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The electroreduction kinetics of silver sulfite complexes

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1. Introduction

Silver electrodeposition from sulfite electrolytes is considered to be one of the most promising processes to replace the extremely toxic traditional cyanide-based silver plating solutions with the additional advantage, that sulfite electrolytes can be successfully applied for silver deposition for micro-electro-mechanical systems (MEMSs).

There are very few works dedicated to the chemistry and electrochemistry of silver sulfite complexes. Most publications related with this subject are concerned with the question of applicability. Silver sulfite complexes are stable in low alkaline solutions, thus the silver plating process based on electroreduction of these complexes is guite a prospective one [1,2]. The authors of [3] have used the rotating disk electrode (RDE) technique to measure the limiting current density of the electroreduction of sulfite complexes in solutions, prepared with 0.025 M free sulfite ions and 0.925 M NaNO₃. The complexes concentrations in the analyzed solutions were 10^{-4} ; 2×10^{-4} and 5×10^{-4} M. Further, the limiting current density was found to depend linearly on the square root of the RDE rotation speed. The diffusion coefficient of Ag(SO₃)₂³⁻ complexes calculated from the experimental data was reported to be 5.6×10^{-6} cm² s⁻¹, a value approximately three times less then the diffusion coefficient of free (hydrated) silver ions 1.55×10^{-5} cm² s⁻¹ as determined in the same study.

ABSTRACT

The electroreduction kinetics of silver sulfite complexes was investigated by rotation disk electrode (RDE) voltammetry, chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS). The stability constants of the silver sulfite complexes, $p\beta_2 = 7.9$ and $p\beta_3 = 8.53$ were determined. For the series of isopotential solutions investigated, a reaction order of 0.67 was obtained, the diffusion coefficient of the silver complexes varies in the range of 3.36×10^{-6} to 5.54×10^{-6} cm² s⁻¹ and the silver degree of complexation (2.31–2.67) were found. The analysis of the RDE, CP data and EIS spectra indicate the existence of a slow stage of the silver electrocrystallization in the region of the equilibrium potential and at stronger polarization of the electrode at initial time moments.

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X-ray photoelectron spectroscopy (XPS) investigation [4], has revealed that in the presence of sulfite ions, the silver dioxide adsorption on a silver monocrystalline (100) surface is accompanied by the build-up of a layer of chemisorbed sulfite. Surface-enhanced Raman scattering (SERS) spectra of electrochemically roughen silver surface [5], have shown that the adsorption behavior of the silver oxianion can be characterized by (i) weak electrostatic adsorption of sulfate and dithionate and (ii) by strong sulfite and tiosulfate chemisorption on the silver surface. The authors of [5] have, thus, assumed that a coating of Ag₂SO₃ builds up on silver surface.

In order to investigate the mechanism of electrochemical reaction, i.e. to identify the complex particle, which directly participates in the charge transfer stage we may apply the well known [6,7] equation which relates the exchange current density, j_0 , to the free ligand concentration C_L :

$$\frac{\partial \ln j_0}{\partial \ln C_L} = R_L + \alpha \frac{ZF}{RT} \frac{\partial E_{(0)}}{\partial \ln C_L}$$
(1)

where R_L is the electrode reaction order depending on the ligand, α is the charge transfer coefficient, and $E_{(0)}$ is the equilibrium electrode potential. As follows from Eq. (1) in order to determine the reaction order, we need to know the value of the charge transfer coefficient. Fortunately, in the case of isopotential solutions Eq. (1) simplifies [7] to:

$$\left(\frac{\partial \ln j_0}{\partial \ln C_L}\right)_{E_{(0)}} = R_L \tag{2}$$

Thus performing the measurements in a series of isopotential solutions we were able to determine the reaction order R_L



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by simple measurement of the exchange current density. Values of the current density measured upon equilibrium potential with the RDE were extrapolated to infinite rotation rate, this, it was possible 'to purify' the charge transfer overvoltage and to determine exchange current density by using the classic kinetic equation [8]:

$$j = j_0 \left[\exp\left(\frac{\alpha zF}{RT} \Delta E_{ct}\right) - \exp\left(-\frac{\beta zF}{RT} \Delta E_{ct}\right) \right]$$
(3)

where α and β are the charge transfer coefficients ($\alpha + \beta = 1$), and ΔE_{ct} is the charge transfer overvoltage. For higher values of the overvoltage, $|\Delta E_{ct}| \gg RT/zF$, one of exponential terms of Eq. (3) becomes negligible and a linear dependence is obtained in the plot of ln (*j*) vs. ΔE_{ct} . An extrapolation towards $\Delta E_{ct} = 0$, thus yields the value of ln j_0 . It should be possible to avoid the requirement $|\Delta E_{ct}| \gg RT/zF$ by applying the coordinates of Allen–Hickling [9], when ln (*Y*) is plotted instead of ln (*j*), where

$$Y = \frac{J}{1 - \exp(\pm zF/RT\Delta E_{ct})}$$
(4)

Here the sign '-' is for anodic currents, whereas '+' is for cathodic currents. Using these new coordinates one of the exponential terms in Eq. (3) will also be eliminated and for the case of a charge transfer controlled process rate the dependence $\ln(Y)$ vs. ΔE_{ct} must be linear even for low polarizations.

During the process of metal electrodeposition a new phase is formed, thus the total rate of the process should also depend on (possibly) slow crystallization phenomena. The deposition can be slowed down by: (i) slow formation of two- and/or three-dimensional crystallization centres and (ii) by slow surface diffusion of ad-atoms [7,10]. Obviously, these two stages are strongly related-the more crystallization centers are formed, the less is the distance, which ad-atoms have to diffuse on the surface. The concentration of crystallization centers very fast increases receding from equilibrium potential [10], i.e. the input of slow crystallization stage decreases. Therefore, the influence of the slow electrocrystallization can be easily avoided by performing measurements at a relatively high electrode polarization, i.e. at potentials rather far from the equilibrium potential. Conversely, in order to investigate the crystallization separately, the electrode potential should be chosen as close as possible to its equilibrium value. In the later case, the electrochemical impedance spectroscopy (EIS) represents the method of choice, because an impedance data can be obtained in a measurement with very low deviation from the equilibrium state. The formation of the crystallization centers, their growth, and the surface diffusion of ad-atoms will show up in the measured impedance spectra, however a good understanding of these processes and their effect on the obtained spectra is to be developed yet [11-13]. Probably the most successful model describing the surface diffusion impedance was proposed in [13]. The authors succeeded in modeling the surface diffusion impedance by parallel connected surface diffusion resistance and capacitance [13]. Unfortunately, these both parameters depend on the alternating current frequency as this is the case with the Warburg impedance. In our analysis we have chosen a simplified approach, taking into account that the non-dimensional alternating current frequency term of the mathematical expressions given in [13] becomes sufficiently large for higher frequencies. As a result, the surface diffusion impedance becomes qualitatively similar to the conventional Warburg impedance, with a constant B characterizing the surface diffusion of ad-atoms instead of the Warburg constant for the case of three-dimensional diffusion:

$$Z' = -Z'' = B\omega^{-1/2}$$
(5)

The specific objectives of this study was to investigate the kinetics of silver sulfite complexes electroreduction, i.e. to determine the limiting stages of the electrochemical reaction; to determine the dependences of the exchange current density on the free sulfite ions concentration in a series of isopotential solutions; to make clear the mechanism of electrochemical reaction (to identify the particle participating in the charge transfer reaction).

2. Experimental

The solutions prepared were based on distilled water and p.a. quality Na_2SO_3 and Ag_2SO_4 . The electrolytes were prepared freshly before every new experimental series, in order to avoid the sulfite ion oxidation by air oxygen. All experiments were performed at 20 °C temperature.

The electroreduction of silver sulfite complexes was investigated using a rotating disk electrode of 0.2 cm² surface area made of a silver rod embedded in Teflon to isolate its side surface. An Ag disk of 25-mm diameter was fitted in parallel to the working area of the working electrode and served as counter electrode.

The silver electrode potential was measured potentiometrically using a saturated Ag/AgCl, KCl electrode as the reference electrode ($E_{\rm H}$ = 0.2 V). In this work, all potentials are referred to the scale of the standard hydrogen electrode: $E_{(0)} = E_{\rm Ag/AgCl} + 0.2$ V.

Chronopotentiometry and EIS measurements were performed using an ordinary three-electrode cell. The working electrode was a platinum wire of 0.5 mm in diameter and 1.08 cm in length, which was coated (10 μ m) with silver galvanostatically (3 mA cm⁻²) in a sulfite-based electrolyte (2 M Na₂SO₃ and 0.3 M AgNO₃) before each measurement. The surface area of the working electrode was 0.17 cm². The counter electrode was made of an Ag spiral of 40 cm². The reference electrode was a saturated Ag/AgCl, KCl electrode, placed as close as possible to the working electrode by means of a Lugin capillary.

The EIS measurements were performed galvanostatically at controlled zero current using a fast Fourier transform (FFT) impedance spectrometer as described in [14,15]. Chronopotentiometry measurements were performed using μ AUTOLAB (Type III) measurement system.

3. Results and discussion

3.1. Stability of complexes

It was determined experimentally that anodic and cathodic yields of the electroreduction of silver sulfite complexes are practically equal to 100%. This shows that electrochemical reaction $Ag(SO_3)_{x}^{1-2x} + e \rightleftharpoons Ag^0 + xSO_3^{2-}$ could be treated as equilibrium.

Since literary data concerning stability of silver sulfite complexes are rather contradictionary [16,17], we attempted to determine the dissociation constants of complexes experimentally. We have measured the silver electrode potential as a function of Na₂SO₃ concentration for different concentrations of Ag(I) in the solution. At higher concentration of the sulfite (>0.3 M), the slopes $(\partial E_{(0)}/\partial \log[SO_3^{2-}])$ of all curves become -150 to -160 mV. Such values can be related to the dominating role of the complex $Ag(SO_3)_3^{5-}$ in the solutions. For lower concentrations of the sulfite ions, the potential dependence on the sulfite concentration becomes more complicated. This may be explained either by the possible coexistence of two kinds of complexes $Ag(SO_3)_2^{3-1}$ and $Ag(SO_3)_3^{5-}$ or by the suggestion that part of the sulfite ions are bounded into complexes, i.e. $[SO_3^{2-}] \neq [Na_2SO_3]$. The less the total concentration of sulfite is, the more these both factors influence the value of the equilibrium potential. In order to describe

the Ag(I)-SO₃²⁻ system, the following system of equations was solved:

$$[Ag^{+}] + [AgSO_{3}^{-}] + [Ag(SO_{3})_{2}^{3-}] + [Ag(SO_{3})_{3}^{5-}] = A;$$

$$\beta_{1}[AgSO_{3}^{-}] = [Ag^{+}] \cdot [SO_{3}^{2-}]; \quad [SO_{3}^{2-}] + [AgSO_{3}^{-}] + 2[Ag(SO_{3})_{2}^{3-}] + 3[Ag(SO_{3})_{3}^{5-}] = L; \qquad \beta_{2}[Ag(SO_{3})_{3}^{3-}] = [Ag^{+}] \cdot [SO_{3}^{2-}]^{2};$$

$$\beta_{3}[Ag(SO_{3})_{3}^{5-}] = [Ag^{+}] \cdot [SO_{3}^{2-}]^{3}$$
(6)

where β_3 , β_2 and β_1 are the stability constants of complex ions $Ag(SO_3)_3^{5-} \rightleftharpoons Ag^+ + 3SO_3^{2-}$; $Ag(SO_3)_2^{3-} \rightleftharpoons Ag^+ + 2SO_3^{2-}$ and $Ag(SO_3)_3^- \rightleftharpoons Ag^+ + SO_3^{2-}$, respectively. *A* is the total concentration of silver complexes, and *L* is the total concentration of sodium sulfite.

Electrochemical system of silver–silver sulfite complexes is stable in aqueous solutions only at $L/A \gg 1$. Analyzing potentiometric data according to Eq. (6) we found that for all investigated solutions expression $[Ag^+]+[AgSO_3^-] \ll [Ag(SO_3)_2^{3-}] + [Ag(SO_3)_3^{5-}]$ is valid. Obtained result characterizes only volumetric concentration of ions, but it does not mean anyhow that in the charge transfer reaction the ions of Ag^+ or/and $AgSO_3^-$ cannot dominate. In that case analytical expressions of Eq. (6) become simpler. Using simplified Eq. (6) and the Nernst equation the equilibrium potential of the silver electrode ($E_{(0)}$) as a function of free sulfite concentration at any values of β_2 and β_3 can be calculated:

$$E_{(0)} = E_{(0)}^{\text{Ag/Ag^+}} + \frac{RT}{F} \ln\left(\frac{A\beta_3}{\beta_3\beta_2^{-1}\left[SO_3^{2-}\right]^2 + \left[SO_3^{2-}\right]^3}\right)$$
(7)

Fig. 1 shows the experimental data (symbols) compared with computer simulated curves (lines) obtained upon best fit of the both constants according to Eq. (7). The best fit value of the product $\beta_3\beta_2^{-1}$ was 0.25. Calculated values of β_3 have an average value of β_3 =2.79×10⁻⁹±0.08 (or $p\beta_3$ =8.53), with $\beta_{3(0.05M)}$ =2.99×10⁻⁹; $\beta_{3(0.01M)}$ =3.57×10⁻⁹; $\beta_{3(0.02M)}$ =2.8×10⁻⁹; $\beta_{3(0.03M)}$ =3.08×10⁻⁹; $\beta_{3(0.04M)}$ =2.57×10⁻⁹ and $\beta_{3(0.05M)}$ =2.79×10⁻⁹. The average value of β =1.2×10⁻⁸, thus $p\beta_2$ =7.9, respectively.

3.2. Slow silver electrocrystallization

At first, in order to investigate the kinetics of the electrochemical reaction, voltammograms were measured in the range around the equilibrium potential, while the rotation speed of the rotating disk electrode was held fixed. Unfortunately, consecutive measurements yielded voltammograms with slightly lower current densities in every further measurement. This complicates the data extrapolation to $\delta = 0$, where δ is the diffusion layer thickness, because the slope of the curves depends additionally on the time interval, the electrode has been immersed into the solution. Therefore, the tactic of the measurements was changed: mechanically (polishing) and electrochemically (deposition of a new Ag layer) prepared rotating disk electrode surface was held for 5 min at a selected potential, and thereafter the current density was measured at five different rotation speeds. Subsequently, the electrode surface was subjected to mechanical and electrochemical preparation again and the experiment was repeated for the next polarization potential value. This measurement sequence has significantly decreased the deviation of measured data. Almost linear dependencies of j^{-1} vs. δ could be found (Fig. 2). This enabled us to find the cathodic and anodic current densities, when $\delta = 0$, i.e. to find how the current density depends on the electrode potential in the case when the process rate is not influenced by diffusion. As an example, this is shown in Fig. 3, curve 1 for a solution containing 0.05 M Ag(I) and 1.0 M Na₂SO₃. This curve is similar to the typical case of a charge transfer reaction. However, unlike the classic charge transfer Eq. (3), characterized by exponential dependence between j and ΔE_{ct} only at considerable deviations from equilibrium ($|\Delta E_{ct}| \gg RT/zF$) in our case the exponential dependence appears already from equilibrium (Fig. 3, curve 1). As a comparison a voltammogram calculated from Eq. (3) for $j_0 = 1.1 \text{ mA cm}^{-2}$, and $\alpha = \beta = 0.5$ is presented in Fig. 3, curve 2. The calculated curve is linear in almost the entire polarization interval of interest with deviations to appear only for $|\Delta E| > 40$ mV. A fit of the experimental data with Eq. (3) provides satisfactory coincidence only when $\alpha \approx \beta > 5$, what is not consistent with the classical kinetic equation. Furthermore, by calculating the polarization resistance $\partial E/\partial i$. when $\Delta E = \pm 5 \text{ mV}$, values of the order of $10^5 \Omega \text{ cm}^2$ was obtained corresponding to an extremely low value $(0.25 \,\mu A \,cm^{-2})$ of the exchange current density. For higher values, $|\Delta E| > 35$ mV, i.e. at the onset of the linear regime (q.v. Fig. 4, filled circles), extrapolation



Fig. 1. Dependence of the equilibrium Ag electrode potential on the concentration of reversible $[SO_3^{2-}]$ concentration in solutions containing Ag(I): (1) 0.01 M; (2) 0.03 M; (3) 0.05 M. Symbols show the experimental data; solid curves are calculated via Eq. (7).



Fig. 2. Dependence of silver dissolution/deposition current densities on the diffusion layer thickness. Solution composition: 0.05 M Ag(I); 1.0 M Na₂SO₃; pH 9.5. The numbers indicate the electrode polarization value.



Fig. 3. Voltammograms determined without influence of diffusion. (1) obtained from experimental data presented in Fig. 2 and (2) theoretically calculated charge transfer voltammogram for $j_0 = 1.1 \text{ mA cm}^{-2}$ and $\alpha = \beta = 0.5$.

towards $\Delta E = 0$, yields $j_0 \approx 0.25$ mA cm⁻², i.e. it is about three orders of magnitude higher. A similar result could be obtained under conditions of equilibrium with the slow crystallization stage determining the total process rate [10]. It can be seen from Fig. 4, open circles, that applying the coordinates of Allen–Hickling extends the linear range, however apparent deviation still remains. This demonstrates, that the charge transfer stage is not the solely rate determining process in the vicinity of the equilibrium potential (±30 mV). The extrapolation of experimental points, far from equilibrium towards $\Delta E = 0$ intercepts $j_0 \approx 0.4$ mA cm⁻², however, the coefficients $\alpha \approx 0.96$ and $\beta \approx 1.1$, found from the slopes, unambiguously show that the cathodic and anodic polarization were not sufficiently high to fully avoid the influence of a slow electrocrystallization stage. Unfortunately, the rotating disk electrode method cannot be applied successfully for higher polarizations.

The slow crystallization stage is most strongly expressed in the region of the equilibrium potential, thus the EIS method was chosen for its investigation. The experimental data were interpreted based



Fig. 4. Dependence of the current density on the electrode polarization (Fig. 3, data from curve 1) in half-logarithmic coordinates (Y=j)-filled circles, and in Allen-Hickling coordinates—open circles.



Fig. 5. Electrochemical FFT impedance spectra. Solution composition: 0.05 M Ag(I), 0.5 M Na₂SO₃, pH 9.5. Time passed after immersing the Ag electrode into the solution: (1) 3 s; (2) 10 s; (3) 26 s; (4) 56 s; (5) 102 s; (6) 193 s; (7) 375 s; (8) 565 s and (9) 748 s.

on the theory proposed in [13]. A freshly prepared silver electrode was quickly immersed into the solution containing 0.05 M Ag(I) and 0.49 M Na₂SO₃ (pH 9.5). Impedance spectra in the range from 1.5 Hz to 5.1 kHz were recorded in galvanostatic regime at zero dc current in order to assure equilibrium potential conditions (Fig. 5). Thereafter, the electrode was held in the solution for 1 h in order to establish an equilibrium surface structure and an electrochemical impedance spectrum was obtained in a frequency range extended in the lower range to 0.0305 Hz, q.v. Fig. 6.

Initially, we tried to fit the impedance data yielded for frequencies above 6.4 Hz using the simplified equation (5) and the typical equivalent circuit taking into account charge transfer, R_{ct} , diffusion, Z_W , and adsorption, R_A , C_A on the surface, as shown in Fig. 7. Afterwards whole spectrum (up to 0.0305 Hz) was analyzed according to model presented in [13]. From the obtained results we succeeded to calculate the silver surface ad-atom diffusion coefficient, D, to mean diffusion distance, r, relation and quite approximately evaluate the mean duration of silver ad-atom diffusion on the surface, τ :

$$D^{1/2}r^{-1} = 3 s^{-1/2}; \quad \tau = D^{-1}r^2 = 0.11 s \cong 0.1 s$$

Analogously, the impedance spectra, Fig. 5, measured after different time intervals of contact with the electrolyte at their equilibrium potential were analyzed. We have attempted to estimate



Fig. 6. Electrochemical FFT impedance spectrum, determined 1 h after the electrode was immersed into the solution. Solution composition as in Fig. 5.



Fig. 7. Equivalent circuit modeling adsorption and charge transfer on the surface of the electrode. R_0 : uncompensated electrolyte resistance; C_D : electrical double layer capacity; R_{ct} : charge transfer resistance; Z_W : diffusion impedance; R_A and C_A : adsorption resistance and capacity.

the single impedance components which mainly determine the impedance. The fluctuation of the adsorption components (C_A and $R_{\rm A}$) was rather large, thus they could not be evaluated accurately, probably due to their negligible effect on the total impedance. The obtained variation of the three major values R_{ct} , B(q.v. Eq. (5)), and $C_{\rm D}$ (Fig. 8) was consistent enough. Initially, during the first 100 s of contact with the electrolyte, C_D increases rather drastically whereas $R_{\rm ct}$ decreases, respectively. This unambiguously could be explained by growing of active silver surface due to recrystallization. Thereafter, this variation stabilizes (C_D even decreases). The coefficient B, which characterizes the silver ad-atom surface diffusion (Eq. (5)), increases with an almost constant rate. This could be explained with the decrease of the number of crystallization centers (or structure defects) during the process of recrystallization. During the first 750s of contact with the electrolyte, B increases from 760 to 1010 Ω cm² s^{1/2}. It is interesting to observe, that this phenomenon lasts further. The measurements performed after 1h of contact with the electrolyte (Fig. 6) yield *B* values of about 1500 Ω cm² s^{1/2}. The electrical double layer capacity $C_{\rm D}$, decreased further to $18.3 \,\mu F \,cm^{-2}$. The charge transfer resistance (and respectively exchange current density) has changed slightly in the first 750 s, $33 \Omega \text{ cm}^2$ ($j_0 = 0.76 \text{ mA cm}^{-2}$) to $27 \Omega \text{ cm}^2$ ($j_0 = 0.95 \text{ mA cm}^{-2}$) but after 1 h its value has increased up to 206 Ω cm² ($j_0 = 0.12$ mA cm⁻²). Even qualitatively, we cannot explain this phenomenon yet. It is important to notice that the exchange current densities determined by the impedance method, are in good agreement with values for j_0 , obtained from voltammogram measurements, analyzed in Allen-Hickling coordinates (Fig. 4).



Fig. 8. Dependence of the electrical double layer capacity (C_D), charge transfer resistance (R_{ct}) and coefficient *B* on the time as determined by analyzing FFT impedance spectra (from Fig. 5).



Fig. 9. Time dependence of the silver electrode polarization. Solution composition (M)–Ag(1): 0.05; Na₂SO₃: 0.49. Cathodic current density: 8 mA cm⁻².

Insofar, the processes under study are complicated by the slow electrocrystallization stage of Ag at equilibrium potential conditions, it would be of interest to perform measurements at relatively high electrode polarization. The chronopotentiometric (CP) method would be the best choice, because at sufficiently large current densities high electrode polarization, even at the early stages could be expected. However, some unexpected results were obtained experimentally—upon subjecting the cell to a cathodic current density of $-8 \,\mathrm{mA}\,\mathrm{cm}^{-2}$. As can be seen from Fig. 9, in contrast, the electrode potential decreases initially, and only after 30 ms starts increasing. Taking in consideration the technical characteristics of our galvanostat, this phenomenon cannot be related to a transitional process of the measurement set-up itself.

Such electrode polarization variation could be explained assuming that despite the comparatively strong deviation from equilibrium, the electroreduction of silver sulfite complexes shortly after the current switching is still controlled by a slow silver electrocrystallization process. In other words, even at sufficiently large electrode polarization, a particular time interval is necessary for a sufficient concentration of crystallization centers to be formed. Otherwise, the limitations of diffusion will assert in the range of longer times. The larger it will become, the more difficult will be to exactly "purify" the charge transfer overvoltage. Thus, for the successful investigation of the charge transfer stage, the identification of the time interval in which the slow electrocrystallization influence is not considerable and limitations of diffusion are not dominating, appears to be essential. This is not very convenient, but still significantly better, as to perform investigations at equilibrium potential range.

3.3. The kinetics of electrochemical reaction

The chronopotentiometry method was chosen for j_0 experimental determination. In many cases, the measured electrode polarization was the sum of the charge transfer and diffusion overvoltages. Since only the diffusion overvoltage depends on time, its effect on the total electrode polarization should be eliminated using coordinates ΔE vs. $t^{1/2}$. Investigating systems without complex ions, the extrapolation of the linear parts of the curves obtained in these coordinates towards $t^{1/2} = 0$, enabled us to determine the exact values of the charge transfer overvoltage. From Fig. 10 it is seen that in our system the experimentally determined ΔE vs. $t^{1/2}$ dependence is not linear, thus the elimination of the effect of diffusion becomes problematical. The determination of the charge



Fig. 10. Time dependence of the silver electrode polarization. Solution composition (M)-Ag(I): 0.1; Na₂SO₃: 0.77. Cathodic current densities used $(mA cm^{-2})$: (1) 10; (2) 12; (3) 14; (4) 16; (5) 18; (6) 20 and (7) 22.

transfer overvoltage becomes complicated as well. In our case the electrochemical reaction proceeds in the presence of complex ions, thus, we attempted to determine the influence of diffusion on the total electrode polarization by taking into account not only the metal complex ions, but also the effect of free ligand molecules on the diffusion overvoltage dependence on time. If a complex compound MeL_x forms in the solution with an equilibrium constant β_x , of the reaction MeL_x \rightleftharpoons Meⁿ⁺ + xL and insert this into the Nernst equation we obtain:

$$E = E_0 + \frac{RT}{zF} \ln \beta_x + \frac{RT}{zF} \ln[\text{MeL}_x] - \frac{xRT}{zF} \ln[\text{L}]$$
(8)

The oxidation–reduction process is proceeding during the electrochemical reaction, thus for the reaction $MeL_x + n\bar{e} \rightleftharpoons Me + xL$ we could write instead of: $[MeL_x] -$ oxidized form C_0 and instead of [L] – reduced form C_R . The electrode equilibrium potential depends on the bulk concentrations of the oxidized and reduced forms C_0^0 and C_R^0 . When current is applied, the electrode potential $E_{(j)}$ is determined by the surface concentrations C_0^S and C_R^S . Since the concentrations are dominant in these equations, the total electrode polarization will be equal to the diffusion overvoltage $\Delta E_{dif} = E_{(j)} - E_{(0)}$ and can be expressed as

$$\Delta E_{\rm dif} = \frac{RT}{zF} \ln C_{\rm O}^{\rm S} - \frac{xRT}{zF} \ln C_{\rm R}^{\rm S} - \frac{RT}{zF} \ln C_{\rm O}^{\rm 0} + \frac{xRT}{zF} \ln C_{\rm R}^{\rm 0}$$
$$= \frac{RT}{zF} \ln \frac{C_{\rm O}^{\rm S}}{C_{\rm O}^{\rm 0}} - \frac{xRT}{zF} \ln \frac{C_{\rm R}^{\rm S}}{C_{\rm R}^{\rm 0}}$$
(9)

If the current passing through the electrochemical system is low enough or the duration of the process is short enough: $2j/zFC^0\sqrt{t/\pi D} \ll 1$, the concentration dependence on time and



Fig. 11. Dependences of the limiting current densities on the rotation speed of the disk electrode. Numbers on the lines correspond to solution numbers as presented in Table 1.

the current density of the cathodic process can be expressed by a simplified Sand equation:

$$\frac{C_{O}^{S}}{C_{O}^{0}} = 1 - \frac{2j}{zFC_{O}^{0}}\sqrt{\frac{t}{\pi D_{O}}} \quad \text{and} \quad \frac{C_{R}^{S}}{C_{R}^{0}} = 1 + \frac{x2j}{zFC_{R}^{0}}\sqrt{\frac{t}{\pi D_{O}}}$$
(10)

where D_0 is the diffusion coefficient of the oxidized form. Introducing the obtained expressions into Eq. (9), we find that the electrode polarization for the cathodic and anodic processes, respectively is equal:

$$\Delta E_{\rm dif} = \frac{RT}{zF} \left[\ln \left(1 \mp \frac{aj}{C_0^0} \sqrt{t} \right) - x \ln \left(1 \pm \frac{axj}{C_R^0} \sqrt{t} \right) \right] \tag{11}$$

where $a = 2/(zF\sqrt{\pi D_0})$. By calculating the diffusion overvoltage of the cathodic process of the electrochemical reaction under study, the '-' sign has to be written in the first term under the logarithm, 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 sulfite ions increases during the cathodic process. The signs in the terms under the logarithms should be opposite for the case of an anodic process.

In order to use the obtained Eq. (11), it is necessary to find the degree of complexation of the silver complex x and its diffusion coefficient D_0 . Both these parameters depend on the solution composition. The diffusion coefficient, D_0 of silver sulfite complexes in all solutions, as presented in Table 1 were determined with a rotating disk electrode. Experimentally determined limiting current densities depend linearly on the square root of RDE rotation speed as shown in Fig. 11. Thus, the values of D_0 were easily calculated for all series of isopotential solutions. As seen from the data presented in Table 1, the values of D_0 decrease by increasing

Table 1

Composition of isopotential solutions ($E_{(0)} = 0.300 \text{ V}$) and parameters of the electrochemical system

No.	Solution composition (M)		System parameters				
	Ag(I)	Na ₂ SO ₃	[SO ₃ ^{2–}](M)	$[Ag(SO_3)_2^{3-}](M)$	$[Ag(SO_3)_3^{5-}](M)$	$D_0 \times 10^6 \ ({\rm cm^2 \ s^{-1}})$	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

the solution concentration. This effect could be due to the Na₂SO₃ influence on the solution viscosity or to migration influence due to decrease of Na₂SO₃ to Ag(SO₃)^{1-2x} concentration ratio.

In Section 3.1, we have proved that in a system of silver–silver sulfite complexes the degree of complexation could vary between 2 and 3. Thus, we can write:

$$x = 2 + \frac{[Ag(SO_3)_3^{5-}]}{A} = 2 + \frac{[SO_3^{2-}]}{[SO_3^{2-}] + \beta_3\beta_2^{-1}}$$
(12)

Under limiting conditions, if $Ag(SO_3)_3^{5-}$ is not formed, i.e. if $[Ag(SO_3)_3^{5-}]=0$, x=2, and if $Ag(SO_3)_3^{5-}$ is formed with a maximum concentration of $[Ag(SO_3)_3^{5-}]=A$, x=3. By using Eq. (12), it is simple to calculate the degree of complexation of silver–silver sulfite complexes in the all isopotential solutions under consideration (q.v. Table 1). Since the surface layer composition changes during the experiments, the degree of complexation depends on time too. We have derived the 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 here.

The diffusion overvoltage of silver sulfite complexes could be simply evaluated knowing all values presented in Eq. (11). Furthermore, following these equations, even before performing detailed calculations, a conclusion might be made that in the case of complex solutions, the dependences ΔE_{dif} vs. $t^{1/2}$ should not be necessarily linear. The dependence of the electrode polarization on time is linear only at small current densities and only for short time intervals.

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. 12, curve c, a practically time-independent polarization was obtained, which can be identified as charge transfer overvoltage. Thus, it becomes possible to avoid a fairly problematical non-linear data extrapolation. It was determined, that for all isopotential solutions, changing the cathodic current densities, the charge transfer overvoltages vary from -60 to -160 mV. Since in the obtained overvoltage region Tafell dependences $\ln j$ vs. ΔE_{ct} were not entirely valid, Allen–Hickling coordinates ($\ln Y$ vs. ΔE_{ct}) were used as shown in Fig. 13. Upon extrapolation of these dependences towards $\Delta E = 0$ yielded the respective exchange current densities



Fig. 12. Chronopotentiograms of silver sulfite complexes: (a) experimentally determined, (b) calculated via Eq. (11) and (c) difference between a and b. Solution composition as in Fig. 10. Cathodic current density: 12 mA cm⁻².



Fig. 13. Dependence of cathodic current density on the polarization of the silver electrode in the coordinates of Allen–Hickling. Numbers on the lines correspond to solution numbers as presented in Table 1.

of the electrochemical reaction. The values determined vary from 0.9 mA cm^{-2} (for solution prepared with 0.003 M Ag(I) and 0.115 M Na₂SO₃) to 2.46 mA cm^{-2} (solution 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 particles, which directly participates in the charge transfer stage, the dependence of the exchange current density on the free sulfite ions concentration was plotted in coordinates $\ln |j_0|$ vs. $\ln[SO_3^{2-}]$ (q.v. Fig. 14). 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 mechanism of the electrochemical system under study not possible. It is very probable, that $AgSO_3^-$ participates in the charge transfer reaction and experimental data can be distorted due to adsorption of sulfite ions or to not exactly estimate slow electrocrystallization of Ag.

We would like to note that any considerations regarding the chemical, mechanical, morphological, etc. properties of the deposited Ag film are not reported in this study because these data were published in our study [18].



Fig. 14. Dependence of the exchange current density on the free sulfite ions concentration.

4. Conclusions

Potentiometry investigations were carried out in order to determine the constants of stability of silver sulfite complexes $(p\beta_2 = 7.9, p\beta_3 = 8.53)$. It was found that the investigation of the electrochemical reaction is hindered by a slow stage of silver electrocrystallization at equilibrium conditions and at higher polarization of the electrode in the range of short times. In a series of isopotential solutions ($E_{(0)} = 0.300 \text{ V}$), the diffusion coefficients of the silver complexes were determined experimentally $(3.36 \times 10^{-6} \text{ to } 5.54 \times 10^{-6}, \text{ cm}^2 \text{ s}^{-1})$, and the respective degree of complexation was calculated (2.31–2.67). The dependence of the exchange current densities on concentration of the free sulfite ions was found. The calculated reaction order (0.67), enables as to explain the mechanism of electrochemical reaction, i.e. permits to make a suggestion that AgSO₃⁻ participates in the charge transfer reaction. Depending on the sulfite ions concentration before charge transfer stage the following chemical reactions are proceeding: $Ag(SO_3)_2^{3-} \rightleftharpoons AgSO_3^{-} + SO_3^{2-}$ and $Ag(SO_3)_3^{5-} \rightleftharpoons AgSO_3^{-} + 2SO_3^{2-}$. Whereas referred chemical reactions do not influence the total rate of electrochemical process, they are very fast definitely. After the reactions of dissociation the slow charge transfer stage is proceeding: $AgSO_3^- + \bar{e} \rightleftharpoons Ag^0 + \bar{e}$ SO_3^{2-} . The slow silver ad-atom diffusion on the surface strongly reduces the total rate of electrochemical process. The mean duration of silver ad-atom diffusion on the surface is approximately equals 0.1 s.

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