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Physicochemical Properties of Low-Dimension Systems: Micellar Solutions of Surfactants and Surfactant/Polymer Complexes

N. N. Kochurova, M. V. Dmitrovskaya, E. R. Airapetova, O. P. Korotkikh, and N. G. Abdulin

St. Petersburg State University,
Universitetskii pr. 26, St. Petersburg, 198504 Russia

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Abstract—As shown in theoretical papers [1] and confirmed by experiments, the transport coefficients in micellar aqueous solutions exhibit a number of anomalies (minima and maxima in the concentration dependences). The studies revealed the existence of four critical micellization concentrations. At approximately 30°C, the critical micellization concentrations have a minimum. Measurements of the dynamic surface tension furnish information on surfactant/polymer complexation.

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Surfactants and surfactant/polymer complexes are widely used in various branches of industry, agriculture, and medicine, in private life, etc. [1, 2]; therefore, it is necessary to study their physicochemical properties, primarily the surface tension, electrical conductivity, viscosity, and critical micellization concentrations (CMCs). A characteristic feature of the systems under consideration is their capability for self-aggregation, due to hydrophobic and electrostatic interactions and to hydrogen bonding. In the process, the physicochemical properties of the system dramatically change. Aggregation of aqueous solutions of surfactants and surfactant/polymer complexes has been studied in numerous papers. However, the region of micellar transition has still been examined poorly. In the first part of this paper we report the results of measuring the viscosity of micellar solutions, and in the second part we analyze the surfactant/polymer complexation on the basis of dynamic surface tension measurements.

Viscosity of micellar solutions. Markina et al. [3] revealed in the region of CMC anomalies in the concentration dependence of the equivalent electrolytic conductivity (maxima and minima), which could be atributed to the concentration dependence of the aggregation number in the course of micelle formation [1, 4].

For Newtonian fluids, the viscosity is a constant depending on temperature and pressure. In micellar solutions of surfactants and surfactant/polymer solutions, specific features of a non-Newtonian fluid are manifested. With increasing concentration, the shape and size of macromolecules and the character of hydrodynamic interaction between them change. The viscosity is no longer a substance constant [5]. Apparently, these features should affect the concentration dependence of the viscosity.

We measured the viscosity of aqueous solutions of a cationic surfactant, dodecylamidoethyldimethylbenzylammonium chloride ($C_{24}H_{42}N_2OCl$).

In this study we used a capillary Ubbelohde viscometer (VPZh-2). The concentration range was 10^{-4}–10^{-1} M. Measurements were performed at 20, 25, 30, 35, and 40°C. The temperature was maintained with an accuracy of 0.05°C. The measurement error did not exceed 0.8%.

The concentration dependence of the relative viscosity $\eta_{rel} = \eta/\eta_0$ (where η and η_0 are the viscosities of the solution and water, respectively) at 20°C is shown in Fig. 1. Similar pattern was obtained for the other temperatures. These data show that there are four areas with a sharp variation of the viscosity. From the variation of the surface tension, we previously determined the first critical micellization concentration (CMC_1) at various temperatures [6]: 4.5×10^{-4}, 3.4×10^{-4}, 2.6×10^{-4}, and 5.5×10^{-4} M at 20, 25, 30, and 35°C, respectively. These values correspond to the concentrations before a maximum in the η_{rel}–$\log c$ curves. Here we obtained a consistent value (Fig. 1): 4.4×10^{-4} M at 20°C. Our experiments show that CMC is a narrow concentration range (rather than a point) in which the self-aggregation occurs. We observe two sharp viscosity jumps: a maximum and a minimum, followed by a smoother increase in the viscosity.

On approaching CMC_2 and CMC_3, the qualitative pattern is reproduced. However, in the region of CMC_4 there is no maximum or minimum. The curve of the viscosity vs. $\log c$ has two linear portions with different slopes; their interception point defines CMC_4 and suggests a new change in the micelle shape. A similar pattern is observed with other surfactants (see, e.g., [6]).

The temperature dependence of all the four CMCs shows an interesting pattern: It is nonmonotonic, with a minimum at about 303 K (Fig. 2). In the literature there are data on the existence of a minimum for different surfactants, with different determination methods: calorimetry, surface tension measurement, etc. [7–9]. Our studies showed [10] that this phenomenon is associated with the open-work structure of the solvent, water, which is smeared at 40°C. The properties of water at different temperatures were studied as early as by D.I. Mendeleev. The temperature of 40°C is termed the Mendeleev point for water. As we showed in [10], the character of hydration of surfactant ions, affecting the hydrophobic effect and CMC, changes in the vicinity of this point. At higher and lower temperatures, higher concentrations of surfactant molecules are required to form micelles.

Possibility of surfactant/polymer complexation, assessed by measuring the dynamic surface tension. We examined the effect of additions of cationic (polydiallyldimethylammonium chloride, compound **I**, $M_w \approx 240000$) and anionic (sodium polystyrenesulfonate, compound **II**, $M_2 \approx 500000$ and 70000; maleic acid–α-methylstyrene copolymer, compound **III**, $M_w \approx 24000$) polyelectrolytes on the adsorption kinetics of aqueous solutions of a cationic surfactant (dodecylamidoethyldimethylbenzylammonium chloride, compound **IV**) at 20°C, using the method of maximal pressure in a gas bubble.

Measurements were performed with a SITA line t60 device (Germany) [11, 12] operating in the time range of up to 1 min. The bubble formation frequency and temperature were monitored automatically. The measurement error was ± 0.5 mN m^{-1}.

Figure 3 shows the results of measuring the dynamic surface tension in solutions containing a cationic polyelectrolyte (**I**) and a cationic surfactant (**IV**). The surfactant concentration was 9.5×10^{-4} M in all the mixtures. Curve *1* shows data for the surfactant without polyelectrolyte, and curves 2–8, for the mixtures containing from 9.7×10^{-5} to 1.5×10^{-3} M polyelectrolyte (concentration ratio z of polyelectrolyte to surfactant from 0.1 to 1.5). It is seen that the surfactant adsorption increases with an increase in the polycation concentration because of the salting-out effect, and the surface activity of the mixtures increases, suggesting formation of aggregates in solution. A similar trend was found in [13] for a mixture of anionic surfactants and a polyelectrolyte. This effect is compared in [13] with the effect exerted by simple salts on surfactant solutions. An increase in adsorption for a mixture of **I** and **IV** relative to the adsorption of the com-

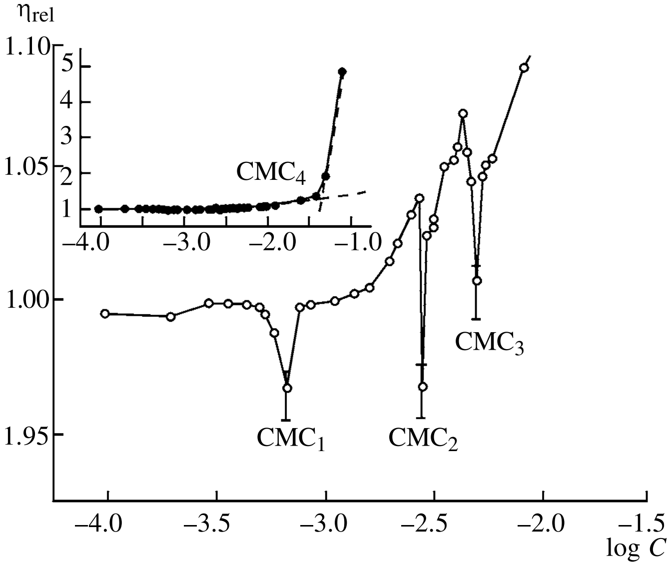

Fig. 1. Relative viscosity of an aqueous solution of **IV** at 293 K.

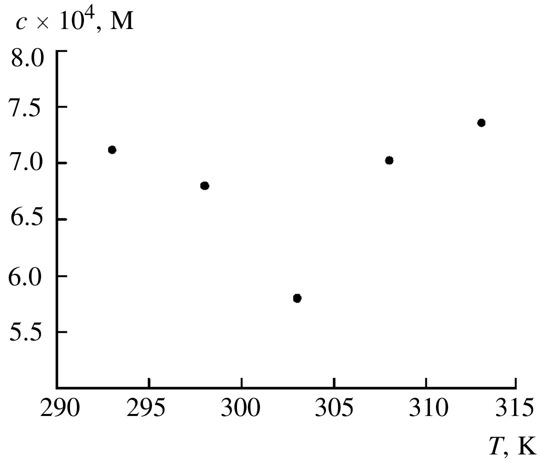

Fig. 2. Temperature dependence of the critical micellization concentration.

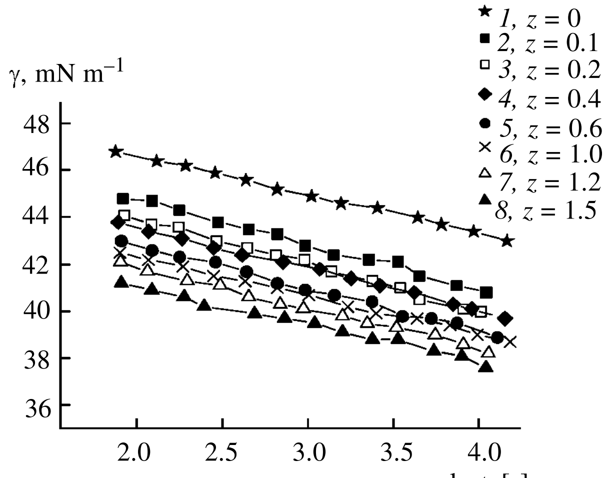

Fig. 3. Dynamic surface tension plots for mixtures of **I** and **IV** at a constant concentration of **IV**, 9.5×10^{-4} M.

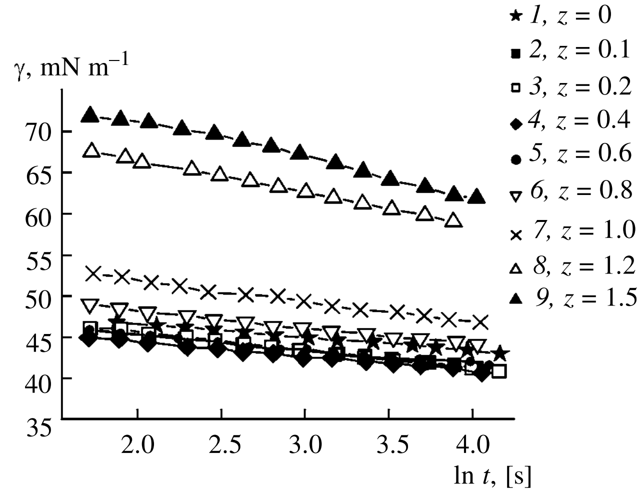

Fig. 4. Dynamic surface tension plots for mixtures of **II** (M_w = 500 000) and **IV** at a constant concentration of **IV**, 9.5×10^{-4} M.

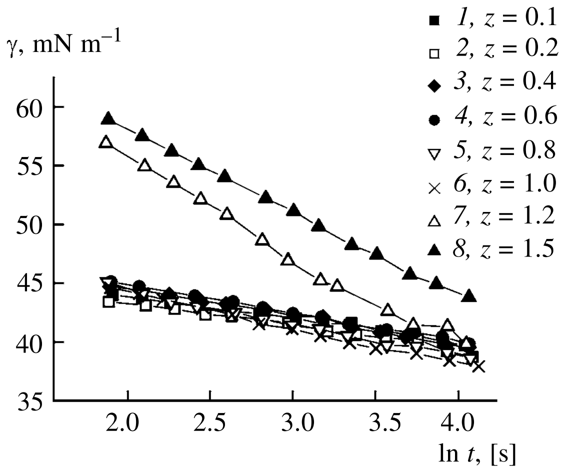

Fig. 5. Dynamic surface tension plots for mixtures of III M_w = 24 000) and **IV** at a constant concentration of **IV**, 9.5×10^{-4} M.

ponents taken separately (a synergic effect) suggests formation of aggregates in solution.

A different pattern is observed when the components are charged differently (mixture of **II**, M_w = 500 000, and **IV**, Fig. 4). The surfactant concentration was 9.5×10^{-4} M in all the mixtures. Curve *1* shows data for the surfactant without polyelectrolyte, and curves 2–9, for the mixtures containing from 9.3×10^{-5} to 1.4×10^{-3} M polyanion (*z* from 0.1 to 1.5). It is seen that small additions of the polyelectrolyte do not noticeably affects the surfactant adsorption, whereas with excess polyelectrolyte the adsorption considerably decreases, i.e., the surface activity of the mixtures decreases. Similar trends were observed with mixtures of **III** and **IV** (Fig. 5), and also of **II** (M_w = 70 000) and **IV**. Similar run of the curves indicates that the major contribution to the adsorption kinetics in mixtures of a surfactant and a polyelectrolyte of different charges is made by compound **IV**. The influence of the structure and molecular weight of anionic polyelectrolytes on the adsorption properties of the solutions is insignificant and consists in that the surface tension of solutions of **IV** changes to a different extent.

Our results show that, in solutions of similarly charged polyelectrolyte and surfactant (**I** + **IV**), the adsorption considerably increases with an increase in the polyelectrolyte concentration, suggesting association between the surfactant and polyelectrolyte molecules through hydrogen bonds and hydrophobic interactions. In systems in which the polyelectrolyte and surfactant are charged differently, electrostatic attraction forces result in aggregation of molecules and decrease in the adsorption ability of the surfactant.

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