MICELLE COUNTERIONS COMPLEXATION BY MACROCYCLIC LIGANDS

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Ion transport across hydrophobic media, selective binding of ions in different solvents, electron transfer across micellar interfaces, enhancement of the quantum yield in photoionization processes, metal cation extraction, production of potentiometric sensors and ion-selective electrodes, recovery of cations from nuclear waste materials, the use as accelerants for cyanoacrylate instant adhesives, and as antioxidant stabilizers for organic polymers and, more generally, host-guest molecular recognition processes are just some of the most important applications of cryptand and calixarenes cavity-shaped macrocyclic molecules.

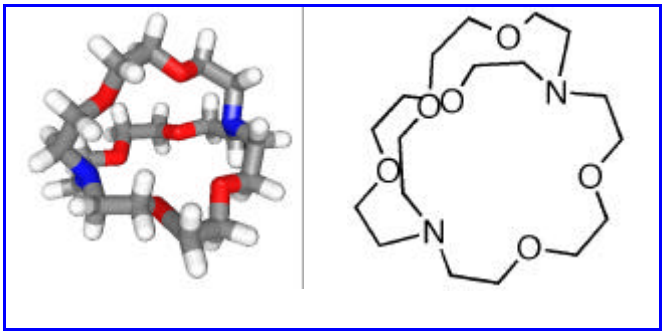

Figure 1. Molecular modeling of the macrocyclic cryptand C222.

In most applications, macrocyclic properties are enhanced by the wide area of supramolecular systems as micelles and microemulsions. The study of the binding of counterions and how they affect the structure of ionic have been already investigated in the past [1-2]. The ligand affinity to complex counterions in solution seems to be the main driving force to significantly change the micellar microstructure and the intermicelle interactions. Lithium dodecyl sulfate (LDS) micelles in aqueous solution have been characterized in the presence of ligands of different type, crown ethers, cryptands, and CESTO molecules [3-4].

In LDS micelles, some SO^{4-} groups remain unscreened because of the migration of the 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 [3-5].

Small-angle neutron scattering (SANS) is a versatile tool for the investigation of these systems.

To characterize the role of C222 addition to SDS aqueous micellar solutions we added to 8% (wt/wt) SDS micellar solution the ligand in a 0.5, 1.0, or 1.5 mole ratio [6].

To study different regions of the system, the C222 location in the SDS micelles and the consequent intermicellar interactions, two systems were investigated:

(i) SDS with C222 in D_2O
(ii) the same system with deuterated surfactant tail (SDSD)/D_2O

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.

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 CH_2 (or CD_2) groups of the surfactant tail that are close to the polar head, the C222 ligand, and hydration water molecules. The C222 ligand is allowed to be partly located in the micelle and partly in the continuous phase. The interparticle structure factor $S(Q)$ has been calculated assuming an analytical solution for the multicomponent ionic liquid with a mean spherical approximation (MMSA).

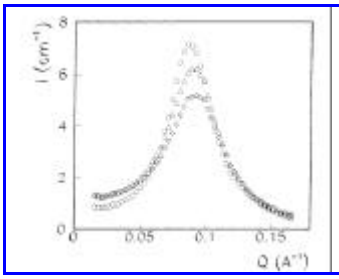

Figure 2. Experimental scattered intensity by SDS aqueous micellar solutions with 8% (wt/wt) concentration for different C222/SDS mole ratios: (O) 0.5 ; (?) 1.0; (open crosses) 1.5.

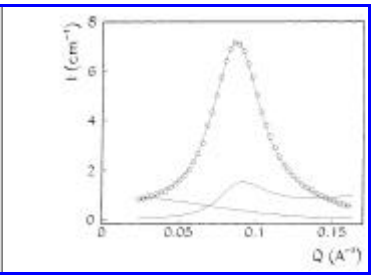

Figure 3. Experimental curve (O) and fitted curve (continuous line) of the 1.0 C222/SDS mole ratio spectrum of Figure 1. The normalized form and structure factors are also shown.

The fit considered two different possible shapes

(a) Ellipsoidal model. Micelles are considered ellipsoidal in shape. The ellipsoidal core of the micelle has a shorter axis equal to the length of

the extended tail of SDS molecule and an external shell around the core.

(b) Polydispersed spheres model. Micelles are considered as polydispersed core-shell spheres, following the Schulz distribution.

The analysis shows that C222 (in spite of its good solubility in water) is partitioned at micellar surface. The ratio C222/SDS increase (from 0.5 to 1.5) is associated to an increase of ligands at the interface (from 40% to 65%). The increase of ligands at the interface produces a decrease of the effective micellar charge from 21 to 12 and of the average aggregation number from 74 to 54. An increase of the shell thickness (from 10 to 12Å) and a decrease of the number of carbons in the hydrophobic core of the micelle (from 12 to 9.5) and of the hydrophobic chain length (18 to 16 Å) are also observed, meaning that the cryptand penetrates below the polar head groups region.

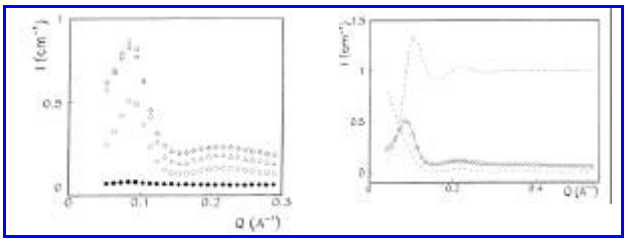

Figure 5. Experimental scattered intensity by deuterated SDS aqueous micellar solutions with 8% (wt/wt) concentration for the C222/SDSD ratios: (O) 0.5; (?) 1.0; (open crosses) 1.5. The full points spec-trum is deuterated SDS without cryptand molecules.

Figure 6. Experimental curve (O) and fitted curve (continuous line) of the 0.5 C222/SDSD mole ratio spectrum of Figure 5. The norma-lized form and structure factors are also shown.

The interaction of cryptand at the micellar surface occurs without any increase of the micellar diameter (55 Å). An increase of the volume fraction of micelles (0.21 to 0.24) is observed, as expected for a macrocycle partitioned at the micellar surface. The number of solvent molecules at the interface increases from 22 to 29 with the increase of the C222/SDS ratio. The micelles are prolate ellipsoids.

In summary, the analysis shows that the sodium/cryptand complex behaves as a "counterion" that migrates from the bulk solution to the interfacial region of the micelles. Once 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. A higher interfacial ligand concentration is observed for the deuterated micelles. Therefore, C222 ligand is more efficient in binding the sodium counterion at the micellar surface of deuterated micelles, probably because of a larger hydrophobic repulsive effect than that in the hydrogenated micellar system.

The proposed mechanism of migration of the sodium/cryptand complex from the bulk phase to the micellar surface agrees with a previous study on the adsorption properties of C222 at a charged macroscopic interface studied as a function of the polarization potential and of the ligand concentration[7]. 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.

We have investigated the most common macrocycles as crown ethers, cryptand, and calixarenes [8-9] as complexing agents for counterions of ionic surfactants (from lithium to cesium, calcium and strontium). SANS has been very powerful in determining the evolution of micelles upon macrocycles addition. Crown ethers, cryptands and calixarenes produce different effects on micelle structure; the evolution of the structure depends on the macrocycle complexing ability and on its location in the micelle. Their use allows the control of the size, shape and charge of ionic disperse systems.

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