Kinetics and Mechanism of Cathodic Processes at Electrolysis of Cu(NO$_3$)$_2$·3H$_2$O Solutions in Dimethyl Sulfoxide

A.K. Mamyrbekova[1,*], A.D. Mamitova[1], G. Turebekova[1], K. Gul[2] and A.K. Mamyrbekova[1]

[1]Department of Chemical Engineering and Biotechnology, M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan
[2]Medical Department, A. Yasawi, International Kazakh-Turkish University, Turkestan, Kazakhstan

*Corresponding author: Fax: +8 7252 210141; Tel: +8 7252 310469; E-mail : aigul_akm@mail.ru

The electrochemical behaviour of copper(II) in dimethyl sulfoxide solutions of copper(II) nitrate trihydrate is investigated. Laws of kinetics of cathodic processes of electrochemical deposition of copper from dimethyl sulfoxide solutions of copper nitrate crystallohydrate have been studied in potentiodynamic mode in 0.004 M solution of Cu(NO$_3$)$_2$·3H$_2$O in DMSO at temperatures 298-328 K. The electroreduction of the complex ions of copper(II) the composition [Cu(DMSO)$_4$(H$_2$O)$_2$]$^{2+}$ is proceeding in two-stage on the adsorbate molecules of organic solvent electrode. The main kinetic parameters: coefficients of transfer (α), heterogeneous constant of speed (k$_s$) and effective energy of activation (A$_{ef}$) of process electroreduction of the ions copper(II) in dimethyl sulfoxide, witnessing about quasi-reversible of process were determined. The general speed of cathodic process brakes of more slow second stage, having the mixed nature of control, as compared with stage transfer of first electron was showed. Researches of kinetic laws of electrode processes at electrodeposition of copper from dimethyl sulfoxide electrolytes have shown that electroreduction of copper(II) ions proceeds in two stages: in the field of potentials 0.1 to 0.2 V the limiting stage is the stage of discharge and in the field of potentials 0.1 to 0.5 V braking of process of copper electrodeposition has diffusion nature.

Keywords: Dimethyl sulfoxide, Copper(II) nitrate crystallohydrate, Voltammogram, Electroreduction, Kinetic parametres.

INTRODUCTION

Organic dipolar solvent – dimethyl sulfoxide (DMSO), is characterized with high donor number (DN = 29.8), possesses ability to formation of complexes with some *d*-metals [1] and high adsorbability on metals [2]. Molecules of (CH$_3$)$_2$SO being cationtropic, form strong complexes with copper(II) ions. It is known, steady in water [(CH$_3$)$_2$SONO$_3$] complexes. The analysis of electronic structure of molecules (CH$_3$)$_2$SO and features of a metal lattice of copper allow to make the conclusion about the most probable orientation of adsorbed molecules of DMSO by atom of oxygen to metal [3]. Earlier we have investigated physical and chemical properties of solutions of copper(II) nitrate crystallohydrate in DMSO in the range of concentrations 0.01-2.0 M and temperature 298 K, the possibility of electro-deposition of copper from these solutions has been shown and on this basis the electrolyte of copper [4] has been developed. Good solubility of copper(II) nitrate trihydrate Cu(NO$_3$)$_2$·3H$_2$O in DMSO has been estab-lished. The water content in mixes with DMSO in molar parities not exceeding sizes of order 1:9 slightly influences on physical and chemical properties of organic solvent.

EXPERIMENTAL

Laws of kinetics of cathodic processes at electrodeposition of copper from dimethyl sulfoxide solutions of copper nitrate trihydrate have been studied by potentiodynamic method. All electrochemical measurements have been done in three electrode thermostated unit at 25-65 °C, with the divided cathodic and anodic space by diaphragm from porous glass. Background electrolyte has been 0.5 M solution of LiClO$_4$. As a comparison electrode the silver electrode Ag/0.01 M AgNO$_3$ in DMSO has been used which potential has been measured by us concerning to sated mercurial-sulphate electrode Hg/Hg$_2$SO$_4$, 1 N H$_2$SO$_4$ in recalculation on a hydrogen scale has made +0.3 V. Working electrode has been Pt wire with the area of 0.0963 cm^2, which has been preliminary activated in the concentrated nitric acid by a technique offered in [5]. Potentiodynamic polarizing measurements have been carried out with the help of potentiostat PI-50.1.1. Curves of current-potential have been registered by self recorder Endim 622.01 at speed of potential development 0.02-0.2 V/s. The unit has been blown by argon during 1 h before expe-rience.

Laws of kinetics of cathodic processes of electrochemical deposition of copper from dimethyl sulfoxide solutions of copper nitrate crystallohydrate have been studied in potentiodynamic mode in 0.004 M solution of $Cu(NO_3)_2 \cdot 3H_2O$ in DMSO at temperatures 298-328 K.

The aim of this work is to study the kinetics and mechanism of electroreduction of copper(II) ions in dimethyl sulfoxide solutions of copper(II) nitrate.

RESULTS AND DISCUSSION

At 298 K cathodic voltammograms represent the curves with two accurately expressed maxima of currents (Fig. 1) that shows on two-stage discharge of solvated complexes of copper(II) $[Cu(DMSO)_4(H_2O)_2]^{2+}$ on adsorbed by molecules of dimethyl sulfoxide electrode which schematically can be presented in the form of:

$$Cu^{2+} + e^- \rightarrow Cu^+ \qquad E = -0.1 \text{ to } -0.2 \text{ V} \qquad (1)$$

$$Cu^+ + e^- \rightarrow Cu^o \qquad E = -0.3 \text{ to } -0.5 \text{ V} \qquad (2)$$

Formation of dimethyl sulfoxide complexes of copper(II) and formation of dense adsorbed layer on the cathode, consisting of molecules of organic solvent, lead to certain braking and shift of potential of copper(II) ions reduction in more electronegative area (E = -0.5 V) which, promotes formation of finely crystalline coverings.
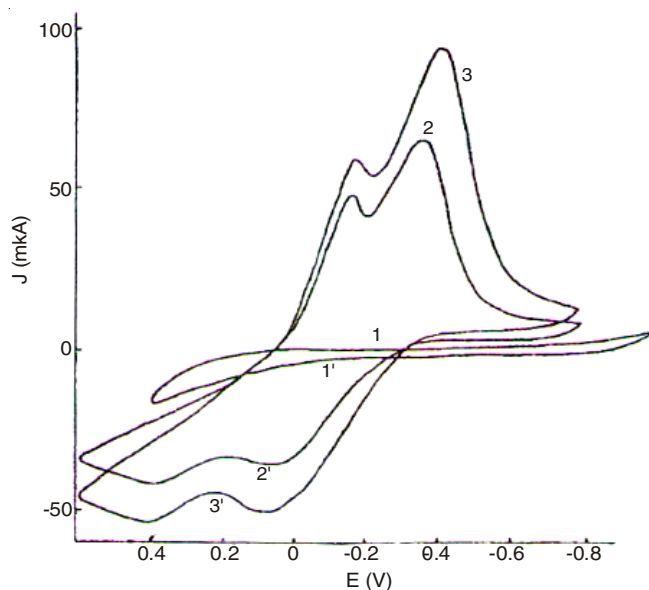

Fig 1. Cyclic polarograms of Cu^{2+} in 0.004 M solution of $Cu(NO_3)_2 \cdot 3H_2O$ in dimethyl sulfoxide at T = 298 K: (1) 0.05 V/s, background of 0.5 M $LiClO_4$ in DMSO; (2) 0.05 V/s; (3) 0.1 V/s.

At 308-328 K on polarizing curves, the third wave (Fig. 2) which lies in deeper area of electronegative potentials is observed. It is possible that this maximum corresponds to reduction of nitrates-ions:

$$NO_3^- + H_2O + 2e^- \rightleftharpoons NO_2^- + 2OH^- \quad E = -1.2 \text{ to } -1.3 \text{ V} \quad (3)$$
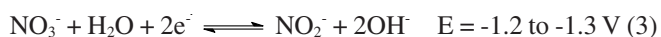
Rise of temperature till 308 K and above, obviously, promotes to partial desorption of solvent, to rupture of hydrogen connections between molecules of H_2O and $(H_3C)_2SO$, causing destruction of heteronuclear complexes, the fluctuations of
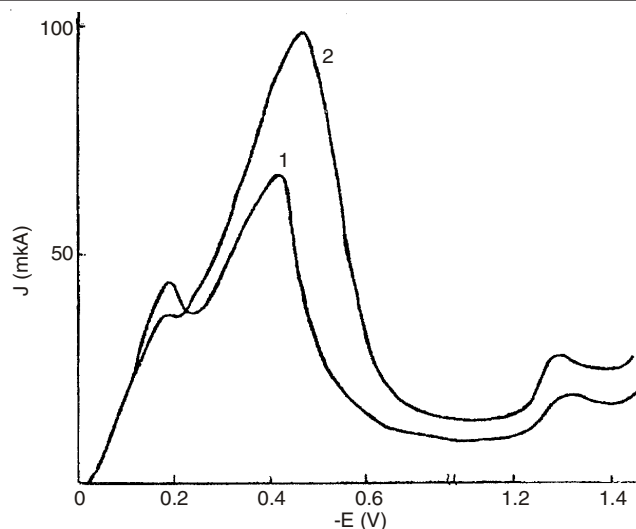

Fig. 2. Cathodic polarizing curves of reduction of copper from 0.004 M of a solution of copper(II) nitrate trihydrate in dimethyl sulfoxide at T = 308 K

structure connected with disintegration of nitrate complexes increase. Hence, these processes favour to acceleration of process of nitrates-ions reduction less solvated by molecules of organic solvent, that causes their high reactionary ability with temperature growth.

Dependences of both peak currents (i_p', i_p''), corresponding to the copper(II) ions discharge, from speed of development of voltage $\sqrt{V}$ at 298-308 K has linear character (Fig. 3a) that is well coordinated with the equation of Delaheya [6] for a current peak of irreversible electrode process. Electrode processes are supervised simultaneously by kinetics of electron transfer and speed of diffusion. Speed of diffusion of copper ions, increasing with temperature growth, apparently, exceeds speed of electron transfer, causing reduction of inclination of direct dependences i_p', i_p'' - $\sqrt{V}$ (Fig. 3b).

With rise of temperature already till 318 K and above this dependence stops to be linear. Temperature growth promotes also to streng thening of collateral process of reduction of the nitrates-ions leading to complication of investigated dependences and infringement of their linear character: at 318 K deviation is still insignificant (Fig. 3c). With the further increase of temperature till 328 K linear character of dependences i_p', $\sqrt{V}$; i_p'', $\sqrt{V}$ - is broken absolutely.

The stated results coordinates with presented by us earlier the data [7] on dependence of volume and transport properties of solutions on temperature. With growth of temperature till 308 K and above hydrogen bonds between molecules H_2O and $(H_3C)_2SO$ are more strongly broken, causing destruction of heteronuclear complexes. Structure fluctuations are increased. Disintegration of difficult nitrate complexes with molecules of DMSO leads to releasing of nitrates-ions, causing their oxidation-reduction interaction in a water-organic solution.

According to polarizing measurements data the coefficient of copper (a) ionstransfer (Table-1), heterogeneous constants of speed (k_s) (Table-2), effective energy of activation of process of electroreduction of copper(II) ions (A_{ef}) are calculated. Calculation of kinetic parametres (a, k_s) is done at 298-308 K.
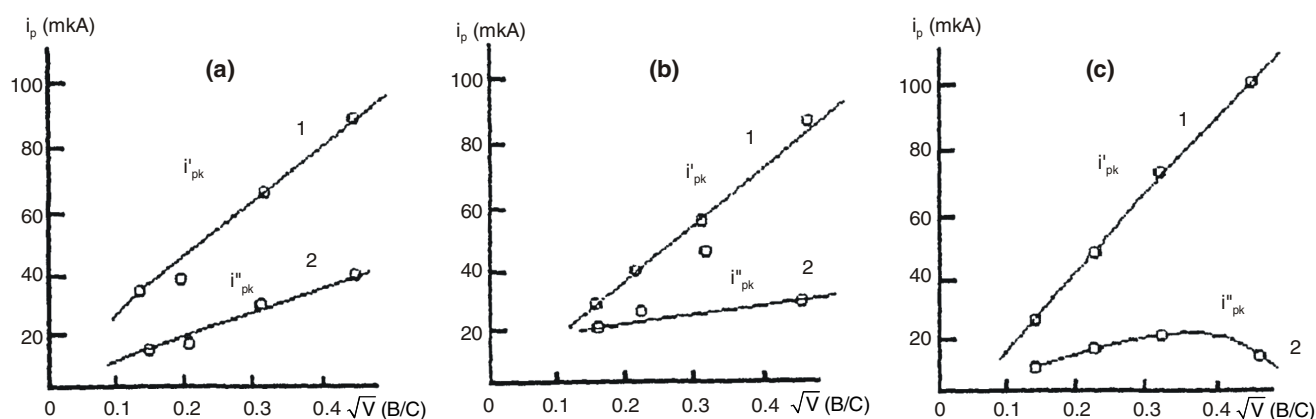
Fig. 3. Dependences of cathodic peaks of currents on speed of development of pressure at various temperatures (K): (a) 298 K; (b) 308 K; (c) 318 K

TABLE-1
VALUES OF TRANSFER COEFFICIENTS (α) OF COPPER(II) IONS DISCHARGE IN DIMETHYL SULFOXIDE

T (K)	V (V/s)			
	0.02	0.05	0.10	0.20
First stage $Cu^{2+} + e^- = Cu^+$ (α_1)				
298	0.34	0.27	0.24	0.20
308	0.41	0.29	0.25	0.24
Second stage $Cu^+ + e^- = Cu$ (α_2)				
298	0.37	0.13	0.15	0.08
308	0.45	0.13	0.23	0.15

TABLE-2
HETEROGENEOUS CONSTANTS OF SPEED (k_s) OF COPPER(II) IONS DISCHARGE IN DIMETHYL SULFOXIDE

T (K)	V (V/s)			
	0.02	0.05	0.10	0.20
First stage ($k_{s1} \times 10^3$, cm s⁻¹) $Cu^{2+} + e^- = Cu^+$				
298	4.55	2.29	2.72	2.13
308	10.80	3.79	3.90	4.04
Second stage ($k_{s2} \times 10^4$, cm s⁻¹) $Cu^+ + e^- = Cu$				
298	2.98	3.24	3.02	3.18
308	2.83	4.65	1.61	4.34

Increase of speed of potential development, as is obvious from Table-1, causes systematic decrease of α_1 size at 298-308 K to values 0.20-0.24 accordingly, that is characteristic for irreversible processes. Values of α_2 for the second stage of the discharge of copper(I) ions at the same temperatures, strengthening difference of parities at small and big speeds of development, show the big irreversibility of process at higher speeds of change of cathode potential.

Low values of transfer factors of copper(II) ions discharge process allow to make the conclusion that the stage of transfer of the second electron is much slower and it is obvious that braking is carried out at actually electrochemical stage.

Calculation of heterogeneous constants of speeds of electrode processes has been spent by the equation of Gorohovskaya and Gorohovsky [8]. As it is obvious from Table-2, heterogeneous constants of speed of the second stage of copper(II) complexes discharge are lower than heterogeneous constants of speeds of the first step of process. Low values of α and k_s, characterizing discharge of copper(II) from dimethyl sulfoxide

electrolyte, allow to consider the second stage as the slowest in total electrode process. The analysis of speeds constants of electrode process of copper(II) complexes reduction, according to criteria on Matsude and Ayabe [9], testify about quasi-reversible course of reduction of copper(II) ions on the cathode. Solving influence on speed of process in whole render the speed of the second stage of copper(II) ions reduction, being slower and having, possibly, the mixed nature of the control.

Calculated from temperature-kinetic dependences the values of effective energy of activation A_{ef} for the first stage of process in the studied temperature interval 298-328 K are equal to 7.52 ± 2.4 kJ/mol, for the second stage of process the slight increase of energy of activation till 17.45 ± 1.6 kJ/mol is observed. The low values of A_{ef} and their independence from overpressure testify about the diffusion control of electrochemical process of copper(II) complexes discharge in dimethyl sulfoxide.

Results of research of kinetic laws allow to make the following conclusion about the mechanism of cathodic processes at electrolysis of dimethyl sulfoxide solutions of copper nitrate.

At electrolysis of solution of copper(II) nitrate trihydrate in DMSO on the cathode the basic process is step reduction of a copper(II) complex $[Cu(DMSO)_4(H_2O)_2]^{2+}$ which is schematically possible to present:

$$Cu^{2+} \longrightarrow Cu^+ \longrightarrow Cu \qquad (4)$$
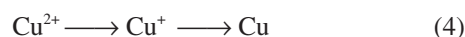
Formation of copper(II) complexes with molecules of DMSO and formation of enough dense adsorptive layer on the cathode, consisting of molecules of organic solvent lead to certain braking and shift of potential of copper(II) ions reduction in more electronegative area (E = -0.5) which promotes formation of qualitative finely crystalline coverings.

It is established that rise of temperature higher than 298 K leads to occurrence of additional wave which lies in the field of potentials E = -1.2 to 1.3 V. It is obvious that this maximum corresponds to reduction of nitrates-ions released as a result of disintegration of anionic complexes with molecules of DMSO of structure $[(CH_3)_2SONO_3]^-$ by the eqn. 3. Increase of temperature till 308 K promotes partial desorption of solvent, on what authors of work [10] specify, promotes rupture of hydrogen bonds in heteroassociates DMSO·2H₂O. Hence, the given processes promote to acceleration of process of nitrates-ions reduction, less solvated by molecules of organic

solvent, that causes their big reactionary ability with temperature growth.

The rise of temperature leads to increase of speed of process of copper(II) ions electro-reduction that is accompanied by increase of values α and k_s.

The analysis of the calculated kinetic parametres (α, k_s, A_{ef}) of electrode processes has shown that discharge of Cu(II) ions is quasi-reversible process. Final influence on speed of process in whole renders speed of the second stage of reduction of copper(II) ions, being slower and having, possibly, mixed nature of the control.

Conclusion

The kinetic laws of electrode processes at electrodeposition of copper from dimethyl sulfoxide electrolytes have shown that electroreduction of copper(II) ions proceeds in two stages: in the field of potentials 0.1-0.2 V the limiting stage is the stage of discharge and in the field of potentials 0.1 to 0.5 V braking of process of copper electrodeposition has diffusion nature.

REFERENCES

1. P.V. Savenko, S.V. Trachuk, Electrodeposition of Copper from Non-Aqueous Solutions; Deposited in Ukrainian SRISTI 858-Uk 88, Kiev (1988) (in Russian).
2. O.V. Guselnikov, S.V. Obraztsov, Electrodeposition of Metals and Alloys from Non-Aqueous Electrolytes; Deposited in SRITEC, Cherkassy, N826-XII 89 (1989) (in Russian).
3. R.S. Vahidov, *Elektrohimiya*, **30**, 1165 (1994) (in Russian).
4. A.K. Mamyrbekova, *Russ. J. Phys. Chem.*, **87**, 414 (2013).
5. N.T. Kudryavtseva and P.M. Vyacheslavova, Practicum on Applied Electrochemistry, Leningrad: Chemistry (1980) (in Russian).
6. Z. Galus, Theoretical Basis of Electrochemical Analysis, Mir, Moscow (2004) (in Russian).
7. A.K. Mamyrbekova, *Russ. J. Gen. Chem.*, **83**, 1799 (2013).
8. V. I. Gorohovskaya and V.M. Gorohovsky, Practicum on Electrochemical Methods of Analysis; Higher School, Moscow (2003) (in Russian).
9. H. Matsuda and Y.Z. Ayabe, *Elektrochemistry*, **59**, 494 (1955).
10. V.V. Kuznetsov and S.P. Shpanko, Inhibiting and Passivation of Metals, Publishing House of RSU, Rostov-on-Don, pp. 164-165 (1989) (in Russian).