APPLICATION OF A COPPERSELECTIVE ELECTRODE COATED WIRE TYPE TO THE DETERMINATION OF COPPER(II) BY POTENTIOMETRIC TITRATIONS WITH ETHYLENEDIAMINE IN AQUEOUS AND NONAQUEOUS SOLUTIONS

Miloš B. Rajković, Borislava D. Vučurović and Dragan Tošković

In this work, potentiometric titrations of the solution of the Cu(II) ione have been executed with ethylenediamine as complexing agent and the copper selective electrode coated wire type/SCE indicator system in aqueous and nonaqueous solvents. Because of the difficult conditions of the formation of the Cu(II)ethylenediamine complex, due to the presence of parallel reactions influencing the position of the basic balance of the formation of the complex, this study discusses and deduces the equations for the calculation of the constant of the formation of the complex as well as the equations for the calculation of the free ethylenediamine. In all the cases a pronounced extreme of the curve of titration has been remarked in the final phase of the titration, whatever diluent was used. Similar results have been obtained using solvents such as: water, alcohol (methanol, ethanol, buthanol), which was expected having in mind the chemical resemblance of these compounds (polar mollecules), while a sharper extreme was obtained in N,N–dymethylformamide, which was expected as well because of the similar basic characteristics with ethylenediamine. The results obtained by this study show the exceptional advantage of ethylenediamine as complexing agent and also the possibility of the application of the copper selective electrode coated wire type/SCE indicating system for the determination of Cu(II) in aqueous and non–aqueous solvents and for the determination of the constants of the determination of the formation of the ethylenediamine complex.

KEY WORDS: *coated wire copper selective electrode, ethylenediamine potentiometric titrations of copper, stability constants of Cu(II)ethylenediamine complex*

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INTRODUCTION

From the seventies the coated wire ion selective electrodes type (CWISE) have an important role in the investigations of various ionic species (and consequently a large variety of compounds) in scientific and research laboratories and in the industrial practice (1–4). The copper selective electrode coated wire type, has also an important place in the analytic practice, having a large application in all fields of research (5– 7).

Ethylenediamine (abbreviation "en" or EN), thanks to the strong donor characteristics of the atom of nitrogen, is a powerful complexing agent. (8) Although detailed research of the ethylenediamine complex have been performed with various ionic species, (for example literature 9–11) its complexing performances *are not completely exploited* for analytic purposes.

This study is a contribution to the research of the properties of ethylenediamine and its applications in the examination of the Cu(II)–ion in protonic and non–protonic solvents and as well a contribution of ethylenediamine to the determination of the constant of the formation of ethylenediamine–copper(II) complex.

EXPERIMENTAL

Reagents

All the chemicals in this study were of the analytical grade purity (p.a.). The solutions of copper(II)–nitrate (Kemika, Zagreb), prepared in different protonic and non–protonic solvents (water, methanol, ethanol, n–buthanol and DMF (N,N–dimethylformamide)), have been used for potentiometric titrations.

The following complexing agents have been used: complexone III (Na_2H_2Y), sodium–citrate, 8–hydroxyquinoline (oxyne) and ethylenediamine. Acetate buffer (pH=5.05), prepared by a usual procedure, has been used during the titrations of the solutions of Cu(II)–ion with complexon III and 8–hydroxyquinoline.

Apparatus

The potential of the solution has been measured by means of an indicator system coated wire copper selective electrode, home-made (5,12,13) /saturated calomel electrode (SCE) K 101, Radiometer Copenhagen). The indicator system was connected to a digital pH–mV meter, Radiometer Copenhagen, and the titrations were executed by an automatic burette Multi–Dosimat E 415, Switzerland. The contact between the tested solution and the reference electrode was realized by a "salt" bridge filled with agar–agar.

Procedure

The solutions of copper(II)–nitrate are made by solving the adequate quantity of copper(II)–nitrate in protonic and non–protonic solvents, which are then titrated by adequate solutions of different complexing agents. The solutions are permanently mixed with a Teflon–coated stirrer. All the potential measurements were done in the temperature interval of 25 ± 0.1°C.

RESULTS AND DISCUSSION

Theory

The properties of ethylenediamine to complex some ionic species

Ethylenediaminetetraacetic acid (EDTA or edta) and his disodium salt (Na_2H_2Y or complexone III – K–III) are a mighty complexing item and the basis of a whole method in the analytic chemistry – the *complexonometry*. It means that its basis, that is to say just the molecule of ethylenediamine from which it obtained by the Stecher reduction *may* also represent a strong comlexing agent. The characteristics of ethylenediamine to get related with some groups are based on the free electron couple possessed by the atom of nitrogen from the amino group ($-\overset{..}{N}H_2$). Thanks to the donor properties of nitrogen, a *coordinative binding* with the central ion is established (with the builder of the complex) – the ion of Cu(II).

An important property of ethylenediamine as a ligand in the complex with the central ion is the coordinative volume or dentantne, determined by the number of places that the ligand occupies in the inner sphere of the complex and it is conditioned by the quantity of donor atoms. Ethylenediamine, having two donor atoms, with free electron couples ($H_2\overset{..}{N}-CH_2-CH_2-\overset{..}{N}H_2$) can occupy not one but *two* positions in the coordination sphere (in the so-called first sphere, right next to the central ion), that is to say, may tie itself with two coordinative bindings to the central ion, so it represents a bidentantne ligand.

The complexes made by ethylenediamine with different ionic species belong to cyclic compound group, but a more specific group, the so–called *chelate* compounds, containing the cyclic complex which includes the central ion and the ligand (11,14).

Ethylenediamine with two donor atoms completely surrounds the central ion, as the claws of the crayfish, so that following the recommendation of Morgan and Drew such complex was named chelate (in Greek "chele" means the claws of the crayfish). The complex of the Cu(II)–ion has the following structure (conformation) (Fig.1) (2,7).

Building their five–member rings, the chelate complexes are very stable, since the molecules of solvents are expulsed from the closed ring structure, which implies a difficult solvability of ethylenediamine complex. It is also considered, that the great stability of the chelates comes from the fact that even if ethylenediamine is expulsed from one coordinative place of the coordinative sphere by a molecule of solvent, it will still stay tied to the central ion.
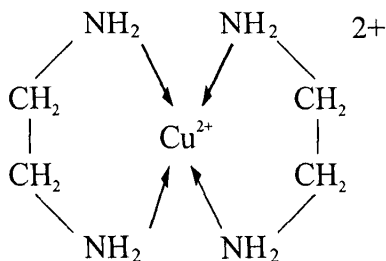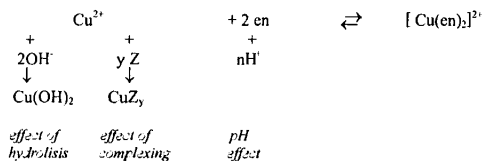

bisethylenediaminecopper(II)–

or $[Cu(en)_2]^{2+}$

Figure 1. The chelate ethylenediaminecopper(II) complex

The formation of the ethylenediaminecopper(II) complex the meshanism and the deduction of the equations for the calculation of the constants of forming (16,17)

The reaction of the complexing of the Cu(II)–ion with ethylenediamine itself is very compsite due to the presence of *parallel* (secundar) balances, which reacting with the ligand (ethylenediamine) or Cu(II)–ion, influence the position of the *basic* balance of the formation of the complex (18):

$$Cu^{2+} \quad\quad +2\,en \quad\quad \rightleftarrows \quad\quad [\,Cu(en)_2]^{2+}$$

$$
\begin{array}{ccc}
+ & + & + \\
2OH^- & y\,Z & nH^+ \\
\downarrow & \downarrow & \\
Cu(OH)_2 & CuZ_y &
\end{array}
$$

$$
\begin{array}{ccc}
\textit{effect of} & \textit{effect of} & pH \\
\textit{hydrolisis} & \textit{complexing} & \textit{effect}
\end{array}
$$

During the reaction of the Cu(II)–ion with ethylenediamine, the following *basic* balances take place:[1]

$$Cu^{2+} + en \overset{\beta_1}{\rightleftarrows} Cu(en)^{2+} \tag{1}$$

$$Cu^{2+} + 2en \overset{\beta_2}{\rightleftarrows} Cu(en)^{2+} \tag{2}$$

The graduated constant of formation b_1 and the total constant of formation b_2 for the Cu(II) –ion complexing processes may be expressed as: (19)

$$\beta_1 = [Cu(en)^{2+}]/[Cu^{2+}]\cdot[en] = 4{,}67\cdot10^{10} \tag{3}$$

$$\beta_2 = [Cu(en)_2^{2+}]/[Cu^{2+}]\cdot[en]^2 = 10^{20} \tag{4}$$

The total concentration of the Cu(II)–ion, $[Cu^{2+}]_{tot}$, and ethylenediamine, $[en]_{tot}$, may be expressed through the equation of the balance of masses:

$$[Cu^{2+}]_{tot} = [Cu^{2+}] + [Cu(en)^{2+}] + [Cu(en)_2^{2+}] \tag{5}$$

where:
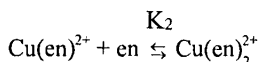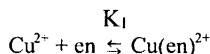
$[Cu^{2+}]_{tot}$ – the *total* concentration of Cu(II)–ion which exists in all forms in the solution;

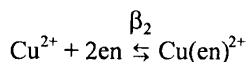$[Cu^{2+}]$ – the concentration of *free* Cu(II)–ion, which has not complexed with the ethylenediamine;

$[Cu(en)^{2+}]$ – the concentration of Cu(II)–ion coming from the dissociation of the complex $Cu(en)^{2+}$;

$[Cu(en)_2^{2+}]$ – the concentration of Cu(II)–ion coming from the dissociation of the complex $Cu(en)_2^{2+}$;

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[1]To be more precise there are *two* basic processes:

$$Cu^{2+} + en \overset{K_1}{\rightleftarrows} Cu(en)^{2+}$$

$$Cu(en)^{2+} + en \overset{K_2}{\rightleftarrows} Cu(en)_2^{2+}$$

which are defined by stability constants K_1 and K_2. By summation this two equations gives:

$$Cu^{2+} + 2en \overset{\beta_2}{\rightleftarrows} Cu(en)^{2+}$$

$$[en]_{tot} = [en] + [Cu(en)^{2+}] + 2[Cu(en)_2^{2+}] \qquad [6]$$

where:

$[en]_{tot}$ – the *total* concentration of ethylenediamine in the solution;

$[en]$ – the concentration of *free* ethylenediamine, which has not reacted with the Cu(II)–ion;

$[Cu(en)^{2+}]$ and

$[Cu(en)_2^{2+}]$ – the concentrations of ethylenediamine coming from the dissociation of the complex $Cu(en)^{2+}$, or $Cu(en)_2^{2+}$.

As the research was done with the copper(II)–nitrate which dissociates completely in the solution, no corrections were made for the parallel processes occurring during the formation (creation) of the complex.

Also, in the further calculations it is supposed that the concentration of the complex $[Cu(en)^{2+}]$ is proportionally low in comparing with the concentrations of the total ethylenediamine and Cu(II)–ion, so its value is neglected.

Combining the shown equations, one can find the expressions for the graduated constant of the formation of the complex β_1, that is to say the total constant of formation β_2.

The deduction of the equation for the graduated constant of formation, β_1

From the equation [6], $[Cu(en)^{2+}]$ may be expressed as:

$$[Cu(en)^{2+}] = [en]_{tot} - [en] - 2 \cdot [Cu(en)_2^{2+}] \qquad [7]$$

If the last member is multiplied and divided by the same value, for example $[Cu^{2+}] \cdot [en]^2$, it does not change its value:

$$[Cu(en)^{2+}] = [en]_{tot} - [en] - 2 \cdot \frac{\left[Cu(en)_2^{2+}\right]}{\left[Cu^{2+}\right] \cdot \left[en\right]^2} \cdot ([Cu^{2+}] \cdot [en]^2) \qquad [8]$$

where: $\dfrac{\left[Cu(en)_2^{2+}\right]}{\left[Cu^{2+}\right] \cdot \left[en\right]^2}$ is the expression of β_2, then

$$[Cu(en)^{2+}] = [en]_{tot} - [en] - 2 \cdot \beta_2 \cdot [Cu^{2+}] \cdot [en]^2 \qquad [9]$$

By substitution of the equation [9] in the equation [3], we have:

$$\beta_1 = \frac{\left[en\right]_{tot} - \left[en\right] - 2 \cdot \beta_2 \cdot \left[Cu^{2+}\right] \cdot \left[en\right]^2}{\left[Cu^{2+}\right] \cdot \left[en\right]} \qquad [10]$$

The deduction of the equation for the total constant of formation, β_2

From the equation [5] follows:

$$[Cu(en)_2^{2+}] = [Cu^{2+}]_{tot} - [Cu^{2+}] - [Cu(en)^{2+}] \qquad [11]$$

and from the equation [6]:

$$[en] = [en]_{tot} - [Cu(en)^{2+}] - 2 \cdot [Cu(en)_2^{2+}] \qquad [12]$$

the combination of those two equations[11] and [12] gives:

$$[en] = [en]_{tot} - [Cu(en)^{2+}] - 2 \cdot ([Cu^{2+}]_{tot} - [Cu^{2+}] - [Cu(en)^{2+}]) \qquad [13]$$

From the condition that $[Cu(en)^{2+}] \ll [Cu^{2+}]_{tot}$ and $[en]_{tot}$, follows that:

$[Cu(en)^{2+}] = [Cu^{2+}]_{tot} - [Cu^{2+}]$, and $\qquad\qquad$ [11–a]

$[en] = [en]_{tot} - 2\cdot([Cu^{2+}]_{tot} - [Cu^{2+}])$ $\qquad\qquad$ [13–a]

The substitution of the equations [11–a] and [13–a] into the expression for the *total* constant of formation β_2 (equation [4]) gives:

$$\beta_2 = \frac{[Cu^{2+}]_{tot} - [Cu^{2+}]}{[Cu^{2+}]\cdot\{[en]_{tot} - 2\cdot([Cu^{2+}]_{tot} - [Cu^{2+}])\}} \qquad\qquad [14]$$

The deduction of the equation for the calculation of the concentration of free ethylenediamine

The concentration of free ethylenediamine, $[en]$, may be calculated from the equation [6]:

$[en] = [en]_{tot} - [Cu(en)^{2+}] - 2\cdot[Cu(en)_2^{2+}]$ $\qquad\qquad$ [15]

From the equation [5]:

$[Cu(en)^{2+}] = [Cu^{2+}]_{tot} - [Cu^{2+}] - [Cu(en)_2^{2+}]$ $\qquad\qquad$ [16]

The substitution of the equations [16] into [15], gives:

$[en] = [en]_{tot} - [Cu^{2+}]_{tot} + [Cu^{2+}] + [Cu(en)_2^{2+}] - 2\cdot[Cu(en)_2^{2+}]$, i.e.

$[en] = [en]_{tot} - [Cu^{2+}]_{tot} + [Cu^{2+}] - [Cu(en)_2^{2+}]$ $\qquad\qquad$ [17]

If, as in the equation [7], the last member is multiplied and divided by the same value, for example $[Cu^{2+}]\cdot[en]^2$, it does not change its value, so it can be written:

$$[en] = [en]_{tot} - [Cu^{2+}]_{tot} + [Cu^{2+}]\frac{[Cu(en)_2^{2+}]}{[Cu^{2+}]\cdot[en]^2}\{[Cu^{2+}]\cdot[en]^2\}$$

where: $\dfrac{[Cu(en)_2^{2+}]}{[Cu^{2+}]\cdot[en]^2}$ is the expression of β_2, then

$[en] - [en]_{tot} + [Cu^{2+}]_{tot} - [Cu^{2+}] + b_2\{[Cu^{2+}]\cdot[en]^2\} = 0$, i.e.

$[en] + [Cu^{2+}]_{tot} + b_2\cdot([Cu^{2+}]\cdot[en]^2) - [en]_{tot} - [Cu^{2+}]_{tot} = 0$ $\qquad\qquad$ [18]

Nikagawa et al. (20) determined the values of the constant of formation of the copper(II)–ethylenediamine complex by application of the Orion copper–selective electrode with a rigid membrane, but in aqueous solutions. Aihara and Oho (21) applied an CuS/Ag_2S electrode for the determination of the constant of formation of the copper(II) – ethylenediamine complex in a water–acetonitrile mixture. Rajković and Vučurović (12,16,22) determined the values of the constant of formation of the copper(II)–ethylenediamine complex by application of the coated wire copper selective electrode in aqueous solutions.

Potentiometric titrations with ethylenediamine with a coated wire copper selective electrode (22)

Based on the previous consideration, a coated wire copper selective electrode as a selective electrode *on* a Cu(II)–ion and ethylenediamine as a selective ligand for the Cu(II)–ion, were applied for the determination of the copper(II)–ethylenediamine complex.
Previously, investigations of the applications of potentiometric titrations of aqueous solutions of the Cu(II)–ion were performed with various complexing agents as titrants, with a coated wire copper

selective electrode/SCE indicator system, and it was observed (Fig.2) that it was with ethylenedi-amine that the most pronounced peak in the final point of the titration and consequently applications in the concentration range $10^{-3} - 10^{-1}$ mol/dm³ (23,24). It is also necessary to state that the shown results were obtained without the previous setting of the pH–value of the Cu(II)–ion solution during the titration with ethylenediamine, which is necessary during the titration with the other complexing agents.
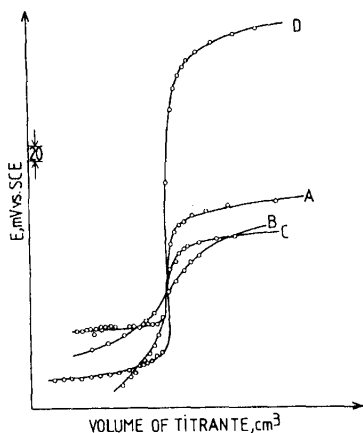

Figure 2. Titrations of Cu(II) solutions with different complexing agents using coated wire copper selective electrode/SCE couple as the indicating system: A. complexone III (Na_2H_2Y) (pH=5.05); B. sodium citrate; C. 8–hydroxyquinoline; D. ethylenediamine

The investigations of the conditions and the species of the complex of the Cu(II)–ion with ethylenediamine in non–proton solvents: acetone, acetonitrile and methanol, performed by Reichnitz et all (25,26), showed that in acetone and in acetonitrile the formation of the complex was 1:1 and in methanol 1:2.

Potentiometric complexometric titrations of the Cu(II) –ion in various solvents: methanol, ethanol, n–buthanol and N,N–dimethylformamide, with a coated wire copper selective electrode/SCE couple as the indicating system, showed the extreme, with ethylenediamine, with a complexing characteristic of ethylenediamine, which consequently brings the response of the electrode couple by means of the pronounced peak on the curve of the titration in its final point (Fig. 3).

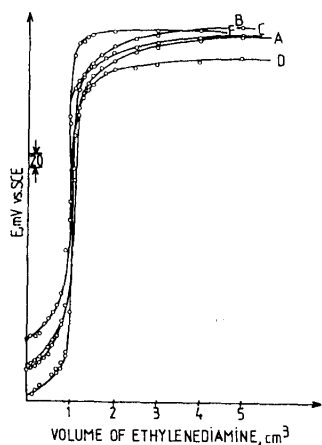
Figure 3. Potentiometric titrations of copper(II)–nitrate in different solvents with ethylenediamine in: A. water; B. methanol; C. ethanol; D. n–buthanol; E. DMF using the coated wire copper selective electrode/SCE couple as the indicating system

The results of the quantitative investigation of the solution of the Cu(II)–ion are shown in the Table 1.

Table 1. Statistical elaboration of results of Cu(II)–ions in different aprotic solvents with ethylenediamine (in methanol) as titrant using the coated wire copper selective electrode/SCE couple as the indicating system

Solvent	Number of measure– ments	Standard deviations (mg)	Mean deviations (mg)	Rel.mean deviation (%)	Taken copper* (mg)	Found copper** (mg)	Error (%)
MeOH	10	0.199	0.063	3.10	4.73	4.87	2.92
EtOH	9	0.208	0.069	3.48	4.73	4.60	2.75
n–BtOH	9	0.236	0.078	3.90	4.73	4.65	1.69
DMF	9	0.343	0.042	2.10	4.73	4.70	0.63

* Copper taken determined gravimetrically;
** Copper found determined by potentiometric titration

In all cases a pronounced peak in the final point of the titration has been noticed, no matter what solvent was used. Similar results have been obtained with water, and alcohol (methanol, ethanol, buthanol), as solvent, which was expected due to the chemical resemblance of these compounds (polar molecules), while a sharper peak is noticed in the N,N–dimethylformamide, which is also expected because of the similar (basic) properties with ethylenediamine. Consequently, the relation copper-nitrogen in a complex compound does not depend on the solvent used, which is in accordance with the investigations of Pool and Sandberg (15).

CONCLUSION

The results of the investigations in this work show the exceptional value of ethylenediamine as a complexing agent in comparison with the other known and recognized complexing agents: complexone III, sodium–citrate and 8–hydroxyquinoline.

Because of the difficult conditions of the formation of the copper(II)–ethylenediamine complex due to the presence of parallel reactions influences the position of the basic balance of the formation of the complex. In this work equations for the calculation of the constant of the formation of the complex have been discussed as well as the equations for the calculation of the free ethylenediamine.

The conditions of the investigations of copper(II)–ethylenediamine have been enlarged with potentiometric method, by use of the coated wire copper selective electrode /SCE indicator system. The use of the coated wire copper selective electrode /SCE electrode for the titration of the Cu(II)– ion with ethylenediamine in non aqueous solutions showed that the best results are obtained when using the solvents having similar (basic) properties with ethylenediamine.

As the discussion of the formation of the copper(II)–ethylenediamine complex and the possible parallel reactions shows, the coated wire copper selective electrode may also be used for the determination of the constant of the formation of the copper(II)–ethylenediamine complex.

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ПРИМЕНА БАКАР–СЕЛЕКТИВНЕ ЕЛЕКТРОДЕ ТИПА ПРЕКРИВЕНА ЖИЦА ЗА ОДРЕЂИВАЊЕ БАКРА(II) ПОТЕНЦИОМЕТРИЈСКОМ ТИТРАЦИЈОМ СА ЕТИЛЕНДИАМИНОМ У ВОДЕНИМ И НЕВОДЕНИМ РАСТВОРИМА

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Формирање комплекса Cu(II) са етилендиамином отежано је постојањем паралелних равнотежа са реактантима, који реагујући са лигандом, етилендиамином, или Cu(II) јоном утичу на положај основне равнотеже грађења комплекса. Полазећи од констатације да својства етилендиамина да гради стабилне комплексе са многобројним јонима у аналитичкој хемији нису довољно искоришћена, у овоме раду извршена је анализа могућих ефеката на положај равнотеже грађења комплекса као и извођење једначина за *укупну* константу образовања β_2 и за израчунавање концентрације слободног етилендиамина.

У раду су извршена потенциометријска испитивања раствора Cu(II) јона са етилендиамином као комплексирајућим агенсом уз бакар–селективна електрода/засићена каломелова електрода (ЗКЕ) индикаторски систем у воденим и неводеним растворима.

Добијени резултати показали су изузетну вредност етилендиамина као комплексирајућег агенса у поређењу са другим, конвенционалним комплексирајућима агенсима, а такође и могућност примене бакар–селективна електрода/ЗКЕ индикаторског система за одређивање константе образовања Cu(en)$_2^{2+}$ комплекса.