

Physicochemical investigations of microemulsification of eucalyptus oil and water using mixed surfactants (AOT + Brij-35) and butanol

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Abstract

Microemulsification of a vegetable oil (eucalyptus) with single and mixed surfactants (AOT and Brij-35), cosurfactant of different lipophilicities (isomers of butanol), and water were studied at different surfactant and cosurfactant mixing ratios. The phase diagrams of the quaternary systems were constructed using unfolded and folded tetrahedron, wherein the phase characteristics of different ternary systems can be underlined. The microemulsion zone was found to be dependent upon the mixing ratios of surfactant and cosurfactant; the largest microemulsion zone was formed with 1:1 (w/w) S:CS. The effects of temperature and additives (NaCl, urea, glucose, and bile salts of different concentrations) on the phase behavior were examined. The mixed microemulsion system showed temperature insensitivity, whereas the Brij-35 (single) stabilized system exhibited a smaller microemulsion zone at elevated temperature. NaCl and glucose increased the microemulsion zone up to a certain concentration, beyond which the microemulsion zones were decreased. These additives decreased the microemulsion zones as temperature was increased. The effect of urea on microemulsion zone was found to be insignificant even at the concentration 3.0 mol dm^{-3} . Little effect on microemulsion zone was shown by NaC (sodium cholate) at 0.25 and 0.5 mol dm^{-3} at different temperatures. The conductance of the single (AOT) and mixed microemulsion system (AOT + Brij-35) depends upon the water content and mixing ratios of the surfactants, and a steep rise in conductance was observed at equal weight percentages of oil and water. Viscosities for both single (AOT) and mixed (AOT + Brij-35) surfactant systems passed through maxima at equal oil and water regions showing structural transition. The viscosities for microemulsion systems increased with increasing Brij-35 content in the AOT + Brij-35 blend. Conductances and viscosities of different monophasic compositions in the absence and presence of additives (NaCl and NaC) were measured at different temperatures. The activation energy of conduction (ΔE_{cond}^*) and the activation enthalpy for viscous flow (ΔH_{vis}^*) were evaluated. It was found that both ΔE_{cond}^* and ΔH_{vis}^* were a function of the nature of the dispersion medium. Considering the phase separation point of maximum solubility, the free energy of dissolution of water or oil (ΔG_s^0) at the microdispersed state in amphiphile medium was estimated and found to be a function of surfactant composition.

Keywords: Eucalyptus oil; AOT; Brij-35; Microemulsion; Phase behavior; Additives; Viscosity; Conductivity; Thermodynamics

1. Introduction

Microemulsions are thermodynamically stable, isotropic dispersions of otherwise immiscible oil and water stabilized by surfactants [1]. Owing to their diphilic nature, surfactants distribute their head and tail parts to the corresponding po-

lar and nonpolar solvents forming a monolayer film between them. This decreases the interfacial tension to an ultralow value, which results in the solubilization of the otherwise immiscible components. Generally, a second surfactant, called cosurfactant, is added into the microemulsion system with reference to various applications in pharmacy and drug delivery and, therefore, its role is well documented [2–8]: (i) prevent formation of rigid structures such as gels, liquid crystals, precipitates, etc.; (ii) lower the viscosity of

the system; (iii) reduce interfacial tension; (iv) increase the fluidity of the interface and thereby increasing the entropy of the system; (v) increase the mobility of the hydrocarbon tail and allow greater penetration of the oil into this region; and (vi) influence the solubility properties of the aqueous and oleic phases due to its partitioning between the phases. Several attempts to substitute traditional cosurfactants with other components [9–14], for example, nonionic surfactants, alkanolic acids, alkanediols, amines, aldehydes, ketones, butyl lactate, and oleic acid, have been carried out from the viewpoint of suitable applications of microemulsions. The roles of cosolvents and additives in the preparation of microemulsions are also reported [15–17]. The structural characteristics of microemulsions and their dynamics and transport behaviors with basic understanding of their formation, state of aggregation, internal composition, and stability with reference to their probable uses have been reviewed in detail by Moulik and Paul [18]. Structural studies of microemulsions stabilized by AOT have been reported by Eastoe et al. [19].

As a consequence of many potential advantages of microemulsions (for example, their clarity, high stability and interfacial area, ease of preparation) interest has rapidly grown in the use of microemulsions starting from tertiary oil recovery to nanoparticle synthesis. A comprehensive account of the phase equilibria characterization, structure, uses, and applications of the microemulsions has been reported by Paul and Moulik [20], Sjoblom et al. [21], De and Maitra [22], Solans and Garcia-Celma [23], Solans and Kunieda [24], Mittal and Kunieda [25], and Mittal and Shah [26]. Recently, microemulsions have been employed as liquid membranes [18,25] to study transport behavior of both polar and nonpolar species across them, which have importance in biology for understanding the fundamentals of membrane transport and offers the prospect as a method of separation. In light of the above, several authors have contributed a good number of publications on the formation of microemulsions using biocompatible and nontoxic ingredients (both surfactant and oils) for applications in pharmaceuticals and drug delivery, cosmetics, food, agrochemical, and micellar enzymology [27–38]. Of these, the systematic investigations made by Moulik et al. on the formulation and development of these systems as mentioned above are noteworthy. Moulik et al. [12,27–30] came up with a series of studies on the formulation and development of multicomponent systems containing biologically occurring components (with biocompatibility and nontoxicity) and their stability, physicochemical properties. The active ingredients used in these systems were Tween-20, Tween-60, Brij-30, Brij-52, Brij-92, and sodium oleate as surfactants; ethanol, isopropyl alcohol, and cinnamic alcohol as cosurfactants; and eucalyptus, coconut, ricebran, clove, isopropyl myristate, and saffola as oils. These systems were found to be fairly stable at 37 °C. The physicochemical properties, viz., viscosity, conductance, compressibility, and specific volumes, of these systems have been reported. In recent studies [29,30],

hydrodynamic diameter, diffusion coefficient, and polydispersity of dispersed droplets of different compositions have been determined from dynamic light scattering (DLS) experiments. In addition, the energetic parameters (free energy, enthalpy, and entropy) have been evaluated from calorimetric measurements to aid the understanding of the formation and stability of these systems. An analysis comprising all these data has been rationalized and presented. The activity of enzyme (alkaline phosphatase) [31] and kinetics of alkali fading of crystal violet [28b] in biological microemulsion media containing vegetable oil (clove and ricebran) and cinnamic alcohol [31] have been presented, and a striking difference in the enzymatic process as well as spectral behavior in microheterogeneous media with both hydrocarbon and vegetable oil has been observed.

A vast literature as cited above concerns mainly the use of single ionic or nonionic surfactants to prepare microemulsions using biocompatible and nontoxic ingredients. Such studies, specially microemulsification of plant/vegetable oils using mixed surfactants, have seldom been carried out, though these oils have several uses in pharmaceutical and industrial preparations [39]. In previous studies [40,41], physicochemical investigations on the microemulsification of oils of different types (plant/vegetable, ester of myristic acid, and hydrocarbon) and water using mixed surfactants of different charges with other characteristics and cosurfactants (alkanols and butyl lactate) in the presence and absence of additives have been reported. The phase behaviors of these systems have been represented by Gibbs triangle and fish-tail diagrams and have compared the efficiency of different surfactants (single and mixed) with respect to the area of monophasic region formed. The structural features of these systems have been investigated using conductivity and viscosity measurements.

The present investigation was taken up to microemulsify eucalyptus oil and water by mixed surfactants [AOT, sodium bis-2(ethylhexyl) sulfosuccinate] and nonionic surfactant [Brij-35, polyoxyethylene(23) lauryl ether] and 1-butanol as cosurfactant at different mixing ratios (w/w) of the surfactants as well as at different ratios (w/w) of surfactant and cosurfactant. The phase behaviors of the pseudoternary mixed systems were examined to understand the mutual solubility and topological nature of the multicomponent mixtures using Gibbs triangle and tetrahedral (both unfolded and folded) representations. The effect of mixing ratio of the surfactants, ratio of surfactant–cosurfactant (S:CS), sodium chloride, urea, glucose, sodium cholate at different concentrations, and temperature on the phase behavior of the microemulsion systems are presented. It is expected that the results of present study will be useful in pharmaceutical and related applications. Therefore, information on the phase behavior and stability of the studied microemulsion systems in the presence of additives of biological relevance and importance would be worthwhile. We herein present the

structural aspects of these mixed systems at different compositions from conductivity and viscosity measurements. The activation energy for conduction, the activation enthalpy for viscous flow, and free energy of solubilization of water-in-oil and oil-in-water systems at different compositions are also estimated to underline the overall comprehension of the microemulsification process of a plant oil like eucalyptus oil.

2. Materials and methods

Sodium bis-2(ethylhexyl) sulfosuccinate (AOT), 99%, was obtained from Sigma, USA. Polyoxyethylene(23) lauryl ether (Brij-35) was a product of Fluka. The surfactants were used without further purification. Eucalyptus oil (EO) was obtained from B.D. Pharmaceutical Works, India. It is a volatile, pale yellow liquid having the characteristic odor and taste of punel. It contains not less than 70% (w/w) eucalyptol (or cineole) of chemical name 1,3,3-trimethyl-2-oxabicyclo-(2,2,2)-octane [29,39]. Its boiling point, refractive index, and density agreed nicely with literature values and the material was used without further purification [29]. 1-Butanol, sodium chloride (NaCl), glucose, and urea were products of SRL, India, and were of AR extrapure grade. Sodium cholate (NaC, sodium salt of $3\alpha,7\alpha,12\alpha$ -trihydroxy-5 β -cholanoic acid) was obtained from Sigma, USA. All the products were used without further purification. Double-distilled water with conductance less than $3 \mu\text{S cm}^{-1}$ was used.

To prepare the phase diagrams, a calculated amount of surfactant, cosurfactant, and oil was taken in a sealed tube, shaken vigorously in a vortex mixture, and equilibrated in a thermostatic bath at the desired temperature. Then water was added into it with the help of a microsyringe, and the mixture was shaken vigorously and then placed in a thermostatic bath. Reading of different phases was taken by visual observation, after conformation of attainment of complete equilibrium. Electrical conductivity of microemulsion systems was measured as a function of weight percentage of water with an automatic temperature compensated Thermo Orion (Model 145 A plus) microprocessor conductivity meter, USA, using Orion cell (of cell constant 1.0 cm^{-1}). Specially designed cylindrical vessels with a certain amount of samples were placed in a refrigerated thermostatic water bath at desired temperatures. The samples were equilibrated for at least 10 min to attain the desired temperature before any conductivity readings were done. All the samples were single phase (1ϕ) and optically transparent under the conditions of the conductivity measurements reported here. The uncertainty in measurement is within $\pm 1\%$.

Viscosities of microemulsions were obtained by measuring the flow times in a calibrated Ostwald viscometer having 100-s efflux time for water at different temperatures. Densities of microemulsions were measured with the help of a calibrated pycnometer. The errors in viscosity measurements were $\pm 1\%$.

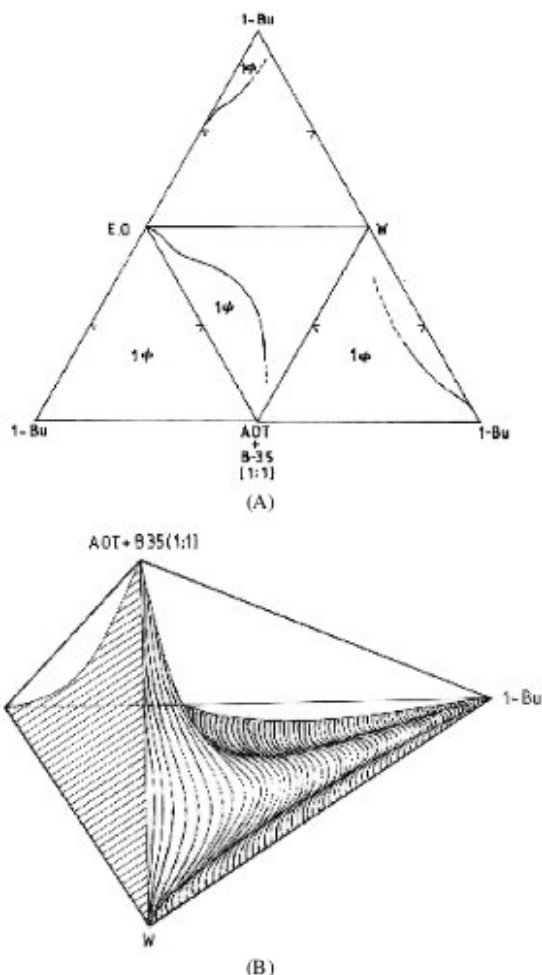


Fig. 1. (A) Unfolded phase tetrahedron with AOT + Brij-35 (1:1, w/w)/EO/water triangles as the base and 1-butanol on top at 303 K. (B) Tetrahedral phase representation of the system AOT + Brij-35 (1:1, w/w)/1-butanol/EO/water at 303 K. The unshaded regions represent clear monophasic domain.

3. Results

3.1. Phase behavior

Fig. 1 represents the unfolded phase tetrahedron of the system AOT + Brij-35 (1:1, w/w) (S)/1-butanol/EO/water at 303 K. Each triangle in the unfolded tetrahedron represents the phase diagram of ternary systems [38]. The uppermost triangle represents the 1-butanol/EO/water system. EO is immiscible in water, but fairly miscible in 1-butanol. A thin monophasic region was formed along the EO–1-butanol axis. The bottom left-hand-side triangle represents the mutual solubility of the S/1-butanol/EO system. It was found that all the components are mutually soluble to all extent and no mutual solubility gap was obtained for this ternary system. The bottom right-hand-side triangle represents the S/1-butanol/water system. 1-Butanol is partially soluble in water [42] and a thin strip of solubility gap was observed along the water–1-butanol axis. The gap was found to be larger for the Brij-35 (single) system and smaller for the AOT (single) system (figure not shown). For the S/EO/water ternary

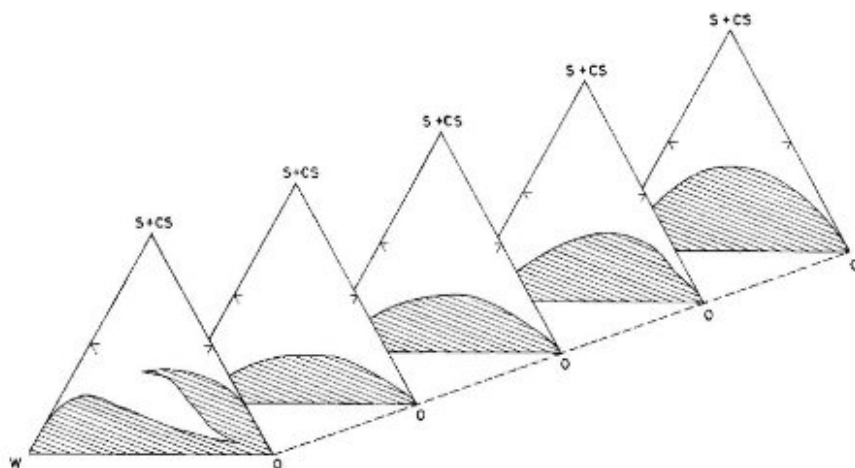


Fig. 2. Triangular phase diagram of AOT/Brij-35/1-butanol/EO/water at 303 K with S:CS = 1:1 (w/w) and varying AOT:Brij-35 ratios (w/w), 1:0, 2:1, 1:1, 1:2, and 0:1 from left to right.

system (middle triangle), it was found that a considerable monophasic zone (1ϕ) was obtained. The monophasic zone was smaller than that formed by AOT alone. The monophasic zone was once more confined to the oil–surfactant axis clearly pointing toward a w/o or L_2 microemulsion formulation. With Brij-35 (single) no monophasic region was obtained. Fig. 1B represents the folded form of the unfolded tetrahedron described in Fig. 1A. The clear area outside the enclosed cage-like biphasic zone represents the monophasic zone. The largest monophasic zone was found along the equal surfactant–cosurfactant region (w/w). The S/1-butanol/water and 1-butanol/EO/water faces were biphasic. The S/1-butanol/EO and S/1-butanol/water faces were mostly monophasic. Such a monophasic zone formed in the tetrahedron was mostly confined between these two faces. Fig. 2 represents the phase diagram (containing Gibbs triangles) for the system AOT/Brij-35/1-butanol/EO/water at 303 K with S:CS = 1:1 (w/w). Five different mixing ratios of AOT and B-35 (1:0, 2:1, 1:1, 1:2, and 0:1, w/w) were used. The terminal two triangles represent systems stabilized by the single surfactants AOT and Brij-35, respectively. AOT formed a large monophasic zone (1ϕ) in the presence of 1-butanol and the extent of the monophasic (1ϕ) zone decreased with increasing extent of Brij-35 into the surfactant mixture. The biphasic region along the water–surfactant axis that appeared in the w/o region for the AOT-stabilized system was not observed for the rest of the systems. In the present study, a microemulsion zone for the mixed surfactant system larger than that for the earlier reported single surfactant systems of Tween 20/1-butanol/EO/water, Tween 20/cinnamic alcohol/EO/water [29], and Brij-30/ethanol/EO/water [30a] was observed.

3.2. Effect of cosurfactant (CS)

Fig. 3A depicts a tetrahedral representation of the phase behavior of the system AOT + Brij-35(1:1)/1-butanol/EO/water at three different S:CS ratios (w/w): 1:1, 1:2, and 1:4. In this system, the extent of monophasic zone decreased

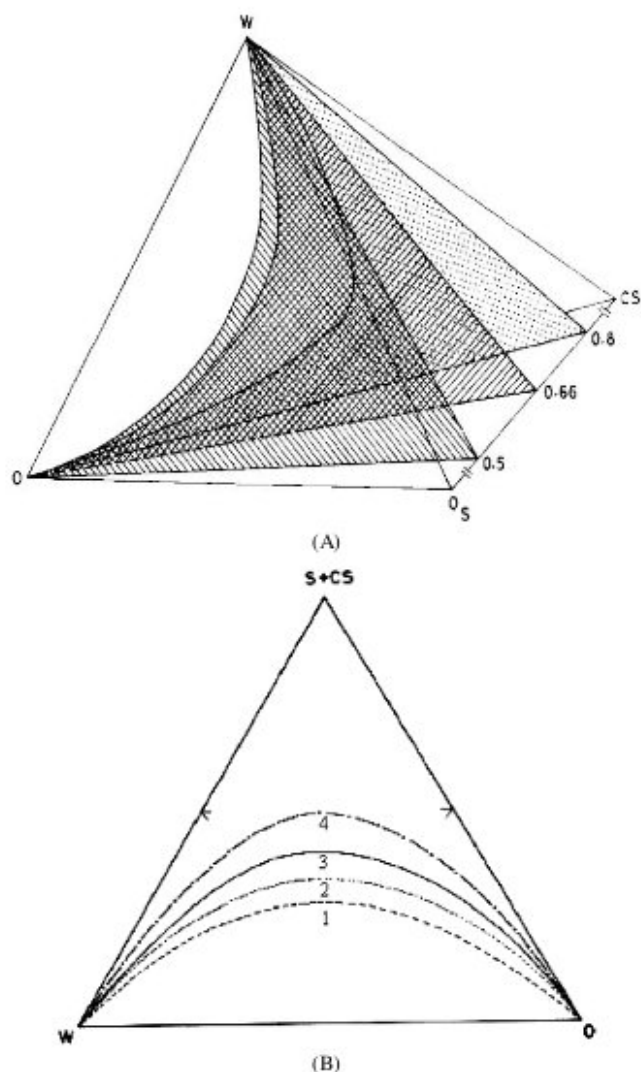


Fig. 3. (A) Tetrahedral representation of AOT/Brij-35/1-butanol/EO/water at 303 K with S:CS = 1:1, 1:2, and 1:4 (w/w). The AOT:Brij-35 ratio was fixed at 1:1 (w/w). The shaded regions represent clear monophasic zone. (B) Triangular phase diagram of AOT + Brij-35 (1:1, w/w)/CS/EO/water with S:CS = 1:1 (w/w) at 303 K with four different CS: (1) 1-butanol, (2) isobutanol, (3) 2-butanol, and (4) *t*-butanol.

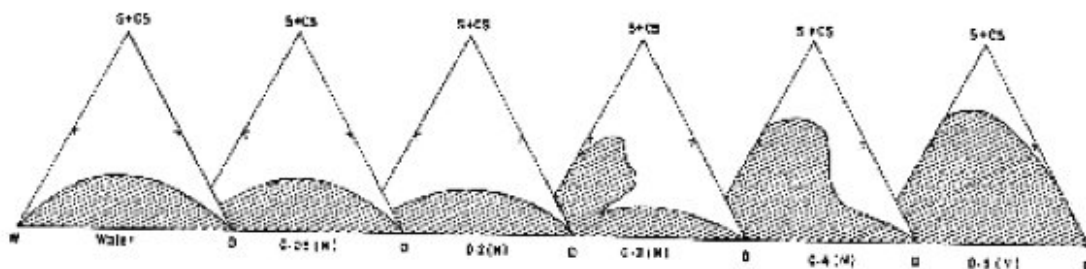


Fig. 4. Triangular phase diagram of AOT/Brij-35/1-butanol/EO/NaCl with S:CS = 1:1 (w/w); AOT:Brij-35 = 1:1 (w/w) at 303 K. Concentration of NaCl: 0.05, 0.2, 0.3, 0.4, and 0.5 mol dm⁻³.

with increasing cosurfactant content. The largest monophasic zone (1ϕ) was obtained at S:CS = 1:1. Single surfactant stabilized systems also followed the same trend (figure not shown) in accordance with earlier reports of Das et al. [43]. In Fig. 3B, the effect of the isomers of butanol (viz., 1-butanol, 2-butanol, isobutanol, and *t*-butanol) on the stability of the microemulsion system AOT + Brij-35(1:1)/CS/EO/water at 303 K with S:CS = 1:1 (w/w) is illustrated. There, 1-butanol formed the largest monophasic zone followed by isobutanol, 2-butanol and *t*-butanol. A similar order has also been observed for the AOT and Brij-35 (single) stabilized systems (figures not shown).

3.3. Effect of temperature

The phase behaviors of the system, AOT and Brij-35 at 1:1 (w/w), butanol, EO and water, were studied at three temperatures, 303, 313, and 323 K (at fixed S:CS ratio of 1:1, w/w). The monophasic (1ϕ) zones for the systems (figure not shown) did not vary much in the studied temperature range. The system with only AOT also exhibited similar temperature independence. But the Brij-35 stabilized system exhibited a decrease in the 1ϕ zone with increasing temperature.

3.4. Effect of NaCl

The phase behavior of the mixed surfactant system is presented in Fig. 4, wherein up to $[\text{NaCl}] = 0.2 \text{ mol dm}^{-3}$ area of the monophasic zone increased. Further increase of $[\text{NaCl}] = 0.3 \text{ mol dm}^{-3}$ decreased it in the o/w region until at $[\text{NaCl}] = 0.5 \text{ mol dm}^{-3}$ only a thin monophasic area was observed. A similar observation was noted for the single surfactant (AOT) system, whereas for the Brij-35 stabilized system, only a little extent of increase of monophasic region was observed with addition of $[\text{NaCl}] = 0.5 \text{ mol dm}^{-3}$. But in the presence of 0.2 mol dm^{-3} NaCl increase of temperature widened the biphasic zones (in the o/w region) of the mixed system (Fig. 5). For the single surfactant system with Brij-35, 0.2 mol dm^{-3} NaCl at S:CS = 1:1 (w/w) the microemulsion zone increased marginally on increasing the temperature from 303 to 313 K, and considerably from 313 to 323 K. For the AOT stabilized system at 0.2 mol dm^{-3} NaCl the monophasic domain shrunk considerably in the o/w region with increasing temperature (figure not shown).

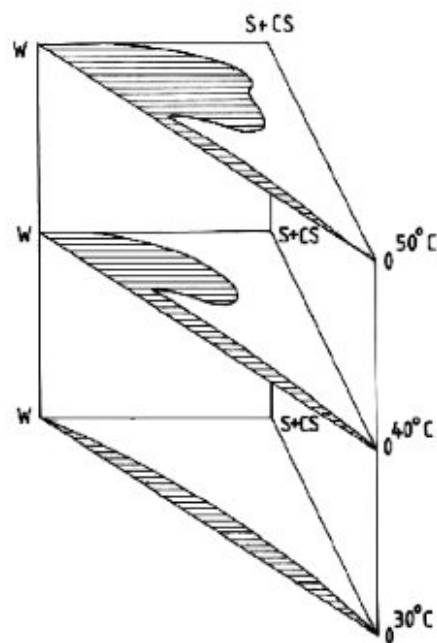


Fig. 5. Triangular phase diagram of AOT/Brij-35/1-butanol/EO/NaCl at 303, 313, and 323 K with S:CS = 1:1 (w/w); AOT:Brij-35 = 1:1 (w/w); concentration of NaCl is 0.2 mol dm^{-3} .

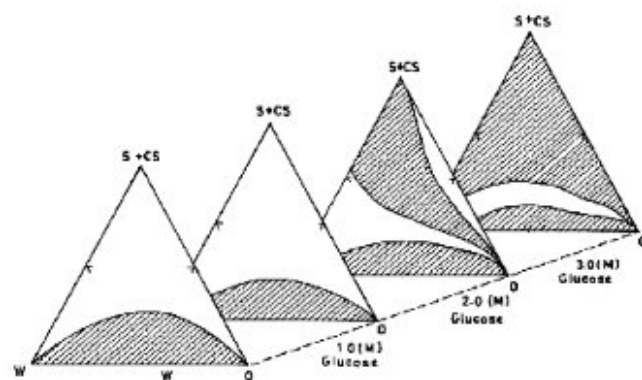


Fig. 6. Triangular phase diagram of AOT/Brij-35/1-butanol/EO/glucose with S:CS = 1:1 (w/w); AOT:Brij-35=1:1 (w/w) at 303 K. Concentrations of glucose: 1.0, 2.0, and 3.0 mol dm^{-3} .

3.5. Effect of glucose, urea, and sodium cholate

Fig. 6 represents the phase diagram of the mixed surfactant system in the presence of glucose at concentra-

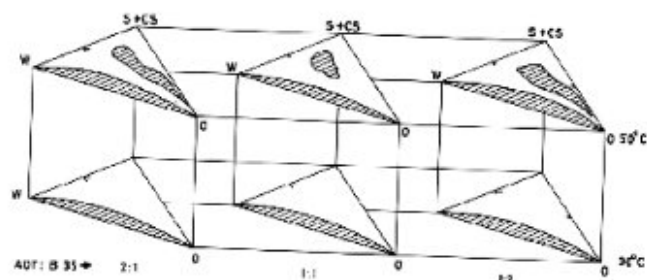


Fig. 7. Triangular phase diagram of AOT/Brij-35/1-butanol/EO/glucose with S:CS = 1:1 (w/w) and AOT:Brij-35 = 2:1, 1:1, and 1:2 (w/w) at 303 and 323 K. Concentration of glucose is 1.0 mol dm^{-3} .

tions 1.0 , 2.0 , and 3.0 mol dm^{-3} at 303 K . At $[\text{glucose}] = 1.0 \text{ mol dm}^{-3}$, the monophasic area increased in comparison with the aqueous system. On further increase to 2.0 mol dm^{-3} , the monophasic area dramatically decreased. Only a thin strip of monophasic zone was observed at 3.0 mol dm^{-3} glucose. Both the single surfactant stabilized systems produced similar behaviors with glucose. The effect of temperature on the phase behavior of the mixed surfactant system with 1.0 mol dm^{-3} glucose at a S:CS ratio of 1:1 (w/w) and three different AOT:Brij-35 mixing ratios, 2:1, 1:1, and 1:2 (w/w), was studied at 303 and 323 K (Fig. 7). The monophasic zone decreased for all three cases when temperature was raised to 323 K. The biphasic zone in the o/w region was found to be the least for the 1:1 mixing ratio compared to 1:2 and 2:1.

The effect of urea up to a concentration of 3.0 mol dm^{-3} on the phase behavior of the mixed surfactant system (not exemplified) was observed to be only mild. A similar effect of urea was observed for both anionic (AOT) and non-ionic (Brij-35) single surfactant stabilized microemulsion systems.

The effect of sodium cholate (NaC, a bile salt) at 0.25 mol dm^{-3} on the phase behavior of the mixed surfactant system at a S:CS ratio of 1:1 (w/w) demonstrated a marginal decrease of the monophasic zone. The increase in temperature from 303 to 323 K insignificantly changed the monophasic zone in the phase diagram. Similar insignificant effect was also demonstrated for the addition of [NaC] up to 0.5 mol dm^{-3} .

3.6. Conductance measurements

Fig. 8 depicts the conductance results of the mixed surfactant system at 303 K at a S + CS weight percent of 40 and a S:CS ratio of 1:1 (w/w). Four different mixing ratios of AOT and Brij-35, viz., 1:0, 2:1, 1:1, and 1:2 (w/w) were chosen for measurements. For all the four mixing ratios the conductivity was initially very low in the oil-rich region, which increased with increasing weight percentage of water. For the AOT system, a sharp increase of conductance with increasing water percentage was observed. After $\sim 30\%$ water, a sharp increase in conductance resembling percolation indicated a structural transition. Such transition for the

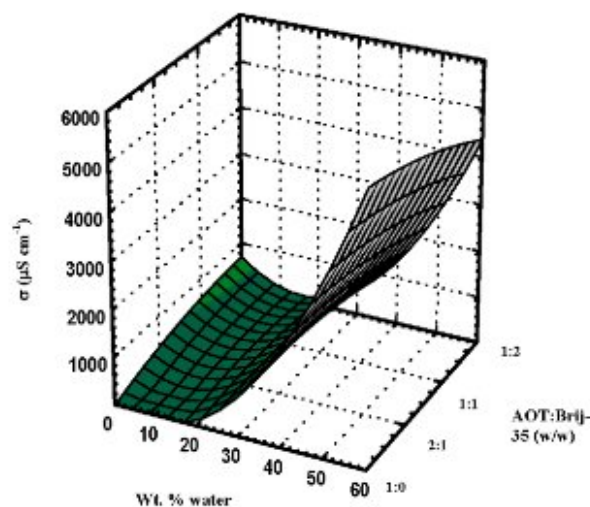


Fig. 8. Conductance of the system AOT/Brij-35/1-butanol/EO/water vs wt% water and AOT:Brij-35 weight ratios (1:0, 2:1, 1:1, and 1:2) with total S + CS = 40% at 303 K.

other mixed (AOT + Brij-35) surfactant systems at different mixing ratios (2:1, 1:1, and 1:2 w/w) was mild. The effect of temperature (298 to 323 K) on conductance for the system AOT + Brij-35/1-butanol/EO/water with varying ratios of AOT:Brij-35 (w/w) (1:0, 2:1, 1:1, 1:2) at three different weight percentage of water (10, 32.5, and 55%) was also studied. For all the studied systems, conductance increased with increasing temperature, but no abrupt change in conductance at a particular temperature (temperature-induced percolation phenomenon) was observed. For the o/w system (55% w/w water), the AOT stabilized system was observed to have the highest conductance values at all the studied temperatures, and the values decreased with increasing weight ratio of Brij-35 in the mixed surfactant. But for the other two compositions (10 and 32.5% water), AOT stabilized systems were observed to have conductance values lower than those of the mixed (AOT + Brij-35) surfactant stabilized systems.

The conductance of the mixed surfactant systems at different temperatures in the presence of additives NaC (0.25 mol dm^{-3}) and NaCl (0.2 mol dm^{-3}) (results not shown) was also studied. Systems containing NaC with composition (S + CS)/O/W = 35/10/55, 35/32.5/32.5, 35/55/10 produced higher conductance compared to the aqueous systems; the increase for the first two compositions was considerable whereas that for the third was marginal. Three compositions for the NaCl systems were chosen as (S + CS)/O/W = 25/65/10, 25/55/20, 25/37.5/37.5. For all the systems conductance increased with temperature, but conductance values were found to be lower than those of the corresponding aqueous systems.

The energetics of conduction flow in microemulsion systems were calculated using an Arrhenius type of equation (see Refs. [12] and [27b]),

$$\sigma = A \exp(\Delta E_{\text{cond}}^* / RT), \quad (1)$$

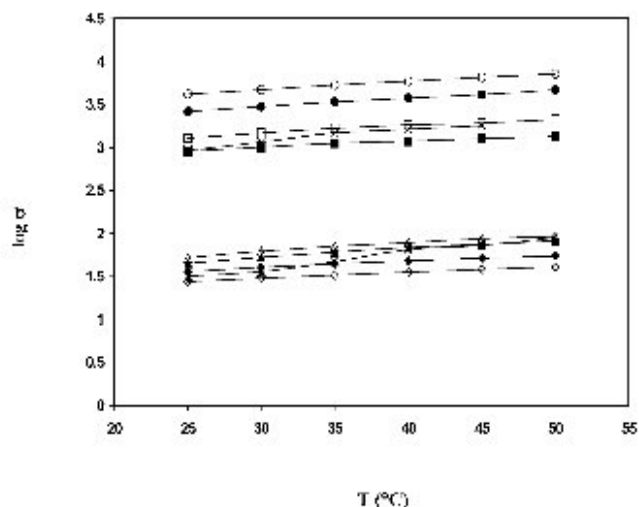


Fig. 9. Conductance vs temperature profile of AOT/Brij-35/1-butanol/EO/water in the presence of additives (0.25 mol dm^{-3} NaC and 0.2 mol dm^{-3} NaCl) at different compositions (S + CS/O/W), (○) NaC (35-10-55); (●) water (35-10-55); (□) NaC (35-37.5-37.5); (■) water (35-37.5-37.5); (△) NaC (35-55-10); (▲) water (35-55-10); (×) NaCl (25-37.5-37.5); (*) NaCl (25-55-20); (◆) NaCl (25-65-10); (◇) water (25-65-10) at AOT:Brij-35 weight ratio of 1:1.

Table 1

Activation energy of conduction (ΔE_{cond}^*) flow of (AOT + Brij-35)/1-butanol/EO/water^a at different mixing ratios (R) of AOT and Brij-35 (w/w)

Composition S + CS/O/W (w/w)	ΔE_{cond}^* (kJ mol^{-1}) ^b			
	AOT	R = 2:1	R = 1:1	R = 1:2
35/10/55	18.3	18.4	18.8	16.1
35/32.5/32.5	23.8	17.4	11.8	10.4
35/55/10	18.9	18.7	17.5	16.1

^a S:CS = 1:1 (w/w).

^b The error limit of ΔE_{cond}^* is $\pm 6\%$.

where σ is the conductance, A is a preexponential constant, and ΔE_{cond}^* is the activation energy of conduction. The plots between $\ln \sigma$ and T^{-1} were obtained for these systems which produced good linear fits (Fig. 9). ΔE_{cond}^* values were calculated from the slopes and are presented in Tables 1 and 2.

3.7. Viscosity measurements

The viscosity of the AOT/Brij-35/1-butanol/EO/water system at different compositions was studied. Newtonian behavior of the fluids was assumed since the systems were found to be low viscous under the studied conditions. Previous studies with microemulsion systems using biocompatible oils like EO, coconut, IPM, and (ricebran + IPM) stabilized by nonionic surfactants (Brij-30, Tween-20, Brij-52 and Brij-92) were found to be non-Newtonian in nature [29,30]. Fig. 10 represents the viscosity values (in cp) of different AOT + Brij-35 mixed surfactant systems at 303 K. The total weight percentage of S + CS was fixed at 40% (w/w). The viscosity curves were all bell-shaped; with

Table 2

Activation energy of conduction^a (ΔE_{cond}^*) and activation enthalpy of viscous flow (ΔH_{vis}^*) of (AOT + Brij-35)/1-butanol/EO/water^b in the presence of additives^c

Composition S + CS/O/W (w/w)	ΔE_{cond}^* (kJ mol^{-1}) ^d		ΔH_{vis}^* (kJ mol^{-1}) ^e	
	NaCl	NaC	NaCl	NaC
25/65/10	26.3	—	22.0	—
25/55/20	42.0	—	27.9	—
25/37.5/37.5	26.0	—	18.9	—
35/10/55	—	17.1	—	27.1
35/32.5/32.5	—	14.6	—	27.2
35/55/10	—	18.2	—	24.6

^a Activation energy for conductance is considered equivalent to the enthalpy of activation as used in the calculation of thermodynamics of the process given in the table.

^b Mixing ratio of AOT and Brij-35 = 1:1 (w/w); S:CS = 1:1 (w/w).

^c [NaCl] = 0.2 mol dm^{-3} ; [NaC] = 0.25 mol dm^{-3} .

^d The error limit of ΔE_{cond}^* is $\pm 4\%$.

^e The error limit of ΔH_{vis}^* is $\pm 6\%$.

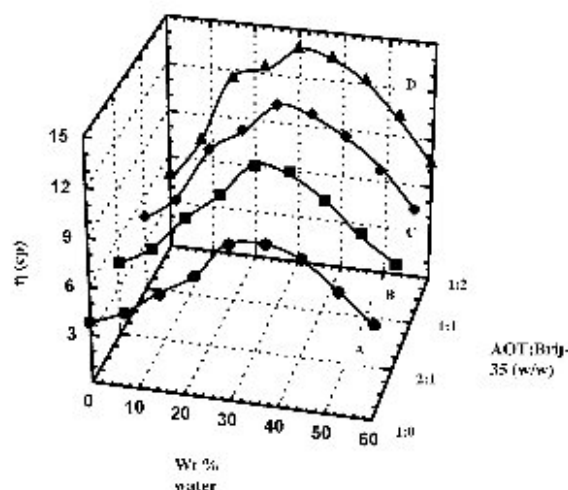


Fig. 10. Viscosity of AOT/Brij-35/1-butanol/EO/water against wt% of water at different AOT:Brij-35 weight ratios: (A) 1:0, (B) 2:1, (C) 1:1, and (D) 1:2, with total S + CS = 40% at 303 K.

increasing weight percentage of water, viscosity of all the systems increased and passed through maxima. The viscosities of the systems at different mixing ratios of individual surfactants (at S + CS = 35%, w/w) were carried out at different temperatures to get the energetics of the viscous flow. Fig. 11 depicts the viscosity behavior of the mixed surfactant systems at different temperatures (298 to 323 K) with three different wt% of water (10, 32.5, and 55%). O/w microemulsion systems have shown viscosities higher than those of the w/o microemulsion systems at all temperatures. However, maximum values of viscosity were obtained for systems containing an equal weight percentage of oil and water at all temperatures and surfactant mixtures.

The viscosity of the mixed surfactant systems with 0.25 mol dm^{-3} NaC produced slightly lower viscosity than that of the system without NaC, except the system with 55 wt% of water (o/w system), in which the NaC-containing system possessed higher viscosity.

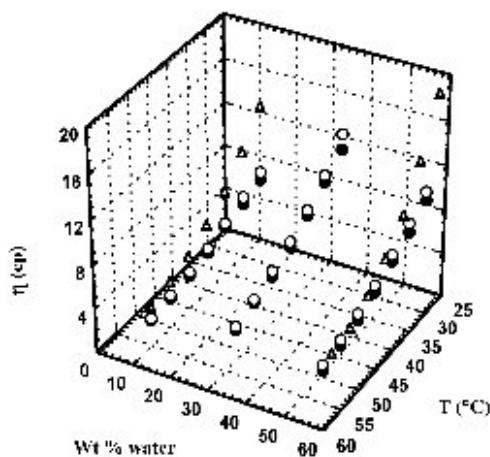


Fig. 11. Viscosity of AOT/Brij-35/1-butanol/EO/water at different temperatures with varying wt% of water with total S + CS = 35%. (Δ) Brij-35; (\circ) AOT + Brij-35 (1:1, w/w); (\bullet) AOT.

The activation enthalpy ΔH_{vis}^* (which can be equated with the energy of activation for viscous flow, ΔE_{vis}^*) was obtained from the equation [29,30]

$$\eta = (Nh/V) \exp(\Delta H_{\text{vis}}^*/RT) \exp(-\Delta S_{\text{vis}}^*/R), \quad (2)$$

where h is the Plank constant, N is the Avogadro number, V is the molar volume, and ΔS_{vis}^* is the entropy of activation for the viscous flow; other terms have their usual significance.

It follows from the equation that

$$\ln \eta = [\ln(Nh/V) - \Delta S_{\text{vis}}^*/R] + \Delta H_{\text{vis}}^*/RT. \quad (3)$$

Assuming ΔS_{vis}^* be independent of temperature, a straight line plot between $\ln \eta$ and T^{-1} is expected from the slope of which ΔH_{vis}^* can be calculated. Herein all the studied systems produced good linear fit for $\ln \eta$ vs T^{-1} (Fig. 12). This observation was in contrast to the reports made by Acharya et al. [30] for microemulsion formulations using EO and other vegetable oils where non-Newtonian flow were observed.

The Gibbs free energy of activation (ΔG_{vis}^*) and the entropy of activation (ΔS_{vis}^*) were obtained from the relations

$$\Delta G_{\text{vis}}^* = RT \ln(\eta V/hN) \quad (4)$$

and

$$\Delta S_{\text{vis}}^* = (\Delta H_{\text{vis}}^* - \Delta G_{\text{vis}}^*)/T. \quad (5)$$

The activation parameters for the viscous flow for different mixed systems at 303 K are given in Table 3.

4. Discussion

4.1. Phase behavior

Addition of ionic AOT to nonionic Brij-35 increased the monophasic domain of the S/1-butanol/EO/water system at

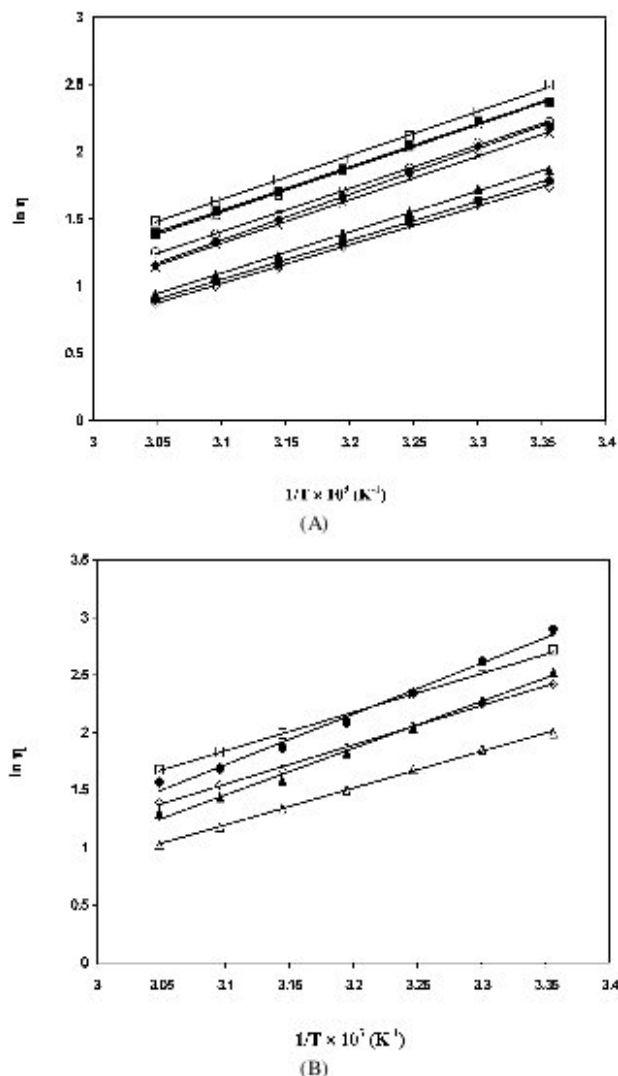


Fig. 12. (A) Plot of $\ln \eta$ vs $1/T$ for different microemulsion systems stabilized by AOT, S + CS/O/W, (\blacklozenge) 35/10/55; (\blacksquare) 35/32.5/32.5; (\diamond) 35/55/10; AOT + Brij-35 (2:1, w/w), (\times) 35/10/55; (\triangle) 35/32.5/32.5; (\bullet) 35/55/10; AOT + Brij-35 (1:1, w/w), (\circ) 35/10/55; (\square) 35/32.5/32.5; (\blacktriangle) 35/55/10. (B) Plot of $\ln \eta$ vs $1/T$ for different microemulsion systems stabilized by AOT + Brij-35 (1:2, w/w), S + CS/O/W, (\diamond) 35/10/55; (\square) 35/32.5/32.5; (\triangle) 35/55/10; Brij-35, (\blacktriangle) 35/7.5/57.5; (\bullet) 35/55/10.

303 K (Fig. 2). AOT formed a considerable L_2 zone in the mixed ternary system (Fig. 1), whereas in its absence the Brij-35 only formed emulsion. Among the isomers of butanol, 1-butanol formed the largest monophasic region (Fig. 3B). These results agreed with our previous work [41] on microemulsion forming systems with anionic (AOT), cationic (CPC), and nonionic (Brij-35) surfactants using the isomers of butanol as cosurfactant. The solubility of these alcohols in water falls in the order t -butanol > 2-butanol > isobutanol > 1-butanol [42]. Due to its higher water solubility, t -butanol molecules moved from the interface to the bulk phases, which in turn caused modification of the interfacial curvature effecting phase separation. Alcohols are reported to be located between the surfactant molecules near the head

Table 3

Thermodynamic parameters for viscous flow of the system AOT/Brij-35/1-butanol/EO/water^a at different mixing ratios (*R*) of AOT and Brij-35 (w/w) at 303 K

Composition (S + CS)/O/W (w/w)	ΔH_{vis}^* (kJ mol ⁻¹) ^b	ΔG_{vis}^* (kJ mol ⁻¹) ^c	ΔS_{vis}^* (J K ⁻¹ mol ⁻¹) ^d
AOT			
35-55-10	24.0	11.1	42.3
35-32.5-32.5	26.9	11.8	49.8
35-10-55	28.4	10.3	59.7
AOT + Brij-35 (<i>R</i> = 2:1)			
35-55-10	24.2	12.0	40.3
35-32.5-32.5	27.3	11.8	50.8
35-10-55	27.0	10.1	55.6
AOT + Brij-35 (<i>R</i> = 1:1)			
35-55-10	25.3	12.3	43.0
35-32.5-32.5	27.4	12.0	50.6
35-10-55	26.8	10.4	54.3
AOT + Brij-35 (<i>R</i> = 1:2)			
35-55-10	26.6	12.6	46.0
35-32.5-32.5	28.1	12.6	51.4
35-10-55	28.4	10.9	58.0
Brij-35			
35-55-10	36.8	13.7	68.4
35-7.5-57.5	34.4	11.7	83.0

^a S:CS = 1:1 (w/w).

^b The error limit of ΔG_{vis}^* is $\pm 4\%$.

^c The error limit of ΔH_{vis}^* is $\pm 6\%$.

^d The error limit of ΔS_{vis}^* is $\pm 8\%$.

groups. But for branched chain alcohols, this configuration is less feasible due to steric difficulty [44]. This might also contribute to the observed result.

4.2. Effect of temperature

According to reports, temperature plays a significant role in solubilization behavior of microemulsion forming systems with special reference to the systems stabilized by nonionic surfactants [45,46]. The hydrophile–lipophile balance of nonionic surfactant changes dramatically with increasing temperature due to the dehydration of the oxyethylene group, which makes nonionic surfactants more lipophilic with increasing temperature. On the other hand, for ionic surfactants, the effect of temperature is less pronounced, and with increasing temperature, the dissociation of ionic group increases and ionic surfactants become more hydrophilic at elevated temperature [47]. In the present study, the Brij-35 stabilized system has been observed to be highly temperature dependent, whereas the AOT and mixed (AOT + Brij-35) stabilized systems were found to be rather insensitive toward temperature. This result highlighted the dominance of ionic surfactant over the nonionic surfactant in the mixed system. Temperature-insensitive microemulsions stabilized by mixed ionic (AOT)–nonionic (dodecylpentaoxyethylene glycol ether, C₁₂E₅) [48] and AOT or SDS/C₁₂EO_{*n*} (where *n* = 2, 3, 6)/brine [49] in hydrocarbon oils have been reported earlier.

4.3. Effect of additives

Inorganic salts are reported to have strong effects on solution behavior of systems stabilized by ionic surfactant [50]. The addition of salt suppresses the dissociation of the ionic hydrophilic group of surfactant and thus makes the surfactant less hydrophilic. Thus, inorganic salts promote cosurfactant penetration into the palisade layer of the surfactant in a water–oil system and the monomeric solubility of cosurfactant tends to decrease [51]. Such effects for nonionic surfactants are less pronounced. The Brij-35 stabilized system was observed to be indifferent toward salinity of the system as expected. For both ionic and mixed systems, the monophasic zones were quenched with increasing [NaCl], specially in the o/w region (Fig. 4). The increasing lipophilicity of the ionic surfactant with increasing electrolyte concentration decreased the water solubility of AOT and hence a biphasic zone was formed in the o/w region. In an o/w microemulsion, the interaction among droplets is generally long-range coulombic repulsion. Increase in electrolyte concentration results in reduction of forces between droplets by shielding polarity of the head group of the surfactant. This may augment a coagulation of droplets and corresponding phase separation [52]. In the present study, the appearance of a biphasic zone in the o/w region for the mixed surfactant system, upon the addition of salt, could be due to the presence of ionic surfactant in the mixture. Hence the dominant role of anionic surfactant in a mixture of (anionic + nonionic, w/w) surfactant was operative. Since

NaCl shields the polar head group of an o/w microemulsion droplet, the cohesive interaction among the droplets increases. With increasing temperature the average kinetic energy of the droplets increases, which in turn may increase the rate of collision among the droplets at an elevated temperature. This may result in a phase separation in the o/w region at a higher temperature (Fig. 5). Glucose molecules are polyols and thereby capable of forming strong hydrogen bonds with polyoxyethylene chains of Brij-35, and hence increased the hydrophilicity of the system. Thus, a reduction in the microemulsion area in the presence of glucose (Fig. 6) was observed. According to Friberg et al. [53] moderate concentrations ($\leq 1.9 \text{ mol dm}^{-3}$) of urea can hardly affect the microemulsion zone for water/tetraethyleneglycol dodecyl ether/Ca-DBS/hexanol-decanol/decane and hexadecane system. But at higher concentrations (6.0 and 8.0 mol dm^{-3}) urea forms a channel compound with hydrocarbons (hexane, heptane, octane) in microemulsion systems stabilized by TX100/butanol/heptane and can disrupt the water structure resulting in a hindrance in micelle formation, and hence can facilitate monophasic formation [54]. Such an increase in monophasic zone has not been observed in the present case. Majhi and Moulik [29] have reported that, at 6.0 mol dm^{-3} , urea marginally increased the monophasic region of the system Tween 20/1-butanol/EO/water and marginally decreased the monophasic area of the system Tween 20/cinnamic alcohol/EO/water at 303 K. Reports are also available which suggest that urea can also decrease the extent of monophasic zone in the microemulsion system TX100/butanol/saffola/water [12]. Mitra et al. [28a] reported that 6.0 mol dm^{-3} urea increased the microemulsion zone of the system Na-oleate/ethanol/clove oil/water. The effect of NaC was quite dissimilar as compared with that of NaCl. This observation supports our earlier studies [40], in which incorporation of NaC to Brij-56/1-butanol/heptane/water was observed to break the hydrophile-lipophile balance by acting as a second anionic surfactant. In aqueous media, bile salts behave in many respects similar to common ionic surfactants due to their amphiphilic nature rather than a common salt like NaCl [55]. On the other hand, there are important differences, such as the pronounced preference of many bile salts to form solution phases rather than lyotropic liquid crystalline phases. This property originates most likely from the molecular architecture of the bile salts, which have a rigid steroid skeleton with a polar surface and an apolar surface instead of the typical "head-and-tail" structure of traditional surfactants. Bile acids do not show a proper CMC but rather a gradual association of low cooperativity [56]. So the phase behavior in the presence of NaC is not similar to that of an electrolyte like NaCl.

4.4. Conductance study

Conductance for the S/1-butanol/EO/water system (where S represents AOT or mixed surfactant) was observed to increase with increasing water content (Fig. 8). For the AOT

system, a sharp increase of conductance with increasing water percentage was observed at about 30% water and 30% oil, which resembled percolation-like phenomenon indicating a structural transition in the bicontinuous form. At higher water percentages, $>30\%$ (o/w microemulsion), conductance decreased in the order $\text{AOT} > \text{AOT} + \text{Brij-35} (2:1) > \text{AOT} + \text{Brij-35} (1:1) > \text{AOT} + \text{Brij-35} (1:2)$. The addition of nonionic surfactant Brij-35 in the o/w system decreased the [AOT] (the charge carrier) at a fixed S + CS concentration and hence conductance decreased. In the region with $<30\%$ water (w/o microemulsion), mixed systems (AOT + Brij-35) produced higher conductance than the AOT stabilized system. The conductance of w/o microemulsion system is mainly driven by the exchange of counterions (or charge carriers) between droplets in close proximity. Incorporation of Brij-56 and Brij-58 into a nonpercolating AOT/IPM/water reverse micellar system made it percolating [57]. This was caused by the increased interfacial fluidity caused by the adsorption of the nonionic surfactants into the interface, which in turn increased the droplet radius, a property guided by the nature and head group area of the added nonionic surfactant. The Brij-35, with a 23 EO chain in the head group, present in the mixed surfactant microemulsion systems herein studied made the interface more fluid and thereby facilitated efficient passage of counterion during interdroplet collision. But with higher water content, the system predominantly became o/w type with charge carriers exposed to the continuous water phase so that the AOT stabilized preparation showed enhanced conductivity than the mixed systems. Also the increased average kinetic energy of the droplets with increasing temperature increased the rate of collision among the droplets resulting in an increase in conductance. In the present study, for the o/w system (55% in an w/w water), the AOT stabilized system was observed to have the highest conductance at all the studied temperatures and the values decreased with increasing weight ratio of Brij-35 in the mixed surfactant. For other two compositions (10 and 32.5% water), AOT stabilized systems were found to have lower conductance than the mixed (AOT + Brij-35) surfactant stabilized systems. The compositions containing 10 and 32.5% water were of w/o and bicontinuous types, respectively, and that with 55% was of o/w type. The conductance results were corroborated by these structural states of the microemulsion systems.

For the systems with equal weight of oil and water [(S + CS)/O/W = 35/32.5/32.5], the ΔE_{cond}^* values were lower than those of the other two systems (w/o, 35/55/10; and o/w, 35/10/55) except for that stabilized by AOT, which produced a higher ΔE_{cond}^* value for the 35/32.5/32.5 system than the other two systems (Table 1). The ΔE_{cond}^* values were found to decrease with increasing Brij-35 content for all the three studied compositions (w/o, o/w, and bicontinuous). The system with NaC produced higher ΔE_{cond}^* (except for (S + CS)/O/W = 35/10/55 composition) than the aqueous systems (Table 2). At all compositions NaCl-containing representatives yielded ΔE_{cond}^* values higher than those of

the aqueous systems (though of not comparable compositions and concentrations), which evidenced lesser availability of Na^+ in reverse micellar environment.

4.5. Viscosity study

The viscosity of the AOT/Brij-35 mixed surfactant system passed through a maximum with increasing water content (Fig. 10). This indicated that the w/o system was converted to the o/w system through a bicontinuous state. Such a behavior was reported earlier for polyoxyethylene [10] oleyl alcohol (Brij-97)/butanol/dodecane/water [58]; SDS/propanol/cyclohexane/water [59]; and CTAB/1-propanol/cyclohexane/water [60] systems. O/w systems have been observed to have viscosity values higher than those of the w/o systems. Viscosity values for a particular weight percentage of water were increased with increasing Brij-35 content in the mixed surfactant. Ajith and Rakshit [61] have also reported that for a mixed SDS + Brij-35/1-propanol/heptane/water system viscosity increased with increasing mole fraction of Brij-35 in the total surfactant content at a fixed microemulsion composition and temperature. The increase in viscosity in oil-rich microemulsions was derived from an increase in dispersed droplet size and enhanced attractive interaction between the droplets [62]. The maxima in viscosity for the studied systems occurred at $\sim 30\%$ water content (Fig. 10) which was well supported by conductance results (Fig. 8), where a structural transition appeared in the 30% water region. Structural transitions from w/o via bicontinuous phase to o/w have been reported by Yagmur et al. [36c] for Winsor IV food grade microemulsions studied by pulsed gradient spin-echo NMR, conductivity, and viscosity measurements. The maximum in viscosity was obtained for systems containing equal weight percentages of oil and water at all temperatures and surfactant mixtures where bicontinuous structure prevailed with radius of curvature tending to infinity resulting in high viscosity.

The ΔG_{vis}^* values steadily decreased with increasing temperature for all the studied systems indicating thinning by the influence of temperature. The positive ΔS_{vis}^* values (Table 3) increased with increasing Brij-35 content in the mixed surfactant for all the compositions, indicating crowding of bulky polar head of Brij-35 at the interface. The ΔH_{vis}^* values of the o/w systems were higher than those of the w/o systems. This observation was quite similar to that of Ajith and Rakshit [61] for Tween 20 + Brij-35/propanol/heptane/water system. ΔH_{vis}^* values increased with increasing Brij-35 content for all the three herein studied compositions (S + CS)/O/W = 35/55/10, 35/32.5/32.5, and 35/10/55). For mixed surfactant microemulsion systems, ΔH_{vis}^* passed through a maximum at equal oil–water (w/w) composition. Addition of Na–cholate did not significantly affect the ΔH_{vis}^* values of the 35/32.5/32.5 system, but that of the 35/10/55 and 35/55/10 systems were slightly higher and lower, respectively, than those of the corresponding aqueous systems.

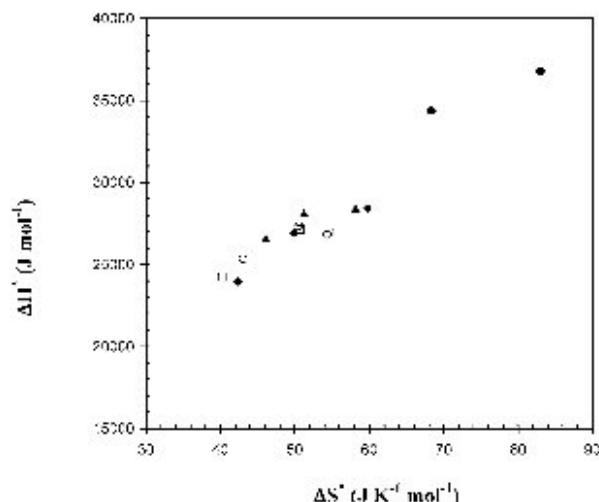


Fig. 13. Plot of ΔH_{vis}^* vs ΔS_{vis}^* for different microemulsion systems. (◆) AOT; (□) AOT + Brij-35 (2:1); (○) AOT + Brij-35 (1:1); (△) AOT + Brij-35 (1:2); (●) Brij-35. A compensation temperature of ~ 309 K was obtained.

The enthalpy–entropy compensation temperature is an important parameter of microemulsion systems. The linearly correlated ΔS_{vis}^* and ΔH_{vis}^* (with a correlation coefficient of 0.9887) for various studied systems at different compositions (mentioned earlier) yielded a compensation temperature of around 309 K (Fig. 13). It refers to an overall temperature that fits the ΔH_{vis}^* and ΔS_{vis}^* data into a linear correlation. In the present case, the value was close to the average of the experimental temperatures, i.e., 313 K. Earlier Acharya et al. [30] obtained compensation temperatures of 298 and 312 K against the average experimental temperatures of 294 and 308 K for viscous flow of Brij-30/ethanol/EO/water and Brij-52/ethanol or isopropanol/coconut oil/water systems, respectively. Such isokinetic effects are very often observed in the dynamics of chemical processes [30,63]. The observed identical compensation temperature for the studied systems revealed interplay of similar internal physical processes.

4.6. Thermodynamics of dissolution

Dissolution of either water in amphiphile/oil medium or oil in amphiphile/water medium up to the phase separation point leading to the formation of w/o or o/w microemulsion can be considered to be the limit of maximum solubility of the dispersing phase. The corresponding free energy of dissolution (ΔG_{s}^0) at a constant temperature T can be obtained from the relation [29,30]

$$\Delta G_{\text{s}}^0 = -RT \ln X_{\text{d}}, \quad (6)$$

where X_{d} is the mole fraction of the dispersed phase (either oil or water) and R is the gas constant. Since the dispersed phase existed in the form of amphiphile-coated droplets, it would be more appropriate to consider X_{d} as the mole fraction of the dispersed droplets. A knowledge of the droplet size was required to estimate X_{d} . This could not be achieved

Table 4

ΔG_s^0 values for the system AOT + Brij-35/1-butanol/EO/water^a at different mixing ratios (*R*) of AOT and Brij-35 (w/w) at 303 K

S + CS wt%	ΔG_s^0 (kJ mol ⁻¹)				
	AOT	R = 2:1	R = 1:1	R = 1:2	Brij-35
O/W systems					
15	9.43	10.9	11.8	12.5	14.9
20	–	9.48	10.5	11.1	12.9
25	–	–	7.60	8.82	11.3
W/O systems					
15	–	1.39	2.00	3.40	5.47
20	–	0.86	1.49	2.29	3.98
25	–	–	1.00	1.4	3.41

^a S:CS = 1:1 (w/w).

at present for want of the necessary facility. The estimation of ΔG_s^0 herein reported was done on the basis of mole fraction of dispersed water or oil. The apparent ΔG_s^0 values reported herein were good enough to exhibit a comparative trend of results obtained under different experimental conditions.

The free energy of dissolution (ΔG_s^0) for both o/w and w/o systems were calculated at three different weight percentage of S + CS (15, 20, and 25%) and the values are given in Table 4. It was found that the ΔG_s^0 values were positive with magnitudes comparable with those reported earlier [29,30]. The o/w systems yielded ΔG_s^0 values higher than those of the w/o systems similar to values obtained by Majhi and Moulik [29] and Acharya et al. [30a]. The ΔG_s^0 values depended on the mixing ratio of the surfactants. They increased with increasing Brij-35 content in the AOT/Brij-35 mixed system and decreased with increasing wt% of S + CS. Ajith and Rakshit [61] calculated the free energy of dissolution at three weight percents of S + CS (40, 50, and 60%) for mixed surfactant microemulsion systems stabilized by (SDS + Brij-35) and (Tween 20 + Brij-35). They also found the Gibbs free energy values to increase with increasing Brij-35 content in the mixed surfactant system. The positive ΔG_s^0 values increased with increasing amount of Brij-35 in the AOT + Brij-35 combination. The phase diagram in Fig. 2 also exhibited a decreased monophasic zone with increasing Brij-35. The ΔG_s^0 values observed in presence of the additives (0.2, 0.25, and 1.0 mol dm⁻³ NaCl, NaC, and glucose, respectively) were also according to their effect on the ternary phase diagrams (Table 5).

5. Conclusions

Large monophasic microemulsion zones were obtained with EO using mixed surfactants AOT + Brij-35 in the presence of 1-butanol. Mixed surfactant systems showed strong resistance toward temperature. The addition of NaCl and glucose caused considerable effect on the phase behavior, whereas that of urea and Na cholate was not significant. Conductance values for AOT-stabilized systems were found to be

Table 5

ΔG_s^0 values for the system AOT + Brij-35/1-butanol/EO/water^a in presence of additives^b at 303 K

S + CS wt%	ΔG_s^0 (kJ mol ⁻¹)					
	NaC		NaCl		Glucose	
	O/W	W/O	O/W	W/O	O/W	W/O
15	11.9	2.40	10.1	0.99	10.5	1.59
20	10.5	2.01	7.37	0.46	8.38	0.90
25	7.75	1.15	–	–	–	–

^a AOT:Brij-35 = 1:1 (w/w); S:CS = 1:1 (w/w).

^b [NaC] = 0.25 mol dm⁻³; [NaCl] = 0.2 mol dm⁻³; [glucose] = 1.0 mol dm⁻³.

less than that for systems containing mixed (AOT + Brij-35) surfactants in the w/o region, whereas in the o/w region the AOT-stabilized system showed the highest conductance. With the addition of water in the mixed systems, a transition from w/o to o/w microstructure was envisaged. The viscosities of both single (AOT) and mixed (AOT + Brij-35) surfactant microemulsion systems passed through maxima at equal oil and water composition showing structural transition. The viscosities of microemulsion systems increased with increasing Brij-35 content in the AOT + Brij-35 blend and decreased with increasing temperature for all the studied systems. The activation energy of conductance (ΔE_{cond}^*) and the activation enthalpy for viscous flow (ΔH_{vis}^*) were found to be composition dependent. The ΔG_s^0 of either water or EO in the surfactant–oil or surfactant–water combination was also composition dependent, and the Gibbs free energy of solution of oil was more positive than the solution of water in the mixed surfactant–dispersant systems.

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