Stability, Interaction, Size, and Microenvironmental Properties of Mixed Micelles of Decanoyl-N-methylglucamide and Sodium Dodecyl Sulfate

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The mixed micellization between the nonionic surfactant decanoyl-N-methylglucamide (MEGA-10) and the common sodium dodecyl sulfate (SDS) in aqueous solutions of 0.1 M NaCl was investigated by the fluorescence probe method. The critical micelle concentrations were determined by the pyrene 1:3 ratio method. The experimental data are discussed in light of two mixing thermodynamic models within the framework of the pseudophase separation model, including the conventional regular solution theory and a recent treatment proposed by Maeda (J. Phys. Chem. B 2004, 108, 6043). This last approach provides a more appropriate description of the mixed system, particularly in two aspects: the nature of the interactions responsible for the stability of the mixed micelle and the behavior of the excess free energy per monomer of the system. By using the static quenching method, the mean micellar aggregation numbers of mixed micelles in the whole range of compositions were obtained. It was found that the micellar aggregation number initially increases with the content of the ionic component, then remains roughly constant, and, finally, decreases slightly for high content of this component. This behavior was analyzed taking into account the effects produced by the presence of the charged headgroups of sodium dodecyl sulfate, as this component increases its participation in the mixed micelle. The micropolarity of the mixed micelles was studied by the pyrene 1:3 ratio index. It was observed that the increasing participation of the ionic component induces the formation of micelles with a more dehydrated structure. Data of micellar microviscosity were obtained by using different methods, including fluorescence intensity measurements of Auramine O and steady-state fluorescence anisotropy of rhodamine B and diphenylbutadiene. The results obtained from these experiments are in good agreement and suggest the formation of mixed micelles with a less ordered structure as the content of SDS increases.

Introduction

The physicochemical properties of the aqueous solutions constituted by two or more surfactants often present a very different character in comparison to those formed by the single surfactants. The change in these properties is due to the occurrence of interactions of a different nature between the component surfactants. The interest in the study of these systems is motivated by aspects of both applied and theoretical character. On one hand, these systems often present superior properties to those with a single surfactant component, showing numerous advantages in many technical applications. For example, mixed micelles of ionic and nonionic surfactants show an expanded colloidal stability when compared with the pure nonionic system. In addition, the size of an ionic micelle, which usually forms small globular aggregates at a low surfactant concentration, may be increased upon the addition of a nonionic surfactant. The improvement of these two properties, stability and size, would enhance the capability of incorporating different solutes in the micellar phase, and this is an important topic in many applications of micellar solutions. Furthermore, there are other important properties of great interest in several applications of surfactants which are determined by the micellar composition. A representative case refers to the microenvironmental properties, which play a decisive role in areas such as micellar catalysis. Note, for instance, that the local polarity or micropolarity can modify not only the velocity but also the mechanism of the reaction. On the other hand, it is also important to get appropriate mixing thermodynamic models able not only to interpret the experimental results but also to predict the behavior of a determined mixed system. Hines’ has reviewed the most relevant advances in theoretical studies of mixed surfactant systems up to 2001. However, new approaches arise continually in this area. Recently, Maeda has reported a phenomenological procedure for analyzing the stability and the synergism of ionic/nonionic mixed micelles in salt solutions.

Among the more frequently studied mixed systems, those constituted by a polyoxyethylene nonionic surfactant and an ionic one have attracted considerable attention due to their wide use in many industrial applications.

(2) Hoffmann, H.; Pössnecker, G. Langmuir 1994, 10, 381.
Recently, alkylpolyglycoside (APG) surfactants have been attracting increasing interest due to their peculiar solution properties. APG surfactants are nonionic and are characterized by having a hydroxyl sugar group as the hydrophilic moiety, and they show a solution behavior substantially different from the ethoxylated nonionic ones. For instance, APG surfactants have both stronger lipophobicity and hydrophilicity, and their temperature dependence of the solution properties is much less pronounced, not showing the clouding phenomenon. This kind of surfactant has a number of properties which make it very interesting in numerous applications in the biomembrane field. In addition, APG surfactants are biodegradable and considered dermatologically safe and, therefore, are very suitable materials in applications related to cosmetic preparations, cleaning products, or food technology. However, the number of studies concerned with mixtures of APG with other surfactants is rather scarce.

This paper deals with a fluorescence probe study on the characterization of the mixed system formed by the APG surfactant decanoyl-N-methylglucamide (MEGA-10) and the conventional ionic one sodium dodecyl sulfate (SDS) in 0.1 M NaCl. The interactions in the system were determined by analyzing the variation of the critical micelle concentration (cmc) through the whole composition range, as determined by the pyrene 1:3 ratio method. The experimental data were analyzed by the regular solution theory, and the results were compared with those obtained by a new approach recently proposed by Maeda. In the second part, by using the static quenching method, we study the variation of the micellar mean aggregation number as a function of the system composition. Finally, by selecting different fluorescent probes, we have obtained information on the microenvironmental properties of the mixed system.

Experimental Section

Materials. The nonionic surfactant MEGA-10 and the quencher cetylpyridinium chloride (CPyC) were obtained from Sigma, whereas SDS was acquired from Fluka. These products were used as received. The fluorescence probes pyrene, auramine O (AO), and rhodamine B (RB) were also from Sigma, and diphenylbutadiene (DPB) was from Aldrich. All these substances were also used without further purification. Stock solutions of surfactants and quencher were prepared in water and those of fluorescence probes in absolute ethanol. Water was doubly distilled, and all the experiments were carried out with freshly prepared solutions.

Apparatus. All fluorescence measurements were recorded on a SPEX FluoroMax-2 spectrofluorometer in the “S” mode. This apparatus is equipped with a thermostated cell housing and fitted with a 150-W xenon lamp and 1 cm × 1 cm quartz cells. Fluorescence anisotropy measurements were recorded 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

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

where the subscripts of the fluorescence intensity values (I) refer to vertical (V) and horizontal (H) polarizer orientation. The software supplied by the manufacturer automatically determined the instrumental configuration factor G, required for the L-format configuration. The anisotropy values were averaged over an integration time of 10 ms, and a minimum number of three measurements were made for each sample. The anisotropy values of the probes in micellar media presented in this work are the mean value of three individual determinations. All the fluorescence measurements were made at 30.0 ± 1 °C.

Methods. The pyrene 1:3 ratio method was used to obtain the cmc values in each binary surfactant mixture. Different aqueous solutions containing MEGA-10 and SDS in several proportions were prepared. The composition of the solutions was expressed in molar fraction (φi) of the respective surfactant, defined as

\[
\phi_i = \frac{[S_i]}{[S_i] + [S_j]}
\]

where [S_i] and [S_j] refer to the molar concentration of the component surfactants. Working solutions of lower concentration were prepared by adding proper volumes of the pyrene ethanolic solution. The volume of this solution was small enough (0.1% of the total volume) so that the solvent did not have an effect on the micellar system. From these solutions, fluorescence emission spectra were recorded using an excitation wavelength of 335 nm, and the fluorescence intensities at the wavelengths corresponding to the first (I1) and third (I3) vibronic bands, located near 373 and 384 nm, were measured. The ratio I3/I1 is the so-called pyrene 1:3 ratio. The cmc determination in each sample was repeated at least two times. When we did not find a good reproducibility, the experiment was repeated a third time. The errors in cmc values are estimated to be <5%.

Micellar aggregation numbers (Nagg) were obtained from luminescence quenching of pyrene using CPyC as a quencher. Stock solutions containing pyrene (3 μM) and MEGA-10/SDS mixtures in different proportions, but with the total surfactant concentration (60 mM) remaining constant, were prepared in 0.1 M NaCl aqueous solutions. Working solutions of lower concentration (1 μM in pyrene and 20 mM in surfactant) were prepared by adding appropriate volumes of quencher solutions. In these studies, the quencher concentrations employed were maintained low enough (<0.18 mM) so as not to interfere with the assembly of pure or mixed micelles. From these solutions, fluorescence intensities were recorded by using excitation and emission wavelengths of 335 and 383 nm, respectively. For each mixture composition, the quenching experiments were repeated three times. The errors in Nagg values are estimated to be <3%.

Micropolarity studies of the mixed micelles were carried out by using the pyrene probing method, under the same optical conditions as those used in the cmc determinations. In this case, the errors in cmc values are estimated to be <5%.
solutions with a total surfactant concentration well above the corresponding cmc (20 mM) were used.

Micellar microviscosity was examined by using different fluorescence probes. First of all, we use the cationic probe AuO, whose fluorescence quantum yield increases with the viscosity of the medium regardless of its polarity. In this case, fluorescence spectra of AuO solubilized in MEGA-10/SDS mixed micelles (20 mM) were recorded using an excitation wavelength of 436 nm. From these spectra, the fluorescence emission was taken at 497 nm. Second, in the fluorescence polarization studies, we used two different probes, a neutral hydrophobic probe (DPB) and a cationic one (RB). In these cases, micellar solutions with a total surfactant concentration of 20 mM with 12 μM DPB or 1 μM RB were prepared. Fluorescence anisotropies were recorded using excitation and emission wavelengths of 334 and 380 nm, respectively, for DPB, and of 557 and 576 nm for RB. All fluorescence anisotropy values reported in this paper are the mean value of three individual determinations.

Results and Discussion

cmc, Interaction, and Micellar Composition. To obtain the cmc values of the MEGA-10/SDS system of different compositions, we have monitored the pyrene 1:3 ratio as a function of the total surfactant concentration. Figure 1 shows representative results of these experiments. In all the cases studied, the pyrene 1:3 ratio curves present a typical sigmoidal decrease. From the plots in Figure 1, the cmc values were obtained as previously described.

Figure 1. Plots of the pyrene 1:3 ratio versus total concentration of surfactant in different MEGA-10/SDS mixtures.

With the aim of evaluating the behavior of our mixed system, we have used the regular solution theory (RST). This approach considers an interaction parameter ($\beta_{12}$) to characterize the interactions between the two surfactants in the mixed micelle. This parameter is defined by

$$\beta_{12} = \frac{N_A(W_{11} + W_{22} - 2W_{12})}{RT} \tag{3}$$

where $N_A$ is Avogadro’s number and $W_i$ are the pairwise interaction energies between monomeric species in the micelle. Note that $\beta_{12}$ is an indication not only of the degree of interaction between the surfactants but also of 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. According to the RST, the activity coefficients in the mixed micelles are expressed as

$$f_1 = \exp[\beta_{12}(1 - x_1)^2] \tag{4}$$

$$f_2 = \exp[\beta_{12}x_1^2] \tag{5}$$

where $x_1$ is the mole fraction of surfactant 1 in the mixed micelle. The interaction parameter ($\beta_{12}$) can be obtained once the cmc for the mixed system ($C^*$) is determined. From this treatment, the following equation can be derived

$$\frac{x_1^2 \ln(a_1C^*/x_1C_1)}{(1 - x_1)^2 \ln((1 - a_1)C^*/(1 - x_1)C_2)} = 1 \tag{6}$$

which relates the mole fraction of surfactant 1 ($x_1$) to the cmc of the binary system, the mole fraction of surfactant 1 in the solution ($a_1$), and the cmc of pure surfactants ($C_1$ and $C_2$). Equation 6 can be solved iteratively for $x_1$, and then, the interaction parameter ($\beta_{12}$) can be determined from the equation

$$\beta_{12} = \frac{\ln(a_1C^*/x_1C_1)}{(1 - x_1)^2} \tag{7}$$

By applying the above procedure, we have obtained $\beta_{12}$ and the micellar composition ($x_{\text{SDS}}$) for each composition of the system. These parameters are reported in Table 1. From the data in Table 1, it is seen that $\beta_{12}$ experiences small variations with the micellar composition. This is probably a consequence of an amplification of random fluctuations in the experimental data. To obtain a unique $\beta_{12}$ value, we have carried out a nonlinear curve fit of our experimental data, by using the following equation:

$$a_1C^* = C_1x_1\exp[\beta_{12}(1 - x_1)^2] \tag{8}$$

which can be easily derived combining the well-known relation $a_1C^* = C_1x_1\beta_{12}$ with eq 4. Figure 2 shows the results of this fit, from which we have obtained a value of $-2.08 \pm 0.02$ for $\beta_{12}$. Figure 3 shows the cmc values obtained.

Table 1. cmc Experimental Values ($C^*$), Mole Fraction of the Ionic Component in the Mixed Micelle ($x_{\text{SDS}}$)RST, and the Corresponding Interaction Parameter ($\beta_{12}$) According to the RST in the Whole Composition Range*

<table>
<thead>
<tr>
<th>$a_{\text{SDS}}$</th>
<th>$C^*$ (mM)</th>
<th>$(x_{\text{SDS}})$RST</th>
<th>$\beta_{12}$</th>
<th>$(x_{\text{SDS}})$M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.00 ± 0.05</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>2.47 ± 0.13</td>
<td>0.387 ± 0.008</td>
<td>-2.15 ± 0.10</td>
<td>0.377 ± 0.004</td>
</tr>
<tr>
<td>0.2</td>
<td>2.00 ± 0.10</td>
<td>0.483 ± 0.006</td>
<td>-2.05 ± 0.07</td>
<td>0.473 ± 0.001</td>
</tr>
<tr>
<td>0.4</td>
<td>1.56 ± 0.08</td>
<td>0.603 ± 0.004</td>
<td>-2.06 ± 0.06</td>
<td>0.593 ± 0.001</td>
</tr>
<tr>
<td>0.6</td>
<td>1.36 ± 0.07</td>
<td>0.695 ± 0.003</td>
<td>-2.12 ± 0.05</td>
<td>0.687 ± 0.001</td>
</tr>
<tr>
<td>0.8</td>
<td>1.35 ± 0.07</td>
<td>0.810 ± 0.003</td>
<td>-1.92 ± 0.03</td>
<td>0.804 ± 0.000</td>
</tr>
<tr>
<td>1</td>
<td>1.43 ± 0.08</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

* The mole fraction of the ionic species ($x_{\text{SDS}}$M) as obtained by Maeda’s approach is also included for comparison.

experimentally as a function of the mole fraction of the ionic component in the solution (\(R_{SDS}\)) together with those obtained by assuming an ideal behavior (dashed line), as well as the best fit of the experimental data using the RST for a fitted \(\alpha_{12}\) parameter of \(-2.08\) (solid line). As discussed above, a negative value of \(\alpha_{12}\) reflects an attractive interaction between anionic and nonionic surfactants, which can be rationalized considering various effects. First of all, it must be taken into account that the intercalation of the nonionic component shields the repulsive interaction between the negatively charged headgroups of SDS, improving the electrostatic stabilization of the mixed micelle. Moreover, the contribution of an attractive ion–dipole interaction is also possible, which could be significant in our system due to the high charge density of the sulfate group of the ionic component. It is also observed in Figure 3 that the cmc value of the mixture is considerably reduced with the addition of a small amount of the ionic component. This effect could be due to the decrease of the steric barrier between the glycoside headgroups of the nonionic micelle when the ionic component is incorporated to form the mixed micelle.

Figure 4 shows the variation of micellar composition, referred to the ionic component (\(x_{SDS}\)), with the composition of the solution (\(\alpha_{SDS}\)). The data in Figure 4 indicate, on one hand, that there is a good agreement between the experimental data and those predicted by the RST and, on the other hand, that small amounts of SDS form mixed micelles with a considerable content in this component. For example, it is observed that for a content of 10% of the ionic surfactant in the solution, its participation in the mixed micelle reaches almost 40%.

As mentioned above, Maeda has recently reported a phenomenological procedure for analyzing the stability and the synergism of ionic/nonionic mixed micelles in salt solutions. This procedure is based on the following assumptions: (i) the ionic strength is independent of the mole fraction of the ionic species in the micelle (\(x_1\)), (ii) the surface charge density varies linearly with \(x_1\), and (iii) the nonelectric contribution to the excess free energy per monomer (\(g^{E,\text{non}}\)) is given by the RST. In this manner, Maeda defines the total excess free energy (\(g^E\)) as the sum of two contributions, the nonelectric contribution (\(g^{E,\text{non}}\)) and the electric one (\(g^{E,\text{el}}\)). This last contribution is related to the parameter \(\beta^E(x_1)\), depending on the micelle composition, by

\[
\beta^E(x_1) = \frac{g^{E,\text{el}}}{x_1(1 - x_1)}
\]

By means of a cumbersome treatment, which we will not reproduce to save space, Maeda obtains an equation for the excess free energy of the mixed micelle as a function of the micellar composition. This equation, particularized for our system, is

\[
g^E = \beta(x_1)x_1(1 - x_1)
\]

where \(\beta(x_1)\) is approximated to change linearly with the composition by

\[
\beta(x_1) = -\{a_1^* + a_2^*(1 + x_1)\}
\]

where \(a_1^*\) and \(a_2^*\) are two parameters that must be obtained by an iterative procedure described in detail in the original paper. Following this procedure, we have determined the above parameters for our mixed system. The values found were \(a_1^* = 2.63\) and \(a_2^* = -0.35\). Once these parameters are obtained, one can determine the micellar composition (\(x_1\)) from the equation with...
\[
\ln(\alpha_1 C^x/x_1 C_1) + a_2 x_1 = \\
\frac{\ln(C^x(1 - \alpha_1)/C_2(1 - x_1))}{x_1^2} - a_2 (1 - x_1) 
\]

The micellar composition values that we have found are also listed in Table 1. It is observed that these values, although close to those obtained by the RST, are systematically lower. Finally, we have calculated \(g^E\) according to eq 10. Figure 5 shows the \(g^E\) values as compared with the results of the RST, evaluated by the following equation:

\[
g^E = \beta_{12}(1 - x_1)x_1
\]

In Figure 5, it can be seen that the minimum position of \(g^E\) is slightly shifted toward \(x_1 \approx 0.5\), with its value being a little more negative than that estimated from the symmetric RST. These results are in excellent agreement with those analyzed by Maeda\(^4\) in the case of mixtures in 0.1 M NaCl.

According to the RST, it is usually stated that the synergism (or negative \(\beta_{12}\) value) of ionic/nonionic mixed micelles is due to the reduction of the electrostatic repulsions by the insertion of the nonionic headgroups. However, from Maeda’s treatment, it can be deduced that the electrostatic interactions are determined not only by the electrostatic free energy of the ionic micelle but also by the dependence of \(\beta_{12}(x_1)\) on the micelle composition (see eq 9). On the other hand, from the RST, one cannot obtain information on the presence of a short-range attractive interaction between the ionic and the nonionic species in the mixed micelle, since these interactions are hidden by the contribution of the electrostatic ones. Maeda has proposed\(^4\) a parameter, \(B_1\), that does not contain the electrostatic free energy contribution. The 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\(^4\) and can be obtained from the equation

\[
B_1 = \ln\left(\frac{C_1}{C_2}\right) + \beta(x_1=0) + \beta_{\text{non}} = \ln\left(\frac{C_1}{C_2}\right) + \beta(x_1=0) 
\]

\(\beta(x_1=0)\) is given by

\[
\beta(x_1=0) = -(a_1^x + a_2^x)
\]

The value of the parameter \(B_1\) that we have determined is \(-3.52\), suggesting a certain attractive interaction of nonelectrostatic nature for the MEGA-10/SDS system. The origin of these short-range interactions resides in the hydrocarbon tail contribution or the hydrocarbon tail dissimilarity of the ionic and nonionic components.\(^4\)

**Micelle Aggregation Numbers.** To determine the mean aggregation number of micelles, we have used the steady-state fluorescence quenching method. This approach, first proposed by Turro and Yekta\(^1\) on the basis of the previous analysis carried out by Tachiya\(^2\) on the kinetics of the fluorescence quenching in micellar solutions, is based on the quenching of a luminescence probe by a known concentration of quencher species and has been successively applied to the determination of mean aggregation numbers of numerous micellar systems.\(^,4^3\)

In our quenching experiments, we have used pyrene as a luminescence probe and CPyC as a quencher; this donor–quencher pair has been found to be appropriate for determining the aggregation number of ionic and nonionic micelles, since it fulfills the suitable requirements.\(^3,4^3\) Namely, (i) the probe and quencher must be solubilized in the micelle and be immobile, remaining within the micelle during the lifetime of the probe; (ii) the quenching rate must be faster than the emission lifetime of the probe, so that fluorescence is observed only from micelles with probe but without quencher; and (iii) the probe and quencher must be distributed among micelles following a Poisson distribution. If the above conditions occur, the ratio between the fluorescence intensities in the presence \(I\) and in the absence \(I_0\) of the quencher is related to the quencher \([Q]\) and micelle \([M]\) concentrations by

\[
\frac{I}{I_0} = \exp\left(- \frac{[Q]}{[M]}\right)
\]

where the micelle concentration \([M]\) is given by

\[
[M] = \frac{[S] - \text{cmc}}{N_{agg}}
\]

with \([S]\) being the total surfactant concentration and \(N_{agg}\) the mean micelle aggregation number. Finally, from eqs 16 and 17, one obtains

\[
\ln\left(\frac{I}{I_0}\right) = \frac{N_{agg}}{[S] - \text{cmc}}[Q]
\]

Figure 6 shows representative quenching plots in micellar solutions containing a fixed total surfactant concentration (20 mM) but different ratios of both surfactants. The solid lines in Figure 6 represent the best fit of experimental data to eq 18. In all the cases, we found an acceptable linear behavior \((r > 0.99)\). From both the slopes of quenching plots and cmc, as obtained by the pyrene 1:3 ratio method, we have obtained the aggregation numbers shown in Figure 7, where we have also included the partial contribution of each component determined taking into account the micellar composition as obtained

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\(^{(40)}\) Maeda, H. *J. Colloid Interface Sci.* **1995**, *172*, 98.


The data in Figure 7 indicate that the aggregation number of micelles initially increases, remaining roughly constant and then decreasing slightly for mixtures with a high content of the ionic component. A similar behavior has been previously observed for mixed systems constituted by SDS and nonionic surfactants in aqueous solutions of 0.1 M NaCl.\textsuperscript{11,44} We can rationalize the trend observed in Figure 7 as follows: At low SDS content, the electrostatic repulsions between the sulfate groups of SDS are weak. When the participation of SDS increases, as the SDS headgroup is smaller than that of MEGA-10, the steric interactions between the larger MEGA-10 heads decrease. This effect results in a smaller steric free energy and, therefore, in a reduction of the area required per surfactant head, allowing the mixed micelle to adopt a structure with lower curvature and leading to the growth of the mixed micelle. However, when the participation of the ionic component increases, the repulsion electrostatics of the ionic headgroups produce an increase in the electrostatic free energy that prevails over the decrease in the steric free energy. This results in an increase of the area per headgroup, which forces the micelle to adopt a higher curvature and, consequently, to form micelles with a lower aggregation number. Another aspect observed in Figure 7 is a clear positive deviation of the aggregation number with respect to the ideal behavior, which seems to be controlled by the high participation of the ionic component in the mixed micelle.

**Microenvironmental Properties.** The interest in the study of the microenvironmental properties of the micellar systems is twofold; on one hand, these properties can be decisive, for example, when the micellar system is used as a reaction medium, and on the other hand, the change in these properties can provide information on the important structural modifications in the system.

It is well-known that the pyrene 1:3 ratio index reflects the polarity of the microenvironment around the probe.\textsuperscript{34,35} Pyrene is solubilized in the palisade layer of micelles, near the polar headgroups, where it senses a relative highly polar environment; therefore, this parameter has been widely used to test changes of local polarity or micropolarity induced by different penetration grades of water molecules in this region of the micelle. We have monitored the pyrene 1:3 ratio index in micellar solutions of concentrations above the cmc (20 mM) as a function of the solution composition. The results of these experiments are shown in Figure 8. It can be seen that the pyrene 1:3 ratio index undergoes a small but systematic reduction as the content of the ionic component increases. However, it must be noted that the behavior observed in Figure 8 is not necessarily related to the dehydration of the micelles, as it could also indicate that pyrene is located in different environments as the micellar composition changes.

It has been previously established\textsuperscript{15} that the decrease in the hydration, as the participation of the ionic component increases, is often accompanied by a reduction of order in the palisade layer of the mixed micelles. Therefore, we have decided to examine the micellar microviscosity
in the MEGA-10/SDS system. First of all, we have studied the behavior of Auramine O (AuO) as a function of the ionic component content. As mentioned above, AuO is a cationic probe whose more peculiar characteristic is that its fluorescence quantum yield increases with the medium viscosity with independence of the solvent polarity. This probe is expected to interact superficially with anionic micelles. In fact, AuO has been used to examine changes in the microviscosity of SDS micelles induced by the addition of urea and NaCl.\(^{(45,46)}\) Figure 9 shows the fluorescence emission spectra of AuO in micellar solutions whose photophysical behavior in micellar media has been characterized. With regards to the stability of the mixed system, as reported by the cmc values, a clear negative deviation with respect to the ideal behavior has been found.\(^{(15)}\) Moreover, the cmc values for the mixed system are higher than those in single SDS micelles, indicating that the structure of the ionic micelles is less tight. This is probably due to two contributions: (i) the electrostatic repulsions between the SDS headgroups and (ii) a smaller hydration of the hydrophilic mantle in the ionic micelles. Second, the data in Figure 10 show that the trend observed for RB is in excellent agreement with that for AuO (Figure 9). That is, the anisotropy of RB initially increases for \(\alpha_{SDS} = 0.1\) and then decreases as the SDS content increases. Third, the behavior of DBP also reflects a reduction of the anisotropy with \(\alpha_{SDS}\), suggesting the formation of micelles with a looser structure as the content of the ionic component increases. It must be noted that the observations obtained from these microenvironmental studies are in good agreement with previous findings\(^{(15)}\) for different mixed systems constituted by ionic and nonionic surfactants and suggest the formation of micelles with a more dehydrated structure as the participation of the ionic component increases. This fact is probably due to the occurrence of ion–dipole interactions between the headgroups of SDS and MEGA-10, producing the release of water molecules from the palisade layer of mixed micelles.

**Conclusions**

The micellar properties of the mixed system constituted by MEGA-10 and SDS in aqueous solutions of 0.1 M NaCl have been characterized. With regards to the stability of the mixed system, as reported by the cmc values, a clear negative deviation with respect to the ideal behavior has been observed. The mixed micellization process is acceptably described by the RST. However, Maeda’s treatment provides a wider perspective about the interactions implied in the system in the sense that, besides the electrostatic interactions, short-range attractive interactions must be considered. In addition, the excess free energy per monomer \((\gamma)\) determined by Maeda’s approach was not found to be symmetric with respect to the micellar composition, and the minimum was deeper than that estimated from the symmetric RST. The observed tendency in the micellar aggregation number with the solution

\[
\frac{r_0}{r} = 1 + \frac{kT \tau}{V \eta}
\]

where \(r_0\) is the limiting value of emission anisotropy obtained 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, \(V\) is the effective molecular volume of the probe, and \(\eta\) is the viscosity around the probe. From Perrin’s equation, it is clear that a larger anisotropy corresponds to a more rigid environment at a fixed temperature. Figure 10 shows the results of the fluorescence polarization studies. From this figure, some interesting conclusions can be drawn. First, it can be seen that the anisotropy values of both probes in pure nonionic micelles are higher than those in single SDS micelles, indicating that the structure of the ionic micelles is less tight. This is probably due to two contributions: (i) the electrostatic repulsions between the SDS headgroups and (ii) a smaller hydration of the hydrophilic mantle in the ionic micelles. Second, the data in Figure 10 show that the trend observed for RB is in excellent agreement with that for AuO (Figure 9). That is, the anisotropy of RB initially increases for \(\alpha_{SDS} = 0.1\) and then decreases as the SDS content increases. Third, the behavior of DBP also reflects a reduction of the anisotropy with \(\alpha_{SDS}\), suggesting the formation of micelles with a looser structure as the content of the ionic component increases. It must be noted that the observations obtained from these microenvironmental studies are in good agreement with previous findings\(^{(15)}\) for different mixed systems constituted by ionic and nonionic surfactants and suggest the formation of micelles with a more dehydrated structure as the participation of the ionic component increases. This fact is probably due to the occurrence of ion–dipole interactions between the headgroups of SDS and MEGA-10, producing the release of water molecules from the palisade layer of mixed micelles.

**Figure 9.** Fluorescence emission spectra of AuO in MEGA-10/SDS micellar solutions of different compositions. Inset: effect of the molar fraction of the ionic component in the solution (\(\alpha_{SDS}\)) on the relative fluorescence intensity of AuO. Absolute temperature, \(k\) is the Boltzmann constant, \(V\) is the effective molecular volume of the probe, and \(\eta\) is the viscosity around the probe. From Perrin’s equation, it is clear that a larger anisotropy corresponds to a more rigid environment at a fixed temperature. Figure 10 shows the results of the fluorescence polarization studies. From this figure, some interesting conclusions can be drawn. First, it can be seen that the anisotropy values of both probes in pure nonionic micelles are higher than those in single SDS micelles, indicating that the structure of the ionic micelles is less tight. This is probably due to two contributions: (i) the electrostatic repulsions between the SDS headgroups and (ii) a smaller hydration of the hydrophilic mantle in the ionic micelles. Second, the data in Figure 10 show that the trend observed for RB is in excellent agreement with that for AuO (Figure 9). That is, the anisotropy of RB initially increases for \(\alpha_{SDS} = 0.1\) and then decreases as the SDS content increases. Third, the behavior of DBP also reflects a reduction of the anisotropy with \(\alpha_{SDS}\), suggesting the formation of micelles with a looser structure as the content of the ionic component increases. It must be noted that the observations obtained from these microenvironmental studies are in good agreement with previous findings\(^{(15)}\) for different mixed systems constituted by ionic and nonionic surfactants and suggest the formation of micelles with a more dehydrated structure as the participation of the ionic component increases. This fact is probably due to the occurrence of ion–dipole interactions between the headgroups of SDS and MEGA-10, producing the release of water molecules from the palisade layer of mixed micelles.
composition was analyzed on the basis of the effect produced by the charged headgroup of SDS when this increases its participation in the mixed micelle. It was established that the micellar size is the result of two opposite contributions: the repulsive interactions between the headgroup of the ionic surfactant, which prevent the micellar increase, and the steric interactions favored by the size of the headgroup of SDS in comparison with that of MEGA-10. Finally, the main conclusions that we can derive from the microenvironmental studies are consistent with a decrease of hydration of the mixed micelles and with an increase of the repulsive interactions between the headgroups of SDS as they replace some MEGA-10 monomers in the mixed micelle, resulting in the formation of less permeated and ordered micelles.

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