Effects of surfactants on complex formation of Cu^{II} with 2-dimethylaminomethylphenol

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The effect of cationic (cetyltrimethylammonium bromide) and nonionic (Triton X-100) surfactants on the complex formation of Cu^{II} with a bifunctional ligand, 2-dimethylaminomethylphenol, in water was studied by spectrophotometry, pH-metry, and mathematical modeling of equilibria in solutions. The character of complex formation depends on the nature and concentration of surfactants. The dependence of complex formation constants on the concentration of surfactants is discussed.

Key words: complex formation, surfactants, 2-dimethylaminomethylphenol, copper(II).

It has been previously[1] shown that in a water-ethanol solution the bifunctional compound 2-dimethylaminomethylphenol (**1**) and Cu^{II} form an unstable ($\log\beta = 2.65$) complex $[CuHL]^{2+}$ (**2**) containing the neutral form of the ligand (HL). It has also been established[2] that compounds **1** and **2** are bifunctional nucleophilic catalysts of hydrolysis of esters of phosphorus acids, which gives grounds to consider compounds **1** and **2** as the simplest models of enzymes and metalloenzymes. Therefore, it is of interest to study the complex formation of compound **1** with Cu^{II} in organized media modeling the functioning of biological membranes. The purpose of the present work was to study the effect of cationic (cetyltrimethylammonium bromide, CTAB) and nonionic (Triton X-100) surfactants on the complex formation of Cu^{II} with compound **1** in water.

Experimental

Ligand **1** was synthesized by the known procedure,[3] and CTAB was prepared and purified as described previously.[4] Triton X-100 was commercially available (Ferak), and $Cu(NO_3)_2$ was of reagent grade. The ionic strength was created by the components of the solution. Optical densities of solutions were recorded on a Specord UV-VIS spectrophotometer. All measurements were performed at 20±0.1 °C. Equilibria were mathematically modeled by the CPESSP program[5] on a PC/AT 286. An error in the determination of constants was not higher than 0.2 logarithm units.

Results and Discussion

The addition of a solution of $Cu(NO_3)_2$ to a solution of compound **1** in the presence of a surfactant results in the appearance of an absorption band with a maximum at 417 nm, whose position is independent of the type of surfactants studied. The complex of Cu^{II} with compound **1**, which is insoluble in water, dissolves in the presence of CTAB and Triton X-100. The values of pK_1 and pK_2 corresponding to the equilibria

$$H_2L^+ \xrightleftharpoons{K_1} HL + H^+ ,$$

$$HL \xrightleftharpoons{K_2} L^- + H^+ ,$$

where H_2L^+ is the protonated at the nitrogen atom form of **1**, HL is the neutral form, and L^- is the phenolate form of compound **1**, were determined in the presence of Triton X-100 as described previously.[6]

The effects of pH of the medium and the content of ligand **1** on the complex formation were studied at variable concentrations of the surfactants (Figs. 1 and 2). The processing of the experimental data "A—pH" (C_1 = const) and "A—C_1" (pH = const) together was performed by the CPESSP program.

In the case of Triton X-100 (at its concentrations of 0.05 and 0.10 mol L^{-1}), mononuclear complex **2** (Scheme 1) is formed together with binuclear complex $[Cu_2(HL)_2L]^{3+}$ (**3**) (Scheme 2).

Scheme 1

$$Cu^{2+} + \underset{\mathbf{1}}{H_2L^+} \xrightleftharpoons{K'_1} \underset{\mathbf{2}}{[CuHL]^{2+}} + H^+$$

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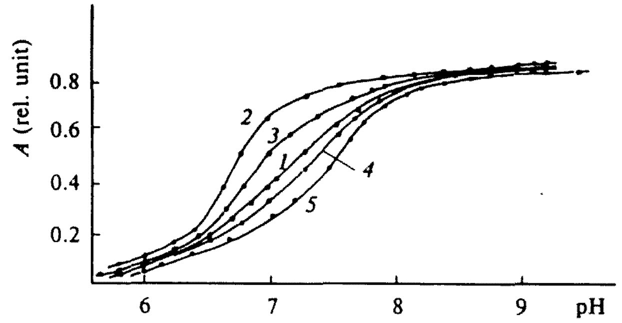

Fig. 1. Dependence of the optical density (A) on pH of the medium ($C_{Cu^{2+}}$ = 1.9 · 10^{-4}, C_l = 0.01 mol L^{-1}) at C_{Tr} = 0.05 mol L^{-1} (*1*) and C_{CTAB} 0.1 (*2*), 0.05 (*3*), 0.005 (*4*), and 0.001 (*5*) mol L^{-1}.

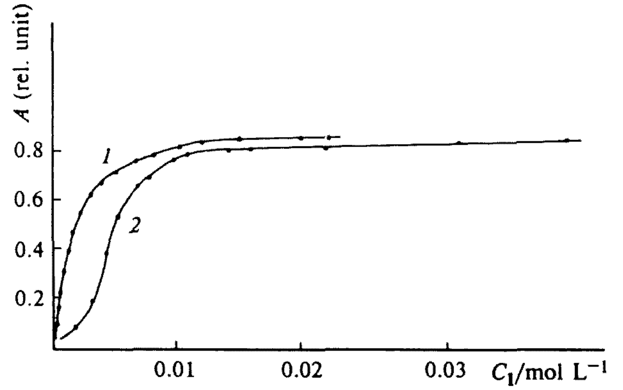

Fig. 2. Dependence of the optical density (A) on C_l ($C_{Cu^{2+}}$ = 1.9 · 10^{-4} mol L^{-1}): *1*, C_{Tr} = 0.05 mol L^{-1}, pH 7.75; *2*, C_{CTAB} = 0.05 mol L^{-1}, pH 7.30.

Scheme 2

$$2Cu^{2+} + 3H_2L^+ \overset{K'_2}{\rightleftharpoons} \underset{\mathbf{3}}{[Cu_2(HL)_2L]^{3+}} + 4H^+$$

The ratio of complex forms **2** and **3** is shown in Fig. 3. A decrease in the concentration of compound **1** decreases the fraction of compound **2**, and its maximum level, as that of binuclear complex **3**, is achieved at higher pH values (Fig. 4). The values of apparent equilibrium constants (K'_1, K'_2) and apparent stability constants of the complexes (Table 1) increase as the surfactant concentration increases. The stability constants of the complexes were calculated from Eqs. (1) and (2).

$$\log\beta_1 = \log K'_1 + pK_1 \qquad (1)$$

$$\log\beta_2 = \log K'_2 + 3pK_1 + pK_2 \qquad (2)$$

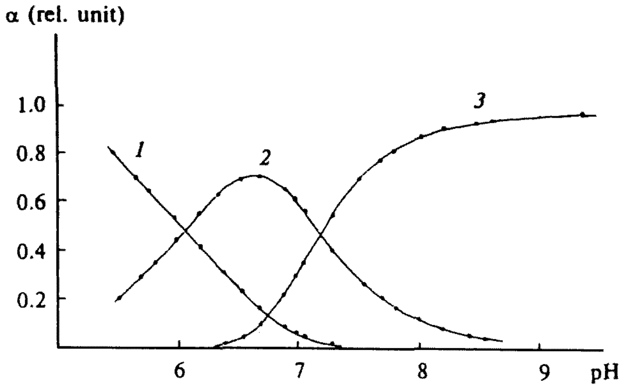

Fig. 3. Ratio of complex forms at various pH of the medium: *1*, Cu^{2+}, *2*, [CuHL]$^{2+}$, and *3*, [Cu$_2$(HL)$_2$L]$^{3+}$. C_{Tr} = 0.05 mol L^{-1}, $C_{Cu^{2+}}$ = 1.9 · 10^{-4} mol L^{-1}, C_l = 1 · 10^{-3} mol L^{-1}.

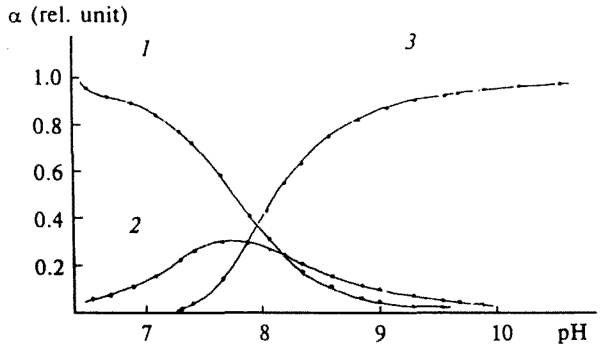

Fig. 4. Ratio of complex forms at various pH of the medium: *1*, Cu^{2+}, *2*, [CuHL]$^{2+}$, and *3*, [Cu$_2$(HL)$_2$L]$^{3+}$. C_{Tr} = 0.05 mol L^{-1}, $C_{Cu^{2+}}$ = 1.9 · 10^{-4} mol L^{-1}, C_l = 1 · 10^{-3} mol L^{-1}.

Table 1. Values of dissociation constants of compound **1**, apparent constants of equilibria (1) and (2), and apparent stability constants of complexes **2** and **3** in the presence of Triton X-100

C_{Tr} /mol L^{-1}	pK_1	pK_2	$-\log K_1$	$-\log K_2$	$\log\beta_1$	$\log\beta_2$
0.05	8.15	10.62	4.08	16.77	4.07	18.30
0.10	8.10	10.60	3.27	14.81	4.83	20.09

The values of pK_1 and pK_2 of apparent dissociation constants in the presence of Triton X-100 are also listed in Table 1. The stability of complex **2** in the presence of the surfactant is considerably higher than that in a mixed water-ethanol solvent.[1] Triton X-100, which is not a potential ligand, favors the formation of the binuclear complex in the micellar pseudo-phase. Perhaps, the phenolate form L$^-$ plays the role of a bridge linking two central ions.

When the concentration of Triton X-100 is lower than that given in Table 1 (C_{Tr} = 0.01 mol L^{-1}), two complex species are formed, which contain two protonated ligands and one neutral ligand (Scheme 3) or one protonated and two neutral ligands (Scheme 4) in the coordination sphere depending on pH of the medium.

Scheme 3

$$Cu^{2+} + 3\,H_2L^+ \xrightleftharpoons{K_3} [Cu(H_2L)_2(HL)]^{4+} + H^+$$

Scheme 4

$$Cu^{2+} + 3\,H_2L^+ \xrightleftharpoons{K_4} [Cu(H_2L)(HL)_2]^{3+} + 2\,H^+$$

Complexes of similar composition are also formed in the whole region of the concentrations studied of the cationic surfactant (CTAB). In this case, we suggested a refined scheme of the complex formation reactions (Schemes 3a and 4a), which includes bromide ions due to the following consideration.

Scheme 3a

$$[CuBr]^+ + 3\,H_2L^+\cdot nBr^- \xrightleftharpoons{K_3}$$
$$\rightleftharpoons \{[CuBr(H_2L)_2(HL)]^{3+}Br_{3n-x}\}^{3-3n+x} + xBr^- + H^+$$

Scheme 4a

$$[CuBr]^+ + 3\,H_2L^+\cdot nBr^- \xrightleftharpoons{K_4}$$
$$\rightleftharpoons \{[CuBr(H_2L)(HL)_2]^{2+}Br_{3n-x}\}^{2-3n+x} + xBr^- + 2H^+$$

It is known that Cu^{II} and bromide ions form complexes containing from one to six bromide ions in the first coordination sphere.[7] However, only the complex with one bromide ion in the coordination sphere has been characterized. It is also known that at high concentrations of bromide ions created by HBr (C_{HBr} = 11—18 mol L^{-1}, $C_{Cu^{2+}} = 2\cdot10^{-4}$—$2\cdot10^{-2}$ mol L^{-1}) Cu^{II} reduces to Cu^{I}, and the solutions decolorize.

It was impossible to study the complex formation of Cu^{II} with bromide ions introduced with CTAB, because CTAB itself, as the Cu^{II} bromide complex, absorbs in the UV spectral range (λ = 280 nm). It is noteworthy that the linear dependence "$A-C_{CTAB}$" is fulfilled in the range of the CTAB concentrations from $1\cdot10^{-3}$ to $1\cdot10^{-1}$ mol L^{-1}. We studied the complex formation of Cu^{II} with bromide ions introduced with potassium bromide ($C_{Cu^{2+}} = 1\cdot10^{-2}$ mol L^{-1}, C_{KBr} = 0.5—4.4 mol L^{-1}). Under these concentration conditions, Cu^{II} is not reduced to Cu^{I}. In the concentration range of bromide ions from $2.5\cdot10^{-2}$ to 0.2 mol L^{-1}, the complex of the composition 1 : 1 is formed in the solution, whose stability (logβ = 0.64±0.21) agrees with the published data.[7] At higher concentrations of bromide ions (C_{Br^-} = 0.5—4.4 mol L^{-1}), the complexes of the compositions 1 : 1 and 1 : 4 coexist in the solution. The maximum fraction of the complex of the composition 1 : 4 is low and comprises only 0.1, and the stability of the complex is low (logβ = −2.60). Thus, the monobromide complex is the predominant form in bromide solutions of Cu^{II}.

In the presence of CTAB, the coordination of protonated molecules of compound **1** is favored by the simultaneous incorporation of bromide ions in the coordination sphere, which is reflected in Schemes 3a and 4a of complex formation reactions. The values of apparent equilibrium constants of the formation of similar complexes in the presence of both surfactants are presented in Table 2. The apparent dissociation constants pK_1 and pK_2 in the presence of CTAB have been determined previously.[6]

As can be seen from the data in Table 2, in the case of low concentrations of CTAB ($1\cdot10^{-3}$ to $5\cdot10^{-3}$ mol L^{-1}), the equilibrium constants K_3 and K_4 depend on the content of the surfactants in the solution according to Schemes 3a and 4a. Therefore, the stability constants of mixed complexes with bromide and aminomethylphenol ligands were calculated taking into account the concentrations of bromide ions of CTAB itself (Eqs. (3) and (4)).

$$\log\beta_1 = \log K_3 + pK_1 + \log\beta_{[CuBr]^+} + \log[Br^-],\quad x = 1 \qquad (3)$$

$$\log\beta_2 = \log K_4 + 2pK_1 + \log\beta_{[CuBr]^+} + \log[Br^-],\quad x = 1 \qquad (4)$$

At these concentrations of CTAB, the stability constants of both complexes are unchanged.

Higher concentrations of CTAB ($5\cdot10^{-2}$ to 0.1 mol L^{-1}) do not affect the constants of the equilibria considered, *i.e.*, the complex formation reactions (Schemes 3b and 4b) are not accompanied by the displacement of bromide ions into the solution.

Table 2. Values of dissociation constants of compound **1**, apparent equilibria constants (K_3, K_4) of the formation of similar complexes in the presence of surfactants, and stability constants of the complexes

C_{surf} /mol L^{-1}	pK_1	pK_2	$-\log K_3$	$-\log K_4$	$\log\beta_1$	$\log\beta_2$
			Triton X-100			
$1\cdot10^{-2}$	8.20	10.62	0.40	6.97	8.60	9.43
			CTAB			
$1\cdot10^{-3}$	8.45	10.90	0.045	7.45	6.14	7.09
$5\cdot10^{-3}$	8.35	10.62	−0.43	7.85	6.26	7.19
$5\cdot10^{-2}$	8.24	10.40	−0.92	8.03	7.92	9.05
$1\cdot10^{-1}$	8.24	10.40	−0.91	7.71	7.92	9.37

Scheme 3b

$$[\mathrm{CuBr}]^+ + 3\mathrm{H_2L^+}\cdot n\mathrm{Br^-} \overset{K_3}{\rightleftharpoons}$$

$$\rightleftharpoons \{[\mathrm{CuBr(H_2L)_2(HL)}]^{3+}\mathrm{Br}_{3n}\}^{3-3n} + \mathrm{H^+}$$

Scheme 4b

$$[\mathrm{CuBr}]^+ + 3\mathrm{H_2L^+}\cdot n\mathrm{Br^-} \overset{K_4}{\rightleftharpoons}$$

$$\rightleftharpoons \{[\mathrm{CuBr(H_2L)(HL)_2}]^{2+}\mathrm{Br}_{3n}\}^{2-3n} + 2\mathrm{H^+}$$

The values of the stability constants of the complexes calculated at these concentrations of CTAB from Eqs. (5) and (6) probably characterize the stability of the complexes in a micellar pseudo-phase, which is less polar than water, and, hence, they are higher than the constants at low concentrations of the sufactant, because in this case the complex formation occurs in an aqueous solution containing ions of the surfactant.

$$\log\beta_1 = \log K_3 + \mathrm{p}K_1 + \log\beta_{[\mathrm{CuBr}]^+} \qquad (5)$$

$$\log\beta_2 = \log K_4 + 2\mathrm{p}K_1 + \log\beta_{[\mathrm{CuBr}]^+} \qquad (6)$$

Thus, the introduction of the surfactant results in a more complicated composition of the complexes compared to those in a water-ethanol solution. An increase in the number of coordinated ligands in the presence of surfactants, which is expalined by loosening of the hydrate shell of a metal ion due to hydrophobic interactions, is documented.[8]

The coordination of protonated ligands is favored by bromide ions of CTAB. It is likely that the formation of hydrogen bonds with ester oxygen atoms of the polyester chain is substantial for the nonionic surfactant Triton X-100. The rather high strength of the complexes can also be the result of the interplanar interaction (stacking[9]) of benzene rings of coordinated ligands. A decrease in the surface tension of water due to the surfactant decreases the work spent for the creation of a cavity in the solution. The plane of the complex-forming agent with donor atoms of the ligand and also its aromatic ring in the case of Triton X-100 are involved in the stacking interaction. This probably is one of the reasons for the assistance of this surfactant in the formation of binuclear complex **3**.

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