

Electroreduction of silver sulphite complexes

Aušra Valiūnienė*,

Alicija Andruškevič,

Gintarė Viselgienė,

Gintaras Baltrūnas

*Department of Physical Chemistry,
Vilnius University, Naugarduko 24,
LT-03225 Vilnius, Lithuania*

In order to investigate the kinetics of silver sulfite complexes, electroreduction rotation disk electrode (RDE) and chronopotentiometry methods were used. In a series of isopotential solutions, the reaction order (0.67) was calculated, and the values of silver complexes diffusion coefficients ($3.36 \cdot 10^{-6} - 5.54 \cdot 10^{-6}$, $\text{cm}^2 \text{s}^{-1}$) and silver complexity degrees (2.31–2.67) were found.

An equation estimating not only metal complexes, but also the impact of free ligand ions on the diffusion overvoltage change vs time has been derived. Using this equation the limitations of diffusion were successfully eliminated and charge transfer overvoltage values were determined.

Key words: silver, sulfite, electroreduction, kinetics

INTRODUCTION

There have been only several investigations carried out in the field of silver sulfite complex chemistry and electrochemistry. In publications related to this subject, applicable questions are predominantly analyzed [1–3]. Silver sulfite complexes are stable in low alkaline solutions [4–5], whereas the silver plating process related to the electroreduction of these complexes is quite perspective. For instance, in study [4], a proposed electrolyte made on the ground of NaAgSO_3 at room temperature without solution mixing ensures the working densities $2-3 \text{ mAcm}^{-2}$ of the cathodic current. An intense mixing provides the possibility to increase them to 50 mAcm^{-2} . In the same study it was emphasized that sulfite electrolyte is characterized by an excellent throwing power, whereas the surfaces coated with galvanic silver are small crystalline and easily polarized. A similar conclusion is deduced in the study [5]. Furthermore, excellent adhesion of silver coating with copper and brass substrate has been taken into consideration. This allowed refusing pre-silver plating or amalgamating procedures. Recently, the throwing power of electrolyte has become particularly important, since it exactly determines one or another application process in microtechnique.

In one of the few publications [6] it has been reported that the employment of the rotating disk electrode (RDE), limiting current densities of the electroreduction of complexes in solutions, prepared with 0.025 M free sulfite ions and 0.925 M NaNO_3 , were measured. The complex concentrations in the analysed solutions were the following: 10^{-4} , $2 \cdot 10^{-4}$ and $5 \cdot 10^{-4}$ M. In the study it was stated that the limiting current densities depended linearly on the square root of RDE rotation speed. The diffusion coefficient of $\text{Ag}(\text{SO}_3)_2^{3-}$ complexes calculated from the experimental data [6], $D = 5.6 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, was approximately three times less than the diffusion coefficient of free (hydrate) silver ions determined in the same study [6] – $D = 1.55 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

The interaction between the silver surface and sulfite ions was investigated by large throwing power of X-ray photoelectron spectroscopy. It was determined [7] that during silver dioxide adsorption on silver monocrystal(100) surface, the coating of the chemisorbed sulfite formed on the surface. The electrochemically roughened silver surface stimulated by Raman scattering (SERS) showed [8] that according to the adsorptional behavior of oxyanion composed with silver, could be divided into two categories: sulfate and dithionate that adsorb on silver surface only electrostatically with weak SER spectrum, and sulfite and tiosulfate clearly chemisorbe on the silver surface causing significant changes in the spectra. An obvious resemblance of the adsorbed sulfite ion SER spectrum to normal Raman spectrum determined to solid silver sulfite allowed the authors [8] to make an assumption that the coating of Ag_2SO_3 developed on the silver surface.

Our provisional electroreduction kinetic study of silver sulfite complexes suggested that in the region of the equilibrium potential the slowest stage was silver electrocrystallization. This highly complicated the research of the charge transfer stage. We had to refuse the methods of the rotating disk electrode and electrochemical impedance. In order to investigate the kinetics of silver sulfite complex electroreduction, the chronopotentiometry method was used, because this method gave us the possibility to perform the measurements at relatively big values of electrode polarization, i. e. when the potential of the investigated electrode was rather far from equilibrium.

EXPERIMENTAL

The solutions were prepared based on distilled water applying Pa qualification Na_2SO_3 and Ag_2SO_4 . The electrolytes were prepared freshly before every new experimental series relating to quite rapid sulphite ion oxidation by air oxygen. All experiments were performed at a temperature of 20 °C.

* Corresponding author. E-mail: ausra.valiuniene@chf.vu.lt

The electroreduction of silver sulphite complexes was investigated using a rotating disk electrode of 0.2 cm² surface area made from a silver rod. The side surface of this electrode was isolated by Teflon. The counter electrode – Ag disk, 25 mm in diameter – was fitted in parallel to the working area of the working electrode.

The chronopotentiometric measurements were performed using a μAUTOLAB (Type III) measurement system with an ordinary three electrode cell. For the working electrode, an Ag wire 0.5 mm in diameter was applied, and for the counter electrode, an Ag wire spiral of 25 cm² area was used. The reference electrode was a saturated Ag/AgCl, KCl electrode. In this work, all potentials are referred to the scale of the standard hydrogen electrode.

RESULTS AND DISCUSSION

The identification of the complex particle, which directly participates in the charge transfer stage, is based on the equation describing the exchange current density (i_0) dependence on free ligand concentration (C_L) [9]:

$$\frac{\ln i_0}{\ln C_L} = R_L + \alpha \frac{nF}{RT} \cdot \frac{E_{(0)}}{\ln C_L}, \quad (1)$$

where R_L is the electrode reaction order depending on ligand (complex composition of particle transferring charge), α is the charge transfer coefficient, and $E_{(0)}$ is the electrode equilibrium potential.

As it follows from eq (1), in order to determine the reaction order, it is necessary to know the value of the charge transfer coefficient. This makes our research much more complicated. In most cases, the use of the method of isopotential solutions [10] is more convenient. In this case, the expression of the reaction order is simplified:

$$\left(\frac{\partial \ln i_0}{\partial \ln C_L} \right)_{E_{(0)}} = R_L \quad (2)$$

The performed measurements of the exchange current densities performed in series of isopotential solutions gave us the possibility to determine the reaction order, even when the charge transfer coefficient was unknown. In order to increase the sulphite ion concentration interval, we chose the isopotential solution series with $E_{(0)} = 0.300$ V. The composition of the investigated electrolytes are presented in Table.

The chronopotentiometry method was chosen for i_0 experimental determination. In many cases, the measured electrode polarization consisted of charge transfer and diffusion overvoltage sum. Since the diffusion overvoltage (opposite to charge transfer overvoltage) depends on time, its input in the total electrode polarization should be eliminated using the coordinates $\Delta E - t^{1/2}$. While investigating systems without complex ions, the extrapolation of straights obtained in these coordinates towards $t^{1/2} = 0$, enabled us to determine the exact values of the charge transfer overvoltage. From Fig. 1 it is seen, that in our investigated system the experimentally determined $\Delta E - t^{1/2}$ dependences are not linear, so the elimination of the diffusion impact becomes problematical. Herewith, the determination of the charge transfer overvoltage becomes complicated.

Since our investigated electrochemical reaction proceeded in the presence of complex ions, we attempted to determine the

influence of diffusion on the total electrode polarization by composing an equation, which estimated not only metal complexes, but also free ligand ion impact on the diffusion overvoltage change in time. If a complex compound MeL_x forms in a solution with equilibrium constant K of the reaction

$MeL_x \rightleftharpoons Me^{n+} + xL$, thus, for the concentration of free metal ions an equation is valid:

$$[Me^{n+}] = \frac{K \cdot [MeL_x]}{[L]^x} \quad (3)$$

Having introduced this into Nernst equation, we obtain:

$$E = E_0 + \frac{RT}{nF} \ln [Me^{n+}] = E_0 + \frac{RT}{nF} \ln K + \frac{RT}{nF} \ln [MeL_x] - \frac{xRT}{nF} \ln [L] \quad (4)$$

The oxidation–reduction process takes place during the electrochemical reaction, thus for the reaction $MeL_x + n\bar{e} \rightleftharpoons Me + xL$ we could introduce the notation: MeL_x – oxidized form (C_O^0) and L – reduced form (C_R^0). Electrode equilibrium potential depends on bulk concentrations of the oxidized and reduced forms (C_O^0) and (C_R^0):

$$E_{(0)} = E_0 + \frac{RT}{nF} \ln K + \frac{RT}{nF} \ln C_O^0 - \frac{xRT}{nF} \ln C_R^0 \quad (5)$$

When the current is applied, the electrode potential ($E_{(i)}$) is determined by the surface concentrations (C_O^S) and (C_R^S):

$$E_{(i)} = E_0 + \frac{RT}{nF} \ln K + \frac{RT}{nF} \ln C_O^S - \frac{xRT}{nF} \ln C_R^S \quad (6)$$

Since only limitations the of concentration are estimated in these equations, total calculated electrode polarization will be equal to diffusion overvoltage ΔE_{dif} which is found from the difference between $E_{(i)}$ and $E_{(0)}$, and can be expressed as follows:

$$\begin{aligned} \Delta E_{dif} &= \frac{RT}{nF} \ln C_O^S - \frac{xRT}{nF} \ln C_R^S - \frac{RT}{nF} \ln C_O^0 + \\ &+ \frac{xRT}{nF} \ln C_R^0 = \frac{RT}{nF} \ln \frac{C_O^S}{C_O^0} - \frac{xRT}{nF} \ln \frac{C_R^S}{C_R^0} \end{aligned} \quad (7)$$

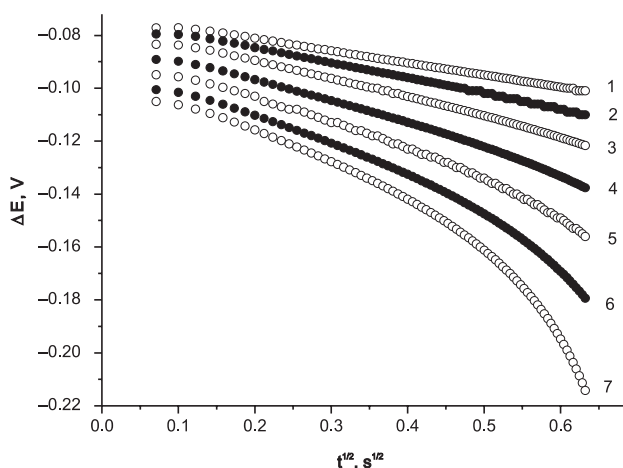


Fig. 1. The dependence of silver electrode polarization on time. Solution composition (M): Ag(I) – 0.1, Na₂SO₃ – 0.77. Cathodic current densities used (mAcm⁻²): 1 – 10, 2 – 12, 3 – 14, 4 – 16, 5 – 18, 6 – 20, 7 – 22

If the current passing through the electrochemical system is weak enough or the duration of the process is short enough:

$\frac{2i}{nFC_O^0} \sqrt{\frac{t}{\pi D_0}} \ll 1$, the concentration dependence on time and the current density of the cathodic process can be expressed by a simplified Sand equation:

$$C_O^S = C_O^0 - \frac{2i}{nF} \sqrt{\frac{t}{\pi D_0}} \quad \text{and} \quad C_R^S = C_R^0 + \frac{x2i}{nF} \sqrt{\frac{t}{\pi D_0}}, \quad (8)$$

where D_0 is an oxidized form diffusion coefficient. Then equation (8) can be rewritten as follows:

$$\frac{C_O^S}{C_O^0} = 1 - \frac{2i}{nFC_O^0} \sqrt{\frac{t}{\pi D_0}} \quad \frac{C_R^S}{C_R^0} = 1 + \frac{x2i}{nFC_R^0} \sqrt{\frac{t}{\pi D_0}}. \quad (9)$$

Having introduced the obtained expressions into equation (7), we find that the electrode polarization for the cathodic and anodic processes respectively is equal:

$$\Delta E_{dif} = \frac{RT}{nF} \left[\ln \left(1 \mp \frac{2i}{nFC_O^0} \sqrt{\frac{t}{\pi D_0}} \right) - x \ln \left(1 \pm \frac{x2i}{nFC_R^0} \sqrt{\frac{t}{\pi D_0}} \right) \right]. \quad (10)$$

While performing the calculations, it is convenient to use a notation $a = 2 / (nF\sqrt{\pi D_0})$. Then equation (10) can be rewritten as follows:

$$\Delta E_{dif} = \frac{RT}{nF} \left[\ln \left(1 \mp \frac{ai}{C_O^0} \sqrt{t} \right) - x \ln \left(1 \pm \frac{axi}{C_R^0} \sqrt{t} \right) \right]. \quad (11)$$

By calculating the diffusion overvoltage of the cathodic process in the investigated electrochemical reaction, the “-” sign in the first term under the logarithm has to be written, because the total concentration of Ag complexes decreases during the cathodic reaction. In the second member we write the “+” sign, because the concentration of free sulphite ions increases during the cathodic process. The signs in the terms under logarithms should be opposite during the investigation of the anodic process.

In order to use the obtained equation, it is necessary to find the silver complexity degree x and the complex diffusion coefficient D_0 . Both these parameters depend on the solution composition.

In order to determine the diffusion coefficients in all solutions (solution compositions are presented in Table), a rotating disk electrode was applied (Fig. 2). Experimentally determined limiting current densities depend linearly on the square root of RDE rotation speed (Fig. 3). Thus, the values of D_0 were easily calculated for all series of isopotential solutions. As seen from the data presented in Table, the values of D_0 are decreased by increasing the solution concentration. Probably it is because of Na_2SO_3 influence on the solution viscosity or because of the migration influence due to a decrease in Na_2SO_3 and $\text{Ag}(\text{SO}_3)_x^{1-2x}$ concentration ratio.

Table. Composition of isopotential solutions ($E_{00} = 0.300$ V) and parameters of electrochemical system

| No | Solution composition, M | | System parameters | | | | |
|----|-------------------------|--------------------------|--------------------------|------------------------------------|------------------------------------|--|------|
| | Ag(I) | Na_2SO_3 | $[\text{SO}_3^{2-}]$, M | $[\text{Ag}(\text{SO}_3)_2^+]$, M | $[\text{Ag}(\text{SO}_3)_3^+]$, M | $D_0 \cdot 10^6$, $\text{cm}^2 \cdot \text{s}^{-1}$ | x |
| 1. | 0.003 | 0.115 | 0.108 | 0.002 | 0.0009 | 5.54 | 2.31 |
| 2. | 0.01 | 0.2 | 0.176 | 0.006 | 0.004 | 5.45 | 2.41 |
| 3. | 0.03 | 0.33 | 0.255 | 0.015 | 0.015 | 4.97 | 2.51 |
| 4. | 0.05 | 0.49 | 0.359 | 0.02 | 0.029 | 4.33 | 2.59 |
| 5. | 0.1 | 0.77 | 0.499 | 0.033 | 0.067 | 3.36 | 2.67 |

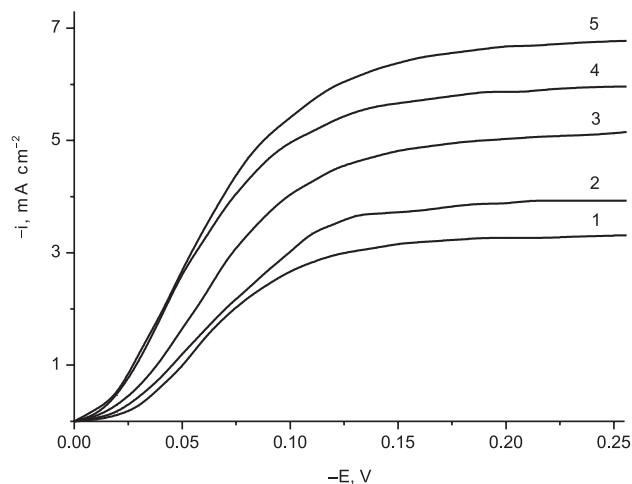


Fig. 2. Voltammograms of electroreduction of silver sulphite complexes. Sweep rate – 0.5 mV/s. Solution composition (M): Ag(I) – 0.01, Na_2SO_3 – 0.2. Rotation speed of the disk electrode (rps): 1 – 10, 2 – 15, 3 – 25, 4 – 35, 5 – 45

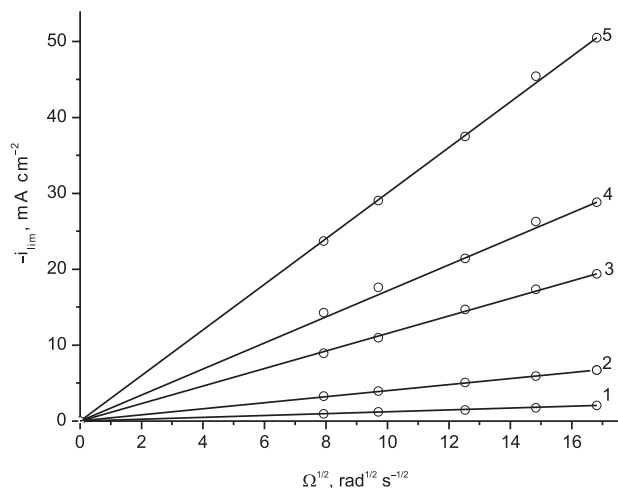


Fig. 3. Dependences of the limiting current densities on the rotation speed of the disk electrode. Numbers on the lines correspond to the solution numbers presented in Table

In our former study [11], it was determined that in a system of silver–silver sulphite complexes, the complexity degree could vary from 2 to 3. Thus, we can write:

$$x = 2 + \frac{[Ag(SO_3)_3^{5-}]}{C_0}, \quad (12)$$

where C_0 is the total concentration of Ag complexes. Under boundary conditions, if $[Ag(SO_3)_3^{5-}]$ is not composed, i. e. if $[Ag(SO_3)_3^{5-}] = 0$, thus $x = 2$, and if $[Ag(SO_3)_3^{5-}]$ is composed in a maximum amount, we get $[Ag(SO_3)_3^{5-}] = C_0$ and $x = 3$.

It is expected that the complex system investigation is labile enough, i. e. thermodynamic equilibrium is reached quite rapidly. Thus, for a partial dissociation of silver sulfite complex, it is possible to form an equation: $[Ag(SO_3)_3^{5-}] \rightleftharpoons [Ag(SO_3)_2^{3-}] + [SO_3^{2-}]$, with the dissociation constant:

$$K = \frac{[Ag(SO_3)_2^{3-}] \cdot [SO_3^{2-}]}{[Ag(SO_3)_3^{5-}]} \quad \text{or} \quad \frac{K}{[SO_3^{2-}]} = \frac{[Ag(SO_3)_2^{3-}]}{[Ag(SO_3)_3^{5-}]} \quad (13)$$

$[SO_3^{2-}] = C_R$, i. e. free sulphite ion concentration.

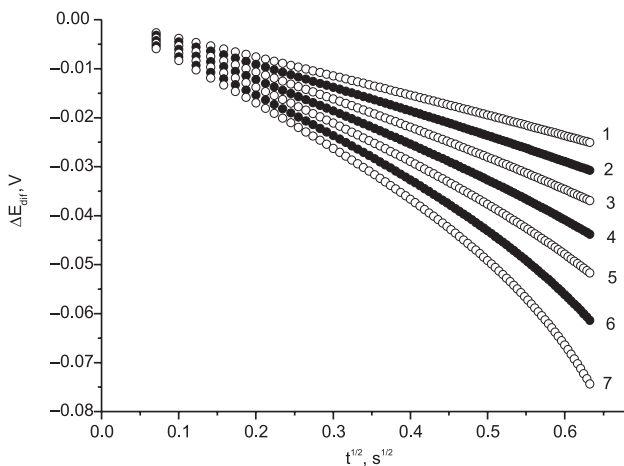


Fig. 4. Dependence of the diffusion overvoltage calculated with eq (11) on time. Solution composition and used cathodic current densities are as in Fig. 1

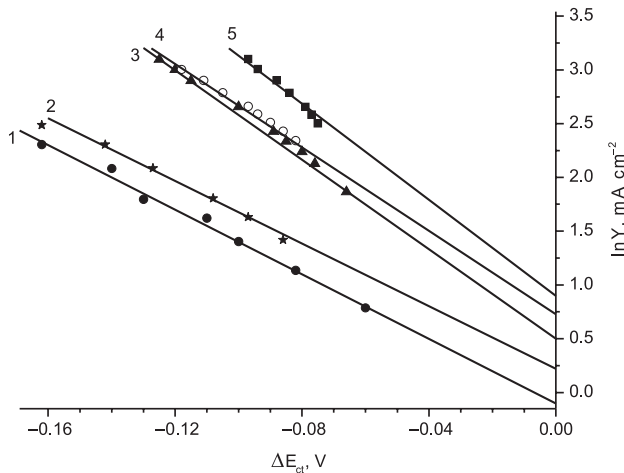


Fig. 6. Dependence of cathodic current density on the polarization of the silver electrode in coordinates Allen–Hickling. Numbers on the lines correspond to the solution numbers presented in Table

Furthermore, it is clear that the total concentration of Ag complexes (C_0) consists of two complex concentrations:

$$[Ag(SO_3)_2^{3-}] + [Ag(SO_3)_3^{5-}] = C_0, \quad \text{i. e.}$$

$$[Ag(SO_3)_2^{3-}] = C_0 - [Ag(SO_3)_3^{5-}] \quad (14)$$

A substitution of (14) into (13) yields:

$$\frac{C_0 - [Ag(SO_3)_3^{5-}]}{[Ag(SO_3)_3^{5-}]} = \frac{K}{C_R} \quad (15)$$

or:

$$\frac{C_0}{[Ag(SO_3)_3^{5-}]} - 1 = \frac{K}{C_R}; \quad (15a)$$

$$\frac{C_0}{[Ag(SO_3)_3^{5-}]} = 1 + \frac{K}{C_R} = \frac{C_R + K}{C_R}; \quad (15b)$$

$$\frac{[Ag(SO_3)_3^{5-}]}{C_0} = \frac{C_R}{C_R + K} \quad (15c)$$

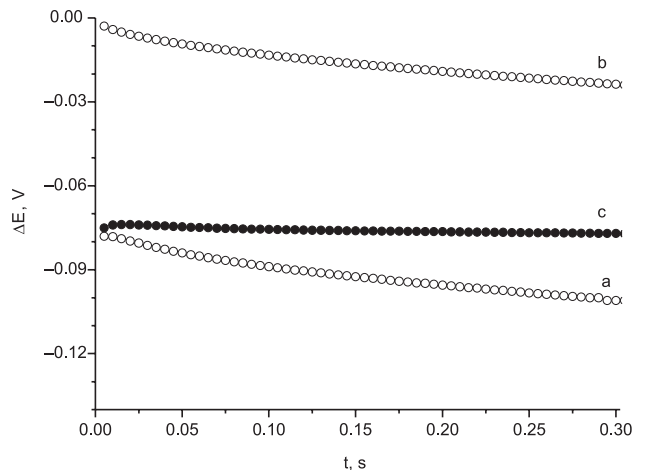


Fig. 5. Chronopotentiograms of silver sulphite complexes: a – experimentally determined, b – calculated with eq (11) and c – the difference between a and b. Solution composition as in Fig. 1. Cathodic current density – 12 mA cm^{-2}

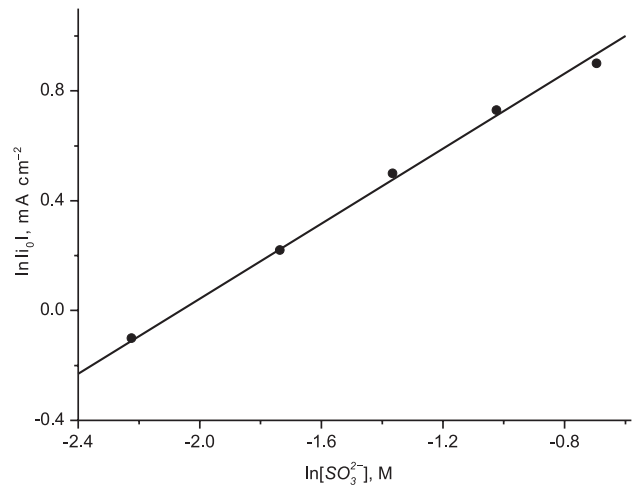


Fig. 7. Dependence of the exchange current density on the free sulphite ions concentration

Having combined (15c) with (12), we can get a complexity degree:

$$x = 2 + \frac{C_R}{C_R + K} \quad (16)$$

Thus, it is simple to calculate the complexity degrees of silver-silver sulphite complexes in all the isopotential solutions investigated (Table). Since the surface layer composition changes during the experiment, the complexity degree depends on time too. We have derived corresponding equations, but the calculations performed showed that a change of x over the time has a negligible influence on the calculated values of ΔE_{dif} . Therefore, we do not present these equations.

The diffusion overvoltage of silver sulphite complexes could be simply evaluated knowing all the values presented in eq (11). Furthermore, following the equation, even before performing detailed calculations, a conclusion suggested itself that in the case of complex solutions, the dependences $\Delta E_{dif} - t^{1/2}$ should not be necessarily linear. As seen from the data presented in Fig. 4, the dependences of the electrode polarization on time are linear only at small current densities and only in short time regions.

For the further analysis, the charge transfer overvoltage (E_{ct}) was found from the experimentally measured total electrode polarization by eliminating the calculated diffusion overvoltage. As seen from Fig. 5, curve c was obtained from a practically time-independent polarization value, which conforms to the charge transfer overvoltage. Thus, there appears a possibility to avoid a fairly problematical non-linear data extrapolation. While changing the cathodic current densities in all isopotential solutions, charge transfer overvoltages varying from -60 mV to -160 mV were determined. Since in the obtained overvoltage region Tafell dependences were not entirely valid, Allen-Hickling [12] coordinates $\ln Y - \Delta E_{ct}$ were used. Fig. 6 shows that the dependences are linear. The extrapolation of these dependences towards $\Delta E = 0$ allows calculating exchange current densities of the electrochemical reaction. The determined values vary from 0.9 mA cm^{-2} (when the solution is prepared with 0.003 M Ag(I) and $0.115 \text{ M Na}_2\text{SO}_3$) to 2.46 mA cm^{-2} (when the solution is prepared with 0.1 M Ag(I) and $0.77 \text{ M Na}_2\text{SO}_3$).

In order to identify the composition of the complex particle, which directly participates in the charge transfer stage, the dependence of the determined exchange current densities on free sulphite ion concentration was plotted in coordinates $\ln |j_0 - \ln[\text{SO}_3^{2-}]$ (Fig. 7). In this figure one can easily find the reaction order to be equal to 0.67. This result suggests that an unambiguous conclusion concerning the investigated electrochemical system mechanism is impossible to make. Probably the particle AgSO_3^- participates in the charge transfer reaction and distortions are caused by the adsorption of sulphite ions or slow electrocrystallization of Ag, which was not taken into account.

CONCLUSIONS

The equation made for complex solutions estimates the influence of the diffusion overvoltage change vs time. Using this equation, the limitations of the diffusion were successfully eliminated and charge transfer overvoltage values were determined.

In a series of isopotential solutions, the values of silver complex diffusion coefficients were determined experimentally

($3.36 \cdot 10^{-6} - 5.54 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), also silver complexity degrees were calculated (2.31–2.67). The dependences of the exchange current densities on free sulphite ion concentration were found. From the calculated reaction order (0.67), any unambiguous conclusions on the composition of species participating in the charge transfer stage cannot be drawn.

Received 30 March 2007

Accepted 22 May 2007

References

1. P. M. Viačeslavov, S. J. Griliches, G. K. Burkat and E. G. Kruglova, *Tauriųjų ir retųjų metalų galvanotechnika*, Mašinostroenie, Leningradas (1970).
2. Gmelins Handbuch der anorganischen Chemie. Auflage 8. Silber. Teil B – 3. Sulfito und Sulfitokomplexe. Weinheim (1971).
3. E. Danilczuk, *Roczniki Chem.*, **44**, 1657 (1970).
4. N. Sysoev, *Necianidinis sidabravimo elektrolitas*, Kazanės cheminės technologijos instituto darbai, **30** (1962).
5. V. G. Kakovkina, V. K. Gabidulina and V. K. Levina, *Metalų apsauga nuo korozijos* (1965).
6. R. R. M. Johnston and M. Spiro, *J. Phys. Chem.*, **71**, 3784 (1967).
7. A. K. Santra, D. P. C. Bird, E. C. H. Sykes, F. J. Williams, A. Goldoni, A. Baraldi and R. M. Lambert, *J. Phys. Chem. B*, **105**, 10062 (2001).
8. L. Rintoul, K. Crawford, H. F. Shurvell and P. M. Fredericks, *Vibrational Spectroscopy*, **15**, 171 (1997).
9. K. Vetter, *Z. Elektrochem.*, **55**, 121 (1951).
10. A. A. Survila, E. I. Morkiavičius and A. A. Dikčius, *Sov. Elektrochem.*, **21**, 1351 (1985).
11. G. Baltrūnas, A. Valiūnienė and H. Cesiulis, *Materials Science*, **7**(4), 234 (2001).
12. P. L. Allen and A. Hickling, *Trans. Faraday Soc.*, **53**, 1626 (1957).

Aušra Valiūnienė, Alicija Andruškevič, Gintarė Viselgienė,
Gintaras Baltrūnas

SIDABRO SULFITINIŲ KOMPLEKSŲ ELEKTROREDUKCIJA

Santrauka

Sidabro sulfitinų kompleksų chemija ir elektrochemija yra palyginti nedaug ištirta. Šia tema paskelbtose publikacijose daugiausia nagrinėjami taikomieji klausimai.

Šiame darbe išvesta lygtis, įvertinanti difuzijos viršštamio kitimą laike kompleksiniuose tirpaluose. Pasinaudojus išvesta lygtimi, buvo sėkmingai eliminuoti difuzijos apribojimai ir nustatyti krūvio pernašos viršštamiai. Izopotencialių ($E_{(0)} = 0,300 \text{ V}$) tirpalų serijoje eksperimentiškai nustatytos sidabro kompleksų difuzijos koeficientų reikšmės ($3,36 \cdot 10^{-6} - 5,54 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) bei apskaičiuoti sidabro užkompleksinimo laipsniai (2,31–2,67). Izopotencialių tirpalų serijoje rastos mainų srovės tankio priklausomybės nuo laisvų sulfito jonų koncentracijos. Iš apskaičiuoto reakcijos laipsnio (0,67) negalima daryti vienareikšmės išvados apie krūvio pernašos stadijoje dalyvaujančios dalelės sudėtį.