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Effect of lithium encapsulation by a macrocyclic aza cage in micellar solutions of lithium dodecyl sulfate

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Abstract

The small macrobicyclic cage (5,12,17-trimethyl-1,5,9,12,17-pentaazobicyclo[7.5.5]nonadecane, CESTO), which can selectively encapsulate lithium ions, has been studied in the presence of micellar solutions of 0.037 M lithium dodecyl sulfate (LDS). The CESTO cage behaves as a fairly strong base in the first protonation step (log $K_1 = 11.83$ where K_1 is the equilibrium constant) and exhibits two different behaviors in LDS micellar solutions. Surface tension, electron spin echo modulation (ESEM), ^{7}Li NMR and small-angle neutron scattering (SANS) measurements show that the macrocyclic cage at about pH 10.2 behaves as a bulkier counterion, while at about pH 12.7 it complexes selectively lithium counterions at the micellar surface. Furthermore, ESEM studies show that CESTO encapsulates lithium ions at the micellar surface by reducing the amount of water at the surfactant polar head groups. SANS results show that, at about pH 12.5, LDS molecules form micelles of quasi-spherical shape with an average aggregation number of 90. The effective ionization of the micelles is about 20%. The addition of CESTO leads to lithium ion complexation with a drastic reduction of the micellar surface charge, and of the hydration number. This is accompanied by the growth of the aggregation number and the micelles become more elongated.

Keywords: Counterion complexation; Lithium dodecyl sulfate; Lithium encapsulation; Macrocyclic ligand; Micelle

1. Introduction

Charge association between ions and macroions or molecular assemblies (micelles, lamellar aggregates, etc.) in aqueous solution is very important. The resulting change in the electrostatic interactions plays a dominant role in determining the thermodynamic and equilibrium structural properties of the solutions at moderate and high surfactant concentrations.

In ionic micellar solutions the counterion properties have been the object of many experimental and theoretical studies [1–10]. In most of these, electrostatic interactions have been studied by changing the ionic strength of the micellar solution (mainly by adding a salt), or by changing the counterion. Another approach, almost unexplored, is the change of the micellar properties by modulation of counterion binding through complexation with macrocyclic ligands. The second method has some advantages, since the micellar properties can be better controlled.

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Macrocyclic compounds, which form stable complexes with alkali and alkaline earth metal ions with good selectivity, have been synthesized in recent years. These compounds have been used successfully in different processes such as ion transport across an oil–water interface, 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 [11,12].

In the present study the small macrobicyclic cage 5,12,17-trimethyl-1,5,9,12,17-pentaazabicyclo [7.5.5]nonadecane (CESTO) is added to micellar solutions of lithium dodecyl sulfate (CDS) to complex the lithium counterions or to interact with the sulfate polar head groups.

Small macrocyclic cages, formed from a 12-membered tetraaza macrocycle in which two trans nitrogen atoms are bridged by two propylene chains bound to a donor atom, have special proton transfer and ligational properties. For example, only small cations, including protons, lithium, copper(II), zinc(II) and cobalt(II) can be encapsulated with a high degree of selectivity [13,14]. In addition, the cage used in the present work is a "fast proton sponge", which shows an extremely high basicity (higher than OH^- ions in aqueous solution) coupled with fast proton exchange. This means that the charge and the complexing ability of the macrocyclic ligand can be modulated simply by controlling the pH of the solution by adding a salt that cannot be complexed by the ligand (NaOH, KOH, etc.). This allows the study of two different effects produced by the addition of the macrocyclic ligand to lithium dodecyl sulfate micellar solutions. One is the complexation of lithium counterions, the other is the interaction of protonated CESTO ($[H(CESTO)]^+$) with the sulfate polar head groups of LDS micelles.

2. Experimental

2.2. Materials

Lithium dodecyl sulfate (LDS), obtained from Eastman Kodak, was recrystallized six times from

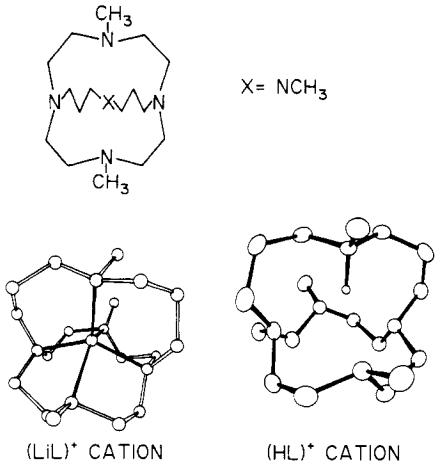

Fig. 1. Chemical structure of CESTO (top) and ORTEP drawings of $[LiCESTO]^+$ and $[H(CESTO)]^+$ cations, indicated as $(LiL)^+$ and $(HL)^+$ respectively.

a mixture of ethanol–diethyl ether (3:1 by volume), and dried under moderate vacuum at 40°C. The macrocycle 5,12,17-trimethyl-1,5,9,12,17-pentaazobicyclo[7.5.5]nonadecane ($(C_{17}H_{37}N_5)HCl \cdot H_2O$, CESTO) was synthesized and purified according to the procedure described earlier [13]. The structural formulae along with the crystal structure of the Li^+ ion complex ($[LiCESTO]^+$) and of the protonated CESTO ($[H(CESTO)]^+$) [13] are shown in Fig. 1. The compounds NaOH, LiCl, ethanol and diethyl ether were supplied by Aldrich, and D_2O was obtained from Carlo Erba, Italy. The 5-doxylstearic acid spin probe (5-DSA) was obtained from Molecular Probes, Eugene, OR, and was used as received. All the measurements were performed at 25°C (for electron spin echo modulation (ESEM) measurements, see below) under a nitrogen atmosphere.

2.3. Methods

2.3.1. Surface tension

Surface tension was measured with the Du Nouy ring method with use of a home-built apparatus stopping at the maximum distension of the meniscus. The accuracy was 0.1 mN m^{-1}.

2.3.2. ESEM

A stock solution of 5-DSA was prepared in chloroform. Films of the probe generated in vials by evaporating the chloroform were dissolved in a 0.29 M solution of LDS in D_2O in a nitrogen atmosphere. The final probe concentration was 1×10^{-4} M. All the samples were sealed in 2 mm i.d. × 3 mm o.d. or 1 mm i.d. × 2 mm o.d. Suprasil quartz tubes, and frozen rapidly in liquid nitrogen. Two-pulse electron spin echo spectra were recorded at 4.2 K on a home-built spectrometer by using 40 ns exciting pulses.

2.3.3. Small-angle neutron scattering (SANS)

SANS measurements were made at the Laboratoire Leon-Brillouin, Saclay, France, using the PAXE spectrometer. Neutrons of wavelength $\lambda = 6.5$ Å and $\Delta\lambda/\lambda = 10\%$ were used. The sample detector distance was fixed at 2.04 m, covering the Q range from 0.02 to 0.28 $Å^{-1}$. Samples were contained in flat quartz cells with a path length of 1 mm. Measurements were made at 25°C with a concentration of 1% LDS.

2.3.4. ^{7}Li NMR

The ^{7}Li NMR spectra were recorded with a Bruker AC-200 spectrometer operating at a frequency of 77.78 MHz, and using a 10^{-3} M $LiCl/D_2O$ solution as reference.

3. Results and discussion

Small cages formed from a 12-membered tetraaza macrocycle in which two trans nitrogen atoms are bridged by two propylene chains bound to a donor atom have been recently synthesized. The molecular topology and size confer special proton transfer and ligational properties to these small cages. The CESTO cage presents extremely high basicity, higher than OH^- ions in aqueous solution, coupled with fast proton exchange. In aqueous solution, the proton transfer properties of CESTO have been investigated by potentiometry. The macrocyclic cage CESTO has four nitrogen atoms that can be protonated and exhibits high basicity in the first step of protonation and moderate and weak basicity in the subsequent steps. The following equilibria are present in solution:

$$H^+ + (CESTO) = [H(CESTO)]^+ \qquad \log K_1 = 11.83$$

$$H^+ + [H(CESTO)]^+ = [H_2(CESTO)]^{2+} \qquad \log K_2 = 9.53$$

$$H^+ + [H_2(CESTO)]^{2+} = [H_3(CESTO)]^{3+} \qquad \log K_3 = 3.43$$

where K_1, K_2 and K_3 are the equilibrium constants.

The amounts of CESTO and CESTO cations present in the solution as a function of pH are shown in Fig. 2. The figure shows that the monoprotonated species of the macrocyclic cage is predominant (approximately 90%) when CESTO is dissolved in pure water (about pH 10.2), while at pH above 12.2 CESTO is about 100% neutral.

It is worthwhile to notice that only neutral CESTO can complex lithium selectively. Therefore it is possible to modulate CESTO activity in LDS micellar solutions simply by controlling the pH of the solution by the addition of sodium or potassium hydroxide, where the cations cannot be complexed by CESTO. In this way it is possible to study two different effects that are produced, in LDS micellar solutions, without changing the steric hindrance of CESTO: (i) the complexation of Li^+ counterions by the "neutral" CESTO; (ii) the interaction of $[H(CESTO)]^+$ with the sulfate head

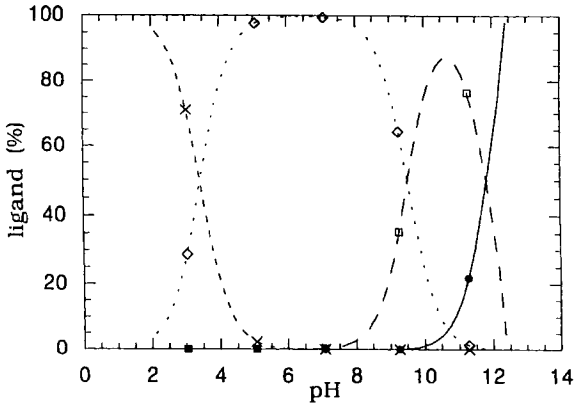

Fig. 2. Concentrations of CESTO and CESTO cations in aqueous solution as a function of the pH of the solutions: ●, CESTO; □, $CESTO^+$; ◇, $CESTO^{2+}$; ×, $CESTO^{3+}$. The percentages of CESTO and CESTO cations were determined by potentiometric titration.

groups. In this work we studied the effects induced by the addition of CESTO to LDS micellar solutions at about pH 10.2 and 12.7, corresponding to the monoprotonated form and the neutral form of CESTO respectively.

3.1. Surface tension

Figure 3 shows the surface tension versus the log of the concentration for LDS, CESTO and two LDS/CESTO equimolar mixtures at about pH 10.2 and 12.7. The figure shows that no breaks are present in the surface tension versus concentration curve for CESTO and only a small decrease in the surface tension is present over two decades of CESTO concentration, indicating that CESTO behaves as an electrolyte. A different trend is present for pure LDS and the two LDS/CESTO mixtures. The curves show, for LDS and the mixtures studied, a break which is indicative of the presence of a CMC in these systems. The addition of CESTO to LDS produces a sharp decrease in the CMC. In particular the CMC is 4.3×10^{-4} M at pH 12.7, and 6.0×10^{-5} M at about pH 10.2. This result is in agreement with the fact that at about pH 10.2, CESTO is monoprotonated and can interact with the negatively charged polar head groups of LDS, while at about pH 12.7, CESTO is neutral and complexes Li^+ ions at the micellar surface. The Li^+ ion encapsulation at the micellar surface is also supported by the decrease in the slope of the surface tension versus log concentration curve below the CMC, which indicates an increase in the area occupied per LDS polar head group.

3.2. ^7Li NMR

In aqueous solution the Li^+ ion is readily encapsulated by CESTO according to the following equilibrium:

$$Li^+(aq) + CESTO(aq) = [LiCESTO]^+(aq)$$

The ^7Li spectrum of the complex, at about pH 12.7 shows a sharp signal at +0.884 ppm shifted with respect to that of the solvated Li^+ ion [13]. This difference between the chemical shifts of complexed and solvated Li^+ ions is similar to shifts found for other cryptands and shows that the resulting complex is very stable [15,16]. It is also remarkable that lithium complex formation requires the removal of all the water molecules that surround the free lithium ion in aqueous solution, and that the complex formation is not

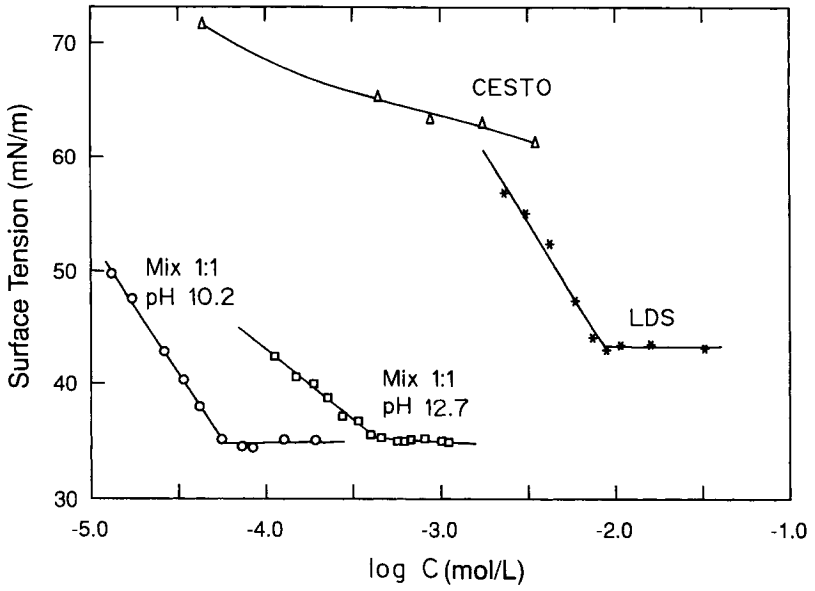

Fig. 3. Surface tension of CESTO, LDS, and two equimolar mixtures of CESTO/LDS at about pH 10.2 and 12.7.

affected by the presence of Na^+ ions, even at very high concentration [13].

Figure 4 reports the ^7Li NMR spectra for LiCl/CESTO and LDS/CESTO solutions at a concentration of 0.037 M, which corresponds to about 1% LDS by weight. In the NMR spectra two peaks are present, corresponding to free (0 ppm) and complexed Li^+ (0.884 ppm) ions. The spectra show that most of Li^+ ions are not complexed at about pH 10.2–10.3 in CESTO/LiCl or CESTO/LDS solutions, where CESTO is mainly positively charged (see Fig. 2). The Li^+ ion complexation occurs at about pH 12.7 for both LiCl and LDS micellar solutions; in these solutions about 91% and 80% of Li^+ ions are encapsulated by the neutral CESTO. It is worthwhile to note that under our experimental conditions, ^7Li NMR gives only the amount of Li^+ ions complexed. This means that in the case of LDS micellar solutions it is not possible to discriminate between the Li^+ ions bound to the LDS micellar surface and the Li^+ ions in the aqueous phase. Further experiments are in progress to elucidate this point.

3.3. ESEM results

Electron spin echo (ESE) spectroscopy is a pulsed version of electron spin resonance spectroscopy. The most common type of pulse sequence consists of a 90° focusing pulse followed by a precession time and then a 180° spin flip pulse which causes the spin to refocus within another precession time period. The refocusing produces a burst of microwave energy, the "echo". The echo intensity is measured as a function of the time between the two pulses to generate an echo decay envelope. In many cases the echo decay envelope is modulated by weak dipolar hyperfine inter-

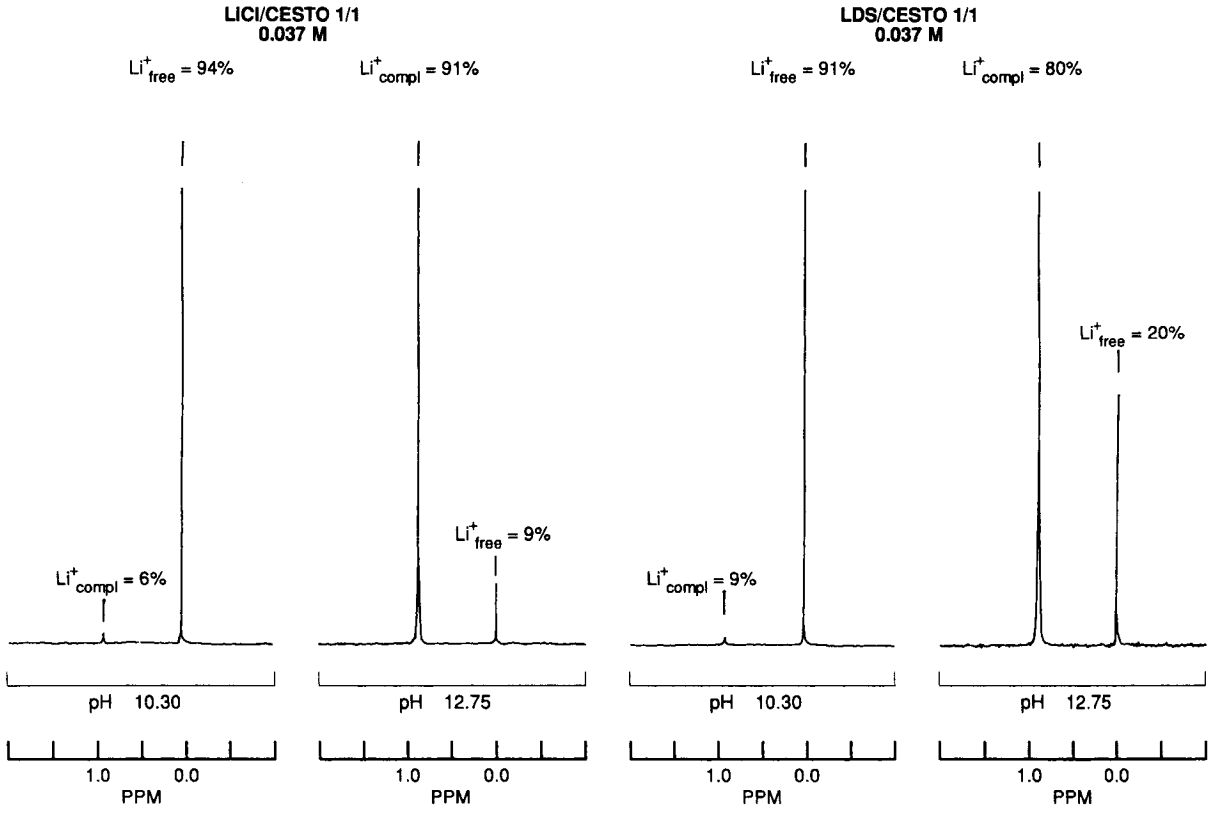

Fig. 4. ^7Li NMR spectra of LiCl/CESTO/D_2O (left) and LDS/CESTO/D_2O (right) solutions at about pH 10.3 and 12.75. The amount of free and complexed Li^+ ions is calculated by peak integration.

actions between the paramagnetic species and neighboring magnetic nuclei (in the present study, deuterium) within the range 0.2–0.6 nm. This modulation is primarily a function of the number and distance of the closest surrounding magnetic nuclei. Analysis of the electron spin echo modulation (ESEM) provides significant structural information which is generally not available from electron spin resonance spectroscopy. In this study the 5-doxylstearic acid spin probe is solubilized in LDS/D_2O micellar solutions to probe the electron–D_2O dipolar interaction. This interaction is primarily a function of the number and distance of the closest surrounding magnetic nuclei and is detectable in 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 deuterium atoms and on their distance from the spin probe, in disordered systems such as micelles, a decrease in the deuterium modulation depth reflects a decrease in the number of water molecules present at the micellar surface [17,18]. In previous studies, it was shown that the 5-DSA spin probe in a micellar solution of ionic and cationic surfactants solubilizes in the micelle with the acidic group at the micellar surface, close to the polar head group [19,20].

Table 1 reports the normalized deuterium modulation depth at two different pH values for pure LDS micellar solutions and for LDS micellar solutions in the presence of CESTO. The normalized deuterium modulation depth is the same for pure LDS micellar solutions at about pH 10.2 and 12.7. The addition of CESTO to LDS micellar solutions leads to a strong decrease in the normalized modulation depth, indicating that the presence of CESTO reduces the amount of water molecules at the micellar surface. Furthermore, this reduction is dependent on the solution pH, i.e. on the presence of CESTO or $[H(CESTO)]^+$ in solution, and it is lower for the system at about pH 12.7. This is in agreement with the surface tension and NMR measurements, which show that only neutral CESTO can complex Li^+ ions. Since ESEM can detect deuterium modulation up to 6 Å from the unpaired electron [17,18] of 5-DSA, and the 5-DSA probe is located at the LDS polar head groups, the above results show that CESTO interacts at the micellar surface by decreasing the local amount of water. In particular the lower modulation depth at about pH 12.7 indicates that the Li^+ ion complexation occurs with the removal of the water molecules that surround the lithium ion.

3.4. SANS results

In the analysis of SANS data a two-shell model is used to calculate the form factor of the micelle. We assume that the micelles have a hydrophobic core of prolate ellipsoidal shape, with principal axes *a*, *b*, *b*, and an outer layer of thickness *d*. The inner core contains hydrocarbon chains (C_2–C_{12}) of LDS. The outer layer is composed of the polar head groups, C_1 of the hydrocarbon chain, a proportion of the counterions, a proportion of CESTO, and water molecules (D_2O).

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

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

where C_M is the number density of the surfactant molecules, N is the average aggregation number of the micelle, $\sum b_i$ is the total scattering length of all

Table 1
Normalized deuterium modulation depth for 5-DSA probe in LDS and LDS/CESTO micellar solutions

Micellar solution	Normalized deuterium modulation depth	
	pH 10.2[a]	pH 12.7[a]
LDS	0.50 ± 0.03	0.48 ± 0.03
LDS/CESTO, 1:1 mole ratio	0.28 ± 0.03	0.16 ± 0.02

[a] Approximate pH value.

atoms in the monomer, including the atoms associated with the 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. More details concerning the data analysis are reported in Refs. 22 and 23.

Table 2 reports the parameters obtained from the analysis of SANS data from the LDS/CESTO system at about pH 12.7. Table 2 shows that, upon the addition of 0.5 and 1 mole ratios of CESTO, the aggregation number increases slightly from 90 to 95, the axial ratio of the ellipsoidal core increases from 1.6 to 1.8, the effective charge decreases, and the counterion fraction in the shell increases, reducing the effective fractional micellar ionization from 18% to 7%. This last effect is due to the complexation of lithium ions by CESTO. In addition, the hydration of the micellar surface decreases, owing to CESTO incorporation at the micellar surface and Li^+ ion complexation.

It is important to notice that the decrease in the hydration of the micellar surface, the solubilization of CESTO at the micellar surface and the complexation of Li^+ ions are qualitatively in agreement with the results obtained by surface tension, ^7Li NMR and ESEM studies.

Table 2
Parameters obtained from the analysis of SANS data for micellar solutions of lithium dodecyl sulfate in the presence of the macrocyclic ligand CESTO at different CESTO/LDS mole ratios

Parameter	[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
Counterion fraction in shell	82%	84%	93%
Short axis, b (Å)	16.7	16.6	16.2
Axial ratio, a/b	1.6	1.7	1.8
Shell thickness, d (Å)	5.56	6.76	6.95
Hydration number	12	10	9

LDS concentration, 0.037M; pH approximately 12.7.

4. Conclusions

Surface tension, ^7Li NMR, ESEM and SANS results show that the addition of the macrocyclic ligand CESTO to micellar solutions of 0.037 M LDS produces different effects which depend on the pH of the solution. In water and in micellar solutions, CESTO is mainly monoprotonated at its "natural" pH (about 10.2) and can be deprotonated by increasing the solution pH, for example by adding sodium hydroxide. Above pH 12, CESTO is neutral and can complex Li^+ ions. The complexation of lithium counterions produces a drastic reduction in the LDS surface charge and in the amount of water molecules at the micellar surface, which are accompanied by the growth of the aggregation number. The quasi-spherical LDS micelle becomes elongated with an axial ratio of 1.8.

At about pH 10.2, $[H(CESTO)]^+$ interacts with the sulfate polar head groups acting as a bulkier counterion, probably replacing the Li^+ counterion. This leads to a decrease in the number of water molecules present at the micellar surface and to a CMC value about 150 times lower than that of pure LDS.

These results show that the interaction of CESTO with LDS changes the "structure" of the interface of LDS micelles. Furthermore, the CESTO–LDS interaction can be controlled and modulated by adjusting the pH of the solution. This might be of considerable importance in micellar catalysis, membrane science, and some specific organic syntheses that use micelles as reaction media.

5. Acknowledgments

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