Interaction, Stability, and Microenvironmental Properties of Mixed Micelles of Triton X100 and n-Alkyltrimethylammonium Bromide: Influence of Alkyl Chain Length

C. Carnero Ruiz* and J. Aguiar

Departamento de Física Aplicada II, Escuela Universitaria Politécnica, Universidad de Málaga, Campus de El Ejido, E-29013 Málaga, Spain

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Micellar properties of binary surfactant systems of Triton X100 (TX100) with three different n-alkyltrimethylammonium bromides (n = 12 (DTAB), 14 (TTAB), and 16 (CTAB)) were investigated by the fluorescence probe technique. The critical micelle concentration (cmc) values of the corresponding mixtures in the whole range of composition were obtained by the pyrene 1:3 ratio method. In order to estimate the interaction between the surfactants in the mixed micelles, the cmc data were treated by using the conventional regular solution approach for mixed micelles. It was found that whereas the interaction parameter values (φ_{12}) remained fairly constant for the TX100–TTAB and TX100–CTAB systems, the TX100–DTAB system was not well modeled by using that theory. However, in all cases the results showed deviation from ideal behavior. The stability of the mixed micelles was also discussed in the light of Maeda’s treatment (J. Colloid Interface Sci. 1995, 172, 98), and the observed differences between the three systems were justified on the basis of a certain steric factor due mainly to the presence of the phenyl group of TX100 in connection with the length of the monomer of the cationic component. The micropolarity of the mixed aggregates was examined by the pyrene 1:3 ratio index in micellar solutions of concentration well above the cmc. It was observed that the increasing participation of the ionic component induces the formation of more closed micelles with a more dehydrated structure. The polarized fluorescence measurements, by using diphenylbutadiene as a probe, were interpreted by using the wobbling in cone model. It was found that the order parameter decreases as the participation of the cationic surfactant in the micelle increases, indicating the formation of a less ordered structure than that of pure TX100 micelles. Data obtained in this investigation allowed to establish a clear correlation between micellar stability and microenvironmental properties of the mixed aggregates.

Introduction

Surfactant solutions are used widely in numerous technical applications such as detergents, cosmetics, pharmaceuticals, enhanced oil recovery or surfactant-based separation processes, to name only a few. However, the systems employed in these applications almost always consist of a mixture of surfactants. This is so because (i) technical-grade surfactants are themselves mixtures, and the purification process may be difficult or excessively expensive, and (ii) the mixed system often behaves better than a single surfactant.6–8 The widespread use of surfactant mixtures for industrial purposes has stimulated the interest of the researchers, and in recent years many papers have been published on the solution properties of mixed surfactant systems. Most of these investigations deal with the study of certain physical properties of the solution. In particular, the variation of the critical micelle concentration (cmc) and of the size or micellar aggregation number with the composition of the system have been the most studied aspects.6–22 Moreover, because the structural properties of the mixed aggregates can become substantially different from those formed only by the single surfactant,1 many recent investigations were concerned with different structural aspects of micelles composed from a two-component surfactant mixture. These studies have commonly been performed by using some spectroscopic techniques, which provide information at a molecular level.23–32 On the other hand, it is widely recognized that

* Corresponding author. E-mail: c.carnero@uma.es.

Mixed Micelles of Triton X100 and D-, T-, and CTAB

The aim of the investigation presented here is double: on the one hand, we have focused on the influence of the alkyl chain length of n-alkyltrimethylammonium bromides in the aggregation behavior of the respective systems and, on the other, we have attempted to establish a correlation between microenvironmental properties and thermodynamic stability of mixed micelles, evaluated on the basis of theoretical mixing model derived parameters.

**Experimental Section**

**Materials.** All surfactants used in this study, TX100 (99.6%), DTAB (99%), TTAB (99%), and CTAB (99%), were obtained from Sigma and due to their high purity were used as received. The samples of pyrene (Sigma) and diphenylbutadiene (Aldrich) were the same as those employed previously and were also used without further purification. Stock solutions of these fluorescence probes were prepared in absolute ethanol. Water was doubly distilled (Millipore) and all experiments were performed with freshly prepared solutions.

**Instrumentation.** All fluorescence measurements were recorded on a SPEX Fluoromax-2 steady-state spectrofluorometer in the "S" mode with band-passes for excitation and emission monochromators of 1.05 nm. The apparatus uses a 150 W xenon lamp as the excitation source and is equipped with a thermostated cell housing. The sample chamber was thermostated to 25 °C using a Julabo F20 circulating water bath, which allowed temperature control to ±0.1 °C. Fluorescence anisotropies were measured in the same apparatus provided with a polarization accessory which uses the L-format instrumental configuration and an automatic interchangeable wheel with Glan-Thompson polarizers. The steady-state fluorescence anisotropy values were determined as

\[
r = \frac{I_V - G_{II}}{I_V + 2G_{II}}
\]

where the subscripts of the fluorescence intensity values (I) refer to vertical (V) and horizontal (H) polarizer orientations. The instrumental correction factor G, required for the L-format configuration, was automatically determined by the software supplied by the manufacturer, and all fluorescence anisotropy values were averaged over an integration time of 20 s.

**Methods.** CMC values in each binary surfactant mixture were obtained by the pyrene 1:3 ratio method. Different binary solutions with a total surfactant concentration of 20 or 40 mM for the three systems investigated were prepared. The composition of the solutions was expressed in molar fraction \(a_i\) of the respective surfactants, defined as

\[
a_i = \frac{[S_i]}{[S_1] + [S_2]}
\]

where \([S_1]\) and \([S_2]\) are the molar concentrations of the surfactants 1 and 2 in the solution. Working solutions of lower concentration were prepared by adding the appropriate amount of a pyrene stock solution in ethanol. The added volume of this solution was 0.1% of the total volume of solution, so that this small amount of solvent had no effect on the micellar system. Fluorescence emission spectra of these solutions were recorded employing an excitation wavelength of 337 nm and the intensities \(I_1\) and \(I_2\) were measured at the wavelengths corresponding to the first and third vibronic band located near 373 and 384 nm. The ratio \(I_1/I_2\) is the so-called pyrene 1:3 ratio (Py 1:3). Some experiments, particularly at high ionic component concentrations, were repeated several times until
values were obtained from the interception of the ex-

obtained were analogous to those measured after 2 h of sonication

resultant solutions were sonicated at least for 10 min at 40 °C,

purpose of achieving a complete solubilization of the probe, the

this amount of solvent had no influence on the system. With the

the added volume of ethanolic solution containing the probe was

í

systems, respectively, and 12

in a number of reference solvents.

by plotting the Py 1:3 values as a function of the dielectric constant

a calibration line obtained, under our experimental conditions,

are estimated to be less than 7%.

Micropolarities of the mixed micelles were obtained following

the pyrene probing method proposed by Turro et al.45 For this

purpose, solutions with a total surfactant concentration well

above the corresponding cmc were prepared. The apparent
dielectric constants of mixed systems were estimated by using

a calibration line obtained, under our experimental conditions,

by plotting the Py 1:3 values as a function of the dielectric constant

in a number of reference solvents.

For the fluorescence polarization studies we have used
diphenylbutadiene (DPB) as a probe. In this case, micellar

solutions with a total surfactant concentration of 20, 40, and 50

mM for the TX100–CTAB, TX100–TTAB, and TX100–DTAB

systems, respectively, and 12 μM in DPB, were prepared. Here

the added volume of ethanolic solution containing the probe was

0.3% of the total volume of the solution. We also checked that

this amount of solvent had no influence on the system. With the

purpose of achieving a complete solubilization of the probe, the

resultant solutions were sonicated at least for 10 min at 40 °C,

as we tested that with this time the fluorescence anisotropy values

obtained were analogous to those measured after 2 h of sonication

at the same temperature. Fluorescence anisotropies were

recorded using excitation and emission wavelengths of 334 and

380 nm, respectively. All fluorescence anisotropy values presented

in this paper are the mean value of three individual determina-

tions. In all cases the errors in the values given for are less than

3%.

Results and Discussion

Cmc, Interaction, and Stability. Figure 1 shows the

variations of Py 1:3 with the total concentration of surfactant in DTAB and a number of mixtures of the

TX100–TTAB system of different compositions. The

results obtained for all mixtures investigated were found to be similar to those shown in Figure 1. In all cases the

Py 1:3 presents a sigmoidal decrease as the micellar concentration increases. Following Zana et al.,29,30 the cmc

values were obtained from the interception of the ex-

trapulations of the rapidly varying part of the plot and of

the nearly horizontal part at high surfactant concentration

(see Figure 1A). The cmc values obtained in the case of

pure surfactants, 0.33 mM for TX100, 15.2 mM for DTAB,

3.83 mM for TTAB, and 1.00 mM for CTAB, compare well

with literature values.21,25,44

In this work we have used Rubingh’s nonideal mixing

model46 to analyze the cmc data of the mixed systems

investigated. Nonideality can be analyzed by using a

regular solution theory,46,47 which introduces an interac-

tion parameter (β12) to characterize the interactions

between the two surfactant species in the mixed micelle.

This interaction parameter is related to the activity

coefficients of the surfactants within the micelle by

\[
f_1 = \exp(\beta_{12}(1 - x_1) x_2) \quad (3a)
\]

\[
f_2 = \exp(\beta_{12} x_1^2) \quad (3b)
\]

where \(x_1\) is the mole fraction of the surfactant 1 in the

mixed micelle, which can be calculated solving iteratively

the eq 4

\[
\frac{x_1^2 \ln \left(\frac{\alpha_1 C^*}{x_1 C_1}\right)}{(1 - x_1)^2 \ln \left(\frac{1 - \alpha_1 C^*}{(1 - x_1) C_2}\right)} = 1 \quad (4)
\]

where \(C^*\) is the cmc of the binary systems and \(C_1\) and \(C_2\)

are the cmc for pure surfactants 1 and 2, respectively.

Subsequently, the interaction parameter \(\beta_{12}\) can be

evaluated from the eq 5

\[
\beta_{12} = \frac{\ln \left(\frac{\alpha_1 C^*}{x_1 C_1}\right)}{(1 - x_1)^2} \quad (5)
\]

\(\beta_{12}\) is an indication not only of the degree of interaction

between the two surfactants but also accounts for the

deviation from ideality. A negative value of \(\beta_{12}\) implies an

attractive interaction; the more negative the \(\beta_{12}\) value the
greater the attraction.

Figures 2–4 show the cmc values obtained experimen-
obtained from eq 4, with the composition of the solution

indicates a certain attractive interaction between the two
an ideal behavior. This negative deviation from ideality
mental values are lower than those obtained by assuming
for the TX100
across the whole mole fraction range stay rather constant
for the TX100
characteristic
of the system were observed. Particularly, we found that
12 value for these systems, we have
1.7 for the TX100
DTAB system, increasing differences appear as the alkyl chain length of the cosurfactant decreases. These
differences can be attributed to experimental errors in
the cmc determination for the TX100–TTAB system, but
the magnitude of the discrepancies in the case of the
TX100–DTAB system could indicate that the TX100–
DTAB system cannot be modeled by using Rubingh’s
approach. With regard to the fact that the regular solution
theory looks fine if represented in terms of the monomer
composition (Figure 2) but gives worse results when plotted
against the micelle composition (Figure 5), as observed in
the case of the TX100–DTAB system, it must be pointed
out that a similar but more pronounced behavior has
recently been reported.23 In any case, from the data in
Figure 5 it can be inferred that at low mole fraction of
cosurfactant the mixed micelle is mostly formed by TX100
monomers and only when the cosurfactant concentration
is high does its participation in the mixed micelle become
significant. This behavior also depends on the length of
the alkyl chain of the cosurfactant. For a fixed composition
of the solution it is observed that the participation of the
cosurfactant in the mixed micelle increases as its alkyl
chain length is greater.

As mentioned above, variations of \( \beta_{12} \) values with
composition for the TX100–TTAB and TX100–DTAB
systems were observed. Particularly, we found that \( \beta_{12} \)
values become more negative as the mole fraction of the
cosurfactant decreases, this trend being more sharp in
the case of TX100–DTAB. In general, this behavior could
be rationalized taking into account the role of the repulsive
interactions of the headgroups of the cationic surfactant
in the stability of the mixed micelles. Note that the
intercalation of nonionic surfactants in the mixed micelle
prevents these repulsive interactions from achieving the
electrostatic stabilization of the micelle. It is interesting
to point out that some authors have justified similar variations of \( \beta_{12} \) with the composition in systems formed
by cationic and nonionic surfactants consisting of poly-
oxethylene (POE) groups, on the basis of the repulsive
interactions between the head cationic groups and oxo-
nium ions formed in the hydrophilic moiety of the nonionic
surfactant. Although this effect could contribute to the
overall electrostatic interactions in the mixed system, as
the cosurfactants employed in this work have the same
headgroup, it seems clear that secondary effects of steric
character may be taken into account to explain the
tendency shown by our experimental data.
Table 1. Interaction Parameters According to Maeda’s Approach for the Different Mixed Surfactant Systems

<table>
<thead>
<tr>
<th>System</th>
<th>$B_0$</th>
<th>$B_1$</th>
<th>$B_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TX100–DTAB</td>
<td>-1.1</td>
<td>1.23</td>
<td>2.6</td>
</tr>
<tr>
<td>TX100–TTAB</td>
<td>-1.1</td>
<td>0.75</td>
<td>1.7</td>
</tr>
<tr>
<td>TX100–CTAB</td>
<td>-1.1</td>
<td>0.11</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Recently, Maeda\(^{34}\) has proposed a new approach for mixed micelles involving ionic species. In the formulation of Maeda, which is based on the phase separation model, the thermodynamic stability is described by $G_{\text{mic}}$, which is given, as a function of the mole fraction of the ionic component in the mixed micelle, by

$$G_{\text{mic}} = \frac{B_0}{RT} + B_1 x_2 + B_2 x_2^2$$  \hspace{2cm} (6)$$

Here $B_0$ is an independent term related to the cmc of the nonionic component by

$$B_0 = \ln C_1$$  \hspace{2cm} (7)$$

The second parameter, $B_1$, is related to the standard free energy change upon replacement of a nonionic monomer in the nonionic pure micelle with an ionic monomer,\(^{34}\) and the last coefficient, $B_2$, is equivalent to $\beta_{12}$ in the regular solution theory, specifically

$$B_2 = -\beta_{12}$$  \hspace{2cm} (8)$$

Finally, the parameters $B_1$ and $B_2$ are related to the cmc values of pure systems by

$$\ln \left( \frac{C_2}{C_1} \right) = B_1 + B_2$$  \hspace{2cm} (9)$$

Consequently, when $B_1$ is evaluated, one can obtain $B_2$ from eq 9. In Table 1 are presented the values of these parameters that we have obtained for our systems. As can be seen, $B_1$ is always positive and small in magnitude but decreases when the length of the alkyl chain of cosurfactant increases. According to Maeda,\(^{34}\) the transfer process of an ionic surfactant monomer to the nonionic pure micelle with an ionic monomer,\(^{34}\) and the last coefficient, $B_2$, is equivalent to $\beta_{12}$ in the regular solution theory, specifically

$$B_2 = -\beta_{12}$$  \hspace{2cm} (8)$$

Finally, the parameters $B_1$ and $B_2$ are related to the cmc values of pure systems by

$$\ln \left( \frac{C_2}{C_1} \right) = B_1 + B_2$$  \hspace{2cm} (9)$$

According to Robson and Dennis,\(^{50}\) we will assume that the TX100 micelle has a prolate ellipsoidal shape with a semiaxis of 52 and 27 Å for the long and short dimension, respectively, its structure consisting of a hydrated POE mantle, which takes up around 83% of the total volume, and a hydrocarbon core, such as shown schematically in Figure 6. On the other hand, we have used the HyperChem molecular calculation package to determine the lengths of the whole molecules of cationic surfactants, obtaining 16.4, 19.0, and 21.5 Å for DTAB, TTAB, and CTAB, respectively. These values as compared with the dimensions of the TX100 micelle explain the trend observed in Figure 7, showing a minor deviation from the ideal behavior.

Finally, we have estimated the stability of the mixed systems as a function of the micellar composition on the basis of the description proposed by Maeda. Figure 7 shows the dependence of $\Delta G_{\text{mic}}/RT$ on micellar composition, where $\Delta G_{\text{mic}}/RT$ is defined as the stability relative to that of TX100 pure micelles. As can be seen in Figure 7, the stability of the three mixed systems decreases when the participation of the cosurfactant increases. This behavior is reasonable as the incorporation of ionic monomers is associated with an increase of the charge density, causing the electrostatic destabilization of the system. In addition, it is also observed that for a fixed micellar composition, i.e., for a $x_2$ constant value, the stability of the mixed system decreases as the alkyl chain length of the cosurfactant becomes smaller. This is consistent with the steric compatibility between the two surfactants in the mixed micelle, as discussed above.

\(^{50}\) Robson, R. J.; Dennis, E. A. J. Phys. Chem. 1977, 81, 1075.
where estimated by using the following relation

\[
\epsilon = x_1\epsilon_1 + x_2\epsilon_2
\]

(10)

where \(\epsilon_1\) and \(\epsilon_2\) are the apparent dielectric constant of pure micelles of components 1 and 2, respectively, and where \(x_1\) and \(x_2\) are the mole fractions of components 1 and 2 in the mixed aggregate. The aforementioned authors also suggest that this method can be used to determine the micellar composition, which was just the procedure followed by Tokuoka et al.\(^\text{41}\) to determine the micellar composition in a number of mixed surfactant systems. In order to apply this procedure to our systems, we have prepared a calibration line in which we have monitored the Py 1:3, measured under our experimental conditions, as a function of the dielectric constant by using a number of reference solvents. Figure 9 shows the calibration line obtained. In this manner, we have estimated the apparent dielectric constants of pure and mixed micelles, denoted by \(\epsilon(x)\). Moreover, by using the \(x_1\) and \(x_2\) values as obtained from the regular solution theory and the eq 10, we have calculated the apparent dielectric constant values for the different mixed systems, denoted as \(\epsilon(x)\). All these values are listed in Table 2. For the TX100–DTAB system it is observed that (i) both \(\epsilon(Py)\) and \(\epsilon(x)\) are roughly insensitive to the system composition, and (ii) there are not large changes between the values obtained from both methods; however, we think that this is due to the fact that the apparent dielectric constant values of both pure systems are very similar. On the other hand, for the TX100–CTAB systems, which are fairly well modeled by the regular solution approach, a continuous decrease is observed for both parameters as the participation of cosurfactant increases in the system. In addition, for these two systems it can be seen that at low participation of cosurfactant there is a reasonable agreement between \(\epsilon(Py)\) and \(\epsilon(x)\). However, when the participation of cosurfactant increases, greater differences are observed in both systems. We have previously found\(^\text{42}\) that, for systems well modeled by the regular solution theory, as the greater the deviations of the ideal behavior, the greater the differences between \(\epsilon(Py)\) and \(\epsilon(x)\) values. From this point of view, the similar trend observed for TX100–DTAB and TX100–CTAB could be interpreted on the basis of an analogous deviation of the ideal behavior for both systems. From these observations and others previously reported,\(^\text{42}\) it can be inferred that the method based on eq 10 for the determination of the micellar composition only can be applied when the mixture is well described by the regular solution theory and at low
The steady-state anisotropy (\(r\)) is related to the viscosity around the probe (\(\eta\)) by Perrin's equation

\[
r = r_0 + r_d \quad (11)
\]

where \(r_0\) is the limiting value of emission anisotropy in the absence of rotational freedom, \(r\) is the average lifetime of the fluorophore excited state, \(T\) is the absolute temperature, \(k\) is the Boltzmann constant, and \(V\) is the effective volume of the probe. Therefore, the anisotropy is considered as an index of the microviscosity or rigidity in the microenvironment of the probe. However, some assumptions inherent to the application of the steady-state depolarization method to obtain microviscosities in micelles have been demonstrated to be not justified. In addition, the concept of microviscosity has recently been critically discussed on the basis of the diffusion coefficients for the molecule probes in micelles. Accordingly, we have focused not on determining absolute values of microviscosities around the probe, but rather on evaluating the relative changes in the micellar structure upon the system composition.

The degree of depolarization of the fluorescence emission of a molecule probe is a measure of its rotational diffusion during the excited lifetime. However, in highly structured microenvironments, the rotational diffusion of the probe is restrained and, as a consequence, the probe does not assume all possible orientations with equal probability. In addition, the dynamic conditions of the medium controlling the speed with which the probe does its motion must also be taken into account. Therefore, the steady-state fluorescence anisotropy can be resolved into two components, one static (\(r_s\)) and another dynamic (\(r_d\)): \(r = r_s + r_d\)

\[
r = r_0 + r_d \quad (12)
\]

According to the wobbling in cone model proposed by Kinosita et al., the rotation of a molecule probe is assumed to occur in a square well potential such that its rotation is unhindered until a certain angle \(\theta_c\) is reached, the rotation beyond this angle being energetically impossible. The region where the movement of the dye molecule takes place is assumed for simplicity as a cone, \(\theta_c\) being the semicone angle. A second important parameter for this model is the order parameter, \(S\), which measures the equilibrium orientational distribution of the probe and which decreases with increasing mobility of the dye in the medium. That is, \(S\) is a structural parameter which gives information about the organization or order of the site of solubilization of the molecule probe.

Table 2. Apparent Dielectric Constant for the Different Mixed Surfactant Systems As Obtained from Both the Calibration Line in Figure 9, \(\epsilon(Py)\), and Eq 10, \(\epsilon(x)\), at 25°C

<table>
<thead>
<tr>
<th>system (\epsilon(x))</th>
<th>(a_2)</th>
<th>(x_2)</th>
<th>(\epsilon(Py))</th>
<th>(\epsilon(x))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TX100–DTAB</td>
<td>0.0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.13</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.13</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.15</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.21</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.00</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>TX100–TTAB</td>
<td>0.0</td>
<td>0.00</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.11</td>
<td>0.30</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.15</td>
<td>0.29</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.24</td>
<td>0.28</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.33</td>
<td>0.28</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.00</td>
<td>0.29</td>
<td>0.29</td>
</tr>
<tr>
<td>TX100–CTAB</td>
<td>0.0</td>
<td>0.00</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.14</td>
<td>0.29</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.26</td>
<td>0.28</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.38</td>
<td>0.27</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.54</td>
<td>0.27</td>
<td>0.29</td>
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<tr>
<td></td>
<td>1.0</td>
<td>1.00</td>
<td>0.26</td>
<td>0.26</td>
</tr>
</tbody>
</table>

\(a\) The total surfactant concentrations used were 50, 40, and 20 mM for the mixtures TX100–DTAB, TX100–TTAB, and TX100–CTAB, respectively. \(a\) The errors in \(\epsilon(Py)\) and \(\epsilon(x)\) are estimated to be within ±7.0% and ±8.0%, respectively.

Cosurfactant content, or in the case that the mixed system behaves ideally.

Fluorescence Anisotropy Studies. As stated above, the structure of TX100 micelles consists of a tightly packed deep core of hydrocarbon and a hydrated POE shell occupying the major part of the volume of the micelle. It is also assumed that the interactions between water molecules and the POE groups play a critical role in the packing of the hydrophilic mantle in the micelle. Therefore, the progressive incorporation of cationic surfactant molecules in the structure of the TX100 micelles will produce a lack of hydration, consistent with a decrease of the hydration layer of the micelle.52 The progressive change in the palisade layer of the micelle.

With the purpose of studying the effect of the cosurfactant participation in the structure of TX100 micelles, we have performed polarized fluorescence measurements by using DPB as a fluorescence probe. The behavior of this probe in micellar media has been previously well characterized by J obe and Verrall,33 and was later used by us to examine structural changes in single44 and mixed micelles.42 The steady-state anisotropy \(r\) is related to the viscosity around the probe \(\eta\) by Perrin's equation

\[
r_0 / r = 1 + kT \eta / V_f \quad (11)
\]

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In the present study we have found that binary systems formed by the nonionic surfactant TX100 and three different n-alkyltrimethylammonium bromides show deviation from the ideal behavior. We have shown that the stability of the mixed micelles depends on the alkyl chain length of the cosurfactant, increasing the stability as the length of its hydrocarbon chain becomes greater. This fact has been interpreted in terms of steric compatibility between the surfactants forming the mixed micelle. From the micropolarity assays, it can be deduced that the progressive participation of cosurfactant on the mixed micelle induces the formation of more closed micelles, in which water penetration is more restricted. This effect also depends on the alkyl chain length of the cosurfactant, the CTAB being the one which causes a major influence due to the greater participation level in the mixed aggregate. The fluorescence depolarization measurements indicate that the incorporation of cosurfactant causes a lack of order in the micellar structure of TX100, which has been attributed to the contribution of two effects: (i) the formation of a more dehydrated structure, and (ii) the increase of the repulsive interactions between the headgroups of the cationic surfactants. Despite the fact that the CTAB is the cosurfactant producing mixed micelles with a more dehydrated structure, it is also the cosurfactant causing the formation of mixed aggregate with more ordered structures. This behavior probably arises from the existence of two compensating effects: (i) the formation of mixed micelles with a more dehydrated structure, as seen in micropolarity studies, and (ii) the tighter packing of the surfactant alkyl chains due to the greater steric compatibility between CTAB and TX100 monomers, as discussed previously.

**Conclusions**

Measurements of steady-state anisotropy provide a simple means of monitoring the processes in which the micellar microstructure is affected in any way. The values for \( r \), \( S \), and \( \theta_c \) obtained for our systems in the whole range of composition are given in Table 3. From its data it is observed that the fluorescence emission of the probe is in all cases highly polarized, indicating a strong interaction between probe and micelle. It can also be seen that the anisotropy values in single nonionic micelles are higher than in single cationic micelles, indicating that the packing is less tight in these systems. This is mainly due to the contribution of two factors: the existence of electrostatic repulsions between the surfactant headgroup and a smaller hydration of the hydrophilic mantle in the ionic systems. On the other hand, the referred data suggest that in the micellar structure experiments there is a lack of order as the presence of cosurfactant increases in the mixed micelle. It is observed that while the order parameter undergoes a progressive decrease, \( \theta_c \) increases with the participation of cosurfactant in the mixed system, indicating that the equilibrium orientational distribution of the molecule probe is less constrained in the mixed system as compared to the pure TX100 system. These observations are consistent with a decrease of hydration of the mixed micelles, as revealed by a reduction in the micellar micropolarity, and with an increase of the repulsive interactions between the headgroups of cationic surfactants as these replace some TX100 molecules in the aggregate. In addition, data in Table 3 indicate that the effect produced in the structure of the micelle, revealed by the order parameter, increases as the alkyl chain length of cosurfactant becomes smaller. Note that although the CTAB is the cosurfactant rising, a greater level of participation in the mixed aggregate produces a minor effect in the order parameter. This behavior probably arises from the existence of two compensating effects: (i) the formation of mixed micelles with a more dehydrated structure, as seen in micropolarity studies, and (ii) the tighter packing of the surfactant alkyl chains due to the greater steric compatibility between CTAB and TX100 monomers, as discussed previously.

**Table 3. Steady-State Fluorescence Anisotropy (r) of DPB Solubilized in the Mixed Surfactant Systems and Structural Parameters (Order Parameter S and Critical Angle \( \theta_c \)) of the Wobbling in Cone Model in Micellar Solutions of Different Compositions, at 25 °C**

<table>
<thead>
<tr>
<th>System</th>
<th>( a_2 )</th>
<th>( r )</th>
<th>( S )</th>
<th>( \theta_c ) [deg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TX100–DTAB</td>
<td>0.0</td>
<td>0.286</td>
<td>0.90</td>
<td>21.3</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.272</td>
<td>0.87</td>
<td>24.4</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.252</td>
<td>0.83</td>
<td>28.1</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.236</td>
<td>0.79</td>
<td>31.5</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.214</td>
<td>0.74</td>
<td>35.4</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.204</td>
<td>0.71</td>
<td>37.6</td>
</tr>
<tr>
<td>TX100–TTAB</td>
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<td>0.286</td>
<td>0.90</td>
<td>21.3</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.260</td>
<td>0.85</td>
<td>26.3</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.242</td>
<td>0.81</td>
<td>29.8</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.228</td>
<td>0.77</td>
<td>33.1</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.223</td>
<td>0.76</td>
<td>33.9</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.221</td>
<td>0.76</td>
<td>33.9</td>
</tr>
<tr>
<td>TX100–CTAB</td>
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<td>0.296</td>
<td>0.92</td>
<td>19.1</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.264</td>
<td>0.86</td>
<td>25.7</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.248</td>
<td>0.82</td>
<td>28.9</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.234</td>
<td>0.79</td>
<td>31.6</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>0.233</td>
<td>0.79</td>
<td>31.6</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.230</td>
<td>0.78</td>
<td>32.0</td>
</tr>
</tbody>
</table>

* Concentrations as in Table 2.