

# Protonation constants and overall constants of complex formation of copper(II) ions with surface-active ligands derived from ethylenediamine

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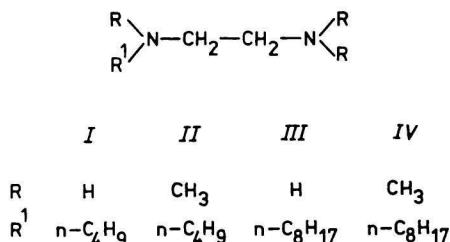
Received 1 July 1987

The protolytic and complex-forming equilibria of the chelates of *N*-substituted ethylenediamine ligands with the central Cu(II) ions were studied, and their capability of formation of the pseudomicellar phase in aqueous solutions as well. The work was predominantly directed to the assessment of possible application for the micellar catalysis enhanced in its action by metal chelates. It was found that substitution on the ethylenediamine nitrogen atoms with longer aliphatic chains (C<sub>4</sub> and C<sub>8</sub>) substantially increases the number of catalytically active particles in solution of a chelate with Cu(II). The formation of pseudomicellar phase, however, brings about to some extent the formation of catalytically inactive dimeric particles.

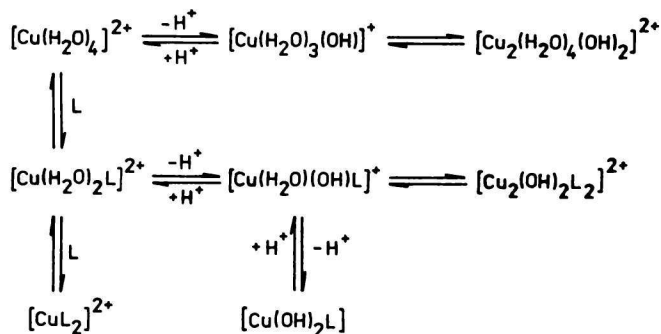
Изучены протолитическое равновесие и равновесие комплексообразования хелатов *N*-замещенных этилендиаминовых лигандов с центральным ионом Cu(II), а также их способность образовывать псевдомицеллярную фазу в водных растворах. Основной целью работы было нахождение возможного применения мицеллярного катализа с усиленным эффектом под действием хелатов металлов. Было обнаружено, что нахождение на атомах азота в этилендиамина длинных алифатических цепочек (C<sub>4</sub> и C<sub>8</sub>) приводит к значительному увеличению числа каталитически активных частиц в растворе хелата с Cu(II). Образование псевдомицеллярной фазы, однако, приводит в некоторой степени к появлению каталитически неактивных димерных частиц.

In the field of micellar catalysis the compounds with reactive polar functional groups and longer aliphatic chains become nowadays more and more utilized as they form the micelles in solution. As the reactive functional groups there are applied the hydroxy groups [1—4], amino groups [5—7], mercapto groups [8, 9], imidazole ring [10—12], hydroxamic anion [13, 14], and the others. Until now there was not studied, however, the effect of micelle formation on the reactions catalyzed by metal ions chelates.

In order to make a consideration on catalytic activity of metal chelates it is necessary to know the concentrations of individual forms of complex particles coexisting in the equilibrium reaction mixture. A catalytically active form of chelate must possess the free coordination sites on a central metal ion enabling to bind the substrate under reaction. In this paper we describe the results of protolytic and complex-forming equilibria of *N*-alkylethylenediamines of the general formula



and their chelates with Cu(II) ions. It is known that similar chelates catalyze the hydrolysis of esters, in which a molecule of water bound in the coordination sphere of metal ion is the main reactive particle [15–18]. The acidity of water molecules coordinated to the central Cu(II) ions is thus remarkably increased, which brings about their stronger ionization (in other words, this can be regarded as a hydrolysis of metal ion). In this way, a mono- and a dihydroxo form of given chelate is formed, occasionally there may be formed dimeric particles by the coupling of two monohydroxo form molecules. In the equilibrium mixture except the hydroxo forms of chelates there may exist Cu(II) ions being coordinated to two molecules of a bifunctional ligand, free hydrated Cu(II) ions, and their corresponding monohydroxo forms and dimers as well. The equilibria of these various particles may be illustrated by the following scheme



## Experimental

*N*-Monoalkylethylenediamines (*I*, *III*) were prepared by the action of 1-alkyl bromides on the excess of ethylenediamine mixed with ethanol at boil of the resultant mixture during several hours. The final products were isolated therefrom by fraction distillation (*I*: b.p. = 75–79 °C at 2.66 kPa; *III*: b.p. = 139–143 °C at 1.5 kPa [19]). From these compounds *N*-alkyl-*N,N',N'*-trimethylethylenediamines (*II*, *IV*) were prepared in the so-called reductive methylation reaction, *i.e.* by the action of formaldehyde and formic acid on amines [20]. They were isolated by fraction distillation, too (*II*: b.p. = 110–113 °C; *IV*: b.p. = 170–175 °C, both at 1.5 kPa). The identity of the synthesized compounds *I–IV* was verified by elemental analysis and <sup>1</sup>H NMR spectroscopy [19].

The protonation constants of *I–IV* as well as the overall constants of complex formation with Cu(II) ions ( $\log \beta_n$ ) were evaluated from the potentiometric titration curves. The measurements were carried out on a digital pH-meter OP-208/1 using a combined glass electrode OP-08087 (both products of Radelkis, Budapest).

All solutions were prepared in deionized water and free of CO<sub>2</sub>. This was done by treating water on the ion-exchange resins and carbon fibres, followed by distillation in a quartz distillation apparatus. The quality of water was verified by conductometry on an OK-102/1 conductometer (Radelkis, Budapest). The conductivity was in the range of 0.5–1.0 μS cm<sup>-1</sup>.

The KOH solution for titrations being free of CO<sub>2</sub> ( $c = 0.1 \text{ mol dm}^{-3}$ ) was prepared from KCl by conversion with AgOH according to *Schwarzenbach* [21]. The solutions titrated were adjusted to the constant ionic strength  $I = 0.1 \text{ mol dm}^{-3}$  with KBr. The titrations were carried out at constant stirring and temperature in an inert atmosphere of N<sub>2</sub>.

For the determination of critical micelle concentration ( $c_K$ ) of compounds under study we used a tensiometer Cenco Du Nouy utilizing the ring method for measurements of surface activity. The solutions of given compounds of pH = 8 were measured at  $\theta = 25^\circ\text{C}$  and ionic strength  $I = 0.1 \text{ mol dm}^{-3}$  (KBr).

The experimental procedure of the  $pK_a$  value determination was verified with NH<sub>4</sub>Cl solution, for which  $pK_a = 9.27$  was found at ionic strength  $I = 6.6 \times 10^{-3} \text{ mol dm}^{-3}$  and  $\theta = 25^\circ\text{C}$ . This agreed with the published data in Ref. [22].

The protonation constants and overall constants of complex formation between Cu(II) ions and ligands *I–IV* were calculated by means of the programs pKAS and BEST. Their principles were published by *Motekaitis* and *Martell* [23, 24].

## Results and discussion

The knowledge of protonation constants is inevitable for the calculation of complex-forming equilibria. Table 1 summarizes the protonation constants obtained by evaluation of titration curves using the program pKAS.

Table 1

Values of successive protonation constants of ligands I–IV  
 $\theta = 25^\circ\text{C}$ ,  $I = 0.1 \text{ mol dm}^{-3}$  (KBr)

Ligand	$\text{p}K_1$	$\text{p}K_2$
I	9.87	7.21
II	9.26	6.11
III	10.18	7.17
IV	9.22	6.20

Comparing the measured and calculated course of titration curves for the ligand IV there were noticed the differences in the area of  $\text{LH}^+ \rightleftharpoons \text{LH}_2^{2+}$  transition, which is typical of the solutions of polyelectrolytes reflecting the effect of close distance of adjacent charges on the protolytic equilibrium. Taking into account the presence of longer aliphatic chain in IV ( $\text{C}_8$ ) we assume that the reason for such behaviour is the formation of micelles, in which the individual molecules are associated in such a manner that can bring about the mutual electrostatic influencing of adjacent molecules of protonated ligands. The behaviour of polyelectrolytes at protonation was studied by *Katchalski* and *Spitnik* [25]. The effect of electrostatic contribution to the protolytic equilibrium they have expressed by the modified Henderson's equation

$$\text{pH} = \text{p}K^\circ + n \log \frac{\alpha}{1 - \alpha}$$

where  $\alpha$  is the value of neutralization degree. Respecting this relationship we got agreement between the measured and calculated courses of titration curves for the ligand IV. For the  $n$  constant there was calculated an average value of 1.15 at concentration  $c_{IV} = 3.71 \times 10^{-3} \text{ mol dm}^{-3}$ . In order to confirm the assumption of micelle formation in solutions of IV the measurements of surface activity in dependence on the concentration were carried out, and the value of critical micelle concentration  $c_K$  at  $\theta = 25^\circ\text{C}$  and ionic strength  $I = 0.1 \text{ mol dm}^{-3}$  (KBr) was therefrom determined:  $c_{K-IV} = 1.12 \times 10^{-4} \text{ mol dm}^{-3}$ . In the case of other ligands (*e.g.* I to III) the micelle formation was not proved.

The complex-forming equilibria were evaluated by means of iterative program BEST. For the initial assessment of overall complex formation constants of  $[\text{Cu}(\text{H}_2\text{O})_2\text{L}]^{2+}$  and  $[\text{CuL}_2]^{2+}$  the titration curves obtained for the ratio  $n(\text{Cu}):n(\text{ligand}) = 1:2$  were used. For the hydroxo forms of the  $[\text{Cu}(\text{H}_2\text{O})(\text{OH})\text{L}]^+$  and  $[\text{Cu}(\text{OH})_2\text{L}]$  chelates and  $[\text{Cu}_2(\text{OH})_2\text{L}_2]^{2+}$  dimer the values of overall stability constants were assessed on the basis of an analogy with those published by *Martell et al.* [18] for similar ligands (*N,N,N',N'*-tetra-

methylethylenediamine — TMEN and  $N,N'$ -dimethylethylenediamine — DMEN). The values for the  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  particles and corresponding dimer  $[\text{Cu}_2(\text{H}_2\text{O})_4(\text{OH})_2]^{2+}$  were taken from Ref. [26]. The calculated values expressed as  $\log \beta_n$  describing the formation of components of the equilibrium mixtures of complexes for the individual ligands (*I*—*IV*) with Cu(II) ions are listed in Table 2.

Table 2

Values of logarithms of the overall constants of complex formation of ligands *I*—*IV* with Cu(II) ions  
 $\theta = 25^\circ\text{C}$ ,  $I = 0.1 \text{ mol dm}^{-3}$  (KBr)

Particle	$\log \beta_n$			
	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>
$[\text{Cu}(\text{OH})(\text{H}_2\text{O})_3]^+$	−8.0	−8.0	−8.0	−8.0
$[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2]^{2+}$	−10.6	−10.6	−10.6	−10.6
$[\text{Cu}(\text{H}_2\text{O})_2\text{L}]^{2+}$	11.43	7.12	11.34	7.33
$[\text{Cu}(\text{H}_2\text{O})(\text{OH})\text{L}]^+$	2.0	0.29	2.13	−1.53
$[\text{Cu}_2(\text{OH})_2\text{L}_2]^{2+}$	11.81	2.36	11.22	3.89
$[\text{Cu}(\text{OH})_2\text{L}]$	−5.35	−8.89	−6.09	−9.36
$[\text{CuL}_2]^{2+}$	14.24	9.04	14.24	19.14

From this table it is obvious that substitution of hydrogen atoms on the nitrogen atoms of ethylenediamine (ligands *I* and *III*) brought about the decrease of  $\log \beta_n$  values for the  $[\text{Cu}(\text{H}_2\text{O})_2\text{L}]^{2+}$  and  $[\text{CuL}_2]^{2+}$  species formation, which is also reflected in the decrease of formation of the same complex types for ligands *II* and *IV*.

The formation of catalytically inactive dimeric particles  $[\text{Cu}_2(\text{OH})_2\text{L}_2]^{2+}$  is mostly suppressed in the case of ligand *II*. From the calculated constants one may deduce that a prone to dimerize increases as follows

$$II < IV \ll III \approx I$$

Therefrom it is also possible to assess the prone of the  $[\text{Cu}(\text{H}_2\text{O})_2\text{L}]^{2+}$  particles to hydrolyze

Hydrolysis to the 1st stage, formation of  $[\text{Cu}(\text{H}_2\text{O})(\text{OH})\text{L}]^+$

$$IV > II \gg I \approx III$$

Hydrolysis to the 2nd stage, formation of  $[\text{Cu}(\text{OH})_2\text{L}]$

$$IV > II > III > I$$

These results are plotted in Fig. 1 as a percentage of individual complex species in dependence on pH. From the plots for ligands *II* and *IV* it is obvious

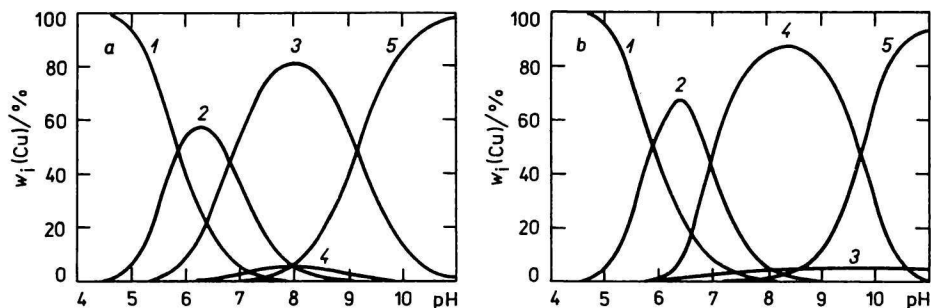


Fig. 1. Distribution of complex particles in per cent in dependence on pH.  $c(\text{Cu(II)}) = 7.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $I = 0.1 \text{ mol dm}^{-3}$  (KBr),  $\theta = 25^\circ\text{C}$ .

a)  $n(\text{II}):n(\text{Cu}) = 1:1$ ; b)  $n(\text{IV}):n(\text{Cu}) = 1:1$ .

Forms of complex particles: 1.  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ; 2.  $[\text{Cu}(\text{H}_2\text{O})_2\text{L}]^{2+}$ ; 3.  $[\text{Cu}(\text{H}_2\text{O})(\text{OH})\text{L}]^+$ ; 4.  $[\text{Cu}_2(\text{OH})_2\text{L}_2]^{2+}$ ; 5.  $[\text{Cu}(\text{OH})_2\text{L}]^{2+}$ .

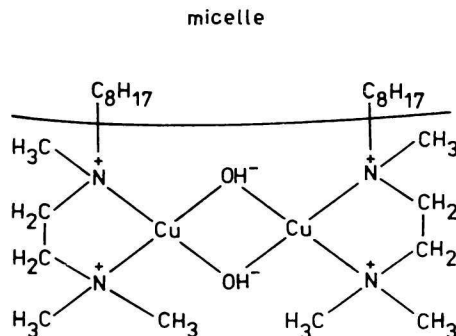


Fig. 2. Schematic representation of a dimer in the micelle of the complex  $\text{Cu(II)—IV}$ .

that in the area of  $\text{pH} = 8\text{--}9$  a suppression of formation of catalytically inefficient dimer  $[\text{Cu}_2(\text{OH})_2\text{L}_2]^{2+}$  is pronounced in the case of ligand *II*. The contrary observation for the ligand *IV* may be explained by micelle formation, in which the coordinated water molecules on  $\text{Cu(II)}$  ions are getting very close to each other and thus probably it supports the undesired formation of dimeric particles. The probable scheme of the dimer is shown in Fig. 2.

## Conclusion

The ligands derived from ethylenediamine (*I—IV*) and their complex compounds with  $\text{Cu(II)}$  ions were studied mainly from the point of view of overall

chelate stability constants of catalytically efficient forms present in the reaction mixtures, whereas the pH value and the effect of micelles in solution have proved to be an important factor.

It was found that substitution of hydrogen atoms on the nitrogen atoms in ethylenediamine leads to an optimal decrease of chelate stabilities along with simultaneous increase of the concentrations of catalytically efficient complex particles. The formation of micellar pseudophase decreases, however, to significant extent the catalytic activity of complex compounds in question due to the support of formation of catalytically inefficient dimeric particles. One may not, however, exclude that at different mechanisms of catalysis by metal chelates the close proximity of chelate reactive centres in a micelle may positively influence the course of reaction to be catalyzed.

## References

1. Meyer, G., *Tetrahedron Lett.* 1972, 4581.
2. Chevion, M., Katzhendler, J., and Sarel, S., Jr., *J. Chem. Soc.* 10, 795 (1975).
3. Martinek, K., Levashov, V. A., and Berezin, I. V., *Tetrahedron Lett.* 1975, 1275.
4. Moss, R. A., Nahas, R. C., and Ramaswani, W. J., *Tetrahedron Lett.* 1975, 3379.
5. Bruice, T. C., Katzhendler, J., and Fedor, R. L., *J. Am. Chem. Soc.* 90, 1333 (1968).
6. Blyth, C. A. and Knowles, J. R., *J. Am. Chem. Soc.* 93, 3071 (1971).
7. Oakenfull, D. G., *J. Chem. Soc., Perkin Trans. 2*, 1006 (1973).
8. Heitmann, P., *Eur. J. Biochem.* 5, 305 (1968).
9. Tagaki, W., Amada, I., Yamashita, Y., and Yano, Y., *J. Chem. Soc.* 1972, 1131.
10. Tagaki, W., Kobayashi, S., and Fukushima, D., *J. Chem. Soc., Chem. Commun.* 1977, 29.
11. Tonellato, U., *J. Chem. Soc., Perkin Trans. 2*, 771 (1976).
12. Tonellato, U., *J. Chem. Soc., Perkin Trans. 2*, 821 (1977).
13. Kunitake, T., Okahata, I., and Sakamoto, T., *Chem. Lett.* 1975, 459.
14. Tabushi, I. and Kuroda, Y., *Tetrahedron Lett.* 1973, 4435.
15. Martell, E. A., Chabereck, S. J., Courtney, R. C., Westerback, S., and Hyyity-Ainen, H., *J. Am. Chem. Soc.* 79, 3036 (1957).
16. Chabereck, S. J., Gustafson, R. L., Courtney, R. C., and Martell, E. A., *J. Am. Chem. Soc.* 81, 1959 (1959).
17. Courtney, R. C., Gustafson, R. L., Chabereck, S. J., and Martell, E. A., *J. Am. Chem. Soc.* 81, 519 (1959).
18. Gustafson, R. L. and Martell, E. A., *J. Am. Chem. Soc.* 81, 525 (1959).
19. Research report No. 573-50/84-Vč. Faculty of Pharmacy, Comenius University, Bratislava, 1984.
20. Naudet, M., Baldy, J., and Desnuelle, P., *Bull. Soc. Chim. Fr.* 1954, 1167.
21. Schwarzenbach, G. and Biederman, W., *Helv. Chim. Acta* 31, 331 (1948).
22. Rabinovich, V. A. and Khavin, Z. Yu., *Krátkii khimicheskii spravochnik*, p. 220. Khimiya, Moscow, 1977.

23. Motekaitis, R. and Martell, E. A., *Can. J. Chem.* 60, 168 (1982).
24. Motekaitis, R. and Martell, E. A., *Can. J. Chem.* 60, 2403 (1982).
25. Katchalski, A. and Spitnik, P., *J. Polym. Sci.* 2, 432 (1947).
26. Berecki-Biedermann, C., *Ark. Kemi* 9, 175 (1956).

Translated by P. Butvin