

Percolation phenomenon in mixed reverse micelles: The effect of additives

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Abstract

The conductivity of AOT/IPM/water reverse micellar systems as a function of temperature, has been found to be non-percolating at three different concentrations (100, 175 and 250 mM), while the addition of nonionic surfactants [polyoxyethylene(10) cetyl ether (Brij-56) and polyoxyethylene(20) cetyl ether (Brij-58)] to these systems exhibits temperature-induced percolation in conductance in non-percolating AOT/isopropyl myristate (IPM)/water system at constant compositions (i.e., at fixed total surfactant concentration, ω and X_{nonionic}). The influence of total surfactant concentration (micellar concentration) on the temperature-induced percolation behaviors of these systems has 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 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 [(EO)₁₃(PO)₃₀(EO)₁₃, Pluronic, PL64], polybutadiene, sucrose esters (sucrose dodecanoates, L-1695 and sucrose monostearate S-1670), formamide distinctively fall in the former category, whereas sodium chloride, cholesteryl palmitate, crown ether, ethylene glycol constitute the latter for both systems. Sucrose dodecanoates (L-595) had almost marginal effect on the process. The observed behavior of these additives on the percolation phenomenon has been explained in terms of critical packing parameter and/or other factors, which influence the texture of the interface and solution properties of the mixed reverse micellar systems. 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 for the first time 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

Reverse micelles (RMs) are generally described as nanometer-sized water droplets dispersed in an apolar solvent with the aid of a surfactant monolayer, forming a thermodynamically stable and optically transparent solution. The entrapped water is heterogeneous in nature and its properties gradually change as a function of ω ($= [\text{H}_2\text{O}]/[\text{surfactant}]$), and depends on the distance from the polar head layer.

Sometimes they contain solubilized water in excess of certain amount and known as w/o microemulsions [1–5]. RMs or w/o microemulsions find applications starting from tertiary oil recovery to nanoparticle synthesis [1,6–10]. Reverse micelles possess highly dynamic structures whose components rearrange themselves over time and space through interactions or collisions, coalescing and redispersing. The structure and properties of reverse micellar systems have been investigated extensively by numerous methods [2,3,6–10]. Of these, the measurement of conductivity is a useful technique in obtaining information on micellar interactions [6,11,12].

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The phenomenon of electrical percolation is 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 [13–17]. 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” [18–21] from droplet to droplet or are transferred by way of “fusion, mass transfer and mass exchange” [22–25]. As a consequence of the ion transfer, the conductance can be enhanced by 100 to 1000 folds. The composition of the system and other environmental conditions such as the presence of additives controls the percolation threshold values [26–30].

AOT can form reverse micelles under wide range of conditions (such as, water content, temperature, solvent, electrolyte type and concentrations) without the need of co-surfactant [31]. 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 [25,27,32–43]. The percolation phenomenon has been shown to occur earlier (assistance) or be delayed (retardation) in presence of additives; however, many of them remained totally ineffective. The “transient-fusion-mass transfer-fission” model has been found to be more applicable over the “hopping” model in most of the cases to explain the percolation phenomenon. Of these studies, the work of Moulik et al. [25,27,32–36], Garcia-Rio et al. [38–40] are noteworthy. Above reports concern mainly the percolation of conductance in water/AOT/hydrocarbon w/o microemulsions. 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. [28], Nazario et al. [44], Eicke et al. [45,46], Li et al. [47,48], Liu et al. [49,50], Bumajdad et al. [51].

In our previous studies, the solubilization behavior of water in anionic (AOT) or cationic didodecyltrimethylammonium bromide (DDAB)/nonionic surfactants (of different chemical structures and physicochemical properties) mixed reverse micellar systems stabilized in isopropyl myristate, isobutyl benzene and cyclohexane at different temperatures has been reported [12,52]. In a subsequent study [6], the effects of water content (ω), micelle concentrations, content of nonionic surfactant of different types (Brijis, Spans, Tweens) on the temperature-induced percolation of conductance of AOT-nonionics and DDAB-nonionics [polyoxyethylene(10) cetyl ether (Brij-56) and polyoxyethylene(20) cetyl ether (Brij-58) only] mixed reverse micelles in a nontoxic oil IPM,

which is widely used in biologically resembling systems, pharmaceutical and drug delivery [53] have been reported.

In continuation of our previous studies, the present study is aimed to measure the electrical conductivity of the water/AOT/Brij-56 or Brij-58/IPM reverse micellar systems in presence of additives of various types with different structures and physical parameters and/or interfacial properties, as they can alter the texture of the interface. Besides, some of the additives are frequently used in the study of mass transfer processes. No study on the effect of additives on the percolation of conductance in mixed reverse micellar systems has yet been reported. 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.

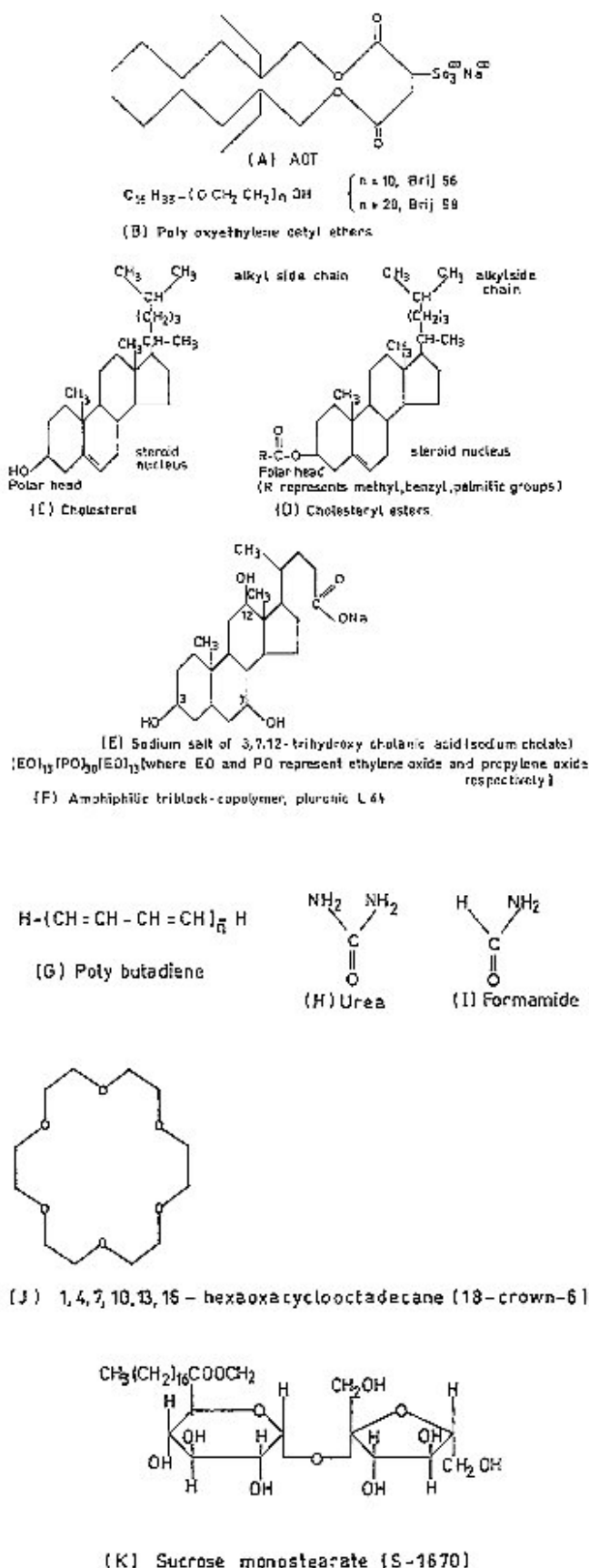
2. Experimental

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 (TI), benzyl alcohol (BA), formamide (FA), ethylene glycol (EG), urea, NaCl are of AR and extrapure grade of SRL, India. Isopropyl myristate (IPM) is a product of Fluka (Switzerland). Two types of sucrose dodecanoates, (L-1695 and HLB, 16.0; L-595 and HLB, 5.0) and sucrose monostearate (S-1670, HLB, 15.0) were gifted by Mitsubishi Chemical Corporation, Yokohama, Japan. L-1695 (sucrose monolaurate) is the mixture of 83.6% sucrose monododecanoate, 15.2% didodecanoate and 1.2% tridodecanoate. L-595 (sucrose dilaurate) is the lipophilic sucrose multi-dodecanoate and the contents of monoester, diester and triester are 30.0, 39.3 and 30.4%, respectively [54,55]. A polymeric surfactant [a triblock copolymer (EO)₁₃(PO)₃₀(EO)₁₃, Pluronic L64, MW = 2900], polybutadiene (PBD), dicyclohexano-18-crown-6 (crown ether, CE) are products of Fluka, Switzerland. Cholesterol (Ch) and its derivatives (cholesteryl acetate, CA, palmitate, CP and benzoate, CB) and sodium cholate (NaC) are products of Sigma, USA. The chemical structures of the surfactants and some of the additives are represented in Scheme 1. Double distilled water was used with conductance less than $3 \mu\text{S cm}^{-1}$.

2.2. Construction of phase diagram

To construct the phase diagram in a Gibbs triangle, calculated amount of surfactant(s) and oil were taken in sealed test tubes and equilibrated at 30°C in a thermostatic water bath accurate to $\pm 0.1^\circ\text{C}$. Then water was added into it in small increment with the help of a micro-syringe, shaken



Scheme 1. Chemical structures of surfactants and some of the additives.

vigorously and placed in the thermostatic water bath. Reading of different phases was taken by visual observation, after conformation of the attainment of complete equilibrium. To study the effect of temperature on these systems, solutions at fixed composition, ω were prepared in sealed test tubes and kept at the desired temperature in the thermostatic water bath. Temperature of the bath was increased at an interval of 1 °C and at each temperature, the test tubes were shaken vigorously and then kept in the thermostat to attain equilibrium. After attainment of equilibrium, phase characteristics were noted at each temperature.

2.3. Solution (sample) preparation for electrical conductivity measurements

The reverse micellar systems were prepared using the blends of AOT and Brij's 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 , in presence of additives (depending upon their solubilities in water and oil) at different concentration levels.

2.4. Measurements of conductivity

Electrical conductivity measurements of samples (in absence and presence of additives) were carried out as a function of temperature 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 readings 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 [21].

3. Results

3.1. Phase behavior of AOT/Brij-56 or Brij-58/IPM/water system

Since the phase boundary of multicomponent systems consisting of surfactant(s), oil and water shifts systematically upon the addition of additives, phase behavior of the quaternary system AOT/Brij-56/IPM/water in absence and presence of additives (NaCl and NaC) has been constructed in a Gibbs triangle at a fixed mole fraction of Brij-56 in total surfactant, ($X_{\text{Brij-56}} = 0.1$) with mass fraction of water,

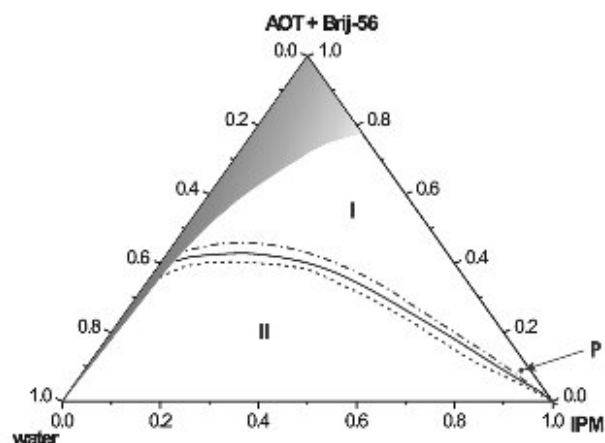


Fig. 1. Triangular phase diagram of the system, AOT/Brij-56/IPM/water in absence of additives (—); in presence of 40 mM NaCl (---) and 25 mM NaCl (- - -) at 300 K. The mole fraction of Brij-56 in total surfactant ($X_{\text{Brij-56}}$) is fixed at 0.1. I and II represents single and biphasic regions, respectively. The shaded region represents viscous phase. The point P denotes the composition chosen for the temperature induced conductivity studies.

IPM and surfactant(s) as the three apexes at 30 °C (Fig. 1). It can be observed from the figure that the phase behavior is characterized by the presence of a considerable single-phase region along the surfactant-IPM axis and a viscous region along the water-surfactant axis. The single-phase region is an oil continuous microemulsion (reverse micellar system) consisting of dispersion of surfactant coated water droplets. A wide biphasic region exists along the IPM-water axis. Additive like 25 mM NaCl has been observed to increase the area of the single-phase region, whereas addition of 40 mM NaCl decreases it. An identical observation has also been obtained with the AOT/Brij-58 blend (figure not shown). It has been reported that the phase separation in a w/o microemulsion is a direct consequence of the interaction among the droplets and the elasticity of the surfactant monolayer, which can be affected by the presence of additives and temperature [52,56]. To understand the combined effect of these two factors, temperature induced phase behavior of the quaternary system AOT/Brij-56/IPM/water has been studied both in absence and presence of additives. The surfactant concentration in oil and the mole fraction of Brij-56 in the total surfactant mixture has been fixed at 175 mM and 0.1, respectively. The water solubilization capacity (ω) has been plotted against temperature (T) and the results are presented in Fig. 2. The phase boundary separates a lower monophasic system (I) from an upper biphasic one (II). The reverse micellar system splits into two distinct phases on reaching a critical temperature, called the “optimum solubilization temperature (T_U)” [52]. It can be observed that T_U decreases with increasing ω for the system without additive. Addition of 40 mM NaCl and 200 mM urea decreases T_U compared to the system without additives, whereas addition of 25 mM NaCl and 13 mM Ch increases it. It can be argued that the former two additives increases the interdroplet interaction as well as the fluidity of the mixed surfactant interface, whereas

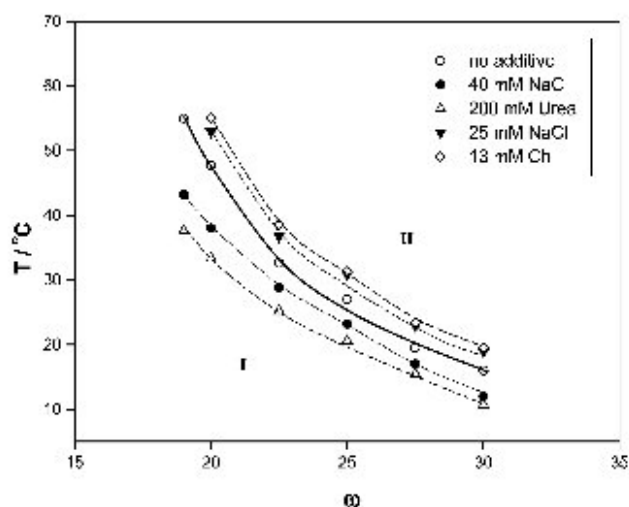


Fig. 2. Temperature dependence of the reverse micellar system AOT/Brij-56/IPM/water in absence and presence of additives. The initial surfactant concentration in oil has been fixed at 175 mM and the mole fraction of Brij-56 in total surfactant ($X_{\text{Brij-56}}$) is fixed at 0.1. I and II represents single and biphasic systems, respectively.

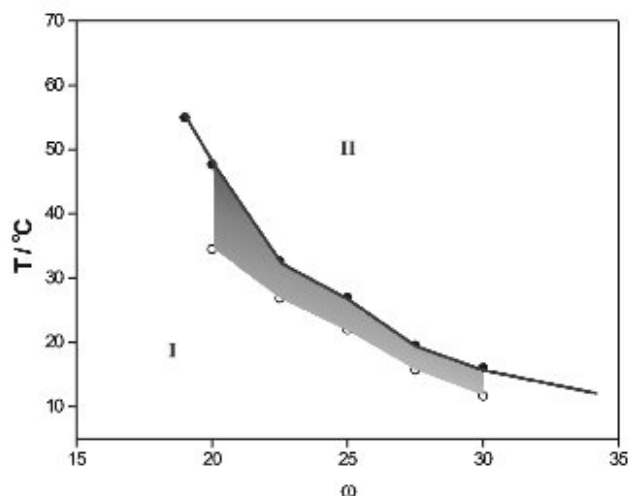


Fig. 3. Temperature dependent phase behavior of the reverse micellar system, AOT/Brij-56/IPM/water with the initial surfactant concentration in oil has been fixed at 175 mM and the mole fraction of Brij-56 in total surfactant ($X_{\text{Brij-56}}$) is fixed at 0.1. Hollow symbols represent percolation threshold temperature (T_p), closed symbols represent optimum solubilization temperature (T_U) and the shaded region represents “percolating region.” I and II represents single and biphasic systems, respectively.

the latter two decreases it, and thereby makes the formulation more stable towards temperature. Since percolation in conductance in w/o microemulsions (or reverse micelles) is a manifestation of the nature of the inter-droplet interaction or the fluidity of the interface, temperature induced conductance study has been carried out for the reverse micellar system AOT/Brij-56/IPM/water at a fix surfactant concentration of 175 mM at different ω 's. The system has been observed to exhibit percolation in conductance (not exemplified) and the threshold percolation temperature (T_p) lies in the vicinity of T_U as shown in Fig. 3. The shaded region

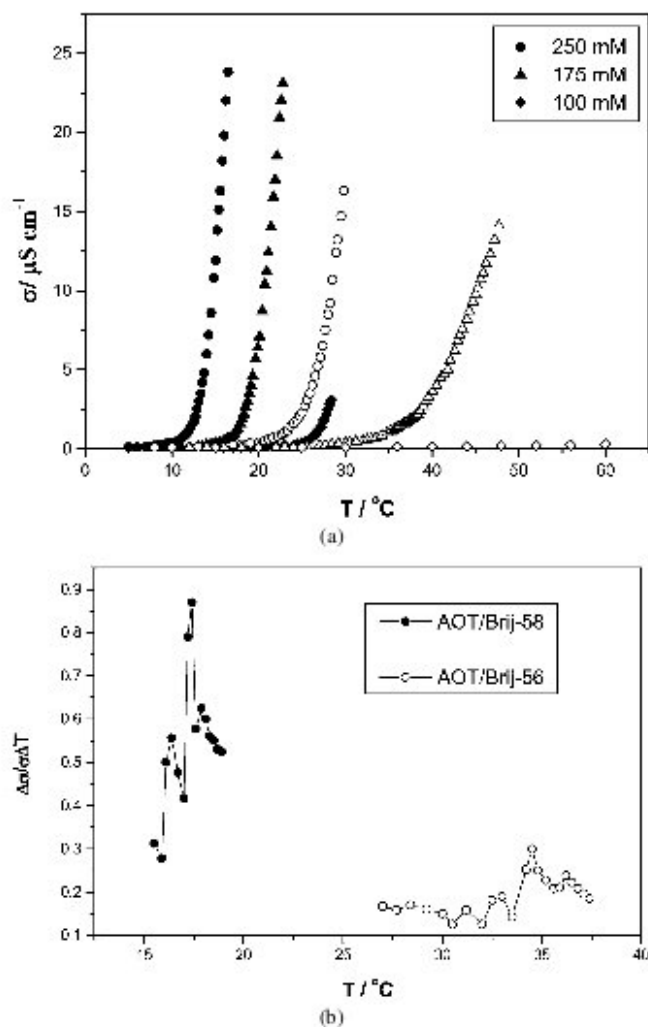


Fig. 4. (a) Conductivity as a function of temperature for AOT/Brij-56 (or Brij-58)/IPM/water mixed reverse micellar systems at different surfactant (micelle) concentrations with $\omega = 20$ and $X_{\text{Brij}} = 0.1$. Open symbols represent Brij-56 systems and closed symbol represent Brij-58 systems. (b) Differential plot for determination of percolation temperature.

in the figure indicates the percolation region, below which the formulation behaves like a non-percolating hard-sphere type system. As it has been observed that additives affects the thermal stability of reverse micellar systems (Fig. 2), temperature-induced conductance studies have been carried out with the reverse micellar system, AOT/Brij-56 (or Brij-58)/IPM/water/additive(s) at fixed initial concentration of surfactant in oil (175 mM), $X_{\text{Brij}} = 0.1$ and fixed water content ($\omega = 20$). The location of the point of study has been demarcated by point P in Fig. 1. The results of conductivity studies are summarized in the following sections.

3.2. 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

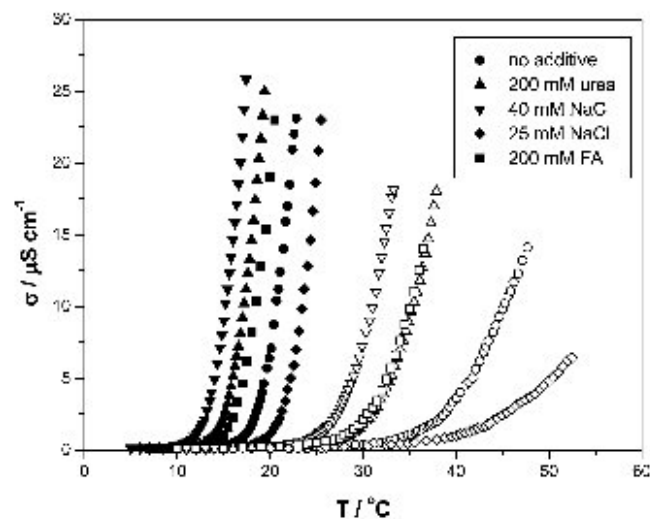


Fig. 5. Conductivity as a function of temperature for AOT/Brij-56 (or Brij-58)/IPM/water mixed reverse micellar systems in presence of additives (urea, NaC, NaCl and FA) with total surfactant concentration 175 mM, $\omega = 20$ and $X_{\text{Brij}} = 0.1$. Open symbols represent Brij-56 systems and closed symbol represent Brij-58 systems.

surfactant concentrations (250, 175 and 100 mM). 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 + nonionic) surfactant concentration ($[S_T]$) as mentioned above and at a fixed $X_{\text{nonionic}} = 0.1$ and $\omega = 20$, a dramatic increase in conductance behavior (except for AOT/Brij-56 system with 100 mM surfactant concentration) is observed as a function of temperature. The results are depicted in Fig. 4a. The differential plot for determination of threshold percolation temperature T_p for both systems is represented in Fig. 4b. The threshold percolation temperature T_p is exhibited at 23.3, 34.5 $^{\circ}\text{C}$ for AOT/Brij-56 system, whereas for the AOT/Brij-58 system, T_p is observed at 12.7, 17.4 and 26.8 $^{\circ}\text{C}$ at the corresponding compositions.

3.3. Influence of third component (additives) on the percolation of conductance in AOT/Brij(s) mixed reverse micelles at fixed ω and X_{nonionic}

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 $X_{\text{nonionic}} = 0.1$ as a function of temperature are presented in Figs. 5–7 and Table 1 and summarized as follows. Addition of NaC (20.0 mM), urea (100 mM) and formamide (200 mM) reduces T_p (15.1, 15.5 and 15.5 $^{\circ}\text{C}$, respectively, for AOT/Brij-58 system, and 32.0, 32.1 and 28.0 $^{\circ}\text{C}$, respectively, for AOT/Brij-56 system), whereas addition of NaCl (25.0 mM) increases T_p (20.1 and 40.0 $^{\circ}\text{C}$ for AOT/Brij-58 and AOT/Brij-56 systems respectively) (Fig. 5 and Table 1). The effect has been found to be more pronounced at higher concentrations of additives. NaC (40.0 mM) and urea (20.0 mM) reduce T_p (12.5 and

Table 1
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 40.0	15.1 12.5	32.0 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 26.0	20.1 20.5	40.5 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 (PL64)	6.9 13.8 27.6	17.0 16.4 13.8	– 34.4 28.0
Polybutadiene (PBD)	11.2	14.0	27.7
	22.4	11.2	22.0
Crown ether (CE)	4.9 18.9	20.2 22.9	42.4 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 dodeca- noates ^b (L-1695)	2%	16.4	32.5
Sucrose dodeca- noates ^b (L-595)	2%	17.0	34.5
Sucrose mono- stearate ^b (S-1670)	2%	16.7	31.5

^a Total surfactant concentration $[S_T] = 0.175 \text{ mol dm}^{-3}$; $X_{\text{Brij}} = 0.1$.

^b Concentration in wt/vol.

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, CP) on T_p for both AOT/Brij-56 and AOT/Brij-58 systems at the compositions mentioned earlier. Addition of Ch (13.0 mM) increases T_p (20.1 and 40.5 °C, respectively) for both these systems. A further increase in the concentration of Ch (26.0 mM), increases the T_p for AOT/Brij-56 system (T_p , 44.5 °C) considerably, whereas for the other system, effect was observed (T_p , 20.5 °C) to be less significant. On the other hand, CA (23.4 mM) and CB (20.4 mM) decrease 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 mM) 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 [(EO)₁₃(PO)₃₀(EO)₁₃, Pluronic, PL64] and polybutadi-

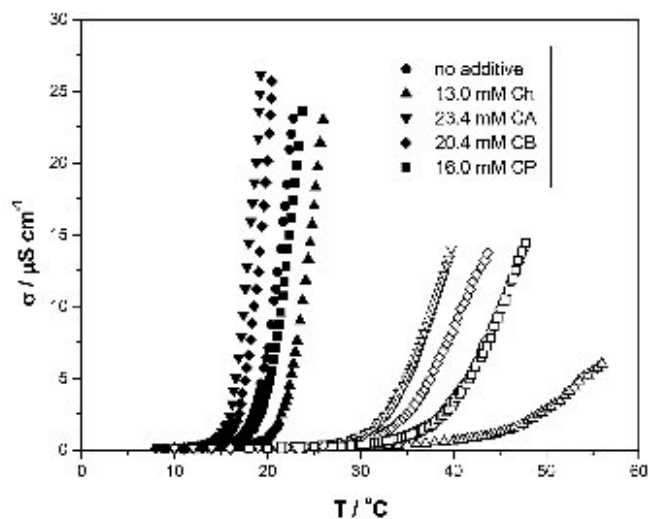


Fig. 6. Conductivity as a function of temperature for AOT/Brij-56 (or Brij-58)/IPM/water mixed reverse micellar systems in presence of additives (Ch, CA, CB and CP) with total surfactant concentration 175 mM, $\omega = 20$ and $X_{\text{Brij}} = 0.1$. Open symbols represent Brij-56 systems and closed symbol represent Brij-58 systems.

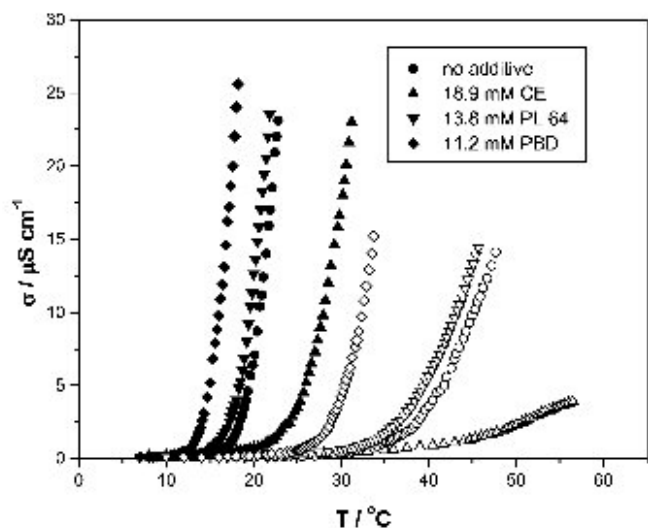


Fig. 7. Conductivity as a function of temperature for AOT/Brij-56 (or Brij-58)/IPM/water mixed reverse micellar systems in presence of additives (PBD, PL64 and CE) with total surfactant concentration 175 mM, $\omega = 20$ and $X_{\text{Brij}} = 0.1$. Open symbols represent Brij-56 systems and closed symbol represent Brij-58 systems.

ene (PBD) (an oil soluble polymer) on T_p are exemplified in Fig. 7. CE (4.9 and 18.9 mM) hinders percolation as reflected through 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 small effect on T_p has been observed by the addition of PL64 (6.9 mM) to both systems. But increasing the concentrations of PL64 (13.8 and 27.6 mM) promotes percolation and T_p decreases for both the systems and T_p is decreased to 13.8 and 28.0 °C for AOT/Brij-58 and AOT/Brij-56 systems respectively at 27.6 mM concentration. PBD (at concentrations of 11.2 and 22.4 mM) also promotes percolation and hence decreases

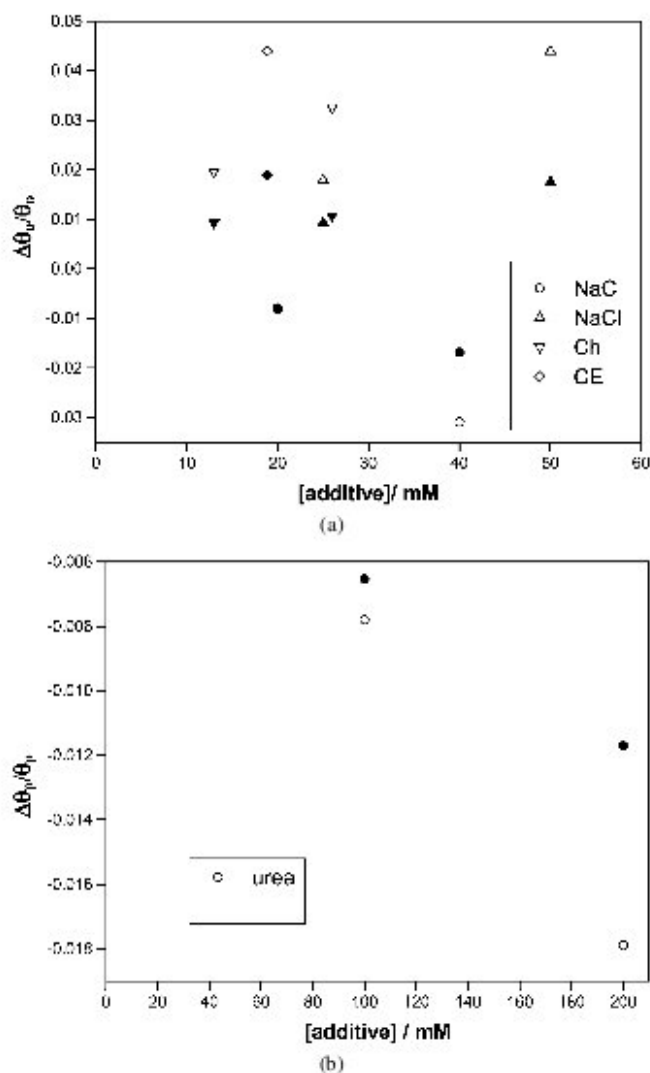


Fig. 8. Relative change in percolation threshold (see text) for AOT/Brij(s)/IPM/water mixed reverse micellar systems in presence of additives with surfactant concentration of 175 mM, $\omega = 20$ and $X_{\text{Brij}} = 0.1$. Open symbols represent Brij-56 systems and closed symbol represent Brij-58 systems. The additives used, (a) NaC, NaCl, Ch and CE; (b) urea.

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 wt%/volume 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 (TI) and benzyl alcohol (BA) (both at 100 mM) are observed to promote percolation, i.e., decreases T_p (16.6 °C) for both systems, whereas TI decreases T_p (33.0 °C) and BA increases T_p (35.0 °C) marginally for AOT/Brij-56 system. Nonaqueous polar solvent, EG (200 mM) increases T_p (18.0 and 35.0 °C) marginally for AOT/Brij-58 and AOT/Brij-56 system, respec-

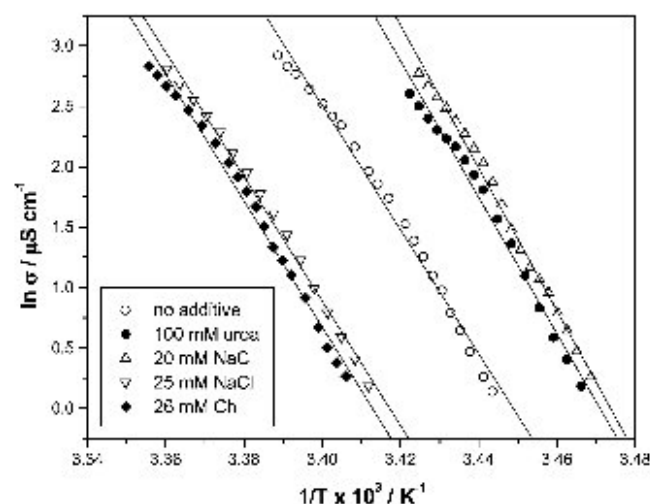


Fig. 9. Plot of $\ln \sigma$ vs $1/T$ to evaluate activation energy for percolation of the system AOT/Brij-58/IPM/water with total surfactant concentration 175 mM, $\omega = 20$ and $X_{\text{Brij}} = 0.1$.

tively. It is interesting to note that T_p values for AOT/Brij-56 systems are almost doubled than that of AOT/Brij-58 systems in most of the cases.

Figs. 8a and 8b 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 absolute scale) without additive and θ'_p is that in presence of additive) in presence of urea, NaC, NaCl, Ch, CE. It can be observed from the figures that the relative change is higher for the AOT/Brij-56 system as compared to the AOT/Brij-58 systems for the all the additives presented herein and it can be inferred that the additives can perturb the former interface more effectively than the latter. It may be due to the larger polar head group size of Brij-58 in comparison to that of Brij-56.

3.4. Activation energy for percolation

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 [25,32–36],

$$\sigma = A \exp(-E_p/RT) \quad (1)$$

or

$$\ln \sigma = \ln A - E_p/RT, \quad (2)$$

where A is a constant and σ is the conductance and R and T have their usual significance. E_p value can be obtained from the slope of $\ln \sigma$ against T^{-1} plot. The results (in absence and in presence of additives) have been presented in Fig. 9 and Table 2.

From Table 2 it is evident that the activation energies, E_p for percolation of conductance in absence of additives for AOT/Brij-58 and AOT/Brij-56 blended systems are 397 and 176 kJ mol^{-1} , respectively. It has been found that E_p increases considerably in presence of the additives, NaC and urea as compared to the systems in absence of additives

Table 2

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. coeff.	E_p (kJ mol ⁻¹)	Corr. coeff.
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 (PL64)	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
	18.9	250	0.9913	82.7	0.9928
Toluene (Tl)	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 wt/vol.

for both AOT/Brij-56 and AOT/Brij-58 systems. However, E_p has also been observed to decrease with increasing concentration of both additives in AOT/Brij-58 system; whereas E_p increased with increase in concentration of both additives for AOT/Brij-56 system. The same trend, in respect of the effects on E_p due to the presence of the additives, viz., NaCl, cholesterol, cholesteryl derivatives at different concentrations, has also been observed for both systems. E_p values of PL64 are not straightforward. A significant increase in E_p has been observed in presence of a polymer, PBD at concentrations of 11.2 and 22.4 mM, respectively, for both systems. Tl increases E_p for both systems, whereas BA has marginal effect on E_p values for these mixed systems. 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 has been decreased by crown ether (CE) for both systems. It has been observed that E_p decreased with increasing crown ether concentration. However, crown ether at 18.9 mM 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 was marginal.

The relative change of activation energy, $\Delta E_p/E_p$, (where $\Delta E_p = E'_p - E_p$, and E_p is the activation energy without additive and E'_p is that with additive) has been plot-

ted against concentration of additives and the results are presented in Figs. 10a and 10b. It can be observed that the magnitude of the relative change of activation energy is higher for the AOT/Brij-56 stabilized system as compared to the AOT/Brij-58 system except for urea and Ch at 100 and 13.0 mM concentrations, respectively. This observation supports the earlier inference drawn from the relative change in T_p (Figs. 8a and 8b), wherein AOT/Brij-56 interface has been inferred to be more perturbed by the additives in comparison to that of the AOT/Brij-58 interface. The lower relative E_p values of AOT/Brij-58 system can be accounted for the larger head group size of Brij-58, which may perhaps ease the droplet fission in presence of additives.

4. Discussion

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 to the passage of cations through the transient channels formed between colliding droplets [39]. This pas-

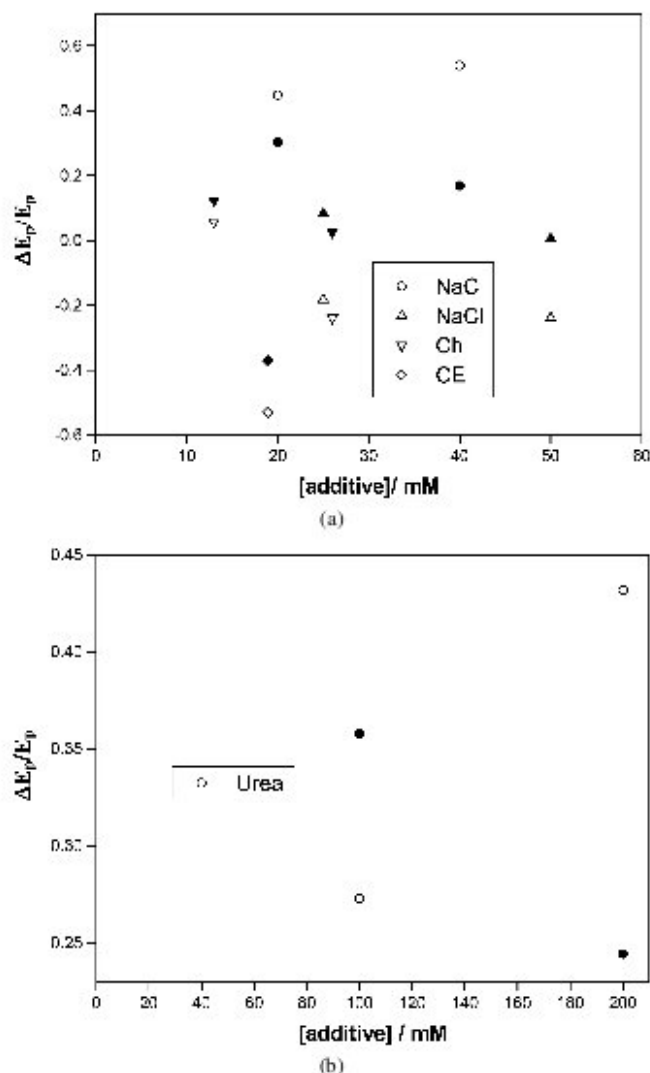


Fig. 10. Relative change in activation energy for percolation (see text) for AOT/Brij(s)/IPM/water mixed reverse micellar systems in presence of additives with surfactant concentration of 175 mM, $\omega = 20$ and $X_{\text{Brij}} = 0.1$. Open symbols represent Brij-56 systems and closed symbol represent Brij-58 systems. The additives used: (a) NaC, NaCl, Ch and CE; (b) urea.

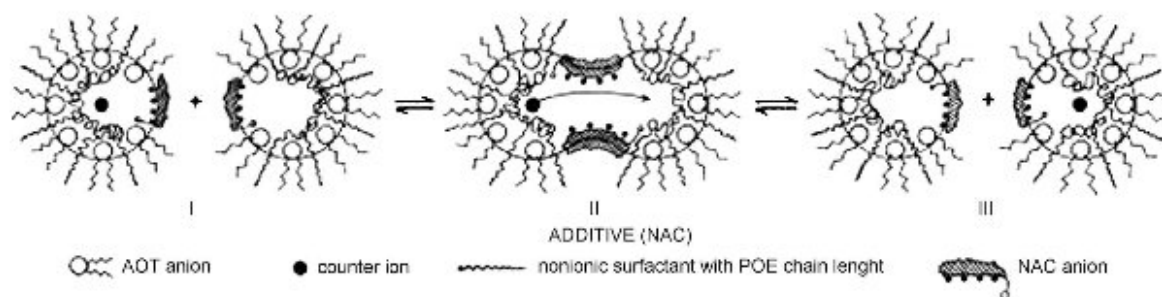
sage is facilitated by the formation of the certain local region of positive curvature in AOT surfactant film [57]. The rigidity of the interface and the attractive interactions among the aggregates are the most important factors that determine the exchange rate of the ions and water molecules during the fusion processes [47,48]. 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 [56], which in turn fails to modify the interface less effectively and thus AOT/IPM system has been observed to be non-percolating. According to Liu et al. [50], for solvents with high viscosity, it is difficult for the droplets to collide and aggregate into clusters, which makes the AOT/IPM system non-percolating.

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 [43,50]. 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. It can be inferred that Brij-58, because of its larger polar head group (polyoxyethylene chains 20) than Brij-56 (polyoxyethylene chains 10), has a stronger effect on perturbing the interface. It is well known that 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) [58]. For a mixed surfactant system, the effective packing parameter P_{eff} can be expressed according to the following relation as modified by Evans and Ninham [59]

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

where x_A and x_B are the mole fractions of AOT and Brij present at the interface respectively, and a , v and l_c are the area of the head group, volume and chain length of the surfactant. Hence, nonionic surfactant with larger polar head group is expected to modify the interface of AOT/Brij(s) mixed reverse micellar systems more efficiently and to percolate at a lower temperature. Our observation may further be supported by the work of Nazario et al. [44,60] who showed that addition of nonionic surfactant, C_iE_j (polyoxyethylene alkyl ethers) resides at the interfacial region of AOT/ C_iE_j mixed interface 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. Both of these configurations supported the increase in droplet size with increasing head group of the nonionic surfactant as evidenced from DLS measurements, and this in turn assisted percolation. Increase in the radius of droplet with the addition of nonionic surfactants (Brij type) into the AOT/heptane/water system has also been reported by Liu et al. [49] from DLS measurements. The droplet size was dependent on the content of the nonionic surfactant and their EO chain length.

The observed effect of additives on the percolation phenomenon in mixed surfactant reverse micelles can be explained by extending the “channel-formation followed by material transfer” mechanism put forward by several workers [22,40,44,61]. A schematic diagram of the mechanism has been presented in Scheme 2. 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. The presence of additives of course, affect the phenomenological process of



Scheme 2. Proposed schemes for "fusion-mass transfer-fission" in presence of additives.

percolation in conductance as a whole in these systems, because of their different structures and difference in degree of their interfacial and physicochemical properties that influence the curvature.

Percolation of conductance in reverse micellar system is associated with the opening-up of the interface in order to produce a local positive curvature followed by the transfer of materials. The formation of the local positive curvature depends upon the fluidity of the interface, which in turn is associated with the effective packing parameter, P_{eff} (Eq. (3)). It has been discussed earlier that addition of Brij-56 and Brij-58 modifies the packing parameter of AOT/IPM system and made this non-percolating system to percolate. The additives further modify the effective packing parameter (P_{eff}) fixed by the composition of the mixed surfactant system 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 nonionic surfactants (Brijs). Thus NaC acts as a percolation-assisting additive as evidenced from Fig. 5 and Table 1. Due to the presence of NaC molecules at the interface, the effective packing parameter of the mixed surfactant monolayer (P_{eff}) is decreased due to the increased area of head group of surfactant, which in turn decreases the percolation threshold (T_p). On the other hand, the addition of Ch and its ester (CP) has a decreasing effect on the intrinsic conductance of the microemulsion, whereas CA and CB have an increasing effect for both the mixed systems. Ch is a small but rigid molecule. In the interface, its hydroxyl group remains attached to the surface of the micro-water droplet and interface becomes stiffer due to the formation of hydrogen bond with the carbonyl ester of AOT [25,37,62]. Thus in the presence of cholesterol, the monolayer of the droplets become more rigid and consequently increases the P_{eff} value of the mixed interface, which in turn increases T_p . Although closer approach of droplets is feasible, the rigidity of the interface restricts transfer of ions between droplets. However, the esters of Ch (CA, CB and CP) impart some degree of hydrophobicity due to the presence of alkyl group of different size. Thus a variation in effectiveness of suppressing the transfer of ions between droplets arising out of the structural features of the cholesterol esters is exhibited. 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 P_{eff} and 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 addition, urea is known to interact with the head group of surfactant present at the interface and also acts as a structure breaker. In the present study, it can be assumed that preferential solvation of the surfactant headgroups by urea results in an increase in the monomer dissociation degree, which leads to an increase in the area per headgroup, and this in turn increases the droplet size of reverse micellar systems in presence of urea, and hence assists percolation. This argument is well supported by Politi et al. for the incorporation of urea in AOT/hexane/water reverse micellar system [63,64].

Addition of NaCl to both these systems resists the percolation process as manifested from the increase of T_p (Table 1) and T_p increases with increasing NaCl concentration. It is known that addition of salt (NaCl) reduces the size of the polar head groups of the ionic surfactant due to the screening effect of the salt on the electrostatic repulsion between the head groups. The presence of salt reduces the effective head group area and thereby increases the "spontaneous negative curvature" of the surfactant and its tendency to form reverse micelles. Thus the curvature parameter of droplets is increased and decreases the attractive interactions among them. As a result T_p is increased. This observation is consistent with that reported by Mejuto et al. [38] 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 crown ether (4.9 to 18.9 mM). Mejuto et al. [39,40] earlier reported that incorporation of crown ether at low concentration to AOT/isooctane/water reverse micellar system increased percolation threshold, whereas at high concentration of crown ether, percolation threshold decreased. Similar observations were reported by Mukhopadhyay et al. [32].

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. This screens the electrostatic charges of the headgroups and decreases the electrostatic repulsion. This in turn decreases the effective head group area of AOT, which correspondingly increases P and thus the natural tendency of AOT to form negative curvature is increased resulting in a decrease in mean droplet size in microemulsions [65] and consequently percolation is retarded.

Both PL64 and PBD assist percolation. 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 resulting in a decrease in T_p . On the other hand PL64 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. This increases the area of head group of the surfactant and promotes exchange of Na^+ between the droplets, which ends up in a lower threshold in the electrical percolation behavior.

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 plus 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 [66,67].

Nonaqueous polar solvent, formamide (FA) (200 mM solution in water) assists percolation, whereas another nonaqueous polar solvent, ethylene glycol (EG) is observed to have only marginal effect on percolation phenomenon with identical concentration. In comparison to water, nonaqueous polar compounds are reported to have enhanced molecular interaction with the hydrophobic compounds [68]. This difference leads to higher penetration of nonaqueous 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, surfactant head group area, a is increased and P is decreased, and thus percolation is facilitated. Two aromatic additives, toluene (Tl) and benzyl alcohol (BA) were observed to decrease T_p for the AOT/Brij-58 system, whereas in AOT/Brij-56 system, Tl decreased T_p and BA increased T_p marginally. Earlier report [24] suggests that Tl increased T_p , whereas BA decreased T_p when added in a small amount (100 and 50 mM, respectively) to AOT/dodecane/water reverse micellar system owing to the interaction of Tl with the AOT hydrophobic moiety (“blocking effect”) and interfacial adsorption of BA (due to the presence polar –OH

group in BA). In the present study, however, both the additives have been observed to assist percolation, except for AOT/Brij-56 system where BA marginally retarded the percolation process.

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/Brij-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. 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 et al. [36] 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 [69]. The magnitude of E_p is 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 nonionic 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.

5. Conclusions

1. The non-percolating system water/AOT/IPM in the temperature range 5–60 °C can be made percolating by the addition of nonionic surfactants (Brij-56 and Brij-58) to the system, and the threshold percolation temperature, T_p depends on the concentration of the surfactant mixtures, and the polar head group size and content of the added nonionic surfactant.
2. 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.
3. The additives NaCl, urea, cholesteryl acetate, cholesteryl benzoate, toluene, pluronic, polybutadiene, sucrose esters (sucrose dodecanoates, L-1695 and sucrose monostearate, S-1670), formamide, decrease T_p , whereas NaCl, cholesteryl palmitate, crown ether, 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 per-

colation 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.

4. The observed behavior of these additives on the percolation phenomenon has been explained in terms of critical packing parameter and/or other factors, which influence the texture of the interface and solution properties of the mixed reverse micellar 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 nonionic 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.

Acknowledgments

The authority of Indian Statistical Institute, Kolkata is acknowledged for financial support in the form of project and Senior Research Fellowship to R.K.M. Mr. A.K. Das of GSU is thankfully acknowledged for preparing some of the illustrations (schemes).

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