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Conductivity of reverse micellar systems of water/AOT + Brij-56 or Brij-58/IPM and their percolation under varied concentrations of amphiphiles and different additives

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Abstract

The conductivity of AOT/Brij-56 or Brij-58/IPM/water reverse micellar systems as a function of temperature, ([water]/[AOT + Brij]) and $X_{\text{non-ionic}}$ (mole fraction of non-ionic in total surfactant) has been studied. The addition of non-ionic surfactants (Brij-56 and Brij-58) exhibits temperature-induced percolation in conductance in non-percolating AOT/IPM/water system at constant compositions (i.e. at fixed total surfactant concentration, ω and $X_{\text{non-ionic}}$). The influence of total surfactant concentration (micellar concentration), water content (ω) and content of non-ionic surfactants on the temperature-induced percolation behaviors of these systems have been investigated. The effect of Brij-58 is more pronounced than that of Brij-56 in inducing percolation. The threshold percolation temperature, T_{p} has been determined for these systems in presence of additives of different molecular structures, physical parameters and/or and interfacial properties. The additives have shown both assisting and resisting effects on the percolation threshold. The additives, bile salt (sodium cholate), urea, formamide, cholesteryl acetate, cholesteryl benzoate, toluene, a triblock copolymer (pluronics, L64), polybutadiene, sucrose esters (sucrose dodecanoates, L-1695 and sucrose monostearate S-1670) and formamide distinctively fall in the former category, whereas sodium chloride, cholesteryl palmitate, crown ether and ethylene glycol constitute the latter for both systems. Sucrose dodecanoates (L-595) had almost marginal effect on the process. The activation energy, E_{p} for the percolation process has been evaluated. E_{p} values for the AOT/Brij-56 systems have been found to be lower than those of AOT/Brij-58 systems. The concentration of additives influence the parameters T_{p} and E_{p} for both systems. A preliminary report on the percolation phenomenon in mixed reverse micelles in presence of additives has been suggested on the basis of these parameters (T_{p} and E_{p}).

Keywords: Mixed reverse micelles; Threshold percolation temperature; Activation energy; Additive effects; AOT; Isopropyl myristate

1. Introduction

Surfactants associate to form reverse micelles (RMs) in non-polar solvents containing a small amount of water with their polar head groups directed towards the aqueous phase and the hydrophobic tails extending outward into the bulk organic solvent phase. RMs can solubilize an appreciable amount of water to form a spherical pool in its centre with low polydispersity. The entrapped water is heterogeneous in nature and its properties gradually change as a function of ω ([H$_2$O]/[surfactant]), and depends on the distance from the polar head layer [1–3]. Shape and sizes of surfactant aggregates depend strongly on the type and concentration of surfactant, on the nature of the counterion and external solvent [4,5] and the presence of a third component [6]. Recent years have witnessed an increasing interest in reverse micelles due to their variety of chemical [3,7–9], photochemical [2,7,10,11], solubilization media for proteins, amino acids and enzymatic reactions [3,9,12–14] in reverse micelles. Furthermore, water entrapped in such aggregates is thought to mimic water close to biological membranes or proteins [1].

Research in the internal dynamics of reverse micelles has largely been concentrated on the phenomenon of electrical percolation characterized by sudden increase in electrical conductivity when either the temperature or the volume fraction of the dispersed phase reaches a certain threshold value. The nature and the basic understanding of the percolation process have been investigated by a number of research workers [15–20]. The enhanced conductance has been considered to take place by

the formation of infinite clusters/association of dispersed water droplets (stabilized by the amphiphiles) in the oil continuous medium. The easy flow of charges (ions) takes place by "hopping" [21–24] from droplet to droplet or are transferred by way of "fusion, mass transfer and mass exchange" [25–29]. As a consequence of the ion transfer, the conductance (σ) can be enhanced by 100–1000-fold. The water content [30] and other environmental conditions, such as temperature [31–34], pressure [35] and the presence of additives control the percolation thresholds.

One of the most commonly used surfactant is AOT [bis(2-ethylhexyl) sodium sulfosuccinate], which can form reverse micelles under wide range of conditions (such as water content, temperature, solvent, electrolyte type and concentrations) without the need of a cosurfactant [36]. Over the past decade a number of studies have been carried out on the effects of various kinds of additives on the electrical conductivity and other properties of water/AOT/hydrocarbon oils reverse micelles by several researchers, viz. Moulik et al. [29,32,37–41], Maitra and co-workers [42]; Garcia-Rio et al. [43–46], Dutkiewicz and Robinson [28], Meier [47], Schubel and Ilgenfritz [48], Wiens and Somasundaran [49], Pileni et al. [50], Papadimitriou et al. [51], Yang et al. [52] and Eicke et al. [53] with a view to understand the roles of additives on percolation, considering that the additives might modify the amphiphilic region and thereby affect the percolation process. The phenomenon has been shown to occur earlier (assistance) or be delayed (retardation) in presence of additives; however, many of them remained totally ineffective. The mechanism proposed by the authors to explain the phenomenon of percolation of conductance in w/o microemulsions or reverse micellar systems was based on either by "transient-fusion-mass transfer-fission" model or by "hopping" model. In most of the cases the former was found to be valid. Of these studies, the work of Moulik et al. [29,32,37–41], Garcia-Rio et al. [43–46] are noteworthy. Moulik et al. [29,32,37–41] made a systematic investigation on the determination of the percolation threshold, performance of scaling equation, the evaluation of the activation energy for percolation, energetics of the droplet clustering, and the dimension, polydispersity and diffusion coefficient of water/AOT/hydrocarbon oils in absence and presence of additives of different types. Temperature-induced percolation of water/AOT/isooctane water-in-oil microemulsion have been reported in the presence of various kinds of additives (such as ureas, thioureas, formamides, ethylene glycol, inorganic salts, crown ethers, kryptand complexes and alkylamides) by Garcia-Rio et al. [43–46].

Investigations on the microstructures and properties of reverse micelles formed with mixed surfactants (i.e. addition of a second surfactant to water/single surfactant/oil system) has seldom been carried out to understand the basic mechanism of the phenomenon taking place inside them. However, reports available on the latter aspect are due to Alexandradis et al. [33], Nazario et al. [54], Eicke et al. [55], Li et al. [56,57], Liu et al. [58–60] and Bumajdad et al. [61].

In our previous studies [62,63], the solubilization behavior of water in anionic (AOT) or cationic (DDAB)/non-ionic

surfactants (of different chemical structures and physicochemical properties) mixed reverse micellar systems stabilized in isopropyl myristate (IPM), isobutyl benzene (IBB) and cyclohexane (Cy) at 303 K has been reported. The mechanism of the solubilization process has been quantitatively interpreted from the percolative conductance in these systems. In continuation of these previous reports, a preliminary study on the temperature-induced percolation behavior of AOT reverse micelles in presence of non-ionic surfactant Brij-56 or Brij-58 in a non-toxic oil IPM, which is widely used in biologically resembling systems, pharmaceuticals and drug delivery [64,65] would be of much importance and significance. Moreover, the study on the effect of additives on the percolation of conductance in mixed reverse micelles has not been reported so far.

In view of the above, the objective of the present study is to measure the electrical conductivity of the AOT/Brij-56 or Brij-58/IPM/ water reverse micellar systems at various temperatures vis-à-vis to determine the threshold percolation temperature (T_p) as a function of surfactant concentrations, content of non-ionic surfactant ($X_{non-ionic}$), water content (ω) and additives of various types with different physical parameters or interfacial properties, as they can alter the texture of the interface. Besides, some of these additives are frequently used in the study of mass transfer processes. This has prompted us to study this area to gain a preliminary understanding of the percolation phenomenon in mixed reverse micellar systems. The activation energy for percolation of conductance of these systems can be interesting and instructive to interpret the percolation phenomenon. Hence, the activation energy has been estimated in presence of additives.

2. Experimental

2.1. Materials and methods

The following surfactants were used without further purification, sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 99%) was purchased from Sigma, USA. Polyoxyethylene (10) cetyl ether (Brij-56), polyoxyethylene (20) cetyl ether (Brij-58) are products of Fluka (Switzerland). Toluene (Tl), benzyl alcohol (BA), formamide (FA), ethylene glycol (EG), urea and NaCl are products of SRL, India and are of AR and extrapure grade. Isopropyl myristate (IPM) is a product of Fluka. Two types of sucrose dodecanoates, (L-1695 and L-595) and sucrose monostearate ($C_{18}S_E$, S-1670) were gifted by Mitsubishi Chemical Corporation, Yokohama, Japan. L-1695 is the mixture of 83.6% sucrose monododecanoate, 15.2% didodecanoate and 1.2% tridodecanoate. L-595 is the lipophilic sucrose multi-dodecanoate and the contents of monoester, diester and triester are 30.0, 39.3 and 30.4%, respectively. A polymeric surfactant [a triblock copolymer $(EO)_{13}(PO)_{30}(EO)_{13}$, Pluronic L64, MW = 2900], polybutadiene (PBD) and dicyclohexano-18-crown-6 (crown ether, CE) are products of Fluka. Cholesterol (Ch) and its derivatives (cholesteryl acetate, CA; palmitate, CP; benzoate, CB) and sodium cholate (NaC) are products of Sigma. Double distilled water was used with conductance less than $3 \, \mu S \, cm^{-1}$.

2.2. Solution (sample) preparation

The reverse micellar systems were prepared using the blends of AOT and Brijs at specified concentration of the surfactant(s) in IPM oil, and then adding calculated amount of water using a microsyringe to obtain the desired ω (=[water]/[surfactant(s)]), in presence of additives (depending upon their solubilities in water and oil) at different concentration levels.

2.3. Measurements

Electrical conductance measurements of samples (in absence and presence of additives) were carried out as a function of temperature or otherwise using an automatic temperature compensated conductivity meter with Thermo Orion, USA (model 145A plus), with cell constant of $1.0\,cm^{-1}$ with uncertainty in measurement within $\pm 1\%$. Dependence of conductivity on temperature at fixed ω, was investigated by changing the temperature in the range of (5–60 °C) in small intervals in a thermostatic water bath accurate to ± 0.1 °C under electromagnetic stirring to eliminate the temperature difference in the conductance cell. The samples were equilibrated for at least 10 min after any temperature change and before any conductivity reading was done; three reading were made for each temperature. All the samples were single phase and optically transparent under the conditions of the conductivity measurements reported here. Differential curve [i.e. $\Delta\sigma/(\sigma\Delta T)$ against T] has been constructed to determine T_p for each system [24].

3. Results and discussion

3.1. Effect of temperature on the conductivity of AOT + Brij-56 or Brij-58 reverse micellar system stabilized in IPM and water

The conductivity of AOT/IPM/water system as a function of temperature has been measured at three different surfactant concentrations (0.25, 0.175 and $0.1\,mol\,dm^{-3}$). It is observed that the system is low conducting and does not exhibit any significant increase in conductivity with temperature (figure not shown). However, the addition of a second surfactant (Brij-56 or Brij-58) to the AOT/IPM/water system with the total (AOT + non-ionic) surfactant concentration ($[S_T]$) as mentioned above and at a fixed $X_{non-ionic} = 0.1$ and $\omega = 20$, a dramatic increase in conductance behavior is observed as a function of temperature (except for AOT/Brij-56 system with $0.1\,mol\,dm^{-3}$ surfactant concentration). The results are depicted in Fig. 1A. The threshold percolation temperature, T_p is exhibited at 23.3 and 34.5 °C for AOT/Brij-56 system, whereas for the AOT/Brij-58 system, T_p is observed at 12.7, 17.4 and 26.8 °C at the corresponding compositions, respectively. The percolation of conductance in reverse micellar systems can be assumed to be a transition from a w/o droplet like structure to a bicontinuous or connected clusters of droplet like microstructure. Owing to its wedge shape, AOT tends to bend around water-in-oil continuous phase forming an interfacial film of negative curvature at the oil–water interface. Electrical conductivity in an AOT-based microemulsion is due
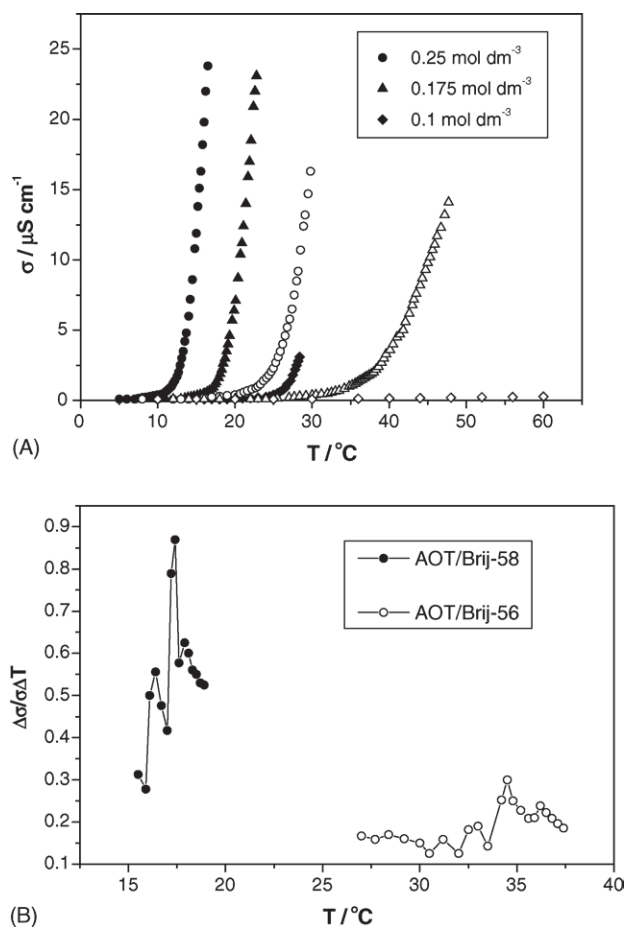

Fig. 1. (A) Conductivity as a function of temperature for AOT/Brij-56 (or Brij-58)/IPM/ water mixed reverse micellar systems at different surfactant (micelle) concentrations with $\omega = 20$ and $X_{Brij} = 0.1$. Open symbols represent Brij-56 systems and closed symbol represent Brij-58 systems. (B) Differential plot for determination of threshold percolation temperature.

to the passage of cations through the transient channels formed between colliding droplets [44]. This passage is facilitated by the formation of the certain local region of positive curvature in AOT surfactant film [66]. The rigidity of the interface and the attractive interactions among the aggregates are the most important factors that determine the exchange rate of the ions and water molecules during the fusion processes [56,57]. The AOT/IPM reverse micellar system can be assumed to be so rigid that it cannot form any such fused droplet network to facilitate percolation. Since IPM possesses high molar volume as well as high viscosity, penetration of this oil into the interface is relatively small [67], which in turn perhaps fails to modify the interface less effectively, which makes the AOT/IPM system non-percolating. The high viscosity of IPM also makes it is difficult for the droplets to collide and aggregate into clusters [60] which in turn makes the AOT/IPM system non-percolating. But addition of Brij-56 and Brij-58 modifies the interface in order to make it less rigid and consequently induce percolation of conductance. It has been observed that the T_p decreases with increase in total surfactant concentration $[S_T]$ for both the systems. High surfactant concentration causes an increase in the number density of the droplets in reverse micellar systems. This

increases interaction between the droplets facilitating percolation by increasing interdroplet collisions and lowering the barrier to electrical conductivity [49,60]. It can further be observed that AOT/Brij-58 system exhibits percolation in conductance at a lower T_p than the AOT/Brij-56 systems for a comparable composition. The droplet size of reverse micellar system depends upon the flexibility of the interface, which in turn is related to the surfactant packing parameter (P) given by the relation [68],

$$P = \frac{v}{al_c} \qquad (1)$$

where a, v and l_c are the area of the head group, volume and chain length of the surfactant (herein AOT), respectively. Lower the value of P, higher would be the interfacial flexibility, and consequently percolation would be facilitated. For a mixed surfactant system (herein AOT + Brij), the packing parameter gets modified due to the presence of different surfactants at the interface and the modified packing parameter (P_{eff}) can be expressed according to the following relation as obtained by Evans and Ninham [69]:

$$P_{eff} = \frac{(xv/al_c)_A + (xv/al_c)_B}{x_A + x_B} \qquad (2)$$

where x_A and x_B are the mole fractions of AOT and Brij present at the interface, respectively. It has been shown that v/al_c of non-ionic surfactants decreases with increased EO chain length and is smaller than that of the ionic surfactant AOT [58]. It follows from Eq. (2) that due to the presence of Brij at the AOT/Brij mixed interface, P_{eff} takes up a lower value than that of P, and consequently the mixed systems acquire larger droplet size than the single AOT/IPM system. Our observation may further be supported by the work of Nazario et al. [54]. They showed that addition of non-ionic surfactant, C_iE_j (polyoxyethylene alkyl ethers) at different micelle concentrations at fixed ω, influenced the percolation temperature on temperature-induced percolation of water/AOT/isooctane reverse micelles. In a subsequent study, they proposed a model that C_iE_j resides at the interfacial region with either immersing its polar head group in the water pool or the polar head group lies in the vicinity of the head group region of the surfactant, AOT using the iodine-laser temperature jump (ILTJ) technique [70]. Both of these configurations supported the increase in droplet size with increasing head group of the non-ionic surfactant as evidenced from DLS measurements, and this in turn assisted percolation. Increase in the radius of droplet with the addition of non-ionic surfactants (Brijs type) into the AOT/heptane/water system has also been reported by Liu et al. [58] from DLS measurements. The droplet size was dependent on the content of the non-ionic surfactant and their EO chain length.

3.2. Influence of content of non-ionic surfactant and POE chain length on the percolation of conductance in AOT/Brij(s) mixed reverse micelles

Fig. 2A and B depicts the conductivity behavior of AOT/Brij-58 (or Brij-56)/IPM/water system as a function of temperature at
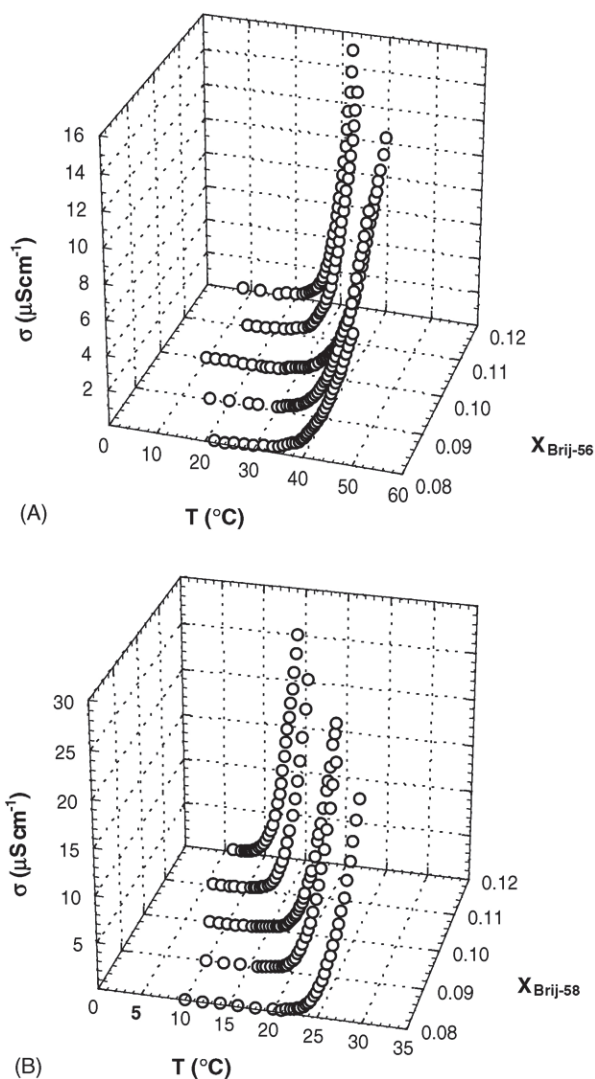

Fig. 2. Conductivity as a function of temperature for AOT/Brij(s)/IPM/water mixed reverse micellar systems at different content of Brij-56 and Brij-58 with surfactant concentration of 0.175 mol dm⁻³ and $\omega = 20$: (A) AOT/Brij-58 and (B) AOT/Brij-56.

five different mole fractions of Brij ($X_{Brij} = 0.08$, 0.09, 0.1, 0.11 and 0.12) at a fixed $[S_T] = 0.175$ mol dm⁻³ and $\omega = 20$. It has been found that T_p decreases with increase in X_{Brij} for both the systems (Table 1). It is evident from Eq. (2) that with increase in X_{Brij}, P_{eff} decreases compared to the AOT/IPM/water system and thereby percolation is facilitated. In order to understand the relative effect of the non-ionic content on percolation threshold (T_p), the relative change in θ_p (percolation threshold temperature in Kelvin scale) ($\Delta\theta_p/\theta_p$) has been plotted against X_{Brij}, where θ_p is the percolation temperature with $X_{Brij} = 0.1$ and $\Delta\theta_p = \theta_p' - \theta_p$, where θ_p' is the percolation temperature at any X_{Brij}. The results are depicted in Fig. 3. It is evident that Brij-58 influences θ_p more effectively than Brij-56 at a particular X_{Brij}. This strongly supports the earlier statement that larger the head group of non-ionic surfactant, larger is the droplet radius, and hence the influence on conductance percolation in mixed micellar systems is more prominent.

Table 1
Percolation threshold (T_p) and activation energy (E_p) for AOT/Brij mixed surfactant systems with different mole fraction (X) of Brij at $[S_T] = 0.175$ mol dm^{-3}

$X_{non-ionic}$	AOT/Brij-56/IPM/water			AOT/Brij-58/IPM/water		
	T_p (°C)	E_p (kJ mol^{-1})	Corr. coefficient	T_p (°C)	E_p (kJ mol^{-1})	Corr. coefficient
0.08	40.2	159.8	0.9903	24.0	404.4	0.9889
0.09	37.5	189.1	0.9873	20.3	460.1	0.9912
0.1	34.5	176.3	0.9923	17.4	396.5	0.9917
0.11	29.0	246.3	0.9955	13.4	488.2	0.9872
0.12	26.1	290.2	0.989	10.1	527.2	0.993

3.3. Influence of water content (ω) at a fixed $X_{non-ionic}$ on the percolation of conductance in AOT/Brij(s) mixed reverse micelles

The conductivity of AOT/Brij-56/IPM/water system at different ω values (20.0, 22.5, 25.0, 27.5 and 30.0) with a total surfactant concentration of 0.175 mol dm^{-3} at $X_{Brij} = 0.1$ as function of temperature has been investigated. The results are presented in Fig. 4. The corresponding T_p values are obtained at 33.4, 26.9, 22.0, 15.7 and 11.7 °C, respectively. It has been found that T_p decreases with increasing ω. The droplets of w/o microemulsions can be assumed to be spherical and increase linearly with increasing ω [39,71]. This in turn increases the droplet interaction facilitating the overlapping of the droplets and percolation initiates at a lower temperature. This observation is supported by other workers [33,38–41,54,60].

3.4. Influence of third component (additives) on the percolation of conductance in AOT/Brij(s) mixed reverse micelles at fixed ω and $X_{non-ionic}$

The results of the effect of additives on the percolation of conductance in AOT/Brij-56 or Brij-58 mixed reverse micelles in IPM at $\omega = 20$ and $X_{Brij} = 0.1$ as a function of temperature are presented in Figs. 5–7 and Table 2 and summarized as follows. Addition of NaC (20.0 mmol dm^{-3}), urea (100 mmol dm^{-3})

and formamide (200 mmol dm^{-3}) reduces T_p (15.1, 15.5 and 15.5 °C, respectively, for AOT/Brij-58 system, and 32.0, 32.1 and 28.0 °C, respectively, for AOT/Brij-56 system), whereas addition of NaCl (25.0 mmol dm^{-3}) increases T_p (20.1 and
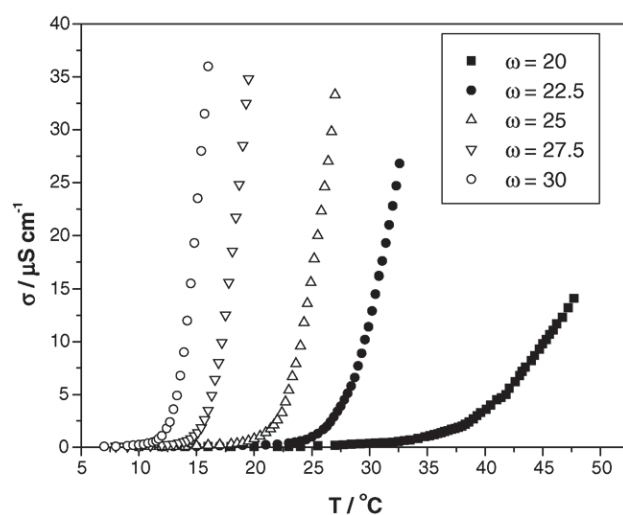
Fig. 4. Conductivity as a function of temperature for AOT/Brij-56/IPM/water mixed reverse micellar systems a different water content (ω) with total surfactant concentration 0.175 mol dm^{-3} and $X_{Brij-56} = 0.1$.

Fig. 3. Relative change in percolation threshold (see text) for AOT/Brij(s)/IPM/water mixed reverse micellar systems with surfactant concentration of 0.175 mol dm^{-3} and $\omega = 20$.

Fig. 5. Conductivity as a function of temperature for AOT/Brij-56 (or Brij-58)/IPM/water mixed reverse micellar systems in presence of additives (urea, NaC, NaCl and FA) with total surfactant concentration 0.175 mol dm^{-3}, $\omega = 20$ and $X_{Brij} = 0.1$. Open symbols represent Brij-56 systems and closed symbol represent Brij-58 systems.

Fig. 6. Conductivity as a function of temperature for AOT/Brij-56 (or Brij-58)/IPM/water mixed reverse micellar systems in presence of additives (Ch, CA, CB and CP) with total surfactant concentration 0.175 mol dm^{-3}, $\omega = 20$ and $X_{Brij} = 0.1$. Open symbols represent Brij-56 systems and closed symbol represent Brij-58 systems.

40.0 °C for AOT/Brij-58 and AOT/Brij-56 systems, respectively) (Fig. 5; Table 2). The effect on T_p is more pronounced at higher concentrations of additives. NaC (40.0 mmol dm^{-3}) and urea (20.0 mmol dm^{-3}) reduce T_p (12.5 and 25.0 °C for AOT/Brij-58 and AOT/Brij-56 systems, respectively) (Fig. 5).

Fig. 6 depicts the influence of cholesterol and its derivatives (Ch, CA, CB and CP) on T_p for both AOT/Brij-56 and AOT/Brij-58 systems at the compositions mentioned earlier. Addition of Ch (13.0 mmol dm^{-3}) increases T_p (20.1 and 40.5 °C, respectively) for both these systems. With a further increase in the concentration of Ch (26.0 mmol dm^{-3}), the influence is much more pronounced for AOT/Brij-56 system (T_p 44.5 °C), whereas for the other system (T_p 20.5 °C) a less significant effect is
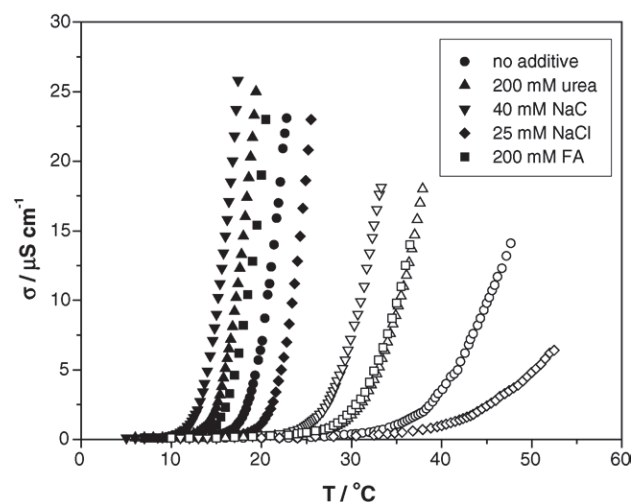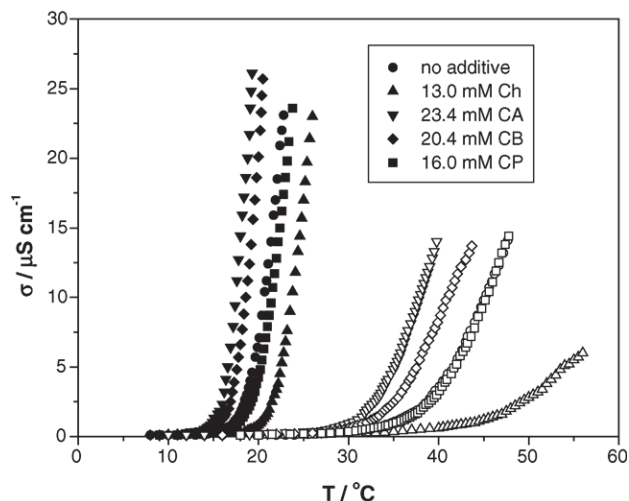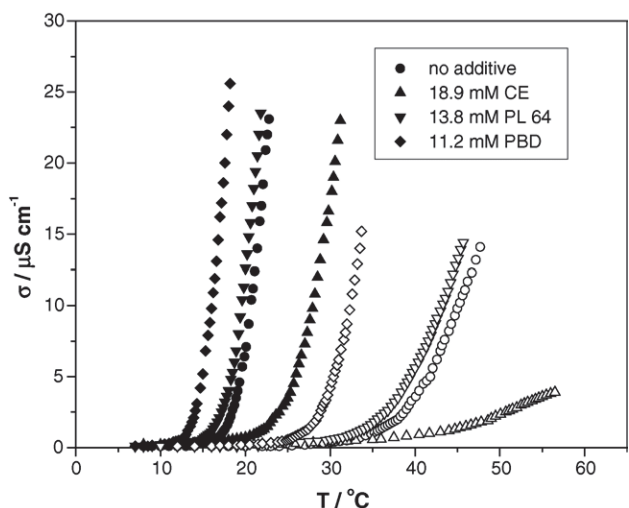

Fig. 7. Conductivity as a function of temperature for AOT/Brij-56 (or Brij-58)/IPM/water mixed reverse micellar systems in presence of additives (PBD, PL 64 and CE) with total surfactant concentration 0.175 mol dm^{-3}, $\omega = 20$ and $X_{Brij} = 0.1$. Open symbols represent Brij-56 systems and closed symbol represent Brij-58 systems.

Table 2
Percolation threshold temperature (T_p) for system water/AOT/Brij-58 (Brij-56)/IPM in the absence and presence of additives at $\omega = 20$[a]

Additive	[Additive] (mmol dm^{-3})	T_p (°C)	
		AOT/ Brij-58	AOT/ Brij-56
No additive	–	17.4	34.5
Na-cholate (NaC)	20.0	15.1	32.0
	40.0	12.5	25.0
Urea	100	15.5	32.1
	200	14.0	29.0
NaCl	25.0	20.1	40.0
	50.0	22.5	49.0
Cholesterol (Ch)	13.0	20.1	40.5
	26.0	20.5	44.5
Cholesteryl acetate (CA)	23.4	16.0	31.8
Cholesteryl benzoate (CB)	20.4	16.7	33.4
Cholesteryl palmitate (CP)	16.0	18.5	37.4
Pluronic (PL 64)	6.9	17.0	–
	13.8	16.4	34.4
	27.6	13.8	28.0
Polybutadiene (PBD)	11.2	14.0	27.7
	22.4	11.2	22.0
Crown ether (CE)	4.9	20.2	42.4
	18.9	22.9	48.0
Toluene (Tl)	100	16.6	33.0
Benzyl alcohol (BA)	100	16.6	35.0
Formamide (FA)	200	15.5	28.0
Ethylene glycol (EG)	200	18.0	35.0
Sucrose dodecanoates[b] (L-1695)	2%	16.4	32.5
Sucrose dodecanoates[b] (L-595)	2%	17.0	34.5
Sucrose monostearate[b] (S-1670)	2%	16.7	31.5

[a] Total surfactant concentration $[S_T] = 0.175$ mol dm^{-3}; $X_{Brij} = 0.1$.
[b] Concentration in w/v.

observed. On the other hand, CA (23.4 mmol dm^{-3}) and CB (20.4 mmol dm^{-3}) decreases T_p for both systems (16.0 and 16.7 °C, respectively, for AOT/Brij-58 system, and 31.8 and 33.5 °C, respectively, for AOT/Brij-56 system). However, CP (16.0 mmol dm^{-3}) increases T_p (18.5 and 37.4 °C, respectively) for both the systems in comparison to that without additive.

The effect of CE, a polymeric surfactant/triblock polymer (Pluronics, PL 64) and polybutadiene (PBD) (an oil-soluble polymer) on T_p are exemplified in Fig. 7. CE (4.9 and 18.9 mmol dm^{-3}) hinders percolation as reflected through an increase in T_p (20.2 and 22.9 °C, respectively, for AOT/Brij-58 system, and 42.4 and 48.0 °C, respectively, for AOT/Brij-56 system). However, a little effect on T_p has been observed upon the addition of PL-64 (6.9 mmol dm^{-3}) to both systems. But increasing the concentrations of PL 64 (13.8 and 27.6 mmol dm^{-3}) promotes percolation and T_p decreases for both the systems. The effect is more pronounced at high concentration of PL-64 (27.6 mmol dm^{-3}) as evidenced from the values of T_p (13.8 and 28.0 °C) for both the mixed systems. PBD (at different concentrations of 11.2 and 22.4 mmol dm^{-3}) also promotes percolation, and hence decreases T_p (14.0 and 11.2 °C for AOT/Brij-58

system and 27.7 and 22.0 °C for AOT/Brij-56 system). Sugar-based surfactants [sucrose dodecanoates, L-1695, sucrose dodecanoates, L-595 and sucrose monostearate, S-1670] at concentration of 2% (w/v) assist percolation marginally. The corresponding T_p values are 16.4, 17.0 and 16.7 °C for AOT/Brij-58 system and 32.5, 34.5 and 31.5 °C for AOT/Brij-56 system (figure not shown).

Two aromatic additives (in absence and presence of hydroxyl group in their structures) toluene (Tl) and benzyl alcohol (BA) (both at 100 mmol dm^{-3}) are observed to promote percolation, i.e. decreases T_p (16.6 °C) for both systems, whereas Tl decreases T_p (33.0 °C) and BA increases T_p (35.0 °C) marginally for AOT/Brij-56 system. Non-aqueous polar solvent, EG (200 mmol dm^{-3}) increases T_p (18.0 °C and 35.0 °C) marginally for AOT/Brij-58 and AOT/Brij-56 system, respectively.

3.4.1. An overall comprehension

The mechanism proposed to explain the electric percolation phenomenon in the present study, i.e. in mixed surfactant reverse micelles is based on the extension of the models as put forward by different authors [26,46,54,72] that the formation of channels exchanging matter between the dispersed water droplets in the continuous phase. The schemes based on the models developed by Moulik et al. [32,38,40,41], are depicted as 1I (in absence of additives) and 1II (in presence of additives). According to this model, it is necessary to have an effective collision between two water droplets of the microemulsion/reverse micelle, causing the droplets to fuse together. Subsequently, an exchange of matter between the water droplets would take place (allowing the charge conduction), which would produce their separation by means of a process of fission (Scheme 1I). The presence of additives of course, affect the phenomenological process of percolation in conductance as a whole in these systems, because of their different structure and difference in degree of their interfacial and physicochemical properties that influence the curvature (Scheme 1II).

It has been discussed earlier that addition of Brij-56 and Brij-58 modifies the packing parameter (P) of AOT/IPM system and made this non-percolating system to percolate. The modified packing parameter (P_{eff}) for the mixed systems has been found to be a function of the content and head group area of the non-ionic surfactant. The additives further modify P_{eff}, and thereby assist or hinder the percolation process.

NaC contains steroid ring and hydroxyl groups, which may enable them to form channels between adjacent droplets by adhering to the water/oil interface, as constituted by both AOT and non-ionic surfactants (Brijs). Thus, NaC acts as a percolation-assisting additive as evidenced from Fig. 5 and Table 2. Due to the presence of NaC molecules at the mixed interface, the area of head group of surfactant, 'a' is increased further with decrease in P_{eff}, which in turn decreases the percolation threshold (T_p). Ch is a small but rigid molecule. In the interface, its hydroxyl group remains attached to the surface of the microwater droplet and interface becomes stiffer due to the formation of hydrogen bond with the carbonyl ester of AOT [29,42,73]. Thus, in the presence of cholesterol, the monolayer of the droplets become more rigid, which in turn increases T_p. Although closer approach of droplets is feasible, the rigidity of the interface restricts transfer of ions between droplets, which hinders percolation. However, the esters of Ch (CA, CB and CP) impart some degree of hydrophobicity due to the presence of alkyl group of different size. The degree of hydrophobicity imparted by the replacement of the hydroxyl hydrogen of Ch by acetate and benzoate groups perhaps perturbs the hydrogen bond formation, which results in an increased fluidity of the interface and a consequence decrease of T_p. But, esterification by palmitate can only partly perturb the hydrogen bond formation, and thus CP exhibits a T_p value in between those of system containing Ch and no additive.

Urea has been found to assist the percolation process for both the mixed systems. Urea is considered to lessen the interfacial rigidity by its property of reducing the amphiphile association, resulting in easier fusion of droplets at lower temperature. In

Scheme 1. Proposed schemes for "fusion-mass transfer-fission" in absence (I) and presence (II) of additives.

addition, urea is known to interact with the head group of surfactant present at the interface and also acts as a structure breaker. It is reported that preferential solubilization of urea at the micelle interface increases the interfacial flexibility and enhances the attractive potential among micelles [74]. Preferential solvation of the surfactant head groups by urea results in an increase in the monomer dissociation degree, which leads to an increase in the area per head group, 'a' [75], which thereby reduces P_{eff} and T_p.

Addition of NaCl to both the systems resists the percolation process. NaCl screens the electrostatic repulsion between the charged head groups, and hence decreases 'a', which in turn increases the packing parameter and percolation is hindered. We have reported earlier [63] that addition of NaCl further enhanced the solubilization capacity and retarded ω-induced percolation of AOT/Brij(s)/IPM/water reverse micellar systems. The decrease in droplet size due to the closer aggregation of surfactant molecules at the interface upon addition of NaCl was argued. A similar trend in temperature-induced percolation has also been registered herein. This observation is consistent with that reported by Mejuto and co-workers [43] for AOT/isooctane/water system. CE increases T_p for both the mixed systems and T_p has been observed to increase with increasing concentration of CE (4.9–18.9 mmol dm^{-3}). Mejuto and co-workers [44,46] earlier reported that incorporation of crown ether in low concentration to AOT/isooctane/water reverse micellar system increased percolation threshold, whereas at high concentration of CE, percolation threshold decreased. Similar observations were reported by Mukhopadhyay et al. [37]. Crown ethers are characterized by their capacity to capture cation. In reverse micellar systems containing AOT, Na$^+$ acts as the counterion and crown ether can capture them. Na$^+$ counterions complexed by CE can penetrate deeply in the interface, which results in an increased screening effect of the interface than that in absence of CE [46]. This in turn decreases the effective head group area, and correspondingly increases the packing parameter of the interface resulting in a decrease in mean droplet size in microemulsions, and consequently percolation is retarded.

Both PL 64 and PBD assist percolation. The effect is more pronounced for PBD than that for PL 64 (Table 2). The additive PBD is soluble in the continuous oil medium, which induces less oil penetration in the interfacial film of the droplets, and hence it increases the interdroplet interaction and the ease of droplet fusion among the droplets. On the other hand, polymers may also act as barriers at the interface for fusion and ion transport. It has been reported that water-soluble POE type of polymers gets adsorbed at the oil–water interface constituted by ionic surfactant (AOT), whereas such effect is absent for interface constituted by non-ionic surfactant (C$_{12}$E$_5$) [76]. As a result, an attractive interaction between the polymer and AOT is produced, which in turn hinders interdroplet interaction and increases T_p. PBD being devoid of any POE chain does not interact with the interface and T_p decreases considerably. But, PL 64 being a hydrophilic polymer, is expected to reside primarily at the oil/water interface and occupy a large surface area on the droplet through polymer–AOT interactions [76]. This increases

the area of head group of the surfactant and promotes exchange of Na$^+$ between the droplets. But the AOT–polymer attractive interaction may also results in increase of T_p. This effect is suppressed by the former one and as a whole T_p is decreased.

Sucrose surfactants [sucrose dodecanoates, L-1695 and L-595 and sucrose monostearate, S-1670] also assist percolation marginally. Because of three factors, viz. reduction of the interfacial area per molecule when these are introduced into a AOT + polyoxyethylene type mixed surfactant layer, low monomeric solubility in oil due to the strong hydrophilicity of its sucrose unit and formation of strong hydrogen bonds between the hydroxyl groups of the sucrose group and water molecules of these additives, counter balances the effect on the interface to be significant to modify the interface, and hence marginal effect in the percolation was observed [77].

Non-aqueous polar solvent, formamide (200 mmol dm^{-3} solution in water) assists percolation, whereas another non-aqueous polar solvent, ethylene glycol is observed to have only marginal effect on percolation phenomenon with identical concentration. In comparison to water, non-aqueous polar compounds are reported to have enhanced molecular interaction with the hydrophobic compounds [78]. This difference leads to higher penetration of non-aqueous polar molecules in the hydrocarbon part of the surfactant. The high penetration induces an increase in cross-sectional area of the surfactant, i.e. the surfactants are closely packed in the interface, 'a' is increased and P_{eff} is decreased, and thus percolation is facilitated owing to a decrease in the packing parameter.

Fig. 8 depicts the relative change in percolation threshold ($\Delta\theta_p/\theta_p$, where $\Delta\theta_p = \theta'_p - \theta_p$, and θ_p is the percolation threshold (in Kelvin scale) without additive and θ'_p is that in presence of additive) in presence of urea, NaC, NaCl, Ch and CE. It can be observed from figure that the relative change is higher for the AOT/Brij-56 system as compared to the AOT/Brij-58 systems for all the additives presented herein and it can be inferred that the additives can perturb the former interface more effectively
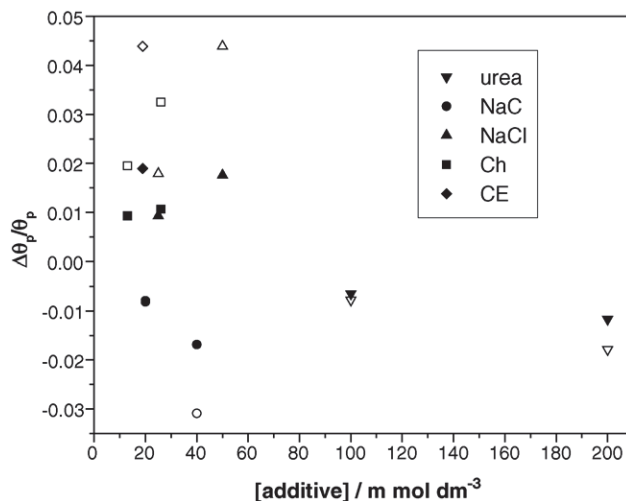

Fig. 8. Relative change in percolation threshold (see text) for AOT/Brij(s)/IPM/water mixed reverse micellar systems in presence of additives with surfactant concentration of 0.175 mol dm^{-3}, $\omega = 20$ and $X_{Brij} = 0.1$. Open symbols represent Brij-56 systems and closed symbol represent Brij-58 systems.

than the latter. This may be due to the smaller polar head group size of the former than the latter.

3.5. Activation energy for percolation in AOT/non-ionics mixed reverse micelles

The activation energy, E_p for percolation of conductance in mixed reverse micelles has been estimated on the basis of an Arrhenius form of relation [29,37–41],

$$\sigma = A \exp\left(\frac{-E_P}{RT}\right) \tag{3}$$

or,

$$\ln\sigma = \ln A - \frac{E_P}{RT} \tag{4}$$

where A is the constant, σ the conductance and R and T have their usual significance. E_p value can be obtained from the slope of $\ln\sigma$ against $1/T$ plot. The results (in absence and in presence of additives) have been presented in Fig. 9 and Table 3.

From Table 3, it is found that E_p in absence of additives for AOT/Brij-58 and AOT/Brij-56 blended systems are 397 and
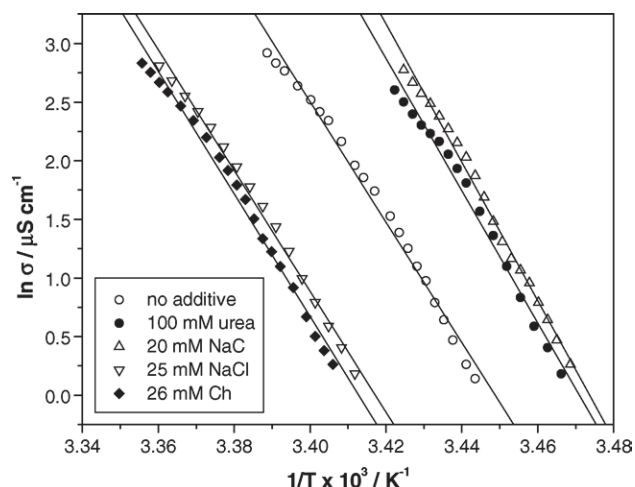
Fig. 9. Plot of $\ln\sigma$ vs. $1/T$ to evaluate activation energy for percolation of the system AOT/Brij-58/IPM/water with total surfactant concentration 0.175 mol dm^{-3}, $\omega = 20$ and $X_{Brij} = 0.1$.

Table 3
Activation energy for percolation (E_p) for system water/AOT/Brij-58 (Brij-56)/IPM in the absence and presence of additives at $\omega = 20$[a]

Additive	[Additive] (mmol dm^{-3})	AOT/Brij-58		AOT/Brij-56	
		E_p (kJ mol^{-1})	Corr. coefficient	E_p (kJ mol^{-1})	Corr. coefficient
No additive	–	397	0.9913	176	0.9932
Na-cholate (NaC)	20.0	517	0.9937	255	0.9921
	40.0	464	0.9915	271	0.9960
Urea	100	539	0.9897	224	0.9851
	200	494	0.9904	252	0.9923
NaCl	25.0	430	0.9935	144	0.9936
	50.0	399	0.9941	134	0.9948
Cholesterol (Ch)	13.0	446	0.9910	186	0.9886
Cholesteryl acetate (CA)	26.0	407	0.9926	134	0.9940
	23.4	502	0.9946	238	0.9975
Cholesteryl benzoate (CB)	20.4	445	0.9877	205	0.9965
Cholesteryl palmitate (CP)	16.0	474	0.9911	199	0.9882
Pluronic (PL 64)	6.9	403	0.9956	–	–
	13.8	393	0.9942	168	0.9948
	27.6	287	0.9947	201	0.9955
Polybutadiene (PBD)	11.2	457	0.9929	303	0.9967
	22.4	740	0.9947	491	0.9944
Crown ether (CE)	4.9	370	0.9905	122	0.9947
Toluene (Tl)	18.9	250	0.9913	82.7	0.9928
	100	416	0.9939	237	0.9964
Benzyl alcohol (BA)	100	393	0.9945	170	0.9905
Formamide (FA)	200	384	0.9921	247	0.9960
Ethylene glycol (EG)	200	391	0.9936	207	0.9919
Sucrose dodecanoates[b] (L-1695)	2%	432	0.9954	192	0.9927
Sucrose dodecanoates[b] (L-595)	2%	401	0.9873	175	0.9914
Sucrose monostearate[b] (S-1670)	2%	416	0.9915	199	0.9947

[a] Total surfactant concentration $[S_T] = 0.175$ mol dm^{-3}; $X_{Brij} = 0.1$.
[b] Concentration in w/v.

$176 \, \text{kJ} \, \text{mol}^{-1}$, respectively. It has been found that E_p increases considerably in presence of the additives, NaC and urea for both the mixed systems. However, E_p has also been observed to decrease with increasing concentration of both the additives in AOT/Brij-58 system, whereas E_p increases with increase in concentration of both additives for AOT/Brij-56 system. A similar trend has also been observed for both systems in presence of the additives, viz. NaCl, cholesterol, cholesteryl derivatives at different concentrations. E_p values of PL 64 are not straight-forward. E_p at lowest concentration ($6.9 \, \text{mmol} \, \text{dm}^{-3}$) of PL 64 increases marginally and gradually decreases with further increase in concentration of PL 64 for AOT/Brij-58 system, whereas for AOT/Brij-56 system, reverse trend is observed and E_p value at highest concentration of PL 64 is higher than that obtained in absence of additive. A significant increase in E_p has been observed in presence of a polymer, PB at concentrations of 11.2 and $22.4 \, \text{mmol} \, \text{dm}^{-3}$, respectively, for both systems. Tl increases E_p for both systems, whereas BA has marginal effect on E_p values. E_p values for both formamide and ethylene glycol have been lowered for AOT/Brij-58 systems, whereas E_p values were higher for AOT/Brij-56 systems. E_p is decreased by CE for both systems. It has been observed that E_p decreased with increasing crown ether concentration. However, CE at $18.9 \, \text{mmol} \, \text{dm}^{-3}$ shows the lowest E_p value for both systems among all the additives. Sucrose esters (L-1695, L-595 and S-1670) are observed to increase E_p for both systems, except L-595 in AOT/Brij-56 system, where the effect on E_p is marginal.

From the results as obtained in the present study, it can be inferred that E_p values have been observed to be affected upon the addition of additives for both the mixed systems stabilized by AOT/Brij-56 and Brij-58 in IPM. E_p values have been shown to be higher for AOT/Brij-58 than AOT/Brij-56 systems, and are almost doubled for AOT/Brij-58 systems (except in some cases) than that of AOT/Bri-56. In most of the cases, E_p values have been found to increase significantly as compared to the systems without additives, irrespective of whether the additive assists or resists percolation of conductance in mixed reverse micellar systems.

From close scrutiny of Table 3, it has been observed that the correlation between the E_p values of percolation-assisting and percolation-resisting additives is not straightforward for both the mixed systems. In general, it has been found that the percolation-assisting additives provide higher E_p values than the percolation-resisting additives for both systems. A plausible explanation for these results may be put forward as argued by Moulik and co-workers [41] for the systems AOT/hydrocarbon oil/water in presence of aromatic methoxy hydrotopes. They considered that fission of the fused droplets is the rate-determining step for the dynamic percolation process [79]. According to them, the fission of bulky droplets into a pair of singlets with associated transfer of counterion (Na^+ ion present in the system) required higher activation energy. The bridging of droplets by an additive reduced T_p, but it was the process of their separation that decided the magnitude of E_p, which resulted high in the presence of an efficient bridging additive.

The magnitude of E_p was, thus, essentially controlled by the separability of the droplets from the "fused" to the "free

state". The contributions of steric and interacting factors of the additives, and also their interaction with non-ionic surfactants (whatever small amount present in these systems) in the process of fission and fusion need to be explored for augmenting the percolation phenomenon in mixed reverse micelles. An elaborate and planned study in this direction is thus wanted.

4. Conclusions

1. The non-percolating system water/AOT/IPM in the temperature range 5–60 °C can be made percolating by the addition of non-ionic surfactants (Brij-56 and Brij-58) to the system, and the threshold percolation temperature, T_p depends on the concentration of the surfactant mixtures, the polar head group size and content of the added non-ionic surfactant.
2. T_p decreases with increasing water content, ω at a fixed composition of non-ionic surfactant content ($X_{\text{Brij-56 or Brij-58}}$).
3. The threshold percolation temperature, T_p of the studied mixed reverse micelles stabilized by AOT/Brij-56 and Brij-58 in IPM and water in absence and presence of additives of different molecular structures, physicochemical parameters and/or interfacial properties, can be obtained from σ–T plot vis-à-vis the differential plot.
4. The additives NaC, urea, cholesteryl acetate, cholesteryl benzoate, toluene, pluronic, polybutadiene, sucrose esters (sucrose dodecanoates, L-1695 and sucrose monostearate, S-1670) and formamide, decrease T_p, whereas NaCl, cholesteryl palmitate, crown ether and ethylene glycol increase it for both the mixed systems. The effect of sucrose dodecanoates (L-595) on T_p is not that much significant. Benzyl alcohol assists the percolation process for AOT/Brij-58 system, whereas it resists percolation process marginally for AOT/Brij-56 system. The relative change of percolation threshold has been found to be higher for the AOT/Brij-56 systems in comparison to that of the AOT/Brij-58 systems.
5. Activation energy (E_p) for percolation in absence and presence of additives for both mixed reverse micellar systems has been evaluated. Both T_p and E_p depends on the type of the non-ionic surfactant blend (i.e. size of the polar head group) in mixed reverse micelles and also on the type of additives and their concentrations.
6. A plausible mechanism for the percolation phenomenon in mixed reverse micelles has been discussed.

Acknowledgements

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