

Interface of AOT/Brij mixed reverse micellar systems: Conductometric and spectrophotometric investigations

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Abstract

Solubilization and conductivity studies are carried out with AOT/Brijs (Brij-30, Brij-35, Brij-52, Brij-56, Brij-58, Brij-72, Brij-76, Brij-78)/isooctane/water mixed reverse micellar systems. Replacement of AOT molecules with large head group Brij molecules (Brij-30, Brij-35, Brij-56, Brij-58, Brij-76, Brij-78) decreases the solubilization capacity, whereas those with smaller polar head groups (Brij-52 and Brij-72) increases it. The former blends assist the conductance percolation whereas the latter retard it. An attempt has been taken to obtain more insight on the interfacial composition of the mixed interface with the help of spectrophotometric studies using 7-hydroxycoumarin as the fluorophore. The results obtained from the solubilization and conductometric studies have been correlated with those obtained from the spectroscopic studies.

Keywords: Solubilization; Conductivity; Mixed reverse micelles; 7-hydroxycoumarin (HCM); Photophysical studies

1. Introduction

Reverse micelles formed by the solubilization of water in oil and surfactant solutions have been extensively studied in recent years. They provide easily controlled model compounds for the behavior of biomembranes and could improve our understanding of reactivities and interactions in confined media. Aerosol OT or sodium bis(2-ethyl-1-hexyl) sulfosuccinate (AOT) is the best known representative of this class of surfactants and has been studied by numerous methods [1]. Alteration of the interface due to the addition of a second surfactant can often give rise to enhancement of the solubilization capacity of mixed surfactant systems, which in turn can provide better performance in the activity of enzyme [2], extraction of protein [3], synthesis of nanoparticles [4,5], and other applications. The mechanism of water solubilization and phase separation due to the coales-

cence of droplets in reverse micellar systems has been modeled by Shah et al. [6–8] and verified by Zana et al. [9,10], Derouiche and Tondre [11], Abuin et al. [12], Paul and Mitra [13] for both single and mixed surfactant systems.

As proposed by Nazario et al. [14], there are two possibilities for the exact solubilization site of nonionic co-surfactant in the (ionic + nonionic) mixed reverse micelles, either immersed in micellar water pool or solubilize in the AOT surfactant head group region. Addition of poly(oxyethylene) polymer in the w/o microemulsion of AOT exhibit an attractive interaction whereas in case of nonionic co-surfactant (pentaethylene glycol monododecyl ether) a repulsive interaction has been reported [15]. Meier [16] reported the alteration of interface of AOT reverse micelle in presence of polyoxyethylenes (POE) of different molecular weights due to attractive interactions between AOT and POE, which lead to polymer adsorption at the interface.

Till date only a few studies have been carried out to underline the interfacial configuration, state of water and location of the second surfactant in the interfacial layer of the mixed reverse micellar systems. Abuin et al. [12] reported the solubility of

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water in w/o microemulsion stabilized by cetyltrimethylammonium surfactants as a function of the surfactant counterion (bromide; CTAB/chloride; CTAC), composition of the oil (chloroform and chloroform/heptane mixtures), salinity of the droplets, and the nature of the salt employed to modify it. Solubility increased abruptly on going from either CTAC- or CTAB-stabilized microemulsions to mixture of both surfactants. The results obtained were explained by considering that, due to the stronger binding of bromide than of chloride to the surfactant heads at the micellar interface, water solubility in solutions of CTAB or CTAC in chloroform is determined by different factors; the curvature of the surfactant film (CTAB) and the interaction between droplets (CTAC). Bumajdad et al. [17] have studied the interface of mixed cationic (DDAB)–cationic (DTAB) [or nonionic ($C_{12}E_5$)–anionic (SDS)] reverse micellar system with small angle neutron scattering measurements, and showed that the $C_{15}E_5$ and DTAB molecules are preferentially co-adsorbed at the DDAB interface, which in turn produce synergism in solubilization. Recently we have initiated a study to determine the synergism in water solubilization capacity of mixed surfactant system stabilized by anionic (AOT)–nonionic (Brijs, Spans, Tweens), cationic (DDAB)–nonionic (Brijs, Spans), and nonionic (Igepal)–nonionic (Brijs, Spans) in different oils (cyclohexane, isobutyl benzene and isopropyl myristate) and the effect of electrolyte and temperature on their stability [13,18]. The occurrence of synergism in solubilization capacity in presence of second nonionic surfactant for AOT and DDAB stabilized systems both in absence and presence of electrolyte has been correlated to the appearance of percolation in conductance in these mixed systems [13].

In the present study, we have investigated the solubilization and conductometric behavior of AOT/Brij mixed reverse micelles in isoctane. To obtain a better understanding of the interfacial composition, photophysical studies have also been carried out with 7-hydroxycoumarin (HCM) used as the fluorophore. Till date, the only report available on the photophysical study of reverse micellar system consisting of mixed (AOT + Brij) surfactants stabilized in *n*-heptane is due to Liu et al. [19]. They used a cationic dye, tris(2,2'-bipyridine) ruthenium dichloride hexahydrate ($Ru(bpy)_3^{2+}$) to study the microenvironment near the surfactant–water interface and an anionic dye 1,8-anilinonaphthalenesulfonic acid to obtain information about the core of the water pool of the mixed reverse micelles. The present paper is the first report of using HCM to obtain information about the configuration of the altered interfacial region of AOT/isoctane reverse micellar system due to the replacement of AOT by Brij molecules.

2. Materials and methods

2.1. Materials

The following surfactants were used without further purification, Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 99%) was purchased from Sigma–Aldrich, USA. Polyoxyethylene(4) lauryl ether (Brij-30), polyoxyethylene(23) lauryl ether (Brij-35), polyoxyethylene(2) cetyl ether (Brij-52), polyoxyethylene-

(10) cetyl ether (Brij-56), polyoxyethylene(20) cetyl ether (Brij-58), polyoxyethylene(2) stearyl ether (Brij-72), polyoxyethylene(10) stearyl ether (Brij-76), polyoxyethylene(20) stearyl ether (Brij-78) were products of Fluka, Switzerland. Isooctane was HPLC grade product of SRL, India. 7-hydroxycoumarin (HCM) was a product of Sigma, USA, and was used as obtained. The absorbance maximum at 261 nm and the maximum at 330 nm in the UV spectra of HCM agree with the values reported in Ref. [20]. Double distilled water of conductivity less than $3 \mu S cm^{-1}$ was used.

2.2. Determination of solubilization capacity

Nonionic surfactants (Brijs) were mixed with AOT at definite mole fractions of Brij (X_{Brij}) and dissolved in isoctane to prepare the stock solutions. The total initial surfactant concentration in oil was fixed at $0.2 mol dm^{-3}$. 5 ml of each solution was taken in sealed test tubes, equilibrated at 303 K in a thermostatic water bath and then water was gradually added into it with the help of microsyringe. The samples were shaken vigorously after each addition in a vortex shaker. Appearance of permanent turbidity indicates the onset of phase separation and the corresponding water solubilization capacity, ω ($=[water]/[surfactant]$) denotes the maximum solubilization capacity ($\omega_{0,max}$) for the mixed system. The process is repeated and the average volume of water was taken.

2.3. Conductance study

Electrical conductivity measurements were carried out as a function of ω using an automatic temperature compensated conductivity meter of Thermo Orion, USA (Model 145A Plus), with cell constant of $1.0 cm^{-1}$ with $\pm 1\%$ uncertainty in measurement. The conductivity of the experimental solutions at different ω 's were measured at each addition of water with the help of a microsyringe, into respective systems at a specified temperature (303 K) after allowing 5–10 min of time to attain equilibrium, in a thermostatic water bath accurate to $\pm 0.1^\circ C$. Differential curves have been constructed to determine the percolation threshold (ω_p) for each system.

2.4. Spectroscopic measurements

Absorption spectra were recorded using a Shimadzu, Japan, UV–vis 1700 spectrophotometer with a matched pair of silica cuvettes. Fluorescence spectra were taken in a F-IIA spectrofluorimeter (Spex, Inc, NJ, USA) with a slit width of 1.25 nm. All the measurements were done thrice. The excitation wavelength was 330 nm. HCM solution in ethanol at 10 mM was prepared as the stock. A requisite amount of it was added to the buffer medium to obtain solutions $\sim 100 \mu M$ with respect to HCM. Phosphate buffer was used for solution preparation of HCM and the analytical concentration of the buffer was $2.5 \times 10^{-2} mol dm^{-3}$. The pH dependent variation of absorbance and the calibration curve (pH vs absorbance and pH vs absorption maximum) has been reproduced to Ref. [20].

3. Results and discussion

3.1. Solubilization study

Fig. 1 depicts the water solubilization capacity of AOT/Brij/isoctane mixed reverse micellar systems at 303 K. It is observed that AOT/isoctane system can solubilize substantial amount of water with $\omega_{0,\max} = 49.5$ and on further addition of water, the system splits into two distinct phases. But, addition of nonionic surfactants Brij-52 and Brij-72 has been observed to increase the solubilization capacity ($\omega_{0,\max}$) [13] of this system up to a certain $X_{\text{Brij},\max}$ beyond which it decreases. For the other AOT/Brij blended systems, the solubilization falls off with increasing X_{Brij} showing no maximum in solubilization. According to the model developed by Shah et al. [6–8], the solubilization in reverse micelles is primarily determined by two opposing factors, namely the radius of curvature of the interface and the interdroplet interaction among the droplets. The former is governed by the spontaneous radius of curvature (R_0) and the latter by the critical radius of curvature (R_c). With increasing water content (ω), reverse micellar droplets grow in size, which in turn increases the interdroplet interaction and leads to the coalescence of droplets followed by phase separation and this limits the solubilization capacity of such systems. Synergism in water solubilization capacity occurs when these two opposing factors are optimized [6]. According to this model, the solubilization capacity in AOT/isoctane system is limited by the interdroplet interaction. The AOT/isoctane interface can be assumed to be fluid and with increasing water content (ω), the droplets grow in size, which in turn increases the interdroplet interaction leading to phase separation. It can be noted from Fig. 1 that the addition of nonionic surfactants with large head groups (viz. Brij-30, Brij-35, Brij-56, Brij-58, Brij-76, and Brij-78) to AOT/isoctane system, phase separation occurs at smaller ω values compared to the AOT/isoctane system, whereas addition of Brijs with smaller head groups (Brij-52 and Brij-72) increases the solubilization capacity. Thus the Brijs with larger head groups increase the fluidity of the in-

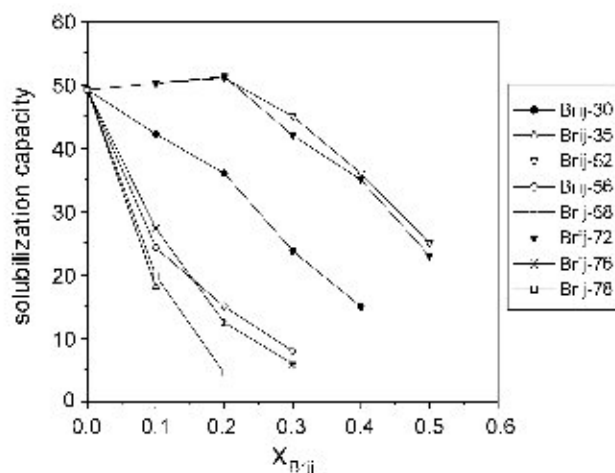


Fig. 1. Solubilization capacity of mixed reverse micellar systems AOT/Brij/isoctane/water at 303 K with initial surfactant concentration of 0.2 mol dm^{-3} in oil.

terface as well as increases the interdroplet interaction, whereas those with smaller head groups decrease both. Since the appearance of percolation in conductance is directly related to the rigidity of the interface, the mixed systems are taken for conductometric measurements.

3.2. Conductometric study

Fig. 2 depicts the conductivity of AOT/Brij/isoctane/water mixed reverse micellar systems as a function of water content (ω). AOT/isoctane/water system has been found to be percolating with the percolation threshold (ω_p) of 44.6. Addition of Brijs, with large head groups (Brij-30, Brij-35, Brij-56, Brij-58, Brij-76, and Brij-78) is observed to facilitate percolation, whereas Brij-52 and Brij-72, having smaller head groups, retard it. In fact, for the AOT/Brij-52 (or Brij-72) blended systems, conductivity remains almost constant throughout the entire solubilization range. The ω_p values for these mixed systems are presented in Table 1. The emulsification failure point (phase separation point) for each system has been demarcated with the help of arrows in Fig. 2. It can be observed that percolation initiates in the vicinity of $\omega_{0,\max}$. Appearance of percolation in conductance in reverse micellar systems can be correlated with the transition from discrete droplet type to connected droplet type microstructures and also the increase of interdroplet interaction as well, which may cause emulsification failure followed

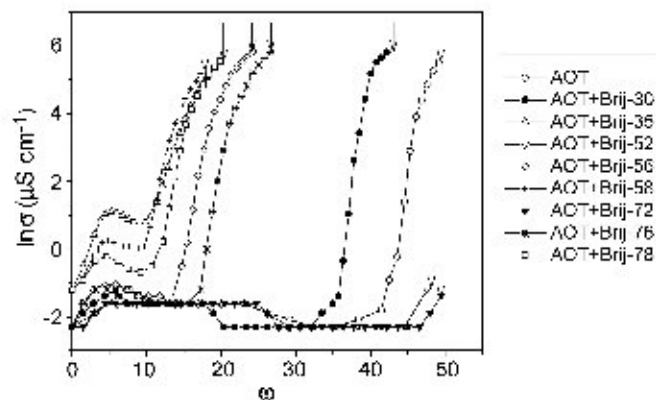


Fig. 2. Conductivity vs ω profile for the mixed reverse micellar systems AOT/Brij/isoctane/water at 303 K with initial surfactant concentration of 0.2 mol dm^{-3} in oil and $X_{\text{Brij}} = 0.1$.

Table 1

Percolation threshold (ω_p) for the AOT/Brij/isoctane/water mixed reverse micellar systems at 303 K with initial surfactant concentration of 0.2 mol dm^{-3} in oil and $X_{\text{Brij}} = 0.1$

Nonionic surfactant	ω_p
–	44.6
Brij-30	37.8
Brij-35	11.3
Brij-52	–
Brij-56	16.5
Brij-58	11.4
Brij-72	–
Brij-76	18.8
Brij-78	12.2

by phase separation. Each conductivity droplet is an insulating surfactant monolayer and conductance takes place either by the displacement current through the capacitance coupling between the droplets or by jump of the charged surfactant ions [21,22]. It is possible for the surfactant ions to leave a droplet and be reabsorbed into a second one. A short-range interaction potential between the droplets may be sufficient to account for the observed percolation phenomenon in these 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 [23]. 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. According to Garcia-Rio et al. [24], 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 [25]. The fluidity 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 [26,27]. Any factor that increases the fluidity of the interface and/or the interdroplet interaction would also increase the ease of conductance percolation. Brij-35, Brij-58, and Brij-78 have 23, 20, and 20 EO chains in their head groups with lauryl, cetyl and stearyl chains in their hydrophobic parts respectively. They produce identical ω_p values following the order, Brij-35 \sim Brij-58 $>$ Brij-78. Likewise, Brij-56 and Brij-76 have 10 EO chains each with cetyl and stearyl groups respectively, and the ω_p values follows the order, Brij-56 $>$ Brij-76. Brij-30 has only 4 EO chains and produces ω_p value in close range to that of the single AOT system. It can be assumed that all these percolation-assisting nonionic surfactants are selectively adsorbed at the interface with their head groups extended toward the water pool. This increases the effective packing parameter (P_{eff}) of mixed surfactant system, which in turn is dependent on the volume, area of head group, and length of the surfactant(s), and on the mixing ratio of the surfactants [28].

Larger the area of head group of nonionic surfactant, larger is the droplet radius and hence smaller would be value of ω_p as has been observed in the recent study. But, it can also be noted that nonionic surfactants with identical head groups but longer methylene chain produce higher ω_p (e.g., Brij-56 vs Brij-76 and Brij-58 vs Brij-78). It is known that during coalescence of droplets, oil molecules are removed from the interface [29] and the easier the removal of oil molecules, easier is the droplet coalescence and hence lower is the value of ω_p . Nonionic surfactants with longer hydrocarbon tail can allow larger oil penetration into the interface and thus makes oil removal from the interface less easier resulting in an increase in ω_p .

Nonionic surfactants with smaller head groups (Brij-52 and Brij-72) resist conductance percolation. It has been reported earlier [14] that long chain alcohols decrease percolation threshold of AOT/isooctane reverse micellar system. It was argued that these long chain alcohols are adsorbed at the palisade layer of the interface, i.e., along the hydrocarbon tail part of

the AOT interface. Brij-52 and Brij-72 can also be assumed to be located at the palisade layer of the interface, whereby it decreases the fluidity of the interface resulting in an increase in solubilization capacity (Fig. 1) and ω_p (Fig. 2). To obtain more insight about the relative position of the nonionic surfactant at the AOT/Brij interface, spectroscopic studies have been carried out using HCM as the fluorophore.

3.3. Photophysical studies

In photophysical study of reverse micelles, the choice of photosensitive probe molecule is important, because its residence depth in the water pool of the reverse micelles is used to estimate the acidity, polarity, viscosity, etc. of the region in which it is located. Compounds with low polarity or high hydrophobicity would reside near the interface, whereas those with high polarity or low hydrophobicity would reside in the interior of the reverse micelle. The pH of the water pool of AOT reverse micelles has been determined by using indicators, viz. methyl red, 4-nitrophenyl-2-sulfonate [30–32], and the fluorescent probe chloro-*N*-ethylrhodofluoresceinamine [33]. Principal-components analysis and multiple linear regression has been used to determine the pK_a of HCM in presence of a series of buffers having different charges [34] and the presence of co-surfactant 1-butanol has been reported to decrease the pH of AOT reverse micelle [20].

HCM is insoluble in hydrocarbon and sparingly soluble in water [20]. It is soluble in hydrocarbons in presence of AOT. The alcoholic dye solution added to the AOT/isooctane/water mixture is expected to reside at the surfactant monolayer formed between the two immiscible phases. The observed physicochemical changes should refer to the properties of the interfacial region. The following findings would refer to the interfacial properties and pH dependent variation of HCM in mixed reverse micellar systems.

3.3.1. Absorption study

The absorption spectra of HCM has been measured at a comparable concentration (in the buffer solution) in w/o microemulsions of different water content, and observed λ_{max} value has been used to estimate the pH of the dispersed aqueous region of the w/o microemulsion. The absorption spectra of HCM in AOT/isooctane reverse micelles at different ω are in Fig. 3a. The absorption maxima in AOT reverse micelle at different ω remains at 324 nm and the absorption maxima (λ_{max}^{abs}) remains unaltered upon the replacement of AOT molecules by Brij. The probe molecule is considered to remain at the interface and its pK_a value does not change with varied compositions of the mixture. The pH-dependent spectral behavior of the probe (HCM) calibrated in the buffer medium is taken to be equally applicable to the aqueous compartment of microemulsions. From the calibration curve of HCM [20], the pH of the AOT/isooctane and AOT/Brij/isooctane reverse micelles have been evaluated and the value is 7.55. From the pH value it may be assumed that HCM resides in an environment having identical pH in both AOT/isooctane and AOT/Brij/isooctane reverse micellar system. With increasing POE chain length at fixed

composition and fixed ω , absorbance increases with no shift in $\lambda_{\text{max}}^{\text{abs}}$. From the spectroscopic study of Safranin T in Brij micelles, it has been reported that with increasing chain length of POE group, polarity of the micelle–water interface enhances [35]. Hence the enhancement of absorbance in mixed reverse micelle with POE group as observed in the present study may be due to enhanced polarity of the interface.

With gradual increase in ω of AOT/isooctane system, the absorbance of HCM decreases and at higher ω ($\omega > 5$) no further decrease of absorbance has been observed. In AOT/Brij/isooctane mixed reverse micelles, absorbance decreases with increasing ω , and at higher ω absorbance levels up. The absorption spectrum of HCM at different ω of mixed reverse micelles (Fig. 3b) passes through an isosbestic point ($\lambda_{\text{max}}^{\text{abs}} = 359$ nm), which may imply formation of dye–reverse micellar complex. The absorption spectra of HCM in AOT/isooctane reverse micelle exhibit no isosbestic point. Spectral presentation of HCM–AOT/isooctane interaction has not been shown here. So, dye–reverse micelle complexation is absent in AOT/isooctane reverse micellar system. Due to incorporation of Brij into the reverse micelle of AOT, an EDA type complexation occurs and this phenomenon has been considered

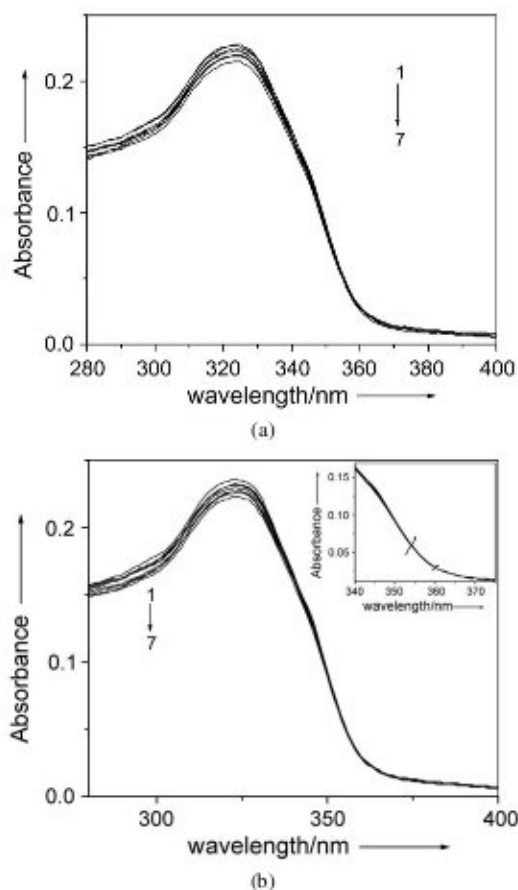


Fig. 3. (a) Absorption spectra of 7-hydroxycoumarin (HCM) in AOT/isooctane/water reverse micelle at (1) $\omega = 2.5$, (2) $\omega = 5$, (3) $\omega = 10$, (4) $\omega = 15$, (5) $\omega = 25$, (6) $\omega = 35$, and (7) $\omega = 45$ with initial surfactant concentration of 0.2 mol dm^{-3} in oil. (b) Absorption spectra of 7-hydroxycoumarin (HCM) in AOT/Brij 52/isooctane/water mixed reverse micelle at (1) $\omega = 2.5$, (2) $\omega = 5$, (3) $\omega = 10$, (4) $\omega = 15$, (5) $\omega = 25$, (6) $\omega = 35$, and (7) $\omega = 47$ with initial surfactant concentration of 0.2 mol dm^{-3} in oil and X_{Brij} of 0.1.

as indirect evidence on the alteration of interface of mixed reverse micelle.

3.3.2. Fluorescence study

Fluorescence study of HCM in mixed reverse micellar medium has been used to predict the extent of solubilization of the fluorophore in the mixed interface and water pool. In AOT reverse micelle HCM has the $\lambda_{\text{max}}^{\text{fl}}$ at 396 nm and the fluorescence intensity gradually decreases with increasing ω of the reverse micelle. At higher ω , a new fluorescence peak appears at 457 nm, which may be due to solubilization of HCM in the pool water, as HCM shows a peak at 457 nm in pure water. In AOT/Brij/isooctane reverse micelle (Fig. 4) with low water content, HCM displays very intense fluorescence intensity with maximum intensity at $\lambda_{\text{max}}^{\text{fl}} = 396$ nm at $\omega = 0.5$ (Fig. 4). Fluorescence intensity at 396 nm is drastically reduced by increasing water content of the reverse micelle with concomitant enhancement of fluorescence intensity at $\lambda_{\text{max}}^{\text{fl}} = 457$ nm. But the fluorescence intensity at $\lambda_{\text{max}}^{\text{fl}} = 396$ nm for HCM is lower in AOT/Brij/isooctane system compared to AOT/isooctane system. From this comparison it can be said that in AOT/Brij/isooctane system, HCM preferably resides in the water pool in comparison to the AOT/isooctane system.

The fluorescence intensity has been plotted against ω for AOT, AOT/Brij-52, AOT/Brij-56, and AOT/Brij-58 system. With increasing water content of the mixed reverse micelle, fluorescence intensity at $\lambda_{\text{max}}^{\text{fl}} = 457$ nm gradually increases and approach a plateau at $\omega = 18$ for AOT/isooctane system. A similar observation has been noticed for the AOT/Brij-52 system at $\omega = 18$, whereas such plateau does not occur for the AOT/Brij-56 and AOT/Brij-58 blends. The plateau is obtained due to localization of HCM in waterpool, i.e., formation of pseudo phase in the reverse micellar systems [36].

The fluorescence intensity of AOT/Brij mixed reverse micellar system at $\lambda_{\text{max}}^{\text{fl}}$ (390 nm) decreases in comparison to the AOT system. The fluorescence intensity follows the order AOT/Brij-30 > AOT/Brij-35, AOT/Brij-52 > AOT/Brij-56, and AOT/Brij-72 > AOT/Brij-76, but for the AOT/Brij-56, AOT/Brij-58 and AOT/Brij-76, AOT/Brij-78 pairs the fluores-

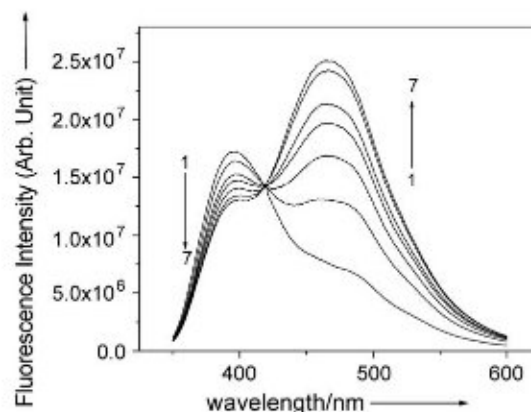


Fig. 4. Fluorescence spectra of 7-hydroxycoumarin (HCM) in AOT/Brij 52/isooctane/water mixed reverse micelle at (1) $\omega = 2.5$, (2) $\omega = 5$, (3) $\omega = 10$, (4) $\omega = 15$, (5) $\omega = 25$, (6) $\omega = 35$, and (7) $\omega = 47$ with initial surfactant concentration of 0.2 mol dm^{-3} in oil and X_{Brij} of 0.1.

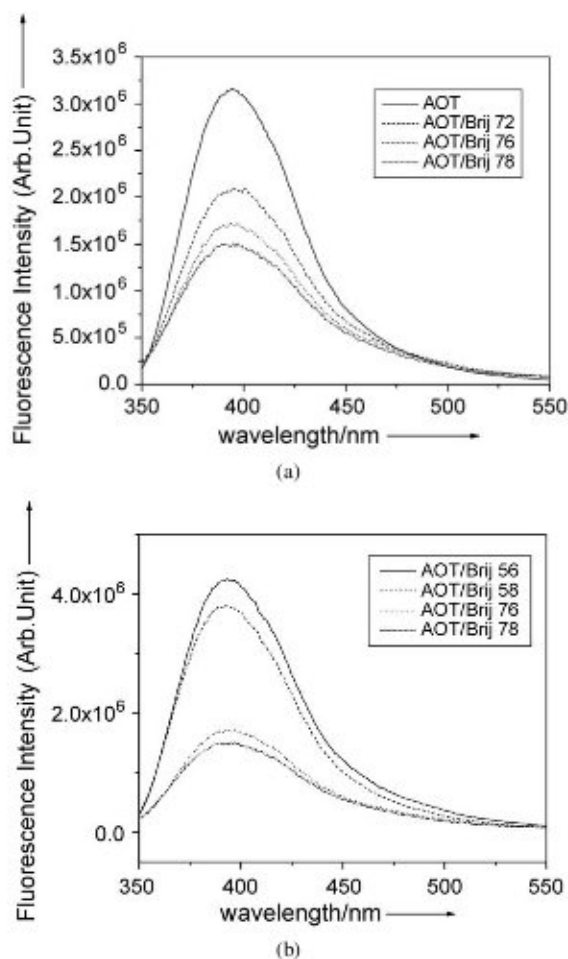


Fig. 5. (a) Fluorescence spectra of 100 μM 7-hydroxycoumarin (HCM) in reverse micelle of AOT/isoctane/water and mixed reverse micelle of AOT/Brij/isoctane/water at $\omega = 3$ with initial surfactant concentration of 0.2 mol dm^{-3} in oil and X_{Brij} of 0.1. (b) Fluorescence spectra of 100 μM 7-hydroxycoumarin (HCM) in mixed reverse micelle of AOT/Brij/isoctane/water at $\omega = 3$ with initial surfactant concentration of 0.2 mol dm^{-3} in oil and X_{Brij} of 0.1.

cence intensity remains almost identical. A representative diagram has been exemplified in Fig. 5a. With increasing numbers of POE groups of Brij (having the same hydrophobic group) fluorescence intensity decreases and for Brij with higher number of POE groups (e.g., Brij-56 and Brij-58 or Brij-76 and Brij-78) it almost levels up. This is possible if Brij molecules with larger POE groups enter into the reverse micellar interface of AOT by ion–dipole interaction forming a sparse interface which is less susceptible to accommodate HCM molecule. Thus HCM preferably resides on the pseudo reverse micellar phase and hence the rate of change in fluorescence intensity decreases. This observation strongly supports the percolation in conductance phenomenon in which incorporation of Brij molecules with large head group size facilitates the percolation phenomenon of mixed system (Table 1) due to the preferential solubilization of the Brij head groups at the surfactant–water interface.

From the fluorescence study of HCM in AOT/Brij-56 and AOT/Brij-58 and AOT/Brij-76 and AOT/Brij-78 reverse micellar systems, it has been observed that for the same number

of POE group fluorescence intensity increases with decreasing chain length of the hydrophobic moiety of the surfactant (Fig. 5b). The fluorescence intensity of AOT/Brij-76 is less than that of AOT/Brij-56 at all ω , even at ω_p . Similar observation has been obtained for the AOT/Brij-58 and AOT/Brij-78 pair. Higher be the fluorescence intensity of HCM at 396 nm in mixed reverse micellar medium, higher will be its probability to reside at the interface. So, mixed reverse micelle having lower chain length can easily accommodate HCM. Based on the fluorescence data, it may be concluded that with decreasing chain length of the hydrophobic moiety, the interface becomes continuously sparse. This confirms the earlier observation obtained from conductivity measurements that both the polar POE group as well as the hydrophobic part of the nonionic surfactant contribute to the alteration of the surfactant coated interface of AOT/ isoctane reverse micellar systems.

4. Conclusions

Replacement of AOT molecules with large head group Brij molecules (Brij-30, Brij-35, Brij-56, Brij-58, Brij-76, Brij-78) decreases the solubilization capacity of AOT/isoctane reverse micellar systems, whereas those with smaller polar head groups (Brij-52 and Brij-72) increases it. The former blends assist the conductance percolation whereas the latter retard it. Absorbance study with HCM shows that the HCM molecule resides in an identical pH environment for both AOT/isoctane and AOT/Brij/isoctane systems. With gradual increase of ω , the absorbance of HCM decreases for all the systems. Fluorescence study reveals that with addition of Brij molecules with larger polar head groups, the fluorescence intensity decreases depending upon both the polar head group and tail part of the added nonionic surfactant.

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