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Complexation of Cu(II) with Glycine in Aqueous Solution of an Anionic Surfactant

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Abstract—The complexation of Cu^{2+} with glycine in aqueous solution of an anionic surfactant, sodium dodecyl sulfate, was studied spectrophotometrically. Sodium dodecyl sulfate in concentrations above the critical micellization concentration participates in the complexation. The composition of the complexes and the equilibrium constants of the complexation were determined.

Complexation of biologically active metals with physiologically active organic ligands is an urgent line of coordination chemistry, because the coordination-bound metal exhibits considerably higher activity and lower toxicity.

Ionic micelles, thanks to their diphilic properties and charged surface, resemble biological membranes and therefore are often chosen as systems simulating the reaction medium of biological substrates [1].

We found previously [2] that comenic acid (5-hydroxy-4-pyrone-2-carboxylic acid used in pharmacology) forms ionic associates of various stoichiometries with a cationic surfactant, cetylpyridinium chloride. This work continues a series of studies on interaction of biologically active compounds with surfactants. We have studied the complexation of Cu(II) with glycine in the presence of an anionic surfactant, sodium dodecyl sulfate. Glycine (aminoacetic acid) is one of the most widely occurring amino acids, a component of proteins; it forms complexes with many metal cations. Copper is a metal of vital importance; its stock in a human body is continuously replenished, and the deficiency of copper causes the damage of vessels.

The interactions in the system were monitored spectrophotometrically. We recorded the absorption spectra containing equimolar amounts of $CuCl_2$ and glycine and variable amounts of sodium dodecyl sulfate. To find in what form (monomeric or micellar) sodium dodecyl sulfate participates in the interaction, we determined stalagmometrically the critical micellization concentration of the ternary system $CuCl_2$–glycine–sodium dodecyl sulfate. The critical micellization concentration was 1.5 mM (Fig. 1), i.e., close to that of copper dodecyl sulfate, 1.2 mM [3]. Addition of sodium dodecyl sulfate to the system $CuCl_2$–glycine in concentrations below the critical micellization concentration did not lead to spectral changes, and at concentrations above the critical micellization concentrations the optical density increased and the absorption maximum shifted toward the short-wave region (Fig. 2), suggesting formation of complexes.

The spectrophotometric data were processed with the FTMT program [4] based on a search for a minimum of the criterial function F by varying $\log K_i$ in each iteration.

The function being minimized has the form

$$F = \sum_{k=1}^{K}\sum_{l=1}^{L}(D_{k,\mathrm{e}} - D_{k,\mathrm{c}})_l^2,$$

where K is the number of wavelengths; L, number of

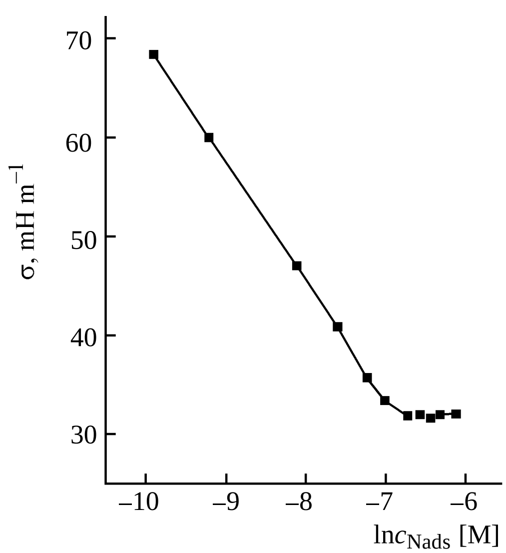

Fig. 1. Isotherms of the surface tension of an aqueous solution of the system $CuCl_2$–glycine (gl)–sodium dodecyl sulfate (Nads). c_{CuCl_2} 0.02, c_{gl} 0.04 M.

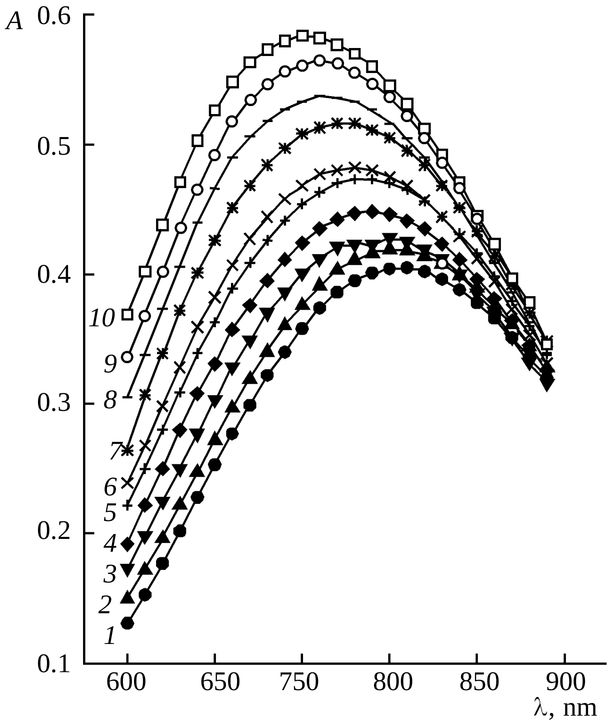

Fig. 2. Absorption spectra of aqueous solutions of Cu^{2+} with glycine (gl) and sodium dodecyl sulfate (Nads). c_{CuCl_2} 0.02, c_{gl} 0.04 M; c_{Nads}, M: (*1*) 0, (*2*) 0.03, (*3*) 0.06, (*4*) 0.07, (*5*) 0.08, (*6*) 0.10, (*7*) 0.12, (*8*) 0.16, (*9*) 0.18, and (*10*) 0.21.

solutions of different compositions; $D_{k,e}$ and $D_{k,c}$, experimentally measured optical density and that calculated at various values of $\log K$.

In mathematical processing of the results, the surfactant was taken into account as the third component of the reaction

$$m\mathrm{M} + n\mathrm{gl} + l\mathrm{ds} \leftrightarrows \{\mathrm{M}_m\mathrm{gl}_n\mathrm{ds}_l\},$$

where M is the metal ion; gl, glycinate anion; ds, surfactant anion; the braces denote that the species is incorporated in a micellar aggregate. A similar approach was used in [5] in studying the complexation of Ni(II) with phosphorus dialkyldithio acid anions in a Triton X-100 solution.

The mathematical model included the following equilibria:

$$Cu^{2+} + 2ds^- \leftrightarrows \{Cuds_2\}, \quad (1)$$

$$Cu^{2+} + gl^- + ds^- \leftrightarrows \{Cuglds\}, \quad (2)$$

$$Cu^{2+} + gl^- + 2ds^- \leftrightarrows \{(Cuglds_2)^-\}, \quad (3)$$

$$Cu^{2+} + gl^- + 3ds^- \leftrightarrows \{(Cuglds_3)^{2-}\}. \quad (4)$$

The calculation gave the following values: $\log K_1$ 4.19±0.73, $\log K_2$ 3.38±0.15, $\log K_3$ 5.77±0.07, and $\log K_4$ 7.07±0.24. Note that the quantity $\log K_1$ characterizing binding of Cu^{2+} ions with dodecyl sulfate is close to the related quantity obtained in [6]: $\log K$ 5.05±0.05. Thus, taking into account the critical micellization concentration of the system under consideration, we can conclude that the complexes Cuglds, $(Cudlds_2)^-$, and $(Cuglds_3)^{2-}$ are incorporated in mixed micelles.

EXPERIMENTAL

In our study we used chemically pure and analytically pure grade chemicals: aminoacetic acid, $CuCl_2 \cdot 2H_2O$, and sodium dodecyl sulfate. The purity of sodium dodecyl sulfate was evaluated according to [7].

The optical density of solutions was measured with an SF-26 spectrophotometer in the wavelength range from 600 to 920 nm in 1-cm quartz cells.

The surface tension of aqueous solutions was measured stalagmometrically [8]. The critical micellization concentration was determined from the inflection of the surface tension isotherm plotted in the σ–$\ln c$ coordinates.

REFERENCES

1. Atherton, S.J. and Dymond, C.M.G., *J. Phys. Chem.*, 1989, vol. 93, no. 18, p. 6809.
2. Vladimirova, T.V., Morgunova, E.E., and Grishina, E.P., *Kolloidn. Zh.*, 2003, vol. 65, no. 6, p. 854.
3. Abramzon, A.A., Bocharov, V.V., and Gaevoi, G.M., *Poverkhnostno-aktivnye veshchestva: Spravochnik* (Surfactants: Handbook), Leningrad: Khimiya, 1979.
4. Vasil'ev, V.P., Borodin, V.A., and Kozlovskii, E.V., *Primenenie EVM v khimiko-analiticheskikh raschetakh* (Use of Computers for Calculations in Analytical Chemistry), Moscow: Vysshaya Shkola, 1993.
5. Amirov, R.R., Skvortsova, E.A., and Matyugicheva, U.V., *Kolloidn. Zh.*, 2002, vol. 64, no. 1, p. 30.
6. Amirov, R.R., Saprykova, Z.A., and Ulakhovich, N.A., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 12, p. 1946.
7. Abramzon, A.A., Zaichenko, L.P., and Faingol'd, S.I., *Poverkhnostno-aktivnye veshchestva* (Surfactants), Leningrad: Khimiya, 1988.
8. Agafonova, E.I., Karpenko, P.G., and Ryabina, L.V., *Praktikum po fizicheskoi i kolloidnoi khimii* (Practical Course of Physical and Colloid Chemistry), Moscow: Vysshaya Shkola, 1985.