Effect of sodium dodecyl sulfate on the reactivity of copper(II) complexes with 2-dimethylaminomethylphenol


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The effects of the anionic surfactant sodium dodecyl sulfate on complex formation of 2-dimethylaminomethylphenol (1) with copper(II) in aqueous solutions and on the kinetics of the reactions of copper(II) complexes of 1 with 4-nitrophenylbis(chloromethyl)phosphinate (2) were studied. The reactivities of the complexes in these reactions are higher than that of 1 at all concentrations of SDS studied (0.010--0.200 mol L$^{-1}$) with pH 7--9.

Key words: complex formation, kinetics; sodium dodecyl sulfate, copper(II), 2-dimethylaminomethylphenol.

It is known$^1$ that the bifunctional nucleophile 2-dimethylaminomethylphenol (1) and its copper complex are catalysts of hydrolysis of esters of phosphorus acids. We have shown$^2$ that sodium dodecyl sulfate (SDS) inhibits the reaction of 1 with 4-nitrophenylbis(chloromethyl) phosphinate (2) mainly due to suppression of the formation of reactive zwitterionic (HL$^-$) and phenolate (L$^-$) forms of compound 1 as a result of the shift of acid-base and tautomeric equilibria. The nonreactive form of 1 protonated at the nitrogen atom (H$_2$L$^+$) is mainly present in solution in the pH 7--9 range studied. In the absence of a surfactant, the reactivity of the copper complex of compound 1, which is reactive in the neutral pH range, is considerably higher than that of ligand 1, and the mechanisms of their effects differ.$^1$ The effects of SDS in forming anionic micelles upon complex formation of 1 with copper(II) and on the reactivity of the complexes formed in the reaction with substrate 2 are studied in this work.

Experimental

Compound 1 (HL) was synthesized by the known procedure.$^3$ SDS was purified and 2 was prepared according to the previously published procedures (see Refs. 4 and 5, respectively). Copper(II) nitrate (reagent grade) was used. The ionic medium was formed by the components of the solution. Complex formation in the copper(II)--ligand 1 system in the presence of SDS was studied at 20±0.1 °C both spectrophotometrically and pH-metrically. The equilibria were simulated by the CPESSP program.$^6$ The simulation is based on the determination of the minimum value of the sum of deviation squares (the nonlinear least-squares method) calculated from the experimentally determined characteristics for all points upon movement along the coordinate, which determines the composition of the equilibrium system (pH, concentration of the ligand, etc.). The optical density of solutions was measured on a Specord UV-VIS spectrophotometer (the length of the absorbing layer was 1 cm), and the pH values of the solutions were measured on a pH-340 instrument. The complexes of copper(II) with 1 are insoluble in an aqueous solution but soluble in the presence of SDS. The dissolution of the complexes results in the appearance of a band with a maximum at 426 nm in the absorption spectrum. The reaction kinetics was studied under pseudo-first-order conditions by increase in the optical density due to the formation of p-nitrophenolate ($\lambda$, 400 nm) at 25±0.1 °C. The observed rate constants ($k_{obs}$) were calculated by a first-order equation by the least-squares method using the known program$^{17}$ (the correlation coefficient was not lower than 0.99). The errors of determination of the apparent equilibrium and stability constants of the complexes were not higher than 0.2 logarithmic units.

Results and Discussion

Investigation of the kinetics of reactions involving metal complexes is closely related to the determination of their structure and the most important quantitative parameters of their complex formation in solutions. This problem becomes more urgent when surfactants are introduced into solution, because it is known$^8,9$ that they substantially affect reactions of metal ions with organic reagents. Therefore, the complex formation of compound 1 with copper(II) should be studied for the investigation of the kinetics of the reaction of substrate 2 with copper complexes 1.
The pH values were varied from 6.0 to 10.2 in five series of solutions with fixed concentrations of copper(II) (5.8 \times 10^{-4} \text{ mol L}^{-1}) and 1 (0.01 \text{ mol L}^{-1}). The constant concentration of SDS was maintained in each series of the solutions. The A–pH dependences are presented in Fig. 1.

The value of the optical density (A) dependent of pH or the concentration of the ligand at the fixed pH value was used as the modelled response. In the case of the inverse problem with various stoichiometric matrices solved according to the CPESSP program, the adequate description of the experimental data (the estimation was performed by the Fischer criterior) is achieved when equilibrium processes (1) and (2) are the determining reactions of complex formation:

\[
\text{Cu}^{2+} + 3\text{H}_2\text{L}^+ \rightleftharpoons [\text{Cu}(\text{H}_2\text{L}^+)_2(\text{HL})]^4^+ + \text{H}_3^+, \quad (1)
\]

\[
\text{Cu}^{2+} + 3\text{H}_2\text{L}^+ \rightleftharpoons [\text{Cu}(\text{H}_2\text{L}^+)(\text{HL})]^3^+ + 2\text{H}_3^+, \quad (2)
\]

where \text{H}_2\text{L}^+ and \text{HL} are the protonated at the nitrogen atom (pK1) and neutral (pK2) forms of compound 1, respectively.

The values of apparent dissociation constants of compound 1, pK1 and pK2, determined at the corresponding SDS concentrations were used for the calculation of the apparent equilibrium constants K1 and K2 (Table 1).

The equilibrium constants of reactions (1) and (2) should be considered as estimation values, because the ionic strength of the solutions was not maintained constant. The values of apparent stability constants of the complexes (β) calculated from Eqs. (3) and (4) are also presented in Table 1.

\[
\log \beta_1 = \log K_1' + pK_1, \quad (3)
\]

\[
\log \beta_2 = \log K_2' + 2pK_1. \quad (4)
\]

Thus, two types of complex species are formed in the solutions studied: depending on pH of the medium, the species contain in the coordination sphere either two protonated ligands H2L+ and one neutral ligand (complex 3) or one protonated and two neutral ligands (complex 4).

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The equilibrium constants of reactions (1) and (2) should be considered as estimation values, because the ionic strength of the solutions was not maintained constant. The values of apparent stability constants of the complexes (β) calculated from Eqs. (3) and (4) are also presented in Table 1.

The dependence of the relative content of each form (in fractions of the total concentration of copper(II)) on pH of the medium is presented in Fig. 2.

The values of the logarithm of the equilibrium constant K2 calculated on the basis of the experimental dependences A–pH and A–CHL (pH 8.60) were −9.29 (CSDS = 0.01 \text{ mol L}^{-1}) and −10.05 (CSDS = 0.10 \text{ mol L}^{-1}) and almost coincided with the data presented in Table 1.

It is known that Cu(DS)2 predominates on the micellar surface in the system containing SDS and copper(II), because the bicharged copper ion is stronger...