

Chapter-VII

Physicochemical investigation of mixed surfactant microemulsion: Water solubilization, thermodynamic properties, microstructure and dynamics

Abstract

In this contribution, we report on systematic investigation of phase behavior and solubilization of water in water-in-heptane or decane aggregates stabilized by mixtures of polyoxyethelene (20) cetyl ether (Brij-58) and cetyltrimethylammonium bromide (CTAB) surfactants with varying compositions in conjugation with 1-pentanol (Pn) at fixed surfactant(s)/Pn ratio and temperature. Synergism in water solubilization was evidenced by the addition of CTAB to Brij-58 stabilized system in close proximity of equimolar composition in both oils. An attempt has been taken up to correlate composition dependent water solubilization and volume induced conductivity study to underline solubilization mechanism of these mixed systems. Conductivity study reveals the ascending curve in water solubilization capacity-(Brij-58: CTAB, w/w) profile as the interdroplet interaction branch indicating percolation of conductance and the descending curve is curvature branch due to the rigidity of the interface in these systems. The microstructure of these systems as a function of surfactant composition has been determined from dynamic light scattering (DLS) and Fourier transform infrared spectroscopy (FTIR) measurements. FTIR study reveals increase and decrease in relative population of bound and bulk-like water, respectively with increase in Brij-58: CTAB (w/w). DLS measurements showed that the hydrodynamic diameter (D_h) of droplets decrease significantly with the increase in Brij-58: CTAB (w/w). Further, the interfacial composition and energetic parameters of transfer of Pn from bulk oil to the interface were evaluated by the dilution method. Formation of temperature-insensitive microemulsions and temperature invariant droplet sizes are evidenced in the vicinity of equimolar composition. A comprehension of the results is suggested.

Keywords: Synergism; Conductance percolation; State of water; Thermodynamic parameter; Temperature-insensitive microemulsion; Droplet diameter.

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1. Introduction

Microemulsions are thermodynamically stable organized assemblies comprising of isotropic mixtures of surfactant, oil, water with or without cosurfactant [1]. These organized assemblies have been receiving a lot of theoretical as well as experimental investigations from time to time due to their potential applications in various fields, viz. aqueous chemical reactions [2], vehicles for drug delivery [3], membrane mimetic systems [4], separation and extraction processes of both metal ions and proteins [5, 6], and nanoparticle and polymer syntheses [7]. Microemulsions consist of a hydrophilic core and a hydrophobic corona. Due to the polar nature of the core in microemulsions, water can be easily solubilized into these micellar solutions. The solubilized water is distinctly different from bulk water in physicochemical properties, such as microviscosity, acidity, and polarity [8, 9], and are very important in areas such as the catalysis of small molecules [9, 10] and biopolymers [8, 11], enhanced oil recovery [12], and models for the study of hydration in membranes and cells [10]. All these applications depend crucially on the water solubilization capacity, which changes in response to the environmental conditions/variables, for example, the chemical structure and physicochemical properties of the amphiphile(s), the nature of the oil phase, the temperature, and the presence of electrolytes [13].

It is well known that the organization of amphiphiles at the interface of a microemulsion plays an important role in solubilization of water in nanoscopic water pool, and warrants an in-depth study of solubilization mechanism for understanding of the phase behavior as well as microstructure of the ordered phases in water/amphiphile(s)/oil systems. Now-a-days, mixing of surfactants is a preferred practice in surfactant industry due to associated performance advantages (synergism) and the inherent difficulty in preparing chemically new surfactants. Among different types of possible mixed surfactant systems, ionic/non-ionic mixed systems, are most frequently making their appearance in commercial and non-commercial products as they provide more flexible physicochemical properties in terms of detergency, solubilization and synergistic performance, which are key parameters in the formulation of cosmetic and medicinal products [14, 15]. Synergism in water solubilization was previously reported for a non-ionic/anionic microemulsion

system designed for pharmaceutical applications, using mixtures of AOT [sodium bis(2-ethylhexyl)sulfosuccinate] and Arlacel-20 (sorbitan laurate) at different proportions [16]. Also, it was reported earlier that the solubilization capacity of nonionic microemulsions increased upon addition of ionic surfactants [17-21], which was attributed to the inhibition of the undulations in the surfactant layer and the consequent gain in surface area [22,23]. The cosurfactant (short chain lipophilic n-alkyl alcohols) plays an important role by blending with surfactant(s) and partitions between the coexisting aqueous and oleic phases to control the bending elasticity of the interfacial layer offering stability to the dispersion as well as affecting the droplet dimensions of the microemulsion systems [24]. In order to quantify the composition of the interfacial layer and the distribution of surfactant and cosurfactant between the oil/water interface, a simple but elegant method (the Schulman method of cosurfactant titration of the oil/water interface or the dilution method, which is accomplished by adding oil at a constant water and surfactant level to destabilize an otherwise stable w/o microemulsion and restabilizing it by adding a requisite amount of cosurfactant with constant composition of the interface and continuous phase) has been employed by a number of workers [25-38].

Numerous studies have been reported for understanding of the interaction and dynamics of the microemulsion droplets in single and mixed surfactant systems using various techniques, such as small-angle X-ray scattering (SAXS), dynamic light scattering (DLS), pulsed-gradient spin-echo nuclear magnetic resonance (PGSE-NMR), steady-state fluorescence spectroscopy, conductance, and viscosity measurements [39-43]. Of these, electrical conductivity provides a convenient, useful, and accessible tool for probing the microstructure of microemulsions. Of the different physical properties of microemulsions, percolation of conductance is striking; where many fold (100-1000 times) increase in conductance can take place after a threshold volume fraction of the dispersant (water) at a constant temperature or after a threshold temperature at a constant composition [44]. Dynamic light scattering is a useful method for detecting the droplet size of microemulsions up to very small dimensions, when the scattering contrast (refractive index) is strong enough for a successful application of this method. Recently, it was shown that DLS can be applied up to very small particle dimensions below 1 nm in size [45]. In order to get a clear understanding of various interactions in the droplet core,

including the type of H-bonding which is operative within the water pool, an excellent and non-invasive technique viz., Fourier transform infrared spectroscopy (FTIR) has been introduced. Several authors were significantly contributed to the understanding of the water dynamics in w/o microemulsion system by studying the state of water using FTIR method [28, 46].

In view of these reports, very recently, we have reported the interfacial composition, thermodynamics of alkanol transfer process, solubilization behavior, transport and microstructural properties, and the dynamics of confined water of mixed surfactant (ionic and non-ionic) w/o microemulsions under different physicochemical conditions, by employing the dilution method, conductivity, viscosity, DLS and FTIR measurements [29, 30, 47-49]. In continuation of our previous studies, we contemplate to undertake studies on the formation and precise characterization vis-à-vis the nature of the oil/ water interface and water in the confined environment of mixed surfactant (non-ionic/ionic) w/o microemulsions [water/polyoxyethylene (20) cetyl ether (Brij-58)/cetyltrimethylammonium bromide (CTAB)/1-pentanol (Pn)/heptane (Hp) or decane (Dc)] as a function of different mixing ratios of Brij-58: CTAB (5:0→0:5, w/w) at 303K. Both of these surfactants are chosen in such a way that they possess similar hydrocarbon tail (comprising 16 carbon atoms in the linear hydrocarbon chain), but they differ in charge type and size of the polar head groups, so that the possible interaction between the hydrocarbon chains of two surfactants gets minimized [50]. In this report, we intend to address non-ionic (Brij-58)/ionic surfactant (CTAB) mixtures at different compositions that exhibit synergism in solubilization of water in w/o mixed surfactant microemulsions. An attempt has also been made to correlate the solubilization capacity of water as a function of mixed surfactant composition with percolation of conductance to underline the microstructure of these mixed surfactant microemulsions. In addition, solubilization mechanism is suggested in terms of the model proposed by Shah et al. [51, 52] (based on curvature of the mixed amphiphilic film separating oil and water, and interaction between microemulsion droplets). Further, microstructure, internal dynamics (dynamics of the confined water) and interfacial composition of the mixed interfacial film of these systems have been characterized by means of the phase study, DLS, FTIR measurements and dilution method as a function of different mixing ratios of surfactant(s). An in-depth

analysis on thermodynamic properties of these microemulsions based on results obtained from the dilution method at different temperatures (303, 308, 313, 318 and 323K), has also been presented. An attempt has been made to rationalize the results in a comprehensive manner. The results are expected to enrich the basic understanding of the role of the amphiphiles (both surfactants and cosurfactant) and oils (of different chain lengths) on the formation, stabilization and characterization of the mixed surfactant microemulsions, which is seldom, reported literature.

2. Experimental

2.1. Materials

Polyoxyethylene (20) cetyl ether (Brij-58, > 98.5%) and cetyltrimethylammonium bromide (CTAB, > 99%) were products of Fluka, Switzerland and Sigma-Aldrich, USA, respectively. 1-Pentanol (Pn, > 98%), heptane (Hp, > 99%) and decane (Dc, > 99%) were products of Lancaster, England and Merck, Germany, respectively. The chemicals were used as received. Eosin blue and Sudan IV were from Aldrich, USA and further purified by re-crystallization from 1:1 aqueous methanol. Dyes were dried at 50°C under vacuum before use. 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 (Brij-58 and CTAB) at different proportions, cosurfactant (Pn), oil (Hp and Dc) and water with constant surfactant and cosurfactant mass ratio (S: CS = 1:2) were formulated in a screw cap glass vials. The samples were monophasic, transparent and stable for over several months. Phase behavior of the chosen systems was constructed at a 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. Optical transparency

The homogeneity and optical isotropy of mixed microemulsions formed were examined by a cross polarizer and visual examination at 303K.

2.2.3 Water solubilization

The initial composition of mixed surfactants (Brij-58 and CTAB at different proportions), cosurfactant (Pn) and oil (Hp and Dc) for water solubilization studies were 23% (w/w), 46% (w/w) and 31% (w/w), respectively. The surfactant and cosurfactant mass ratio was used 1:2 (w/w). Water was added to each solution in steps with a Hamilton micro-syringe, and solubilization capacity was measured after homogenization as a function of water (wt %) at 303K [28].

2.2.4. Dye solubilization experiment

Dye solubilization experiment [48, 51] was performed to estimate the phase separation phenomenon in single (Brij-58 or CTAB) and mixed surfactants (Brij-58 and CTAB) microemulsion by water soluble dye Eosin blue and oil soluble dye Sudan IV at 303K.

2.2.5. Conductivity measurements

The conductivity measurements were performed using Mettler Toledo (Switzerland) digital conductivity bridge (accuracy $\pm 1\%$). The temperature was kept constant within ± 0.1 K by circulating thermostated water, through a jacketed vessel containing the solution. The electrical conductivity of the selected mixed microemulsions was measured at 303K. The repeatability and the accuracy of the measurements were $\pm 0.3\%$ and $\pm 1\%$, respectively.

2.2.6. Dilution method with spectrophotometric measurements

Details of the dilution method were provided in our previous reports [29, 30, 37, 38]. The procedure of this experiment at different physicochemical conditions with theoretical backgrounds (i.e., basics of the dilution method and evaluation of thermodynamic parameters) has been presented in Appendix E (Sec. 1).

2.2.8. DLS measurements

DLS measurements were carried out 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° at 303K. 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 Milipore^(TM) hydrophobic membrane filter of 0.25 μ pore size. Hydrodynamic diameter (D_h) of the microemulsion droplets was estimated from the intensity autocorrelation function of the time-dependent fluctuation in intensity. According to Stokes–Einstein equation, D_h is defined as [49]

$$D_h = k_B T / 3\pi\eta D(1)$$

where, k_B , T , η and D indicate the Boltzman constant, temperature, viscosity and diffusion coefficient of the solution, respectively. To check the reproducibility of the results at least 6 measurements were done.

2.2.9. FTIR measurements

FTIR absorption spectra were recorded in the wave number range of 400-4000 cm^{-1} with a Shimadzu 83000 spectrometer (Japan) using a CaF_2 -IR crystal window (Sigma-Aldrich) equipped with Presslock holder with 100 number scans and spectral resolution of 4 cm^{-1} at 303K. Deconvolution was carried out with the help of Origin 6.0 software.

3. Results and discussion

3.1. Phase behavior

The pseudo-ternary phase behavior of Brij-58/CTAB/Pn/Hp/water system as a function of different mass ratios of mixed surfactant (= 5:0 \rightarrow 0:5) at fixed surfactant and cosurfactant mass ratio (= 1: 2) and at 303 K has been described in Appendix E (Sec. 2) with the help of phase diagrams (Fig. S1).

3.2. Water solubilization capacity

The water solubilization capacity of w/o mixed surfactant microemulsions is one of the important parameters not only from the view point of its wide applications, but also it determines the size of the water core, the rigidity or flexibility of the oil/water interface and morphology of the surfactant aggregates. Further, such studies emphasized on underlying the factors governing solubilization phenomenon in these systems, is of fundamental importance [53, 54].

The solubilization of water in mixed Brij-58: CTAB/Pn/Hp (Dc) microemulsions as a function of composition of mixed surfactants at 303K, has been presented in Fig. 1. It is evident from Fig. 1 that w/o single Brij-58 (Brij-58: CTAB = 5:0, w/w) can solubilize water up to 17 and 15 wt% in Hp and Dc, respectively at constant surfactant/cosurfactant ratio (1: 2, w/w). While Brij-58 has been blended with CTAB at different proportions (for

example, Brij-58 and CTAB = 4:1; 3:2; 2:3; 1:4, w/w), the water solubilization capacity increases up to a maximum value at a certain composition of the mixed surfactants (Brij-58: CTAB = 2:3, w/w), beyond which (Brij-58: CTAB = 1:4 and 0:5, w/w) the solubilization capacity further decreases with increasing CTAB. A plausible explanation for this trend in composition-dependent solubilization phenomenon in mixed microemulsions is not straightforward. However, solubilization of water in w/o microemulsion system depends upon many factors, for example, type of surfactant (as major amphiphile) and cosurfactant (or a second surfactant as auxiliary amphiphile), size of the polar head group and hydrocarbon moiety of both amphiphiles, the composition, oil type etc [53-55]. But the main driving force of such solubilization is the spontaneous film curvature (H^0) (the curvature that the amphiphilic film would like to attain) and the elasticity of the amphiphilic film [52]. If the interfacial curvature and the bending elasticity are fixed, solubilization can be maximized by minimizing the interfacial bending stress of the rigid interface and the attractive interdroplet interaction among droplets [56]. The solubilization of a microemulsion of a fluid interface can be increased by increasing the interfacial rigidity and decreasing the natural radius. Alcohol (cosurfactant) is also an essential factor in promoting interfacial fluidity for the formation of microemulsion [51-54]. It can be seen from Fig. 1 that water solubilization capacity reaches maxima at the close proximity of the middle range composition of Brij-58 and CTAB (i.e., in between 3:2 and 2:3, w/w) in both oils. These results clearly indicate that the addition of CTAB to the nonionic microemulsion (Brij-58) results in obtaining synergism (or maximization) of water solubilization at a specified composition (mentioned earlier). The maximization of solubilization capacity of water in mixed microemulsions can be interpreted as a result of counteracting effects of the attractive interdroplet interaction of the fluid interfaces and bending stress of the rigid interfaces [52]. According to Israelachvili, the molecular packing is determined by a balance between the repulsive force of hydrophilic moieties and the attractive forces of lipophilic moieties [57]. Since nonionic, Brij-58 has 20 POE in hydrophilic moieties, its effective cross sectional area per hydrophilic unit should be larger than that of an ionic CTAB [48, 58]. Hence, the repulsion between the hydrophilic groups is reduced when a part of Brij-58 is replaced by CTAB, which results in a more dense packing of mixed surfactants at

the interface [59]. This is why the added CTAB induces rigidity to the surfactant layer in Brij-58 microemulsions.

Further, attainment of maximum water solubilization using a mixture of ionic/nonionic surfactants can be explained in the light of hydrophilic-lipophilic balance (HLB) of individual surfactants. The HLB is one of the most common methods to correlate surfactant structure with their effectiveness as emulsifiers. The HLB value of a surfactant indicates how surfactant behaves in a solution, and also represents the capability of surfactant solution to solubilize other substances [60]. Huibers and Shah [61] reported earlier that the best solubilization for the mixture occurs when HLB values of its components lie in 9-13 regions. Further, they mentioned that good solubilization occurs when HLB of the surfactant mixture falls in a certain HLB region, which should be neither very water soluble nor oil soluble. As a result of attainment of these conditions, the surfactants are more favorable to partition at the interface. In such a case, solubilization for the mixtures is better than that of either component. Hence, HLB of the present systems at the mixed compositions (i.e., HLB_{mix}) has been evaluated using the concept of Acosta et al. [62],

$$HLB_{mix} = (X_1 HLB_1 + X_2 HLB_2) \quad (2)$$

where, X_1 and X_2 are the mole fraction of surfactant 1 and surfactant 2 in the mixture, respectively. HLB_1 and HLB_2 are the hydrophilic-lipophilic balance of surfactant 1 and surfactant 2, respectively. In these calculations, HLBs of CTAB [63] and Brij-58 [64] are 10 and 16, respectively. A graphical illustration of HLB_{mix} versus Brij-58: CTAB (w/w) has been represented in Fig. 1. It is evident from Fig. 1 that maximum water solubilization occurs at HLB_{mix} equals to 12-13 regions. According to Huibers and Shah [61], synergism in maximum water solubilization in w/o microemulsion was observed at HLB_{mix} equals to 9 for a mixture of nonylphenylethoxylate surfactants ($C_9PhE_{1.5}$ and C_9PhE_{12}) in cyclohexane. Further, synergistic effect must cause the majority of the two surfactants to preferentially partition at the interface that allows larger interfacial area and thus high levels of solubilization [65]. While microemulsions were composed of equal amounts of surfactants, the synergistic effect reported to be more pronounced [65]. In this report, the synergistic effect has been achieved at Brij-58 and CTAB mass ratio of 2:3 and 3:2. Similar result was reported by Fanun for water/propylene glycol/sucrose

monolaurate/ethoxylated mono-di-glyceride/peppermint oil/ethanol microemulsion systems [65].

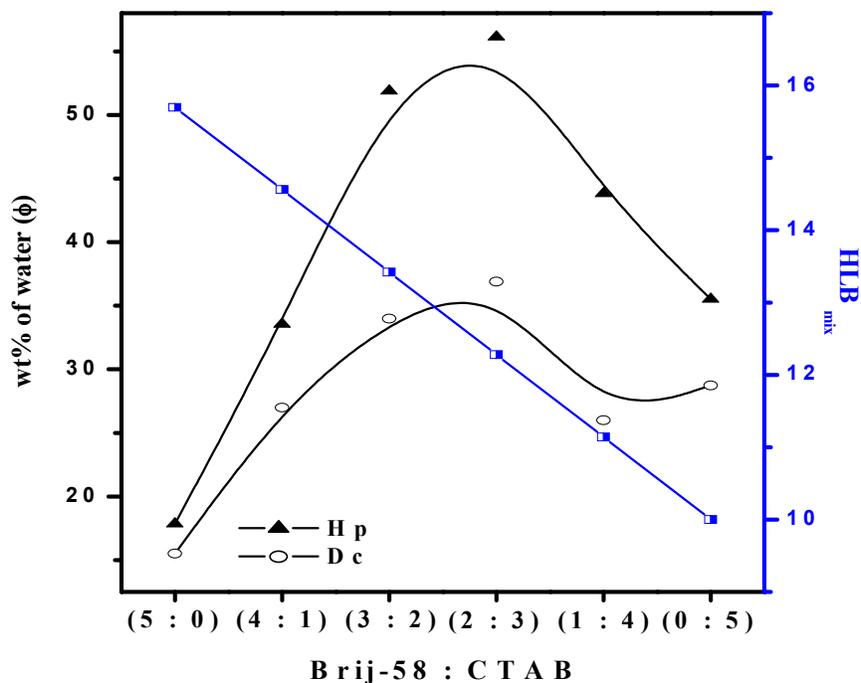


Fig. 1. Water solubilization capacity (wt% of water) and HLB_{mix} of mixed Brij-58/CTAB/1-pentanol/Hp or Dc microemulsions as a function of different mass ratios of mixed surfactant at 303K (Hp: filled triangle and Dc: open circle).

Rodríguez et al. [21] reported on the effect of ionic surfactant (sodium laurate) on the solubilization capacity of w/o microemulsions derived from sucrose ester (water/sucrose dodecanoate/decane). According to them, increase in the solubilization of water by the addition of ionic surfactant was attributed to the increase in repulsion between surfactant layers. At high concentration of ionic surfactant, enhancement in solubilization of water was lost due to the screening of charged groups.

Further, it is evident from Fig. 1 that Dc-based system shows significantly lower water solubilization capacity compared to Hp-based system. Actually increasing oil chain length would gradually reduce the cohesive interaction between the hydrocarbon chains of amphiphiles present at the interface and decrease the interfacial rigidity, due to

decreasing oil penetration. This in turn decrease the water solubilization capacity in Dc [51, 52].

In the present study, phase separation upon the addition of excess water in Brij-58/CTAB/oil(s)/water microemulsion systems has been examined by employing dye solubilization process in both oils [48, 51, 54]. The objective for the dye solubilization experiment is to investigate whether the solubilization process is governed by the curvature effect or the interdroplet interaction effect [53]. A brief description of dye solubilization experiment has been presented in Appendix E (Sec. 3).

3.3. Conductivity measurements

It is known that electrical conductivity measurements can be used to predict qualitatively the interaction between the droplets and thus stability of microemulsion. For example, appearance of an electrical percolation process indicates the existence of large attractive interaction between droplets [28, 53, 58].

In this section, an attempt has been made to correlate the maximum water solubilization with percolation of conductance to underline the microstructure of these mixed surfactant microemulsions. If the droplets are of non-interacting hard sphere type, no significant increase in conductance occurs with increasing water content at constant temperature or with increase in temperature at fixed 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 [53]. In the present investigation, conductance studies have been carried out for mixed surfactant microemulsion systems wherein solubilization maxima (in the vicinity of equimolar composition i.e., at Brij-58: CTAB = 2:3 and 3:2, w/w) are observed. The samples from both sides of the corresponding maxima, i.e., from the ascending branches and the descending branches are chosen.

The conductivity of mixed water/Brij-58/CTAB/Pn/Hp or Dc microemulsion systems at different compositions (Brij-58: CTAB = 5:0; 4:1; 3:2; 2:3; 1:4; 0:5, w/w) [S: CS = 1:2 (w/w)] at 303K as a function of wt% of water has been determined and depicted in Figs. S2A-S2F. Samples chosen from the ascending branch (i.e., at Brij-58: CTAB = 5:0→2:3, w/w) exhibit a nonlinear sharp enhancement in conductivity with the addition of water,

which signifies the volume-induced percolation in conductance (Figs. S2A-S2D). The critical value for sharp enhancement in conductivity with the addition water is considered as volume-induced percolation threshold (ϕ_p). Such percolation in the present systems (i.e., at ascending branch of Fig. 1) shows that the interface of the droplets are fluid enough to coalesce during the collisions followed by material exchange and fusion. Further, it is evident that ϕ_p increases (i.e., percolation process is retarded) with decrease in content of Brij-58 or increase in content of CTAB. On the other hand, no sharp enhancement in conductivity vis-à-vis percolation phenomenon is observed in the descending branch of the solubilization maximum (i.e., at Brij-58: CTAB = 1:4→0:5, w/w) (Figs. S2E-S2F). Further, at a composition of Brij-58: CTAB = 0:5, w/w i.e., single CTAB-derived microemulsion systems, a bell-shaped conductivity profile with flattened maxima is obtained in both oils (Fig. S2F). Further, discussion in this aspect has been dealt in Appendix E (Sec. 4).

3.4. Dilution method

The interfacial composition of water/Brij-58/CTAB/Pn/Hp or Dc microemulsion systems with different mixing ratios of the surfactants (Brij-58: CTAB = 5:0, 4:1, 3:2, 2:3, 1:4 and 0:5, w/w) at a fixed amount of mixed surfactants (5×10^{-4} mol) and water content (2.75×10^{-2} mol), and at five different temperatures of 303K, 308K, 313K, 318K and 323K has been evaluated by the dilution method. From the data collected, graphs were constructed by plotting n_a/n_s against n_o/n_s according to Eq. (S2). Representative illustration is shown in Fig. S3 (Appendix E). The calculated values of compositional variations of amphiphiles (surfactants and Pn) at the interface (n_a^i/n_s) at surfactant compositions mentioned above with varying temperatures are illustrated in Figs. S4A and S4B. The distribution of the cosurfactant (Pn) between the oil and the interface imparts stability to the dispersion. The distribution constant (K_d) at different temperatures lead to the evaluation of energetic of the transfer process. To gain insight into the thermodynamic stability of these systems as a function of different mixing ratios of the surfactants and oil chain length, standard Gibbs free energy change of transfer of alkanol from oil to the interface (ΔG^0_t) has been computed according to Eq. (S4) and Figs. S4A and S4B (Appendix E) and Table 1. Figs. S4A and S4B represent three-dimensional

profiles of n_a^i/n_s and $-\Delta G_t^0$ as a function of both the compositions and temperatures in Hp and Dc, respectively.

It reveals from Figs. S4A and S4B and Table 1 that ΔG_t^0 values for these systems are negative at experimental temperatures and indicate that water/Brij-58/CTAB/Pn/Hp or Dc microemulsion systems form spontaneously no matter which oil or composition was used.

3.4.1. Influence of composition, temperature and oil on n_a^i/n_s and $-\Delta G_t^0$

It is evident from Figs. S4A and S4B that both of the values of n_a^i/n_s and $-\Delta G_t^0$ are found to be higher for (single) CTAB stabilized systems (Brij-58: CTAB = 0:5, w/w) compared to (single) Brij-58 stabilized systems (Brij-58: CTAB = 5:0, w/w) in both oils at all temperatures. The differential behavior of the surfactants toward the above phenomenon may reflect the degree of favorable/unfavorable interaction between the surfactant(s) and the alkanol [25], and can be explained in the following way: it was reported that the interaction between Brij-58 and Pn is of dipole-dipole or dipole-induced dipole or London dispersion type, because of the presence of uncharged or neutral hydroxyl groups (Pn) and POE chains (Brij-58). Whereas, the interaction between CTAB and Pn is of ion-dipole type because of the presence of uncharged or neutral hydroxyl groups (Pn) and charged quaternary ammonium groups $[N(CH_3)_3^+]$. Ion-dipole interaction is very strong compared to dipole-dipole or dipole-induced dipole or London dispersion interactions [66]. Therefore, the association between Pn and CTAB is much more favorable than Pn and Brij-58. As Pn molecules are slightly deprotonated, which assist Pn to associate strongly with cationic CTAB than non-ionic Brij-58, result in stronger association between Pn with CTAB [67]. As a result, both n_a^i/n_s and $-\Delta G_t^0$ for CTAB stabilized systems are higher compared to Brij-58 stabilized systems. Hence, it can be concluded that, the interfacial alkanol affinity can be surfactant specific, which was reported earlier by Bisal et al. [68]. Similar types of results were also reported by Moulik et al. [31], Hait and Moulik [25], Kumar and Kabir-ud-Din [67], Paul and Nandy [36] and De et al. [27].

Table 1. Thermodynamic parameters of transfer of Pn from Hp (or, Dc) to the interface of microemulsion containing 2 ml oil, 0.5 mmol of surfactant and at fixed water content (2.75×10^{-2} mol) with varying compositions (Brij-58: CTAB, w/w) and temperatures. ^a

<u>Temperature (K)</u>			
Brij-58: CTAB = 5:0	$-\Delta G_t^0$ (kJ/mol)	ΔH_t^0 (kJ/mol)	ΔS_t^0 (J/mol/K)
303	2.61 (2.43)	15.74 (10.10)	51.98 (33.36)
308	2.94 (2.66)	17.14 (12.12)	55.68 (39.37)
313	3.25 (2.90)	18.49 (14.07)	59.12 (44.99)
318	3.63 (3.21)	19.81 (15.97)	62.33 (50.24)
323	4.00 (3.51)	21.08 (17.80)	65.29 (55.15)
Brij-58: CTAB = 4:1			
303	1.20 (1.63)	35.71 (21.41)	117.86 (70.68)
308	1.76 (1.96)	31.14 (17.76)	101.13 (57.68)
313	2.26 (2.29)	26.72 (14.22)	85.40 (45.46)
318	2.71 (2.49)	22.44 (10.79)	70.61 (33.98)
323	3.05 (2.69)	18.29 (7.47)	56.68 (23.18)
Brij-58: CTAB = 3:2			
303	2.68 (2.13)	3.03 (1.60)	10.02 (5.31)
308	2.78 (2.18)	3.78 (0.75)	12.31 (2.48)
313	2.89 (2.23)	4.51 (-0.05)	14.45 (-0.15)
318	3.02 (2.25)	5.22 (-0.85)	16.45 (-2.64)
323	3.15 (2.27)	5.91 (-1.61)	18.32 (-4.97)
Brij-58: CTAB = 2:3			
303	3.66 (2.34)	-6.44 (-2.70)	-21.20 (-8.89)
308	3.62 (2.33)	-6.35 (-3.08)	-20.57 (-9.98)
313	3.57 (2.32)	-6.26 (-3.45)	-19.97 (-11.01)
318	3.53 (2.29)	-6.18 (-3.80)	-19.39 (-11.95)
323	3.49 (2.27)	-6.09 (-4.15)	-18.85 (12.83)
Brij-58: CTAB = 1:4			
303	4.89 (3.73)	-14.34 (-10.49)	-47.28 (-34.61)
308	4.67 (3.63)	-19.41 (-9.55)	-62.97 (-30.99)
313	4.44 (3.53)	-24.32 (-8.64)	-77.65 (-27.58)
318	4.03 (3.47)	-29.07 (-7.76)	-91.38 (-24.37)
323	3.63 (3.40)	-33.68 (-6.90)	-104.22 (-21.35)
Brij-58: CTAB = 0:5			
303	6.76 (5.21)	-29.88 (-16.91)	-98.55 (-55.77)
308	6.39 (5.04)	-29.04 (-15.22)	-94.22 (-49.39)
313	6.02 (4.87)	-28.22 (-13.59)	-90.12 (-43.39)
318	5.68 (4.76)	-27.44 (-12.01)	-86.22(-37.74)
323	5.34 (4.65)	-26.67 (-10.48)	-82.52 (-32.41)

^a The error limits of $-\Delta G_t^0$, ΔH_t^0 and ΔS_t^0 are ± 3 , ± 5 and $\pm 8\%$, respectively.

Further, it has been observed that the values of n_a^i/n_s and $-\Delta G_t^0$ did not follow any straight-forward trend as a function of mixing ratios of the surfactants for any of these systems (Figs. S4A and S4B). It has been observed that n_a^i/n_s value first decreases upon the addition of CTAB to Brij-58 stabilized systems (mixed Brij-58: CTAB = 5:0→4:1, w/w) and after that increases gradually (mixed Brij-58: CTAB = 4:1→0:5, w/w) in both oils at all temperatures. In other words, n_a^i/n_s values show minima at composition Brij-58: CTAB = 4:1 (w/w). The interfacial population of cosurfactant vis-à-vis stability of the mixed microemulsion systems is mainly determined by the repulsions between head groups, including electrostatic origin for quaternary ammonium head groups and steric origin for oxyethylene head groups [69]. When CTAB is initially added into Brij-58 stabilized systems, the steric repulsion between head groups of Brij-58 decreases with increasing content of CTAB (X_{CTAB}), but the introduction of quaternary ammonium head groups of CTAB to Brij-58 surfactant molecules brings about a larger electrostatic repulsion between the charged head groups, and subsequently, decreases the area required per surfactant head group, allowing the mixed systems to adopt a conformation with smaller curvature [70]. As a result, n_a^i/n_s values of the mixed systems increase from Brij-58: CTAB = 4:1→0:5, w/w. However, at Brij-58: CTAB = 5:0, w/w (single Brij-58), the electrostatic repulsion is absent and n_a^i/n_s is mainly controlled by steric repulsion between head group of Brij-58 [70]. Hence, it can be concluded that the effective binding between CTAB and/or Brij-58 and Pn at the interface increase in the order of composition, (Brij-58: CTAB, w/w): 4:1 < 3:2 < 2:3 < 1:4, which corroborates well with the degree of spontaneity of the transfer process.

It reveals from Figs. S4A and S4B that, both n_a^i/n_s and $-\Delta G_t^0$ values increase with increase in temperature for pure Brij-58 (Brij-58: CTAB = 5:0, w/w) and Brij-58 rich (Brij-58: CTAB = 4:1, w/w) stabilized systems, whereas reverse trend is observed for pure CTAB (Brij-58: CTAB = 0:5, w/w) and CTAB rich (Brij-58: CTAB = 1:4, w/w) stabilized systems in both oils. This phenomenon can be explained as follows. The effect of temperature on the solubility and hydration of ionic surfactant is opposite to that of non-ionic surfactant. With increase in temperature, dissociation of the ionic head group increases and the ionic surfactant becomes more hydrophilic at higher temperatures [71]. A higher degree of dehydration around the head group region of the non-ionic surfactant

appreciably imparts to the molecules an increase in hydrophobicity, thereby leading to unsuitable molecular geometry at higher temperatures [72, 73]. Addition of alcohol (herein, Pn) effectively changes the originally unfavorable packing geometry of the surfactant molecules and produces a stable surfactant/alcohol mixed interfacial film [26]. Hence, with increasing temperature n_a^i/n_s values increase for pure Brij-58 and Brij-58 rich stabilized systems. However, an interesting result has been observed in the vicinity of equimolar composition (i.e., Brij-58: CTAB = 3:2 and 2:3, w/w) that both n_a^i/n_s and $-\Delta G_t^0$ are found to be invariant with increase in temperature, i.e., temperature-insensitive microemulsions have been formed in both oils. The increased lipophilicity of Brij-58 is suppressed by the increased hydrophilicity of CTAB at elevated temperatures and in consequence, no variation in both of these parameters has been found in vicinity of equimolar composition. Temperature-insensitive microemulsion formation in the vicinity of equimolar composition is further confirmed by the analysis of the results of other thermodynamic parameters (ΔH_t^0 and ΔS_t^0), and has been dealt in subsequent paragraph. ΔG_t^0 values are more negative in Hp continuum than Dc continuum at all compositions of the mixed surfactant microemulsions, indicating the process to be more favorable for the former than the latter. It is suggested that an effective binding (or, a strong interaction) between amphiphiles (Brij-58/CTAB) and alkanol (Pn) at the interface, indicating spontaneity of the transfer process becomes more favored in lower chain length of oils. It may be due to larger penetration of oil (Hp) due to shorter chain length than Dc into the mixed interfacial film of these systems. It is quite likely that the interfacial fluidity may increase with increase in oil chain length and thereby, increasing alcohol partitioning at the interface. Such an increase in interfacial fluidity results in inelastic collisions between droplets, leading to formation of transient dimmers and enhances apparent interdroplet interaction for Dc based systems. At sufficiently strong interdroplet interaction, the microemulsion droplets stabilized in Dc are less stabilized compared to Hp based systems [52]. Similar observations were reported by Moulik et al. [31], Paul and Nandy [36], Mitra et al. [38] and Kundu et al. [29].

3.4.2. Enthalpy and entropy of the transfer process

Due to nonlinear dependence of $(\Delta G_t^0/T)$ on $(1/T)$ (Fig. S5, Appendix E) in terms of a two degree polynomial equation, at each composition of surfactant(s) (Brij-58: CTAB = 5:0→0:5, w/w), five values of ΔH_t^0 and ΔS_t^0 at five temperatures have been evaluated according to Eqs. (S7) and (S8) and presented Table 1. Three-dimensional profiles on the dependence of ΔH_t^0 and $-\Delta S_t^0$ as a function of both the compositions (Brij-58: CTAB = 5:0→0:5, w/w) and temperatures (303K→323K) have been illustrated as Figs. 2A and 2B in Hp and Dc, respectively. These curves are not straightforward upon the addition of ionic surfactant (CTAB) to the non-ionic surfactant (Brij-58) under various physicochemical conditions.

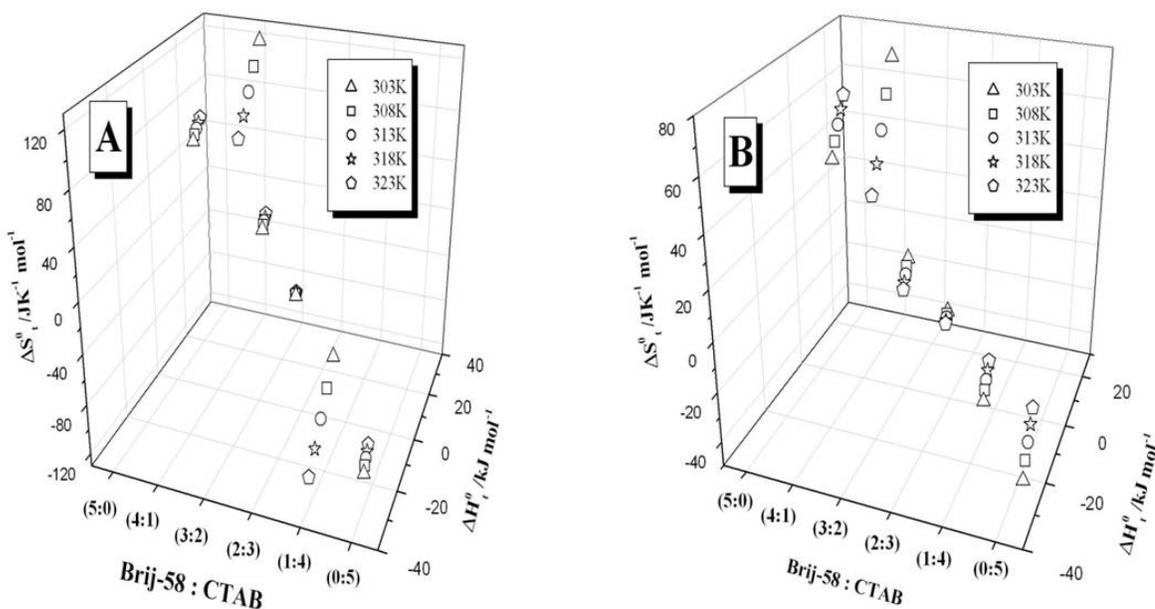


Fig. 2. Plot of ΔH_t^0 and $-\Delta S_t^0$ vs. different mass ratios of mixed surfactant (Brij-58 and CTAB) for w/o microemulsion systems comprising 5×10^{-4} mol of total mixed surfactant, 2.75×10^{-2} mol water, 2 ml of heptane (**Plot: A**) and decane (**Plot: B**) stabilized by 1-pentanol at five different temperatures [303K (open triangle), 308K (open square), 313K (open circle), 318K (open star), 323K (open pentagon)].

Pure Brij-58 and CTAB microemulsion systems

For pure CTAB system (Brij-58: CTAB = 0:5, w/w), the overall transfer process is exothermic at all experimental temperatures with negative entropy change (order) in both oils. So, Pn causes release of heat during transfer process. Consequently, the negative entropy change may be due to more organization of the interface and its surroundings. Therefore, the interface composed of Pn and CTAB is to some extent orderly. Such negative enthalpy and entropy changes were observed by Wang et al. [34] for water or aqueous HCl/cetyltrimethylammonium chloride (CTAC)/alkanol/diesel oil, De et al. [27] for water/DTAB/alkanol/Hp and Digout et al. [35] for CPC derived microemulsion systems stabilized in different chain length of cosurfactants (Bu, Pn, Hx) and oils (pentane/octane/decane). Hait and Moulik [25] and Mohareb et al. [33] reported that the spontaneity of the process of alkanol transfer associated with positive ΔH_t^0 and ΔS_t^0 values for CTAB/1-butanol/IPM/water system. The observed difference in thermodynamic properties for CTAB-stabilized system may be due to the basic difference in type of oils used (for example, ester of fatty acids [25, 33] and long chain alkanes in the present study). For pure Brij-58 stabilized system (Brij-58: CTAB = 5:0, w/w), the process is endothermic with absorption of heat at all experimental temperatures with positive entropy change (disorder) in both oils. The non-ionic surfactant produces insignificant ion-dipolar effect with the alkanol showing endothermic transfer from bulk oil to the interface [33]. The desolvation of head group of Brij-58 during the transfer of Pn in the oil is responsible for both positive enthalpy and entropy change [38]. Similar observation was also reported by De et al. [27] for Tween-20/Bu or Pn/Hp/water and Kundu and Paul [29] for Brij-58 or Brij-78/Pn/Hp or Dc/water microemulsion systems. However, Bardhan et al. [30] reported an opposite behavior of pure Brij-35 based systems stabilized in IPM. The opposite behavior towards temperature of ionic and non-ionic surfactants might be responsible for such variation in enthalpy and entropy values with temperature [74]. The negative entropic change of pure CTAB systems is due to the better organization of the interface and its surroundings. The interfacial film composed of Pn and CTAB indicates more ordered at all experimental temperatures than Brij-58 stabilized systems, which corroborated well with the spontaneity of the transfer process.

Mixed compositions of Brij-58 and CTAB microemulsion systems

At compositions in between two extremes (i.e., Brij-58: CTAB = 4:1, 3:2, 2:3 and 1:4, w/w) in both oils, ΔH_t^0 and ΔS_t^0 values are found to be both positive and negative, respectively at all studied temperatures. It has been observed from Figs. 2A and 2B that, both ΔH_t^0 and ΔS_t^0 values are positive at Brij-58 rich composition (Brij-58: CTAB = 4:1 and 3:2, w/w) and negative at CTAB rich composition (Brij-58: CTAB = 2:3 and 1:4, w/w) in both oils (with some exception at Brij-58: CTAB = 3:2, w/w in Dc). A positive contribution towards ΔH_t^0 can be interpreted as 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 towards ΔH_t^0 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 [75]. However, insignificant changes in these thermodynamic parameters with temperature have been observed in the vicinity of equimolar composition (Brij-58: CTAB = 3:2 and 2:3, w/w), leading to formation of isenthalpic and isentropic microemulsion systems. Similar observation was also reported earlier for mixed surfactant microemulsion systems [29, 30, 37, 76]. Further, it has been observed that both ΔH_t^0 and ΔS_t^0 values are more positive or more negative in Hp stabilized systems compared to Dc stabilized systems at all compositions. The difference in enthalpic and entropic behaviors between these two oils may be attributed to the difference in alkyl chain length between two oils, as reported earlier [29, 37]. It is apparent that different phenomena associated with the transfer process of Pn, viz., changing aggregation number, solvation-desolvation of non-ionic surfactant, electrostatic and steric interactions between hydrophilic head groups of CTAB and Brij-58, steric and other nonspecific processes contribute their shares to ΔH_t^0 and ΔS_t^0 values [77]. 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.

A linear thermodynamic correlation between enthalpy (ΔH^0_t) and entropy (ΔS^0_t) for these systems at 303-323 K (with correlation of coefficients of 0.9999 at each temperature) has been observed. Such figures are not exemplified here. The compensation temperatures (T_{comp}) at each experimental temperature are presented in Table S1. It was reported that the compensation temperatures (T_{comp}) are minorly deviated from the experimental temperatures [25, 29, 31, 35]. The linear correlation suggested that a mutual balance is established between enthalpy and entropy during the alkanol transfer process from the oleic phase to the oil/water interface. The extraordinary correlation between enthalpy and entropy is mainly due to the experimental errors than to chemical variations [36].

3.5. Dynamic light scattering (DLS) measurement

The hydrodynamic diameter (D_h) or droplet size of water/Brij-58/CTAB/Pn/Hp or Dc microemulsions was measured by employing the dynamic light scattering (DLS) technique at different temperatures (303, 308, 313, 318 and 323K). The same compositions were chosen for DLS measurements as employed for the dilution method. The results are depicted in Fig. 3.

3.5.1. Effect of composition on D_h

It reveals from DLS measurements that D_h decreases significantly with the increase in cationic surfactant (CTAB) in the mixed systems (Brij-58: CTAB = 5:0 \rightarrow 0:5, w/w) in both oils at each temperature. It can be argued as follows. The droplet sizes of the mixed surfactant microemulsion systems (herein, reported) is mainly governed by the repulsion between head groups of the surfactants (viz. steric origin for oxyethylene head groups and electrostatic origin for quaternary ammonium head groups), and also by the packing parameters of the surfactants forming the mixture. As discussed above, the initial effect of introducing an ionic surfactant into a nonionic surfactant-based system results in increase in electrostatic repulsive interactions between head groups and, thus decrease the droplet size [78, 79]. From packing parameter consideration, it can be explained as follows. The droplet size of microemulsion depends upon the flexibility of the interface, which in turn is related to the surfactant packing parameter (P) given by the relation, $P = v/al$, where 'v' and 'l' are the volume and the length of hydrophobic chain, respectively, and 'a' the area of polar head group of the surfactant. For a mixed surfactant

microemulsion (herein, Brij-58/CTAB), the effective packing parameter (P_{eff}) can be expressed according to the following relation as obtained by Evans and Ninham[80]:

$$P_{\text{eff}} = [(xv/al)_A + (xv/al)_B]/(x_A + x_B) \quad (3)$$

where, x_A and x_B are the mole fractions of CTAB and Brij-58 present at the interface, respectively. It was reported earlier that, head group area of Brij-58 and CTAB are 1.81 and 0.50 nm² [26, 29]. Hence, v/al of Brij-58 is smaller than that of CTAB. It follows from Eq. (3) that P_{eff} reaches a higher value than that of P due to the presence of CTAB at the mixed interface and consequently, the mixed systems attain lower droplet size than the single Brij-58/oil(s) system.

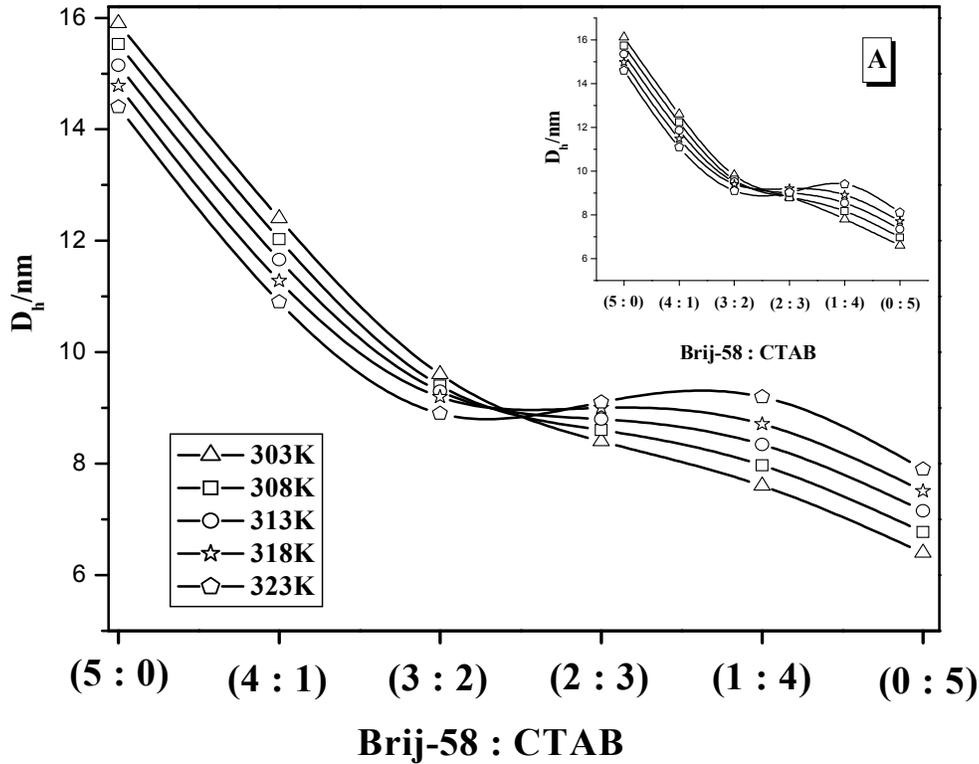


Fig. 3. Plot D_h as a function of mixed surfactant composition for water/Brij-58/CTAB/Pn/Hp or Dc microemulsion systems comprising 5×10^{-4} mol of total mixed surfactant, 2.75×10^{-2} mol of water, 2 ml of Hp or Dc (Inset A) at different temperatures (303K \rightarrow 323K).

3.5.2. Effect of oil on D_h

It can be observed from Fig. 3 that droplet sizes in D_c continuum are larger compared to H_p continuum and can be explained in the following way. It is easier for the solvent with smaller molecular volume (herein, H_p) to penetrate into the hydrocarbon chains of the surfactant(s) existing at the interfacial film of the w/o microemulsions, and, consequently, increases the packing parameter ($P = v/al$) of the surfactant and decrease the diameter of the microdroplets [81]. Similar observation was also reported earlier by Liu et al. [57].

3.5.3. Effect of temperature on D_h

Again, it is evident from Fig. 3 that droplet size (D_h) has been found to decrease with increase in temperature in pure Brij-58 (Brij-58: CTAB = 5:0, w/w) and Brij-58 rich (Brij-58: CTAB = 4:1, w/w) compositions, whereas a reverse effect of temperature on droplet size has been observed for pure CTAB (Brij-58: CTAB = 0:5, w/w) and CTAB rich (Brij-58: CTAB = 1:4, w/w) compositions of the systems in both oils. Further, a negligible effect of temperature on droplet size has been observed in close proximity of equimolar composition of the mixed surfactants (Brij-58: CTAB = 2:3 and 3:2, w/w). This trend can be explained in the following way. It has been observed that n_a^i/n_s values (i.e., compositional variation of P_n at the interface) increase with increase in temperature in Brij-58 rich compositions (Brij-58: CTAB = 5:0 and 4:1, w/w), whereas reverse trend is observed for CTAB rich compositions (Brij-58: CTAB = 0:5 and 1:4, w/w). However, in the vicinity of equimolar composition (Brij-58: CTAB = 3:2 and 2:3, w/w), n_a^i/n_s has been found to be invariant with increase in temperature in both oils (Fig. S4). P_n molecules are mainly located at the micellar interface due to their negligible solubility in water [29]. The total interfacial area becomes larger as alcohol molecules are incorporated at the mixed surfactants interface, which results in increase in the number of droplets and subsequently, the droplet size shrinks. [82]. Further, droplet size depends on the packing parameter (P) of the surfactant(s). The addition of alcohol reduces the average cross-sectional area of the surfactant head group and consequently, effective packing parameter (P_{eff}) becomes larger. This leads to increase in the interface curvature and D_h decreases. Hence, the accommodation of larger P_n molecules at the interface leads to decrease in droplet size [83]. Similar observation was reported earlier by Zhang

et al. [83] for water/AOT/Bu or Pn/IPM microemulsion systems. The polydispersity index (PDI) has been observed in the range between 0.1-0.2, which indicates a monodispersity of the systems [84]. Hence, the reported w/o mixed microemulsions can be exploited as templates for synthesis of the nanoparticle of different sizes.

3.6. FTIR Measurement

It is well known that the nanoscopic confinement of water droplets as well as their sizes has major impact on water hydrogen bond network dynamics regardless of the nature of the interface in w/o microemulsion [85]. But still significant differences in respect of the dynamical nature of water in reverse micelle or w/o microemulsion have been reported for ionic and non-ionic surfactants. Levinger et al. [86, 87] reported that the solvation dynamics of anionic surfactant (AOT) based reverse micelle are slower than nonionic surfactant (Brij-30) based reverse micelle from ultrafast solvation dynamics measurements. This difference in solvation dynamics may be attributed to the difference in interaction between water and charged and uncharged head groups of the surfactants [46]. An interesting question that emerges from these reports is that whether one can tune the dynamics of the confined water in w/o microemulsions by mixing of two surfactants with different charge types. Hence, in order to get a clear picture about the dynamics of the confined water vis-à-vis type of hydrogen bonding network within the water pool of w/o mixed microemulsion systems (water/Brij-58:CTAB/Pn/Hp) as a function of mixed surfactant composition (Brij-58: CTAB = 5:0→0:5, w/w) at fixed water content (2.75×10^{-2} mol), surfactant and cosurfactant mass ratio (1:2) and temperature (303K), we employ a simple noninvasive technique viz. Fourier transform infrared spectroscopy (FTIR). In any reverse micelle or w/o microemulsion formulation, the O-H stretching vibration is a good probe to get an insight into the states of water trapped or confined inside the micellar core. A number of studies have been explored the properties of encapsulated water in a range of sizes and types of w/o microemulsions by FTIR measurement [28, 46, 47, 85, 88]. Small amount of Pn has been used as structure forming cosurfactant in the present study as mentioned earlier. Recently, different states of water species have been reported in single surfactant (CTAB or polyoxyethylene (10) oleyl ether-based) and mixed surfactant [C_n TAB + $C_{16}E_{20}$ (1:1), $n = 12 \rightarrow 18$] w/o microemulsions in presence of cosurfactant (alkanol) [28, 47]. However, the influence of

alkanol vibration on the intensity of O-H stretching vibration of confined water can not be ignored. To get rid of the IR intensity due to O-H stretching vibration of Pn molecule, the spectra of Pn at same concentration has been subtracted from the spectral intensity of O-H stretching band at corresponding ω , and the differential spectra have been analyzed [47]. Different types of hydrogen bonded water molecules exist in reverse micelles or w/o microemulsions, and can broadly be classified into two major classes, namely, head group bound and bulk-like water molecules, as reported earlier by both FTIR and solvation dynamic techniques [46, 47,88]. Hence, the differential spectra obtained in the present study as described above, have been deconvoluted into two peaks at ~ 3500 and ~ 3300 cm^{-1} , corresponding to the O-H stretching frequency of the surfactant head group bound and bulk-like water molecules (droplet core water), respectively [46, 47]. A representative result is depicted in Fig. S6 (Appendix E). Since no coupling effects have been considered, precise calculation of the fractions of different water species cannot be achieved from the present results [89]. However, the values are used for comparative purpose as a measure of the relative abundance of different water species [28, 89].

It is evident from Fig. S6 that the proportion of bound and bulk like water in mixed microemulsion system (Brij-58: CTAB = 5:0 \rightarrow 0:5, w/w) has been found to be affected upon increase in content of CTAB. Further, the decrease in the hydrodynamic diameter (D_h) [15.9 nm (5:0) \rightarrow 6.4 nm (0:5)] has been observed at the prevailing condition as evident from the DLS measurement. It is evident from Fig. S6 that the variation of Gaussian profiles (area fraction) of the normalized spectra of different water species (bound and bulk like water molecules) that the bulk like water and its relative proportion decreases considerably, passing from 58% to 43% with the increase in CTAB content (Brij-58: CTAB = 4:1 \rightarrow 0:5, w/w) vis-à-vis decrease in droplet size from 15.9 nm to 6.4 nm. Meanwhile, contribution of the bound water increases from a proportion of 42% to 57%. In a previous report, FTIR spectra of mixed surfactant (AOT/Brij-30) reverse micelles in isooctane was deconvoluted into two curves peaks at ~ 3300 and 3500 cm^{-1} , with the relative contribution of the former peak (at 3300 cm^{-1}) to be the most prominent one, which indicates the presence of a large fraction of bulk like water in non-ionic rich (Brij-30) composition compare to anionic rich (AOT) composition [46]. On the whole, the features of the FTIR spectra obtained in the present report corroborate well with the

reported system (AOT/Brij-30), although structural variation in polar head groups of AOT and CTAB exists significantly. Hence, it can be inferred that the water molecules interact less strongly with the non-polar head group in comparison to the ionic head group [46]. In a similar experiment, Brubach et al. [85] reported that proportion of different water species significantly changes with the variation of droplet size ($\omega = 1.51 \rightarrow 25.3$, $D_h = 9.4 \text{ nm} \rightarrow 20.9 \text{ nm}$) in nonionic fluorocarbon w/o microemulsion. Further, it was reported that the hydroxyl stretch absorption spectra, vibrational population relaxation times, orientational relaxation rates, and spectral diffusion dynamics as a function of the water nanopool size results in changes from those of bulk properties towards the bound nature as the system moves towards the smaller water nanopool ($\omega = 60 \rightarrow 2$, diameter = $28 \text{ nm} \rightarrow 1.7 \text{ nm}$) for AOT reverse micelles [88]. Hence, it can be concluded that both the parameters, viz., change in mixed surfactant composition (Brij-58: CTAB = 5:0 \rightarrow 0:5, w/w) and droplet size ($D_h = 15.9 \text{ nm} \rightarrow 6.4 \text{ nm}$) significantly affect the dynamics of the confined water vis-à-vis type of hydrogen bonding network within the water pool in mixed surfactant microemulsions.

4. Conclusions

In this report, phase behavior, water solubilization capacity, conductivity, method of dilution, DLS and FTIR techniques were employed for understanding of the physicochemical properties and microstructures of a water-in-oil microemulsion system comprising of Brij-58 and CTAB, and Pn stabilized in Hp or Dc with varying composition (Brij-58: CTAB = 5:0 \rightarrow 0:5, w/w).

Phase study reveals that a single phase (1ϕ) clear microemulsion region has been found to increase with the increase in the ratio of Brij-58 and CTAB in both oils at 303K. Single phase region is larger for Hp stabilized systems compared to Dc stabilized systems. The addition of CTAB in Brij-58/Pn/Hp or Dc microemulsion system induces synergism in water solubilization capacity in the vicinity of equimolar composition (Brij-58: CTAB = 3:2 and 2:3, w/w). The conductivity of mixed surfactant water/Brij-58/CTAB/Pn/Hp or Dc microemulsion with varying composition of surfactant(s) as a function of wt% of water at 303K reveals that the samples chosen from the ascending branch (Brij-58: CTAB = 5:0 \rightarrow 2:3, w/w) of the solubilization capacity versus (Brij-58: CTAB) profile exhibit volume-induced percolation in conductance, whereas no percolation phenomenon

has been observed in the descending branch (Brij-58: CTAB = 1:4→0:5, w/w). Hence, it can be concluded that ascending and descending curves indicate the interdroplet interaction branch (R_c) and the curvature branch (R_o), respectively. The above findings from conductivity measurements also corroborate well with dye solubilization experiment. Understanding of the relationship between microstructure and solubilization capacity of microemulsions is important for preparation and optimization of microemulsions for protein purification process [90] and also for efficient use in drug delivery [91]. Further, FTIR measurements show that bulk water ($\sim 3300 \text{ cm}^{-1}$) and bound water ($\sim 3550 \text{ cm}^{-1}$) gradually decreases and increases, respectively with increasing CTAB content to Brij-58 stabilized systems. It has been argued that the interaction between head group (POE as uncharged) of Brij-58 and water is comparatively weaker than the interaction between charged head group [$\text{N}(\text{CH}_3)_3^+$] of CTAB and water. From the analysis of n_a^i/n_s (compositional variation) and $-\Delta G_t^0$ values (obtained from the dilution method), it can be concluded that the effective binding between CTAB and/or Brij-58 and Pn at the interface increase in the order: 4:1 < 3:2 < 2:3 < 1:4 (w/w). Both n_a^i/n_s and $-\Delta G_t^0$ values increase with increase in temperature for pure Brij-58 and Brij-58 rich systems, whereas reverse trend is observed for pure CTAB and CTAB rich systems in both oils. The phenomenon has been explained from the view point of opposite temperature dependence on the solubility and hydration of ionic and non-ionic surfactants. Both of these properties, have been found to be invariant with increase in temperature (indicating formation of temperature-insensitive microemulsions) in both oils in the vicinity of equimolar compositions (Brij-58: CTAB = 3:2 and 2:3, w/w). Such types of microemulsion formulations have been found to be useful in various commercial and technological processes [92]. The overall transfer process for pure Brij-58 and CTAB systems indicates endothermic and exothermic with positive and negative entropy change, respectively in both oils. However, at compositions in between two extremes, both ΔH_t^0 and ΔS_t^0 values are positive at Brij-58 rich compositions and negative at CTAB rich compositions in both oils. Interestingly, insignificant changes in these parameters with temperature have been observed in the vicinity of equimolar composition (= 3:2 and 2:3, w/w), leading to formation of isenthalpic and isentropic microemulsion systems. Similar to many self-organizing systems, the ΔH_t^0 and ΔS_t^0 values well compensate each

other. It reveals from DLS measurements that D_h decreases remarkably with the increase in CTAB content in the mixed systems at each temperature in both oils. On the other hand, D_h has been found to decrease with increase in temperature in pure Brij-58 and Brij-58 rich stabilized systems, whereas reverse effect of temperature on D_h has been observed in pure CTAB and CTAB rich stabilized systems in both oils. Temperature invariant droplet sizes have also been evidenced in the vicinity of equimolar composition. Also, all these physicochemical parameters have been found to be influenced by oil chain length. The adjustable size of the microemulsion droplets along with the Gibbs free energy change ($-\Delta G_t^0$) [93, 94] could be used for predicting the size of the nanoparticles in mixed surfactant w/o microemulsions, if used as templates. Very recently, it was reported that successful inclusion of 2D allotrope of carbon in CTAB/isooctane/n-hexanol/water microemulsion without compromising the stability of the system, can increase the activity of surface-active enzymes enormously by modulating the amount of cosurfactant at the interface [95]. Further, Singh et al. [96] reported that quantum dots (QDs), which possess potential application in white light emitting devices can be synthesized successfully in CTAB/cyclohexane/1-butanol/water microemulsion systems and the optical properties of QDs can be tuned by changing the experimental parameter, ω (i.e., molar ratio of water to surfactant). In view of these, the evaluation of all these physicochemical and thermodynamic parameters of the present systems could be used as prospective templates for increasing the activity of surface-active enzymes and synthesis of QDs.

References

References are given in BIBLIOGRAPHY under Chapter VII (pp. 253-257).