Micelle formation and microenvironmental properties of sodium dodecyl sulfate in aqueous urea solutions

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Abstract

The critical micelle concentrations (CMC) of sodium dodecyl sulfate (SDS) and the degrees of counterion dissociation in a wide range of urea concentrations have been determined by the electrical conductivity method. While the CMC values are in good agreement with literature values, the values of the degree of counterion dissociation at high urea concentration are greater than those recently published. The micellization process of SDS in different aqueous urea solutions has also been followed through the fluorescence behaviour of pyrene-3-carboxaldehyde (PCA) solubilized in the micellar surface. From this study an attempt was made in order to extract quantitative conclusions about changes in the micropolarity in the micellar surface induced by the presence of urea. Although no definitive conclusions could be derived due to the desolvation of the probe caused by the urea action, the results obtained were interpreted as evidence of a direct interaction of urea with the micellar surface. Changes in the structure of the hydrophobic region of SDS micelles upon addition of urea were studied by using polarized fluorescence measurements of diphenylbutadiene (DPB) solubilized in the micellar phase. The effect of urea on the hydrophobic region of SDS micelles was clearly reflected in the DPB steady-state fluorescence anisotropy measurements, which indicated a more rigid microenvironment around the probe as urea concentration increased. The results obtained in this study support a direct mechanism of urea action, whereby urea participates in the solvation of the hydrophobic chains and the polar headgroups of the amphiphile. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: SDS; Urea; Micellization; Microenvironmental properties

1. Introduction

Micelles are well known for presenting unique structural aspects consisting of a nonpolar inner core and a polar outer surface. This structure allows micellar aggregates to enhance the solubility of hydrophobic materials and to modify environmental features such as viscosity and polarity. However, both dynamic and structural properties of micellar solutions can be altered by the addition of a third component in the solution. This last substance can act through two different mechanisms: by interactions with the surfactant molecules or by changing the solvent nature [1].

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Urea is often used as a denaturing agent for proteins, polypeptides and other biopolymers [2]. Nevertheless, because this denaturing action involves a number of complex factors, there are currently certain controversies for elucidating the mechanism by which this process takes place. Since the denaturation of proteins can be considered to be equivalent to the demicellization of micelles in aqueous urea solutions, in the last years a number of researchers have performed considerable efforts in order to rationalize the effect of urea on micelles [3–28]. These investigations have shown that urea not only increases the CMC of ionic and non-ionic micelles but also increases the extent of ion dissociation from ionic ones, and decreases the micellar size of ionic and non-ionic surfactants. In addition, there are evidences, at a qualitative level, that urea increases the microviscosity and lightly reduces the micropolarity at the micellar interface of ionic micelles. Two different ways of explaining the urea action on aqueous solutions have been proposed: (i) an indirect mechanism, in which urea acts as a ‘water structure breaker’ promoting the solvation of hydrophobic solutes; and (ii) a direct mechanism, whereby urea participates in the solvation of hydrophobic solutes, by replacing some water molecules in the solvation layer of the solute. Traditionally, the indirect mechanism has been the most widely accepted, and some experimental results seem to support this hypothesis [29–32]. However, the results obtained in more recent computer simulations [33–36] and experimental studies [37,38] are consistent with a direct mechanism of urea action.

The literature data on the effects of urea in micellar solutions by using different experimental techniques are to a great extent conflicting. For instance, the results obtained by Causy et al. [11] in an investigation on micellization of dodecyltrimethylammonium bromide, by measuring volumes, heat capacities and conductivities, were interpreted in the sense that urea behaves as a nonpenetrating agent. In contrast, results obtained in studies carried out by using spectroscopic techniques such as ESR [7–9,28] and fluorescence [18–20,22,25–27] based on the analysis of the spectroscopic behaviour of extrinsic probe molecules, have been interpreted as evidence of urea interaction at the micellar surface. The key idea, as previously suggested [7,8], is that only by using experimental techniques providing information at a molecular level it is possible to gain reliable information about the urea action mechanism.

In recent years, we have reported systematic studies on the effect of urea on the aggregation behaviour of both non-ionic [18] and ionic surfactants [19,20], including SDS. In these investigations, 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 micelles. The results obtained in these studies are in accordance with a direct mechanism of urea action, whereby urea replaces some water molecules in the solvation layer of the amphiphile. As a continuation of the above investigations, in this paper we analyze complementary results on the effect of urea on the micellization and on the microenvironmental properties of SDS micelles.

2. Materials and methods

The surfactant SDS was purchased from Fluka and used without further purification. Fluorescent probes: pyrene (Sigma), pyrene-3-carboxaldehyde (Fluke), and diphenylbutadiene (Aldrich) were used as received. Other chemicals used were analytical grade, and water was doubly distilled (Millipore).

Conductivity measurements of aqueous surfactant solutions were carried out in a digital conductivity meter Crison model microCM 2202 using a dip-type cell of cell constant 1.03 cm⁻¹.

All measurements were done in a jacketed vessel, which was maintained at 25.0 ± 0.1°C with a Mendingen E1 temperature bath. Fluorescence measurements were made with a Spex FluoroMax-2 spectrofluorometer, equipped with a thermostated cell housing that allowed temperature control to ±0.1°C. Fluorescence anisotropy measurements were collected with the same apparatus and a polarization accessory which uses the L-format configuration [39] and an automated wheel
with Glan Thompson polarizers. The fluorescence anisotropy ($r$) was determined as

$$r = \frac{I_V - GI_H}{I_V + 2GI_H} \quad (1)$$

where the subscripts of fluorescence intensity values ($I$) refer to orientation of the excitation and emission polarizers (V, vertical; H, horizontal). The instrumental correction factor $G$, which is the ratio of the sensitivities of the detection system for vertically and horizontally polarized light, is required for the L-format configuration and was automatically determined by the software supplied by the manufacturer. The anisotropy values were averaged over an integration time of 10 s and a maximum number of five measurements for each sample. All fluorescence measurements were made at 25.0 $\pm$ 0.1°C.

Conductance measurements of SDS solutions at different urea concentrations were obtained by using a titrametric dilution method. CMC and degree of counterion dissociation ($\beta$) values at each solvent composition were determined by using the conventional method based on the plot of conductivity ($\kappa$) against the surfactant total concentration. The break point in these plots was taken as the CMC, and $\beta$ was determined as the ratio between the slopes of the postmicellar region and that in the pre-micellar region.

Fluorescence spectra of PCA (10 $\mu$M) in SDS micellar solutions of each set containing 13–16 different concentrations at a fixed solvent composition were recorded by using an excitation wavelength of 365 nm. Fluorescence anisotropy values of DPB in micellar solutions were measured using excitation and emission wavelengths of 330 and 377 nm, respectively.

For the microviscosity determination by the depolarization method the fluorescence lifetime ($\tau$) of DPB was estimated from the relation

$$\frac{\tau}{\tau_0} = \frac{I}{I_0} \quad (2)$$

where $\tau_0$ is the fluorescence lifetime taken from the literature, $I_0$ the fluorescence intensity measured under the condition common with the $\tau_0$ measurement, and $I$ the measured fluorescence intensity of the probe in the micellar solution. Eq. (2) can be applied when: (i) the emission decay is monoexponential; (ii) only collisional quenching occurs; and (iii) the probe behaves the same way in the solvent [40]. Jobe and Verral [41] have studied the photophysical behaviour of DPB in several ionic surfactants, and have found that this probe undergoes a monoexponential decay in SDS micelles. Therefore, in the present case, we took 387 ps [41] for DPB in micellar solutions of SDS (50 mM) in the absence of urea as the $\tau_0$ value. In all polarized fluorescence experiments the concentration of SDS was of 50 mM.

3. Results and discussion

3.1. Micelle formation

We have followed the micellization process of SDS at various urea concentrations by using two different methods. In first place, we have employed the common conductance method in which data of specific conductivity were taken as a function of the surfactant concentration. In Fig. 1 we present these plots, where it can be seen that a slower curvature appeared around CMC as urea concentration increased, indicating that the micellization of SDS in the presence of urea takes place in a more gradual way. From plots in Fig. 1 we have obtained the CMC and degree of counterion dissociation ($\beta$) values listed in Table 1, where

![Fig. 1. Specific conductivities vs. concentration of SDS at different aqueous mixtures of urea.](image-url)
Table 1
CMC and degree of counterion dissociation ($\beta$) of SDS in different aqueous solutions of urea at 25°C, as compared with literature value

<table>
<thead>
<tr>
<th>[Urea] (M)</th>
<th>CMC (mM)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.3$^a$</td>
<td>0.39$^a$</td>
</tr>
<tr>
<td></td>
<td>8.0$^b$</td>
<td>0.30$^b$</td>
</tr>
<tr>
<td></td>
<td>8.2$^c$</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8.7$^a$</td>
<td>0.49$^a$</td>
</tr>
<tr>
<td></td>
<td>9.0$^b$</td>
<td>0.40$^b$</td>
</tr>
<tr>
<td></td>
<td>9.2$^c$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>9.6$^a$</td>
<td>0.66$^a$</td>
</tr>
<tr>
<td></td>
<td>9.6$^b$</td>
<td>0.40$^b$</td>
</tr>
<tr>
<td>6</td>
<td>11.2$^a$</td>
<td>0.77$^a$</td>
</tr>
<tr>
<td></td>
<td>11.0$^b$</td>
<td>0.42$^b$</td>
</tr>
<tr>
<td></td>
<td>12.0$^c$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ This work (Conductance method).
$^b$ Data from reference [25] (fluorescence of ANS).
$^c$ Data from reference [9] (electron spin resonance).

literature values are also included for comparison. As can be seen from data in Table 1, the CMC and degree of counterion dissociation ($\beta$) values for low urea content obtained by the conductance method are in reasonable agreement with literature values. However, our values of degree of counterion dissociation in solutions with high urea concentration are greater that those recently obtained by Abuin et al. [25] by using a method based on the fluorescence of 8-anilinophthalene-1-sulfonate (ANS). The increase of the release of the counterion binding with increasing urea concentration has been ascribed to a reduction of the charge density at the micellar surface caused by the decrease in the micellar aggregation number [11,19]. In a recent research [20] we have found that the decrease in the aggregation number of SDS micelles with increasing urea concentration is essentially controlled by a linear increase of the surface area per headgroups. On the other hand, it has previously been demonstrated that the surface area per headgroup, or its inverse, the surface charge density, is the most important controlling factor for micelle size [45]. Therefore, we think that our present results, showing a linear increase ($r = 0.995$) for the degree of counterion dissociation with the urea concentration, are in good accordance with the observed behaviour for the micellar aggregation number of SDS.

The increase of CMC of SDS with increasing the urea concentration is indicative of a reduction of the hydrophobic interactions as a consequence of an enhanced solvation, causing an increase in the solubility of the hydrocarbon tails in the presence of urea. Essentially, two factors can contribute to this effect. First, from the point of view of the direct mechanism, urea increases the solubility of the hydrophobic solutes by reducing the free energy of dissolution in the mixed solvent, resulting from the replacement of water by the larger urea molecule in the solvation layer [34,37]. Moreover, it seems probable that the ability of urea to solvate the headgroups of the surfactant also contributes to the rise in the CMC.

On the other hand, we have also studied the effect of urea on the micellization of SDS by the change in the maximum emission wavelength ($\lambda_{\text{max}}$) of PCA. PCA is a non-charged probe molecule which has a polar carbonyl group, whose $\lambda_{\text{max}}$ undergoes a significant red shift with increasing solvent polarity [42]. This probe is assumed to be micellized near the micelle–water interface, therefore it has been proposed as a luminescent probe to estimate the surface polarity of micelles [42,43]. Fig. 2 shows the change of $\lambda_{\text{max}}$ with the SDS concentration at different urea concentrations. In this figure it can be seen that $\lambda_{\text{max}}$ decreases sharply at a certain concentration
of surfactant, showing a trend towards an asymptotic value ($\lambda_{\text{mic}}$) when a high surfactant concentration is reached. This $\lambda_{\text{mic}}$ value is larger at greater urea concentration. A priori, this fact could be interpreted in the sense that urea induces an increase in the polarity of the micellar surface. However, it has previously been reported [10] that the urea addition causes desolvation of certain surface probes bound to micelles. If this fact occurs in the case of PCA, it is clear that the partitioning of the probe between the micelle and bulk phases will decrease with increasing the urea concentration. In such a case, the result will be reflected by a rise in the $\lambda_{\text{mic}}$. In order to corroborate this expectation it is decisive to estimate the partition coefficient of PCA in the micelle–bulk interface. To obtain this partition coefficient we have applied a new method proposed by Tamory et al. [44] based on the assumption that the PCA maximum emission wavelength ($\lambda_{\text{max}}$) is a linear combination of this parameter in bulk water ($\lambda_w$) and that in the micellar phase ($\lambda_{\text{mic}}$), i.e.

$$\lambda_{\text{max}} = X_{\text{PCA}} \lambda_{\text{mic}} + (1 - X_{\text{PCA}}) \lambda_w$$

(3)

being $X_{\text{PCA}}$ the mol fraction of PCA in the micellar phase. The treatment developed by the aforementioned authors leads to the equation

$$\frac{\Delta \lambda}{\lambda_{\text{max}} - \lambda_{\text{mic}}} = K_{\text{PCA}} v [\text{Surf}] + (1 - K_{\text{PCA}} \text{CMC} v)$$

(4)

where $\Delta \lambda$ is ($\lambda_w - \lambda_{\text{mic}}$), $v$ is the molar volume of the surfactant (248 cm$^3$ mol$^{-1}$ for SDS [44]), $[\text{Surf}]$ is the total surfactant concentration, and $K_{\text{PCA}}$ is the partition coefficient of PCA defined as

$$K_{\text{PCA}} = \frac{[\text{PCA}]_{\text{mic}}}{[\text{PCA}]_w}$$

(5)

According to this approach, the left hand side of Eq. (4) should change linearly with the total surfactant concentration. In this way, this procedure not only allows us to determine $K_{\text{PCA}}$ but also the CMC values. These parameters are related with the slope ($a$) and the intercept ($b$) in Eq. (4) by

$$K_{\text{PCA}} = \frac{a}{v}$$

(6)

and

$$\text{CMC} = \frac{1 - b}{a}$$

(7)

Fig. 3 shows our experimental data plotted according to Eq. (4). These plots present two different parts, a horizontal line corresponding to the premicellar region, and an inclined line corresponding to the postmicellar one. From data in this last region and Eq. (6) and Eq. (7) we have obtained the CMC and $K_{\text{PCA}}$ values presented in Table 2. In this table we also include the $\lambda_{\text{mic}}$ values and the free energy change of PCA in transfer from the bulk to the micellar phase $\Delta G_{\text{PCA}}^0$ as obtained from

$$\Delta G_{\text{PCA}}^0 = -RT \ln K_{\text{PCA}}$$

(8)

From data in Table 2 it is clear that urea causes desolvation of PCA bound to SDS micelles. Therefore, although in the absence or at low urea concentration the CMC values determined by using this method are in good agreement with those obtained by the conductance method, as urea content increases (4 M urea), the CMC value found by using the PCA method becomes greater than that found by the conductance method. Due to the ambiguity in the application of the procedure in the case of 6 M urea, we have preferred not to present the results for this solvent composition. From the results obtained in this experiment it is clear that we cannot extract quantitative
Table 2
Effect of urea on micellization parameters of SDS obtained by fluorescence of PCA, and on the partition parameters of PCA in SDS micelles, at 25°C

<table>
<thead>
<tr>
<th>[Urea] (M)</th>
<th>CMC (mM)</th>
<th>( \lambda_{\text{mic}} ) (nm)</th>
<th>( K_{\text{PCA}} )</th>
<th>(-\Delta G_{\text{PCA}}^0) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.2</td>
<td>458.2</td>
<td>115415</td>
<td>28.9</td>
</tr>
<tr>
<td>2</td>
<td>8.6</td>
<td>459.2</td>
<td>101313</td>
<td>28.6</td>
</tr>
<tr>
<td>4</td>
<td>10.5</td>
<td>460.0</td>
<td>76573</td>
<td>27.9</td>
</tr>
<tr>
<td>6</td>
<td>–</td>
<td>460.0</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Conclusions about changes in micropolarity in the surface of SDS micelles induced by the addition of urea. However, and given that the relative change of \( K_{\text{PCA}} \) is greater than that observed for \( \lambda_{\text{mic}} \), it seems reasonable to assume that urea slightly decreases the polarity of the micellar interface. Finally, it is important to point out that the reduction in \( K_{\text{PCA}} \) is compatible with a direct mechanism of urea action, since the desolation of PCA is probably the result from the direct participation of urea in the solvation layer of the polar headgroups of the surfactant.

3.2. Fluorescence anisotropy studies

Fluorescence depolarization experiments have been extensively carried out to study both structural and dynamics properties of micelles, microemulsions, and other microheterogeneous systems [42]. The degree of depolarization of the fluorescence emission of a fluorophore is an indication of the rotational diffusion during the lifetime of its excited state. The steady-state fluorescence anisotropy (\( r \)) is related to the microviscosity (\( \eta \)) around the probe through the Perrin equation

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

(9)

where \( r_0 \) is the limiting anisotropy obtained in the absence of rotational motion, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( V \) and \( \tau \) are the molecular volume and fluorescence lifetime of the probe, respectively. In structured microenvironments the restrictions imposed by the environment to the free rotational movement of the probe prevent some of the possible orientations which contribute to the polarization of the fluorescence emission. In addition, the dynamic conditions controlling the speed with which the probe does its motion must also be considered. For this reason, the steady-state anisotropy can be resolved into a static component (\( r_{sc} \)), and other dynamic (\( r_d \)) [40,46]:

\[
r = r_{sc} + r_d
\]  

(10)

According to the so-called ‘wobbling-in-cone’ model proposed by Kinoshita et al. [47] the rotation of the fluorophore is assumed to occur in a square-well potential, such that its rotation is unhindered until a certain critical angle \( \theta_c \) is reached, the rotation beyond this angle being energetically impossible. The static component (\( r_{sc} \)) of the steady-state anisotropy is related to the order parameter (\( S \)), which is a measure of the equilibrium orientational distribution of the dye [48], by

\[
\frac{r_{sc}}{r_0} = S^2; \quad 0 \leq S \leq 1
\]  

(11)

This last parameter (\( S \)) is related to the critical angle \( \theta_c \) by Eq. (12)

\[
S = 0.5 \cos \theta_c (1 + \cos \theta_c)
\]  

(12)

Pottel et al. [49], from semiempirical considerations, have proposed a relationship between the order parameter and the steady-state anisotropy given by

\[
r = \frac{S}{r_0} \frac{1}{1 + S - S^2}
\]  

(13)

In this way, from steady-state anisotropy measurements it is possible to determine the order parameter (\( S \)), and hence the critical angle (\( \theta_c \)).
In our polarized fluorescence measurements we have used diphenylbutadiene (DPB) as a fluorescent probe. This probe molecule, whose fluorescence lifetime and quantum yields are very dependent upon the solvent polarity, is hydrophobic in nature and has been previously employed to explore the structural changes in the hydrophobic region of cetyltrimethylammonium bromide micelles induced by the addition of 2-butoxyethanol [41]. In this same research, from the photophysical behaviour of DPB in SDS, among other ionic surfactants, it was proved that the probe is solubilized in the nonpolar region of the micelle, experiencing a monexponential decay.

In Fig. 4 we present the results obtained in our studies of fluorescence emission and fluorescence anisotropy of DPB in SDS micelles using a wide range of urea concentrations as solvent media. As can be seen in Fig. 4, the fluorescence intensity of DPB slightly decreases with increasing urea concentration. This decrease indicates that the probe is experiencing an increasingly polar environment. Two possible explanations can be given for this effect: (i) it can be the result from a greater penetration of solvent in the micellar structure; or (ii) it can be due to a displacement of DPB towards outer region in the micelle. Previously, we have found a similar behaviour by using pyrene as a probe [20]. In that case, on the basis of previous observations about solvent penetration into SDS micelles [6,7], we concluded that the addition of urea promoted the displacement of the probe towards the outer region in the micelle. For this reason, in the present case we think that the decrease in the fluorescence intensity of DPB with increasing urea concentration is the result of a outer localization of the probe in the micelle.

On the other hand, the fluorescence anisotropy of DPB increases with increasing urea concentration (Fig. 4). In Table 3 are listed the experimental values of fluorescence anisotropy together with the order parameter and the critical angle determined according to the ‘wobbling-in-cone’ model, as well as the apparent microviscosity values of the hydrophobic region of SDS micelles determined by the Perrin equation. To manipulate the Perrin equation we have used the literature values for $r_0$, and $V$ (0.346, and 205 Å³, respectively, [41]). All data in Table 3 are indicatives of a more rigid environment sensed by the probe as the urea concentration increases. While the order parameter increases from 0.75 to 0.86, the critical angle $\theta_c$ decreases from 34.5° to 26.7°, indicating that the equilibrium orientational distribution is more constrained as urea concentration is increased. As a consequence, there is both a decrease in the amplitude and in the speed of the Brownian movement of probe molecules in the micelle. It must be noted that this fact in connection to an outer localization of the probe in the micelle is an unexpected result since the rigidity of the environment is expected to decrease in the outer region of

Table 3

<table>
<thead>
<tr>
<th>[Urea] (M)</th>
<th>$r^*$</th>
<th>$S$</th>
<th>$\theta_c$ (°)</th>
<th>$\eta$ (cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.219</td>
<td>0.75</td>
<td>34.5</td>
<td>13.4</td>
</tr>
<tr>
<td>1</td>
<td>0.223</td>
<td>0.76</td>
<td>33.7</td>
<td>14.0</td>
</tr>
<tr>
<td>2</td>
<td>0.228</td>
<td>0.77</td>
<td>32.8</td>
<td>14.2</td>
</tr>
<tr>
<td>3</td>
<td>0.233</td>
<td>0.79</td>
<td>31.8</td>
<td>14.6</td>
</tr>
<tr>
<td>4</td>
<td>0.240</td>
<td>0.80</td>
<td>30.4</td>
<td>15.1</td>
</tr>
<tr>
<td>5</td>
<td>0.248</td>
<td>0.82</td>
<td>28.8</td>
<td>15.7</td>
</tr>
<tr>
<td>6</td>
<td>0.259</td>
<td>0.86</td>
<td>26.7</td>
<td>17.4</td>
</tr>
</tbody>
</table>

$^*$ Mean values of three individual determinations.
the micelle. However, this result can be explained if we assume a direct participation of urea in the solvation layer of the hydrophobic chains of the surfactant in the micelle. In effect, as a urea molecule is \( \approx 2.5 \) times larger than a water molecule, substitution of these molecules by the former will cause an increase in the rigidity of the microenvironment sensed by the probe. It must be pointed out that by using several cationic probes, which are expected to interact superficially with SDS micelles, we have previously shown that urea participates in the solvation layer of the polar headgroups of the surfactant. However, given the hydrophobic nature of DPB, the present results seem to indicate that urea also penetrates below the headgroups by replacing some water molecules in the hydrophobic chain of the amphiphile.

4. Conclusions

In general, the results obtained in this work support the conclusions found in previous studies carried out by other authors and by ourselves. The CMC values that we have determined by using conductometric measurements are in good agreement with those recently obtained by using different experimental techniques. The observed increase in the CMC has been mainly attributed to an increase in the solvation of the hydrocarbon tails of the surfactant in the presence of urea. Although the values of the degree of counterion dissociation that we have found are greater than literature values at high urea concentration, the observed trend in this parameter is in accordance with our previous studies on the change in the aggregation number of SDS micelles induced by the urea addition. In addition, the results obtained in the fluorescence study provided information at a molecular level on the microstructural changes in SDS micelles caused by the presence of urea. The analysis of the fluorescence of PCA shows the interaction of urea with the surface of SDS micelles, to the extent that some PCA molecules are removed from the micellar surface and transferred to the bulk water. Data of fluorescence anisotropy indicated that the interaction of urea not only takes place at a surface level but also penetrates below the surfactant polar headgroups by replacing some water molecules in the solvation layer of the hydrophobic chains of the surfactant in the micelle.

References