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Structure and aggregation of lithium dodecyl sulfate micelles in the presence of a macrocyclic cage: a SANS study

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Abstract: At pH=12, a macrocyclic cage CESTO is a neutral molecule known to complex Li^+ in aqueous solution. We study the effect of addition of CESTO on the aggregation behavior of lithium dodecyl sulfate (LDS) by small angle neutron scattering. In aqueous solutions the LDS molecules form micelles of quasi-spherical shape with aggregation number of 90 and fractional ionization of 18%. Upon addition of 0.5 to 1 and 1 to 1 molar ratios of CESTO to the solutions, the aggregation number increases but the ionization reduces due to the complexation of lithium ions by CESTO. This is also accompanied by the decrease of hydration number on the micellar surface.

1. Introduction

Macrocyclic compounds with strong affinity and high selectivity for metal ions have recently been synthesized. These compounds form stable complexes with cations and anions. They have been successfully used in different processes such as separation of ions, liquid-liquid phase transfer reactions, dissolution in apolar solvents of metals and organic salts, ion-selective electrodes, and isotopes separation, etc. Despite the large use of these compounds as complexing agents in solution, the properties of dispersed systems such as micelles, vesicles, reconstructed membranes, etc., in the presence of macrocyclic compounds are virtually unknown. In the present study 5,12,17 Trimethyl 1,5,9,12,17-pentazabicyclo[7.5.5] nonadecane (CESTO) are added to the micellar solutions of lithium dodecylsulfate (LDS). The form of CESTO is neutral at pH>12 and can complex lithium ions selectively.

2. Small Angle Neutron Scattering (SANS) Experiment

SANS measurements were made at Laboratoire Leon-Brillouin, Saclay, France using PAXE spectrometer. Neutrons with wavelength $\lambda = 6.5 \text{ \AA}$ and $\Delta\lambda / \lambda = 10\%$ were used. The sample to detector distance was fixed at 2.04 m, covering the Q range of 0.02 to 0.28 $\text{\AA}^{-1}$. Samples were contained in flat quartz cell with a path length of 1 mm. Measurements were made with LDS concentrations of 1.48 % at room temperature of 25 °C. In this paper we report only the result of 1% solution.

3. Model for the Normalized Form Factor $\tilde{P}(Q)$

We assume that the micelles have a hydrophobic core of the shape of an ellipsoid with principle axes a, b, b and an outer layer of thickness d . A two-shell model is

used to calculate the form factor. The inner core contains hydrocarbon chains (C2 to C12) of LDS molecules. The outer layer is composed of the head group SO_4^- and C1 of the hydrocarbon chain, certain fraction of counterions, certain fraction of CESTO, and solvent molecules (D_2O). Most of Li^+ ions in the shell are complexed by CESTO.

We can write the orientation dependent form factor as, [1]

$$\begin{aligned} F(Q, \mu) &= f \frac{3j_1(u)}{u} + (1-f) \frac{3j_1(v)}{v} \\ u &= Q[\mu^2 a^2 + (1-\mu^2)b^2]^{1/2} \\ v &= Q[\mu^2(a+d)^2 + (1-\mu^2)(b+d)^2]^{1/2} \\ f &= V_t(\rho_1 - \rho_2) / [\Sigma b_i - V_m \rho_s] \end{aligned} \quad (1)$$

The dry volume of LDS is $V_{\text{LDS}} = 410 \text{ \AA}^3$, and the dry volume of CESTO is assumed to be $V_{\text{CESTO}} = 385 \text{ \AA}^3$. The monomer volume $V_m = V_{\text{LDS}} + N_c V_{\text{CESTO}}$ where N_c is the number of CESTO associated with each LDS molecule. The scattering density of the solvent ρ_s is given by the scattering length of D_2O divided by the volume of water molecule, $30.27 \text{ \AA}^3$. The total scattering length Σb_i is the sum of scattering lengths of all atoms in the monomer including the atoms of associated CESTO molecule. The scattering density of hydrophobic core ρ_1 equals to the scattering length of hydrocarbon chain divided by the the volume of the core. The scattering density of hydrophilic outer layer can be written as $\rho_2 = (b_1 + b_2 + b_3 + b_4) / V_{\text{shell}}$ where $V_{\text{shell}} = 4\pi/3[(a+d)(b+d)^2 - ab^2]$ denotes the volume of the outer layer. The four scattering lengths correspond to: LDS head group $b_1 = \bar{N} b_{\text{HD}}$, counterions remaining in the shell $b_2 = \bar{N}(1-\alpha)b_{\text{Li}^+}$, CESTO associated with the LDS $b_3 = \bar{N} N_c b_{\text{cesto}}$, and solvent molecule $b_4 = \bar{N} N_s b_{\text{solvent}}$, respectively. The hydration number N_s is determined by

$$N_s = \left[\frac{V_{\text{shell}}}{\bar{N}} - (V_m - V_t)(1-\alpha) - (V_m - V_t - V_{\text{Li}^+})\alpha \right] / V_{\text{shell}}$$

In this LDS-CESTO system, the scattering lengths of head group, CESTO, Li^+ , and solvent D_2O are evaluated as 2.4165×10^{-4} , 2.389×10^{-4} , -1.90×10^{-4} , $1.9153 \times 10^{-4} \text{ \AA}$, respectively.

The particle structure factor $\bar{P}(Q)$ is the orientational average of the square of the form factor, namely,

$$\bar{P}(Q) = \int_0^1 d\mu |F(Q, \mu)|^2 \quad (2)$$

The $S(Q)$ is also modified by the orientation effect [2] ,

$$\tilde{S}(Q) = 1 + \frac{\langle |F(Q, \mu)|^2 \rangle}{\langle |F(Q, \mu)|^2 \rangle} [S_{MM}(Q) - 1] \quad (3)$$

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

$$I(Q) = C_M \bar{N} (\Sigma b_i - V_m \rho_s)^2 \tilde{P}(Q) \tilde{S}(Q) \quad (4)$$

where C_M is the number density of surfactant molecules and $\bar{N}$ the average aggregation number in a micelle.

4. Model for the Microion-Microion Structure Factor $S_{MM}(Q)$

Consider a micellar solution as composed of macroions (micelles), counterions and salt ions which interact with each other through electrostatic forces in a dielectric medium of the solvent. A non-additive diameter MSA theory [3,4] was formulated by Ronis and coworkers to reduce this multi-component system into an effective one-component system consisting of microions with a renormalized charge dispersed in the solvent. The effective macroion-macroion (MM) direct correlation function outside the hard core was shown to be a Yukawa form if the counterions and salt ions are taken as point particles. Thus calculation of the MM-structure factor $S_{MM}(Q)$ follows the same procedure as the well known one-component microion (OCM) theory using DLVO potential [5,6]. The renormalized charge Q^* is a function of ionic strength and the macroion hard core diameter and is considerably lower than the aggregation number of micelles. This non-additive MSA theory is, however, more powerful than the OCM theory because it allows one to calculate also other correlation functions such as macroion-counterion correlation function which is useful for evaluation of various thermodynamic properties of the system.

5. Conclusion

We study the aggregation behavior of a LDS micellar solution upon addition of CESTO at pH=12 using SANS. For 1% LDS system, upon addition of 0, 0.5, 1 molar 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 fractional micellar ionization reduces from 18% to 7% due to the complexation of lithium ions by CESTO; and the hydration number of each LDS molecule reduces from 12 to 9 due to incorporation of CESTO on micellar surface. By using a two-shell model for form factor, we can deduce the amount of CESTO associated on the surface of micelle. The

effective charge obtained is qualitatively consistent with a separate NMR study on this system, which shows that about 80% of the free lithium ions are complexed by CESTO [7].

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References:

- [1] E. Y. Sheu and S.H. Chen, J. Phys. Chem., 91, 1535 (1987)
- [2] M. Kotlarchyk and S.H.Chen, J. Phys. Chem, 79, 2466 (1983)
- [3] S. Khan and D. Ronis, Mol. Phys., 60, 637 (1987)
- [4] S. Khan, T.L. Morton and D. Ronis, Phys. Rev. A, 35, 4295 (1987)
- [5] J.B. Hayter and J. Penfold, Mol. Phys, 42, 109 (1981)
- [6] S. H. Chen, E.Y. Sheu, J. Kalus and H. Hoffman, J. Appl. Cryst., 21, 751 (1988)
- [7] P. Baglioni, E. Rivara-Minten and L. Kevan, J. Phys. Chem., 92, 4726 (1988)

[cesto]/[lds]	0	1/2	1.0
aggregation number N	89.7	92.2	94.7
effective charge Q^*	16.2	15.0	6.9
[cesto]/[lds]	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 N _s	12	10	9

Figure 1. Intensity SANS data and fitted curves

Figure 2. Structure Factor curves

Figure 3. Normalized Form Factor curves

- solid line: [cesto]/[lds]=0;
- × dashed line: [cesto]/[lds]=0.5;
- + dash-dotted line: [cesto]/[lds]=1.0.

Table I. Fitted Parameters for [LDS]=1 % at pH=12