}^0$) against mol fraction of nonionic surfactant ($X_{\text{Brij-35}} = 0.0 \rightarrow 1.0$) for w/o microemulsion systems comprising 0.5 mmol of mixed surfactant and 14.0 mmol of IPM oil stabilized by Pn at fixed water content ($\omega = 20$) with different temperature (293K \rightarrow 323K).

As a result, the surfactant molecules are accommodated more closely at the interface and decrease the gaps, resulting from the unsuitable molecular geometry of the surfactants. Hence, the trend of transferring of Pn from oil to the interface is weakened. Again, with increasing ω , the relative retention of Pn in oil has become more (as reflected from values of n_a^0 , Table 1) than its transfer to the interface. In other words, association between surfactant and cosurfactant molecules at the interface becomes less favorable with increase in ω . This type of variation was reported by Hait et al. [18], Zheng et al. [20, 21], Paul et al. [27] and Kundu et al. [29, 30] for single and mixed surfactant microemulsion systems, respectively.

Effect of $X_{nonionic}$ and temperature on $\Delta G^0_{o \rightarrow i}$ of transfer process at a fixed ω

It can be seen from Table 2 that the spontaneity of the transfer of Pn from oil (IPM) to the interface for pure SDS and Brij-35 stabilized systems increases with increasing temperature. This trend corroborates well with our previous report on SDS stabilized systems in Dc with Pn used as cosurfactant [30] and Hait et al. [18] and Mohareb et al. [19] for water/SDS/butanol/IPM and water/SDS/alkanols(C₅–C₉)/IPM w/o microemulsion systems, respectively. The trend of spontaneity of pure Brij-35-derived system stabilized in polar oil (IPM) agrees well with Mehta et al. [25] for water/Brij-96/Pn/ethyl oleate (EO) system. Further, it is evident from Table 2 and representative plot of $-\Delta G^0_{o \rightarrow i}$ vs. $X_{Brij-35}$ at four temperatures in IPM (depicted in Fig. 4) that the $\Delta G^0_{o \rightarrow i}$ values are not straightforward at mixed compositions (i.e. $X_{Brij-35} = 0.2 - 0.8$). $-\Delta G^0_{o \rightarrow i}$ values increase with increase in temperature (293, 313 and 323 K) at all compositions for the mixed surfactant microemulsion systems stabilized in IPM. However, an interesting feature, that is, antagonism in standard Gibbs free energy of transfer ($\Delta G^0_{o \rightarrow i}$) of Pn from the bulk oil phase to the interface is evidenced at equimolar composition of SDS and Brij-35 (i.e. at $X_{Brij-35} = 0.5$) from the plot of $-\Delta G^0_{o \rightarrow i}$ against $X_{Brij-35}$ (Fig. 4). Similar antagonistic behavior was observed for water/SDS/Brij-78/Pn/Hp system at $X_{Brij-78} = 0.4$ [30]. Synergism or antagonism in thermodynamic parameters of surfactant mixtures might arise from the non-ideality of surfactant interactions. It was reported earlier that considerable non-ideality shown by ionic/nonionic mixtures is due to the action of the nonionic component that shields the repulsion between charged ionic head groups and, also, due to the attraction acting between the components, anyway, via ion-dipole interactions [45]. However, antagonism in $-\Delta G^0_{o \rightarrow i}$ at equimolar composition at each temperature might be explained in the following manner. The presence of lower concentration of Pn (i.e. n_a^i as evidenced from Fig. 3) makes the oil/water interface sterically rigid. As it was reported earlier that increasing alcohol partitioning at the interface, increase the degree of interpenetration of droplets and therefore increase the interfacial fluidity or flexibility [46]. Rigid conformation of the hydrophobic tails disrupts steric packaging of the interface and leads to partial hydration of the hydrophobic core of SDS/Brij-35 mixed blends [47]. This partial hydration of the hydrophobic tails in the interface decreases the hydrophobic interactions between the hydrophobic regions of co-

surfactants in the interface, which results in increase in entropy and makes the system more unstable [48]. As a result, at equimolar composition SDS/Brij-35 mixed system shows minima in $-\Delta G_{o \rightarrow i}^0$. A schematic diagram has been presented to represent the correlation between interfacial population of 1-pentanol and antagonism in free energy of its transfer at equimolar composition of mixed surfactant microemulsion (Scheme 1).



Scheme 1. Pictorial representation of correlation between interfacial population of 1-pentanol and antagonism in free energy of its transfer at equimolar composition of mixed surfactant microemulsion.

Effect of X_{nonionic} and temperature on $\Delta H_{o \rightarrow i}^0$ and $\Delta S_{o \rightarrow i}^0$ of transfer process

Due to nonlinear dependence of $(\Delta G_{o \rightarrow i}^0 / T)$ on $1/T$ in terms of a two degree polynomial equation (Figs. are not illustrated), at each composition of a nonionic surfactant (X_{nonionic}), four values of $\Delta H_{o \rightarrow i}^0$ and $\Delta S_{o \rightarrow i}^0$ at four temperatures have been evaluated, and are presented in Table 2. The profile of $\Delta H_{o \rightarrow i}^0$ and $\Delta S_{o \rightarrow i}^0$ with composition ($X_{\text{Brij-35}}$) and temperature [Figs. 5A and 5B] is not straightforward upon the addition of nonionic surfactant (Brij-35 with dodecyl nonpolar tail) to the ionic surfactant (SDS with dodecyl nonpolar tail) under various physicochemical environments (as mentioned earlier).

It is evident from Table 2 that, overall transfer process is endothermic at all experimental temperatures (except at 323 K) with positive entropy change (disorder) in IPM for pure SDS system. So, Pn causes adsorption of heat during transfer process. Consequently, the positive entropy change is due to de-organization of the interface and its surroundings. Therefore, the interface composed of Pn and SDS is to some extent less orderly. Such positive enthalpy and entropy changes were observed by Hait et al. [18] and Mohareb et al. [19] for water/SDS/butanol/IPM and water/SDS/alkanols (C₅–C₉)/IPM w/o microemulsion systems, respectively. For pure Brij-35 stabilized system, the process is exothermic with release of heat at all experimental temperatures (except at 293 K) with negative entropy change (order) in IPM. Negative values of $\Delta S^0_{o \rightarrow i}$ suggest that the entropy as well as enthalpy is involved in the transfer process at the corresponding composition [49]. Such negative enthalpy and entropy changes were observed by Mehta et al. [25] for water/Brij-96/Pn/ethyl oleate (EO) system. Opposite behavior towards temperature for ionic and nonionic surfactants might be responsible for such trend of enthalpy and entropy values with temperature [50].

At compositions in between these two extremes (i.e. $X_{\text{Brij-35}} = 0.2 \rightarrow 0.8$) in IPM, both $\Delta H^0_{o \rightarrow i}$ and $\Delta S^0_{o \rightarrow i}$ values are positive (except at few compositions at 323 K). An interesting feature reveals from the Table 2 and Figs. 5A and 5B that both $\Delta H^0_{o \rightarrow i}$ and $\Delta S^0_{o \rightarrow i}$ values decrease with increase in temperature at all mixed compositions. It may be endothermic to exothermic (at $X_{\text{Brij-35}} = 0.6 \rightarrow 1.0$) or more endothermic to less endothermic (at $X_{\text{Brij-35}} = 0.2 \rightarrow 0.5$). A plausible explanation for exothermicity or endothermicity-derived process may be as follows. A positive contribution to $\Delta H^0_{o \rightarrow i}$ can be the energy required to release the structural water from the hydration layer around the hydrophilic domain. An additional contribution arises from the liberation of water molecules from the water cage around the hydrophilic moiety of the surfactants. The negative contribution to $\Delta H^0_{o \rightarrow i}$ is identified with the transfer of the surfactant tail from water to liquid hydrocarbon state in the interfacial layer and restoring the hydrogen bonding structure of the water around the surfactant head group. With increasing temperature the degree of hydrogen bonding around the surfactant molecules decreases, and therefore, the energy required to break it diminishes i.e., $\Delta H^0_{o \rightarrow i}$ decreases with temperature [51].

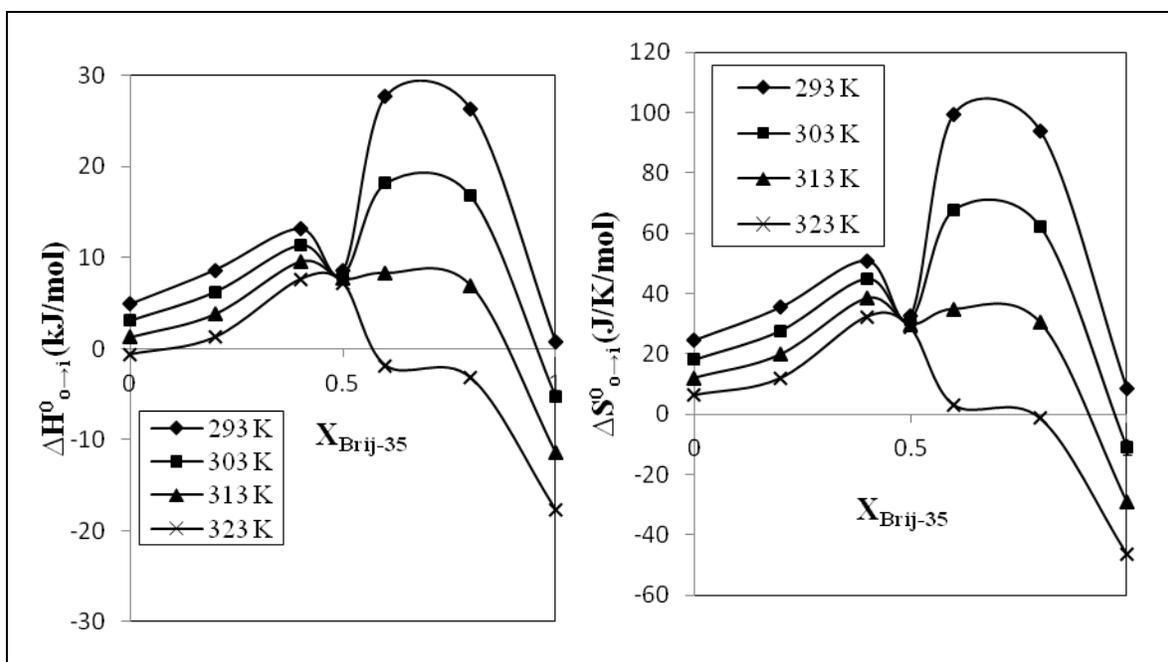


Fig.5(A) Plot of $\Delta H^{\circ}_{o \rightarrow i}$ against $X_{\text{Brij-35}}$ for mixed surfactants water/SDS/Brij-35/Pn/IPM w/o microemulsion system comprising 0.5 mmol surfactant, 10 mmol water and 6.3 mmol IPM oil with varying compositions ($X_{\text{Brij-35}}$) at different temperatures. **(B)** Plot of $\Delta S^{\circ}_{o \rightarrow i}$ against $X_{\text{Brij-35}}$ for the same systems under identical physicochemical environments.

However, insignificant changes in these parameters with temperature have been observed at equimolar composition (at $X_{\text{Brij-35}} = 0.5$), leading to formation of isenthalpic and isentropic microemulsion systems. With increasing temperature the transfer process shows endothermic to exothermic nature mainly in Brij-35 rich combinations ($X_{\text{Brij-35}} = 0.6 \rightarrow 1.0$). Mixed ionic-nonionic surfactant derived athermal microemulsion formulations were reported in literature [28, 50, 52]. The desolvation of the head group of Brij-35 during the transfer in the oil was ended up with absorption of minute amount of heat. Hence, at lower temperature the transfer process shows endothermic nature and converted to exothermic at higher temperature. Similar observation was also reported by our group earlier for water/CPC/Brj-58/Pn/Hp system [29]. It is apparent that different phenomena associated with the transfer process, viz., changing aggregation number, solvation-desolvation of nonionic surfactants, electrostatic and steric interaction between

hydrophilic head group of CPC, steric and other nonspecific processes contribute their shares to the $\Delta H_{o \rightarrow i}^0$ and $\Delta S_{o \rightarrow i}^0$ [53].

Hence, it can be inferred that the overall mixed surfactant microemulsion forming systems can end up with both absorption or release of heat and with ordered or disordered state, depending on their chemical compositions [i.e., the constituent surfactant(s) with their configuration, content and type of oil] and thermal condition.

Since ΔH_t^0 became a function of temperature, the $(\Delta C_p^0)_{o \rightarrow i}$ values have also been obtained at all compositions from the slope of the plots of ΔH_t^0 vs. T (Figs. are not exemplified) according to Eq. (8). All these values are negative (presented in Table S1, Appendix C) and agree well with those reported by Mitra et al. [23] for water/CTAB or its analogues with modified head group/Hx/i-Oc, and Kundu et al. [29, 30] for water/CPC or SDS/Brij-58 or Brij-78/Pn/Hp or Dc microemulsion systems, respectively. Such negative values are usually observed for the self-association of amphiphiles and can be attributed to the removal of large areas of nonpolar surface from contact with water on formation of reverse micelles [54]. It has been observed that $(\Delta C_p^0)_{o \rightarrow i}$ tends to zero at $X_{\text{Brij-35}} = 0.5$, which corroborates well with profile of $\Delta H_{o \rightarrow i}^0$ and $\Delta S_{o \rightarrow i}^0$ vs. $X_{\text{Brij-35}}$ at different temperatures (Figs. 5A and 5B) discussed in preceding paragraph. Kunz et al. [55] reported that formation of temperature-insensitive microemulsions are important for some practical purposes (e.g. for formulation of product), whereas for other applications, such as for extraction and purification process or organic synthesis, the temperature dependence of microemulsions can be desirable. The present report on mixed surfactant microemulsion systems provide such a wide compositions in which both temperature dependent and independent formulations can be found.

Correlation between $\Delta H_{o \rightarrow i}^0$ and $\Delta S_{o \rightarrow i}^0$

In kinetics and equilibrium studies, an extra thermodynamic linear correlation between $\Delta H_{o \rightarrow i}^0$ and $\Delta S_{o \rightarrow i}^0$ changes for the involved process is often reported, called the enthalpy-entropy compensation effect, and such a phenomenon has been observed to be valid also for micelle and microemulsion forming systems [25, 28-30]. In general, the compensation effect can be described by a liner relationship in the form [56]:

$$\Delta H_{o \rightarrow i}^0 = T_{\text{comp}} \cdot \Delta S_{o \rightarrow i}^0 + \Delta(H^0)_{o \rightarrow i}^* \quad (9)$$

where, T_{comp} , is the slope of the compensation plot and $\Delta(H^0)_{\text{o}\rightarrow\text{i}}^*$, the intrinsic enthalpy change of Pn transfer process is the intercept. According to the working scheme of Lumry and Rajender [56] for a compensation phenomenon, the micellization or microemulsification can be described as consisting of two-part processes: (a) the “desolvation” part, i.e., the dehydration of the hydrocarbon tail or polar head of surfactant molecules, and (b) the “chemical” part, i.e., aggregation of the hydrocarbon tails or polar head of surfactant molecules to form micelle or reverse micelle. T_{comp} can be interpreted as a characteristic of solute-solute and solute-solvent interactions, i.e., proposed as a measure of the “desolvation” part. $\Delta(H^0)_{\text{o}\rightarrow\text{i}}^*$ characterizes the solute-solute interaction, i.e., considered as an index of the “chemical” part. The thermodynamic results herein collected were tested for this correlation and illustrated as representative plot for SDS/Brij-35/Pn/IPM/water at 303K [Fig. S3, Appendix C]. A good linear correlation was observed at the temperature of measurement (regression coefficients are 0.9990) i.e. mutual compensation temperature of 301K, which was lesser by 2K than the temperature of measurement (303K). T_{comp} and $\Delta(H^0)_{\text{o}\rightarrow\text{i}}^*$, obtained at different experimental temperatures (293, 303, 313 and 323K) for these systems are presented in Table S2 (Appendix C). T_{comp} temperatures are slightly deviated from the experimental temperatures. Such a deviation is quite common in literature [27-30]. In our previous reports [28], the discrepancy between experimental and compensation temperatures were elaborately discussed. Further, it reveals from Table S2 that the values of $\Delta(H^0)_{\text{o}\rightarrow\text{i}}^*$ lie in the range of -1.93 kJ/mol to - 2.66 kJ/mol. $\Delta(H^0)_{\text{o}\rightarrow\text{i}}^*$ decreases with increase in experimental temperature for SDS/Brij-35 system in IPM. There exists an equilibrium between (free water in bulk solvent + free surfactant molecules with associated water and solvent molecules) and (surfactants with associated water and solvent molecules in the reverse micelles + released solvent molecules). Increasing experimental temperature weakens molecular interactions which results in shifting the surfactant monomer-reverse micelle equilibrium toward the monomer which affects aggregation of surfactant molecules as well as $\Delta(H^0)_{\text{o}\rightarrow\text{i}}^*$ [57]. Similar observation was also reported by Kundu et al. [29, 30].

The aforesaid analysis of the thermodynamics of the studied transfer process can be summarized as follows: $\Delta G^0_{\text{o}\rightarrow\text{i}}$ consists of a number of factors which may account

respectively for the transfer of surfactants (SDS and Brij-35) and Pn tails from water to the interfacial film, the deformation of the tails to satisfy packing constraints, the free energy of formation of the oil/water interface, the steric and ionic interactions among the head groups of SDS as well as interaction arising out of dissimilar head groups of both SDS and Brij-35, the free energy of mixing of surfactants, Pn, and oil (IPM) in the film region [58] and free energy due to formation of hydrated nonionic surfactant (Brij-35) results in formation of different states of water in the pool [59]. As a result of these possible contributions towards $\Delta G_{o \rightarrow i}^0$ at different temperatures, heat involving processes and consequently conformational entropy due to packing restrictions of the hydrocarbon chains, and entropy of mixing the two surfactants in the aggregates make the thermodynamics more complex. Such a comprehensive analysis on the formation and stability of w/o mixed surfactant microemulsions based on “Bowcott and Schulman model” [38] from the view point of thermodynamics, is scarcely reported in literature. Further studies along these series of measurements are in progress to shed more quantitative description of these thermodynamic quantities in quaternary w/o mixed surfactant microemulsions.

4.3. Transport property of single and mixed surfactant based microemulsion

4.3.1. Effect of ω on conductivity of mixed surfactant based microemulsion

It can be observed from Fig. 2 (Inset A) that the conductivity of the studied mixed systems gradually increases with increase in ω ($= 20 \rightarrow 40$). Earlier Bumajdad et al. [60] was shown that the conductivity is governed by droplet charge which is an increasing function of droplet size. Hence, the conductivity behavior shows a characteristic feature of migration of charged water droplets and thereby supports the formation of water-in-oil droplet with increasing size at higher water content ($\omega = 20 \rightarrow 40$).

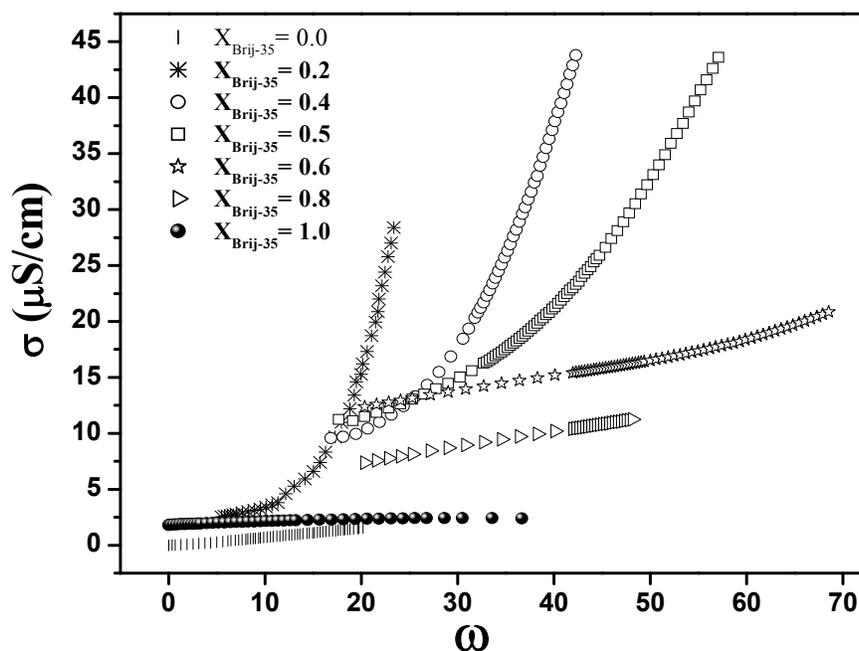


Fig. 6 Conductivity (σ) against ω profile with the variation of $X_{\text{Brij-35}}$ ($= 0.0 \rightarrow 1.0$) for water/SDS/Brij-35/Pn/IPM w/o microemulsion systems at fixed surfactant concentration (0.3 mol. dm^{-3}) and constant temperature (303K).

4.3.2. Effect of X_{nonionic} on conductivity of single and mixed surfactant based microemulsion

The conductivity of water/SDS/Brij-35/Pn/IPM, as a function of water content (ω) has been measured with the variation of Brij-35 ($X_{\text{Brij-35}} = 0.0 \rightarrow 1.0$) at fixed surfactant concentrations (0.3 mol dm^{-3}) and temperature (303K). The results are depicted in Fig. 6. Further, the conductivity measurement of the above systems has been carried out from the appearance of single phase to phase separation on dilution by water with a fixed surfactant and cosurfactant ratio (1:2; w/w). It has been observed that pure SDS microemulsion system ($X_{\text{Brij-35}} = 0.0$) is low conducting and does not exhibit any significant increase in conductivity with ω . However, the addition of nonionic surfactant (Brij-35) to the water/SDS/Pn/IPM system with the total (SDS/Brij-35) surfactant concentration as mentioned above, a dramatic increase in conductance behavior has been observed as a function of ω up to a certain range of mole fraction of Brij-35 ($X_{\text{Brij-35}} =$

0.2→0.5), beyond which ($X_{\text{Brij-35}} = 0.6 \rightarrow 1.0$) decrease in conductivity with increasing ω was observed. An in-depth observation reveals that conductivity increases slowly with ω at $\omega \leq 10.80$, $\omega \leq 24.63$ and $\omega \leq 29.94$, followed by a sharp rising for $X_{\text{Brij-35}} = 0.2$, 0.4 and 0.5 blends, respectively (Fig. 6). The critical value for sharp linear enhancement of conductivity (ω) with the addition water is considered as percolation threshold point [25]. Actually, percolation of conductance extracts information about the nature of interaction among the droplets in mixed surfactant microemulsions. If the droplets are of non-interacting hard sphere type, no significant increase in conductance occurs with increasing water content. But if the interfaces of the droplets are fluid enough to coalesce during these collisions followed by material exchange and fusion, a sharp rise in conductance is evidenced [61]. Percolation of conductance signifies the increase in droplet size, attractive interaction among droplets and exchange rate of materials between the droplets with the addition of water [25, 37].

The antagonistic behavior in interfacial composition (n_a^i) of Pn at $X_{\text{Brij-35}} = 0.5$ might be correlated with the conductivity measurement by the following way. It has been observed that pure ionic system ($X_{\text{Brij-35}} = 0$) is non-percolating. After addition of nonionic surfactant, critical packing parameter (CPP) of mixed microemulsion system decreases and thereby leads to increase in the droplet radius with increase in $X_{\text{Brij-35}}$ [37]. Further, it can be observed from Fig. 3 that n_a^i value increase with increasing $X_{\text{Brij-35}}$ up to 0.4 and thereafter minima observed at $X_{\text{Brij-35}} = 0.5$ at a fixed temperature. Two opposite effects are observed after addition of alcohol and nonionic surfactant to single surfactant based system on the interfacial rigidity or flexibility. It was reported that with increasing alcohol partitioning at the interface, increase the interfacial flexibility (or fluidity), so that the degree of interpenetration of droplets increases during the collision of the droplets. On the other hand, addition of long chain nonionic surfactant makes the interface more rigid and decreases the strength of attraction between microemulsion droplets [46]. So, beyond $X_{\text{Brij-35}} = 0.6$, effect of alcohol partitioning at the interface overcomes the effect of increasing concentration of nonionic surfactant and therefore, percolation of conductance has been observed up to $X_{\text{Brij-35}} = 0.5$. Threshold value of volume-induced percolation has been found to be higher at $X_{\text{Brij-35}} = 0.5$, that is due to minimum amount of alcohol concentration at the interface (minima of n_a^i at equimolar composition i.e., antagonism in

n_a^i). But beyond $X_{\text{Brij-35}} = 0.5$, when concentration of nonionic surfactant are sufficiently large, effect of increasing content of nonionic surfactant start dominating over the effect of alcohol partitioning at the interface, which makes the interface more rigid. Therefore, no percolation has been observed beyond equimolar composition. Similar studies on percolation of conductance phenomenon were already reported for nonionic (Brij-96) and ionic (CTAB or SDS or OTAB or AOT) surfactant derived microemulsion systems at their individual state in presence of alcohol (cosurfactant) [24, 25, 62].

4.4. Droplet dimension of single and mixed surfactant based microemulsion by DLS studies

4.4.1. Effect of X_{nonionic} and ω

The droplet size (hydrodynamic diameter, D_h) and the size distribution in w/o microemulsion have been measured by the dynamic light scattering techniques (DLS) and analyzed in terms of count rate and the polydispersity index (PDI) of the droplets for mixed microemulsion systems reported herein [63, 64]. The results are presented in Table 3 (A and B). The same composition of w/o mixed (SDS/Brij-35) surfactant microemulsion systems has been chosen for DLS measurement, as that was used in Schulman's cosurfactant titration as function of X_{nonionic} ($X_{\text{Brij-35}} = 0.0 \rightarrow 1.0$) and ω (= 20, 25, 30, 35, 40) at constant temperature of 303K. It has been observed that values of D_h of the microemulsion droplets increase remarkably from 9.8 nm to 18.91 nm in IPM oil with the increase in proportion of nonionic surfactant ($X_{\text{Brij-35}} = 0.0 \rightarrow 1.0$) in the mixed systems, whereas about 1.6 fold decrease of droplets count rate has been observed under the prevailing condition (Table 3A). The degradation of droplets count rate indicates that the total number of microemulsion droplets decreases with increasing the content of Brij-35. It is known that the addition nonionic surfactant (with large POE-chain as polar head group) resides at the interfacial region of the mixed interface (herein SDS/Brij-35) either immersing its polar head group in the water pool or the polar head group lies in the vicinity of the head group region of the ionic surfactant depending upon the content of ω . Hence, both of these configurations supported the increase in droplet size with increasing head group of nonionic surfactant by increasing its proportion in mixed system ($X_{\text{Brij-35}} = 0.0 \rightarrow 1.0$), as evident from DLS measurement [65].

Table 3[A]. Hydrodynamic diameter (D_h) and count rate of water droplets in w/o mixed surfactant microemulsion at fixed water content ($\omega = 20$) and temperature (303K)^a

System: water/SDS/Brij-35/Pn/IPM							
$X_{\text{Brij-35}}$	0.0	0.2	0.4	0.5	0.6	0.8	1.0
D_h/nm	9.80	11.02	12.67	14.55	15.86	17.03	18.91
Count Rate/kcps	99.30	92.80	85.60	78.90	73.20	68.40	61.50

Table 3[B]. Hydrodynamic diameter (D_h) and count rate of water droplets in w/o mixed surfactant microemulsion at increase in water content ($\omega = 20 \rightarrow 40$) and fixed $X_{\text{Brij-35}}$ (**0.5**), temperature (303K)^a

System: water/SDS/Brij-35/Pn/IPM						
ω	20	25	30	35	40	
D_h/nm	14.55	17.71	22.54	25.26	27.63	
Count Rate/kcps	78.90	67.50	55.30	44.80	36.50	

^a All the mixed microemulsion systems are formed using constant amount of mixed surfactant (0.5 mmol) and oil (14.0 mmol).

Further, the droplet size (D_h) obviously increases from 14.55 nm to 27.63 nm with increasing water content ($\omega = 20 \rightarrow 40$) and decreasing droplet count rate (Table 3B) [64]. Typical values of polydispersity index (PDI) obtained here are in the range between 0.1-0.2, which indicates the monodispersity of the sample [66]. Furthermore, the D_h values indicate the presence of comparatively larger dimension of droplets in IPM derived systems than reported hydrocarbon oil based w/o microemulsions at comparable water content [67]. However, such a larger dimension of water droplet has been reported earlier for IPM derived systems in presence of nonionic surfactant (polyoxyethylene lauryl ether or polysorbate and sorbitol) [68-70]. For example, D_h was found to be 34.4 nm for IPM (63 wt%)/[polyoxyethylene (4) lauryl ether/isopropyl alcohol] (32 wt%)/water (5 wt%)

system at 308K [68]. Actually IPM, being amphiphilic polar oil, is not solubilized in the palisade layer, rather than it has a swelling tendency in the oil domain. Thus, swelling causes an increase in repulsion between the hydrophilic moieties of surfactant, and hence, the surfactant layer curvature becomes more positive, which leads to increase in droplet size [71, 72].

5. Conclusion

The present study is focused on the characterization of quaternary water-in-oil microemulsions comprising of anionic sodium dodecylsulfate (SDS) and nonionic polyoxyethylene (23) lauryl ether (Brij-35), 1-pentanol (Pn) and isopropyl myristate (IPM) with a detailed description of the phase behavior and the dependence of the partition equilibria (of Pn) on the system composition. The formation of a single phase microemulsion zone (1 ϕ) has found to be dependent on the composition of mixed surfactant (SDS and Brij-35; $X_{\text{Brij-35}} = 0.0 \rightarrow 1.0$) at a fixed surfactant-cosurfactant ratio (= 1:2) and constant temperature (303K). The interfacial and bulk compositions as well as the distribution of Pn between the interface and bulk oil (evaluated by the Schulman's titration at the oil/water interface) depend on the interaction between the surfactant(s) at the interface, vis-à-vis their compositions, and temperature. The transfer process of Pn from the bulk oil phase to the interface $\Delta G_{\text{o}\rightarrow\text{i}}^0$ is spontaneous for all the systems, but the degree of spontaneity depends on ω , composition of nonionic surfactant ($X_{\text{Brij-35}} = 0.0 \rightarrow 1.0$) and temperature (293K \rightarrow 323K). Further, an interesting feature of antagonism in the standard Gibbs free energy of transfer, $\Delta G_{\text{o}\rightarrow\text{i}}^0$ of alkanol from the bulk oil phase to the interface has been observed at an equimolar composition of SDS and Brij-35 (i.e. at $X_{\text{Brij-35}} = 0.5$). The values of $\Delta H_{\text{o}\rightarrow\text{i}}^0$ and $\Delta S_{\text{o}\rightarrow\text{i}}^0$ well compensate each other. Temperature insensitive microemulsions with zero $(\Delta C_{\text{p}}^0)_{\text{o}\rightarrow\text{i}}$ have been formed at specific compositions for these mixed surfactant systems due to opposite behavior of ionic and nonionic surfactant towards temperature [50]. Such types of microemulsion formulations have been found to be useful in various commercial and technological processes [55]. Conductivity studies reveal that incorporation of Brij-35 in nonpercolating water/SDS/pentanol/IPM systems is favorable for water content (ω) induced percolation behavior up to $X_{\text{Brij-35}} \leq 0.5$. But further addition of nonionic surfactant ($X_{\text{Brij-35}} \geq 0.6$) causes a decrease in conductivity with increasing ω . Furthermore, it is observed from

DLS measurement that the values of D_h of the microemulsion droplets increase remarkably as a function of both $X_{\text{Brij-35}} = 0.0 \rightarrow 1.0$ and ω in IPM oil. However, the decrease of light scattering count rate is observed under these conditions. Hence, the adjustable radius of the water pool [20, 21, 27] along with the Gibbs free energy change ($\Delta G^0_{o \rightarrow i}$) [73, 74] could be used for predicting the size of the nanoparticles in w/o microemulsions if used as templates. Further, these microemulsion systems may be used to study the activity of an enzyme (CV-lipase, HRP [75] and HLADH [76]), as it was reported that nonionic surfactants and concentration of Pn not only influence the enzymatic activity, and also are useful complements for the investigation of microemulsion structures.

References

References are given in BIBLIOGRAPHY under Chapter V (pp. 246-250).