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Reaction of *N*,*N*-Dimethyl-*N*'-(2-hydroxybenzyl)ethylenediamine with Copper(II) in the Presence of Surfactants

Yu. I. Sal'nikov, G. A. Boos, I. S. Ryzhkina, and E. R. Ganieva

Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia

Kazan State University, Kazan, Tatarstan, Russia

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Abstract — The protolytic properties of *N*,*N*-dimethyl-*N*'-(2-hydroxybenzyl)ethylenediamine (HL) and its complexation with copper(II) in the presence of cationic (cetyltrimethylammonium bromide) and nonionic (Triton X-100) surfactants were studied by pH-metry, spectrophotometry, and mathematical simulation of the equilibria. Cetyltrimethylammonium bromide affects the $H_2L_2 \rightleftarrows 2HL$ equilibrium. Along with the protonated monomeric and dimeric species, triprotonated tetrameric species were revealed in surfactant solutions, as in aqueous solutions of isopropyl alcohol. The surfactants affect the complexation of HL with Cu(II). The 1 : 2 complex with the phenolate form in solutions of cetyltrimethylammonium bromide is formed in a more acidic medium (pH ~5.5) compared to an aqueous solution of isopropyl alcohol (pH ~11). The apparent stability constants of the complexes increase in the presence of surfactants, especially of cetyltrimethylammonium bromide.

2-Aminomethylphenols and their complexes with metal ions are of interest as biologically active compounds and catalysts of hydrolysis of phosphorus acid esters in aqueous-organic and micellar solutions of surfactants [1, 2]. Surfactants can exert an appreciable effect on the protolytic and complexing properties of organic reagents [3]; this effect depends on the surfactant type.

In this work we studied the acid–base properties of *N*,*N*-dimethyl-*N*'-(2-hydroxybenzyl)ethylenediamine and its complexation with Cu(II) in solutions of cationic (cetyltrimethylammonium bromide) and nonionic (Triton X-100) surfactants. Along with the surfactants, the solutions contained 5 vol % of isopropyl alcohol.

Introduction of the ethylenediamine fragment into the 2-aminomethylphenol molecule affects its properties, including the acid–base properties. In particular, *N*,*N*-dimethyl-*N*'-(2-hydroxybenzyl)ethylenediamine exists in an aqueous solution of isopropyl alcohol [40 vol % $(CH_3)_2CHOH$] mainly in the form of a dimer, H_2L_2. This dimer, depending on the acidity of the medium, forms mono-, di-, and triprotonated species: $H_3L_2^+$, $H_4L_2^{2+}$, and $H_5L_2^{3+}$, respectively. The maximal content of the diprotonated monomeric species H_3L^{2+} is low, 0.09 [4].

The quantitative characteristics of the protolytic equilibria involving *N*,*N*-dimethyl-*N*'-(2-hydroxybenzyl)ethylenediamine in the presence of the surfactants are listed in the table. The pH values corresponding to the maximal accumulation of a given species are denoted as pH_{max}.

In the presence of both surfactants, as in aqueous solution of isopropyl alcohol, the protonated form of the tetramer, $H_7L_4^{3+}$, is formed (in neutral solution, pH ~7.02, α_{max} ~0.65). The apparent constants of formation of this species in the surfactant solutions are close. A certain decrease in the constants is observed in going from the submicellar concentrations to cationic micelles of cetyltrimethylammonium bromide (the critical micellization concentration is 8×10^{-4} M [5]). The acid properties of the protonated dimeric species, as those of $H_7L_4^{3+}$, also tend to increase with increasing concentration of cetyltrimethylammonium bromide.

It is particularly remarkable that the cationic surfactant in a concentration below the critical micellization concentration favors formation of noticeable amounts of the monomeric species HL, *N*,*N*-dimethyl-*N*'-(2-hydroxybenzyl)ethylenediamine (α_{max} 0.17). Under these conditions, the cationic surfactant occurring in the solution as ions [3, 6], apparently, blocks the centers responsible for the dimerization: the OH group and terminal nitrogen atom of the neutral form, or the phenolate group and protonated terminal nitrogen atom of the zwitter-ionic form of the compound. On the contrary, at micellar concentrations of cetyltrimethylammonium bromide and Triton X-100 (critical micellization concentration 3.35×10^{-4} M [7]), the

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Logarithms of constants (with confidence ranges for $P = 0.95$) of protolytic equilibria in solutions of *N*,*N*-dimethyl-*N*'-(2-hydroxybenzyl)ethylenediamine, containing cetyltrimethylammonium bromide (CTAB) and Triton X-100 (TX)

Equilibrium	log *K*	α_{max}	pH_{max}
c_{CTAB} 5×10^{-4} M			
$2L^- + 2H^+ \leftrightarrows H_2L_2$	22.81 ± 0.52	0.61	9.52
$H_2L_2 + H^+ \leftrightarrows H_3L_2^+$	8.83 ± 0.30	0.40	8.53
$H_2L_2 + 2H^+ \leftrightarrows H_4L_2^{2+}$	16.14 ± 0.23	0.43	6.15
$H_2L_2 + 3H^+ \leftrightarrows H_5L_2^{3+}$	22.07 ± 0.21	0.81	4.69
$0.5H_2L_2 + 2H^+ \leftrightarrows H_3L^{2+}$	11.46 ± 0.12	0.36	3.79
$2H_2L_2 + 3H^+ \leftrightarrows H_7L_4^{3+}$	28.80 ± 0.42	0.64	7.32
$0.5H_2L_2 \leftrightarrows HL$	–1.69 ± 1.1	0.17	9.73
$L^- + H^+ \leftrightarrows HL$	9.73 ± 1.1	0.17	9.73
c_{CTAB} 1×10^{-3} M			
$2L^- + 2H^+ \leftrightarrows H_2L_2$	22.96 ± 0.33	0.77	9.53
$H_2L_2 + H^+ \leftrightarrows H_3L_2^+$	8.72 ± 0.21	0.45	8.43
$H_2L_2 + 2H^+ \leftrightarrows H_4L_2^{2+}$	15.93 ± 0.18	0.41	6.09
$H_2L_2 + 3H^+ \leftrightarrows H_5L_2^{3+}$	21.89 ± 0.16	0.80	4.93
$0.5H_2L_2 + 2H^+ \leftrightarrows H_3L^{2+}$	11.44 ± 0.09	0.38	3.90
$2H_2L_2 + 3H^+ \leftrightarrows H_7L_4^{3+}$	28.41 ± 0.34	0.63	7.35
$0.5H_2L_2 \leftrightarrows HL$	(–3.15)	6×10^{-3}	9.80
c_{CTAB} 5×10^{-3} M			
$2L^- + 2H^+ \leftrightarrows H_2L_2$	22.56 ± 0.12	0.77	9.42
$H_2L_2 + H^+ \leftrightarrows H_3L_2^+$	8.56 ± 0.19	0.40	8.36
$H_2L_2 + 2H^+ \leftrightarrows H_4L_2^{2+}$	15.78 ± 0.17	0.39	6.09
$H_2L_2 + 3H^+ \leftrightarrows H_5L_2^{3+}$	21.75 ± 0.15	0.76	5.06
$0.5H_2L_2 + 2H^+ \leftrightarrows H_3L^{2+}$	11.48 ± 0.08	0.41	4.03
$2H_2L_2 + 3H^+ \leftrightarrows H_7L_4^{3+}$	28.18 ± 0.30	0.66	7.33
$0.5H_2L_2 \leftrightarrows HL$	(–5.16)	6×10^{-5}	9.60
c_{TX} 5×10^{-3} M			
$2L^- + 2H^+ \leftrightarrows H_2L_2$	23.04 ± 0.27	0.81	9.52
$H_2L_2 + H^+ \leftrightarrows H_3L_2^+$	8.60 ± 0.52	0.39	8.50
$H_2L_2 + 2H^+ \leftrightarrows H_4L_2^{2+}$	15.72 ± 0.46	0.28	6.27
$H_2L_2 + 3H^+ \leftrightarrows H_5L_2^{3+}$	22.04 ± 0.37	0.76	5.34
$0.5H_2L_2 + 2H^+ \leftrightarrows H_3L^{2+}$	11.82 ± 0.19	0.69	3.69
$2H_2L_2 + 3H^+ \leftrightarrows H_7L_4^{3+}$	28.29 ± 0.74	0.69	7.30
$0.5H_2L_2 \leftrightarrows HL$	(–5.40)	3×10^{-5}	9.70

compound is dimeric, as in aqueous solution of isopropyl alcohol.

One more feature is that the diprotonated monomer species H_3L^{2+} in the presence of surfactants is formed in a less acidic medium (pH 2.6 and 3.6–4.0, respectively). The relative content and apparent formation constant of this species increase, especially in the presence of the nonionic surfactant.

Complexation of copper(II) with *N*,*N*-dimethyl-*N*'-(2-hydroxybenzyl)ethylenediamine in surfactant solutions has certain features. Addition of copper(II) to an *N*,*N*-dimethyl-*N*'-(2-hydroxybenzyl)ethylenediamine solution, both in the absence and in the presence of surfactants, gives rise to two bands in the absorption spectrum with maxima at 390–400 and 660–700 nm. The first strong band may originate from intraligand transitions [8], and the second medium-intensity band is most probably due to *d*–*d* transitions. The long-wave band is broader and is shifted bathochromically relative to the related band in the spectra of copper(II) ethylenediamine complexes (pH ≥ 5.2, λ_{max} 550 nm, ε 60 [9]). The position and intensity of the bands are virtually independent of the type of surfactants; however, in aqueous solutions of $(CH_3)_2CHOH$ the absorption intensity is by a factor of ~1.2 higher. We studied the influence exerted on the complexation by the solution pH and by the ligand and Cu(II) concentrations. The processes were monitored by absorption at 400 nm (the strongest band).

The pH dependences of the molar extinction coefficients, recorded in solutions of cetyltrimethylammonium bromide and Triton X-100 (figure, curves *1*–*3*), do not contain the second step observed in aqueous isopropyl alcohol (curve *4*). The curves recorded in the presence of the surfactants become similar in shape to those characteristic of the reaction of Cu(II) with ethylenediamine [9] or with 2-butylaminomethylphenol in aqueous ethanol [10]. In an aqueous solution of isopropyl alcohol [40 vol % $(CH_3)_2CHOH$], six complexes are formed [here and hereinafter, in parentheses are, respectively, the pH corresponding to the maximal accumulation of the given species, the maximal relative content of this species, and the logarithm of the equilibrium constant of the corresponding reaction of Cu(II) with H_2L_2; the fourth figure is the logarithm of the stability constant of the complex]: $[Cu(HL)]^{2+}$ (3.65, 0.63, 7.57); $[Cu_2(HL)_2]^{4+}$ (3.65, 0.14, 17.25, 20.5); $[Cu(HL)_2]^{2+}$ (5.25, 0.98, 13.14); $[Cu_2(HL)_2L_2]^{2+}$ (7.91, 0.94, 16.58); $[CuL_2]$ (11.0, 0.77, –2.59, 20.3); $[CuL_2OH]^-$ (11.0, 0.23, –14.08, 23.60) [4]. At cetyltrimethylammonium bromide concentrations of 5×10^{-4} and 5×10^{-3} M (below and above the critical micellization concentration, respectively), four complexes were revealed; their quantitative characteristics were only slightly dependent on the surfactant concentration. For the cationic surfactant concentration of 5×10^{-4} M, the data are as follows: $[Cu_2(HL)_2]^{4+}$ (3.75, 0.95, 19.33, 22.71); $[Cu_2(HL)_4]^{4+}$ (4.43, 0.25, 30.87, 37.6); $[CuL_2]$ (5.66, 0.999, 5.08, 27.9); $[CuL_2OH]^-$ (11.0, 0.987, –3.84,

33.0). As seen, in the presence of cetyltrimethylammonium bromide, the number of complexes containing the HL species decreases. The 1 : 2 complex with the phenolate form of the ligand starts to form even in weakly acidic solutions, with the maximal accumulation at pH ~5.5. Note that a decrease in the pH of complexation with acidic reagents is generally characteristic of cationic surfactants [11].

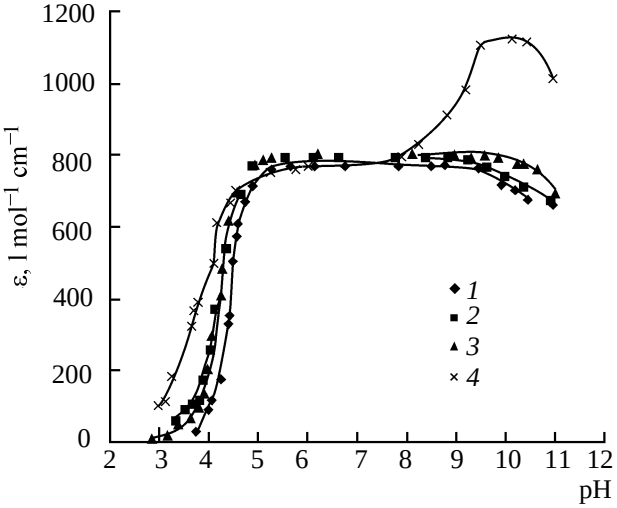
The neutral and anionic complexes in cetyltrimethylammonium bromide solutions are highly stable. Their apparent stability constants are considerably higher (by 7–9 log units) than in 40% $(CH_3)_2CHOH$. By analogy with [3, 6], we can assume that the cationic surfactant before reaching the critical micellization concentration substitutes the phenolic proton and forms an associate with the anionic ligand species. In interaction of this modified ligand with Cu(II), the bidentate coordination via the ethylenediamine moiety may be preferable. However, the absorption spectra of the Cu(II) complexes do not rule out the coordination via the aminophenolate moiety also. Complexes with a mixed coordination mode may also form. If several alternative coordination modes are realized, the complexes are present as sets of isomers, and their apparent stability constants can be considered as the averaged quantities [12, 13].

When a cationic surfactant forms micelles, the anionic ligand species is adsorbed on their surface, which also favors the complexation.

Participation of bromide ions in the inner-sphere coordination is improbable because of the low stability of copper(II) bromide complexes [14]. Nevertheless, these ions may stabilize the cationic complexes by outer-sphere coordination.

In solutions of Triton X-100 (TX) of micellar concentrations (c_{TX} 5.1×10^{-3} M), six complexes are formed: $[Cu(HL)]^{2+}$ (3.91, 0.09, 6.45); $[Cu_2(HL)_2]^{4+}$ (3.91, 0.61, 17.69); $[Cu_2(HL)_4]^{4+}$ (4.23, 0.34, 29.96); $[Cu(HL)L]^{+}$ (6.20, 0.99, 9.17); $[CuL_2]$ (10.6, 0.58, –0.91, 22.1); $[Cu_2L_2(OH)_2]$ (11.0, 0.70, –1.74, 50.3). Three of them, namely, $[Cu_2(HL)_2]^{4+}$, $[Cu_2(HL)_4]^{4+}$, and $[CuL_2]$, also exist in solutions of the cationic surfactant. In the solution of the nonionic surfactant, the conditions of formation and the stability of the complexes change, especially for the complex $[CuL_2]$, which is formed in alkaline solution, as in the case of aqueous isopropyl alcohol. The relative content of this complex and its apparent stability constant are considerably lower than in the presence of cetyltrimethylammonium bromide.

Instead of the anionic hydroxo complex revealed in the presence of the cationic surfactant, in the presence of the nonionic surfactant at the same pH a neutral hydroxo complex is formed, $[Cu_2L_2(OH)_2]$. The complex $[Cu(HL)]^{2+}$ exists only in solutions of Triton X-100 and in aqueous isopropyl alcohol. Thus, complexation processes in solutions of the nonionic surfactant and in aqueous isopropyl alcohol have more in common, compared to the processes in the presence of the cationic surfactant.



Molar extinction coefficient at 400 nm as a function of pH in the system Cu(II)–HL (*1*–*3*) in the presence and (*4*) in the absence of surfactants. $c_{alcohol}$, vol %: (*1*–*3*) 5 and (*4*) 40. $c_{Cu^{2+}}$ 5.8×10^{-4} M. c_{HL}, M: (*1*–*3*) 4.8×10^{-3} and (*4*) 9.87×10^{-3}. c_{CTAB}, M: (*1*) 5×10^{-3} and (*2*) 5×10^{-4}. (*3*) c_{Triton} 5.1×10^{-3} M.

EXPERIMENTAL

N,*N*-Dimethyl-*N*'-(2-hydroxybenzyl)ethylenediamine was prepared as described in [15] and was identified by the melting point and refractive index. Isopropyl alcohol was purified by distillation [16]. Triton X-100 (Ferak) was used without additional purification. Cetyltrimethylammonium bromide was prepared and purified as described in [3]. The other chemicals were of chemically pure grade.

As starting compounds we used a solution of *N*,*N*-dimethyl-*N*'-(2-hydroxybenzyl)ethylenediamine in isopropyl alcohol and aqueous solutions of Triton X-100, cetyltrimethylammonium bromide, and other reagents. All the solutions, along with the surfactants, contained isopropyl alcohol (5 vol %).

The processes were studied by pH-metric titration and spectrophotometry at 298 K. An MV-88 pH meter–millivoltmeter were used. The glass electrode was calibrated in aqueous solutions of isopropyl alcohol [17]. The ionic strength of solutions containing

a surfactant and 5 vol % isopropyl alcohol was provided by the solution components, and in 40% isopropyl alcohol it was maintained at a level of 0.1 (KNO_3). The constants of the protolytic equilibria were determined by titration of HL solutions (c_{HL} 5×10^{-3}, 0.01 M) with solutions of HNO_3 or HCl and of KOH. In the course of titration, the solutions were stirred with a magnetic stirrer.

The electronic absorption spectra were taken on Spekol-11 and Perkin–Elmer Lambda-EZ-210 spectrophotometers in 1-cm quartz cells. The experimental data were processed with the CPESSP program [18].

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