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DIFFRACTION AND SCATTERING OF NEUTRONS

Small-Angle Neutron Scattering Study of the Structure of Mixed Micellar Solutions Based on Heptaethylene Glycol Monotetradecyl Ether and Cesium Dodecyl Sulfate

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Abstract—The micellization in mixed aqueous systems based on a nonionic surfactant, heptaethylene glycol monotetradecyl ether ($C_{14}E_7$), and an anionic surfactant, cesium dodecyl sulfate, has been investigated by small-angle neutron scattering. Preliminary data on the behavior of the $C_{14}E_7$ aqueous solutions (with three concentrations, 0.17, 0.5, and 1%) mixed with a small amount of anionic surfactant, cesium dodecyl sulfate, are reported.

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INTRODUCTION

Mixed micelles, containing more than one surfactant in their composition, are very important for both fundamental and technological studies in pharmaceutics and biology. Mixtures if ionic and nonionic surfactants are more promising for practical applications, because they have better properties than individual surfactants. Rather often a mixture of ionic and nonionic surfactants exhibits "nonideal" behavior. The critical micellization concentration (CMC) for a mixture is lower than for solutions of individual surfactants. The addition of a nonionic surfactant to an ionic one reduces the electrostatic repulsion between charged heads of ion surfactant molecules and increases the micelle sizes [1–9, 12–21]. The nonideal behavior of ionic–nonionic systems is also determined by some other structural characteristics of the two surfactants, such as the difference in sizes of groups of heads and the length of tails of surfactant molecules. The interaction of surfactant molecules in mixed solutions is a very complex process, especially in the case of mixed systems of surfactants of different types. The purpose of our study, which is devoted to mixed aqueous solutions of an anionic surfactant, cesium dodecyl sulfate (CDS), and a nonionic surfactant, heptaethylene glycol monotetradecyl ether ($C_{14}E_7$), is to clarify the specific features of this interaction.

EXPERIMENTAL

Chemical Materials

All the solutions under study were prepared in heavy water (D_2O, degree of deuteration 99.9%). We used surfactant samples, heptaethylene glycol monotetradecyl ether ($C_{14}E_7$) and CDS (Sigma-Aldrich), without additional purification.

CMC Measurements

Tensiometric CMC measurements were performed by the ring method. The surface tension of aqueous surfactant solutions decreased very rapidly with an increase in their concentration to the CMC level, after which they remained constant. The CMC values for the surfactants under study were determined from the dependence of the surface tension on the logarithm of surfactant concentration. The CMC for $C_{14}E_7$ in a D_2O solution was found to be 1.42×10^{-5} mol/L at room temperature.

SANS Measurements

All SANS measurements were carried out on a time-of-flight small-angle YuMO diffractometer installed on the IBR-2 pulsed reactor at the Joint Institute for Nuclear Research, Dubna. Some specific features of the spectrometer were described in details in [10]. Neutrons with wavelengths in the range of 0.7–10 Å^{-1} were used. Solutions were poured into 2-mm-thick closely capped quartz cells (Hellma). A thermostat was applied to maintain the temperature in

Average distances between micelles and aggregation numbers in micellar solutions for three $C_{14}E_7$ + CDS + D_2O mixtures (CMC = 1.20×10^{-5} mol/L) with different concentrations of nonionic surfactant

Sample	$C_{14}E_7$ concentration		CDS concentration, mol/L	Aggregation number N	Average distance between micelles d, Å
	%	mol/L			
1	0.17	3.25	0.216	206	418
2	0.17	3.25	1.083	105	314
3	0.17	3.25	2.160	82	310
4	0.5	9.56	0.372	240	300
5	0.5	9.56	1.860	141	224
6	0.5	9.56	3.720	93	209
7	1	19.12	0.573	330	289
8	1	19.12	2.866	151	208
9	1	19.12	5.733	98	157

the cells constant during measurements: 25 ± 0.5°C. The measured differential neutron-scattering cross section was calibrated with the aid of a vanadium standard. Primary data processing was performed using the SAS program [11]]. Heavy water D_2O was used as a solvent for all samples to implement good contrast conditions. Experimental results were processed using the PCG Software 2.0 (Austria).

RESULTS

The experiment was performed for nine mixed solutions of $C_{14}E_7$ in D_2O: three non-ionic-surfactant concentrations (0.17, 05, 1%) and nine different concentrations of ionic surfactant CDS (see table). The SANS results are presented in Figs. 1–3.

Figure 1 shows experimental SANS data for three mixtures with concentration c of non-ionic-surfactant in D_2O equal to 0.17%. These mixtures differ by the concentration of conventional anionic surfactant: CDS. For a $C_{14}E_7$ content of 0.17%, the intersection point of the curves ($Q = 0.027989$ Å^{-1}) is independent of the amount of added anionic surfactant. Figure 2 presents a set of SANS curves for three concentrations of anionic surfactant CDS: $c_1 = 0.372$ mmol/L, $c_2 = 1.860$ mmol/L, and $c_3 = 3.720$ mmol/L (the content of $C_{14}E_7$ in D_2O is 0.5% in all three cases). At a $C_{14}E_7$ content of 0.5%, the intersection point of the curves ($Q = 0.02865$ Å^{-1}), like for the concentration of 0.17%, is independent of the amount of added anionic surfactant.

Figure 3 shows experimental scattering curves for three mixed systems with $c_7 = 0.573$ mmol/L, $c_8 =$

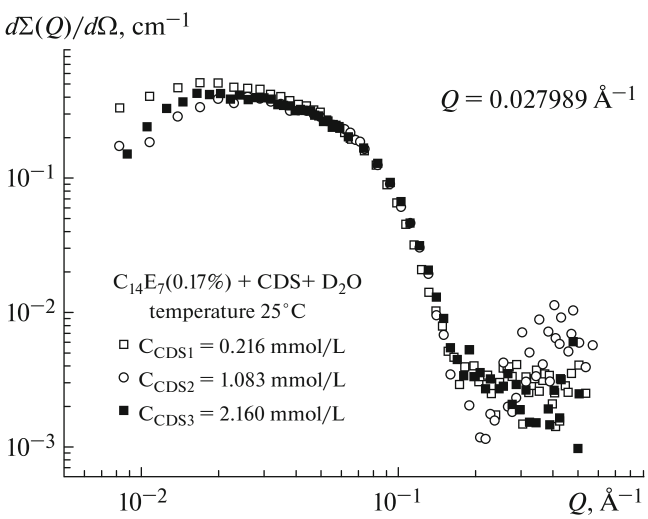

Fig. 1. Dependences of the neutron scattering intensity on the scattering vector modulus for a $C_{14}E_7$ + D_2O + CDS mixture. The $C_{14}E_7$ + D_2O content is $c = 0.17\%$; the CDS contents are $c_1 = 0.216$ mmol/L, $c_2 = 1.083$ mmol/L, and $c_3 = 2.160$ mmol/L.

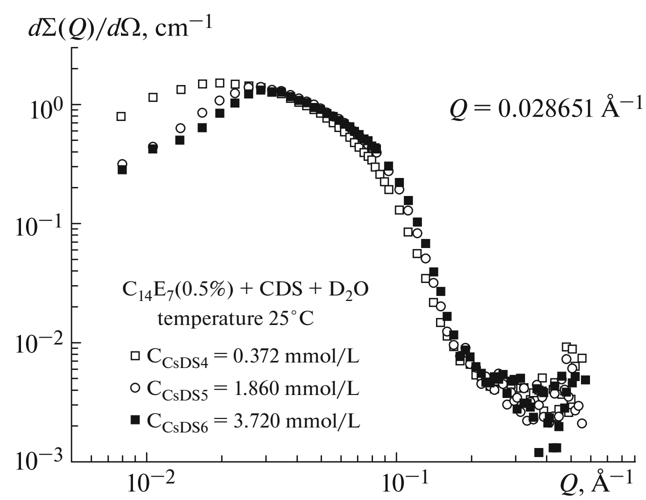

Fig. 2. Dependences of the neutron scattering intensity on the scattering vector modulus for a $C_{14}E_7$ + D_2O + CDS mixture. The $C_{14}E_7$ + D_2O content is $c = 0.50\%$; the CDS contents are $c_4 = 0.372$ mmol/L, $c_5 = 1.860$ mmol/L, and $c_6 = 3.720$ mmol/L.

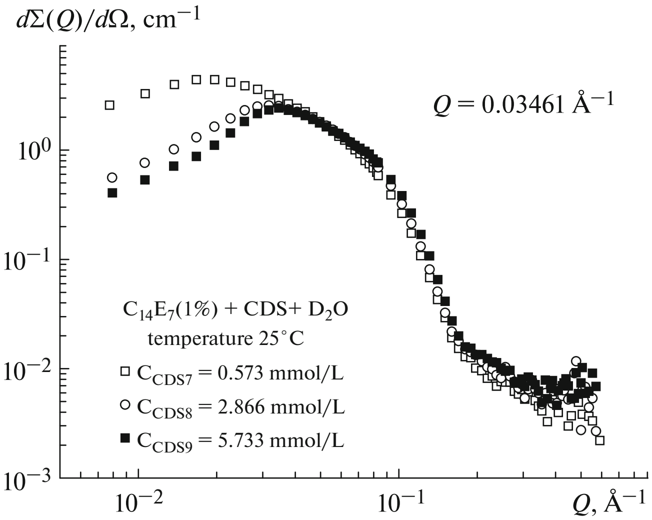

Fig. 3. Dependences of the neutron scattering intensity on the scattering vector modulus for a $C_{14}E_7$ + D_2O + CDS mixture. The $C_{14}E_7$ + D_2O content is c = 1%; the CDS contents are c_7 = 0.573 mmol/L, c_8 = 2.866 mmol/L, and c_9 = 5.733 mmol/L.

2.866 mmol/L, and c_8 = 5.733 mmol/L (the content of $C_{14}E_7$ in D_2O is c = 1%). The intersection point of these curves is $Q = 0.03461$ Å^{-1}.

These experimental data indicate that the scattering curves for the $C_{14}E_7$ + D_2O solutions with an additive of anionic surfactant CDS contain a singularity that arbitrarily divides the curves into two regions. Below this point (where Q is small but larger than the Q value found from the average distance between micelles, $d = 2\pi/Q$), the scattering curves for solutions with higher concentrations are located above the curves for the solutions with lower concentration, whereas after this point the situation is the other way around. In other words, for solutions with higher concentrations, the scattering intensity decreases (these solutions contain more small micelles), but only at scattering vectors below a certain value. To the right of this singularity (intermediate and large values of scattering vector Q), solutions with lower concentrations contain more micelles of a larger size.

Thus, the intersection point of scattering curves (dependences of scattering intensity on the momentum transfer) is determined by the amount of anionic surfactant (CDS) added to the solution and the concentration of nonionic surfactant $C_{14}E_7$ in the initial solution.

The SANS curves for the $C_{14}E_7$ + D_2O + CDS ternary system (0.5, 1% nonionic surfactant) differ from those for a concentration of 0.17%. The scattering curves for the two highest concentrations of nonionic surfactant with CDS added (0.5% with c_5 = 1.860 mmol/L, c_6 = 3.720 mmol/L and 1% with c_6 = 2.866 mmol/L, c_9 = 5.733 mmol/L) show that the interaction between micelles is obviously stronger for the highest concentrations in the ternary system.

CONCLUSIONS

The aggregation number for the $C_{14}E_7$ + D_2O + CDS 0.17% solutions was found to be smaller than for the $C_{14}E_7$ + D_2O + CDS 0.5% and $C_{14}E_7$ + D_2O + CDS 1% solutions. The average distance between micelles in the $C_{14}E_7$ + D_2O + CDS 0.5% solutions with three different CDS concentrations decreases with an increase in the ionic-surfactant concentration. The electrostatic interaction between micelles for the solutions with a higher content of CDS is stronger than for $C_{14}E_7$ + D_2O + CDS 0.17%. The scattering curves for all the solutions under study contain a singularity: an intersection point.

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