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The role of macrocyclic ligands in the structure of LDS micellar solutions

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The role of macrocyclic ligands in the structure of LDS micellar solutions

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Abstract

We have studied the effect of macrocyclic ligands on the aggregation behavior of lithium dodecyl sulfate (LDS) micellar solutions. Two different classes of macrocyclic compounds are investigated: crown-ethers and cryptands. We show that macrocyclic ligands solubilize at the micellar surface by decreasing the micellar surface charge and the micellar aggregation number and increasing the thickness of the micellar polar head group region. These effects are dependent on the shape and size of the macrocyclic ligand.

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]. The role of these ligands in the inter-micellar interactions has been discussed recently [2,3]. Within one possible interpretation, the ligand makes complexes with the counter-ions which are then removed from the close environment of the polar heads of the surfactant [4,5]. Within another interpretation, the ligand remains attached to the micelles screening, at least partly, the macro-ionic charge [2,3].

The purpose of our experiment is to test the applicability of these schemes to a LDS micellar aqueous solution in the presence of different macrocyclic ligands. These ligands differ for the shape of the molecule and the binding constant to form macrocyclic ligand-Li⁺ complexes. If the first interpretation is appropriate, one expects an increase in the net charge of the micelles and

a subsequent reduction of the aggregation number. Instead, within the second interpretation, the net charge will be reduced and the aggregation number will change according to the size and location at the micellar surface to the macrocyclic ligand. Moreover, it is clear that the structure factor of the system, which depends on the inter-micellar interactions, will be enhanced in the first case, as compared with that of the simple LDS/water system.

2. Experimental

The experiments have been performed on 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 far apart. The overall momentum resolution was equal to 10%, mainly imposed by the mechanical velocity selector.

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The samples were prepared starting from two aqueous micellar solutions of 0.147 and 0.294 M lithium dodecyl sulfate (LDS). The macrocyclic ligand was added to the solution in molar ratio 1/1 of ligand to LDS. Cryptands C221 and C222 as well as 18-crown-6 and 15-crown-5 ethers were obtained from Merck. LDS, obtained from Eastman Kodak, was recrystallized from a mixture of ethanol-diethyl ether 3:1 by volume, and dried under moderate vacuum at 40°C. D₂O was obtained from Carlo Erba. The temperature of the experiments was 25 ± 0.1 °C.

3. Results and discussion

Some typical raw spectra are shown in Fig. 1. They are characterized by a very sharp structural peak at around 0.08 \AA^{-1} . This peak is a manifestation of the strong interactions between the charged particles.

The treatment of the data followed the analysis recently performed by Chen et al. [6] for the CESTO/LDS/water system. It is based on a liquid theory of Khan and Ronis [7] and an algorithm of Hayter and Penfold [8] which proved to be very useful, giving precise information about the net charge, aggregation number, hydration level, micellar size, i.e. essentially all the physical parameters characterizing the system.

The main problem consists of separating of the scattered intensity into two factors, $P(Q)$ and $S(Q)$, related respectively to the shape and size of the micelles and to the spatial distribution of their centers of masses. Q represents the value of the scattering wave vector. Figs. 2 and 3 show two typical examples of this decomposition. The form factor corresponds to slightly elongated ellipsoids. The structure factor reproduces the strong interac-

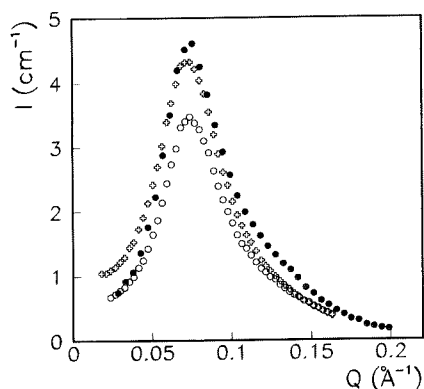


Fig. 1. Scattered intensity by aqueous solutions of 0.147 M LDS: pure LDS (full circles); LDS and C222 (open circles) and LDS and C221 (open crosses) at LDS/cryptand mole ratio of 1.

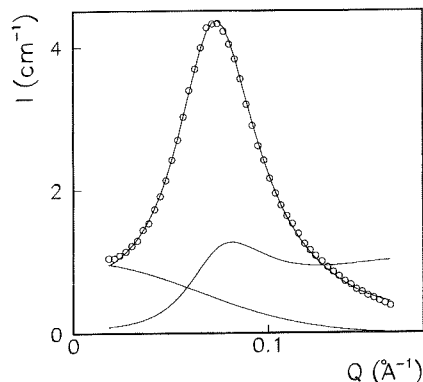


Fig. 2. Experimental curve (open circles) and fitted curve (continuous line) for 0.147 M LDS micellar solution with C221. $P(Q)$ and $S(Q)$ are also shown.

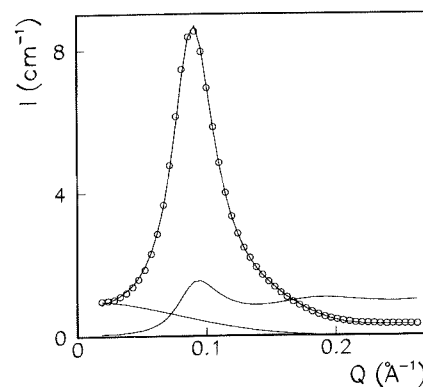


Fig. 3. Experimental curve (open circles) and fitted curve (continuous line) for 0.294 M LDS micellar solution with 15C5. $P(Q)$ and $S(Q)$ are also shown.

tions among micelles. The fitting parameters are summarized in Table 1, where the parameters of pure LDS micellar solutions are also reported for comparison. The addition of C222, C221, 18C6 and 15C5 to LDS micellar solutions in equimolar ratio between ligand and surfactant produces changes in the micelle parameters. In the presence of both C222 and C221 cryptands, the net charge and the aggregation number decrease. The interfacial thickness increases and the micellar size is also increased due to the large amount of ligand at the interface (from 0.5 to 1 molecule for one LDS molecule). The micellar ellipsoidal shape is less elongated. In the presence of crown-ethers the percentage of ligand at the interface is lower and both the interfacial thickness of the micelle and the diameter are unchanged. The shape variation is also weaker.

Table 1

Net charge (Q^*), aggregation number (N), interfacial thickness (t), percentage of ligand molecules for surfactant molecules at the interface (n_{mi}), micelle diameter (D) and ellipsoid axial ratio (a/b) of the micelle, for LDS aqueous micellar solutions 0.147 and 0.294 M without ligands and with ligands C222, C221, 18C6 and 15C5 added to the solutions in 1/1 ratio of ligand to surfactant

		Q^*	N	$t(\text{\AA})$	$n_{mi}(\%)$	$D(\text{\AA})$	a/b
LDS	0.147 M	25	77	5.5	—	48	1.38
	C221	15	68	9.5	87	55	1.24
	C222	19	68	9.5	48	55	1.22
	18C6	27	73	5.5	6.6	48	1.31
	15C5	26	75	5.5	10	48	1.36
LDS	0.294 M	30	83	5.5	—	49	1.49
	C221	16	68	9.4	100	55	1.23
	C222	19	68	9.7	48	55	1.22
	18C6	27	74	5.5	11.5	48	1.44
	15C5	28	78	5.5	12.4	49	1.41

The C222 and C221 cryptands are stronger complexing agents than the 18C6 and 15C5 crown-ethers [1]. They modify substantially the size of the micelles due to their hemispherical cage-like shape and to their larger

dimensions. On the contrary, the crown-ethers form smaller cages and fit more easily between the polar head groups of the surfactant. All these effects are clearly seen in Table 1. We emphasize that neutron-scattering experiment can provide in a single experiment information otherwise accessible only through diverse and indirect techniques.

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