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Formation of Binuclear EDTA and Cu(II) Complexes in Aqueous Solutions

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EDTA (ethylenediaminetetraacetate) is one of the most powerful chelating agents widely used in industry to enhance the metal ion solubility or to avoid the formation of insoluble metal compounds. It enters into strong complexes with heavy metal ions at the ratio 1:1. Such a peculiarity of EDTA hinders the metal recovery in the form of insoluble compounds, which is the common practice for the treatment of spent solutions containing heavy metal ions. Metals are removed from complexing agent containing solutions, as a rule, only after the oxidative destruction of ligands [1,2]. In order to diminish the treatment costs and the environmental impact the possibilities to recover and reuse ligands have also been investigated. Scarcely soluble H_4EDTA in acidic (pH 0.5–1.5) solutions has been proposed for recycling copper plating solutions [3,4]. EDTA can be removed from solutions in the form of low soluble $Cu_2EDTA \cdot 4H_2O$ as well [5]. The formation of the low soluble $Cu_2EDTA \cdot 4H_2O$ compound from $Cu(OH)_2$ and H_4EDTA is known [6]. The structure and formation of M_2EDTA compounds in suspension of insoluble metal compounds by H_4EDTA, where M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}, were studied at high temperatures [7,8]. The reaction between Ag(I) and EDTA and the formation of insoluble Ag_4EDTA were described in [9].

This study examines the interactions of Cu(II) and H_2EDTA^{2-} in solutions when the insoluble $Cu_2EDTA \cdot 4H_2O$ is produced with the purpose to assess its composition, dissociation and solubility. The insoluble form of $Cu_2EDTA \cdot 4H_2O$ is precipitated in aqueous solutions when the concentration of Cu(II) exceeds the concentration of EDTA and the range of pH is rather narrow (Fig. 1). The formation begins approximately at pH 2 and is most complete at pH 5.6. At higher pH the hydrolysis of Cu_2EDTA begins.

The interactions between Cu^{2+} and excess of EDTA were thoroughly investigated. In this case the stable complex $CuEDTA^{2-}$ ($pK = 18.8$) is formed [10]. However, the influence of Cu^{2+} ion excess on the complex formation has not been investigated so far. For this purpose conductometric and potentiometric titration of H_2EDTA^{2-} with Cu^{2+} was carried out (Fig. 2a and b). A sharp potential jump at constant pH (Fig. 2b)

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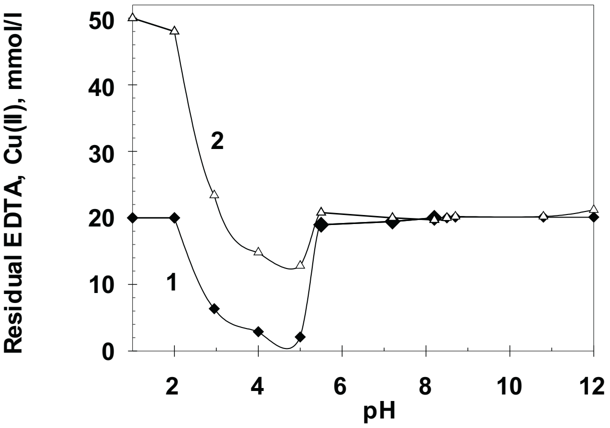

Figure 1. Influence of pH on the residual EDTA (curve 1) and Cu(II) (curve 2) concentrations in solution, containing 50 mmol/l Cu(II) and 20 mmol/l EDTA.

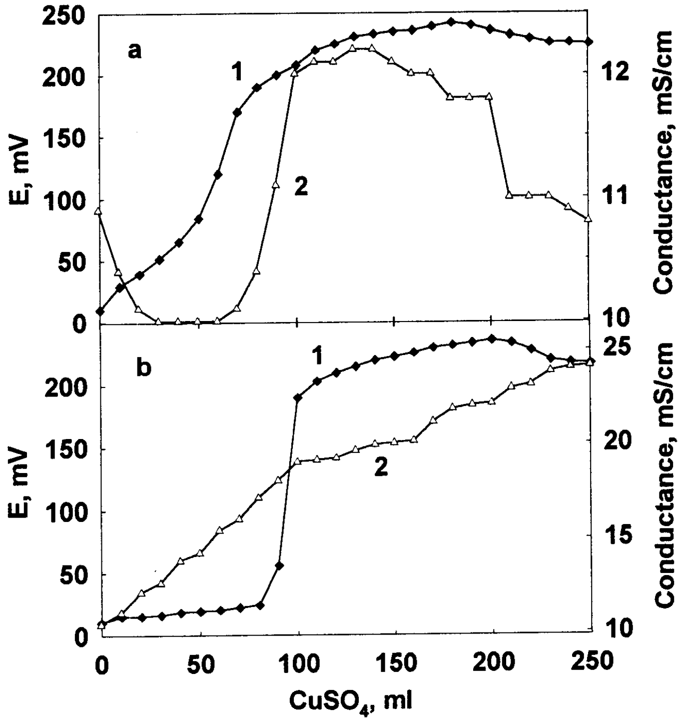

Figure 2. Potentiometric (curve 1) and conductometric (curve 2) titration of 100 ml solution, containing 100 mmol/l Na_2H_2EDTA (pH = 4) with 100 mmol/l $CuSO_4$ (pH = 4) solution: a – without adjusting pH, b – at pH = 4.

and a conductance jump without pH adjusting (Fig. 2a) are found, while titrating the Na_2H_2EDTA solution with the $CuSO_4$ solution indicates the formation of $CuEDTA^{2-}$ complex. The decrease in potential and conductance (Fig. 2a) with a further titration of H_2EDTA^{2-} containing solutions with Cu^{2+} indicates the interaction between the formed $CuEDTA^{2-}$ complex and Cu^{2+} ions. Further investigations were carried out by titration of the formed $CuEDTA^{2-}$ complex with Cu^{2+}. For this purpose a $CuEDTA^{2-}$ complex solution was prepared by potentiometric titration of Na_2EDTA with $CuSO_4$ up to the potential jump at pH 4.

When the $CuSO_4$ solution (pH 4.0) is added to the $CuEDTA^{2-}$ solution (pH 4.0), the total Cu(II) concentration is constant in the entire range of the added amounts of $CuSO_4$. It is worth noting that the form of the conductometric and potentiometric curves depends on the titration rate. Therefore, 5 ml of the $CuSO_4$ solution were added to the $CuEDTA^{2-}$ solution every 2 min in order to achieve a better reproducibility. The formation of a distinct Cu_2EDTA precipitate begins after the addition of 50 ml of 0.1 mol/l $CuSO_4$ to 150 ml of 0.1 mol/l $CuEDTA^{2-}$ solution. At the same time the pH begins to decrease (Fig. 3a, curve 1) and an additional amount of NaOH is needed to maintain a constant pH. The concentration of free Cu^{2+}, which was determined using an ion selective electrode, considerably differs from that, which was calculated from the added $CuSO_4$. This difference is observed after the addition of 10–15 ml of $CuSO_4$. Simultaneously the decrease in conductance also proceeds (Fig. 3a and b, curves 2).

Such results are due to the formation of a soluble Cu_2EDTA compound at the initial stage of titration. Its precipitation begins at a higher $CuSO_4$ amount, when the pH begins to decrease. For the formation of 1 mol of the Cu_2EDTA precipitate 0.02 mol of NaOH is needed. In comparison, 2 mols of NaOH are used for the formation of 1mol of $CuEDTA^{2-}$ complex.

The pH-metric titration of Cu^{2+}, $CuEDTA^{2-}$ and $CuEDTA^{2-} + Cu^{2+}$ solutions (Fig. 4) indicates the formation of more stable compounds in the latter solution. In this case the formation of the insoluble $Cu(OH)_2$ precipitate in a $CuSO_4$ solution proceeds at pH 5.2, while in the solution containing $CuEDTA^{2-}$, $Cu(OH)_2$ precipitates at pH 5.8. If we assume that the formation of Cu_2EDTA proceeds according to:

$$Cu^{2+} + CuEDTA^{2-} \rightleftarrows Cu_2EDTA, \tag{1}$$

a free Cu^{2+} ion concentration can be calculated from the solubility product

$$[Cu^{2+}] = \frac{S}{[OH]^2} \tag{2}$$

The solubility product (S) of $Cu(OH)_2$ equals $5 \cdot 10^{-20}$ [11], thus, the calculated dissociation constant K_d is $1.28 \cdot 10^4$ l/mol. The spectrophotometric method of continuous variation was used to determine the complex dissociation constant and to confirm the complex composition. The measurements were carried out at a different ratio and constant total concentration (40 mmol/l) of $Cu^{2+} + CuEDTA^{2-}$

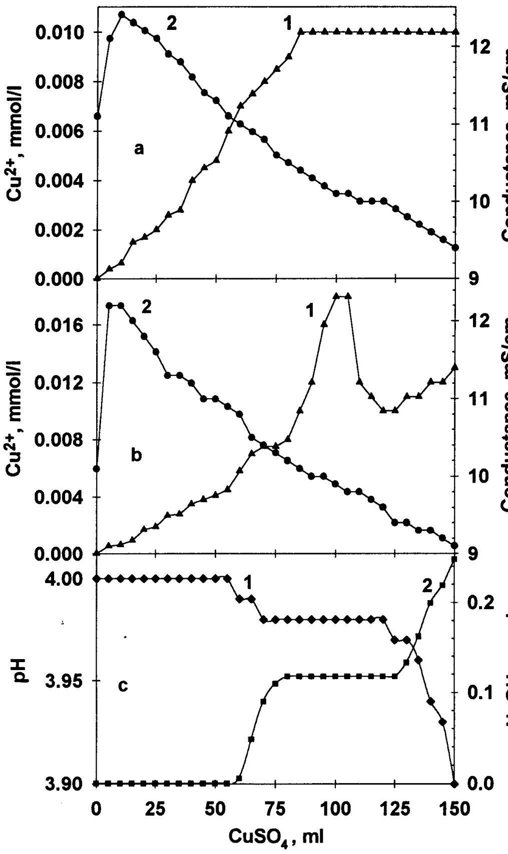

Figure 3. Potentiometric (curve 1) and conductometric (curve 2) titration of 150 ml solution containing 100 mmol/l CuEDTA^{2-} (pH = 4.0) with 100 mmol/l $CuSO_4$ solution (pH = 4.0): a – without adjusting pH; b – at pH = 4.0; c – pH change without adjusting pH (curve 1) and amount of NaOH used for adjusting of pH (curve 2).

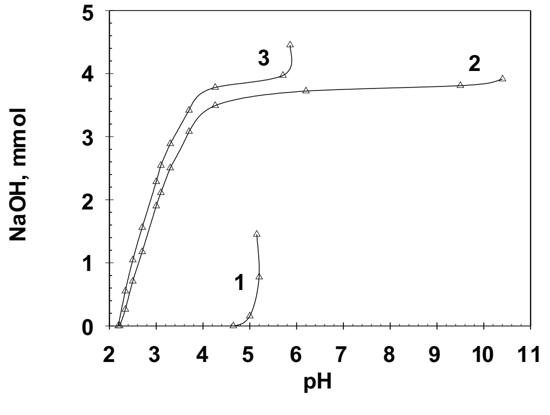

Figure 4. pH-metric titration of 100 ml solutions, containing 20 mmol/l $CuSO_4$ (curve 1), 20 mmol/l – CuEDTA^{2-} (curve 2) and 20 mmol/l $CuSO_4$ + 20 mmol/l CuEDTA^{2-} (curve 3).

in 0.5 M Na_2SO_4 solution. The empirical formula of the complex established is 1:1. K_d calculated at different Cu^{2+} and $CuEDTA^{2-}$ concentrations [7,12]

$$\frac{c^{\circ}_{Cu^{2+}} \cdot c^{\circ}_{CuEDTA^{2-}}}{\Delta A} = \left(c^{\circ}_{Cu^{2+}} + c^{\circ}_{CuEDTA^{2-}} + \frac{1}{K_d} \right) \cdot \frac{1}{\Delta A} - \frac{\Delta A}{(\Delta\varepsilon)^2} \tag{3}$$

is equal to $3.4 \cdot 10^3$.

According to [13] this equation for 1:1 complexes is applicable, when $K_d (c^{\circ}_{Cu^{2+}} + c^{\circ}_{CuEDTA^{2-}}) > 100$ and in our case it is equal to 136. The influence of different cations and ionic strength on the solubility of $Cu_2EDTA \cdot 4H_2O$ is shown in Table 1.

Table 1. Influence of ionic strength on solubility parameters of $Cu_2EDTA \cdot 4H_2O$ precipitates.

Background electrolyte	Ionic strength	pH	Free Cu^{2+}, mmol/l	Total Cu(II) in saturated solution, mmol/l	K_d	S
			1.0	6.0	$2 \cdot 10^3$	$1.0 \cdot 10^{-6}$
Na_2SO_4	0.25	5.12	2.4	17.2	$1.1 \cdot 10^3$	$5.7 \cdot 10^{-6}$
	1.25	5.18	2.1	31.8	$3.1 \cdot 10^3$	$4.4 \cdot 10^{-6}$
	2.5	5.18	1.6	39	$7 \cdot 10^3$	$2.6 \cdot 10^{-6}$
K_2SO_4	0.25	5.03	2.0	16.4	$1.5 \cdot 10^3$	$4.0 \cdot 10^{-6}$
	1.25	5.23	1.4	32.5	$7.8 \cdot 10^3$	$2.0 \cdot 10^{-6}$
	2.5	5.28	1.4	41	$10.0 \cdot 10^3$	$2.0 \cdot 10^{-6}$
$(NH_4)_2SO_4$	0.25	4.80	2.0	16.6	$1.5 \cdot 10^3$	$4.0 \cdot 10^{-6}$
	1.25	4.40	1.0	36	$1.7 \cdot 10^3$	$1.0 \cdot 10^{-6}$
	2.5	4.20	0.6	49	$6.6 \cdot 10^4$	$3.6 \cdot 10^{-7}$

Cu^{2+}concentration determined using the copper ion selective electrode.

The concentration of free Cu^{2+} in the solutions was determined using an ion selective electrode. With the increase in solution ionic strength the solubility of precipitate and dissociation constant increase, whereas the solubility product (S) decreases. It may be attributed partly to the formation of bihomonuclear Cu_2EDTA complexes in the solutions of high ionic strength [7]. The solubility of the precipitate was investigated using an excess of $CuSO_4$ and $CuEDTA^{2-}$. In both cases the solubility of the $Cu_2EDTA \cdot 4H_2O$ compound decreased with the increase in the concentrations of both components. When the concentration of $CuSO_4$ or $CuEDTA^{2-}$ was exceeding 150 mmol/l, the dissolved $Cu_2EDTA \cdot 4H_2O$ precipitate, the dissociation constant (K_d) and solubility product (S) could be calculated

$$c_s = K_d \cdot S + \frac{S}{c^{\circ}_{CuEDTA^{2-}}} \tag{4}$$

where c_s is the Cu^{2+} concentration in the solution after dissolving $Cu_2EDTA \cdot 4H_2O$. In Cu^{2+} and $CuEDTA^{2-}$ concentration range from 200 to 400 mmol/l calculated $K_d = 2.4 \cdot 10^3$ l/mol and $S = 2 \cdot 10^{-5}$ mol^2 /l^2.

In the pH range 2–6 the free EDTA is in the form of H_2EDTA^{2-}. Its two nitrogen atoms and two oxygen atoms from two COOH groups act as powerful chelating agents for Cu^{2+} ion [10]. The two residual COOH groups are free and capable of forming ionic or complexing bonds with Cu^{2+}. For the investigations of the interactions between Cu^{2+} and the ligand the FT-IR spectra were recorded for H_4EDTA, which contained undissociated COOH groups, Na_2H_2EDTA, contained dissociated and undissociated COOH, and $Cu_2EDTA \cdot 4H_2O$ (Table 2). The poorly defined band at 1686 cm^{-1} indicates that the $Cu_2EDTA \cdot 4H_2O$ compound contains a partly undissociated COOH. The well-defined bands at 1638 cm^{-1} and 1617 cm^{-1} indicate the presence of coordinated as well as dissociated COOH groups.

Table 2. COOH wavenumbers of EDTA in FT-IR spectra.

Group	Wavenumber, cm^{-1}		
	H_4EDTA	Na_2H_2EDTA	$Cu_2EDTA \cdot 4H_2O$
COOH undissociated (ν_{as})	1690	1673	1686
COO^- dissociated (ν_{as})	–	1627	1617
COOH coordinated (ν_{as})	–	–	1638
COOH valence symmetric vibration (ν_s)	1420	1397	1391
C–N	1214	1193	1091

The packing in the solid state may be broken by the dissolution in polar solvents. Therefore, the results are not always applicable for the complexes existing in an aqueous solution, but the nature of bindings are the same in the crystal and in the solution. The results of FT-IR investigations indicate that Cu_2EDTA may form by interaction of the undissociated CuH_2EDTA as well as dissociated $CuEDTA^{2-}$ with Cu^{2+} ions. The decrease in conductivity during the $CuEDTA^{2-}$ titration with Cu^{2+}, the formation of insoluble $Cu(OH)_2$ at higher pH values in Cu_2EDTA solutions and deflection from absorbance additivity, indicate the complex formation. Each of the two Cu^{2+} ions is bound in $Cu_2EDTA \cdot 4H_2O$ compound by different bonds and therefore forms complexes of different stability (pK ~18 for $CuEDTA^{2-}$ and pK ~3 for Cu_2EDTA). Thus, the resulting Cu_2EDTA is not a bihomonuclear complex compound.

REFERENCES

1. Chaudhary A.J., Donaldson J.D., Grimes M.-ul- Hassen S.M. and Spencer R.J.. *J. Chem. Techn. and Biotechn.,* **75**, 353 (2000).
2. Brooks C.S., *Separation Science and Technology*, **28** (1–3), 579 (1993).
3. Czepluch H. and Bissinger W.D.H., *Galvanotechnik*, **90**, 4427 (1989).
4. Gylienė O. and Šalkauskas M., *Plating and Surface Finishing,* **83**(10), 61 (1995).
5. Gylienė O., Aikaitė J. and Šalkauskas M., *Galvanotechnik*, **92**, 2222 (2001).
6. Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Kupfer. Teil B–Lieferung 4. System Nummer 60, 1955, Verlag Chemie – GmBH, Wernheim/Bergstr., S. 1670.
7. Leonteva M.V. and Fridman A.Y., *Koordinatsionaia khimiia*, **14**, 320 (1988) (in Russian).
8. Leonteva M.V. and D'iatlova N.M., *Koordinatsionaia khimiia,* **16**, 823 (1990) (in Russian).
9. Saran L., Cavalheiro E. and Neves E.A., *Talanta*, **42**, 2027 (1995).
10. D'iatlova N.M., Temkina V.I. and Popov K.I., Kompleksony i kompleksonaty metallov (Complexing Agents and Metal Complexes), Khimiia, Moskva, 544 p. (1998) (in Russian).
11. Lur'e Iu., Spravochnik analiticheskoi khimii (Handbook of Analytical Chemistry), Khimiia, Moskva, 1989 (in Russian).
12. Mc Bryde W.A.E., *Talanta*, **21**, 979 (1974).
13. Budisinsky B.W., *J. Inorg. Nucl. Chem.*, **31**, 1345 (1969).