Organization of amphiphiles
Part X: Studies on the interaction between polyoxyethylated (30) octylphenol and cetyltrimethylammonium bromide in aqueous solution

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ABSTRACT

The solution behavior of the mixture of cetyltrimethylammonium bromide (CTAB) and polyoxyethylene (30) octylphenol (OP-30) has been investigated by measuring the conductance, fluorescence intensity, surface tension and absorbance of the surfactant mixtures. A strong interaction between the two surfactants is indicated from each of the measurements. The critical micelle concentration of CTAB is found to increase with increase in the amount of OP-30 in the mixture. This delaying in micellization of CTAB has been attributed to the diminution of its effective hydrophobicity due to interaction with monomers or micelles of OP-30. Below CMC of OP-30, the monomeric concentration of CTAB decreases due to the formation of a hydrophobic complex between OP-30 and CTAB. Above CMC of OP-30, CTAB monomers get solubilized into micellar core of OP-30 in 1:1 stoichiometric ratio. Micropolarity and the aggregation numbers of the mixed systems have been determined from fluorescence studies. The thermodynamics of micelle formation of CTAB coupled with fluorescence studies of the mixtures indicates that the complex grows in size with increase of OP-30 concentration till the micelle of latter is formed at higher concentrations. The treatment of theoretical model to the interaction of OP-30 and CTAB yields a positive interaction parameter showing antagonism behavior. A schematic model of interaction of OP-30 with CTAB below and above its CMC has been suggested.

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1. Introduction

There has been a tremendous upsurge in interest in the physicochemical properties of surfactant solutions particularly that of mixtures of surfactants, largely due to their wide scope of applications in both industrial and household processes, such as detergents, dyes, mineral flotation, surface modification, and personal care. In most of the applications surfactant mixtures rather than pure species are preferably used as they are naturally prevalent and hence require less cost than single surfactant systems [1]. Further, the mixed surfactant systems show many kinds of blending effects compared to the single surfactant systems. The mixtures of nonionic/ionic surfactant systems, in particular, are receiving much more attention than that of ionic/ionic surfactant mixtures since insertion of the nonionic surfactant into ionic surfactant reduces the electrostatic repulsion between its charged head group and hence shows a drastic change in the surface activity of ionic surfactant [2]. Both a synergism behavior [3–6] and an antagonism behavior [7,8] are exhibited by the mixture, depending on the surfactant structure and the properties of the medium.

Because of the unique structural characteristic, polyoxyethylated surfactants have been of special interest to surface chemists as well as industrialists during the past three decades [9]. Many papers are concerned with investigations on the physicochemical behavior of mixtures of nonionic polyoxyethylene surfactants with both anionic and cationic surfactants [10,11]. Ruiz and Aguilar [12] have studied the micellization process of binary mixtures formed by octaethylenamine monodecyl ether and different alkyltrimethylammonium bromides by a fluorescence probing method and have explained the experimental data considering the electrostatic interactions of the head group and the hydrophobic chain length of the bromides. They have suggested the formation of open micelles with a lot of penetrated water. The solution properties of polyoxyethylene alkyl ether and N-decanolyl-N-methylglucamine and their mixtures have been studied by Sulthana et al. [13]. They have seen the formation of more spontaneous micelles for the mixture than that of the individual micelles. While studying the mutual interaction of nonionic and ionic detergents, Mandal et al. [14] have seen that the nonionic surfactant, TX-100, decreases the micellization tendency of both cationic and anionic surfactants, leading to
an antagonistic effect. Dar et al. [15] have studied the cationic–nonionic mixed system and have concluded that the mixed surfactant system improves the performance of surfactant-enhanced remediation of soil, thereby leading to a decrease in the remediation cost. Ruiz and Aguiar [16] have shown that the stability of a binary system formed by Triton X-100 and a series of cationic surfactants, n-alkyltrimethylammonium bromides, depends on the length of the hydrocarbon chain of the cationic surfactant. A literature survey, however, reveals that most of the nonionic–ionic mixture involves linear nonionic surfactants with short chain oxyethylene units, the work on surfactants with long oxyethylene chains and phenyl moieties being scanty. Further, very few scientific reports are available in which the mechanism of mixed interaction has been elucidated at the molecular level by coupling theoretical treatment with experimental findings.

In the present study we have explored the mechanism of interaction of a nonionic surfactant, polyoxyethylene (30) octyphenol, OP-30, with an ionic surfactant cetyltrimethylammonium bromide, CTAB, in aqueous medium. OP-30 with 30 oxyethylene units as its hydrophilic moiety and a phenyl ring in its nonpolar part is judiciously selected because of its applications in industrial and household processes [17,18]. In our earlier studies [19,20] we have also seen that this type of polyoxyethylated alkyl surfactants aggregates with substantial exposure of their hydrophobic groups to the bulk water and hence they can be readily accessible to the incoming substrates for hydrophobic interaction. In order to investigate the role of the molecular state of the surfactants on the interactions, the process of micelle formation of CTAB has been studied in the presence of OP-30, both below and above its critical micelle concentration (CMC). The organization pattern before and after CMC has been suggested on the basis of determination of the aggregation number, micropolarity, and thermodynamic parameters of micelles.

2. Materials and methods

2.1. Materials

The polyoxyethylated alkyl phenol, OP-30, obtained from Nikko Chemicals, Japan, was used as supplied. CTAB (Sigma, USA) was used after purification [21,22]. The absence of a minimum in the surface tension–concentration curve of both surfactants confirmed the high purity (>99%) of these surfactants [23–25], CPC (cetyltrimethylpyridinium chloride) and pyrene (Aldrich, USA) were used without further purification. Triple distilled water (conductance = 1 × 10⁻⁶ mho) was used within 7 days of its preparation. Surfactant solutions were prepared in triple distilled water fresh just before measurement.

2.2. Conductivity measurement

Specific conductivities of solutions of the surfactants at different compositions were measured by a Systronic direct reading conductivity meter (D.D.R. conductivity meter type 303), in the micro range. A dip-type cell with cell constant 1 cm⁻¹ was used. The reproducibility of the conductance value was within experimental error (±0.2%). The CMCs of CTAB were determined in the presence of various concentrations of OP-30 by measuring the conductivity of the surfactants mixtures. A break in the plot of conductance versus [surfactant] indicates the onset of micelle formation and the point of intersection is referred to as the CMC of the surfactants [26]. During the determination of the intersection point (CMC) weight has been given to obtain two lines above and below the break (CMC) with different slopes and better regression coefficients. This method was standardized by determining the CMCs of CTAB and SDS, which compares well with literature values [27].

2.3. Surface tension measurement

The surface tensions of surfactant solutions of various concentrations of CTAB were measured by using a Nima Manual Tensiometer, Model ST 500-man (Nima Tech, England), at 303 K in the presence of variable amounts of OP-30. The surface tension of the pure and mixed surfactant systems is found to decrease with the increase of surfactant concentration and ultimately it attains a minimum value beyond which there is no change in the surface tension values.

2.4. UV–vis studies

The absorbance of the surfactant samples at the appropriate wavelength was taken using a UV–vis double beam spectrophotometer type 2201 (Systronics, Ahmedabad, India).

2.5. Fluorescence measurement

2.5.1. Determination of CMC

Fluorescence spectral measurements were made on a Hitachi Model No. F 4500 Fluorimeter. Stock solution of the fluorescence probe, pyrene, was prepared in pure methanol (Anal R grade, Sisco-chem). A very low concentration of pyrene (1 × 10⁻⁶ M) was used in the sample to avoid the formation of excimer as well as perturbation to the organized system [28]. The emission spectra in between 350 and 600 nm were recorded by exciting the surfactant mixture containing various concentrations of CTAB in the presence and absence of OP-30 at 335 nm (λmax of pyrene). Pyrene has a structured monomeric emission with five peaks out of which the first peak at 370 nm (I₁) and third peak at 380 nm (I₃) are sensitive to the polarity of the medium [29] and hence the ratio I₃/I₁ is called the polarity parameter [29,30]. CMC was determined by noting the variation of polarity parameter with the concentration of the surfactant. The appearance of a plateau in the polarity parameter versus [surfactant] curve has been attributed to a consequence of micelle formation and the concentration at the onset of plateau of this curve is considered to be CMC [31,32] (Supplementary Fig. S1).

2.5.2. Determination of aggregation number

The aggregation numbers (N) of OP-30 (10 mM) alone and CTAB (15 mM) were determined in the absence and presence of OP-30 (various concentrations) following the Turro and Yekta model [33]. The aggregation numbers were determined by measuring the quenching of pyrene fluorescence using cetylpyridinium chloride as the quencher. Surfactant solutions containing 15 mM CTAB with various concentrations of OP-30 and quencher (0.02–0.2 mM) were subjected to excitation at 335 nm and the fluorescence emission intensity at 372 nm was recorded. Using the linear plot of ln(I₀/I) versus quencher concentration the aggregation number was calculated.

3. Results and discussion

3.1. Conductivity studies

The conductivity of CTAB solution is decreased instantly with the addition of OP-30. This decrease is significant before the CMC value of the mixture (break point) in the presence of all concentrations of OP-30. However, beyond CMC of the mixture, the conductance values do not change appreciably when low concentrations of OP-30, i.e., 1 × 10⁻⁵, 5 × 10⁻⁵, and 1 × 10⁻⁴ M (well below its CMC = [OP-30]CMC = 1 × 10⁻³ M [24]) are added to the mixture. But as the added concentration of OP-30 nearly approaches CMC or above (= 5 × 10⁻⁴ and 2 × 10⁻³ M), the conductance value
of the mixture is found to increase remarkably above the CMC of the mixture. These observations clearly suggest the interaction between CTAB and OP-30 [14,34].

Table 1 shows the CMC of CTAB in the presence of various concentrations of OP-30 at three different temperatures, 303, 308, and 318 K. The CMC is found to increase with increase in concentration of OP-30 as well as temperature of the system (Figs. 1 and 2) in all cases. The degree of dissociation (α) values of the micelle (ratio of postmicellar slope to the premicellar slope of the specific conductance versus concentration of surfactant plot) in the absence and in the presence of OP-30 at these temperatures are given in Table 1. The increase in CMC and α values with the increase of the concentration of OP-30 in the mixture as well as temperature suggests that the formation of micelle is hindered by both OP-30 concentration and temperature.

The aggregation phenomena of surfactant systems involve contributions from both repulsive interactions, originating primarily from electrostatic repulsions between the polar head groups [35,36], and attractive interactions between nonpolar tails (hydrophobic interactions) of the surfactant monomers [36,37]. This delicate interplay among nonpolar tails and hydrophilic heads results in surfactant aggregation only when hydrophobic interactions dominate over electrostatic repulsions. The increase in CMC value of CTAB with addition of various concentrations of OP-30 in the present case may be attributed to the reduction of its effective hydrophobicity due to the interaction with OP-30 monomers or micelles. The methylene groups of CTAB may interact favorably with a nonylphenyl chain of OP-30 forming small hydrophobic aggregates. The trimethylammonium group of CTAB may be located near the first oxyethylene group immediately next to the phenoxy ring of OP-30 and the methyl groups of CTAB may be placed close to that of octylphenyl chain of OP-30 [38], thus favoring their association. In our earlier studies [32,39] we have seen that polyoxyethylated alkyl ether and alkyl phenol surfactants associate to form micelles in a stepwise manner, i.e., through formation of premicellar aggregates, such as dimmers and trimmers. The increase in conductance values of the mixture beyond CMC of the mixture may be attributed to the increase in monomer concentration of CTAB due to greater interactions with such premicelles and micelles of OP-30.

Usually nonionic surfactant promotes micellization of ionic surfactant by reducing the electrostatic repulsion between the head groups during insertion. But in the present case this does not happen, probably due to the presence of a phenyl ring in its nonpolar moiety and long oxyethylene chain, nonionic surfactant cannot penetrate compatibly into the palisade layer of CTAB micelles. Further, the favorable interaction of 30 oxyethylene units with water molecules through H-bonds possibly compels OP-30 molecules to stay back in bulk water rather than inside CTAB micelles. The hydrophobic interaction of the octylphenyl unit with a cetyl chain of CTAB surfactant is superseded by this interaction. Such increase in CMC with the addition of nonionic surfactant to ionic surfactant has been reported earlier [14,40].
3.2. Effect of temperature: Analysis of thermodynamics of micellization

The thermodynamic parameters are calculated applying the phase separation model of micelle formation. The standard free energy change of micellization is calculated by using Eq. (1) [27, 41–43]

\[
\Delta G_m^0 = RT \ln X_{\text{CMC}}.
\]

Neglecting the activity coefficient, the free energy change of transfer of CTAB from water to the micellar pseudophase is calculated from Eq. (2) [43]

\[
\Delta G_m^0 = RT \ln [\text{[CMC]}_d/\text{[CMC]}_w].
\]

The enthalpy change of micellization and entropy change of micellization are calculated using Eqs. (3) and (4) respectively [41,43]

\[
\Delta H_m^0 = -RT^2 (\ln X_{\text{CMC}}/dT).
\]

\[
\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0)/T.
\]

The values of \(\Delta G_m^0\), \(\Delta H_m^0\), and \(\Delta S_m^0\) in the absence and presence of different concentrations of OP-30 are given in Table 2. The \(\Delta G_m^0\) values at different temperatures without OP-30 compare well with the literature values [27].

On examination of the thermodynamic parameters (Table 2) it is seen that at constant temperature the standard free energy of micellization, \(\Delta G_m^0\), becomes less negative with increase in concentration of OP-30 in the mixture. But keeping [OP-30] constant, \(\Delta G_m^0\) values become more negative as the temperature increases. At higher temperatures, the nonionic surfactant may become dehydrated and hence may prefer to associate among themselves strongly rather than interacting with the surrounding CTAB monomers. Thus the interaction between OP-30 and CTAB is outweighed by the association of CTAB monomers to form micelles. The trend of enthalpy change of micellization is also commensurate with that of free energy change of micellization. The positive values of free energy change of transfer, \(\Delta G_m^0\) (Supplementary Table S1), indicate that the transfer of the surfactant monomer to the micelle is less favored as the amount of OP-30 increases in the mixture.

The positive value of entropy change of micellization clearly indicates that the formation of micelle is an entropy-directed process [44,45]. During the dissolution of a surfactant in water, the water molecules arrange themselves around the hydrocarbon chain to form a solvation layer. Thus due to the formation of the solvation layer with highly ordered water molecules, the entropy of the systems decreases remarkably, making the dissolution of hydrocarbon chains highly unfavorable. The clustering of amphiphiles into surfactant aggregates (micelles) within which hydrocarbon chains are located in the interior and the molecules are anchored at the interface by hydrophilic head groups (remaining in contact with water), however, decreases the extent of solvation layer. This aggregation releases the mobility constraint on the water molecules and, therefore, results in a favorable increase in entropy.
possibly due to partitioning of OP-30 monomers to the interface. The CMC, however, increases from 0.9 mM to around 1.8 mM in the presence of 0.1 mM OP-30. This may be attributed to the formation of the hydrophobic complex between OP-30 and CTAB, thereby reducing the monomeric concentration of CTAB. In presence of 2 mM OP-30 surface tension decreases substantially; nevertheless a clear-cut CMC is not observed due to the presence of OP-30 micelles from the beginning and CTAB micelles beyond CMC later on simultaneously.

3.5. Fluorescence behavior of pyrene in mixed systems

Some representative emission spectra of pyrene in the presence of various concentrations of CTAB with and without OP-30 (of various concentrations) at 303 K are shown in Figs. 5 and 6. In the presence of CTAB alone, the $I_3/I_1$ ratio remains constant ~0.63 at low concentrations and undergoes a sharp change to attain a value of ~0.98 beyond which the value does not change appreciably (plateau of Supplementary Fig. S1). The plateau sets off at around [CTAB] = 0.9 mM which is the same as its CMC found from the literature [25]. Pyrene being a hydrophobic molecule partitions preferably to micelle as soon as the latter appears in solution. Unlike a slanting middle arm found in our earlier studies [32,39] the appearance of a sharp middle arm in the plot of $I_3/I_1$ versus surfactant concentration in the present case (Supplementary Fig. S1) suggests the one-step association of CTAB monomers to form micelles [29,32,39], possibly due to greater hydrophobicity of its cetyl chain. A stepwise association of surfactant monomers in our earlier studies has been attributed to its long oxyethylene chain which hinders easy association among its hydrophobic chains [32,39]. The change in pattern of the emission spectrum of pyrene (intensity and shape) with gradual increase of OP-30 in the mixture indicates change of environment of pyrene. This change is dependent on the concentration of OP-30 added (below or above CMC).

3.5.1. Below CMC of OP-30

When [OP-30] < CMC is added to various concentrations of CTAB, the characteristic monomer peak with $I_3/I_1$ value = 0.63–0.70 appears at low concentrations of CTAB. The $I_3/I_1$ values undergo a gradual change (Supplementary Fig. S1, Fig. 7) till the onset of a plateau appears. Such sigmoidal plots suggest the formation of small aggregates prior to the formation of micelles [32,39]. From conductivity studies we have suggested the formation of a complex between OP-30 and CTAB monomers. The pyrene may preferably reside in the hydrophobic environment of these complexes compared to water. Due to the formation of the aggregates in stepwise manner, the $I_3/I_1$ suffers a gradual change. But as the micelles of CTAB appear in bulk solution, pyrene molecule partitions to the micellar environment of micelles due to its greater hydrophobicity compared to that of the domain of the hydrophobic complex. Thus in the three-armed plot, the first arm represents the aqueous environment containing surfactant monomers, followed by the small aggregates OP-30 and CTAB in the middle arm and micellar environment at the plateau. The $I_3/I_1$ values at the plateau undergo slight change from 0.98 to 0.95 as the OP-30 concentration is increased in the mixture.

In the transition zone (middle arm) where pyrene starts partitioning slowly from aqueous environment to the nonpolar environment of the complex aggregates an additional peak appears at 480 nm. This peak is not observed in the presence of either CTAB or OP-30 alone under the experimental concentrations studied. The plot of the intensity of the peak with [surfactant] is a sine curve having a maximum at a concentration just below the CMC of the surfactant. The maximum intensity value of the excimer
In fragmented media [50,51] composed of micelles or other smaller aggregates in which pyrene is solubilized, the probability of the excited singlet P to leave one micelle and interacting with a ground-state pyrene from another micelle during its excimer lifetime is very low. This is because the exit of pyrene from micelles occurs on the millisecond scale whereas fluorescence occurs on the nanosecond scale [52,53]. Thus, the excimer formation is essentially an intramicellar process. Only those micelle/aggregates which contain more than one pyrene at a suitable distance during the instance of flash excitation and within the lifetime of the species can give rise to excimer. Due to the small size of the aggregates of the CTAB and OP-30 complex, a ground-state pyrene can collide easily with excited pyrene present in the same domain to form an excimer. The frequency of collision decreases as the aggregates grow in size, leading to a decrease in the probability of excimer formation. Finally the excimer does not form due to the solubilization of the probes in large domains of hydrophobic complexes/micelles. The absence of an excimer peak in the presence of OP-30 micelles alone is due to its long oxyethylene chain which decreases its relative hydrophobicity [28,54].

3.5.2. Above CMC of OP-30

In presence of [OP-30] = 2 × 10^{-3} M (>OP-30_{CMC} = 1 × 10^{-3} M), the pyrene exhibits an emission spectrum with $I_2/I_1$ value of 0.83 at low concentrations of CTAB, slowly increasing to value of 0.94 at 1.9 × 10^{-3} M (Fig. 8). The high value of $I_2/I_1 = 0.83$ even at low concentrations of CTAB is because of the formation of OP-30 micelles which provide a relatively nonpolar environment to pyrene molecules in comparison to water. After the formation of CTAB micelles in the medium, pyrene preferably partitions to the CTAB micelles due to its greater hydrophobicity. The excimer does not appear here due to the solubilization of pyrene in the large domain of OP-30 and CTAB micelles. The increase in CMC of CTAB at this concentration is due to the decrease of its relative hydrophobicity as CTAB monomers become solubilized into OP-30 micelles.

In order to quantify the extent of binding between CTAB to OP-30 micelles the mass-action principle is applied for the formation of CTAB–OP-30 micelle complex as per the following equation [55]

$$\text{(OP-30)}_n + n(\text{CTAB})_m \rightleftharpoons \text{OP-30} – (\text{CTAB})_{3n}. \quad (5)$$

where $n$ number of molecules of ionic CTAB associated to a single OP-30 micelle (complex) with the association constant $K_A$. This equation on further rearrangement yields

$$\log [\Delta \text{[CTAB]}] = \log (K_A n(\text{OP-30})/N) - n \log [\text{CTAB}]_r. \quad (6)$$

The plots of $\log [\Delta \text{[CTAB]}]$ versus $\log [\text{CTAB}]_r$ are linear at all temperatures with correlation coefficient more than 0.99. The values of $n$ and $K_A$ are calculated from these plots and are given in Table 3. The value of $n$'s, approximately equals to 1, and indicates that the association of CTAB monomer with OP-30 micelles is in 1:1 ratio. The high value of $K_A$ indicates the strong interaction between CTAB monomer with OP-30 micelles. The decrease of $K_A$ with increase of temperature is due to the increase in kinetic energy of both surfactants, thereby decreasing their association. This is commensurate with the result obtained in Section 3.2.

The ideality in the interaction of CTAB with OP-30 has been studied further, by considering the pseudophase thermodynamic model proposed by Clint [56]. The ideal CMC of the mixed system has been calculated by using the Clint equation in the following form and the value is given in Table 4,

$$\frac{1}{\text{CMC}^*} = \frac{\alpha_1}{\text{CMC}_1} +\frac{(1-\alpha_1)}{\text{CMC}_2}, \quad (7)$$

where CMC$_1$, CMC$_2$, and CMC$^*$ are the critical micellar concentrations of the surfactant CTAB, OP-30, and the mixtures, respectively. $\alpha_1$ is the mole fraction of the surfactant CTAB in total mixed solute at CMC. The higher value of experimental CMC compared to that of the ideal CMC indicates that the mixing of OP-30 with CTAB is unfavorable in the mixed state.

In order to quantify the unfavorable mixing behavior, the micellar composition in the nonideal state $x_1$ and ideal state $X_1_{ideal}$ is calculated using regular solution approximation [57] (Eq. (8)) and Motomura approximation [58] (Eq. (9)), respectively, and are given in Table 4.

$$x_1^2 \ln(CMC\alpha_1/(CMC\times x_1)) \quad (1-x_1)^2\ln\left(CMC(1-\alpha_1)/(CMC(1-x_1))\right) = 1, \quad (8)$$

$$X_1,_{ideal} = \frac{\alpha_1 \text{CMC}_2}{\alpha_1 \text{CMC}_2 + (1-\alpha_1) \text{CMC}_1}. \quad (9)$$

### Table 3

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$n$ (no of ionic surfactant bound with single micelle of OP-30)</th>
<th>$K_A$ (association constant)</th>
</tr>
</thead>
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<tr>
<td>303</td>
<td>1.966</td>
<td>8956</td>
</tr>
<tr>
<td>308</td>
<td>1.918</td>
<td>7434</td>
</tr>
<tr>
<td>318</td>
<td>1.0095</td>
<td>2015</td>
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</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Mole fraction at CMC</th>
<th>Experimental CMC</th>
<th>Theoretical CMC (ideal CMC)</th>
<th>Ideal micellar composition</th>
<th>Nonideal micellar composition</th>
<th>Interaction parameter ($\beta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.48</td>
<td>1.9 × 10^{-3} M</td>
<td>0.94 × 10^{-4} M</td>
<td>0.51</td>
<td>0.48</td>
<td>2.76</td>
</tr>
</tbody>
</table>

Fig. 8. Plot of $I_2/I_1$ (polarity parameter, pp) of pyrene in the presence of various concentrations of cetyltrimethylammonium bromide solution containing [OP-30] = 2 × 10^{-3} M.
The smaller value of $x_1$ than $X_{1(1)}$ suggests that the micellar composition of CTAB is less in the mixed state in the presence of $2 \times 10^{-3}$ M OP-30 ($[\text{OP-30}] > \text{CMC}$). This may possibly be due to the solubilization of some of CTAB monomers in OP-30 micelles in the mixed state. The interaction parameter ($\beta$) is calculated by using [57,59]

$$\beta = \frac{\ln(CMC_{\alpha_1}/CMC_{\lambda_1})}{(1 - x_1)^2}. \quad (10)$$

The positive value of the interaction parameter (2.76) suggests bluntly that the interaction between CTAB and OP-30 is antagonistic in nature [60] and hence formation of CTAB micelles is not assisted by the OP-30 surfactants.

### 3.6. Micropolarity and aggregation number of mixed systems

Pyrene because of its nonpolar character always prefers partitioning to the nonpolar environment and hence its $I_{3}/I_{1}$ ratio indicates the polarity of the environment where it resides. In the absence of OP-30 the value $I_{3}/I_{1}$ ratio $= 0.98$ is because of the formation of CTAB micelles in solution. Even though this ratio at plateau does not suffer drastically with addition of OP-30, still a steady decrease of the value from 0.98 to 0.94 is observed as the concentration of OP-30 is increased in the mixture. In the presence of OP-30 micelles alone, the value is around 0.80 [28,39]. A value greater than 0.80 at higher concentrations of CTAB (both in the presence and in the absence of OP-30) suggests clearly the preferred site of pyrene to be CTAB micelle/OP-30-CTAB complex due to their greater nonpolar environment compared to OP-30 alone.

On partitioning from an aqueous environment to complexes of increasing size, the pyrene molecule experiences a gradual decrease in the polarity of the surrounding. This is indicated by the gradual increase in the $I_{3}/I_{1}$ value in the middle arm of the sigmoidal curve (Fig. 7). The polarity of the SDS micelle, as estimated by the $^{14}\text{N}$ hyperfine coupling constants of the indicator, is also reported to decrease along with an increase in the micelle size [60].

The $E_{T}(30)$ [61], a solvent parameter value, which indicates the polarity of a medium, is estimated from the plot of $I_{3}/I_{1}$ versus $E_{T}(30)$ plot [32] and an alcohol-like environment is proposed for pyrene in CTAB micelles, both in the presence and in the absence of the OP-30. From earlier studies [19,20] we have seen that CTAB forms a micelle with some fatty patches exposed to water [62]. Studies on the hydroxylation of Rosaline hydrochloride in the presence of CTAB [19] suggest that about 9% of hydrophobic

![Fig. 9. Schematic representation of the formation of micelles of CTAB in the presence and absence of OP-30: (A) in water alone, (B) in the presence of [OP-30] below CMC, and (C) in the presence of [OP-30] > CMC.](image-url)
patches are exposed to water. Pyrene molecules sitting on such fatty patches become exposed to a water environment and hence an alcohol-like environment is experienced. The relatively lower value of $I_3/I_1$ in the presence of CTAB micelles with addition of OP-30 may be attributed to greater interaction of the pyrene molecule with surrounding bulk solution due to the presence of OP-30. In the absence of OP-30 micelles, pyrene stays relatively away from the interfacial region of CTAB micelles to avoid the polar environment of bulk water as well as the ionic atmosphere of CTAB micelles.

The mean aggregation number $N$'s for CTAB alone, CTAB with OP-30, and pure OP-30 systems are calculated from the slope of plot of $\ln(I_0/I)$ against system [Q] for a fixed CTAB concentration = 15 mM. The aggregation numbers of 15 mM CTAB with varying concentrations of OP-30 are found to be 64, 61, 55, 52, and 36, respectively, in the presence of various concentrations of OP-30 chosen in this study. For pure OP-30 and CTAB systems the $N$'s are found to be 27 and 66, respectively. It is known that the aggregation number, i.e., the number of monomers per unit micelle depends on the nature of the environment. Usually for a very polar surrounding the aggregation number is high to minimize strong solvophobic interactions [19,63]. A steady decrease in aggregation number of CTAB micelles with increase in concentration of OP-30 in the bulk solution is observed due to favorable interaction of CTAB surfactants with OP-30 monomers/micelles of the bulk medium.

4. Mechanism of interaction

CTAB alone forms compact micelles with polarity parameter value $I_3/I_1 = 0.98$ of pyrene, indicating CTAB micelles to be non-polar with less penetrated water. On addition of OP-30 (below CMC) a complex is formed between OP-30 and CTAB, thereby leading to the decrease in the monomeric concentration of CTAB. This in turn reduces the hydrophobic interaction of CTAB and hence CTAB agglomerates at higher concentration. The facts that (i) the OP-30–CTAB complex is destabilized with the increase in temperature (as indicated by increase in released free energy change of micellization) and that (ii) the $I_3/I_1$ value of the pyrene increases with increase of OP-30 concentration suggests the nature of the complex to be hydrophobic. The appearance of the excimer at relatively lower concentrations of CTAB with increase of added OP-30 concentration is a direct evidence of the strong interaction of CTAB with OP-30. The gradual decrease of intensity of the excimer with increase of OP-30 concentration in solution suggests that OP-30 micelle is built up in a stepwise manner. At high concentrations of OP-30 (beyond CMC), the CTAB monomer becomes solubilized in OP-30 micelles in a 1:1 stoichiometric ratio. The complex, therefore, acts as a seed corn for the formation and growth of the OP-30 micelle. The favorable interaction between solute (CTAB) and solvent (OP-30 solution) becomes stronger, resulting in the decrease of aggregation number with increase of OP-30 concentration in solution. On the whole the aggregation of the CTAB micelle/CTAB-OP-30 complex is compensated by the disorder they produce in the surrounding due to the release of hydrated water molecules (present around the surfactant monomers) to bulk water. The positive value of interaction parameter ($\beta$) obtained from theoretical treatment of the mixed system is in support of the antagonistic behavior of OP-30 toward CTAB micellization. All experiments carried out here to pursue the micellization study of the binary mixture of CTAB and OP-30 at different solution compositions coherently suggest the progress of the overall process to be as represented schematically in Fig. 9.

5. Summary

The interest in solution behavior of surfactant mixtures lies in the fact that the technical grade surfactants are themselves mixtures and the purification process may be difficult or excessively expensive and the mixed systems often behave better than a single surfactant [16]. Understanding the process of micellization and investigating the molecular organization in the aggregates of the surfactant mixtures with variation of solution compositions are, therefore, of prime importance for Colloid Science from a fundamental viewpoint. The systematic study of a surfactant mixture of an ionic surfactant (CTAB) and nonionic surfactant (OP-30) both below and above CMC presented in this paper reveals that the length of the oxyethylene chain and the phenyl group play a vital role in the mixed interaction in addition to the hydrocarbon chain length of the nonionic surfactant. In contrast to the frequently observed synergism behavior in binary mixtures of cationic surfactant and nonionic surfactant the antagonism behavior has been observed in the present study due to the strong interaction of the long oxyethylene chain with bulk water and incompatible packing of the phenyl group in the aggregates. The antagonism behavior OP-30 toward CTAB micellization has been suggested by two phenomena occurring simultaneously: (i) the delay in micellization of CTAB due to interaction with the OP-30 present in bulk water (evidenced by the positive value of interaction parameter, $\beta$) and (ii) formation of a 1:1 complex between CTAB monomer and OP-30 micelle (evidenced by high value of association constant and unity value of $n$ values).

Because of the similarities of the nonionic surfactants assemblies with globular protein [64,65] this study has an important implication in investigating protein folding problems. The strong interaction of cationic surfactant with OP-30 (a model protein) suggests that the aggregation behavior of a protein can be also be tuned by adding varied amounts of cationic surfactant and hence could be highly useful for divulging the mechanism of interaction of protein with surfactants and subsequent applications. The mechanisms behind denaturation and renaturation phenomena of protein could also be understood by carrying out similar studies with protein and surfactants.

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Supplementary data

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