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## Study by Small-Angle Neutron Scattering of Sodium Dodecyl Sulfate Micelles with the Macrocyclic Ligand [2.2.2]Cryptand

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The addition of [2.2.2]cryptand (C222) to sodium dodecyl sulfate (SDS) micelles in aqueous solution is studied by small-angle neutron scattering (SANS). Hydrogenated and perdeuterated SDS micelles with 8% (wt/wt) concentration have been studied in the presence of 0.5, 1.0, and 1.5 mole ratio C222/surfactant. SANS analysis was performed using a two-shell model for the micelle form factor (core plus interfacial layer) and a screened Coulomb interactive potential for the interparticles potential. For both deuterated and hydrogenated surfactant, C222 ligand complexes the sodium micellar counterion and is mainly located at the interface partially screening the micelle surface charge. Counterion complexation produces, as compared to pure SDS micellar solutions, an increase of the interfacial layer thickness and a decrease of the micellar surface charge, of the contact potential, and of the average aggregation number. We report a detailed analysis of the micelle structure and intermicellar interaction potential.

### Introduction

The study of the binding of counterions and how they affect the structure of ionic micelles in aqueous solution has been extensively investigated.<sup>1</sup> Most of these studies follow two different approaches, chemical substitution of the surfactant counterion<sup>2</sup> or addition of specific counterion complexing molecules, such as macrocyclic ligands.<sup>3–7</sup> In this last case, the ligand affinity to complex counterions in solution seems to be the main driving force to significantly change the micellar microstructure and the intermicellar interactions. In particular, lithium dodecyl sulfate (LDS) micelles in aqueous solution<sup>3</sup> have been characterized in the presence of ligands of different type, crown ethers, cryptands, and CESTO molecules.<sup>4–5</sup> It is a general property that ionic micelles in water are partially charged because some counterions migrate from the interfacial shell to the bulk solution. In LDS micelles, some  $\text{SO}_4^-$  groups remain unscreened because of the migration of the  $\text{Li}^+$  ion toward the bulk water phase, resulting in a net surface charge at the micellar surface. The addition of crown ethers or cryptands leads to important changes in the micellar structure,<sup>4</sup> whereas the addition of the CESTO ligand, which is highly specific for lithium ion, gives consistent changes of the micellar structure.<sup>5</sup> In fact, CESTO counterion complexation at the micellar surface produces practically uncharged micelles with high micellar aggregation number and high ellipsoidal axial ratio.

This paper reports a small-angle neutron scattering (SANS) study of sodium dodecyl sulfate (SDS) micelles in water in the

presence of cryptand C222, which is a specific complexing agent for sodium with a complexing constant of 7000.<sup>8</sup> A previous study of SDS micelles in water with C222 gave preliminary results without being conclusive in relation to the question of whether the micelles are ellipsoidal or spherical and the location of the cryptand.<sup>9</sup> The used model (two-shell ellipsoidal micelle) gave axial ratios  $a/b$  (where  $a$  is the major axis and  $b$  is the minor axis) in the range 1.1–1.3, which indicates a slight ellipticity. The model of ellipsoids, in this case, can be equivalent<sup>10</sup> to that of polydisperse two-shell spheres. The purpose of the present paper is to better characterize the role of the C222 ligand in SDS aqueous micellar solutions. For this reason, C222 was added to the 8% (wt/wt) SDS micellar solution in C222/SDS = 0.5, 1.0, or 1.5 mole ratios. Moreover, to accurately study different regions of the system microstructure, the C222 location in the micellar system, and the consequent intermicellar interactions, two systems were investigated: (i) SDS micellar system with C222 as above-described and (ii) a similar system with deuterated surfactant tail (SDSD), both in deuterated water. These systems differ for the contrast. In system i the main contrast is between the solvent and the whole micelle, while in system ii, the contrast is between the interfacial region and the core or the solvent.

We have to point out that the deuteration of the surfactant tail implies an isotopic substitution of the hydrogen atoms in the surfactant molecules. In principle, this substitution might change the phase behavior of the micellar system as found for other self-assembled systems.<sup>11–13</sup> However, we expect that the structural changes due to the isotopic substitution are quite small because the system is quite far from any phase transition. Protonated SDS micelles in  $\text{D}_2\text{O}$  and deuterated SDS micelles in  $\text{H}_2\text{O}$  have been studied by SANS in ref 12 with a surfactant

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concentration of 2% (wt/wt). The micelle aggregation number and surface charge are 73.6 and 28 for the protonated surfactant micelles, whereas they are 68.1 and 24 for the deuterated surfactant micelles. These values lead to a ionization degree of 0.38 and 0.35 for protonated and deuterated micelles, respectively. The authors conclude that the effect of deuteration on the micellar structure was small as also previously found in ref 11 for the same micellar systems with added salt.

### Modeling Micelles

The micellar particle structure factor  $P(Q)$  has been modeled as a two-shell particle formed of a core containing most of the surfactant aliphatic chains and an interfacial layer containing the surfactant polar headgroups, some  $\text{CH}_2$  (or  $\text{CD}_2$ ) groups of the surfactant tail that are close to the polar head, the C222 ligand, and hydration water molecules. The interparticle structure factor  $S(Q)$  has been calculated assuming an analytical solution for the multicomponent ionic liquid with a mean spherical approximation (MMSA).<sup>14–18</sup> For the micellar system here investigated,  $S(Q)$  is the result of hard-sphere repulsion and screened Coulombic repulsion between micelles.<sup>19–23</sup> The multicomponent system was reduced to an effective one-component macroion (OCM) system<sup>24</sup> under the Gillan's condition.<sup>25</sup> A detailed description of the theoretical framework is reported in refs 5 and 23. According to theory, the total neutron cross section per unit volume of the sample can be written<sup>26</sup>

$$I(Q) = C_M N \left( \sum_i b_i - V_m \rho_S \right)^2 P(Q) S(Q) + I_{\text{back}} \quad (1)$$

where  $C_M = C - \text{cmc}$  represents the number of monomers aggregated in micelles ( $C$  is the surfactant concentration;  $\text{cmc}$  is the critical micellar concentration),  $N$  is the average aggregation number of a micelle,  $\sum_i b_i$  is the sum of the scattering length of all of the atoms in the monomer including the associated C222 molecules,  $V_m$  is the monomer volume,  $\rho_S$  is the scattering density of solvent,  $P(Q)$  is the normalized form factor,  $S(Q)$  is the structure factor, and  $I_{\text{back}}$  is the background term. For the hydrogenated surfactant, the monomer volume is defined by<sup>5</sup>  $V_m = V_{\text{SDS}} + N_L V_{\text{C222}}$ , where  $V_{\text{SDS}} = 414.6 \text{ \AA}^3$  is the dry volume of SDS<sup>6</sup> and  $V_{\text{C222}} = 567 \text{ \AA}^3$  is the volume of C222 with the complexed ion  $\text{Na}^+$ .<sup>6</sup> We point out that the sodium/cryptand complex has a volume equal to sodium plus cryptand because of the cryptand complexation process.<sup>8</sup>  $N_L$  is the mole fraction of ligand molecules for each polar head at the micellar interface. The scattering density of solvent,  $\rho_S$ , is given by the  $\text{D}_2\text{O}$  scattering length divided by the  $\text{D}_2\text{O}$  molecule volume. The term  $(\sum_i b_i - V_m \rho_S)$  represents the contrast, that is, the difference between the scattering length of the dry monomer above-defined and the solvent molecules of equivalent volume. We can define the scattering length density of the two parts of a micelle.  $\rho_1$  is the density of the hydrophobic core, which is equal to the total scattering length of the SDS tail divided by the tail volume,  $V_T$ .  $V_T$  is given by the Tanford empirical relationship,<sup>27</sup>  $V_T = (27.4 + 26.9N_C) \text{ \AA}^3$ , where  $N_C$  is the number of carbon atoms of a SDS molecule in the core.  $\rho_2$  is the scattering length density of the shell, which is given by the sum of the scattering lengths of the atoms in the shell divided by the shell volume,  $V_{\text{shell}}$ , and can be written as follows:

$$\rho_2 = \frac{N}{V_{\text{shell}}} [N_S b_{\text{D}_2\text{O}} + b_{\text{SO}_4^-} + N_L b_{\text{C222}} + (12 - N_C) b_{\text{CH}_2} + (1 - \alpha) b_{\text{Na}^+}]$$

where  $\alpha = Z/N$  is the fractional ionization and represents the number of free  $\text{Na}^+$  counterions surrounding each micelle (they do not belong to the interfacial layer),  $(1 - \alpha)$  is the number of  $\text{Na}^+$  ions per surfactant molecule in the micellar shell, and  $(12 - N_C)$  is the number of  $\text{CH}_2$  groups per surfactant molecule in the shell.  $N_S$  is the hydration number per surfactant molecule defined by<sup>5</sup>

$$N_S = \left[ \frac{V_{\text{shell}}}{N} - (V_m - V_T)(1 - \alpha) - (V_m - V_T - V_{\text{Na}^+})\alpha \right] \frac{1}{V_{\text{D}_2\text{O}}}$$

$V_{\text{Na}^+}$  is the volume of a dry sodium ion,  $9.1 \text{ \AA}^3$ .<sup>28</sup> For the deuterated surfactant, in the relationship of  $\rho_2$  the scattering length of the group  $\text{CD}_2$  substitutes that of the  $\text{CH}_2$  group. The macroion–macroion interaction effective potential<sup>21</sup> is

$$u(x) = V_1 \frac{\exp(-k(x-1))}{x}$$

for  $x > 1$ , where  $x = r/D$ ;  $r$  is the distance from the center of the micelle,  $D$  is the micelle diameter,  $k = k_D D$  is the screen constant where  $k_D$  is the inverse of the Debye length, and  $V_1$  is the contact potential, that is, the potential on the micellar surface ( $r = D$ ):

$$V_1 = \frac{(Ze)^2}{D\epsilon \left(1 + \frac{k}{2}\right)^2}$$

where  $e$  is the electronic charge,  $Z$  is the number of charges, and  $\epsilon = \epsilon_0 \epsilon_r$  is the product of dielectric constant of vacuum and the dielectric constant of solvent. The macroion structure factor was calculated using a revised version of the Hayter-Penfold's Fortran package.<sup>21</sup>

**(a) Ellipsoidal Model.** In this model, micelles are considered ellipsoidal in shape. The ellipsoidal core of the micelle has a shorter axis,  $b$ , equal to the length of the extended tail of a SDS molecule, which can be obtained by the empirical Tanford rule:<sup>27</sup>

$$b = 1.5 + 1.265N_C$$

The longer core axis of the micelle is indicated with  $a$ . The external shell around the core has a constant thickness  $d$ .

The form factor of the two-shell single particle is

$$F(Q, \mu) = f \frac{3j_1(u)}{u} + (1-f) \frac{3j_1(v)}{v} \quad (2)$$

where

$$\begin{aligned} u &= Q[\mu^2 a^2 + (1 - \mu^2) b^2]^{1/2} \\ v &= Q[\mu^2 (a+d)^2 + (1 - \mu^2) (b+d)^2]^{1/2} \\ \mu &= \cos \vartheta \\ f &= \frac{V_T (\rho_1 - \rho_2)}{\left( \sum_i b_i - V_m \rho_S \right)} \end{aligned}$$

where  $\vartheta$  is the angle between the direction of the  $Q$  vector and the longer symmetry axis ( $a$ ) of the ellipsoid and  $j_1(u)$  and  $j_1(v)$

are the first-order Bessel functions of argument  $u$  and  $v$ , respectively.

The overall form factor of a micelle must consider all of the possible orientations of the micelles; the form factor  $P(Q)$  in relationship 1 thus is<sup>10</sup>

$$P(Q) = \int_0^1 d\mu |F(Q,\mu)|^2 \quad (3)$$

The internal equivalent radius of a micelle is equal to hard core length  $R_{hc} = (ab^2)^{1/3}$ .

(b) **Polydispersed Spheres Model.** The micelles are considered as polydispersed spheres in the solution. The form factor  $P(Q)$  therefore is

$$P(Q) = \int_0^{\infty} f(R) |F(Q,R)|^2 dR \quad (4)$$

where  $f(R)$  is the normalized probability of a sphere having a total radius between  $R$  and  $R + dR$ .<sup>10</sup> The distribution that describes better the polydispersity in the micellar solutions is the Schulz distribution:<sup>10</sup>

$$f(R) = \left(\frac{z+1}{\bar{R}}\right)^{z+1} \frac{R^z}{\Gamma(z+1)} \exp\left(-\frac{z+1}{\bar{R}}R\right)$$

where  $\bar{R}$  is the average radius of the particle,  $\Gamma(z+1)$  is the gamma function, and  $z$  is the width parameter of the Schulz distribution ( $z > 0$ ).  $z$  is related to the value of polydispersity,  $\xi$ , of the system as follows:

$$\xi = \frac{1}{\sqrt{z+1}}$$

Within the two-shell micellar model, if  $R$  is the total radius of the micelle (core + shell) and  $pR$  is the core radius (where  $p$  is a real parameter with values  $0 < p < 1$ ), the form factor of single particle can be written<sup>29</sup>

$$F(Q,R) = p^3(\rho_1 - \rho_2)V F_0(QpR) + (\rho_2 - \rho_S)V F_0(QR) \quad (5)$$

where

$$F_0(QpR) = \frac{3j_1(QpR)}{QpR}$$

$$F_0(QR) = \frac{3j_1(QR)}{QR}$$

where  $V$  is the total volume of the micelle, and  $j_1$  is the first-order Bessel function. Assuming a Schulz distribution, the form factor of single particle is

$$\langle F(Q) \rangle = \int_0^{\infty} f(R) F(Q) dR = p^3(\rho_1 - \rho_2)V t_1(Qp\bar{R}) + (\rho_2 - \rho_S)V t_2(Q\bar{R})$$

while the overall micellar form factor  $P(Q)$  is<sup>29</sup>

$$P(Q) = p^6(\rho_1 - \rho_2)^2 V^2 t_2(Qp\bar{R}) + (\rho_2 - \rho_S)^2 V^2 t_2(Q\bar{R}) + 2(\rho_1 - \rho_2)(\rho_2 - \rho_S) V^2 t_3(Q\bar{R}, p) \quad (6)$$

The whole expression for the functions  $t_1$ ,  $t_2$ , and  $t_3$  is in ref 29.

The coherent scattered intensity for a system of polydispersed spheres is as follows:

$$I(Q) = \left(\frac{N}{V}\right) P(Q) [1 + \beta(Q)(S(Q) - 1)] \quad (7)$$

where

$$\beta(Q) = \frac{|\langle F(Q) \rangle|^2}{P(Q)}$$

(in the case of monodispersed spheres  $\beta = 1^{10}$ ).

## Experiments

**Materials.** SDS, obtained from Eastman Kodak, was recrystallized twice from a mixture of ethanol/diethyl ether 3:1 by volume, and dried under moderate vacuum at 40 °C. SDS was obtained from Isotec and cryptand C222 from Merck, both used as received. In ref 9, the chemical structure and a molecular model of the cryptand C222 molecule are reported. D<sub>2</sub>O was obtained from Carlo Erba.

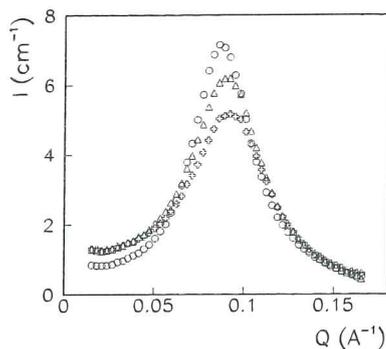
The micellar solution had approximately a surfactant concentration of 8% in weight fraction in D<sub>2</sub>O. The critical micelle concentration for the micellar solution is 8.1 mM. The addition of C222 cryptand to the surfactant micellar solution was in 0.5, 1.0, and 1.5 C222/surfactant molar ratios. The aqueous surfactant molar concentration was 0.265, 0.254, and 0.243 M for the hydrogenated SDS micellar solutions in the increasing order of C222/surfactant ratio. For the deuterated SDS micellar solutions, the molar concentration was 0.246, 0.236, and 0.227 M in the increasing C222/surfactant ratio. On the basis of the knowledge of the structural evolution of LDS and SDS micellar solutions as a function of the surfactant concentration,<sup>14,15</sup> the concentration differences for the deuterated and the hydrogenated systems are small enough to allow safe comparison for the two systems.

**Method.** The SANS experiments were performed at the small-angle spectrometer PAXE of the Laboratoire Léon Brillouin at Saclay (France). The distance between the sample and the detector was 2.5 m, and the incident neutron wavelength was 5 Å with wavelength spread  $\Delta\lambda/\lambda < \pm 5\%$ . The samples were contained in quartz cells and studied at constant temperature of  $25 \pm 0.1$  °C. The intensity was corrected for the empty cell contribution and normalized to absolute scale by means of a secondary standard of known cross section.

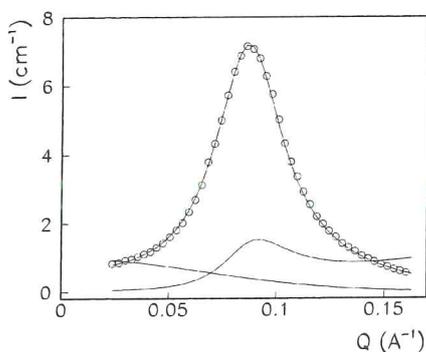
## Results

The experimental scattered neutron intensity,  $I$  (differential cross section per unit volume of the sample,  $\text{cm}^{-1}$ ), as a function of the scattering wave vector  $Q$  ( $\text{\AA}^{-1}$ ) has been analyzed for a surfactant concentration of 8% (wt/wt) in aqueous solution prepared as reported in previous paragraphs. We will report separately the results of the hydrogenated and deuterated micellar systems.

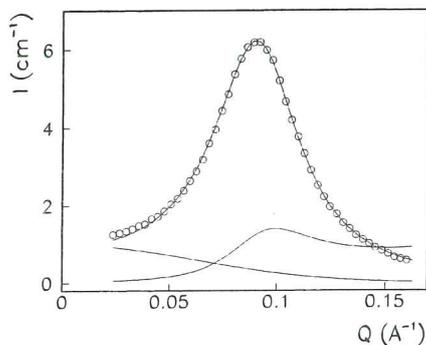
**Hydrogenated SDS Micelles.** In Figure 1, the experimental spectra of SDS micelles, with 8% (wt/wt) concentration, are shown for the cryptand/surfactant molar ratios 0.5, 1.0, and 1.5. The data analysis has been performed as above-reported assuming ellipsoidal particles. The fitted curves and the respective form factors and structure factors for each sample are shown in Figures 2–4. The values of the parameters obtained by the data analysis are reported in Table 1. The experimental spectra for the three C222/SDS ratios show a marked maximum that shifts to higher  $Q$  values and decreases in height as the ligand/surfactant ratio increases from 0.5 to 1.5. The model used to



**Figure 1.** Experimental scattered intensity by SDS aqueous micellar solutions with 8% (wt/wt) concentration for different C222/SDS mole ratios: (O) 0.5; ( $\Delta$ ) 1.0; (open crosses) 1.5. The experimental errors are smaller than the symbols used.

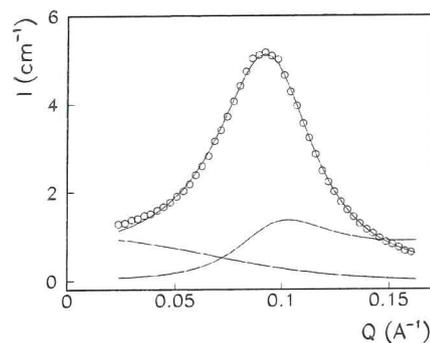


**Figure 2.** Experimental curve (O) and fitted curve (continuous line) of the 0.5 C222/SDS mole ratio spectrum of Figure 1. The normalized form factor and structure factor extracted from the fit to the data are reported. The vertical scale is dimensionless for the structure and form factors of all of the figures.



**Figure 3.** Experimental curve (O) and fitted curve (continuous line) of the 1.0 C222/SDS mole ratio spectrum of Figure 1. The normalized form and structure factors are also shown.

analyze the spectra contains six free fitting parameters: the micellar surface charge  $Z$ , the average aggregation number  $N$ , the thickness of the interfacial region  $d$ , the percentage of interfacial ligand molecules in relation to the total surfactant molecules  $N_L$ , the number of carbon atoms for a monomer in the core  $N_C$ , and the background parameter. These parameters are reported in Table 1 in which other useful parameters, calculated as above detailed, are also reported. The comparison of the parameters shows that when the ratio C222/SDS increases from 0.5 to 1.5, there is an increase of ligands molecules  $N_L$  at the interface from 40% to 65%. With the increase of ligands molecules at the interface, we observe a decrease of the effective micellar charge  $Z$  from 21 to 12 and of the average aggregation



**Figure 4.** Experimental curve (O) and fitted curve (continuous line) of the 1.5 C222/SDS mole ratio spectrum of Figure 1. The normalized form and structure factors are also shown.

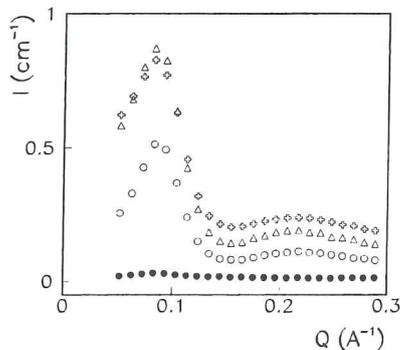
number  $N$  from 74 to 54. At the same time, we observe a slight increase of the shell thickness, from 10 to 12 Å, and a slight decrease of the parameters  $N_C$ , from 12 to 9.5, and  $R_{hc}$ , from 18 to 16 Å. The whole micelle diameter  $D$  remains practically constant, 55 Å. The Debye length ( $1/k_D$ ) is constant, 16 Å, whereas the contact potential decreases from 6.7 to 2.3  $K_B T$  units as the C222/SDS ratio increases. Furthermore, we observe a slight increase of  $\eta$ , the volume fraction of micelles, from 0.21 to 0.24. The number of solvent molecules at the interface,  $N_S$ , slightly increases from 22 to 29 with the increase of the C222/SDS ratio. Ellipsoids are prolate because the ellipsoidal axial ratio is larger than 1, and the latter increases slightly with the increase of C222 in the micellar solution from 1.3 to 1.5. The quality of the fitted curve is better for Figure 2 (C222/SDS = 0.5) than for Figures 3 and 4. In fact, we can observe that the fitted curve passes through all experimental points for the ratio C222/SDS = 0.5, whereas for the ratios C222/SDS = 1.0 and C222/SDS = 1.5, the fitted curves shift down for the low  $Q$  points. The reduced  $\chi^2$  is 3 for the C222/SDS ratio 0.5, 8 for the ratio 1.0, and 5 for the ratio 1.5. Compared with the results obtained for hydrogenated 8% (wt/wt) LDS (lithium dodecyl sulfate) and SDS micelles without C222,<sup>14–15</sup> composed by prolate ellipsoidal aggregates, we observe that the effect of the C222 addition to SDS micellar solutions does not change the micellar form of prolate ellipsoids but increases the thickness of the outer layer of the micelles from 5.5<sup>14,15</sup> to 10–12 Å. At the same time, we observe a decrease of the effective micellar charge from 30<sup>14,15</sup> to 10–20 and of the average aggregation number from 75<sup>14,15</sup> to 55–75. The other parameters,  $a/b$  and  $N_C$ , are similar to SDS micelles without C222, whereas the micellar diameter is larger for micelles with C222, 55 Å, than for micelles without C222, 48 Å.<sup>14–15</sup> The Debye length and the contact potential for the pure SDS micellar solution with 8% concentration are 4 Å and 15  $K_B T$  units,<sup>14–15</sup> respectively, and become 16 Å and 7–2  $K_B T$  units, respectively, in the presence of C222. The spectra of Figure 1 have been also analyzed by the two-shell polydispersed spheres model without success.

**Deuterated SDS Micelles.** In Figure 5, the experimental spectra of SDS micelles, with 8% of concentration in weight fraction, are shown for the different C222/surfactant ratios, 0.5, 1.0, and 1.5. In the same figure, the experimental spectrum of a SDS sample without C222 is also shown. The latter spectrum cannot be analyzed because of the small coherent part, and it is explicative of the effect of cryptand addition to the micellar solution. For all of the spectra, there is a peak at low  $Q$  that is highly emphasized by cryptand addition, and the peak maximum depends on the ligand/surfactant ratio. A broad less-pronounced

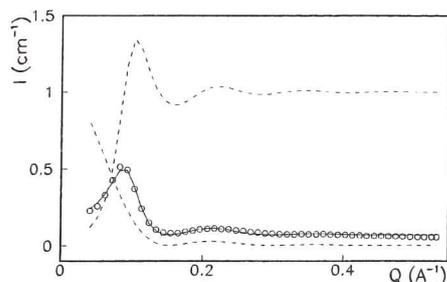
TABLE 1.

C222/SDS	Z	N	$d^a$	$N_C$	back <sup>b</sup>	$N_L$	$N_S$	a/b	$D^a$	$1/k_D^a$	$R_{hc}^a$	$V_1^c$	$\eta^d$
0.5	21	74	10	12	0.198	0.40	22	1.3	57	16	18	6.7	0.206
1.0	15	59	11	8.9	0.288	0.68	21	1.8	54	17	16	4.1	0.211
1.5	12	54	12	9.5	0.359	0.65	29	1.5	56	16	16	2.3	0.242

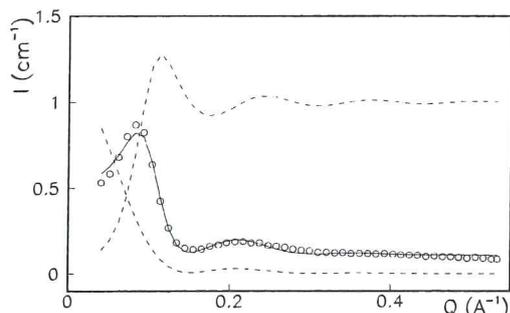
<sup>a</sup> Expressed in units of Å. <sup>b</sup> Background parameter. <sup>c</sup> Contact potential in  $K_B T$  units. <sup>d</sup> Volume fraction of the micelles.



**Figure 5.** Experimental scattered intensity by deuterated SDS aqueous micellar solutions with 8% (wt/wt) concentration for the C222/SDS ratios: (○) 0.5; (△) 1.0; (open crosses) 1.5. The full points (●) spectrum is that of the same micellar solution without the cryptand molecules. The experimental errors are smaller than the symbols used.

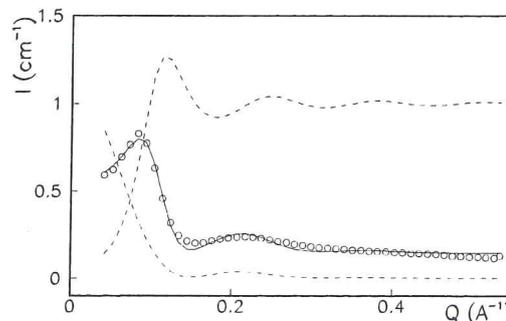


**Figure 6.** Experimental curve (○) and fitted curve (continuous line) of the 0.5 C222/SDS mole ratio spectrum of Figure 5. The normalized form and structure factors are also shown.



**Figure 7.** Experimental curve (○) and fitted curve (continuous line) of the 1.0 C222/SDS mole ratio spectrum of Figure 5. The normalized form and structure factors are also shown.

maximum is also shown by the spectra with ligand. Also in this case, the data analysis of the spectra of Figure 5 was performed as above-reported using a two-shell ellipsoidal model for the particles. This analysis did not lead to reasonable results. Thus, the two-shell polydispersed spheres model was used. The fitted curves of the spectra with ligand, as well as the normalized form and structure factors, are reported in Figures 6–8. The values of the parameters deduced by the fit and those calculated are reported in Table 2. The core radius of the micelle,  $pR$  (see eq 5), is reported as  $R_{hc}$  in Table 2. The model contains seven



**Figure 8.** Experimental curve (○) and fitted curve (continuous line) of the 1.5 C222/SDS mole ratio spectrum of Figure 5. The normalized form and structure factors are also shown.

free fitting parameters: the micellar surface charge  $Z$ , the average aggregation number  $N$ , the thickness of the interfacial region  $d$ , the percentage of interfacial ligand molecules in relation to the total surfactant molecules  $N_L$ , the core radius  $R_{hc}$ , the size polydispersity, and the background. Analysis of Table 2 shows that when the C222/SDS ratio increases from 0.5 to 1.5, there is a decrease of the effective micellar charge from 15 to 9.4 and of the aggregation number from 51 to 38, whereas the percentage of ligand at the interface increases from 52% to 80%, and the thickness of the outer layer increases slightly from 7.4 to 9 Å. We point out that the internal micellar radius decreases slightly from 17 to 15 Å, whereas the micellar diameter  $D$  remains around 49 Å for the three ratios, and the polydispersity remains very small (5%–8%). The Debye length slightly increases from 16 to 18 Å, and the micellar volume fraction  $\eta$  increases slightly. The decrease of the effective micellar charge is coupled to the decrease of the contact potential  $V_1$  from 4.8 to 2.3  $K_B T$  units. The number of the solvent molecules in the outer layer increases from 16 to 23. The reduced  $\chi^2$ , 12, 26, and 46 at ligand/surfactant ratio = 0.5, 1.0, and 1.5, respectively, represent the best fit in this case.

## Discussion

The results of the hydrogenated micellar solution with cryptand and the comparison of these results with those of the micellar solution without cryptand give a strong indication that the sodium/cryptand complex behaves as a counterion that migrates from the bulk solution to the interfacial region of the micelles. Once it is at the micellar surface, it screens the micelle surface charge, which leads to a reduction of the contact potential and to an increase of the Debye length. The comparison of the results for hydrogenated and deuterated micellar solutions, reported in Tables 1 and 2, shows that the trend of change and the entity of the parameters  $Z$ ,  $N$ ,  $N_L$ ,  $d$ ,  $R_{hc}$ ,  $(1/k_D)$ ,  $V_1$ , and  $N_S$  caused by the ligand/surfactant ratio increase are the same for hydrogenated and deuterated micellar solutions. The micelle diameter is constant in both cases. Furthermore, for the same ligand/surfactant ratio, the average aggregation number  $N$ , the micelle diameter  $D$ , and the micelle surface charge  $Z$  are lower for the deuterated micelles. A higher interfacial ligand concentration is observed for the deuterated micelles and seems responsible for the smaller aggregation

TABLE 2.

C222/SDSD	Z	N	$d^a$	back <sup>b</sup>	$N_L$	$N_S$	poly	$D^a$	$1/k_D^a$	$R_{hc}^a$	$V_1^c$	$\eta^d$
0.5	15	51	7.4	0.067	0.52	16	5%	49	16	17	4.8	0.176
1.0	10	42	8.6	0.108	0.76	20	8%	49	18	16	2.6	0.206
1.5	9.4	38	9.1	0.145	0.80	23	8%	48	18	15	2.3	0.212

<sup>a</sup> Expressed in units of Å. <sup>b</sup> Background parameter. <sup>c</sup> Contact potential in  $K_B T$  units. <sup>d</sup> Volume fraction of the micelles.

number and micellar size because a higher migration of the sodium/cryptand complex to the micellar surface induces a higher decrease of the surface charge. The thickness of the external shell  $d$  is slightly lower for the deuterated micelles (7–9 Å) with respect to hydrogenated ones (10–12 Å), and the interfacial water amount for surfactant molecule is also lower for deuterated micelles. The Debye length is similar for both hydrogenated and deuterated micelles, almost constant (in fact the change vs the increase of the C222/surfactant ratio is weak), whereas the contact potential decreases from 7 to 2 and from 5 to 2  $K_B T$  units for hydrogenated and deuterated micelles, respectively, caused by the C222/surfactant ratio increase. The study of the deuterated micellar system reinforces the previous findings of the hydrogenated micellar system. The proposed mechanism of migration of the sodium/cryptand complex from the bulk phase to the micellar surface, which well explains the body of the results, is in agreement with the results of a previous study<sup>30</sup> on the adsorption properties of the cryptand C222 at a charged macroscopic interface studied as a function of the polarization potential and of the ligand concentration. In the latter work, the C222 ligand was dispersed in an electrolytic solution of sodium chloride. The interfacial adsorption of the C222 ligand has been demonstrated to be driven by the hydrophobic repulsion of the exposed surfaces in the presence of an intermolecular repulsive electrostatic contribution due to sodium cation trapped inside the ligand cage.

On the basis of the results, however, we cannot conclude that the two micellar solutions differ for the form. In fact, slightly elongated ellipsoids and slightly polydispersed spheres cannot be distinguished.<sup>10,29</sup> However it was possible to study hydrogenated micelles only with the ellipsoidal model and deuterated micelles only with the polydispersed spheres model, in our opinion, because this last model contains one additional fitting parameter. This indetermination of the micellar form was also present in the study performed on 4% SDS micellar solutions with C222/surfactant ratios 0.5, 1.0, and 1.5.<sup>9</sup> In that case, only the hydrogenated micelles were studied and the ellipsoidal ratio was in the range 1.1 to 1.3. The size of the micelles and of the submicellar dimensions, shell, and core is practically the same for 8% and 4% micellar solutions, whereas a higher amount of ligand molecules is found in the interfacial region of the 8% system.

It remains to be discussed the differences between hydrogenated and deuterated micellar solutions. A higher amount of ligand at the micellar surface is present for deuterated micelles and leads to smaller surface charge and contact potential. It is a result of this paper that the C222 ligand is more efficient in binding sodium counterion at the micellar surface of deuterated micelles, probably because of a larger hydrophobic repulsive effect than that present in the hydrogenated micellar system.

## Conclusions

In summary, hydrogenated and deuterated micelles have approximately the same micellar core radius and Debye length. For both micelles, the ligand that complexes the sodium counterion of the surfactant migrates toward the interface in large amount leading to a consistent screening of the micellar surface charge due to the neutralizing effect of the surfactant

polar headgroup. This decreases the average aggregation number and the contact potential, whereas the whole volume fraction of the dispersed phase increases. The average shell thickness value, 11 and 8.4 Å for hydrogenated and deuterated micelles, respectively, is justified by the ligand migration from the bulk phase to the micelle surface. In fact, the interfacial layer thickness of SDS micelles without ligand is 5.5 Å. The micelle diameter, 55 Å for hydrogenated and 49 Å for deuterated micelles, is independent of the C222/surfactant ratio. Deuterated micelles reach a higher ligand concentration in the interfacial region than hydrogenated micelles, which leads to lower values of surface charge, average aggregation number, and shell thickness. These results highlight the possibility of micelle surface charge and aggregation number control by complexing micellar counterions for ionic surfactants.

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