

Investigation on percolation in conductance of mixed reverse micelles

Rajib K. Mitra, Bidyut K. Paul*

Geological Studies Unit, Indian Statistical Institute, 203 B.T. Road, Kolkata 700108, India

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Abstract

The addition of nonionic surfactants (Brij-56 and Brij-58) induces ω induced percolation in conductance in nonpercolating AOT/IPM/water system at constant temperature. The percolation threshold (ω_p) depends upon the content of the nonionic surfactants. The addition of NaCl at different concentrations shifts the ω_p towards higher values of ω for both systems. The influence of total concentration of surfactants on the conductance behavior of (AOT + Brij)s at fixed X_{nonionic} (mole fraction of nonionic in total surfactant) at constant temperature has been investigated, and as the concentration increases, ω_p shifts towards lower ω . The effect of Brij-58 is more pronounced than that of Brij-56 in inducing percolation. The temperature induced percolation behaviors of AOT reverse micelles in presence of nonionic surfactants of different types (Brij)s, Spans, Tweens) have been studied. The effects of water content (ω), micelle concentrations, content of nonionics (X_{nonionic}), solvent (hydrocarbon oils and IPM) have also been investigated. The threshold percolation temperature (T_p) of the mixed reverse micellar systems has been found to be dependent on the type, head group configuration and content of the added nonionic surfactant, oil. The temperature induced percolation in mixed anionic (AOT)–nonionic (Igepal CO 520) and cationic (DDAB) and nonionics (Brij-56 and Brij-58) in IPM have been studied, and percolation and reverse percolation in conductance have been observed respectively. An attempt has been made to give an insight to the mechanism of percolation in conductance and microstructures in mixed reverse micellar systems. The activation energy, E_p has been estimated for the percolation process of AOT-nonionic(s) mixed reverse micellar systems. This parameter has been utilized to interpret the percolation phenomenon in these systems.

Keywords: Mixed reverse micelles; Temperature induced percolation; DDAB; IPM; Nonionic surfactants

1. Introduction

Reverse micelles (RMs) are thermodynamically stable isotropic dispersions consisting of microdomains of water in oil solubilized by an interfacial film of surfactant. They are aggregates of surfactant molecules with their polar groups concentrated in the interior of the aggregate with their hydrophobic moieties extended into and are surrounded by the bulk apolar solvent. Water molecules are readily solubilized in this polar core, forming a so-called water pool. Reverse micelles containing solubilized water in excess of a certain amount are known as w/o microemulsions [1–8]. Shapes and sizes of surfactant aggregates in apolar solvents depend strongly

on the type and concentration of surfactant and on the nature of the counterion and solvent. Reverse micelles can host all kinds of substrate molecules whether hydrophilic, hydrophobic or amphiphilic due to the dynamic nature of the water pool and the interface formed by the surfactant layer. But solubilities and aggregation of surfactants in organic solvents are dramatically affected by the presence of a third component. The water content in a reverse micelle is usually characterized by the molar ratio, $\omega = [\text{water}]/[\text{surfactant}]$, which significantly affects the physical properties, for example, the sizes of reverse micelles and water pool, polarity of water pool of reverse micelles, etc. The properties of water molecules localized in the interior of reverse micelles are physicochemically different from those of bulk water, and the difference becoming progressively smaller as the water content in the micellar system increases. This indicates different states of

solubilized water in reverse micelles. The bound water exists overwhelmingly below $\omega = 10$ regardless of cationic and anionic surfactants [1,7–10]. The state of the interface between the water pool and surfactant monolayer depends strongly on the hydrophilic group of the surfactant, and accordingly one can control the electrostatic field by changing the hydrophilic group. Thus the chemical structure of the surfactant and ω can play a key role on the reactions in the water pool.

Reverse micelles or w/o microemulsion (hereafter referred to as reverse micelles) have drawn attention of many research workers from various fields of science and technology, owing to their power to solubilize otherwise immiscible substances. Because of their unique physicochemical properties (as mentioned above), reverse micelles find applications starting from tertiary oil recovery to nanoparticle synthesis [1,2,5–14]. The structure and properties of reverse micellar systems have been investigated extensively by employing a variety of physicochemical techniques, for example, IR [15–20], NMR [21], fluorescence spectroscopy [22–25], scattering techniques [20,26,27], calorimetry [28–30], DLS [31,32] and conductivity [33–70]. Among these, electrical conductivity provides a particularly convenient, useful and accessible tool for probing the structure and phase phenomena of reverse micelles/microemulsions. Of the different physical properties of reverse micelles, percolation of conductance is striking where manyfold (100–1000 times) increase in conductance can take place after a threshold volume fraction of the dispersant (water) at a constant temperature or after a threshold temperature at a constant composition [6,33,35,58,60]. In general discrete droplets, aggregational clusters or bicontinuous structure can easily be distinguished from the conductivity variation. The enhancement in conductance can be attributed due to two probable mechanisms, namely the “hopping” of ions from droplet to droplet beyond a threshold volume fraction of the dispersed phase is reached [43,56,66] and/or by exchanging droplet contents during droplet collisions known as “transient-fusion–mass transfer-fission” mechanism [34–36,65,67] on reaching a threshold temperature. According to Borkovec et al. [67] the sudden increase in conductance is caused due to a sharp transition from w/o dispersion to the bicontinuous aqueous phase. This mechanism is commonly known as the “static” (or frozen) percolation model. According to the “dynamic” percolation model [37–42,69] the increase in conductivity is effected by the formation of clusters of the aqueous droplets, which permits charge transport. This area has been intensively studied and quantification with adequate theories has been attempted [35,61–63]. Recently Antalek et al. [70] proposed an equilibrium model of a mixture of such structures, i.e. bicontinuous structure coexists in equilibrium with clusters and isolated droplets. In recent years, numerous studies on the effect of additives (other than surfactants) and other factors on the percolation of conductance (both volume and temperature-induced) have been carried out in water/AOT/hydrocarbon oil(s) systems since it can form reverse micelles under a wide range of conditions without the need of a cosurfactant. The

percolation phenomenon has been shown to occur earlier (assisting effect) or be delayed (resisting effect) in the presence of certain additives; however, many of them may also remain totally ineffective. These results enabled a better understanding of the factors that influence mass transfer in reverse micelles and revealed the significance of small amounts of additives on the behavior and properties of these systems. Of these studies, the work of Moulik and co-workers [35–42], Mathew et al. [43], Garcia-Rio et al. [44,45], Costa Amaral et al. [46], Dutkiewicz and Robinson [65] are noteworthy. A systematic investigation on the determination of the percolation threshold, performance of scaling equation, the evaluation of the activation energy for percolation, the energetics of clustering, and the dimension, polydispersity, and diffusion coefficient of water/AOT/hydrocarbon oil(s) in absence and presence of additives of different types have been examined and rationalized the results on a physicochemical basis by Moulik and co-workers [35–42]. This section has been dealt in a subsequent paper.

Alexandridis et al. [47] made a comprehensive study on temperature induced percolation of AOT/oil(s)/water-in-oil microemulsion (oils used were hexane, isooctane, decane and dodecane) to understand the effect of solvent, ω and micelle concentration. They estimated the thermodynamic parameters (enthalpy and entropy) associated with the formation of percolation clusters using an “association” model. They concluded that the percolating temperature decreased with increase in water content, micelle concentration and molecular weight of the solvent, and also concluded that the percolating process was enthalpically disfavored.

Reports on the microstructural study (with reference to conductivity measurements) using double chain cationic surfactant, di-*n*-dodecyldimethyl ammonium bromide (DDAB) are rarely reported [48].

Investigations on the microstructures and properties of reverse micelles formed with mixed surfactants (or addition of a second surfactant to single surfactant/oil/water) by conductivity measurements has seldom been carried out, which prevents one from completely understanding the basic mechanisms of the phenomenon taking place inside them. However, reports available on this aspect, are due to Li et al. [56], Liu et al. [53–55], Nazario et al. [49], Eicke and co-workers [50,51], Bumajdad and co-workers [26,57].

Li et al. [56] reported temperature induced percolation in water/AOT + HDEHP [bis(2-ethylhexyl)phosphoric acid]/heptane system, and the percolation threshold was found to decrease with increasing water content and/or HDEHP content, whereas for the NaDEHP + HDEHP system, conductance decreased with temperature and then increased marginally. The results were explained on the basis of different aggregation states of the surfactants and the different transition mechanism of charge carriers in these systems. In a subsequent work [56] they observed conductance percolation with the addition of NaCl in AOT/Hp/water system, and the onset water content increased with increasing NaCl concentration, whereas no percolation was observed

with increasing water content in presence of HDEHP. The influence of these additives on the conductance behaviors have been explained on the basis of their effects on the rigidity of oil/water interface and the attractive interactions of the surfactant aggregates.

Nazario et al. [49] analyzed the effect of several alkanols (C_6 , C_8 and C_{10}) and nonionic surfactants, poly (oxyethylene) alkyl ethers (C_iE_j , $i=10, 12$; and $j=1, 4, 6$ and 8) upon the percolation temperature and the apparent hydrodynamic radius of AOT/*i*-Oc/water microemulsion. The effects of both types of additives were opposite in regard to threshold percolation temperature. Using the experimental results and an association model, the clustering enthalpy and entropy were determined. The clustering process was found to be endothermic and entropically driven. Eicke et al. [50] studied the structure of water-in-isooctane microemulsion systems stabilized by AOT- $C_{12}E_5$ blends. They have shown that at low temperature, and for $\omega=25$ and $X_{\text{nonionic}} < 0.1$, the measured specific conductivity remained essentially constant. It was indicated that addition of a small amount of $C_{12}E_5$, has no effect on the droplet shape or volume. For $X_{\text{nonionic}} > 0.1$, the conductance decreased which implied a change in the droplet shape and/or volume. A spherical or oblate ellipsoid transition at $X_{\text{nonionic}} = 0.1$ was proposed by the authors. The percolation temperature was shown to be a decreasing function of X_{nonionic} . They [51] observed a typical conductivity (a reverse percolation type) of (AOT + $C_{12}E_5$)/*n*-octane/water as a function of temperature for varying interfacial mole fractions of AOT. The diffused double layer at the oil/water interface of the droplets has been considered to be highly compressed which accounts for reduced mobility and surface conductivity. The properties and microstructures of w/o microemulsion stabilized by mixed reverse micelles of AOT-nonionics (Brijs) in *n*-heptane were investigated by Liu et al. [53,54] using conductivity and dynamic light scattering. They reported that the shift in conductance maximum to a smaller ω_0 ([water]/[surfactant]) for both AOT-Bri-56 and AOT-Brij-58 mixed reverse micellar systems from conductance versus water solubilization curves compared with pure AOT microemulsions. They found that the shift of the conductivity maximum to a smaller ω_0 depends on the content of the nonionic surfactant. The intensity of the maximum was found to depend on the type and molar volume of the oils used. They further observed that the percolation temperature of AOT reverse micelles was decreased by adding nonionic surfactants, and more pronounced effects were obtained with increase of EO chain length and content of the nonionic surfactant [55].

The electrical conductivity of D_2O -in-heptane (or in *p*-xylene) microemulsions stabilized by a mixture of the cationic surfactant, DDAB and either the nonionic surfactants C_iE_j or polymeric nonionic surfactants of the type PEO-PPO-PEO, Pluronic[®], was investigated as a function of D_2O content and surfactant mixture composition by Bumajdad and Eastoe et al. [57]. It was found that the change in conductivity as a result of partially replacing the cationic

surfactant by the nonionic due to the change in droplet size, and not a decrease in ionic strength. The experimentally measured conductivity was found to agree with charge fluctuation model (CFM) predictions, even though the mole fraction of $C_{12}E_5$ was varied.

In our previous report [71] conductometric studies were carried out for the systems showing solubilization maximum, and it has been found that the occurrence of ω induced conductance percolation in mixed reverse micellar systems stabilized by AOT-nonionics (Brijs, Tweens, Spans, Igepals) and DDAB-Brijs in isopropyl myristate (IPM), isobutyl benzene (IBB), heptane and water at the vicinity of solubilization maximum ($\omega_{0,\text{max}}$). The threshold conductance percolation (ω_p) has been found to be dependent on the type of oil (or its molar volume) and also on the content and type of the nonionics in the blends, at which the solubilization maximum of water or NaCl was exhibited. These results have been used to correlate the two opposing factors (namely the interfacial curvature effect and the interdroplet interaction effect) that govern the solubilization maximum in mixed surfactant reverse micellar systems.

In continuation of our previous report [71], we have undertaken a comprehensive study on the conductance behaviors of anionic-nonionic(s) (AOT/Brijs, AOT/Tweens, AOT/Spans and AOT/Igepal CO 520) and cationic-nonionic (DDAB/Brij-56 and Brij-58) in isopropyl myristate (IPM, a hydrophilic oil with high viscosity) and water at different temperatures. IPM is a non-toxic oil, which was been widely used in biologically resembling systems, pharmaceuticals and drug delivery [72–75]. The phase characteristics of IPM-based reverse micellar systems have been studied, but microstructural studies with this type of systems, in particular to conductivity measurements, have not been found in literature. Hence the purpose of this investigation is to underline the effect of water content, types of nonionic surfactants and their contents (compositions), the micelle concentration, hydrocarbon oils of different molar volumes, the electrolyte concentration in solubilized water on the percolative conductance behavior. The evaluation of activation energy for the percolation process in mixed reverse micellar systems is hardly available in the literature. Therefore, these studies have also been undertaken to give an insight to the mechanism of percolation in conductance in mixed reverse micellar systems.

2. Experimental

2.1. Materials and methods

The following surfactants were used without further purification, Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 99%), polyoxyethylene(20) sorbitan monolaurate (Tween-20), polyoxyethylene(20) sorbitan monopalmitate (Tween-40) and nonylphenyl ethoxylates (Igepal CO 520) were purchased from Sigma, USA and Aldrich, USA, respectively. Polyoxyethylene(4) lauryl ether (Brij-30), polyoxyethylene(10)

lauryl ether (Brij-35), polyoxyethylene(2) cetyl ether (Brij-52), polyoxyethylene(10) cetyl ether (Brij-56), polyoxyethylene(20) cetyl ether (Brij-58), polyoxyethylene(10) stearyl ether (Brij-76), sorbitan monolaurate (Span-20), sorbitan monooleate (Span-80), didodecyltrimethylammonium bromide (DDAB) are products of Fluka (Switzerland). Hexane (Hx), heptane (Hp), octane (Oc), *iso*-octane (*i*-Oc), NaCl are of AR and extrapure grade of SRL, India and are of AR and extrapure grade. Isopropyl myristate (IPM) and decane are products of Fluka (Switzerland). Double distilled water was used with conductance less than $3 \mu\text{S cm}^{-1}$.

2.2. Solution preparation

The reverse micellar systems were prepared using the blends of AOT/nonionics and DDAB/nonionics at specified concentration of the surfactant(s) in oils (of different molar volumes) and then adding calculated amount of water using a microsyringe to obtain the desired ω ($[\text{water}]/[\text{surfactant(s)}]$).

2.3. Measurements

Electrical conductance measurements 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 $\pm 1\%$. The conductance of the experimental solutions at different ω 's was measured at each addition of water with the help of a microsyringe, into respective systems at a specified temperature (303 K) after allowing 30 min of time to attain equilibrium, in a thermostatic water bath accurate to $\pm 0.1^\circ\text{C}$. Dependence of conductivity on temperature at fixed ω , was investigated by changing the temperature in the range of (5–60 °C) in a thermostatic water bath under electromagnetic stirring to eliminate the temperature difference in the conductance cell. Differential curves have been constructed to determine ω_p and T_p for each system.

3. Results and discussion

3.1. Influence of water content on the percolation of AOT/Brijs mixed reverse micelles

Reverse micelles formed by AOT in IPM oil can solubilize water up to $\omega_{\text{max}} \sim 22$ with 0.1 mol dm^{-3} surfactant in oil at 303 K [71]. Conductance of AOT/IPM/water reverse micellar system was investigated at 303 K against varying ω . It was observed that the conductance remained almost constant throughout the studied ω (~ 22 , beyond which the formation became unstable), and conductivity was extremely low ($\sim 0.1 \mu\text{S cm}^{-1}$), which corresponds to that for non-conducting oil phase. But addition of a second surfactant (nonionic) into AOT/IPM system was observed to increase the conductivity of such mixed system. Fig. 1A depicted

conductivity of AOT/Brij-56/IPM/water system as a function of ω at three different $X_{\text{Brij-56}}$ (mole fractions of Brij-56 to total surfactants; 0.1, 0.15, 0.2) values at 303 K. It was found that after certain ω values, conductance increased suddenly, indicating a percolation in conductance phenomenon for such mixed surfactant reverse micellar systems. Conductivity reached a high value of $\sim 9.0 \mu\text{S cm}^{-1}$ of this formulation. Fig. 1B represents conductivity against ω profile of AOT/Brij-58/IPM/water reverse micellar systems at different $X_{\text{Brij-58}}$ (0.05, 0.1, 0.15, 0.2) and a sudden increase in conductance (percolation) was obtained for these systems too. For both the systems, a shift in threshold percolation in ω (ω_p) has been observed to be dependent on X_{Brij} . As X_{Brij} increases, percolation threshold is shifted towards lower ω -values. For AOT/Brij-56/IPM/water system, the percolation was exhibited at a highest ω value of 25.6 with a lowest $X_{\text{Brij-56}} = 0.1$, whereas in the AOT/Brij-58/IPM/water system the percolation started at a highest ω -value of 27.0 with a lowest $X_{\text{Brij-58}} = 0.05$. Thus the exhibition of percolation in conductance for both systems differed in respect of ω and X_{Brij} . It may be due to the difference in size of the polar head groups, i.e. EO chains of the Brij-56 (10 EO chains) and Brij-58 (20 EO chains). The effect of factors (like the type, area of polar head group, hydrophobic moiety, etc.) of the added nonionic surfactants on percolation phenomenon has been dealt in details in subsequent sections. This result can be correlated with the water solubilization behavior of AOT/Brij/IPM/water system [71]. The differential plot for determining ω_p for AOT/Brijs/IPM/water is presented in Fig. 1C. Fig. 2 shows the water solubilization behavior of AOT/Brij/IPM/water reverse micellar system at 303 K and the shaded region denotes the percolating region. For both the mixed surfactant systems, AOT/Brij-56 and AOT/Brij-58, maximum in water solubilization ($\omega_{0,\text{max}}$) was obtained with corresponding $X_{\text{Brij,max}} = 0.1$ and 0.05, respectively. It was found that percolation started in the vicinity of the maximum solubilization limit for both the systems and extended beyond the X_{max} limit. Appearance of percolation in 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, which may cause the emulsification failure and phase separation. Each conductivity droplet is coated with an insulating layer of surfactant on the interface, and it can be assumed that conductance takes place either by the displacement current through the capacitance coupling between the droplets or by jumps of the charged surfactant anions [69,76]. It is possible for the surfactant anions to leave the droplets and be reabsorbed into the second droplet. A short-range interaction potential between the droplets may be sufficient to account for the observed percolation threshold in colloidal systems provided that a conduction shell with an appropriate thickness around each droplet can be defined, so that the effective conductive phase volume reaches the percolation limit [77]. Owing to its wedge shape, AOT tends to bend around water in oil continuous phase forming an interfacial film of negative cur-

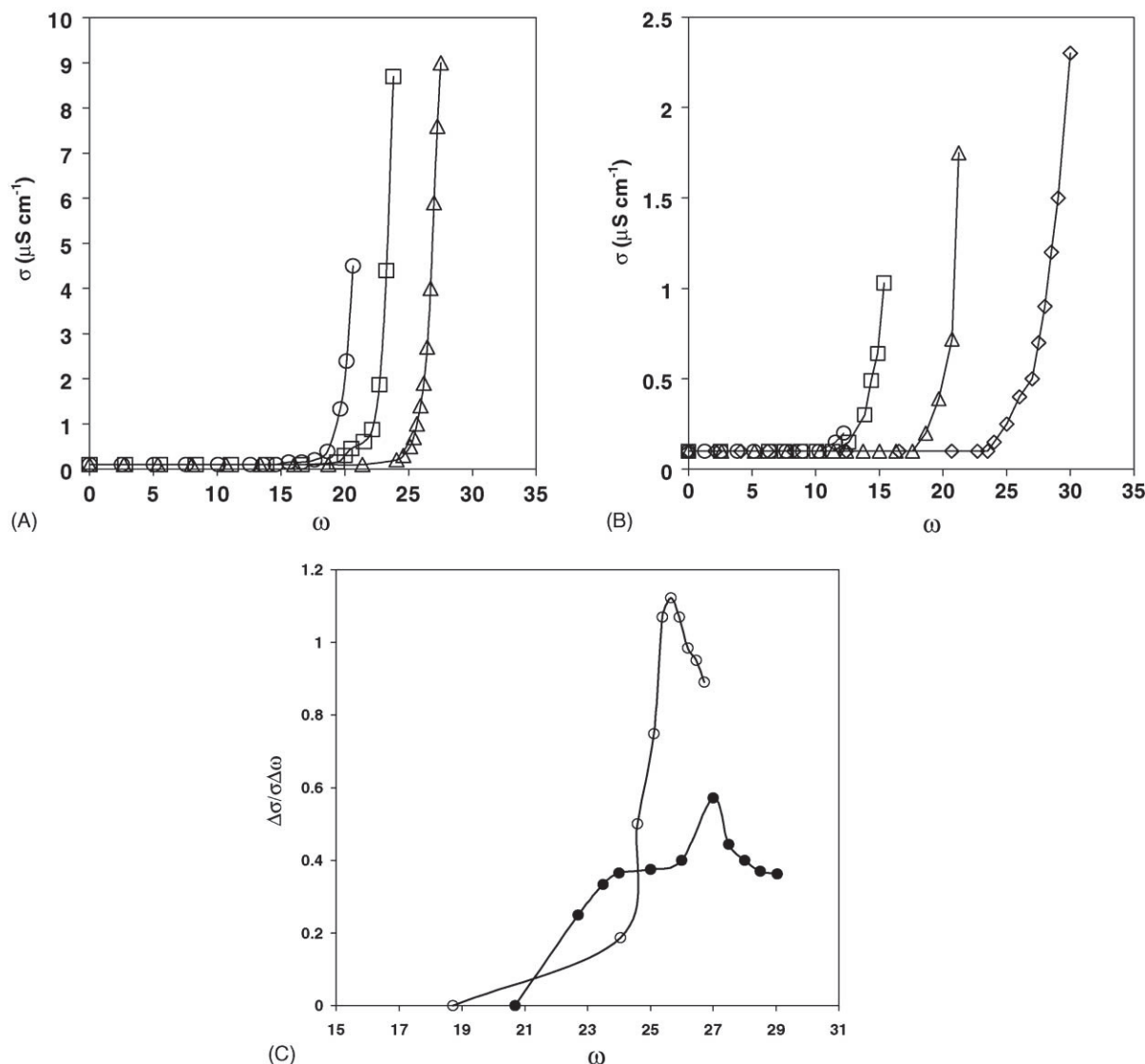


Fig. 1. Conductivity of the system AOT/Brij/IPM/water with $[S]=0.1 \text{ mol dm}^{-3}$ at 303 K (A) AOT/Brij-56: (Δ) $X=0.1$; (\square) $X=0.15$; (\circ) $X=0.2$; (B) AOT/Brij-58: (\diamond) $X=0.05$; (Δ) $X=0.1$; (\square) $X=0.15$; (\circ) $X=0.2$. Differential plot for determining ω_p : (\circ) AOT/Brij-56/IPM/water with $X_{\text{Brij-56}}=0.1$; (\bullet) AOT/Brij-58/IPM/water with $X_{\text{Brij-58}}=0.05$. (C) Differential plot for determining ω_p for the system; (\circ) AOT/Brij-56/IPM/water; (\bullet) AOT/Brij-58/IPM/water with $S_T=0.1 \text{ mol dm}^{-3}$ and $X_{\text{nonionic}}=0.1$.

vature at the oil-water interface. According to Garcia-Rio et al. [45], electrical conductivity in an AOT-based microemulsion is due to the passage of cations through the transient channels formed between colliding droplets. This passage is facilitated by the formation of the certain local region of positive curvature in AOT surfactant film [78]. The rigidity of the interface and the attractive interactions among the aggregates are probably the most important factors that determine the exchange rate of the ions and water molecules during the fusion processes [56]. 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. IPM also has a high molar volume. Since IPM possesses high molar volume as well as high viscosity, penetration of this oil into the interface is relatively small [79], which in turn perhaps fails

to modify the interface less effectively and thus AOT/IPM system was observed to be non-percolating. According to Liu et al. [55], 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. But incorporation of a second nonionic surfactant like Brij-56 and Brij-58 into AOT/IPM system modifies the interface in such a way that the interface becomes more flexible to incorporate more water and to facilitate droplet fusion and hence the percolation process. It may be due to the presence of the head group of nonionic surfactant at the interface shields the head group repulsion of AOT molecules, and make the interface more flexible. The inter droplet attractive interaction in AOT w/o microemulsions increases with increasing chain length of the oil [80], which in turn increases the overlap volume

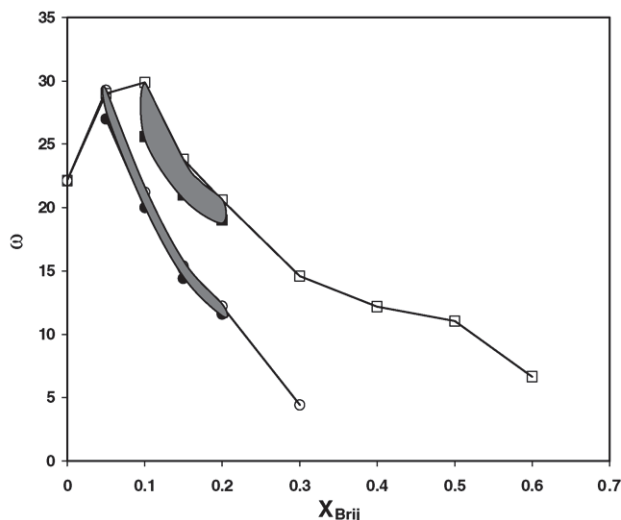


Fig. 2. Percolating region of mixed reverse micellar system: AOT/Brij/IPM/water with surfactant concentration 0.1 mol dm^{-3} in oil at 303 K. The shaded region represents percolation region; (\square) AOT/Brij-56; (\circ) AOT/Brij-58.

between droplets and consequently percolation process is facilitated.

3.2. Effect of NaCl concentration on the percolation water content

Effect of NaCl on conductivity of the mixed surfactant reverse micellar systems AOT/Brij-56/IPM/water and AOT/Brij-58/IPM/water at fixed $X_{\text{Brij}} = 0.1$ and 0.05 , respectively and total surfactant concentration (S_T) 0.1 mol dm^{-3} , have also been studied at 303 K and depicted in Fig. 3A and B. It was found that with increasing NaCl concentration (0.05 – 0.1 mol dm^{-3}), conductance percolation threshold (ω_p) was shifted towards higher ω -values compared to the aqueous systems. No percolation was observed at 0.15 mol dm^{-3} of NaCl in both the systems. NaCl increases the rigidity of the interfacial film, thus increasing the negative curvature of the surfactant layer by reducing the head group repulsion of the ionic surfactant. Consequently, the packing parameter $P = v/al_c$ (where v : volume of head group, a : area of head group and l_c : chain length of surfactant) of the surfactant molecules is increased as ‘ a ’ is decreased, and thereby the radius of the droplets is decreased [53,81]. This made the systems containing NaCl to percolate at a higher ω . The increase in ω_p with increasing NaCl concentration can be correlated with the solubilization behavior of AOT/Brij/IPM/aqueous NaCl system at 303 K [71]. It was observed that solubilization capacity passed through a maximum value (ω_{max}) at a certain NaCl concentration ($[\text{NaCl}]_{\text{max}}$) at constant temperature. The increased solubilization capacity can be related to the increased rigidity of the interface with addition of electrolyte, which made the droplets more stable and in turn enable to accommodate more water. It has also been observed that NaCl had no effect on water solubilization behavior of reverse mi-

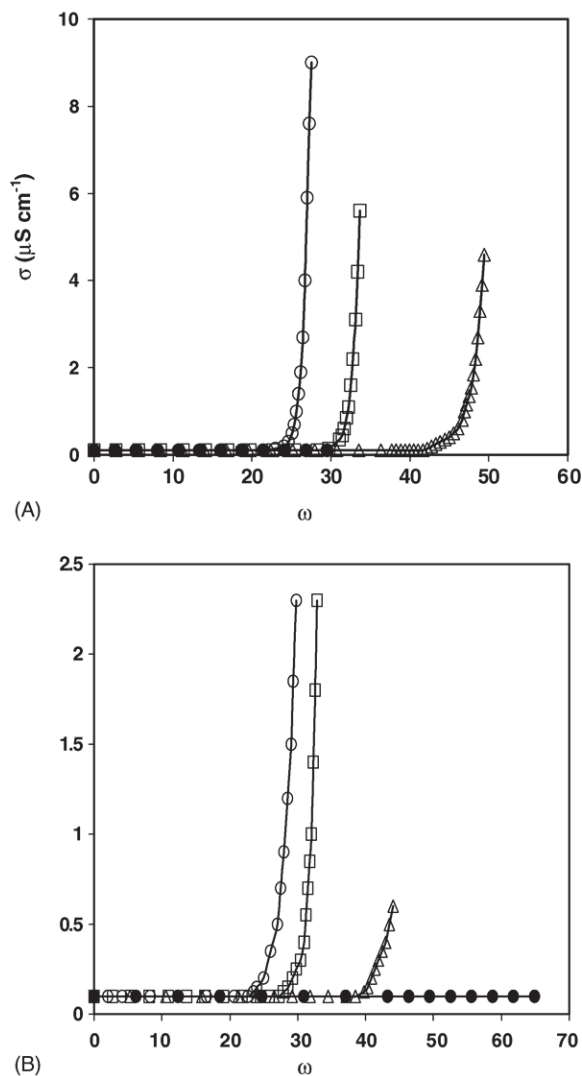
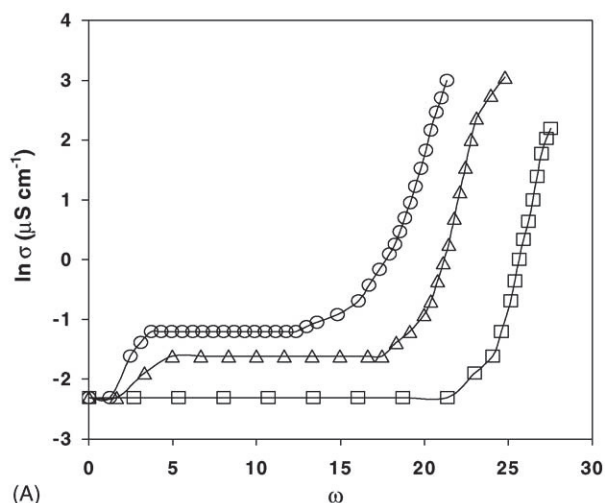


Fig. 3. Effect of NaCl on percolation behavior of AOT/Brij/IPM/water mixed reverse micellar system with surfactant concentration 0.1 mol dm^{-3} at 303 K. (A) AOT/Brij-56 with $X_{\text{Brij-56}} = 0.1$: (\circ) water; (\square) 0.05 mol dm^{-3} NaCl; (\triangle) 0.1 mol dm^{-3} NaCl; (\bullet) 0.15 mol dm^{-3} NaCl. (B) AOT/Brij-58 with $X_{\text{Brij-58}} = 0.05$: (\circ) water; (\square) 0.05 mol dm^{-3} NaCl; (\triangle) 0.1 mol dm^{-3} NaCl; (\bullet) 0.15 mol dm^{-3} NaCl.

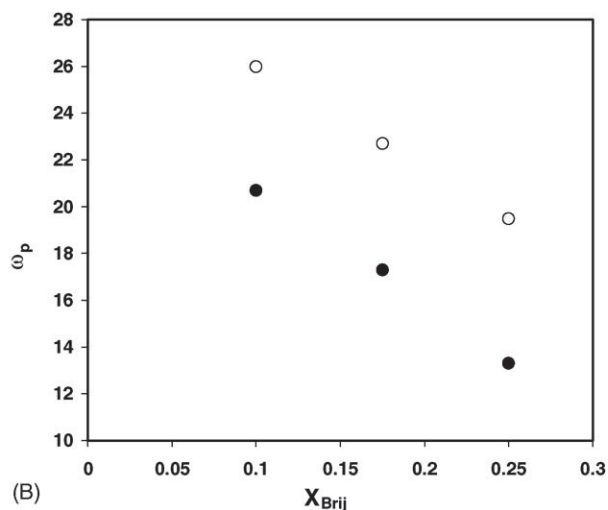
cellar systems stabilized by mixed nonionic–nonionic (Igepal CO 520/Brij-56) surfactant [71]. So it is the presence of AOT in the AOT/Brij mixed surfactant interface, that made the effect of NaCl pronounced to make the interface rigid and increase ω_p .

3.3. Influence of surfactant concentration on the percolation water content

Fig. 4A depicts conductivity of AOT/Brij-56 and Brij-58 blends in IPM and water system as a function of ω with three different total surfactant concentrations (S_T) (viz. 0.1 , 0.175 and 0.25 mol dm^{-3}) at 303 K. It was found that with increasing surfactant concentration, percolation threshold (ω_p) was decreased. High surfactant concentration induces higher



(A)



(B)

Fig. 4. (A) Conductivity vs. ω profile for AOT/Brij-56/IPM/water system with different surfactant concentrations at 303 K and $X_{\text{Brij-56}} = 0.1$: (\square) 0.1 mol dm^{-3} ; (\triangle) $0.175 \text{ mol dm}^{-3}$; (\circ) 0.25 mol dm^{-3} . (B) ω_p (percolation threshold) values for AOT/Brij/IPM/water mixed surfactant systems at three different surfactant concentrations ($0.1, 0.175$ and 0.25 mol dm^{-3}) and $X_{\text{Brij}} = 0.1$: (\circ) AOT/Brij-56; (\bullet) AOT/Brij-58 at 303 K.

number density of droplets in reverse micellar system, which in turn facilitate interdroplet interactions and hence also facilitated percolation. To determine the relative effect of added nonionic surfactant in altering the interface to induce percolation, ω_p has been plotted against concentration of surfactant for two mixed surfactant systems, AOT/Brij-56 and AOT/Brij-58 (Fig. 4B). It has been found that for all three studied surfactant concentrations, ω_p had lower values for the AOT/Brij-58 systems in comparison to AOT/Brij-56 systems. So it can be inferred that Brij-58 modifies the interface more effectively than Brij-56. Brij-58 has a larger polar head group than Brij-56, and hence Brij-58 has stronger effect on perturbing the interface. It is well known that the droplet size of reverse micellar systems depends on the flexibility of the interface, which in turn is related to the surfactant packing

parameter (P), as mentioned earlier [81]. 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 [82]:

$$P_{\text{eff}} = \frac{(xv/al_c)_A + (xv/al_c)_B}{x_A + x_B} \quad (1)$$

where x is the mole fraction of the surfactant present at the interface. For nonionic surfactants P decreases with increasing EO chain length [83] and are generally smaller than that of AOT. So it is evident from the equation that P_{eff} will be less for Brij-58 (containing 20 EO chains) compared to Brij-56 (containing 10 EO chains). Hence droplet size would be larger for the former resulting in a lower value of ω_p .

3.4. Temperature-induced percolation of AOT/Brijs mixed reverse micelles

Like the increase of the conducting aqueous phase, increase in temperature can also induce conductance percolation in w/o microemulsion/reverse micelles. Increasing temperature enhances droplet collisions, which can result in an exchange of mass between the colliding droplets and facilitate percolation. Conductivity in a reverse micellar system emanates from the formation of short-lived dimers followed by their separation [78,84]. The monolayer must deform in order to form the dimers. At low water content, the surfactant aggregates behave as dispersion of conducting particles inside non-conducting oil. Fluctuation of ion contents induces ionization causing charged droplets. Transport of charged droplets conducts electricity. An increase in temperature increases the frequency of charge fluctuation and Brownian movement of the droplets in an oil medium, which in turn can induce sharp increase in conductance [56]. According to Alexandridis et al. [47] with increasing temperature, surfactant monolayer bending elasticity decreases for a given droplet size. This increases the frequency of droplet clustering, surfactant monolayer deforming, droplets exchanging materials and increasing conductivity. In the present study conductance was studied against varying temperature of AOT/IPM/water reverse micellar system with total surfactant concentration (S_T) of $0.175 \text{ mol dm}^{-3}$ and $\omega = 20$. It was found that conductance increased only marginally up to a temperature of as high as 333 K. In order to exhibit percolation in conductance for AOT/hydrocarbon oil/water reverse micellar systems, the water droplets in the oil continuum must undergo 'sticky collisions' to form transient expanded clusters through which Na^+ can migrate easily increasing the conductivity sharply. The opening of surfactant film to form transient clusters involve large activation energy in order to form local positive curvature [78]. The high viscosity of IPM and the rigidity of the AOT/IPM interface (as discussed in the preceding sections) perhaps hindered the percolation process in AOT/IPM/water reverse micellar system. To underline the effect of added nonionic surfactant to AOT/IPM/water reverse micellar system, conducto-

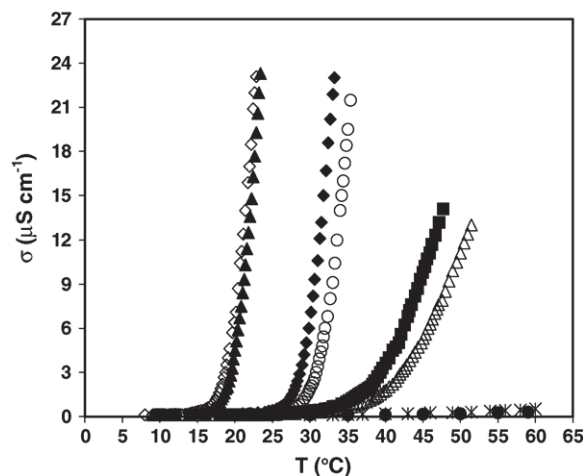


Fig. 5. Conductivity as a function of temperature for AOT/nonionic/IPM/water mixed reverse micellar systems with $[S] = 0.175 \text{ mol dm}^{-3}$; $X_{\text{nonionic}} = 0.1$ and $\omega = 20$: (\diamond) Brij-58; (\blacktriangle) Brij-35; (\blacklozenge) Tween-20; (\circ) Tween-40; (\blacksquare) Brij-56; (\triangle) Brij-76; ($*$) Brij-52; (\bullet) Brij-30.

metric studies were carried out for AOT/nonionic/IPM/water reverse micellar systems at the same composition and compared the contributions due to the size of polar head groups (EO chain length), hydrophobic moiety, and type of the added nonionic surfactant in conductance behavior. It may be noted that all these contributions were observed to play a significant role as reflected from the solubilization capacity of water vis-à-vis the conductance versus ω profile as reported earlier [71]. Fig. 5 shows the temperature dependence on conductivity for the AOT/nonionic/IPM/water system with different nonionic surfactants (Brij-30, Brij-35, Brij-52, Brij-56, Brij-58, Brij-76, Tween-20, Tween-40, Span-20 and Span-80) at $\omega = 20$ and $X_{\text{nonionic}} = 0.1$ with total surfactant concentration of $0.175 \text{ mol dm}^{-3}$. It was found that for all the mixed systems (except AOT/Brij-30, AOT/Brij-52 and AOT/Span blends) conductance increased sharply after certain threshold temperature indicating a percolation phenomenon. For all these mixed reverse micellar systems, mole fraction of the nonionic component in total surfactant was fixed. So the effective packing parameter (P_{eff}) and hence the radius of droplets was dependent mainly on the polar head group area and chain length of the nonionic surfactants [53,81]. Increasing EO chain length increases hydrodynamic radius of mixed reverse micellar systems (according to Eq. (1)) and hence expected to percolate at a lower temperature. Nazario et al. [49] showed that in AOT/*iso*-octane/water reverse micellar system, addition of nonionic surfactant, C_iE_j assisted conductance percolation, and it was assumed that C_iE_j resided at the interfacial region with its polar head either immersed in the water pool or in the surfactant (AOT) head group region. Both these conformations accord with the increase in droplet size and assisting percolation. The present observation strongly supports this argument. Table 1 provides the T_p (percolation threshold temperature) values for the mixed

Table 1

Threshold percolation temperature (T_p) and activation energy (E_p) of AOT/nonionic mixed surfactant reverse micellar systems in IPM at $X_{\text{nonionic}} = 0.1$ and $[S_T] = 0.175 \text{ mol dm}^{-3}$

Nonionic surfactant	T_p ($^{\circ}\text{C}$)	E_p (kJ mol^{-1})
Brij-35	18.0	469
Brij-56	34.5	176
Brij-58	17.4	397
Brij-76	39.0	177
Tween-20	28.1	391
Tween-40	29.3	386

reverse micellar systems. T_p increases with decreasing EO chain length. Brij-58 and Brij-35 have 20 and 23 EO chains in their hydrophilic part, but differs in their hydrophobic moiety. They have identical T_p values. Brij-56 and Brij-76 have identical EO chains (10), but different carbon number in their hydrophobic moiety (C_{16} and C_{18} , respectively). So the penetration of oil into the interfacial layer is different for these two systems. Consequently AOT/Brij-56/IPM system has lower T_p than AOT/Brij-76/IPM system. However, AOT/Brij-56 and AOT/Brij-76 blends have higher T_p values in respect to the AOT/Brij-35 and AOT/Brij-58 blends. Both Tween-20 and Tween-40 have 20 EO chains in their head groups, but AOT/Tween systems exhibited T_p values larger than those of AOT/Brij-35 and AOT/Brij-58 systems (Table 1). A probable explanation for this may be put forward from the bulky nature of these surfactant head groups (unlike Brij it does not have a straight EO chain head group) which hinders these surfactants to be adsorbed at the interface in an extent similar to those of Brij-35 or Brij-58. Tweens (ethoxylated derivatives of sorbitan esters) are interesting family of the surfactants. The substitution of the hydroxyl groups on the sorbitan ring with polyoxyethylene groups increases the hydrophilicity of the surfactants. Among these two Tweens, Tween-20 (HLB = 16.7) is more hydrophilic than Tween-40 (HLB = 15.6) and hence it exhibited a lower T_p , as observed previously that nonionic surfactants (Brij-35 and Brij-58) with higher HLB number (16.9 and 15.7) showed percolation at a lower T_p in comparison to nonionic surfactants (Brij-56 and Brij-76) with lower HLB numbers (12.9 and 12.4). Thus it can be inferred that the polar oxyethylene chain length of the nonionic surfactant vis-à-vis its size which originates from the type of the surfactant have strong influence on governing the percolation phenomenon in AOT/nonionic mixed surfactant reverse micellar system; though the effect of the hydrocarbon moiety cannot be neglected. Brij-30 (HLB, 9.7) and Brij-52 (HLB, 5.2) having only four and two EO chains, respectively in their head groups, could not modify the interface significantly at the chosen composition (according to Eq. (1)) and hence percolation did not occur for AOT/Brij-30/IPM/water and AOT/Brij-52/IPM/water reverse micellar systems. Span-20 and Span-80 does not have any EO chains in their head group (HLB, 8.6 and 4.3) and the AOT/Span/IPM/water systems did not exhibit any percolation. However, at higher S_T (0.25 mol dm^{-3}) and X_{nonionic} (0.3), the AOT/Brij-52, Span-

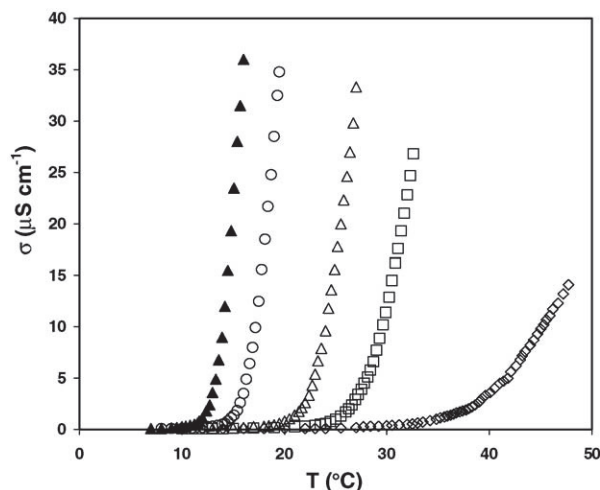


Fig. 6. Conductivity as a function of temperature for AOT/Brij-56/IPM/water mixed reverse micellar systems at different water content (ω) with surfactant concentration $0.175 \text{ mol dm}^{-3}$ and $X_{\text{Brij-56}} = 0.1$: (\diamond) $\omega = 20$; (\square) $\omega = 22.5$; (\triangle) $\omega = 25$; (\circ) $\omega = 27.5$; (\blacktriangle) $\omega = 30$.

20 and Span-80 blends in IPM/water exhibited temperature induced conductance percolation at higher ω (>40) (figure not shown).

Fig. 6 shows conductivity of the AOT/Brij-56/IPM/water mixed reverse micellar system with different ω -values (20.0, 22.5, 25.0, 27.5 and 30.0) at $X_{\text{Brij-56}} = 0.1$ and total surfactant concentration of $0.175 \text{ mol dm}^{-3}$. The corresponding T_p values were obtained at 34.5, 26.9, 22.0, 15.7 and 11.7°C , respectively. It has been found that T_p decreased with increasing ω . The droplets of w/o microemulsions can be assumed to be spherical and increase linearly with increasing ω [40,85]. This in turn increases droplet interaction facilitating overlapping of the droplets and percolation initiates at a lower temperature. This observation is supported by other workers [40–42,47,49,55].

Conductance studies have been carried out at three different total surfactant concentrations (0.1 , 0.175 and 0.25 mol dm^{-3}). Fig. 7 shows conductivity of AOT/Brij-56 and Brij-58/IPM/water reverse micellar systems with three different initial concentration of the surfactant at fixed $X_{\text{nonionic}} = 0.1$ and $\omega = 20$. It was found that T_p decreased with increasing surfactant concentration. Higher the total concentration of the mixed surfactants, lower is the T_p for both systems. AOT/Brij-56/IPM/water system with 0.1 mol dm^{-3} surfactant concentration did not show any significant increase in conductance with temperature. High surfactant concentration causes an increase in the number density of droplets in reverse micellar systems. This increases interaction between droplets facilitating percolation by increasing interdroplet collisions and lowering the barrier to electrical conductivity [32,55]. AOT/Brij-58 systems exhibited conductance percolation at a lower T_p than the AOT/Brij-56 systems for any particular composition as intuited from preceding discussions.

It has been reported earlier that increase in Brij-30 content (from $X_{\text{Brij}} = 0$ to 0.2) in an AOT/Brij-30 blend in hep-

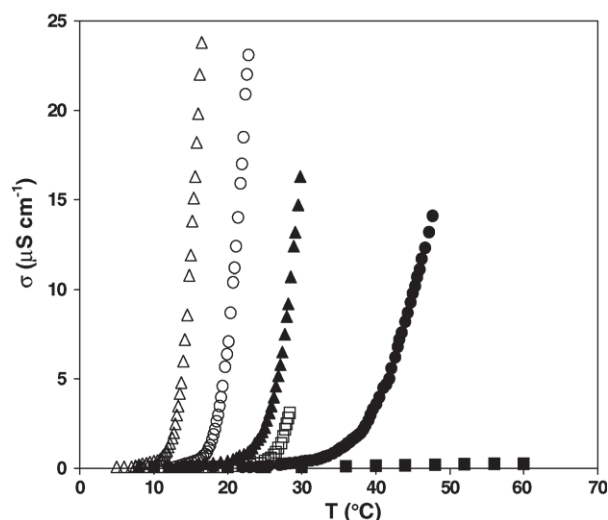


Fig. 7. Conductivity as a function of temperature for AOT/Brij-56(58)/IPM/water mixed reverse micellar systems at different total surfactant (micelle) concentrations with $\omega = 20$ and $X_{\text{Brij}} = 0.1$. Open symbols represent Brij-58 systems and closed symbols represent Brij-56 systems. Triangle: 0.25 mol dm^{-3} ; circle: $0.175 \text{ mol dm}^{-3}$; square: 0.1 mol dm^{-3} .

tane/water reverse micellar system, T_p decreased [49]. In the present investigation, conductance was studied more elaborately at five different mole fractions of Brij-56 and Brij-58 ($X_{\text{Brij}} = 0.08, 0.09, 0.1, 0.11$ and 0.12) with fixed $\omega = 20$ and total surfactant concentration of $0.175 \text{ mol dm}^{-3}$ for the system to underline the effect of content of nonionic surfactants Brij-56 and Brij-58 in AOT/IPM/water system. It was found that with increasing nonionic content, percolation threshold temperature decreased for both the mixed systems (Fig. 8A and B). The corresponding T_p values have been presented in Table 2. Addition of Brij-56 and Brij-58 makes the rigid AOT/IPM interface more fluid to form the required local positive curvature to induce droplet fusion followed by mass transfer and hence percolation phenomenon is facilitated with increasing nonionic content. It is evident from Eq. (1) that with increasing X_{nonionic} , P_{eff} decreases compared to the single AOT/oil/water system and thereby percolation is facilitated. To study the relative effect of the nonionic content on percolation threshold, the relative change in θ_p (percolation threshold temperature in Kelvin scale), $(\Delta\theta_p/\theta_p)$ has been plotted against X_{Brij} (Fig. 9), where θ_p is the percolation temperature with $X_{\text{Brij}} = 0.1$ and $\Delta\theta_p = \theta'_p - \theta_p$, where θ'_p is the percolation temperature at any X_{Brij} . It is evident

Table 2
Percolation threshold (T_p) of AOT/Brij mixed surfactant systems with different mole fraction (X) of Brij at $[S_T] = 0.175 \text{ mol dm}^{-3}$ at $\omega = 20$

X_{nonionic}	AOT/Brij-56/IPM/water: T_p ($^\circ\text{C}$)	AOT/Brij-58/IPM/water: T_p ($^\circ\text{C}$)
0.08	40.2	24.0
0.09	37.5	20.3
0.1	34.5	17.4
0.11	29.0	13.4
0.12	26.1	10.1

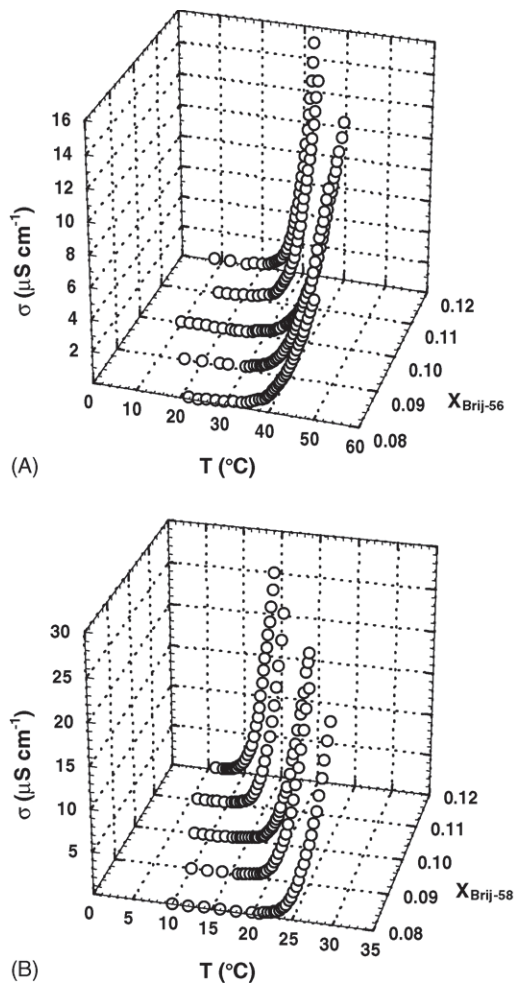


Fig. 8. Conductivity as a function of temperature for AOT/Brijs/IPM/water mixed reverse micellar systems at different content of Brij-56 and Brij-58 ($X_{\text{Brij}}=0.08, 0.09, 0.1, 0.11, 0.12$) with surfactant concentration $0.175 \text{ mol dm}^{-3}$ and $\omega=20$: (A) AOT/Brij-58; (B) AOT/Brij-56.

from the figure that for a certain X_{Brij} , Brij-58 influences θ_p more effectively than Brij-56 does. This supports the earlier statement that larger the size of the polar head group of anionic surfactant, larger is the droplet radius and hence more is the influence on conductance percolation in mixed reverse micellar systems.

3.5. Effect of oils (hydrocarbon and IPM) on percolation of AOT/Brijs mixed reverse micelles

Conductance behavior of mixed reverse micellar system (AOT/Brij-56) have been studied at different ω 's (20, 22.5, 25, 27.5 and 30) in different oils (Hx, Hp, Oc, *i*-Oc, Dc and IPM) with $X_{\text{Brij-56}}=0.1$ and total surfactant concentration of $0.175 \text{ mol dm}^{-3}$ (Fig. 10) and results are presented in Table 3. It has been observed that T_p decreased with increasing molar volume of the hydrocarbon oils at a fixed $\omega=20$, whereas IPM being an oil with a high molar volume ($317 \text{ cm}^3 \text{ mol}^{-1}$) exhibited T_p in the range of that of heptane (molar volume $146 \text{ cm}^3 \text{ mol}^{-1}$). From Table 3 it is evident that T_p depends on

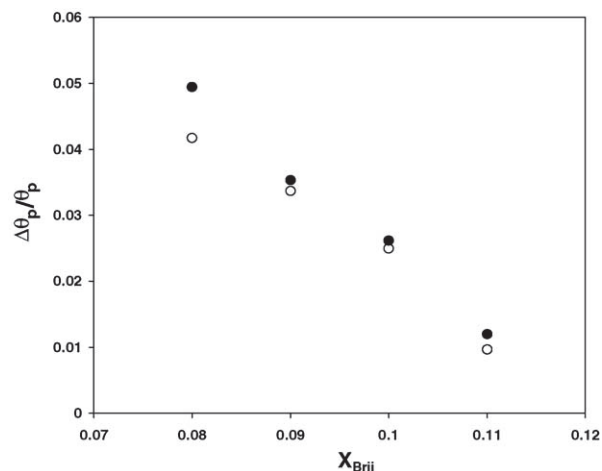


Fig. 9. Relative change in percolation threshold, $\Delta\theta_p/\theta_p$, where the percolation threshold temperatures have been expressed in kelvin scale (see text), vs. content of nonionic surfactant (X_{Brij}) profile for AOT/Brijs/IPM/water mixed reverse micellar systems with surfactant concentration $0.175 \text{ mol dm}^{-3}$ and $\omega=20$. Open circles represent Brij-56 systems and closed circles represent Brij-58 systems.

ω , and larger the ω -value, smaller was the value of T_p . Our observation is well supported from the finding of other authors which can be summarized as follows; the molecular weight or molecular volume or chain length of oils (alkanes) is reported to have strong influence over percolation phenomenon in w/o reverse micellar systems [34,42,47,49,55,86,87]. Liu et al. [55] explained the shifting of the T_p to a lower value with an increase in molar volume of alkane solvents for mixed reverse micellar systems on the basis of increased droplet radius and the increased interdroplet interactions with chain length of the oil. A large attractive interaction between the droplets in a reverse micellar system is a major factor that limits the

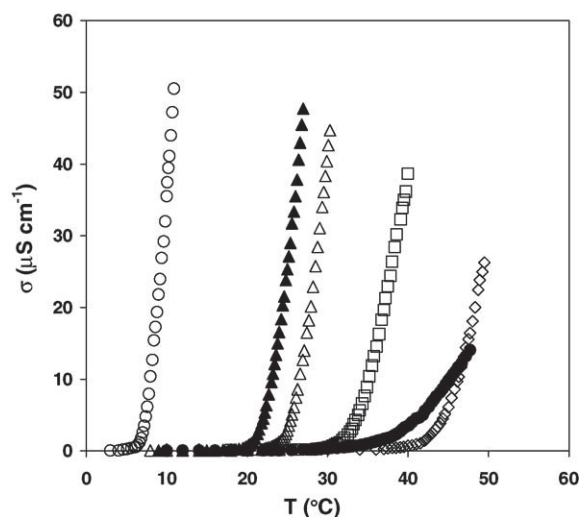


Fig. 10. Conductivity as a function of temperature for AOT/Brij-56/oil/water mixed reverse micellar systems in different oils with surfactant concentration $0.175 \text{ mol dm}^{-3}$, $X_{\text{Brij-56}}=0.1$ and (A) $\omega=20$; (B) $\omega=30$: (\diamond) *n*-hexane; (\bullet) IPM; (\square) *n*-heptane; (\triangle) *iso*-octane; (\blacktriangle) *n*-octane; (\circ) *n*-decane.

Table 3

Threshold percolation temperature (T_p) of AOT/Brij-56 mixed surfactant reverse micellar systems with different oils at $X_{\text{Brij-56}} = 0.1$ and $[S_T] = 0.175 \text{ mol dm}^{-3}$

Oil	Molar volume ($\text{cm}^3 \text{ mol}^{-1}$)	$\omega = 20$: T_p ($^{\circ}\text{C}$)	$\omega = 22.5$: T_p ($^{\circ}\text{C}$)	$\omega = 25$: T_p ($^{\circ}\text{C}$)	$\omega = 27.5$: T_p ($^{\circ}\text{C}$)	$\omega = 30$: T_p ($^{\circ}\text{C}$)
Hx	131	42.8	38.2	32.2	29.1	23.0
Hp	146	32.1	26.8	23.1	20.0	14.2
Oc	163	24.5	–	–	–	–
<i>i</i> -Oc	165	21.6	21.8	19.1	15.6	13.0
Dc	195	7.0	–	–	–	–
IPM	317	34.5	26.9	22.0	15.7	11.7

stability of the system [80]. The exchange rate of droplet contents increases with increasing apolar solvent chain length in AOT/hydrocarbon oil systems, and as a consequence percolation threshold decreases. As the chain length of oil is increased, penetration of it into the interface is decreased resulting in greater interdroplet attraction and consequent reduction of T_p [47,49]. The increase in the molar mass of the hydrocarbon oil decreased the density of the continuous phase enabling easier approach of the interacting droplets for mass transfer [42]. Increased droplet radius also increases the overlap volume between two droplets when they form cluster, which in turn increases interacting potential and thus facilitates conductance percolation. According to Mays et al. [86], the percolation threshold was moved towards higher temperature with alkanes of lower molecular weight as solvent. It was further observed [87] that the changing of the droplet size via ω leads to clearer differences between the conductivity curves for AOT/Hp/water system.

Higher the ω , lower was the T_p . It was concluded that percolation was favored in w/o microemulsions with smaller droplets and occurred at considerably higher temperature. The molar volume of IPM is higher than the studied hydrocarbon oils (alkanes), and percolation in conductance for AOT/Brij-56/IPM occurred at a temperature between that of hexane and heptane. In order to understand this unusual behavior of IPM, the relative change of percolation threshold ($\Delta\theta_p/\theta_p$) has been plotted against ω for different oils (Fig. 11). It was observed that the slope of the curve decreased steadily with increasing molar volume of oil. But for IPM the slope was higher than any of the hydrocarbon oils studied. Since all the other factors (type, head group configuration, hydrophobic moiety, mole fraction of non-ionic surfactant, total surfactant concentration, ω) remained constant, oil characteristic played the key role in this relative change, and thus it can be inferred that not only molar volume, but other parameters (like hydrophilicity, viscosity, branching of chains of oils, etc.) can play important role in determining percolation phenomenon.

3.6. Temperature-induced percolation of AOT/Igepal and DDAB/Brij mixed reverse micelles

In this section, temperature induced percolation in mixed reverse micellar systems stabilized by AOT and Igepal CO 520 (a nonionic surfactant belonging to the family of nonyl phenyl ethoxylates and contains five EO chains) which can

solubilize substantial amount of water when dissolved in IPM, is presented. A blend of AOT and Igepal CO 520 with a total surfactant concentration of 0.1 mol dm^{-3} at $X_{\text{Igepal}} = 0.2$ (as maximum water solubilization was observed at this mole fraction of Igepal in an AOT/Igepal blend) was used to form reverse micelle in IPM oil. The conductivity of these systems at three ω -values, 28, 32 and 34 was measured at different temperatures. The results are depicted in Fig. 12. A normal conductance percolation like curves were obtained, wherein T_p decreased with increasing ω , resembling other mixed reverse micellar systems. In an AOT/Igepal/IPM blend with $X_{\text{Igepal}} = 0.2$, Igepal thus acts in the same way a non-ionic surfactant does in AOT/Brij, Tweens blends. Ilgenfritz and co-workers [88] have studied the conductance behavior of Igepal/cyclohexane + *n*-hexane (1:1)/aqueous KCl system. They reported that Igepal/hydrocarbon oil system exhibited a reverse percolation in conductance phenomenon, wherein conductivity decreased with increasing temperature. They concluded a bicontinuous structure for the w/o microemulsion systems at low temperature, and on increase in temperature, the microstructure changed into discrete droplets due to the dehydration of the nonionic Igepal. It has also been reported that the opposite temperature dependence of surfactant hydration and solubility in water of these two surfactants are

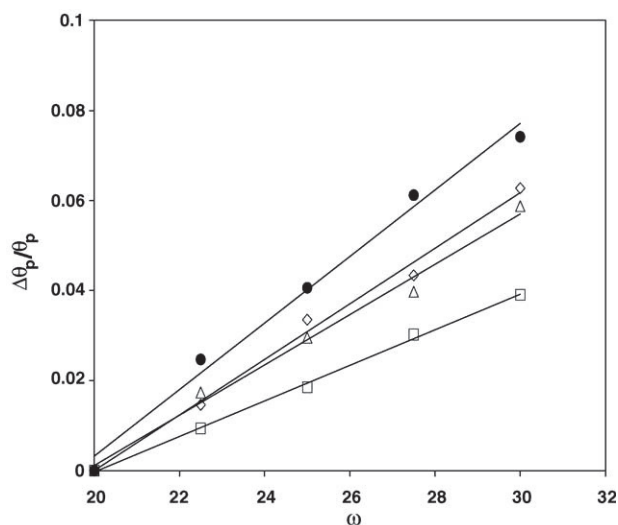


Fig. 11. Relative change in percolation threshold, $\Delta\theta_p/\theta_p$ vs. ω profile for AOT/Brij-56/oil/water reverse micellar systems with surfactant concentration $0.175 \text{ mol dm}^{-3}$ in oil; $X_{\text{Brij-56}} = 0.1$: (\diamond) *n*-hexane; (\bullet) IPM; (\square) *iso*-octane; (\triangle) *n*-heptane.

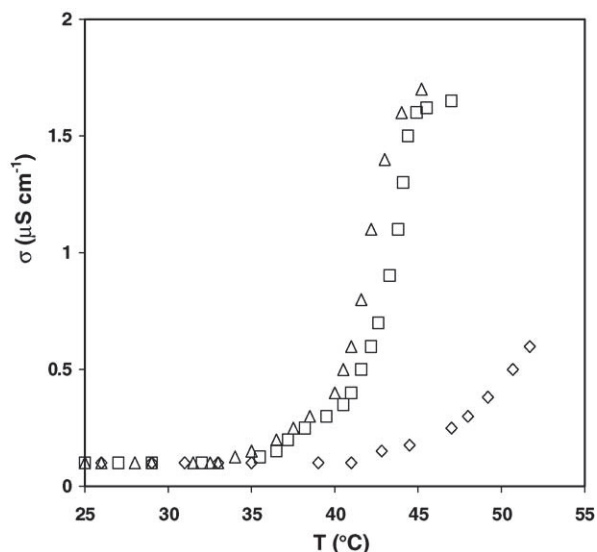


Fig. 12. Conductivity as a function of temperature for AOT/Igepal/IPM/water mixed reverse micellar systems with surfactant concentration 0.1 mol dm^{-3} in oil and $X_{\text{Igepal}} = 0.2$: (\diamond) $\omega = 28$; (\square) $\omega = 32$; (\triangle) $\omega = 34$.

reflected in electrical conductivity study [89]. In the present investigation, the effect of the anionic surfactant (AOT) has been observed to overwhelm the effect of nonionic surfactant (Igepal).

DDAB (known to have a negligible solubility in both oil and water) is a double chain cationic surfactant, which forms reverse micelle in hydrocarbon and aromatic oils [20,31,48,68,90,91]. DDAB/hydrocarbon oil/water reverse micellar system is reported to have a bicontinuous structure at low water content, which gets inverted into a droplet type surfactant on increasing water content and hence a reverse percolation type phenomena was observed for such systems [90]. In the present study, the conductance behavior of DDAB/IPM/water system with increasing water content at total surfactant concentration of 0.1 mol dm^{-3} (fixed) has been studied at 303 K. It was found that conductivity did not change appreciably with increasing ω . When Brij-56 and Brij-58 was blended with DDAB at $X_{\text{Brij}} \leq 0.3$, it was found that sudden jump in conductance occurred for both the blended systems (Fig. 13A and B), and the percolation threshold (ω_p) was found to be in the vicinity of water solubilization limit of these formulations (Fig. 13C). With increasing X_{Brij} , ω_p was shifted to a lower value of ω . The effect of addition of Brij-58 to DDAB/IPM system has been observed to be more pronounced than that of Brij-56 in modifying the interface, and made the system to percolate at a lower ω_p at comparable composition. Similar behaviors were observed for AOT/Brij's blend in IPM as presented earlier. In the present investigation, DDAB/IPM system was low-conducting. So the structure may be assumed to be of the discrete droplet type. Addition of the nonionics (Brij's) made the system to percolate. It may be assumed that Brij's can modify the interface in order to change the discrete droplet structure to connected droplet type with increasing

water content. Earlier Bumajdad et al. [26] reported that the additions of cationic surfactant (DTAB) and nonionic surfactant ($C_{12}E_5$) to DDAB/Hp/water reverse micellar systems enhanced water solubilization capacity, while addition of anionic surfactant (SDS) to DDAB/Hp system decreased the water solubilization capacity. The DDAB/DTAB/Hp/water mixed reverse micellar system exhibited sharp increase in conductivity with increasing X_{DTAB} at constant temperature, while the other two mixed systems, DDAB/ $C_{12}E_5$ and DDAB/SDS has shown decrease in conductivity with increasing X . The increase in conductivity for DDAB/DTAB blend has been correlated with a transition from droplet to bicontinuous structure. In a subsequent study, they [57] investigated the conductance of mixed surfactant systems, DDAB/ C_iE_j /Hp or *p*-xylene/ D_2O and DDAB/Pluronic/Hp or *p*-xylene/ D_2O as a function of D_2O content and surfactant mixture composition. They found that the partial replacement of DDAB by nonionics (C_iE_j or pluronic) affects the conductivity and the reason may be due to the change in droplet size on addition of nonionics. No conductance percolation was observed for any of these systems and the conductivity agreed with the charge fluctuation model. Olla et al. [91] reported an interacting w/o close domain (discrete droplet) structure at low [surfactant]/[oil] ratio (reflected by maximum in conductance curve) and existence of a water continuous network at high [surfactant]/[oil] ratio (reflected by high conductance values) for DDAB/toluene or trifluoro methyl benzene/water reverse micellar systems. A transition from connected to disconnected water domain with increasing oil content along the water dilution line was suggested. The transition has been reported not to be significantly dependent on the type of the aromatic oil. On the other hand, Testard and Zemb [68] have shown that DDAB/dodecane/water reverse micellar system exhibited a decrease in conductance with increasing water content at a fixed surfactant to oil ratio. Addition of lindane and phenol in dodecane was observed to shift the percolation threshold to a lower weight fraction of water.

In the present study, the oil used, IPM is of high molar volume, but DDAB/IPM/water system has been observed to be low-conducting in comparison to that of DDAB/tetradecane system [48,68,90]. It has been reported that DDAB/alkane (C_6 – C_{14})/water system is highly conducting and with increasing water content conductance decreases [48,68,90]. In DDAB, surfactant chains pack flexibly because they are fluid at room temperature. At low water content, inter-connected conduits filled with water are formed with surfactant monolayer separating the water and oil phases. Adding water causes the conduits to increase in diameter and begins to depart from the optimum curvature set by the head group repulsion and oil penetration. One way for the structure to maintain optimum curvature is to transfer from conduits to spheres. As extended conduit structure gradually breaks down, conductance decreases. It has also been reported that oils with low molecular volume (Hx, Oc) form droplet structure at a low water content (owing to their higher penetration into the sur-

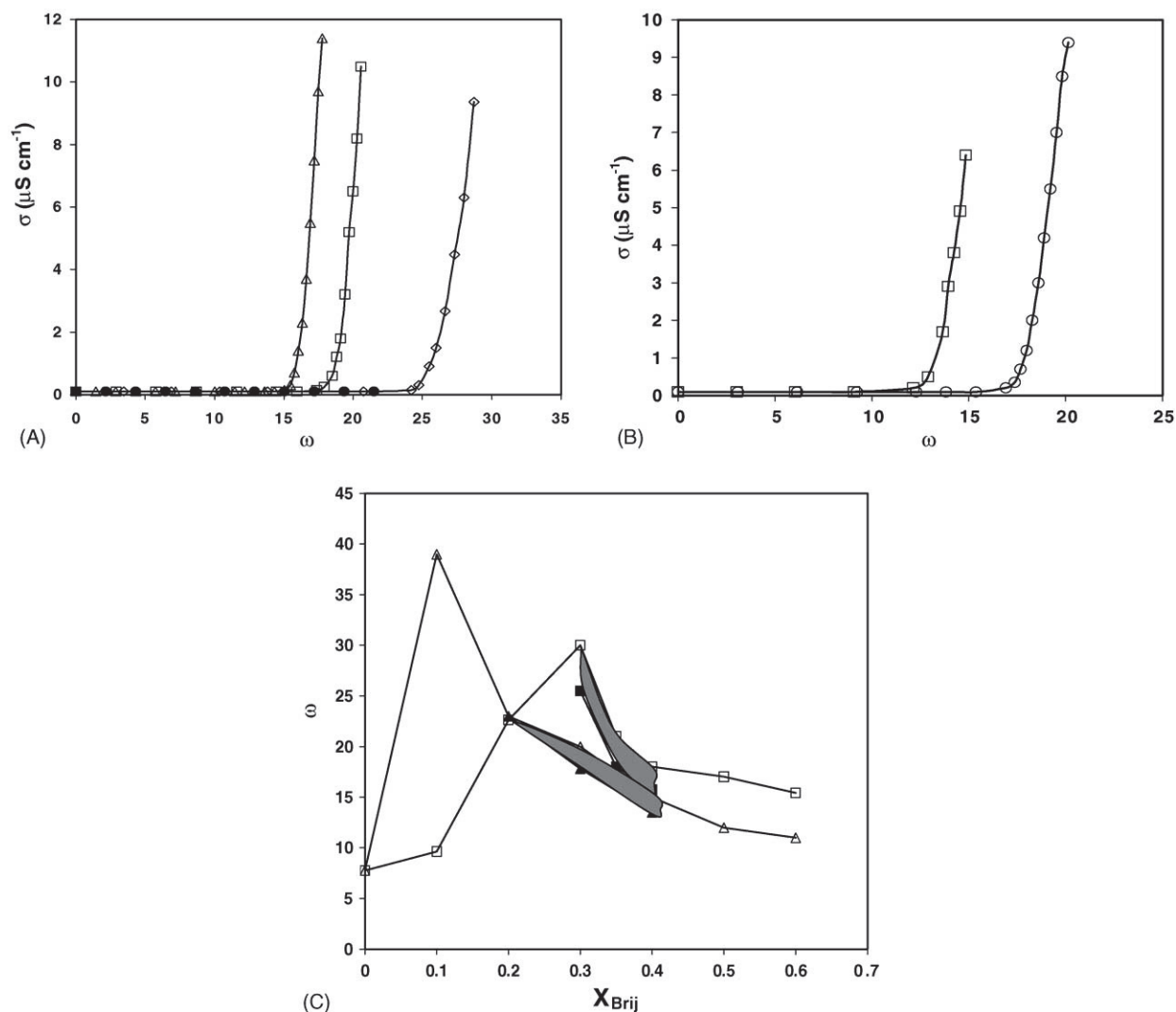


Fig. 13. (A) Water content (ω) induced percolation of conductance of DDAB/Brij-56/IPM/water mixed reverse micellar systems with surfactant concentration 0.1 mol dm^{-3} and $X_{\text{Brij-56}} = 0.2$ (\bullet); 0.3 (\diamond); 0.35 (\square); 0.4 (\triangle) at 303 K. (B) Water content (ω) induced percolation of conductance of DDAB/Brij-58/IPM/water mixed reverse micellar systems with surfactant concentration 0.1 mol dm^{-3} and $X_{\text{Brij-56}} = 0.3$ (\circ); 0.4 (\square) at 303 K. (C) Percolation region of the mixed surfactant reverse micellar systems: (\square) DDAB/Brij-56/IPM/water; (\triangle) DDAB/Brij-58/IPM/water at 303 K with total surfactant concentration of 0.1 mol dm^{-3} . The shaded portions represent percolation regions.

factant monolayer), whereas for oil of high molar volume (tetradecane), the conduit structure was retained throughout the solubilization limit and no decrease in conductance was observed with increasing water content [68,90]. This difference between IPM and alkanes may arise due to the polar nature and high viscosity of IPM.

When conductivity measurements of the mixed surfactant systems DDAB/Brij-56/IPM/water at different ω (25.0, 27.5, 30.0, 32.5 and 35 for AOT/Brij-56 blend and 18.0, 19.0 and 20.0 for DDAB/Brij-58 blend) and $S_T = 0.1 \text{ mol dm}^{-3}$ fixed) were carried out as a function of temperature, reverse percolation type of curves were obtained for both the mixed systems, wherein conductance decreased with increasing temperature at a fixed ω (Fig. 14A and B). It was observed that with increasing ω the conductance curves were shifted towards higher temperature. The systems may be assumed to have a

connected structure at lower temperature and the structure was converted into droplet type with increasing temperature, as revealed from the decrease in conductance against temperature.

3.7. Activation energy for percolation in AOT/nonionics mixed reverse micelles

The effect of temperature on conductance has three distinct stages (pre-percolation, percolation and post-percolation). The activation energies for conductance are lower in the pre- and post-percolation range; they are in the order of normal electrolyte conductance [39–42]. It is considered that lower activation energy suggests a more open structure. The particles in the cluster merge to form conduits or channels for easier transport of ions more or less

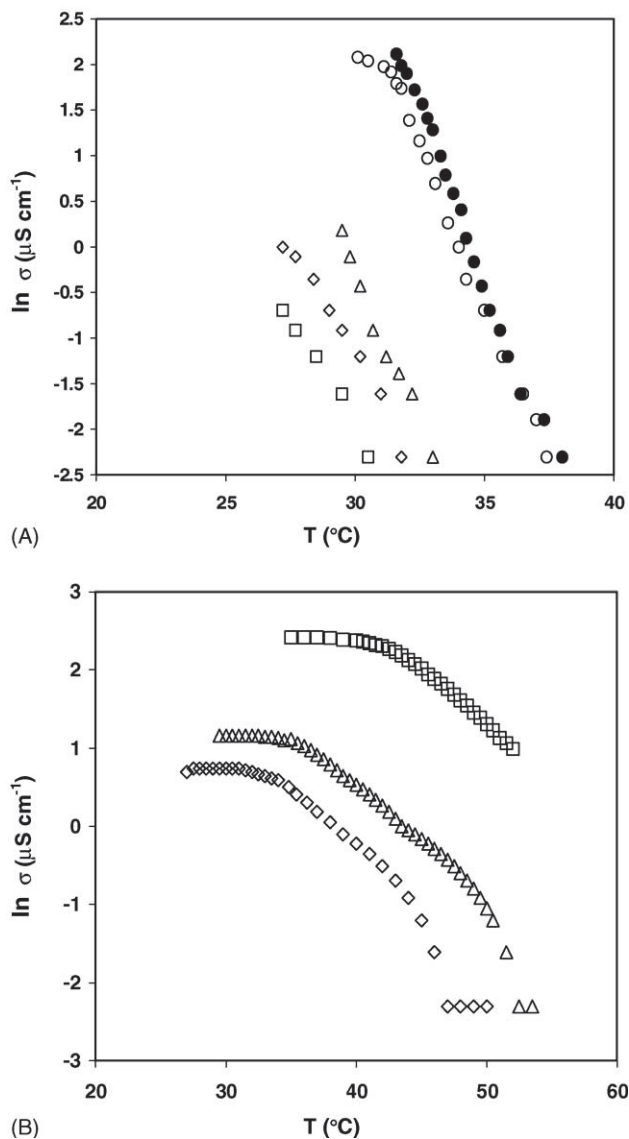


Fig. 14. (A) Conductivity as a function of temperature for DDAB/Brij-56/IPM/water reverse micellar systems with $X_{\text{Brij}} = 0.3$ and $S_{\text{T}} = 0.1 \text{ mol dm}^{-3}$ at $\omega = 25$ (\square); 27.5 (\diamond); 30 (\triangle); 32.5 (\circ); 35 (\bullet). (B) Conductivity as a function of temperature for DDAB/Brij-58/IPM/water reverse micellar systems with $X_{\text{Brij}} = 0.3$ and $S_{\text{T}} = 0.1 \text{ mol dm}^{-3}$ at $\omega = 18$ (\diamond); 19 (\triangle); 20 (\square).

like normal ion conduction; the mechanism of hopping and transient-fusion and mass exchange contribute mainly to the percolation process. This is the first report on the estimation of activation energies in mixed reverse micellar systems.

The activation energy (E_p) of percolation for w/o microemulsions/reverse micelles has been estimated on the basis of an Arrhenius form of relation [39–42,87]:

$$\sigma = A \exp\left(-\frac{E_p}{RT}\right) \quad (2)$$

or

$$\ln \sigma = \ln A - \frac{E_p}{RT} \quad (3)$$

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. Several contributions may accompany the values of E_p [78,92,93]. Some of these factors may arise due to the facts that bending forces must be overcome to deform the surfactant monolayer as the droplets come close for sticky collisions. Also compression of the surfactant hydrocarbon chains or surfactant flipping into the oil continuum, both to reduce the film area in the transition state of merging droplets, are endothermic processes. E_p values may not strictly follow a trend in presence of additives [39–42]. It may increase or decrease steadily with ω or may pass through a maximum or minimum.

From Table 1, it can be seen that E_p values depend on the number of polyoxyethylene chains (POE) of the nonionic surfactants. Nonionic surfactants with smaller chain lengths (10 POE chains for Brij-56 and Brij-76) have lower E_p values (of the order $\sim 177 \text{ kJ mol}^{-1}$), whereas for Brij-35, having 23 POE chains, it is in the order of $469.3 \text{ kJ mol}^{-1}$. Other three nonionic surfactants, Brij-58, Tween-20 and Tween-40 (with 20 POE chains) have E_p values in the order of $\sim 390 \text{ kJ mol}^{-1}$.

Fig. 15 represents the E_p values of AOT/Brij-56/oil/water systems against the molar volume of oils ($\text{C}_6\text{--C}_{10}$ and IPM) at two different ω values (20 and 30) with $X_{\text{nonionic}} = 0.1$ and at $\omega = 20$ with $X_{\text{nonionic}} = 0.075$. The total surfactant concentration was fixed at $0.175 \text{ mol dm}^{-3}$. It was observed that E_p value increased regularly with increasing molar volume of oil for hydrocarbons at fixed ω and X_{nonionic} . This can be explained from the fact that long chain alkanes are stiff within the monolayer or can hardly be removed into the oil continuous phase [86]. Thus oils with higher molecular volume can be expected to overcome high activation energy as obtained in the present study for the series of alkanes, $\text{C}_6\text{--C}_{10}$ (Table 4). But IPM having a higher molar volume than these

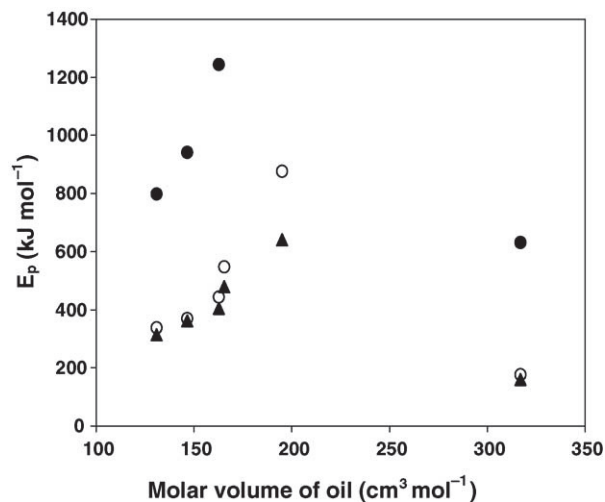


Fig. 15. Activation energy of percolation in conductance (E_p) vs. molar volume of oils profile for AOT/Brij-56/oil/water mixed reverse micellar systems with surfactant concentration 0.175 mol l^{-1} in oil: (\circ) $X_{\text{Brij-56}} = 0.1$ and $\omega = 20$; (\bullet) $X_{\text{Brij-56}} = 0.1$ and $\omega = 30$; (\blacktriangle) $X_{\text{Brij-56}} = 0.075$ and $\omega = 20$.

Table 4

Activation energy of percolation (E_p) of AOT/Brij-56 mixed surfactant reverse micellar systems with different oils at $X_{\text{Brij-56}} = 0.1$ and $[S_T] = 0.175 \text{ mol dm}^{-3}$

Oil	$\omega = 20: E_p \text{ (kJ mol}^{-1}\text{)}$	$\omega = 22.5: E_p \text{ (kJ mol}^{-1}\text{)}$	$\omega = 25: E_p \text{ (kJ mol}^{-1}\text{)}$	$\omega = 27.5: E_p \text{ (kJ mol}^{-1}\text{)}$	$\omega = 30: E_p \text{ (kJ mol}^{-1}\text{)}$
Hx	338	450	519	728	799
Hp	370	479	530	830	942
Oc	406	–	–	–	–
<i>i</i> -Oc	547	608	661	890	1150
Dc	876	–	–	–	–
IPM	176	313	372	506	632

alkanes, observed to have the lowest E_p value. For IPM oil, the E_p value was observed to be lower than any of the studied hydrocarbon oils. So in this context also, the percolation behavior in IPM oil is quite different from other hydrocarbon oils.

It has also been observed from Table 4 that E_p increased steadily with increasing ω at a fixed X_{nonionic} for reverse micellar systems stabilized by alkanes and IPM. The large value of E_p may be attributed to the large energy barrier that has to be overcome in order to initiate percolation. The activation energy depends upon the droplet size [94] and can be represented by a second order polynomial in ω [87]. In the present study, E_p has been plotted against ω for four mixed systems, AOT/Brij-56 system stabilized in hexane, heptane, isooctane and IPM (Fig. 16). A good fit in second order polynomial was obtained for the IPM system, whereas those for the hexane, heptane and *iso*-octane systems, were not good. The increase of E_p with ω have been reported earlier [92,94,95]. Free energy calculations for transition states of bilayer membranes also propose an increase of E_p with the aggregate radius [87], which in turn is linearly dependent on ω . With increasing ω droplet size increases and an exchange between larger droplets may require higher activation energy in order to deform a larger area of interface. When the droplets coalesce

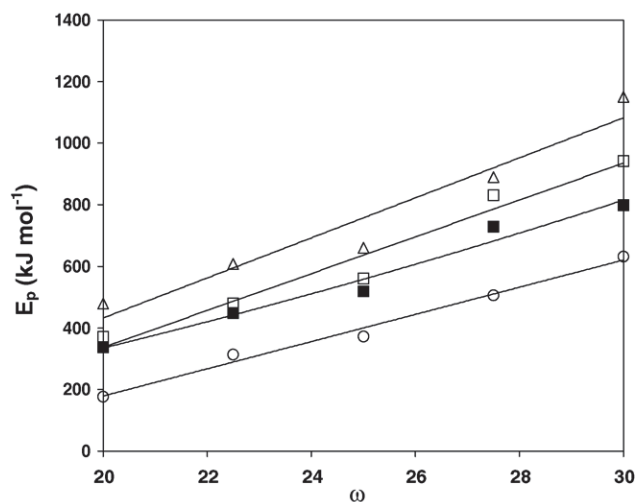


Fig. 16. Activation energy of percolation in conductance (E_p) against ω profile for AOT/Brij-56/oil/water mixed reverse micellar systems with $S_T = 0.175 \text{ mol dm}^{-3}$ and $X_{\text{nonionic}} = 0.1$: (○) IPM; (■) Hx; (□) Hp; (△) *i*-Oc. The solid lines represent the best fitted second order polynomials.

Table 5

Threshold percolation temperature (T_p) and activation energy (E_p) of AOT/Brij-56 mixed surfactant reverse micellar systems with different oils at $\omega = 20$ and $[S_T] = 0.175 \text{ mol dm}^{-3}$

Oil	$X_{\text{Brij}} = 0.1$		$X_{\text{Brij}} = 0.075$	
	$T_p \text{ (}^\circ\text{C)}$	$E_p \text{ (kJ mol}^{-1}\text{)}$	$T_p \text{ (}^\circ\text{C)}$	$E_p \text{ (kJ mol}^{-1}\text{)}$
Hx	42.8	338	53.1	314
Hp	32.1	370	41.0	361
Oc	24.6	406	29.9	404
<i>i</i> -Oc	21.5	547	34.0	479
Dc	7.0	876	12.8	640
IPM	34.5	176	41.1	160

the penetrating oil molecules are compressed within pore removed from the monolayer of the merging clusters [87]. At high ω , larger pores are formed which require higher energy, to avoid energetically unfavorable highly curved monolayers. Hence, E_p value increases with increasing ω .

It has also been observed (Table 5) that with decreasing mole fraction of Brij-56 (from 0.1 to 0.075) in AOT/Brij-56/oil (alkanes and IPM)/water reverse micellar systems, E_p decreased at fixed ω . It has been discussed earlier that with increasing Brij content, droplet size increases in AOT/Brij/oil/water system, which in turn increases E_p with increasing X_{Brij} .

4. Conclusions

1. AOT/IPM/water reverse micellar system is nonpercolating, but addition of nonionic surfactants (Brij-56 and Brij-58) to this system, favors ω -induced percolation in conductance at constant temperature (303 K). The percolation threshold (ω_p) depends upon the type, head group configuration and content (X_{nonionic}) of the added nonionic surfactants.
2. Electrolyte (NaCl) increases the percolation threshold (ω_p) for the mixed surfactant systems (AOT/Brijs/IPM) at constant temperature, and is dependent on the concentration of NaCl.
3. AOT/IPM/water reverse micellar system does not exhibit temperature-induced percolation, but addition of nonionic surfactants (Brij-35, Brij-56, Brij-58, Brij-76, Tween-20, Tween-40) induces temperature induced percolation in the AOT/IPM system. Percolation threshold temperature (T_p)

is found to be dependent on the type, head group configuration and content of the added nonionic (X_{nonionic}) surfactant. Nonionic surfactant with low hydrophilicity (Brij-52, Spans) does not induce percolation in AOT/IPM system.

4. Percolation behavior is dependent on the molar volume of oils in AOT/Brij/hydrocarbon oils (Hx, Hp, Oc, *i*-Oc, Dc)/water systems, whereas for IPM stabilized systems (being a different kind of oil), is not straightforwardly dependent on its molar volume.
5. Incorporation of Brij-56 and Brij-58 in nonpercolating DDAB/IPM/water reverse micellar system makes the system favorable for water content (ω) induced percolation behavior, but the mixed DDAB/Brij-56 and Brij-58 blends in IPM/water exhibits temperature induced reverse percolation phenomenon. AOT/Igepal CO 520/IPM/water system exhibits conductance percolation though the reverse micellar systems stabilized with both the single surfactants (Igepal and AOT) in IPM and water are non-percolating.
6. Activation energies for percolation for AOT/Brij-58/IPM/water systems are higher than that of AOT/Brij-56/IPM/water systems. E_p values are dependent on the content of water (ω), content, size of the polar head group and its configuration, hydrophobic moiety of nonionic surfactant, type of oil.

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