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Complexation of counter-ions in ionic micellar solutions: a small-angle neutron scattering study[1]

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COLLOIDS AND SURFACES A

Complexation of counter-ions in ionic micellar solutions: a small-angle neutron scattering study[1]

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Abstract

The properties of LDS and SDS micellar solutions upon the addition of [2.2.2]-cryptand (C222) are studied by small-angle neutron scattering (SANS). The interfacial thickness of the micelle for three ligand to surfactant molar ratios ($L/S=0.5$, 1.0 and 1.5) increases from 5.5 Å (interfacial thickness of the micelles without ligand) to 10 Å, indicating that the ligand is located at the interface. The micellar net surface charge and the average aggregation number decrease as L/S increases, producing a slight decrease of the micellar size and a more spherical shape. The ionization degree of the LDS micelles is almost constant as L/S increases, whereas it decreases slightly for SDS micelles. This supports the higher binding ability of C222 for sodium ions. The ligand/surfactant molar ratio at the interface is at most 1/2 when the ligand is added to the surfactant solution (LDS and SDS) in equimolar amounts. This implies that only half of the total amount is partitioned at the interface, while the remaining ligand molecules are in the bulk solution. Further addition of the ligand increases its amount in the bulk solution.

Keywords: Counterion complexation; Cryptand; Macrocycle; Micellar solution; Neutron scattering

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1. Introduction

Macrocyclic compounds can form stable complexes with metal ions. The shape and size of these molecules enables them to recognize specific ions and/or small organic molecules [1]. This ability can be measured in terms of the binding constant of a given ion. These properties give rise to a large number of applications, such as the separation of ions and isotopes, transport across oil–water interfaces, liquid–liquid and liquid–solid phase-transfer reactions, dissolution of organic salts in apolar solvents, ion-selective electrodes, etc. [2–5].

The role of the macrocyclic ligands on the properties of micellar solutions is a subject of growing interest [6–13]. The crucial point is to understand how the complexation ability of a macrocyclic molecule changes when the ion is a counter-ion of a surfactant which forms micelles in water. An example is the complexation of lithium or sodium counter-ions in lithium dodecyl sulfate (LDS) or sodium dodecyl sulfate (SDS) aqueous micellar solutions. It is known that the ionic micelles in water are partially charged because some counter-ions form a diffuse layer.

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For example, in LDS micelles, some SO_4^- groups remain unscreened because of the migration of the Li^+ ion towards the bulk, resulting in a net surface charge at the micellar surface. It is expected that the addition of a ligand to the micellar solution changes this net surface charge, depending on the complexing ability of the counter-ion. It is also expected that such a variation can change the shape and size of the micelles and the inter-micellar interactions. In this paper, we extend the work of previous investigations performed by small-angle neutron scattering (SANS) on LDS micellar solutions with two different crown ethers and two cryptands added in an equimolar ratio of ligand to surfactant (L/S) [14]. The effect of cryptand C222 in 0.5, 1.0 and 1.5 molar ratios is reported here for a 0.13 M LDS micellar solution. Furthermore, the same study is performed on a 0.13 M SDS micellar solution.

2. Experimental

LDS and SDS, obtained from Eastman Kodak, were recrystallized from a mixture of ethanol–diethyl ether 3:1 by volume, and dried under moderate vacuum at 40°C. D_2O was obtained from Carlo Erba. Cryptand C222 was obtained from Merck. The critical micelle concentration for the LDS micellar solution with an equimolar ratio of C222 to surfactant is 2.1 mM [6], whereas that for the SDS micellar solution is 1.6 mM [7]. The chemical formula of C222 is reported in Fig. 1, showing the cavity where the ion can be complexed.

The experiments were performed at the small-angle spectrometers PAXY and PAXE of the Laboratoire Léon Brillouin at Saclay. The sample–detector distance was 2 m and the incident neutron wavelength was 5 Å. Collimation was achieved by two slits of 12 and 7 mm placed 2.5 m apart. The overall momentum resolution was equal to 10%, mainly imposed by the mechanical selector monochromator.

The temperature of the experiments was 25 ± 0.1°C.

3. Results and discussion

In Figs. 2 and 3 we report the experimental scattered neutron intensity I as a function of the scattering wave vector Q for 0.13 M LDS and SDS micellar solutions, with L/S ratios of 0.5, 1.0 and 1.5, respectively. The spectra are characterized by the presence of sharp interaction peaks. Figs. 2 and 3 show that the increase of the ligand-to-surfactant ratio from 0.5 to 1.5 produces a decrease in the maximum intensity and an increase in the peak width.

SANS data were analysed assuming a two-shell model for the micellar particle structure factor $P(Q)$ and an analytical solution of a multicomponent ionic liquid in a mean spherical approximation (MMSA) for the interparticle structure factor $S(Q)$ of the charged micelles in solution, as already used for LDS and SDS micellar solutions [15–19]. The interparticle structure factor $S(Q)$ is the result of a screened Coulombic repulsion between micelles, in addition to hard-sphere repulsion [20–23]. More details on the theory for the determination of $S(Q)$ on ionic micellar solutions and on the storical evolution of the theory are given in Refs. [13,24]. In this paper, the multi-component system is reduced to an effective one-component system [25] under Gillan's condition [26].

Strictly speaking, the scattering cross-section for a system of interacting particles can be calculated from $P(Q)$ and $S(Q)$ only for a system consisting of monodisperse spherical particles. However, not too large deviations from sphericity or monodispersity have been shown to give the addition of a background to the scattered intensity, which may be modelled and subtracted from the data [27,28]. In the case of a polydispersed sample, the oscillations in the apparent interparticle structure factor $S'(Q)$ are significantly damped in comparison to those of the "true" structure factor $S(Q)$. For non-spherical particles, the orientational averaging affects $S'(Q)$ in a similar way.

The micellar solution is assumed to be composed of monomeric surfactants at the critical micellar concentration, and uniform-sized elliptical micelles with a mean aggregation number N and an effective charge Z. The fractional ionization is defined as $\alpha = Z/N$. The particle structure factor $P(Q)$ is

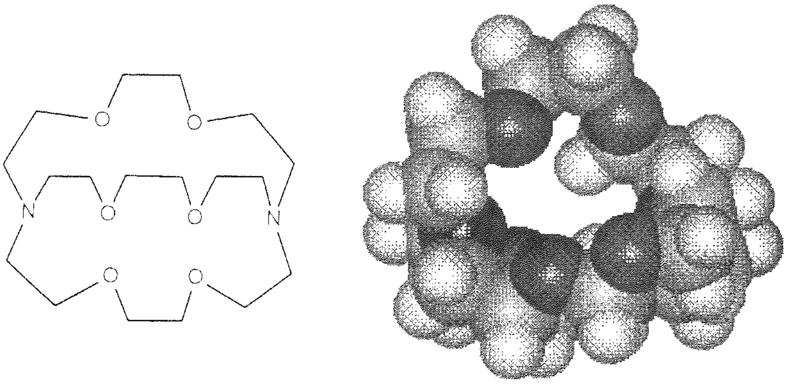

Fig. 1. The chemical structure of C222 (left) and a molecular model of C222 (right). The molecular model was obtained by using a modified MM$^+$ method [29].

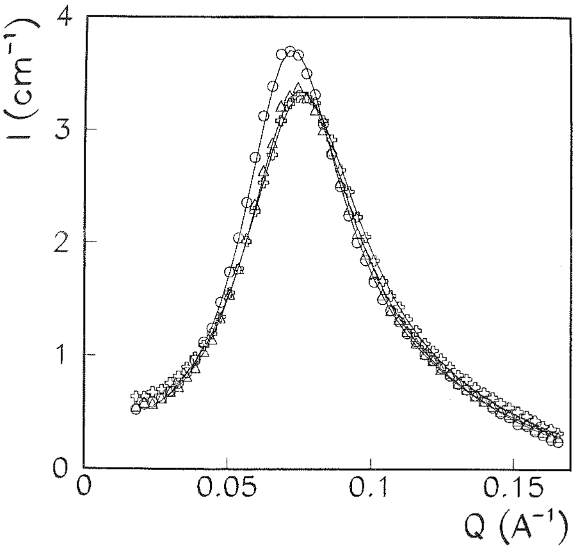

Fig. 2. Experimental scattered intensity by 0.13 M LDS micellar aqueous solutions with different C222 ligand-to-surfactant ratios: 0.5 (circles), 1.0 (triangles) and 1.5 (crosses). The error bars are smaller than the symbols used. The continuous lines represent the calculated curves.

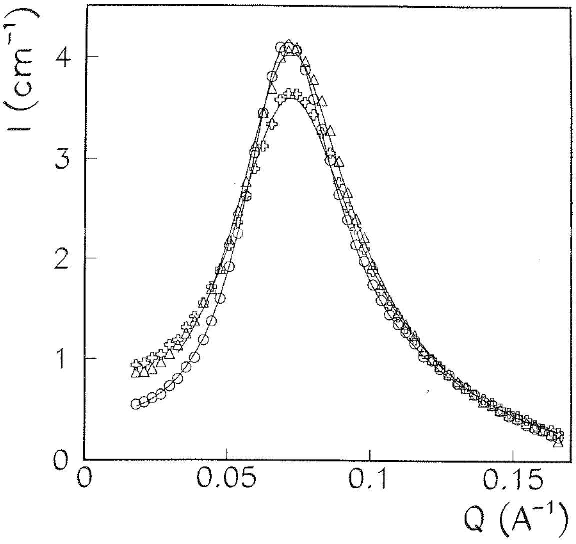

Fig. 3. Experimental scattered intensity by 0.13 M SDS micellar aqueous solutions with different C222 ligand-to-surfactant ratios: 0.5 (circles), 1.0 (triangles) and 1.5 (crosses). The error bars are smaller than the symbols used. The continuous lines represent the calculated curves.

computed assuming a two-shell model. In this model, the micelles have a hydrophobic core composed of close-packed hydrocarbon tails of the dodecyl sulfate, a hydrated hydrophilic shell composed of head groups (SO_4^-), some fraction of counter-ions (Li^+ or Na^+), the complexed ligand, and the solvent molecules. We assume that the hydrophobic core is of elliptical shape with principal axes a, b, b and the hydrophilic layer has a thickness t, as found for the LDS and SDS micellar solutions without a ligand [15–19], and with a ligand named CESTO of a chemical composition similar to C222 [13]. The elliptical shape of the micelles is related to thermodynamic considerations [18] when the major driving force of the formation of aggregates is the hydrophobic effect. In this case, the aggregates grow to minimize the surface-to-volume ratio, which decreases from a spherical to an elliptical shape. A further hypothesis, i.e. that the ligand does not completely change the self-associating regimen, is also necessary to use the model.

The scattering contribution from the counterions in the vicinity of the micelle is orders of magnitude weaker than that from the macro-ions for neutron scattering. Consequently, scattering from species other than the macro-ions is treated as a flat background added to the incoherent scattering from all the hydrogen atoms in the solution. The total scattered intensity $I(Q)$, under the previous hypotheses, can thus be written:

$$I(Q) = C_{\mathrm{M}} N \left(\sum b_i - V_{\mathrm{m}} \rho_{\mathrm{s}} \right)^2 P(Q) S(Q) + I_{bcgd}$$

where C_{M} is the number density of the surfactant molecules ($C_{\mathrm{M}} = C - \mathrm{cmc}$, with C being the surfactant concentration and cmc the critical micelle concentration), $\Sigma\, b_i$ is the total scattering length of all atoms in the monomer, including the atoms associated with the ligand molecule, V_{m} is the monomer volume defined as $V_{\mathrm{m}} = V_{\mathrm{surf}} + N_{\mathrm{l}} V_{\mathrm{l}}$ (where V_{surf} and V_{l} are the volume of the surfactant and ligand molecules, respectively), N_{l} is the number of ligand molecules associated with each surfactant molecule, and ρ_{s} is the scattering density of the solvent. The SANS spectra calculated according to the above model are reported as continuous lines in Figs. 2 and 3. The agreement between the experimental and the calculated curves is quite good. The quality of the fit was deduced by the reduced χ^2 value, which is between 2 and 4 for the data in this work. The free fitting parameters, some of which are reported in Table 1, are the micellar charge Z, the average aggregation number N, the thickness of the interfacial region t, the percentage of interfacial ligand molecules in relation to surfactant molecules at the interface N_{l}, the micelle small-axis value and the axial ratio of the ellipsoidal shaped micelles a/b. The micellar diameter and the ionization degree, evaluated by the free parameters of the fitting, are also reported in Table 1, along with the accuracy of the parameters.

Analysis of Table 1 shows that for both micellar solutions the thickness of the interfacial region of the micelle (the outer layer in the two-shell model) does not change on increasing the ligand/surfactant ratio. The value of about 10 Å for the interfacial thickness of LDS and SDS micelles suggests that some of the macrocycle has solubilysed at the micellar interface. In fact, the interfacial thickness of the pure LDS and SDS micelle is about 5.5 Å [15,16]. We point out that the pure SDS 0.13 M micellar solution, measured at 23°C, has an effective charge of 23, an aggregation number of 100 and a size of 66 Å [18]. The corresponding values of the C222/SDS micellar solutions are lower also at the smaller C222-to-SDS ratio (see Table 1). At 23°C, the pure LDS micellar solutions with concentrations of 0.078 and 0.156 M show diameters of 66 and 61 Å, aggregation numbers 67 and 73 and effective charges of 24 and 28, respectively [18]. Thus we expect, for a 0.13 M LDS micellar solution, a diameter of

Table 1
Net surface charge (Z), average aggregation number (N), interfacial thickness (t), percentage of ligand molecules for surfactant molecules at the interface (N_{l}), degree of ionization α, micelle diameter D and micelle ellipsoidal axial ratio a/b (a = major axis and b = minor axis) for LDS and SDS aqueous micellar solutions 0.13 M, with C222 in molar ratio to surfactant 0.5, 1.0 and 1.5

C222/SDS molar ratio	Z	N	t (Å)	N_{l} (%)	α	D (Å)	a/b
0.5	20.0 ± 0.8	72 ± 1	10.0 ± 1.0	35 ± 5	0.275 ± 0.015	56.0 ± 1.0	1.29 ± 0.02
1.0	15.5 ± 0.5	63 ± 1	10.3 ± 0.7	55 ± 5	0.245 ± 0.015	54.4 ± 1.4	1.20 ± 0.05
1.5	14.0 ± 0.5	61 ± 2	10.5 ± 1.0	59 ± 9	0.230 ± 0.02	53.1 ± 0.4	1.11 ± 0.01
C222/LDS molar ratio							
0.5	19.0 ± 0.5	74 ± 1	9.5 ± 0.5	28 ± 3	0.257 ± 0.01	56.0 ± 1.0	1.31 ± 0.02
1.0	17.0 ± 0.5	62 ± 2	10.5 ± 0.5	48 ± 7	0.270 ± 0.01	55.0 ± 2.0	1.16 ± 0.05
1.5	16.0 ± 0.2	60 ± 2	9.0 ± 1.0	38 ± 3	0.260 ± 0.01	53.0 ± 1.0	1.05 ± 0.04

60 Å, an aggregation number of 70 and a charge of 25. The addition of C222 to LDS micellar solutions decreases the charge, the aggregation number and the size, as for SDS micellar solutions. The effect of C222 addition to LDS and SDS micellar solutions is to increase the outer layer thickness of the micelles, producing a decrease in the effective charge of the micelle, a decrease in the aggregation number (smaller for LDS micelles) and in the micellar size. Considering that the ellipticity observed is very small (axial ratio $\leq 1.3:1$), no final conclusion by simple data analysis can be deduced on the real shape of the micelle (weakly polydispersed spheres or slightly ellipsoidal particles).

At different ligand-to-surfactant ratios, for both SDS and LDS micellar solutions, effective charge, aggregation number, micellar diameter and ellipticity of the micelle decrease as the ligand concentration increases. The micelles becomes smaller and more spherical. The variation of the amount of C222 at the interface is different in the two micellar systems. It is higher for SDS than for LDS micelles, suggesting that C222 complexes better sodium than lithium counter-ions at the micellar interface. This is in agreement with the complexation constant of C222 [1] in solution. Moreover, the amount of macrocycle at the interface increases as the ligand-to-surfactant ratio increases, and stabilizes at the equimolar ratio. A further addition of macrocycle above the 1:1 ratio only increases the amount of ligand in the bulk. Table 1 shows that the maximum amount of macrocycle at the interface is about 50% for SDS and LDS micellar solutions. Counter-ion complexation at the micellar interface is also shown by the decrease of the Z parameter. In fact, for both micellar solutions, the charge and the aggregation number decrease as a function of the L/S increase. These variations produce a slight decrease of the degree of ionization only for SDS micelles. Another interesting effect due to complexation of counter-ions is related to the micellar shape. The presence of C222 at the interface slightly decreases the ellipticity of the micelles, which become more spherical as the amount of ligand at the interface increases.

4. Conclusions

LDS and SDS micellar solutions with the macrocyclic ligand C222 have been studied at $T=25°C$ as a function of the ligand-to-surfactant ratio increase (0.5, 1.0 and 1.5). The micelles are modelled as two-shell ellipsoids which incorporate counterions (Li^+ or Na^+), ligand–counter-ion complexes and the associated water molecules in the outer layers, whereas the surfactant dodecyl chains are in the core. The inter-micellar correlations are calculated according to a multicomponent primitive model in a mean spherical approximation with non-additive diameters. It is found that C222 complexes the interfacial counter-ions, and that the sodium counter-ion is better complexed than the lithium counter-ion, in agreement with the complexation constant measured for solutions [1]. For both counter-ions, the interfacial macrocyclic amount increases as the ligand-to-surfactant ratio increases from 0.5 to 1.0, stabilizing at about 50%. Above the 1:1 ratio, only the amount of ligand in the bulk increases. The effective charge and the average aggregation numbers decrease as a function of the L/S increase, leading to slightly smaller and more spherical micelles.

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