

## Effect of Urea and Alkylureas on Micelle Formation by a Nonionic Surfactant with Short Hydrophobic Tail at 25 °C

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The effect of urea, *N*-monomethylurea, and *N,N'*-dimethylurea on the micellization of the nonionic ethoxylated tenside pentaethyleneglycolmonohexyl ether ( $C_6E_5$ ) was investigated through intradiffusion coefficient measurements (Pulsed-gradient spin-echo-NMR method) at 25 °C. The presence of the additive causes, in all cases, an almost linear increase in the critical micellar composition (cmc), while a decrease in the aggregation number occurs. Furthermore, both the monomer–monomer and micelle–micelle interactions increase. The analysis of the intradiffusion coefficients shows the presence of additive molecules in the hydration shell of the tenside, in both its monomeric and micellar forms. A comparison with the results obtained for the water–pentaethyleneglycol (PEG5)–urea or alkylurea systems suggests that the additive molecules are mainly positioned near the tenside ethoxylic chain. The number of alkylurea molecules in the solvation shell of each  $C_6E_5$  and PEG5 molecule was computed and commented. The experimental cmc values in water– $C_6E_5$ –urea mixtures are in quite good agreement with those predicted through a molecular thermodynamic model.

### Introduction

Urea and its derivatives are well-known denaturants of proteins,<sup>1,2</sup> because of their ability to weaken hydrophobic interactions in aqueous solution.<sup>3</sup> For the same reason, one expects that ureas may have a profound effect on the properties of micellar solutions, which are determined by a delicate balance of hydrophobic/hydrophilic interactions of surfactants with water.<sup>4,5</sup> Indeed, urea has been shown to increase the critical micellar concentration (cmc) of ionic<sup>6–8</sup> and nonionic<sup>9</sup> surfactants and decrease the mean micellar hydrodynamic radius of ionic micelles.<sup>10</sup>

Two different mechanisms for the urea action have been proposed: an indirect mechanism, whereby urea changes the structure of interfacial water surrounding the solute,<sup>11–13</sup> and a direct mechanism, whereby urea replaces some of the water molecules in the hydration shell of the solute.<sup>14–16</sup> The indirect mechanism has received most of the attention and has been widely accepted in the past. According to different authors,<sup>17–20</sup> urea acts as a “water-structure breaker”, destroying the long-range order characteristic of pure water and reducing the degree of water–water hydrogen bonding without replacing these interactions by strong urea–water hydrogen bonds. However, most of the experimental techniques used in these studies did not provide information at a molecular level, and conflicting interpretations of urea action have been proposed.<sup>21,22</sup> On the other hand, computer simulations<sup>23–26</sup> seem to indicate that urea has a negligible effect on water structure; at the same time, some studies using electron-spin resonance spectroscopy,<sup>27,28</sup> which have probed the system at a molecular level, show that urea mainly replaces some water molecules in the hydration shell around the solute. These findings seem to support the direct mechanism of urea action.

Briganti et al.<sup>29</sup> extensively studied the effect of urea on micellization of a nonionic ethoxylated surfactant with a long hydrophobic tail (hexaethylene glycol monododecyl ether,  $C_{12}E_6$ ). These authors interpreted surface-tension and light-scattering measurements in terms of a direct urea–surfactant interaction mechanism; they also compared the experimental results with those predicted through a molecular thermodynamic model they had previously developed,<sup>30</sup> showing good agreement.

Much less attention has been paid, in the past, to the effect of the alkylureas on the micellization of surfactants in aqueous solution. Contrary to urea, alkylureas are considered to be, to a different extent, water-structuring agents.<sup>31,32</sup> Nevertheless, they weaken the hydrophobic effect in aqueous solution.<sup>33</sup>

In this work the influence of urea (U), *N*-monomethylurea (MMU), and *N,N'*-dimethylurea (DMU) on the micellization of a nonionic ethoxylated tenside in heavy water is detected through the determination of the intradiffusion coefficients by the pulsed-gradient spin-echo (PGSE)-NMR technique and analyzed.

The aggregation process of the chosen tenside, pentaethylene glycol monohexyl ether ( $C_6E_5$ ), has been widely studied in our laboratory;<sup>34–36</sup>  $C_6E_5$  has a short hydrophobic chain so that its cmc value is high enough to allow an experimental study in the premicellar composition range.<sup>37,38</sup> The  $C_6E_5$  hydrophilic headgroup is a pentamer of the ethylene glycol (PEG5) whose thermodynamic and dynamic properties in aqueous solution were studied in the past.<sup>39,40</sup> In addition, in the present work, the ternary systems heavy water–PEG5–urea or alkylurea have been considered.

The experimental evidence reported in the present work support a model in which alkylureas replace several water molecules that solvate the tenside molecule, in both its monomeric and micellized states. In particular, intradiffusion coefficients furnished clear experimental evidence of direct alkylurea–

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surfactant interaction, allowing us to compute the number of alkylurea molecules in the solvation shell of each C<sub>6</sub>E<sub>5</sub> and PEG5 molecule.

Finally, the effect of urea on C<sub>6</sub>E<sub>5</sub> micellization has been compared with the theoretical prediction obtained through the molecular thermodynamic theory developed by Briganti et al.<sup>29</sup>

## Experimental Section

**Materials.** Pentaethylene glycol monohexyl ether (C<sub>6</sub>E<sub>5</sub>), a Bachem product with a declared purity of more than 99%, was used as received. Urea (U), a Sigma product with a declared purity of >99.9%; *N*-monomethylurea (MMU), a Sigma product with a declared purity of >99.9%; and *N,N'*-dimethylurea (DMU), a Sigma product with a declared purity of ~98%, were dried under vacuum in a desiccator containing P<sub>2</sub>O<sub>5</sub> and were used without further purification. Pentaethylene glycol (PEG5) was purchased from Aldrich and used as received. The solvent used was D<sub>2</sub>O, obtained from Sigma (>99.96% isotopic purity). All solutions were prepared by weight.

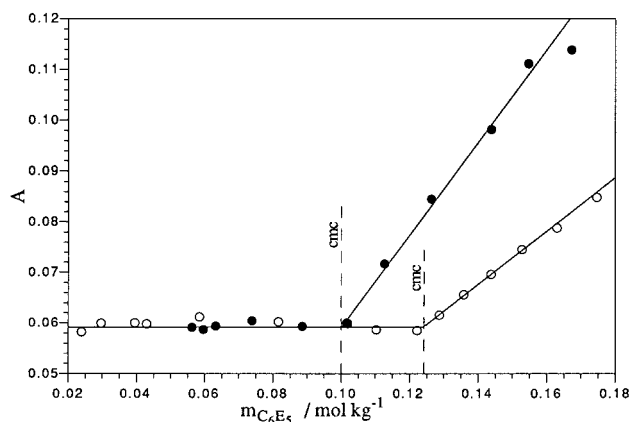
**Intradiffusion Measurements.** The intradiffusion coefficients were obtained by using the FT-PGSE-NMR technique.<sup>41,42</sup> A spectrometer operating in the <sup>1</sup>H mode at 80 MHz, and equipped with a pulsed magnetic field gradient unit, made by Stelar (Mede, Italy), was employed. The temperature was controlled to within 0.1 °C with a Stelar variable temperature controller, model VTC87. The individual spin-echo peak amplitude, *A*, for a given line, is given by the equation

$$A = A_0 \exp \left[ -\gamma^2 g^2 D_a \xi^2 \left( \Delta - \frac{\xi}{3} \right) \right] \quad (1)$$

where *A*<sub>0</sub> is a constant for a given set of experimental conditions,  $\gamma$  is the gyromagnetic ratio of the proton, *D*<sub>a</sub> is the intradiffusion coefficient of the species responsible for the NMR signal, *g* is the strength of the applied gradient, and  $\Delta$  and  $\xi$  are time parameters in the pulse sequence. The time between the 180° and 90° pulses,  $\Delta$ , was kept constant. The duration of the two gradient pulses,  $\xi$ , was varied over a suitable range to observe the decay of the spin-echo signal *A*. The above equation was fit by a nonlinear least-squares routine to the experimental decay of *A* as a function of  $\xi$ . To evaluate the intradiffusion coefficients, the *g* term must be known. Measurements to establish its value were performed on a reference sample with known intradiffusion coefficient; we used heavy water with trace amounts of light water (*D*<sub>HDO</sub> = 1.872 × 10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup>).<sup>43</sup> The errors on the experimental data were generally less than 2%.

The PGSE-NMR method allowed us to determine the C<sub>6</sub>E<sub>5</sub> and PEG5 intradiffusion coefficients by following the ethoxilic group signal intensities ( $\delta$  = 3.7). The MMU and DMU intradiffusion coefficients were measured using the methyl groups signal ( $\delta$  = 2.7). The urea intradiffusion coefficient was not determined because the proton exchange between the urea NH's and the water OH's is much faster than the single spin-echo sequence, and a unique urea-solvent signal ( $\delta$  = 4.7) could be detected in the D<sub>2</sub>O-C<sub>6</sub>E<sub>5</sub>-U and D<sub>2</sub>O-PEG5-U systems. Under these conditions, only a mean intradiffusion coefficient could be determined, *D*<sub>OH-NH</sub>, which is an average of the intradiffusion coefficients of all of the species containing OH or NH groups.

For the D<sub>2</sub>O-PEG5-alkylurea systems, the experimental *D*<sub>OH-NH</sub> value allowed us to compute *D*<sub>HDO</sub>, the intradiffusion coefficient of HDO molecules present in trace in D<sub>2</sub>O. *D*<sub>HDO</sub> is representative of solvent mobility in the considered mixtures.<sup>34,38</sup>



**Figure 1.** BAA absorbance at 315 nm vs C<sub>6</sub>E<sub>5</sub> molality: (●) D<sub>2</sub>O-C<sub>6</sub>E<sub>5</sub> binary system and (○) D<sub>2</sub>O-C<sub>6</sub>E<sub>5</sub>-DMU ternary system (*m*<sub>DMU</sub> = 1.040 mol kg<sup>-1</sup>).

As the D<sub>2</sub>O-PEG5-MMU system is considered, the following relation holds

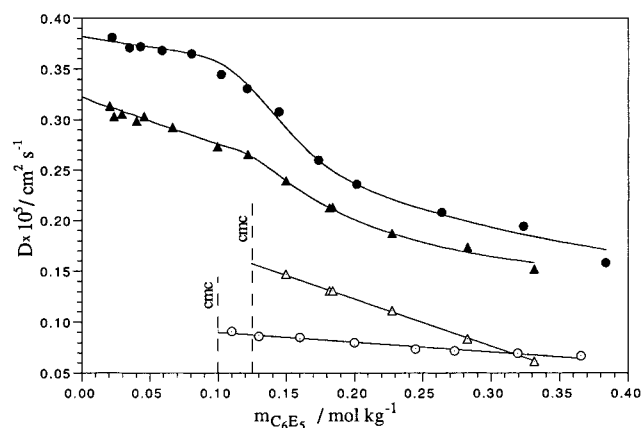
$$D_{\text{OH-NH}} = \frac{2 \times 55.5}{2 \times 55.5 + 2 \times m_{\text{PEG5}} + 3 \times m_{\text{MMU}}} D_{\text{HDO}} + \frac{2 \times m_{\text{PEG5}}}{2 \times 55.5 + 2 \times m_{\text{PEG5}} + 3 \times m_{\text{MMU}}} D_{\text{PEG5}} + \frac{3 \times m_{\text{MMU}}}{2 \times 55.5 + 2 \times m_{\text{PEG5}} + 3 \times m_{\text{MMU}}} D_{\text{MMU}} \quad (2)$$

The isotopic substitution of the solvent might result in an alteration of the structural properties of the micellar aggregates (cmc, aggregation number). In fact, D<sub>2</sub>O is thought to be slightly more structured than H<sub>2</sub>O.<sup>44</sup> Berr<sup>45</sup> showed that these differences are very small and become appreciable only for surfactants with long hydrophobic chains. Furthermore, no significant differences in behavior between H<sub>2</sub>O and D<sub>2</sub>O binary mixture with urea have been detected in the past.<sup>46</sup> Consequently, it is reasonable to assume that the micellization parameters in the systems under consideration are almost unaffected by the isotopic change of the solvent.

All of the experimental intradiffusion coefficients are collected in the tables provided in the Supporting Information.

**Absorption Spectrometry Measurements.** The surfactant cmc's in the binary system D<sub>2</sub>O-C<sub>6</sub>E<sub>5</sub> and in the ternary systems D<sub>2</sub>O-C<sub>6</sub>E<sub>5</sub>-U, D<sub>2</sub>O-C<sub>6</sub>E<sub>5</sub>-MMU, and D<sub>2</sub>O-C<sub>6</sub>E<sub>5</sub>-DMU were determined following the changes occurring in the absorption spectrum of *α*-benzoylacetanilide (BAA, an Aldrich product with a declared purity of 98%), which shows two peaks near 250 and 315 nm corresponding to the ketonic and enolic forms, respectively. As the percentage of the enolic form is much higher in an apolar environment, the absorbance at 315 nm strongly increases when the BAA molecules are solubilized into the micellar aggregates.<sup>47</sup> In this work, a D<sub>2</sub>O-C<sub>6</sub>E<sub>5</sub>-additive mixture, well above the surfactant cmc, was diluted with small amounts of D<sub>2</sub>O. Both the titrating and titrated solutions contained BAA in a very low and constant concentration (1.0 × 10<sup>-5</sup> mol kg<sup>-1</sup>). As the micellar concentration decreases, the absorbance at 315 nm diminishes, reaching an almost constant value in the premicellar composition range. The experimental results for the D<sub>2</sub>O-C<sub>6</sub>E<sub>5</sub> binary system and for the D<sub>2</sub>O-C<sub>6</sub>E<sub>5</sub>-DMU ternary system (*m*<sub>DMU</sub> = 1.040 mol kg<sup>-1</sup>) are shown in Figure 1.

The absorption measurements were made, in analogy with the intradiffusion measurements, using heavy water as solvent;



**Figure 2.** Intradiffusion coefficients vs  $C_6E_5$  molality: (●)  $D_{C_6E_5}$  and (○)  $D_{C_6E_5}^M$  in the binary  $D_2O$ – $C_6E_5$  mixtures and (▲)  $D_{C_6E_5}$  and (△)  $D_{C_6E_5}^M$  in the ternary  $D_2O$ – $C_6E_5$ –DMU mixtures ( $m_{DMU} = 1.040$  mol  $kg^{-1}$ ).

however, some measurements were repeated also in degassed and doubly distilled light water, with exactly the same results obtained.

**Viscosity and Density Measurements.** The viscosities of the system  $H_2O$ – $C_6E_5$ –DMU ( $m_{DMU} = 1.040$  mol  $kg^{-1}$ ) were determined to evaluate quantitatively the viscosity influence on the intradiffusion coefficient. Furthermore, the viscosity at the cmc of each considered system was measured in order to evaluate, through the Stokes–Einstein relation, the hydrodynamic radii of the micellar aggregates from their intradiffusion coefficients. The viscosity measurements were carried out with a Ubbelohde viscometer with a relatively long water flow time (203 s) to minimize the kinetic energy correction and to obtain more accurate data in the dilute range.

All measurements were carried out in a water bath (mgw Lauda CS) at  $25.000 \pm 0.005$  °C. At least 3 runs were carried out on each solution with times differing by no more than 0.05 s among them. The estimated error of our relative viscosity data is less than  $8 \times 10^{-4}$ . To evaluate the viscosities in heavy water from those measured in light water, the experimental data were multiplied by the  $\eta_{D_2O}^*/\eta_{H_2O}^* = 1.23$  ratio, where  $\eta_{D_2O}^*$  and  $\eta_{H_2O}^*$  are the viscosities of pure heavy and light water, respectively.

The density measurements necessary to compute the dynamic viscosity from the kinematic value were performed with an Anton Paar DMA 60 vibrating-tube densimeter operating at  $25.00 \pm 0.01$  °C, using distilled water and air (at measured pressure and humidity) for calibration.

## Results and Discussion

Both the  $C_6E_5$  premicellar and micellar composition ranges were considered. Different sets of measurements were made at constant urea or alkylurea molality, varying the  $C_6E_5$  molality. Five urea or alkylurea molalities were considered ( $\sim 0.1$ ,  $0.2$ ,  $0.4$ ,  $1.0$ , and  $2.0$  mol  $kg^{-1}$ ). Figure 2 shows, as an example, the surfactant intradiffusion coefficients for the  $D_2O$ – $C_6E_5$  binary system and the  $D_2O$ – $C_6E_5$ –DMU ternary system ( $m_{DMU} = 1.040$  mol  $kg^{-1}$ ).

The  $C_6E_5$  intradiffusion coefficients in the  $D_2O$ – $C_6E_5$  binary system and  $D_2O$ – $C_6E_5$ –urea or alkylurea ternary system present qualitatively similar trends: a slope change can be detected where the molecules start to aggregate, so that the cmc composition can be evaluated, although with a sensible experimental error.<sup>34</sup> The values obtained for the systems under consideration are almost coincident with the cmc evaluated

**TABLE 1: Tenside cmc in the  $D_2O$ – $C_6E_5$ –Urea or Alkylurea System<sup>a</sup>**

$m_U$ mol $kg^{-1}$	cmc mol $kg^{-1}$	$m_{MMU}$ mol $kg^{-1}$	cmc mol $kg^{-1}$	$m_{DMU}$ mol $kg^{-1}$	cmc mol $kg^{-1}$
0.1060	0.10	0.1252	0.10	0.1137	0.10
0.1603	0.10	0.3061	0.11	0.2967	0.11
0.3537	0.11	0.4054	0.11	0.4025	0.12
1.0490	0.11	0.4468	0.11	1.0401	0.13
1.7557	0.13	1.8825	0.14	2.0437	0.15
4.0623	0.16	3.9612	0.17	3.9980	0.18

<sup>a</sup> Evaluated through the spectrophotometric technique.

through the more accurate spectrophotometric technique. The cmc values are collected in Table 1.

In the premicellar composition range, a smooth decrease in the  $C_6E_5$  intradiffusion coefficient can be seen. Above the cmc, the presence of aggregates causes a sudden  $D_{C_6E_5}$  decrease; in this composition range, the experimental data are a mean value of free and micellized molecules.

$$D_{C_6E_5} = \frac{m_{C_6E_5}^F}{m_{C_6E_5}} D_{C_6E_5}^F + \frac{m_{C_6E_5}^M}{m_{C_6E_5}} D_{C_6E_5}^M \quad (3)$$

$D_{C_6E_5}^F$  is the intradiffusion coefficient of the molecules in the solution bulk;  $D_{C_6E_5}^M$  is the micelle intradiffusion coefficient;  $m_{C_6E_5}^F$  and  $m_{C_6E_5}^M$  are the molalities of free and micellized surfactant, respectively; and  $m_{C_6E_5}$  is the total surfactant molality in the system.

$D_{C_6E_5}^M$  was determined experimentally by the addition of tetramethylsilane (TMS, Sigma product, purity 99.9%) to the system. TMS is a strongly hydrophobic molecule and is solubilized only in the micellar core. By following its NMR signal, the micelle intradiffusion coefficient can be measured directly.<sup>48</sup> To be sure that the TMS insertion does not change the shape and dimension of the micelles, two measurements were performed for each solution, before and after the TMS addition, to verify that the surfactant intradiffusion coefficient was the same. For all samples, a single-exponential decay of the echo amplitude was observed for the TMS signal, signifying a nonappreciable polydispersity in the micelle's dimension.<sup>49</sup>

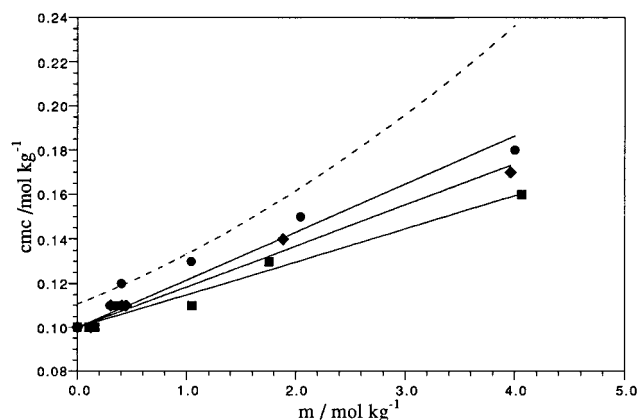
The effects of the urea and alkylurea presence in the system are the following: (i) the  $C_6E_5$  cmc value increases, confirming the trend already reported in the literature<sup>29</sup> concerning  $C_{12}E_6$ ; (ii)  $D_{C_6E_5}^M$  shows a tendency to assume higher values but, at the same time, the slope of its trend increases; and (iii) the  $D_{C_6E_5}$  premicellar slope increases, and the value extrapolated at infinite dilution,  $D_{C_6E_5}^\infty$ , changes. The extent of these effects depends on the additive molality in the system.

**Surfactant–Additive Interaction Mechanism.** The presence of urea or alkylurea in the system causes an almost linear increase of the  $C_6E_5$  cmc (Table 1 and Figure 3). Quantitatively, the effect of urea and alkylurea on the cmc values is small, considering the high concentration necessary to obtain an appreciable variation. U, MMU, and DMU have similar effects, in the following strength order:

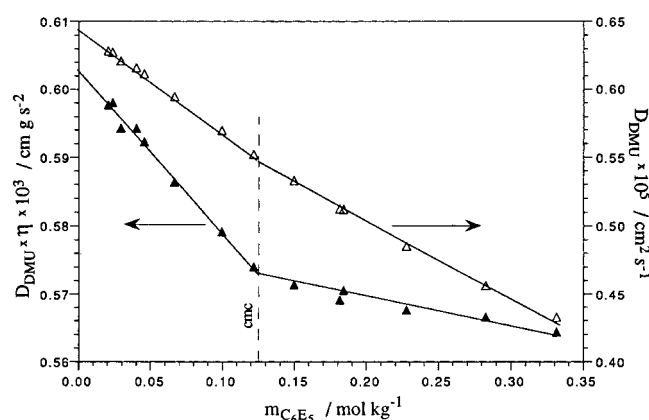
$$U < MMU < DMU$$

The change in the cmc value provides clear evidence that urea and alkylurea appreciably influence the hydrophobic effect that is the driving force of the micellization process, even if thermodynamic interpretations in terms of cmc changes alone have been shown to be uncertain.<sup>50</sup>

Because urea, which is a weak water-structure breaker, and the alkylureas, which are structure makers, show qualitatively



**Figure 3.** C<sub>6</sub>E<sub>5</sub> critical micellar composition vs additive composition in the ternary H<sub>2</sub>O–C<sub>6</sub>E<sub>5</sub>–urea or alkylurea mixtures: (■) H<sub>2</sub>O–C<sub>6</sub>E<sub>5</sub>–U system, (◆) H<sub>2</sub>O–C<sub>6</sub>E<sub>5</sub>–MMU system, and (●) H<sub>2</sub>O–C<sub>6</sub>E<sub>5</sub>–DMU system. The dashed line is the prediction of the molecular thermodynamic approach for the H<sub>2</sub>O–C<sub>6</sub>E<sub>5</sub>–U system.



**Figure 4.** DMU intradiffusion coefficients,  $D_{\text{DMU}}$ , and  $D_{\text{DMU}} \cdot \eta$  product vs C<sub>6</sub>E<sub>5</sub> molality in the ternary D<sub>2</sub>O–C<sub>6</sub>E<sub>5</sub>–DMU mixtures ( $m_{\text{DMU}} = 1.040 \text{ mol kg}^{-1}$ ).

**TABLE 2: Density and Viscosity Data for the H<sub>2</sub>O–C<sub>6</sub>E<sub>5</sub>–DMU System ( $m_{\text{DMU}} = 1.040 \text{ mol kg}^{-1}$ )**

$m_{\text{DMU}}$ mol kg <sup>-1</sup>	$d$ mol dm <sup>-3</sup>	$m_{\text{DMU}}$ mol kg <sup>-1</sup>	$\eta$ cp
0.0000	1.005350	0.0000	1.172
0.0396	1.006278	0.0476	1.199
0.0837	1.007170	0.0634	1.210
0.1278	1.007962	0.0828	1.230
0.1473	1.008321	0.1057	1.258
0.1924	1.008933	0.1269	1.280
0.2166	1.009658	0.1586	1.331
0.2486	1.010457	0.1903	1.379
0.2755	1.011068	0.2115	1.419
		0.2359	1.452
		0.2719	1.510

the same effects, the direct mechanism seems more reasonable in explaining the experimental results. The intradiffusion coefficient analysis clearly confirms this hypothesis.

The DMU intradiffusion coefficients,  $D_{\text{DMU}}$ , for the D<sub>2</sub>O–C<sub>6</sub>E<sub>5</sub>–DMU ternary system ( $m_{\text{DMU}} = 1.040 \text{ mol kg}^{-1}$ ) are reported in Figure 4 as a function of the C<sub>6</sub>E<sub>5</sub> molality. With increasing the tenside molality,  $D_{\text{DMU}}$  decreases. This behavior could, in principle, be imputed to the increasing viscosity of the system. To test this hypothesis, we measured the viscosities of the system H<sub>2</sub>O–C<sub>6</sub>E<sub>5</sub>–DMU ( $m_{\text{DMU}} = 1.040 \text{ mol kg}^{-1}$ , Table 2). Because diffusion and viscosity belong to different tensorial ranges, any correlation at the macroscopic level between them is incorrect according to the Curie's theorem.<sup>51,52</sup>

However, some information can be obtained by computing the  $D_{\text{DMU}} \cdot \eta$  product, which is also a decreasing function of the C<sub>6</sub>E<sub>5</sub> molality, as shown in Figure 4.

Furthermore, we estimated that  $D_{\text{DMU}}$  is weakly affected by the obstruction effect<sup>53</sup> because of the presence of the C<sub>6</sub>E<sub>5</sub> aggregates in the system (<5%). For these reasons, the decrease in the  $D_{\text{DMU}}$  trend can only be due to some DMU–tenside direct interactions.

In the premicellar composition range, the DMU intradiffusion coefficient is a mean value between the intradiffusion coefficient of the free DMU molecules present in the solution bulk,  $D_{\text{DMU}}^{\text{F}}$ , and that of the molecules involved in the solvation shell of the tenside molecules in their monomeric form,  $D_{\text{DMU}}^{\text{BF}}$ .<sup>54</sup>

$$D_{\text{DMU}} = p_{\text{DMU}}^{\text{F}} D_{\text{DMU}}^{\text{F}} + p_{\text{DMU}}^{\text{BF}} D_{\text{DMU}}^{\text{BF}} \quad (4)$$

where  $p_{\text{DMU}}^{\text{F}}$  is the fraction of free DMU molecules and  $p_{\text{DMU}}^{\text{BF}}$  is that of bound molecules.

$$p_{\text{DMU}}^{\text{BF}} = \frac{n_{\text{DMU}}^{\text{BF}} m_{\text{C}_6\text{E}_5}}{m_{\text{DMU}}} \quad p_{\text{DMU}}^{\text{F}} = 1 - p_{\text{DMU}}^{\text{BF}} \quad (5)$$

The superscript F refers to free additive molecules in the solution bulk, while BF refers to molecules involved in the solvation shell of the C<sub>6</sub>E<sub>5</sub> molecules in the premicellar composition range.  $n_{\text{DMU}}^{\text{BF}}$  is the number of DMU molecules coordinated to each tenside molecule; it was considered to be independent of the tenside molality.  $D_{\text{DMU}}^{\text{F}}$  was assumed to be equal to the intradiffusion coefficient measured in the binary system D<sub>2</sub>O–DMU, while  $D_{\text{DMU}}^{\text{BF}}$  coincides with the C<sub>6</sub>E<sub>5</sub> intradiffusion coefficient,  $D_{\text{C}_6\text{E}_5}$ . Substituting eq 5 into eq 4, one obtains

$$m_{\text{DMU}}(D_{\text{DMU}}^{\text{F}} - D_{\text{DMU}}) = n_{\text{DMU}}^{\text{BF}} m_{\text{C}_6\text{E}_5} (D_{\text{DMU}}^{\text{F}} - D_{\text{C}_6\text{E}_5}) \quad (6)$$

Hence,  $D_{\text{DMU}}^{\text{BF}}$  can be computed as the slope of  $m_{\text{DMU}}(D_{\text{DMU}}^{\text{F}} - D_{\text{DMU}})$  plotted as a function of  $m_{\text{C}_6\text{E}_5}(D_{\text{DMU}}^{\text{F}} - D_{\text{C}_6\text{E}_5})$ .

In the micellar composition range, a fraction  $p_{\text{DMU}}^{\text{BM}}$  of DMU molecules is bound to the micellized surfactant.

$$D_{\text{DMU}} = p_{\text{DMU}}^{\text{F}} D_{\text{DMU}}^{\text{F}} + p_{\text{DMU}}^{\text{BF}} D_{\text{DMU}}^{\text{BF}} + p_{\text{DMU}}^{\text{BM}} D_{\text{DMU}}^{\text{BM}} \quad (7)$$

$p_{\text{DMU}}^{\text{BF}}$  is the fraction of DMU molecules interacting with the monomeric surfactant. The superscripts BF and BM refer to additive molecules involved in the solvation shell of monomeric and micellized C<sub>6</sub>E<sub>5</sub> molecules in the micellar composition range, respectively.  $D_{\text{DMU}}^{\text{BF}}$  is the intradiffusion coefficient of the DMU molecules bound to the monomeric C<sub>6</sub>E<sub>5</sub>, considered to be coincident with the intradiffusion coefficient of the nonmicellized surfactant,  $D_{\text{C}_6\text{E}_5}^{\text{F}}$ ; in solutions where the micelles are not very concentrated, this coefficient can be assumed to be equal to that of the tenside at the cmc,  $D_{\text{C}_6\text{E}_5}^{\text{cmc}}$ .  $D_{\text{DMU}}^{\text{BM}}$  is the intradiffusion coefficient of the DMU molecules bound to the micellized C<sub>6</sub>E<sub>5</sub>, coincident with the micelle intradiffusion coefficient,  $D_{\text{C}_6\text{E}_5}^{\text{M}}$ .

The DMU molecule fractions can be written as

$$p_{\text{DMU}}^{\text{BF}} = \frac{n_{\text{DMU}}^{\text{BF}} m_{\text{C}_6\text{E}_5}^{\text{F}}}{m_{\text{DMU}}} \quad p_{\text{DMU}}^{\text{BM}} = \frac{n_{\text{DMU}}^{\text{BM}} m_{\text{C}_6\text{E}_5}^{\text{M}}}{m_{\text{DMU}}} \quad (8)$$

$$p_{\text{DMU}}^{\text{F}} = 1 - p_{\text{DMU}}^{\text{BF}} - p_{\text{DMU}}^{\text{BM}}$$

where  $n_{\text{DMU}}^{\text{BF}}$  is the number of DMU molecules bound to each C<sub>6</sub>E<sub>5</sub> monomer, as computed in the premicellar composition



**TABLE 3: Physicochemical Parameters Derived from Intradiffusion Data for the D<sub>2</sub>O–C<sub>6</sub>E<sub>5</sub>–Urea or Alkylurea Mixtures at 298.15 K**

$m_U$ mol kg <sup>-1</sup>	$n^{BF}$	$n^{BM}$	$D_{C_6E_5}^\infty \times 10^5$ cm <sup>2</sup> s <sup>-1</sup>	$\alpha$ kg mol <sup>-1</sup>	$D_{C_6E_5}^{M,cmc} \times 10^5$ cm <sup>2</sup> s <sup>-1</sup>	$k_d$ kg mol <sup>-1</sup>	$\eta^{cmc}$ kg s <sup>-1</sup> m <sup>-1</sup>	$R_{app}$ Å	$s$
U									
0.0000			0.382	−0.62	0.092	1.2	0.8904	18	
0.1060			0.392	−0.98	0.097	1.7	0.9010	17	
0.1603			0.398	−1.34	0.098	1.8	0.9090	17	
0.3537			0.421	−1.85	0.097	2.3	0.9409	15	
1.0490			0.426	−2.04	0.11	2.3	1.070	15	
1.7557			0.445	−2.48	0.10	1.7	1.123	14	
MMU									
0.1252	0.26	0.18	0.372	−0.82	0.098	1.5	0.9179	16	16
0.3061	0.33	0.28	0.354	−0.98	0.10	1.8	0.9614	17	19
0.4054	0.41	0.36	0.368	−1.46	0.099	1.7	0.9880	14	11
0.4468	1.5	0.51	0.361	−1.63	0.11	1.9	0.9960	13	9
1.8825	2.9	1.0	0.358	−2.41	0.10	1.9	1.320	12	7
DMU									
0.1137	0.11	0.06	0.380	−0.75	0.10	1.8	0.9330	16	16
0.1463	0.26	0.08	0.379	−0.77	0.10	1.6	0.9490	15	13
0.2967	0.35	0.18	0.366	−0.90	0.11	1.9	0.9980	13	8
0.4025	0.59	0.21	0.343	−1.25	0.12	1.5	1.039	13	8
1.0401	1.8	0.66	0.319	−1.38	0.13	2.6	1.293	11	5
2.0437	3.5	0.89	0.292	−2.36	0.12	2.4	1.632	10	4

range; and  $n_{DMU}^{BM}$  is the number of DMU molecules in the solvation shell of the micellized surfactant. By substituting eq 8 into eq 7, the following relation is obtained:

$$m_{DMU}(D_{DMU}^F - D_{DMU}) = n_{DMU}^{BF} cmc(D_{DMU}^{BF} - D_{C_6E_5}^{cmc}) + n_{DMU}^{BM}(m_{C_6E_5} - cmc)(D_{DMU}^F - D_{C_6E_5}^M) \quad (9)$$

$n_{DMU}^{BM}$  can be computed as the slope of  $m_{DMU}(D_{DMU}^F - D_{DMU})$  plotted as a function of  $(m_{C_6E_5} - cmc)(D_{DMU}^F - D_{C_6E_5}^M)$ .

The same treatment can be applied to the data at the various DMU molalities and for the D<sub>2</sub>O–C<sub>6</sub>E<sub>5</sub>–MMU systems. The lack of U intradiffusion data does not allow us to consider the D<sub>2</sub>O–C<sub>6</sub>E<sub>5</sub>–U systems. The obtained  $n_{MMU}^{BF}$ ,  $n_{DMU}^{BF}$ ,  $n_{MMU}^{BM}$ , and  $n_{DMU}^{BM}$  values are reported in Table 3. It can be seen that  $n_{DMU}^{BM}$  is lower than  $n_{DMU}^{BF}$ . This evidence can be imputed to the release of the DMU molecules bound to the hydrophobic tail as the surfactant molecules micellize; furthermore, the interactions among the ethoxylic chain in the micellar hydrophilic layer can also lead to the loss of some DMU molecules participating in the solvation shell of the surfactant headgroup. The MMU behavior is similar to that of DMU, even if it seems that the number of MMU molecules bound to the surfactant is slightly lower. Because urea and the alkylureas have similar effects on the micellization parameters, most probably the interaction mechanism is the same, i.e., urea molecules enter the solvation shell of the tenside, substituting some water molecules.

**Premicellar  $D_{C_6E_5}$  Trend.** In the composition range below the cmc, the following relation can be fit to the experimental intradiffusion coefficients:

$$D_{C_6E_5} = D_{C_6E_5}^\infty(1 + \alpha m_{C_6E_5}) \quad (10)$$

where  $D_{C_6E_5}^\infty$  is the C<sub>6</sub>E<sub>5</sub> intradiffusion coefficient extrapolated at infinite C<sub>6</sub>E<sub>5</sub> dilution and  $\alpha$  is an empirical fitting parameter. The  $D_{C_6E_5}^\infty$  and  $\alpha$  values for the considered systems are collected in Table 3.

The presence of U causes an increase of the  $D_{C_6E_5}^\infty$  values, whereas these values decrease upon the addition of MMU and DMU to the system (see Table 3). According to Berman and

Kirkwood's approach,<sup>55</sup> the  $D_{C_6E_5}^\infty$  value depends on the solvent–surfactant interactions. The presence of U in the solvation shell of the surfactant molecules has a destructuring effect on the icelike domains formed by water molecules surrounding the hydrophobic moieties of these solutes. For this reason, the microviscosity near the surfactant molecules decreases, leading to higher  $D_{C_6E_5}^\infty$  values. On the contrary, MMU and DMU have a structure-making effect on the aqueous medium. For this reason, the microviscosity near the surfactant molecules increases so that their limiting intradiffusion coefficient decreases.

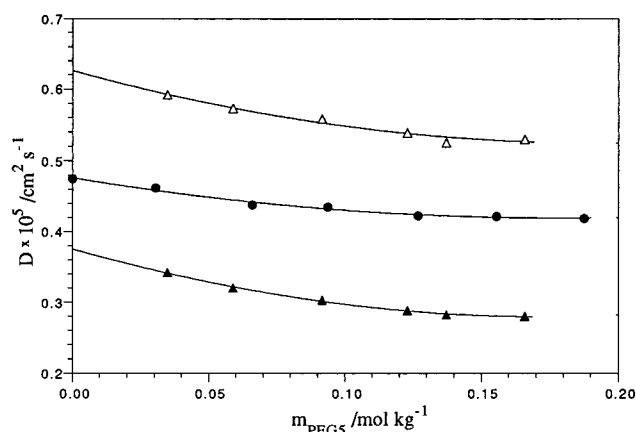
In the past, the  $\alpha$  value has been interpreted in terms of premicellar surfactant–surfactant interactions.<sup>38</sup> In our case, this increase cannot be due to some increasing hydrophobic interactions. In fact, a larger hydrophobic effect should lead to a lower cmc value, which is not the experimental evidence. Consequently, an increasing of the interactions among the surfactant hydrophilic heads, which correspond to pentamers of the ethylene glycol (PEG5), must be supposed. To test this hypothesis, the D<sub>2</sub>O–PEG5 binary system and the D<sub>2</sub>O–PEG5–U, D<sub>2</sub>O–PEG5–MMU, and D<sub>2</sub>O–PEG5–DMU ternary systems were studied. The PEG5 molality was varied within the range 0–0.2 m; for each additive, two sets of measurement were made, in which the additive molality was held constant (0.3 and 1 m).

A comparison between the surfactant intradiffusion coefficient in the D<sub>2</sub>O–PEG5 binary system and D<sub>2</sub>O–PEG5–DMU ternary system ( $m_{DMU} = 0.9852$  mol kg<sup>-1</sup>) is shown in Figure 5. The presence of DMU causes an evident changes in the  $D_{PEG5}$  values. In the considered composition range the PEG intradiffusion coefficient can be interpolated by the following empirical relation:

$$D_{PEG5} = D_{PEG5}^\infty(1 + \phi m_{C_6E_5} + \psi m_{C_6E_5}^2) \quad (11)$$

where  $D_{PEG5}^\infty$  is the PEG5 intradiffusion coefficient extrapolated at infinite dilution, while  $\phi$  and  $\psi$  are empirical fitting parameters. The  $D_{PEG5}^\infty$ ,  $\phi$ , and  $\psi$  values depend on the additive and its molality in the system; they are reported in Table 4.

The  $D_{PEG5}^\infty$  value increases in the presence of U and decreases in the presence of MMU and DMU. This behavior, as discussed concerning  $D_{C_6E_5}^\infty$ , is related to the structuring or



**Figure 5.** Intradiffusion coefficients vs PEG5 molality: (●)  $D_{\text{PEG5}}$  in the binary  $\text{D}_2\text{O}$ –PEG5 mixtures and (▲)  $D_{\text{PEG5}}$  and (△)  $D_{\text{DMU}}$  in the ternary  $\text{D}_2\text{O}$ –PEG5–DMU mixtures ( $m_{\text{DMU}} = 0.9852 \text{ mol kg}^{-1}$ ).

**TABLE 4: Fitting Parameters for the Intradiffusion Data in  $\text{D}_2\text{O}$ –PEG5–Urea or Alkylurea Mixtures at 298.15 K**

$m_{\text{additive}} / \text{mol kg}^{-1}$	$D_{\text{PEG5}}^\infty \times 10^5$	$\phi / \text{kg mol}^{-1}$	$\psi / \text{kg}^2 \text{mol}^{-2}$	$n^B$	$n_{\text{D}_2\text{O}}^B$
U					
0	0.475	−1.27	3.5		97
0.3125	0.492	−1.32	2.7		74
1.0141	0.515	−1.43	1.9		56
MMU					
0.2996	0.469	−1.57	4.2	0.39	81
1.0087	0.450	−1.80	4.3	1.4	68
DMU					
0.3056	0.449	−2.00	5.7	0.45	74
0.9652	0.377	−2.98	8.6	1.93	66

destructuring power of the additive on the aqueous medium. The increasing of the  $\phi$  value in the presence of U, MMU, and DMU should be due to the strengthening of the PEG5–PEG5 interactions.

Some studies are present in the literature concerning the effect of organic additives on solution properties of poly(ethylene glycol),<sup>56,57</sup> indicating that, in aqueous urea solutions, the ethoxylic chain is more extended. In this situation, the intramolecular interactions are substituted by intermolecular association, thus explaining the  $D_{\text{PEG5}}$  decrease.

For the  $\text{D}_2\text{O}$ –PEG5–MMU and  $\text{D}_2\text{O}$ –PEG5–DMU systems, the additive intradiffusion coefficients could be measured. The DMU intradiffusion coefficients in the  $\text{D}_2\text{O}$ –PEG5–DMU system ( $m_{\text{DMU}} = 0.9852 \text{ mol kg}^{-1}$ ) are shown in Figure 5.  $D_{\text{DMU}}$  is a mean value between the intradiffusion coefficient of the free molecules present in the solution bulk,  $D_{\text{DMU}}^F$ , and that of the molecules involved in the solvation shell of PEG5 molecules,  $D_{\text{DMU}}^B$ .

$$D_{\text{DMU}} = p_{\text{DMU}}^F D_{\text{DMU}}^F + p_{\text{DMU}}^B D_{\text{DMU}}^B \quad (12)$$

where  $p_{\text{DMU}}^F$  is the fraction of free DMU molecules and  $p_{\text{DMU}}^B$  is that of bound molecules.

$$p_{\text{DMU}}^B = \frac{n_{\text{DMU}}^B m_{\text{PEG5}}}{m_{\text{DMU}}} \quad p_{\text{DMU}}^F = 1 - p_{\text{DMU}}^B \quad (13)$$

$D_{\text{DMU}}^F$  is assumed to be equal to the intradiffusion coefficient measured in the binary system  $\text{D}_2\text{O}$ –DMU, while  $D_{\text{DMU}}^B$  is assumed to be equal to the PEG5 intradiffusion coefficient;  $n_{\text{DMU}}^B$  is the number of DMU's in the solvation shell of a

pentamer molecule. Substituting eq 13 into eq 12, one obtains

$$m_{\text{DMU}}(D_{\text{DMU}}^F - D_{\text{DMU}}) = n_{\text{DMU}}^B m_{\text{PEG5}}(D_{\text{DMU}}^F - D_{\text{DMU}}^B) \quad (14)$$

Hence,  $n_{\text{DMU}}^B$  can be computed as the slope of the trend of  $m_{\text{DMU}}(D_{\text{DMU}}^F - D_{\text{DMU}})$  plotted as a function of  $m_{\text{PEG5}}(D_{\text{DMU}}^F - D_{\text{DMU}}^B)$ . The same treatment can be applied to the data at the various DMU molalities and for the  $\text{D}_2\text{O}$ – $\text{C}_6\text{E}_5$ –MMU systems. The computed  $n_{\text{MMU}}^B$  and  $n_{\text{DMU}}^B$  values are reported in Table 4. They depend on the additive molality in the system, and  $n_{\text{MMU}}^B$  is lower than  $n_{\text{DMU}}^B$ .

The number of MMU and DMU molecules bound to a PEG5 molecule is similar to the number of additive molecules bound to the  $\text{C}_6\text{E}_5$  free molecule. As a consequence, it can be argued that the additive molecules bound to a free  $\text{C}_6\text{E}_5$  molecule are positioned near the surfactant headgroup, forming hydrogen bonds with the ether oxygens.

When  $\text{D}_2\text{O}$ –PEG5–DMU mixtures at constant DMU composition are considered, the solvent intradiffusion coefficient,  $D_{\text{HDO}}$ , allows us to estimate the number of solvent molecules present in the PEG5 solvation shell,  $n_{\text{D}_2\text{O}}^B$ , and the impact of the presence of the additive on this number.  $D_{\text{HDO}}$  is a mean value between the intradiffusion coefficient of the heavy water molecules in the heavy water–DMU solution bulk,  $D_{\text{HDO}}^F$ , and that of the molecules involved in the solvation shell of the PEG5 molecules,  $D_{\text{HDO}}^B$ .

$$D_{\text{HDO}} = p_{\text{D}_2\text{O}}^F D_{\text{HDO}}^F + p_{\text{D}_2\text{O}}^B D_{\text{HDO}}^B \quad (15)$$

where  $p_{\text{D}_2\text{O}}^F$  is the fraction of solvent molecules not involved in the PEG5 solvation shell and  $p_{\text{D}_2\text{O}}^B$  is that of solvent molecules directly interacting with PEG5.

$$p_{\text{D}_2\text{O}}^B = \frac{n_{\text{D}_2\text{O}}^B m_{\text{PEG5}}}{n_{\text{D}_2\text{O}}} \quad p_{\text{D}_2\text{O}}^F = 1 - p_{\text{D}_2\text{O}}^B \quad (16)$$

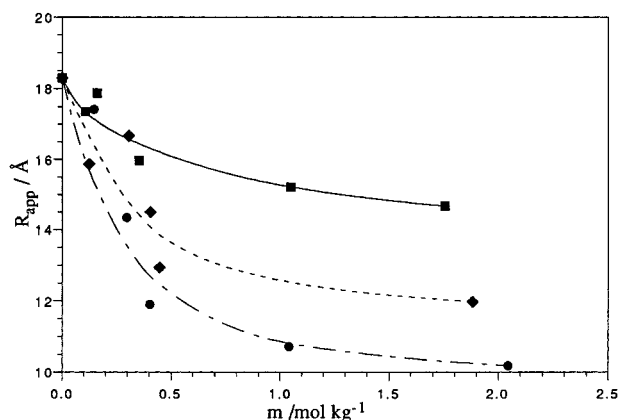
$D_{\text{HDO}}^F$  is assumed to be equal to the solvent intradiffusion coefficient measured in the binary system  $\text{D}_2\text{O}$ –DMU, while  $D_{\text{HDO}}^B$  is assumed to be equal to the PEG5 intradiffusion coefficient;  $n_{\text{D}_2\text{O}} = 49.9 \text{ mol}$  is the number of  $\text{D}_2\text{O}$  moles in 1000 g.

The  $n_{\text{D}_2\text{O}}^B$  values are collected in Table 4. The number of water molecules in the solvation shell of a PEG5 molecule was estimated to be nearly 100, i.e., 20 for each ethoxylic unit, in agreement with the value of 18 computed in the past for ethoxylated surfactants in the nonmicellized form;<sup>38</sup> this value is reduced by 30 or 40% because of the insertion of a MMU or DMU molecule, respectively.

**Hydrodynamic Dimension of the Micellar Aggregates.** The micellar intradiffusion coefficient, measured by following the NMR signal of the solubilized TMS, shows a linear dependence on the micellized tenside molality.

$$D_{\text{C}_6\text{E}_5}^M = D_{\text{C}_6\text{E}_5}^{\text{M.cmc}} [1 - k_d(m_{\text{C}_6\text{E}_5} - \text{cmc})] \quad (17)$$

$D_{\text{C}_6\text{E}_5}^M$  is the micellar intradiffusion coefficient extrapolated at the cmc, which represents the condition of micellar infinite dilution, and  $k_d$  is the intermicellar interaction parameter.<sup>58</sup> The computed  $D_{\text{C}_6\text{E}_5}^{\text{M.cmc}}$  and  $k_d$  values are collected in Table 3. It is possible to relate  $D_{\text{C}_6\text{E}_5}^{\text{M.cmc}}$  to the hydrodynamic size of the micellar aggregates using the Stokes–Einstein equation to



**Figure 6.**  $R_{app}$ , micelle apparent radius, vs urea or alkylurea molality: (■) in the ternary  $D_2O$ – $C_6E_5$ – $U$  mixtures, (◆) in the ternary  $D_2O$ – $C_6E_5$ – $MMU$  mixtures, and (●) in the ternary  $D_2O$ – $C_6E_5$ – $DMU$  mixtures.

calculate the apparent radius

$$D_{C_6E_5}^{M,cmc} = \frac{k_B T}{6\pi\eta^{cmc} R_{app}} \quad (18)$$

where  $k_B$  is the Boltzmann constant,  $T$  the absolute temperature, and  $\eta^{cmc}$  the viscosity of the medium, assumed to be that of the mixture at the cmc. The measured  $\eta^{cmc}$  and the computed  $R_{app}$  values are collected in Table 3. The presence of the additive in the system causes an  $R_{app}$  decrease in the order  $DMU > MMU > U$  (Figure 6). This evidence is in agreement with the results obtained by Briganti et al.<sup>29</sup> for the system water– $C_{12}E_6$ –urea. Baglioni et al.<sup>28</sup> interpreting ESR data, suggested that the urea molecules on the micellar hydrophilic layer decrease the surface tension, leading to the formation of smaller aggregates.

An attempt to evaluate the surfactant aggregation number from the apparent radius data was made. Assuming a spherical micelle, the aggregation number can be computed by the ratio between the experimental and calculated hydrodynamic volumes. For the  $D_2O$ – $C_6E_5$ – $DMU$  systems

$$s = \frac{(4/3)\pi R_{app}^3}{V_{C_6E_5}^M + n_{DMU}^{BM} V_{DMU} + n_{D_2O}^{BM} V_{D_2O}} \quad (19)$$

where  $V_{C_6E_5}^M = 309.75 \text{ cm}^3 \text{ mol}^{-1}$  is the volume of micellized  $C_6E_5$ ,<sup>37,39</sup> and  $V_{D_2O} = 18.04 \text{ cm}^3 \text{ mol}^{-1}$  and  $V_{DMU} = 76.48 \text{ cm}^3 \text{ mol}^{-1}$  ( $V_{MMU} = 62.41 \text{ cm}^3 \text{ mol}^{-1}$ ) are the volume of water and alkylurea<sup>59</sup> molecules, respectively. In a previous paper, we found that the ethoxylic head of  $C_6E_5$  in the micellized form is surrounded by 20 water molecules;<sup>39</sup> we assumed the percentage of water molecules removed from the hydration shell because of the insertion of an alkylurea molecule to be the same as that computed for PEG5 in aqueous solution.

The estimated aggregation numbers are collected in Table 3. Because, in the computation, the possibility that the same additive molecule participates in the solvation shell of two or more hydrophilic heads, thereby replacing a higher number of water molecules, is neglected, the obtained values could be underestimated. The presence of alkylurea in the system causes a decrease that is higher in the case of DMU.

The intermicellar interaction parameter,  $k_d$ , increases with additive molality. Urea and the alkylureas, favoring a more extended conformation of the ethoxylic chain, could enhance the interaction between micelles.

**TABLE 5: Critical Micellar Composition in  $H_2O$ – $C_6E_5$ –Urea Mixtures as Computed through the Blankschtein Approach at 298.15 K**

$m_U$ mol kg <sup>-1</sup>	cmc mol kg <sup>-1</sup>
0	0.134
0.1	0.139
0.2	0.139
0.4	0.141
1	0.151
2	0.162
4	0.192

**Prediction of the cmc through a Molecular Thermodynamic Model.** A prediction of micellar properties for surfactants with short hydrophobic tails, which form aggregates with loose structures and less extensive association behaviors,<sup>60,61</sup> is usually very difficult and often leads to unreasonable results. For this reason, we thought it interesting to test a molecular thermodynamic model proposed by Blankschtein et al.<sup>29,30,62</sup> as a predictive method to estimate the cmc of  $C_6E_5$  and its variation in the presence of urea and alkylureas.

The approach proposed by Blankschtein et al. blends a molecular model, describing the micellization process from a microscopic point of view, and a thermodynamic framework, which captures the salient features of the micellar solution at the macroscopic level.

The free energy of micellization, which represents the free energy change when a surfactant molecule is transferred from the aqueous medium to a micellar aggregate, is computed as the sum of the contributions of the different steps into which the process can be conceptually divided, and its knowledge allows the prediction of the cmc.

The values assumed for the free energy of micellization in the binary water– $C_6E_5$  and the ternary water– $C_6E_5$ – $U$  systems were computed as described in the original works by Briganti et al.<sup>29</sup> and Puvvada et al.<sup>30</sup>

These authors do not consider the carbon atom of the hydrophobic tail nearest to the hydrophilic head to be part of the micellar core. However, some of us, analyzing volumetric data, found that the change in the  $C_6E_5$  isothermal volume upon micellization is almost coincident with the volume change related to the transfer of a 1-hexanol molecule from water to the pure alcohol;<sup>34</sup> this is clear evidence that, for this surfactant with a short hydrophobic tail, the whole hydrocarbon chain participates in the micellar core formation. For this reason, while computing the cmc according to the Blankschtein's model, we considered the micellar hydrophobic core to be formed by all six carbon atoms of the surfactant tail.

The cmc values predicted for the considered systems are given in Table 5. The experimental and computed cmc values are compared in Figure 3. The molecular thermodynamic method furnishes a quite good estimation of cmc values in water–urea mixtures. However, the predicted values are systematically higher than the experimental ones, and the additive effect in increasing the tenside cmc is generally overestimated.

## Conclusions

The presence of urea or alkylurea causes an increase in the  $C_6E_5$  cmc in aqueous solution. The analysis of the isothermal intradiffusion coefficients in water–surfactant and water–surfactant–urea or alkylurea mixtures provides quite a great deal of information on the structure and behavior of these systems. Particularly, the micelle intradiffusion coefficients show that the aggregate radius diminishes. At the same time, the

alkylurea intradiffusion coefficients provide clear experimental evidence of the additive presence in the tenside solvation shell and allows a quantitative estimation of the number of additive molecules related to each tenside molecule.

The comparisons with the intradiffusion coefficients measured for the ternary systems water–pentaethylene glycol–urea or alkylurea show that the additive molecules are mainly located in the solvation shell of the surfactant hydrophilic head.

The experimental cmc's were compared with values predicted through a molecular thermodynamic model, and reasonable agreement was found.

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**Supporting Information Available:** Four tables containing intradiffusion coefficients in  $\text{D}_2\text{O}$ – $\text{C}_6\text{H}_5$ –U,  $\text{D}_2\text{O}$ – $\text{C}_6\text{H}_5$ –MMU,  $\text{D}_2\text{O}$ – $\text{C}_6\text{H}_5$ –DMU, and  $\text{D}_2\text{O}$ –PEG5–U,  $\text{D}_2\text{O}$ –PEG5–MMU,  $\text{D}_2\text{O}$ –PEG5–DMU mixtures at 298.15 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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