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ORIGINAL CONTRIBUTION

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A photophysical study of the urea effect on micellar properties of sodium dodecylsulfate aqueous solutions

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Abstract With the aim of studying the effect of urea on micellar properties of aqueous solutions of sodium dodecylsulfate (SDS), steady-state fluorescence experiments were carried out with different luminescence probes incorporated into the micellar phase. The increase of critical micelle concentration (CMC) of the surfactant with urea addition was followed by changes in the relative intensities of the vibrational fine structure of the pyrene fluorescence spectra. Micellar aggregation numbers were obtained from the analysis of fluorescence quenching data using ruthenium tris(bipyridyl) chloride and 9-mehylanthracene as a donor-quencher pair. It was found that the decrease in the aggregation number is mainly controlled by rise in the surface area per headgroup of the surfactant. From fluorescence measurements, using several ionic probes (8-anilino-1-naphthalen-sulfonic acid, rhodamine B, and auramine O), it was found that urea decreases the polarity and increases the microviscosity of the micellar interface. These effects, which are dependent on the concentration of urea, can be explained according to a direct interaction of urea at the micellar surface.

Key words SDS – urea – fluorescence techniques – micellar properties

Introduction

The aggregational and interfacial properties of aqueous micellar solutions can be modified by addition of electrolyte or nonelectrolyte substances [1, 2]. The presence of cosolutes and other additives can affect the micellization process either through specific interactions with the surfactant molecules or by changing the solvent nature [2]. Urea and its derivatives, which are well known denaturants of proteins, are very efficient as modifiers of the aqueous solution properties. Since the micellar formation arises as a result of a delicate balance between hydrophobic and hydrophilic interactions, it is not surprising that urea has a sharp influence on the properties of micellar solutions. In recent years, a number of studies concerning the effect of urea and its derivatives on the aggregation behavior of micellar aqueous solutions has been published [3–21]. From these investigations, it has been found that urea increases the CMC of ionic [7, 12, 14, 15, 19] and nonionic surfactants [12, 13, 21], as well as the cloud point of nonionic surfactants [9, 13, 21], whereas it decreases the micellar size of ionic [4] and nonionic micelles [13], and the cloud point of zwitterionic surfactants [8]. In spite of the work carried out, the role of urea it is still not entirely clear. To explain the urea action two different mechanisms have been proposed: i) an indirect mechanism, in which urea acts as a water "structure breaker" facilitating the solvation of the hydrocarbon chain of the amphiphile, and ii) a direct mechanism, whereby urea participates in the

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solvation of hydrophobic chain and the polar headgroups of the amphiphile, by replacing some water molecules in the solvation layer. The indirect mechanism is the most widely accepted, and many experimental studies seem to support this hypothesis [22–27]. However, more recent investigations [28–30] indicate that urea has a negligible effect on water structure, suggesting that the urea action is based on the direct mechanism.

Photophysical techniques based on the behavior of fluorescence probes solubilized in micelles have been widely used for obtaining information about both structural and dynamic micellar properties [31–33]. The main advantage in the use of luminescence probes is that the nature of the probe environment is reflected in their emission properties, thus providing information at a molecular level. However, a correct interpretation of the results requires to know the solubilization site of the probe in the micelle.

This paper describes the effects of urea addition to SDS micellar solutions studied by using fluorescence techniques. A few studies on the effect of certain additives, including urea, on SDS micelles by using fluorescence techniques have been previously published [4–6]. In these works only some partial aspects about the urea action were investigated, but in all cases the results were interpreted at the light of the indirect mechanism. Recently, we obtained reliable information concerning the effect of urea on micellar properties of aqueous micellar solutions of Triton X-100 [21], and the results obtained were explained according to a direct mechanism of urea action.

Experimental

Materials

Fluorescence probes: pyrene, 8-anilino-1-naphthalensulfonic acid (ANS), rhodamine B (RB) and auramine O (AuO) were obtained from Sigma Chemical Co., ruthenium tris(bipyridyl) chloride ($Ru(bpy)_3^{2+}$) and 9-methylanthracene (9-MA) were acquired from Aldrich. All fluorescence probes were used as received. The surfactant SDS and urea were obtained from Sigma and used without further purification. Other chemicals used were analytical grade, and water was doubly distilled (Millipore). Stock solutions (1 mM) of hydrophobic probes were prepared in absolute ethanol, whereas hydrophilic probes stock solutions (1 mM) were prepared in water.

Methods

Fluorescence measurements were made with a Perkin-Elmer LS50 luminescence spectrometer equipped with a thermostated cell housing, and fitted with a xenon lamp (9.9 W) pulsed at line frequency, 1 × 1 cm quartz cells, and R928 Hamamatsu photomultiplier. Polarization emissions were collected with the same apparatus, which uses the L-format and an automatic interchangeable wheel with film polarizers. The polarization values were averaged over an integration time of 20 s. All fluorescence measurements were made at 25.0 ± 0.1 °C.

In order to determine the CMC of SDS, fluorescence emission spectra of pyrene (0.5 μM) in SDS micellar solutions were recorded by using slit widths for both monochromators of 2.5 nm, a scan speed of 240 nm/min, and an excitation wavelength of 338 nm. In these spectra fluorescence intensities were measured at 373 nm (peak 1) and 384 nm (peak 3). Aggregation numbers of micelles were obtained from luminescence quenching of $Ru(bpy)_3^{2+}$ using 9-MA as a quencher. A stock solution of $Ru(bpy)_3^{2+}$ (0.03 mM) in SDS (0.5 M) was prepared as follows: a suitable volume of $Ru(bpy)_3^{2+}$ stock solution was placed in a volumetric flask, the surfactant was then added, and the solution was sonicated for 1 h. Working solutions of lower concentration were prepared by adding appropriate volumes of quencher solutions. Fluorescence intensities were obtained by using an excitation wavelength of 460 nm and an emission wavelength of 612 nm. Micellar solutions of ANS (5 μM), RB (2 μM) and AuO (10 μM) were prepared by taking an aliquot of stock solution and adding the surfactant solution; the resultant solutions were sonicated for few minutes. Fluorescence measurements were made using excitation and emission wavelengths, respectively, of 389 nm and 494 nm for ANS, 557 nm and 576 nm for RB, and 436 nm and 501 nm for AuO.

Results and discussions

CMC determination

The CMC of SDS at different urea concentrations was determined by using the pyrene 1:3 ratio method [32, 34, 35]. This procedure is based on the sensitivity to the microenvironment nature of the pyrene vibrational structure. Below the CMC, when there still are no micelles present, the pyrene fluorescence spectrum corresponds to a polar environment. But when the micelles are formed, pyrene is solubilized inside the micelle, and the polarity of its microenvironment decreases sharply, as also does the pyrene 1:3 ratio value. We have monitored the pyrene 1:3 ratio as a function of the SDS concentration in water and in the presence of different urea concentrations. Figure 1 presents the results of these experiments. It must be pointed out that the characteristic vibrational fine structure of pyrene did not modify in the presence of urea, and

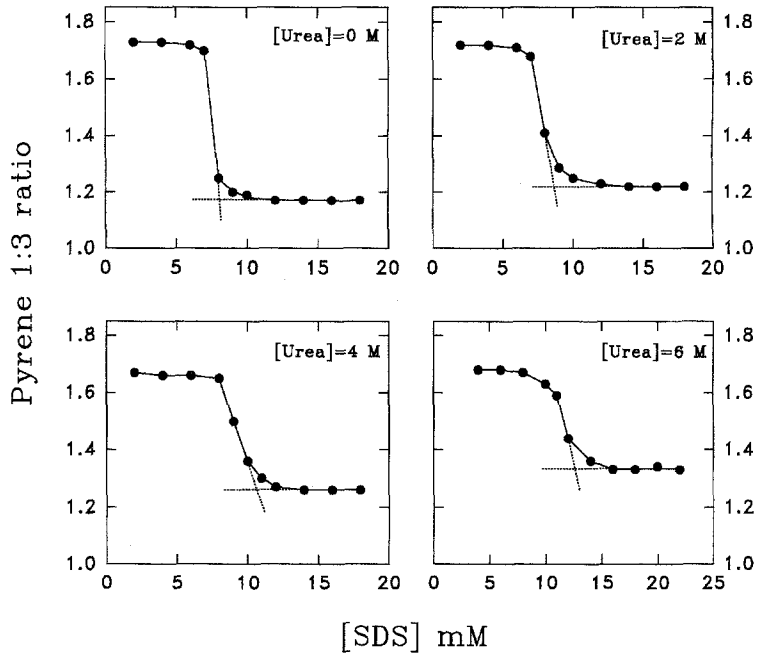

Fig. 1 Plots of pyrene 1:3 ratio versus concentration of SDS in water and in the presence of different urea concentrations

only changes in the intensity of vibronic bands (1:3) were observed (Fig. 1). This means that no interaction between probe and urea occurs, and that changes in the pyrene 1:3 ratio are due to a decrease in the polarity around the probe induced by micellization. The CMC values, which were obtained from the abrupt turning points in the plots of Fig. 1, are listed in Table 1. These CMC values are in good agreement with those recently obtained by using electron spin resonance spectroscopy [14], but are lower than those obtained by using conductivity measurements [7].

The mechanism of micelle formation in water is controlled by the cohesive interactions between the hydrophobic tails of the monomers. Therefore, the thermodynamics of micelle formation can be considered as the formation of a different micellar phase at the CMC, which is in equilibrium with the monomeric surfactant; the concentration of the monomer remains constant after the micellization. The standard Gibbs free energy of micellization (ΔG_m^0) in the case of ionic surfactants (1:1) can be calculated from [36]

$$\Delta G_m^0 = 2RT \ln \mathrm{CMC} . \quad (1)$$

The effect of a cosolute or additive on micellization process, given by ΔG_M^0, can be calculated by [36]

$$\Delta G_M^0 = \Delta G_m^0(\text{additive}) - \Delta G_m^0(\text{water}) , \quad (2)$$

which can be finally expressed as

$$\Delta G_M^0 = 2RT \ln \frac{(\mathrm{CMC})_A}{(\mathrm{CMC})_W} , \quad (3)$$

Table 1 Effect of urea on micellization parameters of SDS at 25 °C

[Urea] M	CMC (mM)	ΔG_M^0 (kJ/mol)
0	8.2 (8.2)[a]	0
2	8.7 (9.2)[a]	0.15
4	10.5	0.61
6	12.7 (12.0)[a]	1.08

[a] In parentheses, values from ref. [14]

where $(\mathrm{CMC})_A$ is the CMC value in the presence of the additive, and $(\mathrm{CMC})_W$ is the CMC in water. The ΔG_M^0 values calculated from Eq. (3) are also presented in Table 1. It can be seen from data in Table 1 that the CMC and ΔG_M^0 increase non-linearly with increasing urea concentration. The increase in ΔG_M^0 indicates a reduction of the hydrophobic interaction, resulting in a significant increase of the solubility of the hydrocarbon tails in the presence of urea, and definitively in an increase of CMC. According to the direct mechanism, the fact that urea raises the solubility of hydrophobic solutes is ascribed to an improved solvation caused by the displacement of a number of water molecules by the larger urea molecule in the solvation layer [29, 30]. In addition, the influence of urea on the hydrogen bonding structure in the apolar region must help the solvation of hydrophobic solutes. Probably, the observed increase of CMC is also favored by the increase of solvation of headgroups induced by the action of urea.

Micellar aggregation numbers. Micellar size

In order to determine the mean aggregation number of micelles, the steady-state fluorescence quenching method has been used. This method, first proposed by Turro and Yekta [37], is based on the quenching of a luminescence probe by a known amount of quencher species, and has been successively applied to the determination of mean aggregation numbers of SDS micelles in water and in the presence of additives [4, 37, 38]. In our quenching studies, we have used $Ru(bpy)_3^{2+}$ as a luminescence probe and 9-MA as a quencher; this donor-quencher pair has been found to be a suitable for determining the aggregation number of ionic surfactants in micellar solutions.

When the steady-state fluorescence quenching method is applicable, the ratio of luminescence intensities (I/I_0) with and without the quencher Q is related to the aggregate concentration M as shown in [37]

$$\frac{I}{I_0} = \exp\left(-\frac{[Q]}{[M]}\right). \tag{4}$$

The micelle concentration is given by

$$[M] = \frac{S - \mathrm{CMC}}{N_{agg}}, \tag{5}$$

where S is the total surfactant concentration, and N_{agg} is the micelle aggregation number. Combining Eqs. (4) and (5) yields

$$\ln\frac{I_0}{I} = \frac{N_{agg}}{S - \mathrm{CMC}}[Q]. \tag{6}$$

Figure 2 shows the results of our quenching studies (data for urea 4 M no presented). In all cases we found a good linearity, as the model predicted. From the slopes of these plots, and assuming the CMC values in Table 1, we obtained the aggregation numbers listed in Table 2. Almgren and Swarup [4] used this same method to study the effect of urea, among other additives, on the size of SDS micelles, but they employed a smaller range of urea concentration, and roughly estimated the CMC values required for determining the micelle concentration M.

It has been demonstrated that the surface area per headgroup (a_0), or its inverse, the surface charge density, is the most important controlling factor for micelle size [39]. In accord with Tanford [40], the hydrophobic chain volume of the micelle (v) and the critical chain length (l_c), were obtained from

$$v = 27.4 + 26.9\, n(\text{Å}^3) \tag{7}$$

$$l_c = 1.5 + 1.265\, n(\text{Å}), \tag{8}$$

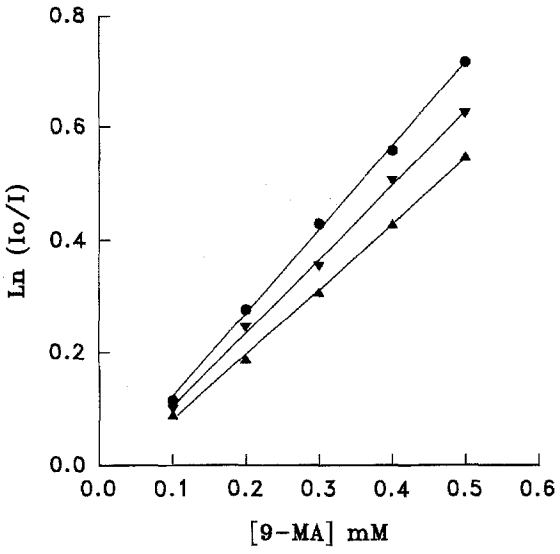

Fig. 2 Quenching of $Ru(bpy)_3^{2+}$ fluorescence by 9-MA in 0.05 M SDS aqueous solutions at different urea concentrations: ● 0 M, ▼ 2 M, and ▲ 6 M

Table 2 Effect of urea on aggregation number and size of SDS micelles at 25 °C

[Urea] M	N_{agg}	$R^{(a)}$ (Å)	$a_0^{(b)}$ (Å^2)	$v/a_0 l_c^{(c)}$
0	62	17.3	60.7	0.34
2	54	16.5	63.4	0.33
4	49	16.0	65.6	0.32
6	43	15.3	68.4	0.31

(a) Micellar radius calculated assuming spherical micelles
(b) Surface area per headgroups
(c) Critical packing parameter

where n is the number of carbon atoms of the chain. The micellar radius (R) and the surface area per headgroup were then obtained assuming a spherical shape. In Table 2 are presented the obtained values together with the critical packing parameter ($v/a_0 l_c$), which is a parameter controlling the micelle shape [39]. From data in Table 2 some interesting aspects can be derived. On the one hand, the reduction in the critical packing parameter indicates that the urea addition favors the formation of smaller spherical micelles. On the other hand, the surface area per headgroup increases linearly with urea concentration, as shown in Fig. 3. Similar results were obtained by Briganti et al. [13] in the study of the effect of urea on micellar properties of the nonionic surfactant n-dodecyl hexaethylene oxide ($C_{12}E_6$). These authors interpreted this fact according to a direct mechanism of urea action. In effect, since a urea molecule is approximately 2.5 times larger than a water molecule, if urea replaces some water molecules in the solvation layer of the micelle headgroups, an

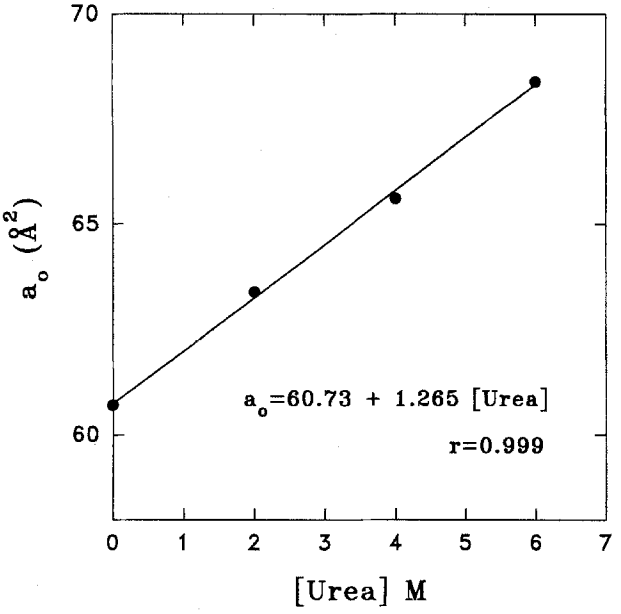

Fig. 3 Surface area per headgroups (a_0) of SDS micelles versus urea concentration

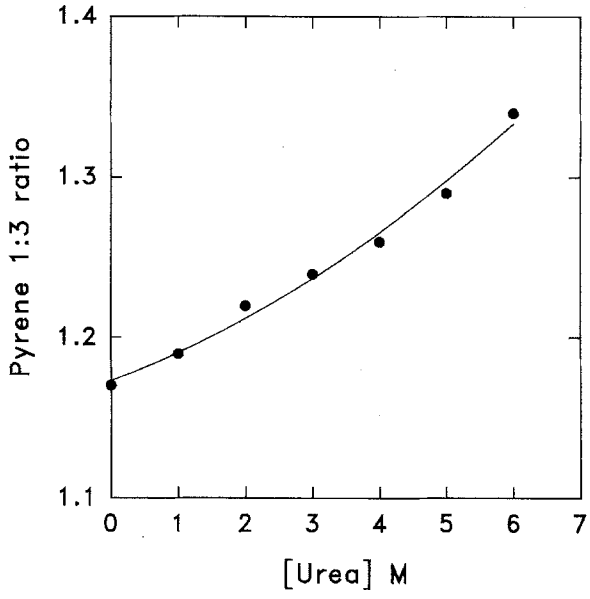

Fig. 4 Variation of pyrene 1:3 ratio against urea concentration in micellar solutions of SDS (0.02 M)

increase of urea concentration will produce an increase of the surface area per headgroup.

Polarity and microviscosity studies

As stated above, the pyrene 1:3 ratio reflects the polarity of the microenvironment around the probe, therefore this parameter could be used to detect changes of polarity in micelles upon modification of the micellar solution. In the course of the experiments leading to the CMC determination, we observed that the pyrene 1:3 ratio value in micellar region increased with increasing urea concentration, so that we decided to study this aspect. The relationship between pyrene 1:3 ratio and the urea concentration is shown in Fig. 4. The observed behavior in Fig. 4 apparently suggests that the polarity of the pyrene microenvironment increased with urea addition. However, we will see that two possible explanations can be given for this fact. It is known that pyrene is solubilized in the palisade layer of micelles, near the polar headgroups, where it senses a relative highly polar environment [41]. This is probably due to the presence of water molecules intercalated between the headgroups in the palisade layer. When urea is added to the solution, the surface area per headgroups increases, inducing the incorporation of a greater number of water molecules to the palisade layer. As a consequence, the polarity sensed by the probe would increase. On the other hand, it is also possible that the increase of surface area per headgroup forces the probe to be located outward in the micelle, which would contribute to a more polar environment. Nevertheless, recent results obtained by using electron spin echo modulation [11] and electron spin resonance spectroscopy [10] indicate that urea does interact with the micellar surface and it does not increase the water penetration at the micelle surface. Consequently, it seems that the increase of pyrene 1:3 ratio induced by urea addition is due to the displacement of the probe towards outer region in the micelle. In summary, the behavior of pyrene 1:3 ratio shown in Fig. 4 does not reflect changes in micellar polarity, but rather different locations of the probe in the micelle.

In order to clarify the influence of urea on micellar polarity, we decided to study the photophysical behavior of two ionic probes, ANS and RB, which are expected to interact superficially with anionic micelles such as SDS. The fluorescence properties of ANS and RB have been widely exploited to gain information about the micellar microenvironment. The spectral behavior of ANS is particularly interesting because their emission properties are very sensitive not only to the polarity of the medium, but also to the viscosity in the environment of the probe [42, 43]. It is well known that ANS, which is almost non-fluorescent in aqueous solutions, exhibits a larger fluorescence enhancement on binding to the micellar surface. This fluorescence enhancement has been explained in terms of the polarity-dependent twisted intramolecular charge transfer (TICT) concept [44–46]. When ANS molecules are transferred from the highly polar aqueous medium to the relatively non-polar micellar surface, the

reduction in polarity and the increase in microviscosity leads to a decrease in the rate of non-radiative TICT process. Inhibition of non-radiative TICT pathways results in an increase of the emission quantum yield and lifetime. In contrast to ANS, the lifetime of RB does not change in a dramatic way with the polarity of the system. Figure 5 shows the relative fluorescence intensity and the degree of polarization for ANS and RB as a function of urea concentration. In both cases it is found that both the relative intensity and the degree of polarization increase and approach a plateau value with increasing urea concentration. In addition, we found that both the emission maximum wavelengths and the spectral shapes of ANS and RB remained invariable with addition of urea, suggesting that no interactions between probes and urea took place.

From Perrin's equation, the degree of fluorescence polarization (P) is related to the microviscosity in the vicinity of the probes and fluorescence lifetime by

$$\frac{1/P - 1/3}{1/P_0 - 1/3} = 1 + \frac{kT\tau}{\eta V}, \qquad (9)$$

where P_0 is the fluorescence polarization in a solvent of extremely high viscosity, k is Boltzmann's constant, T is absolute temperature, and V and τ are effective volume and fluorescence lifetime of the probe, respectively. Hence, the polarization values are proportional to the ratio η/τ. Although ANS and RB present a different behavior against changes in polarity, in both cases in increase in the lifetime, greater in ANS, with decreasing polarity is expected. Moreover, depolarization of light emitted from probes associated with micelles can originate from two different rotational processes: i) movement of the probe in the micelle, and ii) rotation of the micelle itself. As the size of the micelle becomes continuously smaller with urea addition, the second rotational process will increase. Therefore, the increase of polarization shown in Fig. 5 is the result of two opposite effects: a) an increase of the polarization due to a greater rigidity of the microenvironment around the probe, and b) a depolarization caused by the rotation of the micelle as a result of the reduction in the micelle size with increasing urea concentration. In consequence, it seems reasonable to explain the data in Fig. 5 in terms of a reduction in the polarity and an increase in the microviscosity of the micellar interface with urea addition. Similar conclusions were obtained by Baglioni et al. [10] from electron spin resonance spectroscopy studies.

With the aim of confirming the effect of urea on micellar viscosity, we have also studied the influence of urea addition on fluorescence of AuO solubilized in SDS micelles. AuO is a cationic probe whose fluorescence

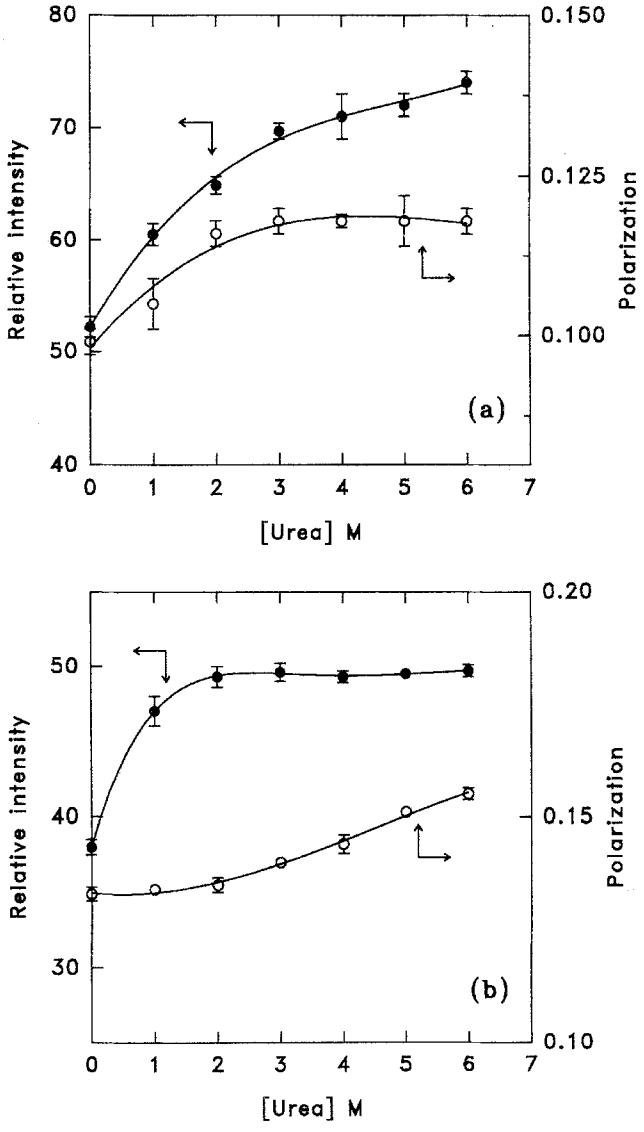

Fig. 5 Relative fluorescence intensity and degree of polarization of ANS (a) and RB (b) in SDS (0.025 M) versus urea concentration (triplicate experiments)

quantum yield increases with the viscosity of the medium regardless of the solvent polarity [47]. This probe, like ANS and RB, is expected to interact superficially with SDS micelles. Therefore, AuO will provide information about the microviscosity in the micellar interface. In fact, AuO has been used to test changes in microviscosity of SDS micelles induced by addition of urea and NaCl [6], but the results of this investigation were explained in terms of an indirect modification of the microenvironment. Oster and Nishijima [47] studied the fluorescence of AuO in glycerol at various temperatures and in dextrose-glycerol-water mixtures at room temperature. These authors found that the fluorescence intensity of AuO is related to the viscosity

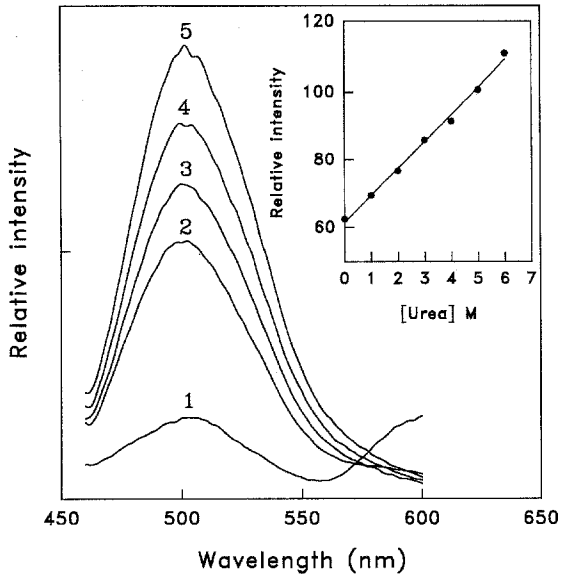

Fig. 6 Fluorescence emission spectra of AuO (10 μM) in water (1) and in SDS micellar solutions (0.05 M) at different urea concentrations: 2 (0 M), 3 (2 M), 4 (4 M), and 5 (6 M). Inset: effect of the concentration of urea on the relative fluorescence intensity of AuO in SDS micellar solutions ($\lambda_{exc} = 436$ nm, $\lambda_{em} = 501$ nm)

of the medium by

$$I = \frac{\eta/T}{\alpha + \beta(\eta/T)}, \tag{10}$$

where α and β are constants, and η and T are the viscosity and the absolute temperature of the medium, respectively. If the temperature remains constant and assuming that $\alpha \gg \beta$, Eq. (10) can be expressed as

$$I = K\eta, \tag{11}$$

where K is a constant.

Figure 6 shows the fluorescence emission spectra of AuO in water and in SDS micellar solutions at different urea concentrations. The maintenance of the spectral characteristics of AuO reveals that no interaction occurs between this and urea. In the same figure the dependence of the relative fluorescence intensity of AuO on urea concentration is plotted. As can be seen in Fig. 6, the fluorescence intensity of AuO rises considerably when SDS micelles are present, indicating a remarkable interaction between probe and micelle. Moreover, a very significant linear dependence between fluorescence intensity and urea concentration is observed. This fact clearly suggests that the micellar surface structure is strongly affected by the urea addition, increasing the local viscosity of the micellar interface. These results confirm the conclusions obtained from ANS and RB.

As commented above, results previously reported [4–6] about the urea effect on micellar properties by using fluorescence techniques were analyzed under the supposition that urea cannot be solubilized in the micelle. In order to explain the increase in microviscosity, several arguments have been suggested. For instance, Grieser et al. [5] proposed that the increase in micellar microviscosity is mainly due to an increase of hydration of headgroups, but it seems clear that this effect would lead to an enhancement in the polarity of the micellar interface.

Conclusions

By using steady-state fluorescence measurements of luminescence probes solubilized in the micellar phase, we have obtained information about structural changes induced by urea in SDS micelles. We have shown that the urea addition produces: 1) an increase on CMC, which is mainly due to an increase of solubility of hydrocarbon tails of the surfactant, 2) a decrease in the micellar aggregation number, which is essentially controlled by the increase of the surface area per headgroups, and 3) a decrease of the polarity and an increase the microviscosity of the micellar interface. These results are in agreement with recent investigations carried out using different experimental techniques [10–14], and can be explained according to a direct mechanism of urea action, whereby urea replaces some water molecules in the solvation layer of the amphiphile.

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