# On the Urea Action Mechanism: A Comparative Study on the Self-Assembly of Two Sugar-Based Surfactants

**ARTICLE** *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · MAY 2009

Impact Factor: 3.3 · DOI: 10.1021/jp811198d · Source: PubMed



**3 AUTHORS:**

Jose Hierrezuelo
Dublin City University
**28** PUBLICATIONS **334** CITATIONS
SEE PROFILE

Jose A Molina-Bolívar
University of Malaga
**64** PUBLICATIONS **1,129** CITATIONS
SEE PROFILE

Cristóbal Carnero Ruiz
University of Malaga
**72** PUBLICATIONS **1,765** CITATIONS
SEE PROFILE

# On the Urea Action Mechanism: A Comparative Study on the Self-Assembly of Two Sugar-Based Surfactants

**J. M. Hierrezuelo, J. A. Molina-Bolívar, and C. Carnero Ruiz***

*Grupo de Fluidos Estructurados y Sistemas Anfifílicos, Departamento de Física Aplicada II, Escuela Universitaria Politécnica, Universidad de Málaga, Campus de El Ejido, 29071-Málaga, Spain*

*Received: December 18, 2008; Revised Manuscript Received: February 23, 2009*

Studies on the effect of urea on micelle formation and structure of *n*-octyl-*β*-D-thioglucoside (OTG) and *N*-decanoyl-*N*-methylglucamide (MEGA-10) were carried out by using the steady-state and time-resolved fluorescence techniques, together with combined static and dynamic light scattering measurements. A similar increase in the critical micelle concentration with the urea addition was observed for both surfactants. This behavior was attributed to a rise in the solubility of hydrocarbon tails and the increase of solvation of the headgroup of the surfactants in the presence of urea. Structural studies mainly based on the analysis of the hydrodynamic radius and aggregation number of micelles revealed that urea induces changes much more significant on micelles of OTG. Particularly, it was found that, whereas the surface area per headgroup of OTG increases with the urea concentration, it does decrease in the case of MEGA-10. This fact suggests that different action mechanisms operate for both surfactants. Accordingly, investigations on the micellar microstructure based on the study of microenvironmental properties such as micropolarity and microviscosity also indicated a more pronounced effect in the case of OTG. Although changes were not observed in the hydrophobic inner region of both micellar systems, a significant increase of polarity and viscosity in the micellar interface of OTG suggests a direct participation of urea in the micellar solvation layer. The differences between the observed behaviors for both micellar systems were interpreted on the basis of two features: the weaker hydration and greater rigidity of the OTG headgroup as compared with MEGA-10.

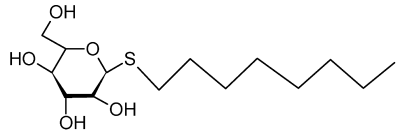
## Introduction

It is well-known that the dynamic and structural properties of micelles can be altered by the presence of a third component in the medium. In fact, during much time a great number of thermodynamic, kinetic, and structural studies about the micellization process in aqueous surfactant solutions, including the effect of additives, have been carried out.[1] In addition, the real systems of industrial interest, as those used in detergency, solubilization, oil recovery, and particularly in many biotechnological applications, are formed by several components and often show a very complex behavior being difficult to investigate. Therefore, the study of surfactant solutions with additives or cosolutes is very important to achieve a better understanding about the behavior of these multicomponent systems.

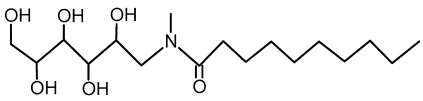
The presence of an additive in the solution can affect the micellar formation either through specific interactions with surfactant molecules or by changing the solvent nature.[2] Urea and its derivatives, which are very efficient as modifiers of the aqueous solution properties, have received considerable attention because they are often used as denaturing agents for proteins, polypeptides, and other biopolymers.[3] However, since this denaturing action involves a number of complex factors, there are still some controversies about the mechanism by which that process occurs, as well as the effect produced on several physicochemical properties of various molecular assemblies. Because the demicellization of micelles in aqueous urea solutions resembles the denaturation of proteins, considerable effort has been performed in the past to rationalize the way in which urea affects micellar solution properties.[4−43] These studies have revealed the ability of urea in weakening the hydrophobic interactions in aqueous solutions. So, it has been found that urea increases the critical micelle concentration (cmc) of ionic and nonionic surfactants, reduces the size of both kinds of micelles, and inhibits the clouding of nonionic surfactants.[10,13,23] Furthermore, there is evidence, at a qualitative level, that urea increases the microviscosity and decreases the micropolarity of the micellar interface of ionic micelles.[11,12,25] To explain the urea action two different mechanisms have been proposed: (i) an indirect mechanism, whereby urea acts as a "water-structure breaker" favoring the solvation of the hydrophobic solutes, and (ii) a direct mechanism, in which urea replaces some of the water molecules in the hydration shell of the solute, participating in its solvation layer.[13] For much time, the indirect mechanism has been the most widely accepted, and many studies seem to support this hypothesis.[4−7] However, later results obtained by both computer simulations and experimental investigations are consistent with a direct mechanism of urea action.[44−49] Recently, Politi's group[37] have proposed that urea neither breaks the water-structure nor acts through a direct mechanism, but simply it increases the water polarity enhancing the solvation of the polar groups of the surfactant. This view has been reinforced by later studies carried out by the same group, by using a chemical trapping method, in which they found that the urea concentration in the interfacial regions of cationic, anionic, and zwitterionic micelles is the same than in the bulk solution.[38] Finally, in a recent study about the urea effect on Triton X-100 micelles based on the fluorescence probe technique, Raghuraman et al.[39] suggest an increased accessibility from the aqueous phase at higher urea concentrations, which could result from better solvation of the polar headgroups of the surfactant by urea−water

* Corresponding author. E-mail: ccarnero@uma.es.

10.1021/jp811198d CCC: $40.75 
Published on Web 04/24/2009



*n*-Octyl-β-D-thioglucopyranoside (OTG)



*N*-Decanoyl-*N*-methylglucamide (MEGA-10)

**Figure 1.** Molecular structures of the surfactants studied in the present investigation.

mixture than water alone. Essentially, these conclusions agree with those obtained by Politi's group.

In this paper, we report the effect of urea on micellar properties of two sugar-based surfactants: *n*-octyl-*β*-D-thioglucoside (OTG) and *N*-decanoyl-*N*-methylglucamide (MEGA-10), belonging to the two most representative groups of this kind of surfactants, alkyl polyglucosides and fatty acid glucamides, respectively. These surfactants differ essentially in the nature of their headgroups, which are mainly characterized by the presence of the methylamine moiety and an open conformation, in the case of MEGA-10, and a glucose ring in the case of OTG (see Figure 1). Because of their favorable environmental profile, "mild" character, and other much interesting physicochemical properties, sugar-based surfactants are currently receiving increasing attention, and new literature is emerging on this subject.[50] The motivation of this study was twofold. First of all, sugar-based surfactants show a solution behavior substantially different from the ethoxylated nonionic ones. Particularly, this fact stems from the strength of the hydrogen bonds between the hydroxyl groups of the sugar group and water. Consequently, the dehydration process in these surfactants is considerably more difficult.[51,52] Second, in recent studies carried out in our laboratory we have examined the effect of temperature and salt addition on micellar properties of OTG and MEGA-10.[53−55] In these studies we have found that the properties of MEGA-10 are much more insensitive to an increased temperature and the presence of salt than OTG. These differences were ascribed to the stronger hydration and a minor rigidity of the sugar head of MEGA-10 as compared with OTG. Since urea is preferentially interacting with the micelle−water interface, a comparative study between these two surfactants has a lot of interest. In addition, as far as we know the literature data on the effect of urea on the solution behavior of sugar-based surfactants are lacking.

The outline of this paper is as follows. First, by using the pyrene 1:3 ratio method, we have obtained information on the change of the cmc of both surfactants induced by the presence of urea. Second, the effect of the additive on the micellar size was analyzed by using light scattering, static fluorescence quenching, and complementary viscosity measurements. Finally, changes in the microstructure micellar upon urea addition were examined by using both steady-state fluorescence anisotropy and time-resolved fluorescence measurements of probes solubilized in the micellar phase.

## Experimental Section

**Materials.** The samples of MEGA-10, OTG, the fluorescence probes pyrene, coumarin 6 (C6), and the quencher cetylpyridinium chloride (CPyC) were purchased from Sigma Co., whereas 8-anilinonaphthalene-1-sulfonate (ANS) was acquired from Fluka. Due to their high purity, these compounds were used as received. Stock solutions of surfactants were prepared in water, whereas those of the fluorescence probes were prepared in absolute ethanol and stored at 4 °C. Working solutions of lower concentration were used immediately after preparation. Ultrapure water (resistivity ∼18 MΩ·cm) for the preparation of the solutions was obtained by passing deionized water through an ultrahigh quality polishing system (UHQ-PS, ELGA). All chemical used were of analytical grade quality.

**Steady-State Fluorescence Measurements.** A SPEX FluoroMax-2 spectrofluorometer in the "S" mode was used to record all the steady-state fluorescence measurements. This apparatus is equipped with a thermostatted cell housing and fitted with a 150 W xenon lamp and 1 cm × 1 cm quartz cells. Fluorescence emission spectra of surfactant containing around 1 $\mu$M pyrene were recorded between 360 and 500 nm by using an excitation wavelength of 335 nm. From these spectra the intensities $I_1$ and $I_3$ were measured at the wavelengths corresponding to the first and third vibronic band located near 373 and 384 nm. The ratio $I_1/I_3$ is the so-called pyrene 1:3 ratio index.

The steady-state fluorescence quenching method[56] was used to determine the mean micellar aggregation number ($N_{agg}$). In all the quenching experiments pyrene was used as a luminescence probe and CPyC as a quencher. Stock solutions containing pyrene and surfactant were prepared in either pure water or urea solutions of different concentration. Working solutions of lower concentration (1 $\mu$M in pyrene and 30 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 micelles. From these solutions, fluorescence intensities were recorded by using excitation and emission wavelengths of 335 and 383 nm, respectively. Triplicate experiments were carried out for each aqueous system with different urea content. The errors in $N_{agg}$, in terms of the standard deviation of three individual determinations, are estimated to be less than 3%.

Fluorescence polarization measurements were recorded in the same apparatus equipped with a polarization accessory, which uses the L-format instrumental configuration[57] and an automatic interchangeable wheel with Glan−Thompson polarizers. From the fluorescence polarization measurements, the steady-state fluorescence anisotropy ($r_{ss}$) values were determined as

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

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 20 s, and a maximum number of three measurements was 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.

**Time-Resolved Fluorescence Measurements.** Fluorescence lifetimes of ANS solubilized in micelles were determined from time-resolved fluorescence intensity decays using an Edinburgh Instruments FLS920 luminescence spectrometer in the time-correlated single-photon counting mode. The excitation source was a 375 nm picosecond laser (PicoQuant PDL 800B), and the emission was recorded at 490 nm. To optimize the signal-

to-noise ratio, $10^4$ photon counts were collected in the peak channel. The instrumental response function was regularly obtained by measuring the scattering of a Ludox solution. The decay curves were deconvoluted with the help of the F900 software package of Edinburgh Instruments. Intensity decay curves were fitted as a sum of exponential terms:

$$I(t) = \sum_i A_i \exp\left(\frac{t}{\tau_i}\right) \tag{2}$$

where $A_i$ is a pre-exponential factor of the component $i$ with a lifetime $\tau_i$. In all the cases, the best fit was obtained for a biexponential decay curve ($\chi^2 \leq 1.18$). From these two-component contributions, average fluorescence lifetimes $\langle\tau\rangle$ were calculated using the following equation:[57]

$$\langle\tau\rangle = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i} \tag{3}$$

The relative concentration or fractional amount of each component, $\alpha_i$, was determined by

$$\alpha_i = \frac{A_i}{\sum_i A_i} \tag{4}$$

**Light Scattering Measurements.** Light scattering measurements were carried out with a Zetasizer Nano-S instrument (Malvern Instrument, U.K.). This apparatus, which uses the backscattering detection (scattering angle $\theta = 173°$) and an avalanche photodiode detector (APD), is equipped with a helium−neon laser source (wavelength 633 nm; power 4.0 mW) and a thermostatted sample chamber controlled by a thermoelectric Peltier. The sample cells were soaked in nitric acid, rinsed with distilled water, and finally with freshly distilled acetone before use. To remove any dust particles present, surfactant solutions were filtered once through a 0.1 $\mu$m Millipore filter directly into the cell and sealed until use.

Dynamic light scattering (DLS) measurements were carried out to determine the diffusion coefficient of the micelles ($D_c$), as described in previous papers.[53−55] This diffusion coefficient, which is concentration-dependent, reflects the micelle diffusion as affected by the intermicellar interaction. At elevated micelle concentrations, these interactions are two sorts: direct interaction (such as repulsive excluded volume effects and attractive van der Waals interactions) and hydrodynamic interactions (in which the motions of one particle are communicated to other particles via the flow of the solvent). For dilute solutions, where the intermicellar interactions can be considered absent, the apparent diffusion coefficient varies linearly with the surfactant concentration:[58]

$$D_c = D_0[1 + k_D(c - \mathrm{cmc})] \tag{5}$$

where $k_D$ is a constant. The actual diffusion coefficient at infinite dilution, $D_0$, can be calculated by extrapolation of the apparent diffusion coefficient to zero concentration. In any case, the diffusion coefficient values ($D$) can be used to provide information on micellar size, by using the Stokes−Einstein relation to deduce the apparent hydrodynamic radius $R_H$:[59]

$$R_H = \frac{k_B T}{6\pi\eta_0 D} \tag{6}$$

where $k_BT$ is the thermal energy factor and $\eta_0$ is the solvent viscosity.

Static light scattering (SLS) data provide information on the average molecular weight of the micelles $M_w$. According to the Rayleigh−Gans−Debye theory, the scattered intensity of light from a dilute solution of weakly interacting particles with dimensions small compared with the wavelength of the incident light (i.e., diameter $< \lambda/20$) may be approximated by

$$\frac{K(c - \mathrm{cmc})}{\Delta R_\theta} = \frac{1}{M_w P(q)} + 2B_2(c - \mathrm{cmc}) \tag{7}$$

where $c$ is the total surfactant concentration, cmc is the critical micelle concentration, $M_w$ is the micelle molecular weight, $P(q)$ is the particle form factor, $B_2$ is the second virial coefficient and $K$ is an optical constant given by

$$K = \frac{4\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2}{N_A \lambda_0^4} \tag{8}$$

here $\mathrm{d}n/\mathrm{d}c$ is the refractive index increment of the micellar solution. In the case of dilution where the particle interactions are negligible, $B_2$ is practically zero, and eq 7 can be rewritten as

$$\frac{K(c - \mathrm{cmc})}{\Delta R_\theta} = \frac{1}{M_w P(q)} \tag{9}$$

As is well-known, the micellar weight in solutions of association colloids can be calculated from this equation only for the concentration range directly above the cmc. The refractive index values of the solvent and micellar solutions were measured using a digital Abbe refractometer (WYA-1S). The refractive index increment was determined by fitting $n$ as a linear function of the surfactant concentration. In the case of MEGA-10, this parameter ranged from $2.019 \times 10^{-4}$ L g$^{-1}$ in water to $1.196 \times 10^{-4}$ L g$^{-1}$ in 3 M urea, and for OTG from $2.215 \times 10^{-4}$ L g$^{-1}$ in water to $1.763 \times 10^{-4}$ L g$^{-1}$ in 2 M urea. If the particle size is much smaller than the wavelength of light the scattering intensity shows generally a very low angle dependence, and the contribution of the particle form factor can be neglected (i.e., $P(q) = 1$).[60] This analysis is valid if the micelle molecular weight remains constant in the explored surfactant concentration domain.

The excess scattering ratio of the micelles is given by $\Delta R_\theta$ which represents the difference in the Rayleigh ratio between the micellar solution and the solvent solution in the absence of micelles, $\Delta R_\theta = R_\theta - R_\theta^0$. On the other hand, the Rayleigh ratio of the sample solution is determined using toluene as a standard according to the relationship

$$R_\theta = \frac{I_\theta}{I_{tol}} R_{tol} \tag{10}$$

where $I_\theta$ and $I_{tol}$ are the scattered intensity of the sample solution and the toluene, respectively, and $R_{tol}$ is the Rayleigh ratio of toluene. This value was assumed to be $1.3523 \times 10^{-3}$ m$^{-1}$ at 633 nm. The intensity of scattered light was measured at least five times for each sample. The overall error in the micelle molecular weights and the micelle aggregation numbers determined by SLS was estimated to be approximately 5%.

**Viscosity and Density Measurements.** The dynamic viscosity ($\eta$) of the surfactant solutions was obtained with an automated microviscometer AMVn (Anton Paar). The measuring principle of this apparatus is based on Stoke's law. The apparatus determines the falling time of a small steel ball between a fixed distance into a Peltier-thermostatted capillary. For each sample, the run time was recorded at least four times and the temperature was controlled within 0.01 °C.

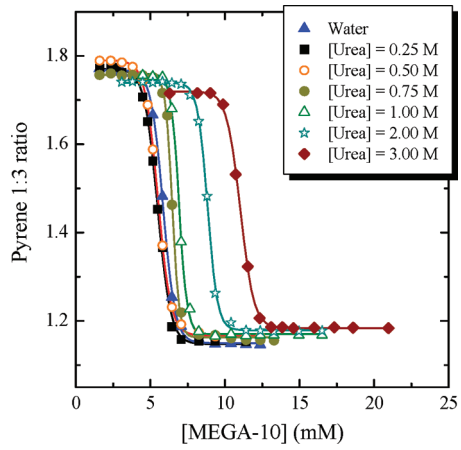



**Figure 2.** Plots of pyrene 1:3 ratio vs the total concentration of MEGA-10 in water and at different urea concentrations.

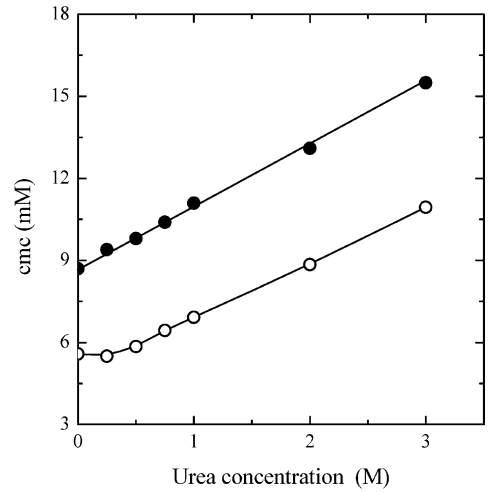



**Figure 3.** Effect of the urea concentration on the cmc of the surfactants: (●) OTG and (○) MEGA-10.

The density measurements necessary to compute the dynamic viscosity were performed with an Anton Paar DMA 58 density meter. This apparatus determines the density value by placing the sample in a U-shaped tube and measuring its period of oscillation. The instrument has an accuracy of $\pm 10^{-5}$ g/cm$^3$, and it was calibrated with air and water. The temperature was controlled within ±0.01 °C. These density measurements were also used to determine the partial specific volume, $\upsilon$, of micelles and the so-called dry micelle radius, $R_0$, by using the procedure previously described.[55]

Finally, the work temperature used in the case of OTG was 25 °C. However, to avoid solubility problems with MEGA-10, a temperature of 30 °C was employed for this surfactant in all the experimental work.

## Results and Discussion

**Effect of Urea on the cmc.** The micellar formation process of both surfactants in solutions of increasing urea concentrations was studied by using the well-established pyrene 1:3 ratio method.[61] Figure 2 shows representative plots of the experiments carried out in the case of MEGA-10; similar results were obtained in the case of OTG (see Figure SI1 in the Supporting Information). As can be seen in Figure 2 all plots show a typical sigmoidal decrease with the surfactant concentration. Below the cmc the pyrene 1:3 ratio index corresponds to a polar environment; as the surfactant concentration increases this index decreases rapidly, indicating that the probe is sensing a more hydrophobic environment. Above the cmc, the pyrene 1:3 ratio index reaches a roughly constant value due to the incorporation of the probe into the hydrophobic region of micelles. From plots in Figure 2, the cmc values were obtained by using the procedure previously described.[62] Briefly, the experimental data were fitted to a sigmoid (Boltzmann-type) curve, and the center of the sigmoid was identified as the cmc. The cmc values so obtained are plotted in Figure 3. From this figure, it is apparent that the cmc of OTG is more sensitive to the presence of urea in the medium. However, starting from a certain urea concentration both surfactants show practically the same behavior. The increase in the cmc with increasing the urea concentration can be explained if we consider two effects: the enhancement of the solubility of hydrocarbon tails and the increase of solvation of the headgroup of the surfactant in the presence of urea.[34] Note that this explanation is consistent, on the one hand, with the ability of urea to weaken the hydrophobic interactions responsible for the formation and maintenance of the micellar assembly in aqueous solution[39] and, on the other, with the fact that urea enhances the hydrophilic character of water which results in more strongly solvated polar headgroups. In other words, the urea−water mixture solvates the polar groups in micellar aggregates better than water alone.[37,39]

It is interesting to compare the observed effect of urea on the cmc values of OTG and MEGA-10 with the one previously reported for other surfactants. For instance, for a 2 M urea concentration, the cmc increases around 60% and 51% for OTG and MEGA-10, respectively. At the same urea concentration, it has been reported that the cmc increases 52% for the nonionic surfactant Triton X-100,[23] 8% for the anionic surfactant sodium dodecyl sulfate (SDS),[34] and 17% for the cationic surfactant cetyltrimethylammonium bromide (CTAB).[24] Clearly, the behavior of these sugar-based surfactants is similar, as for the observed trend in the cmc values, to that of the nonionic oxyethylene-based surfactant Triton X-100.

**Effect of Urea on the Micellar Size.** In order to examine the effect of the urea concentration on the micellar size of OTG and MEGA-10, we have carried out DLS measurements. First of all, we have determined the apparent hydrodynamic radius as a function of urea concentration for solutions containing 10 g/L (32.4 mM) and 25 g/L (71.5 mM) of OTG and MEGA-10, respectively (see Figure 4). From Figure 4 it can be seen that the presence of urea in the solution induces a strong decrease in the OTG size. Probably, this reduction in the micellar size is accompanied with a change in the micellar shape. In fact, the hydrodynamic radius of OTG micelles in water corresponds to nonspherical micelles, whereas in 3 M urea the micelles could be spheres.[53,54] It is also seen that the effect of the additive on MEGA-10 micelles is much less significant, showing a slight reduction in the micellar apparent hydrodynamic radius with the urea concentration. In this case, no changes in the micellar morphology are expected. In regard to the hydrodynamic radius values it is plausible to assume that MEGA-10 forms spherical micelles.[55]

On the other hand, we have also investigated the concentration dependence of the apparent diffusion coefficients of micelles. The data obtained for OTG solutions in 1 and 2 M urea are presented in Figure 5. It should be noted that it was not possible to collect data for 3 M urea due to the low intensity of dispersed light by the micelles at low surfactant concentration. It is evident from this figure that there is a rapid initial decrease in the apparent diffusion coefficient ($D_c$) with increasing surfactant

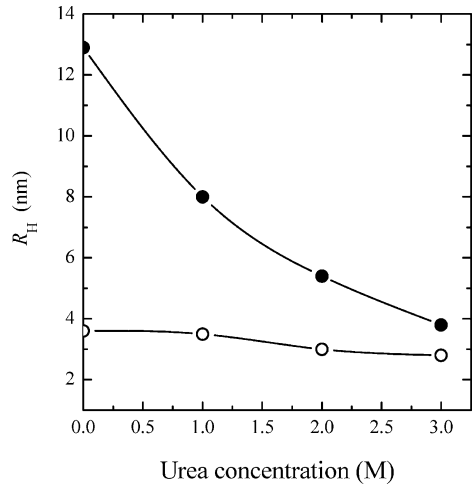



**Figure 4.** Effect of the urea addition on the apparent hydrodynamic radius of micelles for (●) OTG (10 g/L or 32.4 mM) and (○) MEGA-10 (25 g/L or 71.5 mM).

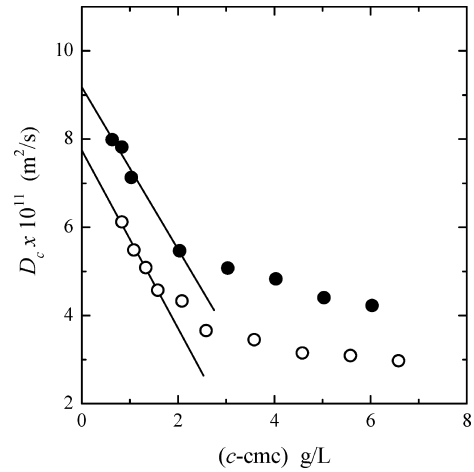



**Figure 5.** Apparent diffusion coefficients $D_c$ vs surfactant concentration for OTG in urea solutions: (○) 1 M and (●) 2 M. Solid lines are the best fit of data to eq 5.

concentration, and beyond a critical concentration $D_c$ values show no further significant decrease. As indicated in the Experimental Section, in the region of dilute solution, micelles are small and it is plausible to suppose that they have a spherical shape. In this region, the actual diffusion coefficient $D_0$ can be deduced by extrapolating the apparent diffusion coefficient to the cmc, and hence the micellar hydrodynamic radius at infinite solution, $R_H^0$, can be evaluated by eq 6. The so-obtained $R_H^0$ values are listed in Table 1, where one sees significant changes in the radius of OTG micelles. The size of OTG micelles decreases with increasing the urea concentration. The behavior of the apparent diffusion coefficients at elevated surfactant concentration could be attributed to a micellar growth with the subsequent change in the micelle shape from sphere to rodlike.[53] In the case of MEGA-10 micelles, the micelle size remains roughly constant with the surfactant concentration (data not shown). The actual diffusion coefficient values obtained are listed in Table 1, where it is noteworthy that the hydrodynamic radius of MEGA-10 micelles is practically constant within the experimental error. It is to be noted that previous studies on the effect of urea on nonionic ethoxylated surfactants reported a decrease the micelle hydrodynamic radius with the urea concentration.[13,36]

To obtain additional information regarding the different influence of urea on the micelle size of OTG and MEGA-10,

**TABLE 1: Structural Parameters of MEGA-10 and OTG as a Function of the Urea Concentration, at 30 °C for MEGA-10 and at 25 °C for OTG**

| micellar media | urea (M) | $R_H^0$ (nm) | $M_w$ (Da) | $N_{agg}$ | $N_{agg}$[a] | $R_0$ (nm) | $a_0$ (Å$^2$) |
|---|---|---|---|---|---|---|---|
| MEGA-10 | 0.0 | 2.6 | 25514 | 73 | 75 ± 1 | 2.1 | 75.9 |
| | 1.0 | 2.7 | 25186 | 72 | 74 ± 1 | 2.1 | 74.1 |
| | 2.0 | 2.6 | 24638 | 70 | 71 ± 1 | 2.0 | 71.8 |
| | 3.0 | 2.5 | 22685 | 65 | 64 ± 1 | 1.9 | 69.7 |
| OTG | 0.0 | 3.5 | 35040 | 114[b] | 74 ± 1 | 2.3 | 58.3 |
| | 1.0 | 3.1 | 29376 | 95[b] | 72 ± 1 | 2.2 | 61.1 |
| | 2.0 | 2.5 | 20974 | 37 | 68 ± 2[b] | 1.9 | 67.8 |
| | 3.0 | | 17581 | | 57 ± 1[b] | 1.8 | 71.0 |

[a] Number aggregation values as obtained by the static quenching method. [b] Values of $N_{agg}$ used for determining the values of the surface area per headgroup, $a_0$, for OTG.

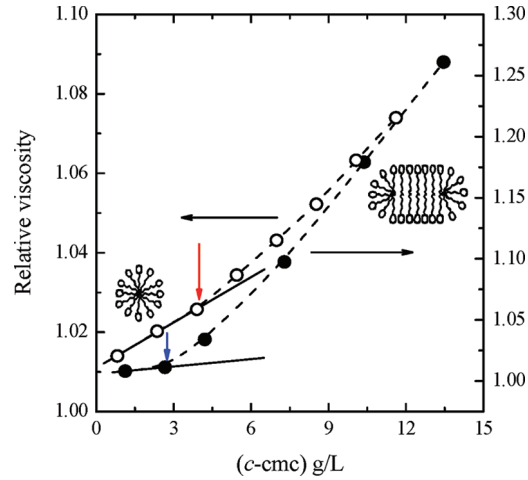



**Figure 6.** Relative viscosity of OTG micellar solutions in (●) water and (○) 3 M urea.

we carried out viscosity measurements of micellar solutions of both surfactants. It is well-known that viscosity is a property which is very sensitive to structural changes of the aggregates in solution.[63] Surfactant solutions containing spherical micelles are isotropic and of low viscosity. The presence of anisotropic micelles (e.g., rod-shaped) in the solution causes a distinct rise in viscosity due to mutual interactions (entanglement).[64,65] In this regard, we have studied the effect of the addition of urea on the viscosity of MEGA-10 and OTG solutions. In the case of MEGA-10, the plots of the relative viscosity versus surfactant concentration (see Figure SI2 in the Supporting Information) present a linear dependence ($r > 0.998$), indicating that the micelles are approximately spherical or that they do not grow enough for the viscosity measurement to detect the growth.[66] This result indicates that very little change occurs in the micelle structure of MEGA-10 when urea is present. However, in the case of OTG the viscosity is not linear with surfactant concentration (see Figure 6), indicating micellar growth. The viscosity increases slightly at low surfactant concentration, but from a certain surfactant concentration the relative viscosity undergoes an abrupt increase. Higher viscosities correspond to larger micelles. This change in the relative viscosity is less pronounced in urea solution than in water. These results suggest the existence of a sphere to rodlike transition of the micelles of OTG. It is noteworthy that the presence of urea causes a shift of the surfactant concentration when the transition occurs, i.e., the urea provokes a retardation of the sphere to rodlike transition. In fact, Romsted et al.[38] have observed that the sphere to rodlike transition of tetradecyltrimethylammonium bromide (TTAB) micelles shifts to significantly higher concentrations in the

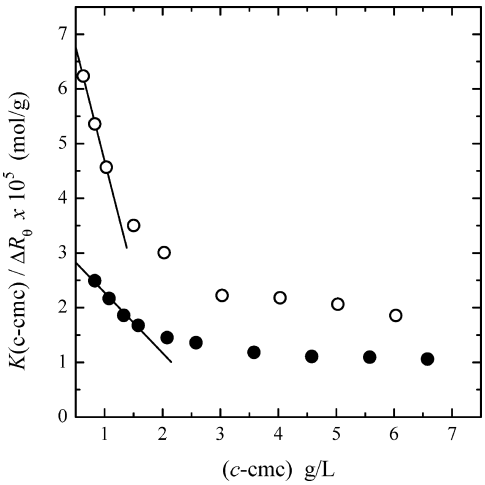



**Figure 7.** Debye plots for OTG micellar solutions in urea solutions: (●) 1 M and (○) 2 M.

presence of 3 M urea. Also, it has been observed that urea shifted to higher values the temperature where the transition from sphere to rodlike of $C_{12}E_6$ micelles occurs.[13] Definitively, our viscosity results indicate that urea induces a considerable reduction in the size of OTG micelles, shifting to higher concentration values the transition from sphere to rodlike.

The size of micelles is determined by two factors: the solvation degree and the mean micellar aggregation number. In order to examine the contribution of both factors, we have determined the mean micellar aggregation number, $N_{agg}$, by using two different experimental techniques: SLS and fluorescence static quenching. First of all, we have performed light scattering measurements of micellar solutions as a function of the surfactant concentration in media of different urea contents. From these experiments we have found two different behaviors. In the case of MEGA-10, the micellar system behaved as a noninteracting one, in such a way that eq 9 applies. In this case, the micellar molecular weight can be directly determined from the plot of the excess scattering ratio of the micelles, $\Delta R_\theta$, as a function of the surfactant concentration, as described in the Experimental Section. Our SLS results with MEGA-10, plotted according eq 9 (see Figure SI3 in the Supporting Information), showed an acceptable linearity ($r > 0.99$) and allows us to suggest that essentially the micellar molecular weight is independent of the surfactant concentration over the studied range. The $N_{agg}$ values obtained for MEGA-10 are listed in Table 1. As can be seen, only the presence of 3 M urea induces a significant reduction (around 17%) in $N_{agg}$.

In the case of OTG, due to the appearance of intermicellar interactions favored by the micellar growth, SLS results were treated according to eq 7. Figure 7 shows the so-called Debye plots, where a strong initial decrease with increasing surfactant concentration can be seen and then levels off at high concentrations. It must be pointed out that we found reproducibility problems with the experiments in 3 M urea, due to the high scattering of the medium compared with the small particles size. Data in Figure 7 shows an apparent linearity in the range of low surfactant concentration (where spherical micelles are present), from which we may infer that the micelle growth is promoted by the increase in surfactant concentration above a certain value. From this point, the monomers associate in larger micelles and the profile deviates downward from a straight line.[53] Linear regression analysis of the initial part of the data in Figure 7 (assuming that $P(\theta) = 1$) was used to estimate the micellar molecular weight of OTG micelles in the respective urea concentrations. The calculated values are listed in Table 1. It is noteworthy that $N_{agg}$ decreases around 68% in 2 M urea. In comparing both surfactants, the relative insensitivity of the MEGA-10 micelle aggregation number to the urea concentration is in contrast with the significant reduction for OTG.

Alternatively, we have also determined the $N_{agg}$ values by using the well-established steady-state fluorescence quenching method.[56] In these experiments, pyrene was used as a luminescence probe and CPyC as a quencher, and the results were analyzed by using the following equation:

$$\ln \frac{I_0}{I} = \frac{N_{agg}}{c - \mathrm{cmc}}[\mathrm{Q}] \tag{11}$$

where $I_0$ and $I$ are the fluorescence intensities in the absence and presence of quencher, respectively, $c$ is the total surfactant concentration, and [Q] is the quencher concentration. We have plotted our quenching results according to eq 11 (Figure SI4, in the Supporting Information, shows some representative plots obtained in the quenching studies). From the slope of these plots, and using the corresponding cmc values, we have determined the mean aggregation numbers of micelles, which are listed in Table 1. With regards to data of $N_{agg}$ presented in Table 1, an excellent concordance between the values obtained by both experimental techniques in the case of MEGA-10 can be observed. However, the agreement is rather poor for OTG. It should be pointed out that the $N_{agg}$ values for MEGA-10 in water agree well with those previously reported in the literature.[55] In the case of OTG, only the $N_{agg}$ value in water determined by SLS is in good agreement with that previously obtained by Frindi et al.[67] It seems reasonable to think that in water and at low urea concentration (1 M) the OTG micelles are very large and the static quenching method provides underestimated values. On the other hand, as previously mentioned, our light scattering experiments at high urea concentrations were little reproducible. This fact is clearly due to the strong reduction in the micellar size of OTG accompanied with the increasing scattering of the medium at 2 and 3 M urea. In addition, it seems obvious that the reduction observed in $N_{agg}$ for 2 M urea (from 114 to 37, around 68%) is not consistent with that observed for $R_H^0$ (around 29%) at the same urea concentration. For all these reasons, we decided to adopt as acceptable the $N_{agg}$ values obtained by SLS in water and 1 M of urea and those obtained by the quenching method for 2 and 3 M urea. In any case, we can conclude that the reduction observed in $N_{agg}$ for OTG is much more significant than for MEGA-10, in good agreement with our observations from DLS and viscosity measurements.

On the other hand, if we assume a spherical geometry, it is possible to estimate the "dry" micelle radius, $R_0$, from the "dry" micellar volume, $V_0$, which can be obtained from the relationship:

$$V_0 = \frac{\upsilon M_w}{N_A} \tag{12}$$

where $\upsilon$ is the partial specific volume of micelle which can be determined from density measurements. For this purpose, we have carried out density measurements of MEGA-10 and OTG micellar solutions of varying surfactant concentrations in media of different urea concentrations (see Figure SI5 in the Supporting Information). The $R_0$ values calculated are presented in Table 1. As can be seen, for both surfactants the "dry" micellar size becomes smaller with increasing urea concentration, this reduction again being more pronounced in the case of OTG micelles. Finally, in Table 1 are also listed the estimated values of the surface area per headgroup, $a_0$, which is the most important

controlling factor for micelle size.[68] According to Israelachvili,[68] an increase in $a_0$ will lead to an increased stability of a spherical shape but to a destabilization of a planar arrangement of the surfactant molecule. In such spherical arrangement, the packing of the surfactant molecules can be less dense as a consequence of the higher headgroup area. From data in Table 1, an interesting aspect is that the value of $a_0$ increases in the presence of urea in the case of OTG, whereas it decreases for MEGA-10. These results suggest that the micellar solvation layers of both micellar systems are affected in a different way by the presence of urea in the medium.

It is to be pointed out that previous studies revealed a similar behavior to that observed in the case of OTG, that is, an increase of $a_0$ with the urea concentration, in both ionic[24,25] and nonionic micelles.[13] In these cases, this fact was considered as an indication of the participation of urea in micellar solvation layer, contributing to the solvation of the headgroups of the surfactant and, therefore, acting through a direct mechanism. In this sense, it was assumed that as a urea molecule is larger than a water molecule, replacing of water molecules by urea molecules would cause an increase in the surface area per headgroup. However, it must be recognized that our results for OTG can be also interpreted on the basis of an enhanced solvation of the headgroups of the surfactant induced by the presence of urea but without the participation of the additive in the micellar solvation layer, in agreement with recent observations performed by Politi and co-workers[37,38] and by Raghuraman et al.[39] However, it is evident that neither of the two mechanisms can be invoked in the case of MEGA-10. This fact suggests that the urea action mechanism is not only due to the intrinsic properties of this substance, but rather it also depends on the characteristics of the surfactant and, mainly, of those of its headgroup. If we assume that the role of urea is the enhancement of the hydrophilic properties of water, resulting in more strongly solvated polar headgroup of monomers in the micelle,[37−39] this mechanism should operate in all cases. Nevertheless, if the urea action consists in the replacement of water molecules in the micellar hydration shell, this mechanism should be dependent on both the strength of the hydration of the headgroups and of the rigidity of these groups, as this would control the penetration of urea molecules in the micellar solvation layer. As previously mentioned, we have observed that the different behaviors of OTG and MEGA-10 against temperature could be related with the stronger hydration and a minor rigidity of the sugar head of MEGA-10 as compared with OTG. From this view, the observed differences of the urea effect on the structure of MEGA-10 and OTG could be explained on the basis of these same points. Indeed, in the case of OTG, having a weaker hydration and a major rigidity, it is plausible to assume that some water molecules can be replaced by urea molecules inducing a thicker solvation layer and, hence, a greater surface area per headgroup. In the case of MEGA-10, two aspects would oppose to the direct mechanism: on the one hand, the accessibility of urea molecules to the solvation layer should be impeded by the tighter packing of the headgroups and, on the other, the replacement of water molecules for some urea ones should be hindered by the stronger hydration of the headgroups.

**Effect of Urea on Microenvironmental Properties.** Additional information about the effect of urea can be obtained through alterations in the microstructure of micelles revealed by changes in two important microenvironmental properties: micropolarity and microviscosity. To check possible modifications of these properties induced by the urea addition, we have carried out studies based on the fluorescence probe technique by using probe molecules with different character and luminescence properties. First of all, to examine the effect of urea in the inner micellar region, two hydrophobic probes such as pyrene and C6 were used. We performed measurements of the pyrene 1:3 ratio index and steady-state fluorescence anisotropy ($r_{ss}$) of C6 in micellar solutions at surfactant concentrations well above the cmc (20 mM). In both cases no significant changes were observed. The main conclusion attained by these studies, of which a detailed description is given in the Supporting Information, is that the microstructure of the inner region of micelles of OTG and MEGA-10 is not affected by the presence of urea in the medium.

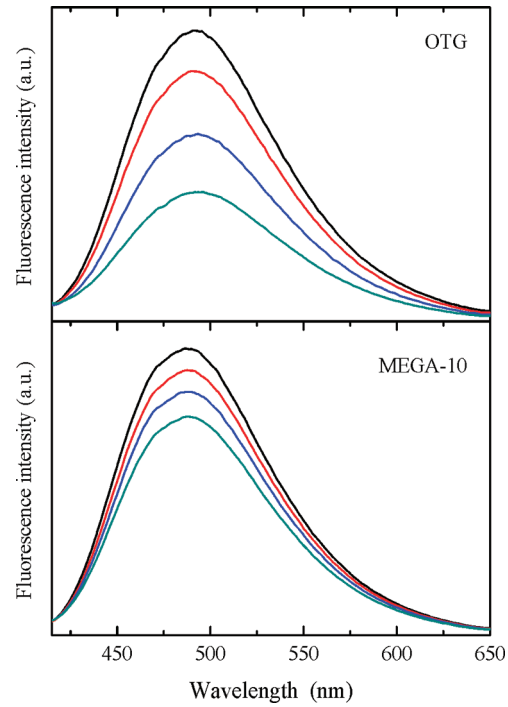



**Figure 8.** Fluorescence spectra of ANS in micellar media at different urea concentrations: water (black), 1 M urea (red), 2 M urea (blue), 3 M urea (green).

With the purpose of evaluating the effect of the urea addition on the micellar interface we have used a surface probe such as ANS. The spectral behavior of ANS is very interesting in the context of our study because its luminescence properties (emission maximum and fluorescence quantum yield) are very sensitive not only to the polarity but also to the viscosity around the probe.[69,70] In accordance with its molecular structure, it is expected that ANS binds to micelles in the surface region, where the nonpolar part of the ANS molecule would be submerged in the direction of the palisade layer while the sulfonate group projects outward and lies at the level of the polar headgroups of the micelle. When ANS molecules are transferred from a polar aqueous environment to the relatively nonpolar micellar microenvironment the reduction in polarity and the increase in viscosity leads to an increase of the emission quantum yield and lifetime. This behavior has been explained in terms of the twisted intramolecular charge-transfer (TICT) concept.[71,72] In contrast to C6, the fluorescence lifetime of ANS does change in a dramatic way with the polarity and viscosity of the medium. Therefore, we decided to study the behavior of this probe by using not only steady-state measurements but also time-resolved studies. Figure 8 shows the emission spectra of ANS solubilized in OTG and MEGA-10 micellar media. From this figure, two aspects can be observed: (i) the emission maximum, $\lambda_{max}$, is

**TABLE 2: Fluorescence Decay Parameters of ANS in OTG and MEGA-10 Micelles at Different Urea Concentrations**

| micellar media | urea (M) | $\alpha_1$ | $\tau_1$ (ns) | $\alpha_2$ | $\tau_2$ (ns) | $\langle\tau\rangle$ (ns) | $\chi^2$ |
|---|---|---|---|---|---|---|---|
| OTG | 0 | 0.19 | 1.32 | 0.81 | 3.36 | 3.19 | 1.03 |
| | 1 | 0.20 | 1.37 | 0.80 | 3.24 | 3.06 | 1.07 |
| | 2 | 0.31 | 1.58 | 0.69 | 3.33 | 3.02 | 1.11 |
| | 3 | 0.37 | 1.49 | 0.63 | 3.24 | 2.87 | 1.18 |
| MEGA-10 | 0 | 0.18 | 1.88 | 0.82 | 4.34 | 4.13 | 1.10 |
| | 1 | 0.16 | 1.58 | 0.84 | 4.12 | 3.95 | 1.11 |
| | 2 | 0.13 | 1.50 | 0.87 | 3.97 | 3.84 | 1.04 |
| | 3 | 0.13 | 1.41 | 0.87 | 3.90 | 3.77 | 1.11 |

not shifted with increasing urea concentration, but whereas in the case of OTG it is located to 492 nm, in the case of MEGA-10 it is close to 487 nm, and (ii) the fluorescence intensity is much more reduced in the case of OTG. The former indicates that the probe senses a more hydrophobic environment in the case of MEGA-10 (minor $\lambda_{max}$). However, the reduction in the fluorescence intensity with urea addition can be due to either an increase in the polarity sensed by the probe in the micelle or the result of the displacement of ANS molecules from the interfacial region to the bulk. In this respect, it is important to remember that it has been previously observed that urea can induce desolvation and removal of ANS,[31] and other related probes such as *p*-toluidino naphthalene sulfonate (TNS),[15] from the interfacial region of micelles decreasing the partitioning of the probe toward the micelles. Since time-resolved measurements can serve as a sensitive indicator of the local environment in which a probe molecule is solubilized, we carried out a time-resolved fluorescence study of ANS in OTG and MEGA-10 micellar media. (Figure SI6, in the Supporting Information, shows representative fluorescence decay profiles of ANS in MEGA-10 micellar solutions). Table 2 lists the obtained fluorescence lifetimes of micelle-bound ANS at various concentrations of urea. From data in Table 2, it is apparent that all fluorescence decay could be fitted well with a biexponential function. The appearance of multiple lifetimes for probes solubilized in microheterogeneous media is a usual observation[39,70] that should not necessarily be attributed to the existence of several populations. Rather, it could reveal the microenvironments experienced by the probe that are collectively reflected in more that one lifetime.[57] In our case, data in Table 2 indicate that the probe is partitioned between a relatively hydrophobic environment and the solvent-accessible region. In both micellar systems the major contribution corresponds to the hydrophobic region, given by a decay profile with the longest decay component ($\tau_2$) as revealed from the fraction of the each decay component. However, data in Table 2 indicate different tendencies in both micellar systems. Whereas in the case of OTG the predominant fraction decreases, a slight increase of this fraction is seen in the case of MEGA-10. In addition, the longest decay lifetimes are systematically higher in the MEGA-10 micelles, indicating a more hydrophobic environment sensed by the probe, in good agreement with the emission maximum values observed from the steady-state fluorescence spectra. The average lifetimes $\langle\tau\rangle$ listed in Table 2 were calculated using eq 3. A continuous decrease of $\langle\tau\rangle$ with increasing urea concentration is seen in both micellar media. Furthermore, the decreasing rate in both cases is similar, around 10% and 9% for OTG and MEGA-10, respectively, when urea concentration is increased from 0 to 3 M. It is to be noted that a similar behavior has been recently observed by Raghuraman et al.[39] by using different fluorescent probes to examine the effect of urea on Triton X-100 micelles.

Table 3 shows the steady-state fluorescence anisotropy of ANS solubilized in OTG and MEGA-10 micelles with increasing urea concentrations. In the case of OTG, a steady reduction of the anisotropy with the urea concentration is observed, indicating that the rotational diffusion of ANS is increased in the presence of urea. However, in the case of MEGA-10, the anisotropy remains rather constant. To check the effect of the change of the ANS lifetime on the steady-state fluorescence anisotropy, we determined the apparent rotational correlation times for the probe in micellar media, $\tau_c$, by using the Perrin's equation:[57]

**TABLE 3: Steady-State Anisotropy and Rotational Correlation Times of ANS in OTG and MEGA-10 Micelles as a Function of Urea Concentration**

| micellar media | urea (M) | $r_{ss}$[a] | $\tau_c$ (ns) |
|---|---|---|---|
| OTG | 0 | $0.123 \pm 0.003$ | 1.85 |
| | 1 | $0.110 \pm 0.002$ | 1.50 |
| | 2 | $0.103 \pm 0.004$ | 1.34 |
| | 3 | $0.098 \pm 0.002$ | 1.19 |
| MEGA-10 | 0 | $0.100 \pm 0.005$ | 1.76 |
| | 1 | $0.099 \pm 0.004$ | 1.66 |
| | 2 | $0.100 \pm 0.002$ | 1.63 |
| | 3 | $0.106 \pm 0.004$ | 1.75 |

[a] Mean value ± standard deviation of three individual measurements.

$$\tau_c = \frac{\langle\tau\rangle r_{ss}}{r_0 - r_{ss}} \tag{13}$$

where $r_0$ is the limiting anisotropy of ANS and $r_{ss}$ and $\langle\tau\rangle$ have their usual meaning. It has been previously established that although Perrin's equation is not strictly applicable to these systems, it can be assumed as an acceptable approximation if the average fluorescence lifetime is used to determine $\tau_c$.[39] In addition, it can be argued that as the micellized ANS contributes to the fluorescence intensity signals overwhelmingly, the steady-state anisotropy computed from steady-state fluorescence intensity signals could adequately reflect the constraint experienced by the probe within the micelle. The values of $\tau_c$ calculated by using a value of $r_0$ of 0.335[70] are listed in Table 3. From data in Table 3, it is observed that there is a decrease in $\tau_c$ values for OTG, suggesting a less tight environment as the urea concentration increases. However, in the case of MEGA-10, it seems that the $\tau_c$ value remains constant within the experimental error. Again, one can observe different behaviors for both micellar systems. Data in Table 3, and also those shown in Table 2 and Figure 8, can be interpreted in the sense that the micellar interface of OTG is much more affected by the presence of urea in the medium than that of MEGA-10, in good agreement with our results discussed in previous sections. Again, we think that this different behavior can be explained considering the characteristics of the headgroups of OTG and MEGA-10. If we take into account that the OTG headgroups are more rigid and less strongly hydrated than those of MEGA-10, we can assume that the solvation layer of OTG is more vulnerable to the urea effects. Although with quantitative differences, we have found that in both micellar systems an increase of polarity in the micellar interface occurs (minor fluorescence intensity and lifetime) as the urea concentration increases. This can be due to increased water penetration in micelles. In addition, the fact that OTG micelles become a more open structure as the urea concentration increases could favor the concomitant penetration of some urea molecules into the micellar solvation layer of OTG, according to a direct mechanism. Note that this view is consistent with the increase in the

surface area per headgroup of OTG with increasing urea concentration, as previously discussed.

## Conclusions

A comparative study on the effect of urea on the aggregation behavior of OTG and MEGA-10 has been carried out. Our results indicate that the cmc's of both surfactants increase similarly with the urea concentration, which has been interpreted invoking two effects: the enhancement of the solubility of hydrocarbon tails and the increase of solvation of the headgroup of the surfactants in the presence of urea. The structural study revealed that urea induces a reduction in the micellar size of both surfactants. However, the effect is much more pronounced in the case of OTG. In addition, the observed changes in the surface area per headgroup suggest that different urea action mechanisms operate in both cases. Whereas for OTG a direct mechanism seems to explain the observed behavior, the participation of urea in the micellar solvation layer of MEGA-10 cannot be argued. Our studies based on the fluorescence probe technique support this same view, indicating a different behavior of both micellar systems. In general, an increase of polarity in the micellar interface is observed, more significant in the case of OTG, suggesting the formation of more permeated micelles in the presence of urea. Nevertheless, the increase of microviscosity observed in the micellar interface of OTG could be explained by assuming a certain participation of the additive in the micellar solvation layer. In summary, the present investigation shows that it is not adequate to tell, in general terms, of a direct or indirect mechanism to refer to the action of urea on micellization of surfactants, but it seems that this mechanism depends on the way in which solvation occurs in a specific micellar system.

**Acknowledgment.** This work has been financially supported by "Consejería de Innovación, Ciencia y Empresa de la Junta de Andalucía" (Project P07-FQM-02762).

**Supporting Information Available:** Six figures corresponding to cmc determination of OTG, relative viscosity of MEGA-10 vs surfactant concentration, excess scattering ratio vs surfactant concentration of MEGA-10, quenching plots in MEGA-10 micellar solutions, plots of density of micellar solutions vs concentration, and representative fluorescence decay profiles of ANS in MEGA-10 micellar solutions, and also a detailed discussion on the microviscosity and micropolarity of micelles in the inner micellar region. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) De Lisi, R.; Milioto, S. *Chem. Soc. Rev.* **1994**, *23*, 67.
(2) Myers, D. *Surfactants Science and Technology*, 2nd ed.; VCH: New York, 1992.
(3) Creighton, T. E. *Proteins: Structures and Molecular Principles*; Freeman: New York, 1993; Chapter 7.
(4) Kresheck, G. C.; Scheraga, H. A. *J. Phys. Chem.* **1965**, *69*, 1704.
(5) MacDonald, J. C.; Serpilis, J.; Guerreva, J. J. *J. Phys. Chem.* **1973**, *77*, 370.
(6) Herskovits, T. T.; Kelly, T. M. *J. Phys. Chem.* **1973**, *77*, 381.
(7) Manabe, M.; Koda, M.; Shirahama, K. *J. Colloid Interface Sci.* **1980**, *77*, 189.
(8) Carvalho, B. L.; Briganti, G.; Chen, S.-H. *J. Phys. Chem.* **1989**, *93*, 4282.
(9) Das Gupta, P. K.; Moulik, S. P. *Colloid Polym. Sci.* **1989**, *267*, 246.
(10) Han, S. K.; Lee, S. M.; Kim, M.; Schott, H. *J. Colloid Interface Sci.* **1989**, *132*, 444.
(11) Baglioni, P.; Ferroni, E.; Kevan, L. *J. Phys. Chem.* **1990**, *94*, 4296.
(12) Baglioni, P.; Rivara-Minten, E.; Dei, L.; Ferroni, E. *J. Phys. Chem.* **1990**, *94*, 8218.
(13) Briganti, G.; Puvvada, S.; Blankschtein, D. *J. Phys. Chem.* **1991**, *95*, 8989 and references therein.
(14) Baglioni, P.; Dei, L.; Ferroni, E.; Kevan, L. *Prog. Colloid Polym. Sci.* **1991**, *84*, 55.
(15) Sarkar, N.; Bhattacharyya, K. *Chem. Phys. Lett.* **1991**, *180*, 283.
(16) Causi, S.; De Lisi, R.; Milioto, S.; Tirone, N. *J. Phys. Chem.* **1991**, *95*, 5664.
(17) Caponetti, S.; Causi, S.; De Lisi, R.; Floriano, M. A.; Milioto, S.; Triolo, R. *J. Phys. Chem.* **1992**, *96*, 4950.
(18) Kang, Y. S.; McManus, J. D.; Kevan, L. *J. Phys. Chem.* **1992**, *96*, 10049.
(19) Kang, Y. S.; McManus, J. D.; Kevan, L. *J. Phys. Chem.* **1992**, *96*, 10055.
(20) Calvaruso, G.; Cavasino, F. P.; Sbriziolo, C.; Liveri, M. L. T. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1373.
(21) Jha, R.; Ahluwalia, J. C. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3465.
(22) Kundu, S.; Chattopadhyay, N. *Chem. Phys. Lett.* **1994**, *228*, 79.
(23) Carnero Ruiz, C.; Garcia Sanchez, F. *J. Colloid Interface Sci.* **1994**, *165*, 110.
(24) Carnero Ruiz, C. *Mol. Phys.* **1995**, *86*, 535.
(25) Carnero Ruiz, C. *Colloid Polym. Sci.* **1995**, *273*, 1033.
(26) Briganti, G.; Bonicontro, A. *Colloids Surf., A* **1995**, *103*, 105.
(27) Alexandridis, P.; Athanassiou, V.; Hatton, T. A. *Langmuir* **1995**, *11*, 2442.
(28) Asakawa, T.; Hashikawa, M.; Amada, K.; Miyagishi, S. *Langmuir* **1995**, *11*, 2376.
(29) Florenzano, F. H.; Cardoso dos Santos, L. G.; Cucovia, I. M.; Scarpa, M. V.; Chaimovich, H.; Politi, M. J. *Langmuir* **1996**, *12*, 1166.
(30) Abuin, E. B.; Lissi, E. A.; Borsarelli, C. *J. Colloid Interface Sci.,* **1996**, *184*, 652.
(31) Abuin, E. B.; Lissi, E. A.; Aspee, A.; Gonzalez, F. D.; Varas, J. M. *J. Colloid Interface Sci.* **1997**, *186*, 332.
(32) Shen, X.; Belletete, M.; Durocher, G. *J. Phys. Chem. B* **1997**, *101*, 8212.
(33) Hao, J.; Wang, T.; Shi, S.; Lu, R.; Wang, H. *Langmuir* **1997**, *13*, 1897.
(34) Carnero Ruiz, C. *Colloids Surf., A* **1999**, *147*, 349.
(35) Berberich, K. A.; Reinsborough, V. C. *Langmuir* **1999**, *15*, 966.
(36) Constantino, L.; D'Errico, G.; Roscigno, P.; Vitagliano, V. *J. Phys. Chem. B* **2000**, *104*, 7326.
(37) Dias, L. G.; Florenzano, F. H.; Reed, W. F.; Baptista, M. S.; Souza, S. M. B.; Alvarez, E. B.; Chaimovich, H.; Cuccovia, I. M.; Amaral, C. L. C.; Brasil, C. R.; Romsted, L. S.; Politi, M. J. *Langmuir* **2002**, *18*, 319.
(38) Romsted, L. S.; Zhang, J.; Cuccovia, I. M.; Politi, M. J.; Chaimovich, H. *Langmuir* **2003**, *19*, 9179.
(39) Raghuraman, H.; Pradhan, S. K.; Chattopadhayay, A. *J. Phys. Chem. B* **2004**, *106*, 2489.
(40) Kumar, S.; Parveen, N.; Kabir-ud-Din, *J. Phys. Chem. B* **2004**, *108*, 9588.
(41) Roy, S.; Dey, J. *J. Colloid Interface Sci.* **2005**, *290*, 526.
(42) Kumar, S.; Sharma, D.; Ghosh, G.; Kabir-ud-Din, *Langmuir* **2005**, *21*, 9446.
(43) Kumar, S.; Sharma, D.; Ghosh, G.; Kabir-ud-Din, *Colloids Surf., A* **2005**, *264*, 203.
(44) Kuharsky, R. A.; Rossky, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 5786.
(45) Kuharsky, R. A.; Rossky, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 5794.
(46) Tanaka, H.; Touhara, H.; Nakanishi, K.; Watanabe, N. *J. Chem. Phys.* **1984**, *80*, 5170.
(47) Cristinziano, P.; Lelj, F.; Amodeo, P.; Barone, G.; Barone, V. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 621.
(48) Mizutani, Y.; Kamogawa, K.; Nakanishi, K. *J. Phys. Chem.* **1989**, *93*, 5650.
(49) Breslow, R.; Guo, T. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 167.
(50) Carnero Ruiz, C., Ed. *Sugar-Based Surfactants: Fundamentals and Applications*; Surfactant Science Series, Vol. 143; CRC Press: New York, 2008.
(51) Söderman, O.; Johansson, I. *Curr. Opin. Colloid Interface Sci.* **2000**, *4*, 391.
(52) Stubenrauch, C. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 160.
(53) Molina-Bolívar, J. A.; Aguiar, J.; Peula-García, J. M.; Carnero Ruiz, C. *J. Phys. Chem. B* **2004**, *108*, 12813.
(54) Molina-Bolívar, J. M.; Hierrezuelo, J. M.; Carnero Ruiz, C. *J. Phys. Chem. B* **2006**, *110*, 12089.
(55) Molina-Bolívar, J. A.; Hierrezuelo, J. M.; Carnero Ruiz, C. *J. Colloid Interface Sci.* **2007**, *313*, 656 and references therein.
(56) Turro, N. J.; Yekta, A. *J. Am. Chem. Soc.* **1978**, *100*, 5951.
(57) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 3rd ed.; Springer: New York, 2006.
(58) Cichocki, B.; Felderhof, B. U. *Phys. Rev. A* **1990**, *42*, 6024.

(59) Mazer, N. A. In *Dynamic Light Scattering: Applications of Photon Correlation Spectroscopy*; Pecora, R., Ed.; Plenum Press: New York, 1985; Chapter 8.
(60) Tontikakis, A.; Hilfiker, R. B.; Chu, B. *J. Colloid Interface Sci.* **1990**, *135*, 427.
(61) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039.
(62) Aguiar, J.; Carpena, P.; Molina-Bolívar, J. A.; Carnero Ruiz, C. *J. Colloid Interface Sci.* **2003**, *258*, 116.
(63) Larson, R. G. *The Structure and Rheology of Complex Fluids*; Oxford University Press: New York, 1999.
(64) Kohler, H. H.; Strnad, J. *J. Phys. Chem.* **1990**, *94*, 7628.
(65) Rehage, H.; Hoffman, H. *J. Phys. Chem.* **1988**, *92*, 4712.
(66) Shiloach, A.; Blankschtein, D. *Langmuir* **1998**, *14*, 7166.
(67) Frindi, M.; Michels, B.; Zana, R. *J. Phys. Chem.* **1992**, *96*, 8137.
(68) Israelachvili, J. N. In *Physics of Amphiphiles: Micelles, Vesicles, and Microemulsions*; Degiorgio, V., Corti, V., Eds.; North Holland: Amsterdam, The Netherlands, 1985; p 24.
(69) Thomas, J. K. *Chem. Rev.* **1980**, *80*, 283.
(70) Slavik, J. *Biochim. Biophys. Acta* **1982**, *694*, 1.
(71) Das, K.; Sarkar, N.; Nath, D.; Bhattacharyya, K. *Spectrochim. Acta* **1992**, *48A*, 1701.
(72) Bhattacharyya, K.; Chowdhury, M. *Chem. Rev.* **1993**, *93*, 507.

JP811198D