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Original Citation:

Structure and aggregation of lithium dodecylsulfate micellar solutions in the presence of a macrocyclic cage / Baglioni, Piero; Bencini, Andrea; Dei, Luigi; Gambi, CECILIA MARIA CRISTINA; LO NOSTRO, Pierandrea; Chen, S. H.; Liu, Y. C.; Teixeira, J.; Kevan, L.. - In: JOURNAL OF PHYSICS. CONDENSED MATTER. - ISSN 0953-8984. - STAMPA. - 6(1994), pp. A369-A373. [10.1088/0953-8984/6/23A/061]

Availability:

This version is available at: 2158/212980 since:

Published version:

DOI: 10.1088/0953-8984/6/23A/061

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Structure and aggregation of lithium dodecyl sulphate micellar solutions in the presence of a macrocyclic cage

P Baglioni†*, A Bencini†, L Dei†, C M C Gambi‡, P Lo Nostro†, S H Chen§, Y C Liu§, J Teixeira¶ and L Kevan||

† Department of Chemistry, University of Florence, 50121 Florence, Italy

‡ Department of Physics, University of Florence, 50125 Florence, Italy

§ Department of Nuclear Engineering, MIT, Cambridge, MA 02139, USA

¶ Laboratoire Léon Brillouin, CEN-CNRS-Saclay, F-91191 Gif sur Yvette Cédex, France

|| Department of Chemistry, University of Houston, Houston, TX 77204-5641, USA

Received 22 October 1993

Abstract. We study the effects of addition of the macrocyclic cage CESTO (5,12,17-trimethyl-1,5,9,12,17-pentaazabicyclo[7.5.5]nonadecane) on the aggregation behaviour of lithium dodecylsulphate (LDS) in aqueous solution at a $\text{pH} \approx 12.7$. At this pH CESTO is neutral and binds selectively Li counter-ion. Electron spin-echo modulation results show that CESTO interacts with LDS micelles by decreasing the amount of water at the LDS polar headgroups region. Small-angle neutron scattering shows that LDS forms micelles of quasi-spherical shape. Upon addition of CESTO to 1% LDS micellar solution (1/1 mole ratio) we observed a dramatic lowering of the micellar charge, a small growth of the aggregation number, and increased elongation of micelles.

1. Introduction

In ionic micellar solutions the counter-ion properties have been the object of many experimental and theoretical studies [1–6]. An approach almost unexplored in the study of electrostatic interactions in ionic micellar solutions is the change of the micellar properties by modulation of counter-ion binding through complexation with macrocyclic ligands. This method allows the study of two different effects: (i) the counter-ion complexation, and (ii) the almost complete screening of the micellar charge by macrocycle interaction with the micellar polar headgroups. Macrocycles are compounds capable of forming stable complexes with alkali, alkaline earth and transition metal ions with a good selectivity. These compounds have been successfully used in different processes such as ion transport across oil–water interfaces, separation of ions, liquid–liquid or solid–liquid phase-transfer reactions, dissolution in apolar solvents of metals and organic salts, ion-selective electrodes, isotope separations, and in the understanding of some natural processes through mimicry of metalloenzymes [6].

In the present study the small macrobicyclic cage known as CESTO (basket), so-called because the shape of the molecule is similar to a basket, is added to micellar solutions of lithium dodecylsulphate to investigate its ability to complex lithium counter-ion (Li^+), or interact with the sulphate polar headgroups (SO_4^-). CESTO molecules have special proton and ligational properties in solution. They can encapsulate only small cations (H^+ , Li^+ , Cu^{2+} , Co^{2+} , and Zn^{2+}) with a high degree of selectivity [7]. Preliminary results show that, in

* To whom correspondence should be addressed.

micellar solution of lithium dodecylsulphate, the micellar charge and the complexing ability of Li^+ by CESTO can be controlled, without changing the steric hindrance of the CESTO molecule. In particular, by controlling the pH of the solution, two different effects can be studied: (i) the complexation of Li^+ counter-ions at a $\text{pH} > 12$, and (ii) the interaction of protonated CESTO, $[\text{H}(\text{CESTO})]^+$, with the sulphate polar headgroups of LDS micelle at a $\text{pH} < 12$.

This paper reports results at a $\text{pH} \simeq 12.7$, focusing on ESEM and SANS measurements.

2. Experimental

The materials and methods used in this study have been already reported in [8].

3. Results and discussion

The structure of the CESTO molecule is reported in figure 1. CESTO has four nitrogens that can be protonated. Their protonation depends on the pH of the solution, as shown in figure 2. The figure shows that the monoprotinated species of the macrocyclic cage is predominant ($> 90\%$) when CESTO is dissolved in pure water (note that, because of the peculiar behaviour of CESTO, the pH differs from that of pure water, i.e. $\text{pH} \simeq 10.2$), while at a $\text{pH} > 12.0$ CESTO is about 100% neutral.

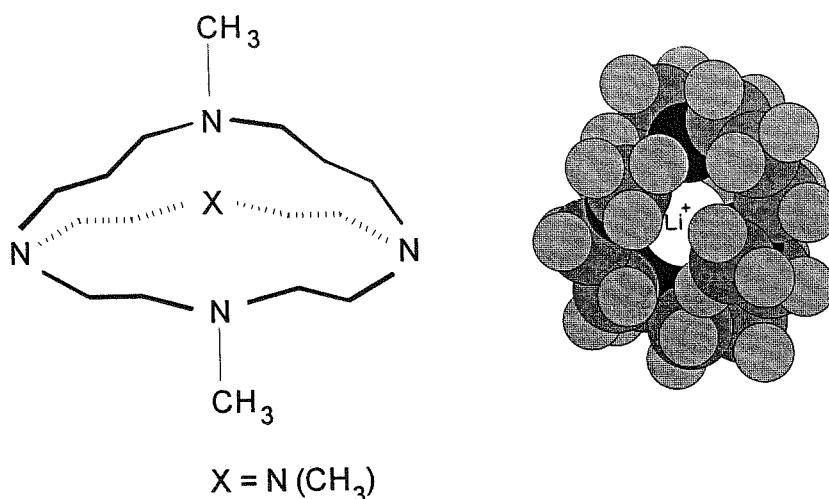


Figure 1. The chemical structure of CESTO (left) and a molecular model of $[\text{LiCESTO}]^+$ (right). The molecular model was obtained by using a modified MM^+ method [17] and minimizing the energy to $0.01 \text{ Kcal mol}^{-1}$.

It is worthwhile noting that only neutral CESTO can complex lithium selectively [7]. Therefore, it is possible to modulate CESTO behaviour in LDS micellar solutions by controlling the pH of the solution. This can be accomplished by adding sodium or potassium hydroxide, which cannot be complexed by CESTO. In this way, it is possible to study two different effects that are produced in LDS micellar solutions: (i) the complexation of Li^+ by the 'neutral' CESTO, and (ii) the interaction of $[\text{H}(\text{CESTO})]^+$ with the sulphate headgroups.

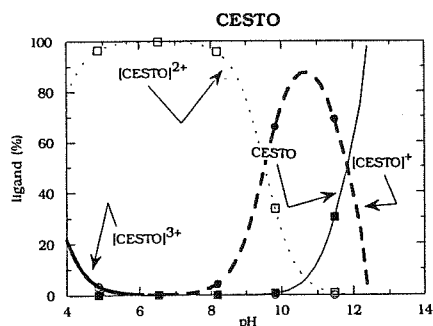


Figure 2. Concentrations of CESTO and CESTO cations in water solution as a function of the pH of the solutions. The percentage of CESTO and CESTO cations have been obtained by potentiometric titration.

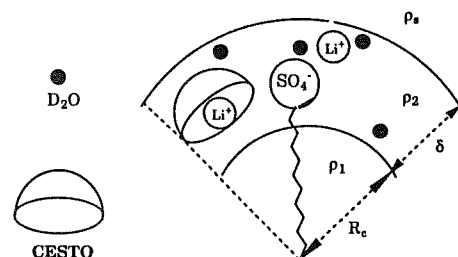


Figure 3. Schematic drawing of the two-shell model used for SANS analysis.

We will report here only the results obtained for the complexation of lithium counter-ion in LDS micellar solutions.

4. ESEM results

The ESEM results are analysed in terms of the normalized deuterium modulation depth that is related to the strength of the electron–deuterium dipolar interaction [9, 10]. In this study 5-doxylostearic acid spin probe is solubilized in LDS/D₂O micellar solutions to probe the electron–D₂O dipolar interaction. This interaction is primarily a function of the number and distance of the closest surrounding magnetic nuclei and is detectable at the X-band up to a distance of about 6 Å from the unpaired electron. Since the deuterium modulation depth depends on the number of interacting deuteriums and on their distance from the spin probe, in disordered systems such as micelles, a decrease in the normalized deuterium modulation depth reflects a decrease in the number of water molecules at the micellar surface [9, 10]. It was shown that the 5-DSA spin probe in micellar solutions is located in the micelle with the acidic group at the micellar surface, close to the polar headgroups [11, 12].

Table 1. Normalized deuterium modulation depth for a 5-DSA probe in LDS and LDS/CESTO micellar solutions at a pH \approx 10.2 and \approx 12.7.

	pH \approx 10.2	pH \approx 12.7
LDS	0.50 ± 0.03	0.48 ± 0.03
LDS/CESTO (1:1 mole ratio)	0.28 ± 0.03	0.16 ± 0.02

Table 1 reports the normalized deuterium modulation depth at a pH \approx 12.7 for pure LDS micellar solutions and for LDS micellar solutions in the presence of CESTO. The addition of CESTO to LDS micellar solution leads to a strong (about 30%) decrease of the normalized modulation depth. Since ESEM can detect deuterium modulation up to 6 Å from the unpaired electron [9, 10] of 5-DSA, and the 5-DSA probe is located at the LDS polar headgroups, the above results show that CESTO interacts at the micellar surface decreasing the number of water molecules at the polar headgroups region.

5. SANS results

In the analysis of the SANS data a two-shell model is used to calculate the form factor of the micelle [13]. We assume that the micellar hydrophobic core has a prolate ellipsoidal shape, with principal axes a, b, b , and an outer layer of thickness d . The inner core contains hydrocarbon chains (C_2 to C_{12}) of LDS. The outer layer is composed of the polar headgroups, C_1 of the hydrocarbon chain, a fraction of the counter-ions, a fraction of CESTO and water molecules (D_2O). In figure 3, a schematic representation of the two-shell model is reported.

The experimental scattering intensity $I(Q)$ is expressed as

$$I(Q) = C_M N \left(\sum b_i - V_m \rho_s \right)^2 P(Q) S(Q)$$

where C_M is the number density of the surfactant molecules, N is the average aggregation number of the micelle and $\sum b_i$ is the total scattering length of all atoms in the monomer, including the atoms associated with CESTO molecule; V_m is the monomer volume defined as $V_m = V_{LDS} + N_c V_{CESTO}$, where N_c is the number of CESTO molecules associated with each LDS molecule; ρ_s is the scattering density of the solvent, $P(Q)$ is the particle form factor, and $S(Q)$ is the structure factor. The $S(Q)$ factor is calculated by using a non-additive radius mean spherical approximation theory (NAR-MSA) [13, 14] formulated to reduce this multi-component system into one-component system consisting of macro-ions with a renormalized charge dispersed in the solvent [15, 16]. The effective macro-ion-macro-ion direct correlation function outside the hard core was shown to be of Yukawa form if the counter-ion and salt ions are taken as point particles. The application of the NAR-MSA theory allows us to calculate the macro-ion-macro-ion structure factor, S_{MM} , and macro-ion-counter-ion structure factor, S_{MC} . Table 2 reports the parameters obtained from the analysis of the SANS data from the LDS/CESTO system at a pH $\simeq 12.7$. An analysis of the table shows that, upon addition of 0.5 and 1 mole ratio of CESTO, the aggregation number slightly increases from 90 to 95, the axial ratio of the ellipsoidal core increases from 1.6 to 1.8, the effective charge decreases, the counter-ion fraction in the shell increases, reducing the effective fractional micellar ionization from 18% to 7% due to the complexation of lithium ions by CESTO, and the hydration of the micellar surface decreases, due to the CESTO incorporation at the micellar surface and Li^+ complexation.

Table 2. Parameters obtained from an analysis of the SANS data of micellar solution of lithium dodecylsulphate in the presence of the macrocyclic ligand CESTO, at different CESTO/LDS mole ratio. [CESTO]/[LDS] = 0, 0.5 and 1; LDS = 0.037 M, pH $\simeq 12.7$.

[CESTO]/[LDS]	0	0.5	1
Aggregation number, N	90	92	95
Effective charge, Q^*	16.2	15	6.9
[CESTO]/[LDS] in shell	0	0.47	0.53
Counter-ion fraction in shell	82%	84%	93%
Short-axis, $b(\text{\AA})$	16.7	16.6	16.2
Axial-ratio, a/b	1.6	1.7	1.8
Shell thickness, $d(\text{\AA})$	5.56	6.76	6.95
Hydration number	12	10	9

It is important to note that the decrease of the hydration of the micellar surface, the solubilization of CESTO at the micellar surface and the complexation of Li^+ are qualitatively in agreement with the results obtained by 7Li NMR and ESEM studies [8]. In fact, CESTO increases the shell thickness, decreasing by about 30% the number of water molecules (see the hydration number in table 2) in the micellar interfacial region.

6. Conclusions

^7Li NMR, electron-spin-echo modulation and small-angle neutron scattering results show that addition of the macrocyclic ligand, CESTO, to micellar solutions of 0.037 M LDS produces different effects that depend on the pH of the solution. At a pH > 12, CESTO is neutral and can complex Li^+ . The complexation of lithium micellar counter-ions produces a drastic reduction of the LDS surface charge and of the amount of water molecules at the micellar surface, accompanied by a growth of the aggregation number. The quasi-spherical LDS micelle becomes elongated with an axial ratio of 1.8.

The results show that the interaction of CESTO with LDS changes the 'structure' of the interface of the LDS micelle. Moreover, the CESTO-LDS interaction can be controlled and modulated by adjusting the pH of the solution [8]. This might be of considerable importance in micellar catalysis, membrane science and some specific organic syntheses that use micelles as reaction media. Furthermore, since the counter-ion distribution can be controlled and modulated, the CESTO/LDS system is particularly appealing for testing liquid state 'models'.

Acknowledgments

Thanks are due to the Italian National Council of Research (CNR) and to MURST for financial support. The research by Y C Liu and S H Chen has been supported by DOE grant DEFG02-90-ER45429. Research at the University of Houston was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy.

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