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On the application of Koutecky–Levich analysis to electrochemical processes involving metal complexes.
2. Experimental examples

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Cathodic RDE voltammograms obtained for the reduction of Ag(I) complexes with glycine, sulfite and cyanide were analysed using a modified Koutecky–Levich approach. To extend this method to processes involving ligands, the composition of the electrically active complex was taken into account. For this purpose, the initial experimental data were modified using special correction functions. Experimental data were analysed with the involvement of information on the complexation characteristics and the mechanism of charge transfer. The scope of the basic model and factors requiring further evaluation were discussed.

Keywords: Koutecky–Levich analysis, silver complexes, glycine, sulfite, cyanide

INTRODUCTION

The method of analysing RDE voltammograms known as the Koutecky–Levich (KL) approach was proposed for simple redox processes controlled by diffusion and charge transfer [1]. Its application made available the determination of charge transfer kinetics undistorted by diffusive mass transport. Later attempts were aimed at the extension of this method to more complex reactions containing a different sequence of chemical and electrochemical stages [2]. Due to their rather complicated kinetics, successful quantifications have proven to be feasible only in the case of a limited number of chemical steps (usually one).

The applicability of the KL approach for the processes involving labile metal complexes was considered in our previous communication [3]. The KL analysis was found to be acceptable for an unlimited number of chemical stages if they do not control the rate of the total process. However, specific modifications of the initial voltammetric data, taking into account the surface distribution of complexes and ligands, are required in this case. The necessary corrections of experimental RDE voltammograms considering the specifics of complex systems have been expressed as analytical functions.

Undoubtedly, any theoretical approach needs to be experimentally tested to identify the limits of its application and to bring to light the problems arising therefrom. The present communication is a continuation of the initiated study [3] and deals with experimental data obtained for some systems containing metal complexes. To exclude from consideration the problems associated with the consecutive transfer of several electrons, we turned to one-electron processes, an example of which can be the reduction of silver(I) complexes. In addition to the results of our studies, some voltammetric data available in the literature were also used.

EXPERIMENTAL

Electrochemical measurements were carried out with solutions containing glycine, sulfite or cyanide

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complexes of Ag(I). For their preparation deionised water and the following chemicals were used: Ag_2SO_4 (Acros Organics BVBA, the highest purity), glycine (99.7%, Aldrich) and Na_2SO_3 (VWR Chemicals, an analytical reagent). Cyanide solutions were prepared with $KAg(CN)_2$ and KCN (both Reakhim, Russia). In all cases, 0.3 M $NaClO_4 \cdot H_2O$ (>98%, Fluka) was introduced as a supporting electrolyte. The pH was adjusted by adding KOH. To prepare the working electrodes, Pt disc with a surface area of 0.07 cm^2 was coated at 10 mA cm^{-2} with a 5–7 μm thick Ag layer in the cyanide bath containing (g dm^{-3}): $KAg(CN)_2$ – 35, KCN – 30, K_2CO_3 – 40 (pH 9.95).

RDE voltammograms were recorded using an Autolab PGSTAT302 potentiostat. Each curve was obtained at different rotation speeds applying a sufficiently low (5 mV s^{-1}) potential sweep rate and using a freshly prepared electrode. The solutions were deaerated before the experiments with an argon stream for over 0.5 h. Electrode potentials were measured in reference to the Hg | Hg_2SO_4 | K_2SO_4 (sat) electrode and were converted to the standard hydrogen scale. All experiments were performed at 20°C.

RESULTS AND DISCUSSION

The basic theoretical model discussed here assumes compliance with certain requirements imposed on the kinetics of electrochemical processes. First, it is supposed that diffusion and charge transfer should control their rate. In addition, the system must be labile and contain sufficiently fast chemical steps. One of the signs of lability is the subordination of the limiting current density i_d to the modification of Levich equation,

$$i_d = -0.62\, nFD^{2/3}\nu^{-1/6}\omega^{1/2}c_{M,b}, \tag{1}$$

where D is treated as the average (effective) diffusion coefficient, and $c_{M,b}$ is the total metal concentration in the bulk of solution [4].

Further, the original KL approach [1] assumes the parallelism of KL graphs represented as dependencies $1/i$ on $1/\sqrt{\omega}$ (ω is the rotation velocity of electrode). According to Ref. [3], this condition is also satisfied in the case of complex systems if a certain modification of RDE voltammograms is performed using the certain correction functions $F(i)$ defined by Eq. (11) in Ref. [3]. Then the electrochemical analysis should be carried out according to the following relation:

$$F(i)/i = 1/i_K + F(i)/i_d = 1/i_K + F(i)/(k\sqrt{\omega}\, c_{M,b}). \tag{2}$$

Both the applicability of Eq. (1) and the parallelism of KL plots are checked below. Hereinafter surface and bulk concentrations are labelled with *s* and *b*, respectively; cathodic overvoltage and current are considered negative.

Ag(I)–glycine system

Glycine (amino acetic acid) form complexes with numerous metal ions including Ag^+. In alkaline media, AgL and AgL_2^- complexes prevail. Their relatively high stability is achieved due to rather strong coordination bonds between the Ag^+ ion and the deprotonated nitrogen atom in the glycinate anion L^-. Stability constants of mono- and diligand complexes (β_1 and β_2, respectively) somewhat depend on the ionic strength of solutions and the nature of the supporting electrolyte but differ little. According to various sources [5–11], log β_1 = 3.2–3.8 and log β_2 = 6.3–6.8.

The high complexation degree of the Ag(I)–glycine system causes a significant (about –0.3 V) shift of the equilibrium potential of the Ag electrode relative to its value in the absence of a ligand. Cathodic RDE voltammograms have the typical configuration involving a well-defined plateau of the limiting current

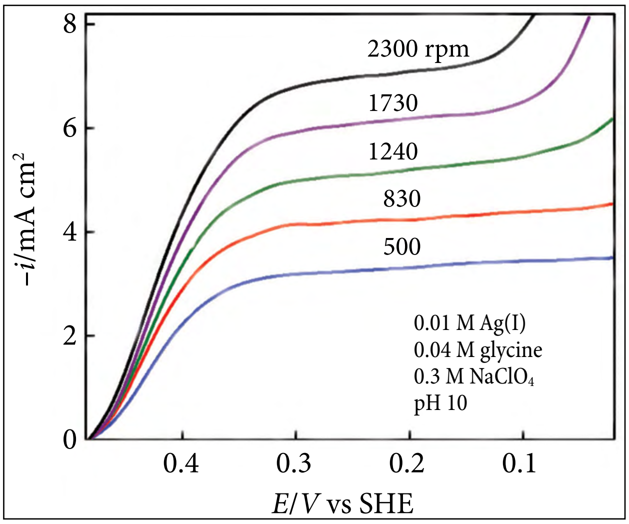

Fig. 1. RDE voltammograms of the Ag(I)-glycine system at different rotating velocities. Revolutions per minute (rpm) are indicated at the respective curves

density, which increases with intensity of forced convection (Fig. 1). In moderately alkaline solutions, pH has no noticeable effect on their shape. Increasing the alkalinity of solutions leads only to a slight shift of all curves towards more negative potentials. For example, at rise of pH from 9.5 to 10, this shift makes ~ –40 mV. The main reason for this behaviour seems to be the increase in the fraction of the active form of the ligand (glycinate anion L^-).

It is noteworthy that voltammetric data normalized with respect to the limiting current density (i/i_d) fall on one common curve at different electrode rotation speeds (symbols in Fig. 2). The cathodic i_d varies linearly with $\sqrt{\omega}$ (inset in Fig. 2) and obeys Eq. (1) with $D = 6.9 \times 10^{-6}$ cm^2 s^{-1}. Similar quantities, $(6.5–6.7) \times 10^{-6}$ cm^2 s^{-1}, are also characteristic of alkaline Cu(II)–glycine solutions [12–14].

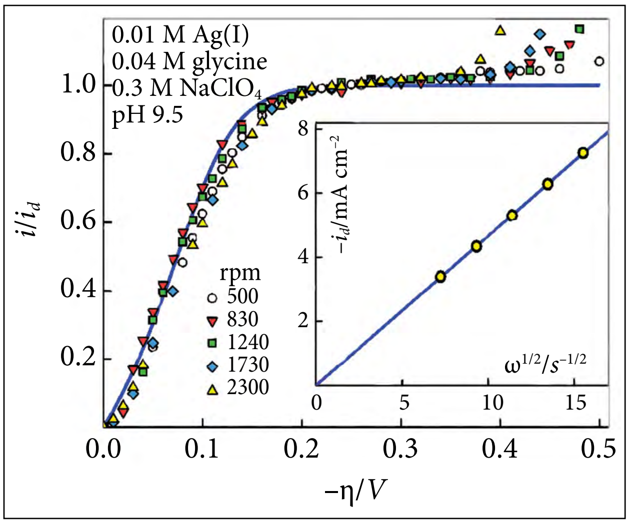

Fig. 2. Normalized RDE voltammograms of Ag(I)–glycine system at different rotating velocities (symbols). A solid line represents the simulated reversible voltammogram. The Levich plot is shown in the inset

The display of the experimental data as ordinary KL plots shows that they can be approximated by straight lines with slopes depending on the potential (Fig. 3). The diffusion coefficients following from the conventional KL analysis vary from 1.8×10^{-6} to 5.3×10^{-6} cm^2 s^{-1} and are below their actual value given above. It can be also seen that the $1/i$ quantities when extrapolated to $1/\sqrt{\omega} \to 0$ yield small intercepts.

Since the most effects observed are typical of reversible processes, we performed the simulation of reversible voltammograms using procedures that are described in detail elsewhere [3, 4]. The equation

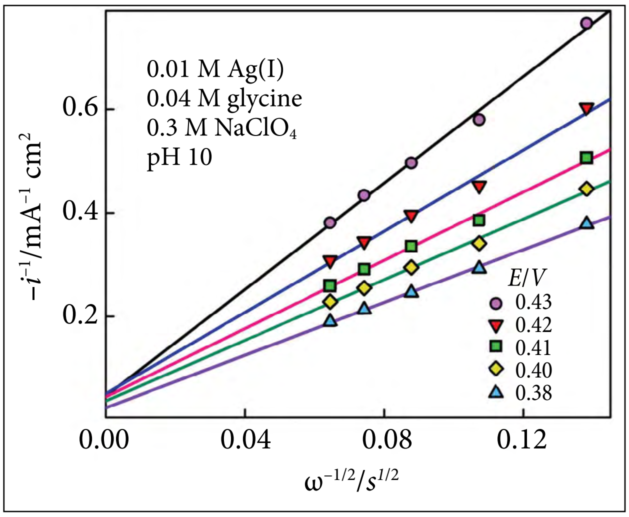

Fig. 3. Conventional KL plots obtained at different potentials for the Ag(I)–glycine system using experimental RDE voltammograms given in Fig. 1

$$i = i_d\,(1 - c_{M,s}/c_{M,b}) \qquad (3)$$

was used to relate surface concentrations to current density, where c_M is the total concentration of Ag(I). Next, the distribution of individual species of complexes and ligands was determined using the material balance equations supplemented with expressions for respective stability constants. Finally, a convenient modification of the Nernst equation

$$\eta = RT/F \ln\,[Ag^+]_s/[Ag^+]_b \qquad (4)$$

was used to calculate the voltammogram. The close position of calculated and experimental data (Fig. 3) indicates a substantial reversibility of the reduction of Ag(I)–glycine complexes (according to the preliminary estimation, the exchange current density in these solutions $i_0 \sim 5$ mA cm^{-2}). This circumstance accompanied by insufficient accuracy of extrapolation to the infinite intensity of forced convection makes further KL-analysis problematic.

Ag(I)–sulfite system

One of the reasons for the interest in this system was the need to replace cyanide baths with less toxic solutions. Major previous studies have addressed the prospects of using Ag(I)–sulfite complexes for silver plating [15] or reduction [16]. In contrast to the glycine system, the characteristics of complexation are less well investigated. It is believed that the coordination sphere of the Ag^+ ion can contain up to 3 sulfite anions, although the existence of a three-ligand complex is quite often ignored. There is also a significant discrepancy in the stability constants, and their values given in various sources [5, 8, 16–19] differ by two orders of magnitude. After all, there is a lack of reliable data on the kinetics of chemical interactions involving sulfite anions. This makes it difficult to assess the lability of the system and, consequently, the quantitative processing of voltammograms.

The RDE voltammograms obtained for glycine and sulfite systems are similar in shape (cf. Figs. 1 and 4). However, the open-circuit potentials of the latter system are more negative that is indicative of a somewhat higher complexation degree of Ag(I)-sulfite solutions. Other above-mentioned properties are characteristic as well. Linear Levich plots pass through the origin (inset in Fig. 4). Besides, limiting currents agree well with the i_d values observed in Ref. [20] at high sulfite excess but in the absence of additional supporting electrolyte. All these data combined with Eq. (1) yield $D = 6.0 \times 10^{-6}$ cm^2 s^{-1}. A close quantity (5.6×10^{-6} cm^2 s^{-1}) follows from the analysis of limiting currents obtained for solutions containing a 250-fold excess of ligand [20], provided that the concentration in Levitch's equation refers to the total amount of Ag(I).

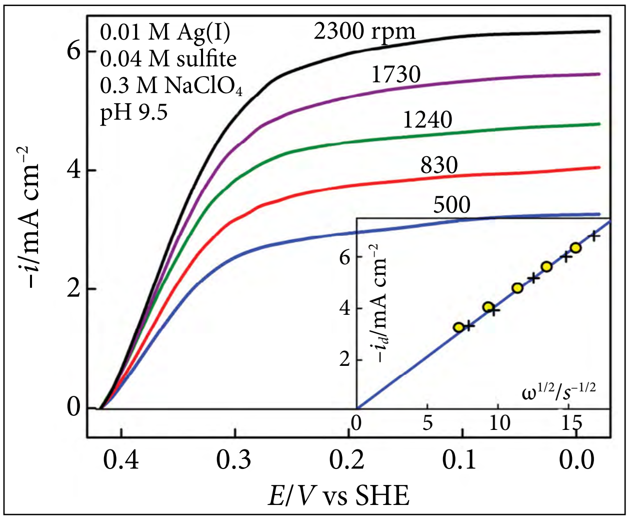

Fig. 4. RDE voltammograms of the Ag(I)–sulfite system at different rotating velocities. The data of the present work (circles) and the voltammograms published in Ref. [20] (crosses) were used in constructing Levich plots (inset)

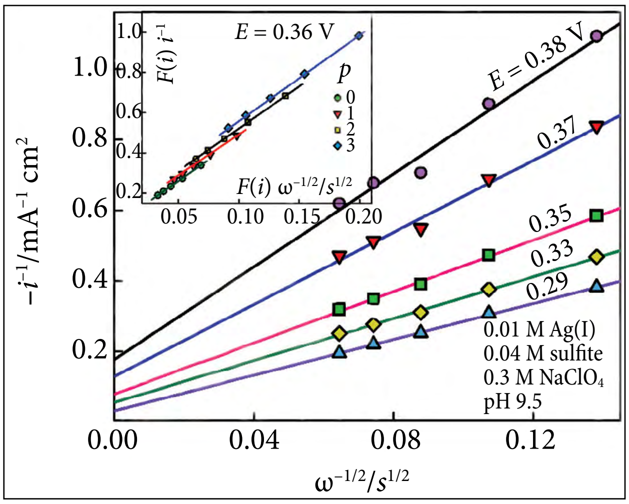

Fig. 5. Conventional KL plots obtained at different potentials for the Ag(I)–sulfite system using the experimental RDE voltammograms given in Fig. 4. The effect of corrections made for different electrically active complexes AgL_p^{1-2p} is shown in the inset

As in the case of Ag(I)–glycine system, ordinary KL plots are essentially linear with slopes depending on the potential (cf. Figs. 3 and 5). However, the intercepts for sulfite solutions are higher. It was of interest to analyse the experimental data according to Eq. (2). The expression of $F(i)$ function depends on the number of ligands (sulfite anions) bonded in the electrically active complex (EAC) that is directly involved in the charge transfer process [3]. When there is no sound information about the mechanism of this stage, one must consider all possible variants. In the case of Ag(I)–sulfite system, this task becomes even more complicated due to the lack of reliable data on the characteristics of complex formation (see above). In this connection, we have considered two options. One of them admits the existence of a trisulfite complex, and the other ignores it. In addition, possible pH changes at the electrode surface were taken into account by evaluating material balance for proton donors and acceptors [4]. The results obtained (Fig. 6) show that in both cases $F(i)$ for mono- and diligand EAC are very close. This seems to follow from the fact that the triligand complex is not predominant.

The modification of RDE voltammograms by means of $F(i)$ functions insignificantly changes the character of KL plots. Their linear characteristics (slope and intercept) remain approximately the same over a wide range of cathodic polarizations. Moreover, the result of the procedures performed does not depend on the assumption of

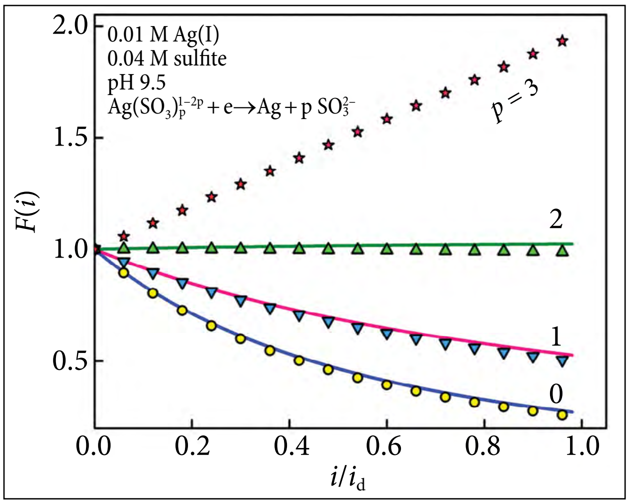

Fig. 6. Correction functions $F(i)$ simulated for different electrically active Ag(I)–sulfite complexes with log β_1 = 5.4, log β_2 = 8.4 and log β_3 = 8.4 (symbols). The case of no tri-ligand complex (β_3 = 0) is shown by lines. Used protonation constants of sulfite are log $\beta_1^H = 7.2$ and log $\beta_2^H = 9.0$

which Ag(I)–sulfite species is treated as EAC. This observation is illustrated by an example given in the inset of Fig. 5.

According to Refs. [19, 20], the order of the exchange current density with respect to the concentration of free sulfite ions is equal to 0.67. The authors suppose that it is very probable that $AgSO_3^-$ species participate in the charge transfer reaction, but an unambiguous termination of the mechanism is impossible. It should be noted that a similar conclusion about the monoligand composition of EAC was drawn from the RDE voltammetry data obtained for the Au(I)–sulfite system [21]. Nevertheless, the question of the composition of electrically active Ag(I)–sulfite complexes remains open and the above KL analysis cannot provide a definite solution to this problem.

Ag(I)–cyanide system

Silver plating electrolytes based on Ag(I)–cyanide complexes have been known for more than 100 years. During this period, along with works of applied character, investigations aimed at understanding the mechanism and kinetics of electrode processes were also carried out. A considerable number of studies in this area was considered earlier [4]. Here we will limit ourselves to citing only those works that are directly relevant to the KL analysis.

In some cases, RDE voltammograms of this system can be quite complex. Therefore, when analysed, they are often divided into several characteristic regions [22]. Two such areas can be also distinguished in the curves shown in Fig. 7. At small cathodic polarizations, a pre-wave can be detected, which at sufficiently high electrode rotation speeds ceases to grow regularly with the intensity of forced convection. Somewhat similar pre-waves have been also observed in more concentrated solutions containing 0.27 M K_2CO_3 as a supporting electrolyte [23]. Further, a gradual decrease in current rise is observed, but the plateau of the expected limiting current is less pronounced than in the previous systems. Near the potential E = – 1 V, the current density obeys Eq. (1) with $D = 1.26 \times 10^{-5}$ cm^2 s^{-1} (inset in Fig. 7). D values of the same order were presented in the monograph [24]. The slightly higher value of $D = 1.6 \times 10^{-5}$ cm^2 s^{-1} obtained from anodic voltammograms [25] should obviously be attributed to the diffusion of cyanide anions.

In contrast to systems containing glycine or sulfite, the equilibrium potential in cyanide solutions is shifted relative to the standard potential of the Ag | Ag$^+$ electrode by a significant value exceeding 1 V. This indicates the presence of strong coordination bonds in the coordination sphere of Ag$^+$, which can contain up to 4 cyanide anions. A wide variety of reports concerning the composition of EAC can be found in the literature. For example, according to Ref. [22], all four complex species

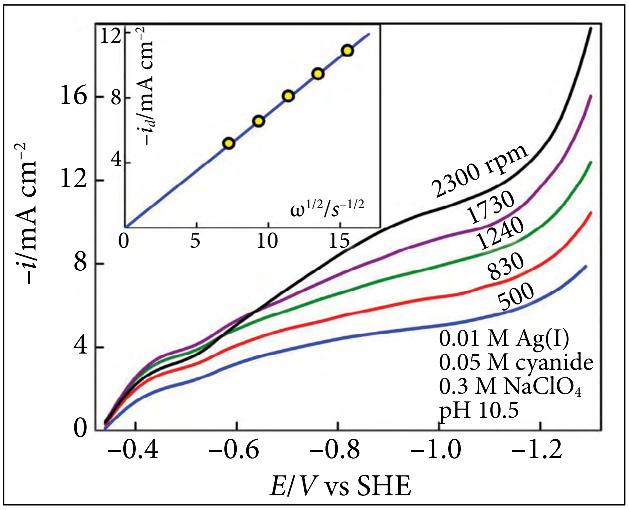

Fig. 7. RDE voltammograms obtained at different rotating velocities for the Ag(I)–cyanide system with an excess of ligand. The Levich behaviour of the limiting current density detected at E = –1.05 V is shown in the inset

can be electrically active in different potential regions. However, the view expressed 70 years ago [26], according to which mono- and diligand complexes can participate in the charge transfer step, still prevails [23, 25, 27–30]. It was generally thought that in the region of low cathodic polarizations (or in the absence of excess ligand) the adsorbed AgCN is reduced, but at more negative potentials its role is taken over by $Ag(CN)_2^-$.

Ordinary KL data constructed for the second region ($E < -0.7$ V) are shown in Fig. 8 by filled symbols. They are well approximated by almost parallel straight lines. The analysis of these unmodified data using equations (1) and (2) gives D values, which range from 1.2×10^{-5} to 1.4×10^{-5} cm^2 s^{-1}. These magnitudes are not too different from the above D obtained from the analysis of limiting currents.

To carry out the modification of KL plots, the $F(i)$ functions for each supposed EAC were calculated. For this purpose, the following stability constants were chosen from the reference literature [5, 6]: log β_1 = 15, log β_2 = 21.1, log β_3 = 21.8 and log β_4 = 20.68. These values agree well with our studies of open-circuit potentials, which were found to have an equilibrium character [4]. The results obtained show (Fig. 9) that $F(i)$ functions depend substantially on which complex is considered as electrically active. It is noteworthy that in the case of discharge of diligand complex (p = 2), the $F(i)$ function is close to 1 since $Ag(CN)_2^-$ dominates in the bulk of solution. According to the calculations performed, this species takes more than 90% of the total Ag(I). The remaining part falls on the complex $Ag(CN)_3^{2-}$. A consequence of the above is the result of correction using the function calculated at p = 2 (crosses in Fig. 8). As follows from the basic model [3], in the case of EAC dominating in the solution, these corrections are insignificant.

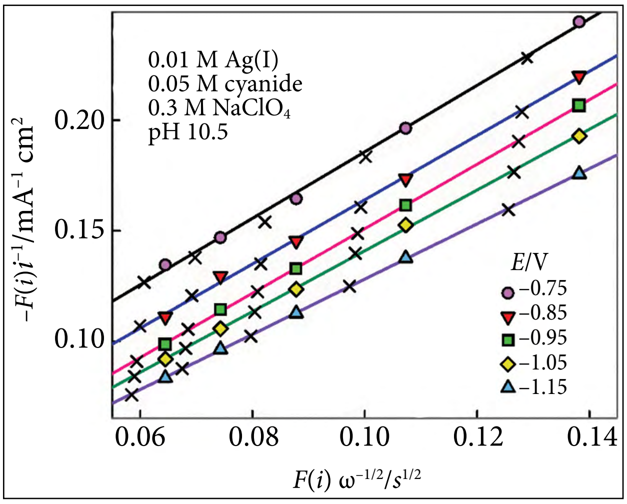

Fig. 8. Conventional (filled symbols) and corrected (crosses) KL plots obtained at different potentials for the Ag(I)–cyanide system from the experimental RDE voltammograms shown in Fig. 7

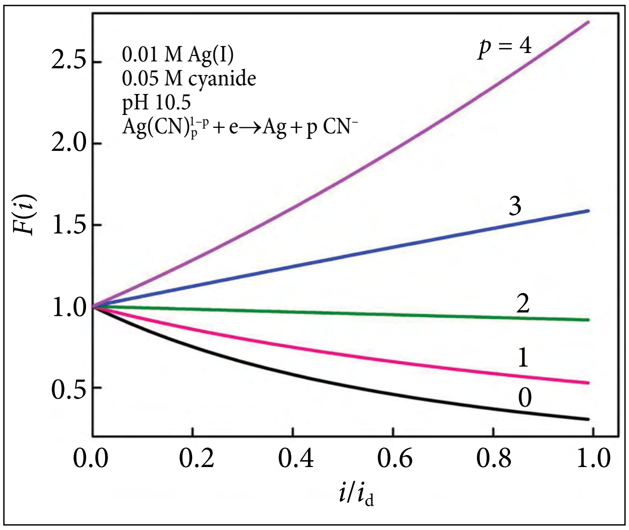

Fig. 9. Functions $F(i)$ vs normalized cathodic current density simulated for different electrically active Ag(I)–cyanide complexes

Further analysis requires extrapolation of KL plots to the infinite intensity of forced convection, i.e. to $1/\sqrt{\omega} \to 0$. The inverse values of the resulting intercepts are kinetic currents not distorted by diffusive mass transfer processes. These data can be used to construct linear Tafel plots, the analysis of which allows us to determine kinetic parameters of the charge transfer step. The revision of the experimental data obtained by us has shown that insignificant deviations from the parallelism of the KL plots lead to considerable errors in the determination of kinetic currents. To alleviate this disadvantage, experimental data obtained at much higher electrode rotation speeds are desirable. Considering the above, we present the data plotted in Tafel coordinates at different ω (Fig. 10). The slopes of these straight lines give the value of the cathodic charge transfer coefficient α = 0.15. According to the rough estimate of the exchange current density, $i_0 \approx$ 2–6 mA cm^{-2}. Note that $\alpha \approx 0.1$ was obtained for the reduction of $Cu(CN)_2^-$ complexes [31]. Its low value was explained by effects of the adsorption of complex ions and cyanide at the copper surface.

At a final point, we note that the KL plots

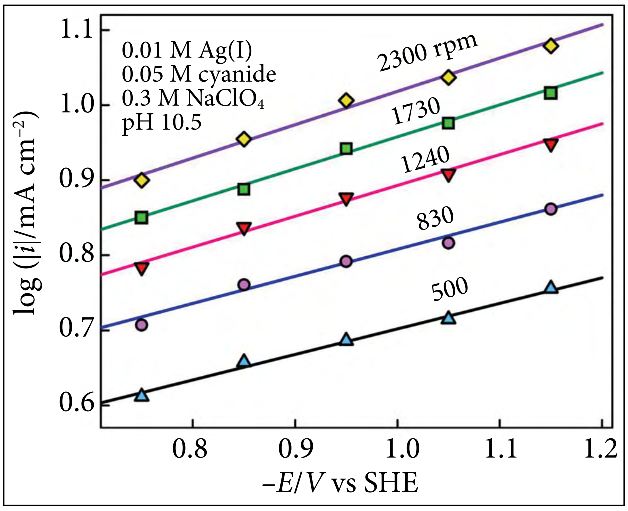

Fig. 10. Tafel plots obtained for the Ag(I)–cyanide system at different rotation velocities

constructed for tri- and tetraligand EACs are extrapolated to the region of anodic kinetic currents. This anomalous result gives grounds to conclude that species $Ag(CN)_3^{2-}$ and $Ag(CN)_4^{3-}$ are electrically inactive.

CONCLUSIONS

1. The advantage of KL analysis, consisting in a relatively simple determination of kinetic currents of simple redox processes, is difficult to realise in the case of reduction of metal complexes. An adequate approach requires preliminary information on the characteristics of complexation and the mechanism of charge transfer.

2. Corrections of experimental RDE voltammograms, which take into account the composition of the electrically active complex, are necessary but insufficient. Factors related to the lability of the system, adsorption of components, crystallization, etc. should be considered additionally.

3. Despite certain limitations, the KL approach can be used as an auxiliary (complementary) method to study the kinetics of electrochemical processes involving metal complexes.

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DĖL KOUTECKIO-LEVIČIAUS ANALIZĖS TAIKYMO ELEKTROCHEMINIAMS PROCESAMS, KURIUOSE DALYVAUJA METALŲ KOMPLEKSAI. 2. EKSPERIMENTINIAI PAVYZDŽIAI

Santrauka

Naudojant modifikuotą Kouteckio-Levičiaus metodą, atlikta analizė katodinių RDE voltamperogramų, gautų redukuojant Ag(I) kompleksus su glicinu, sulfitu ir cianidu. Taikant šį metodą procesams, kuriuose dalyvauja ligandai, buvo atsižvelgta į elektriškai aktyvaus komplekso sudėtį. Šiuo tikslu pradiniai eksperimentiniai duomenys buvo modifikuoti naudojant specialias korekcines funkcijas. Eksperimentiniai duomenys buvo analizuojami, pasitelkiant informaciją apie kompleksinimo charakteristikas ir krūvio pernašą. Aptarta pagrindinio modelio taikymo sritis ir veiksniai, reikalaujantys tolesnio vertinimo.