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Characteristic of the Ag(II)/Ag(I) System in the Presence of 2,2′:6′,2″-Terpyridine in Acetonitrile

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Summary. Composition of complexes of Ag(II) and Ag(I) ions with 2,2′:6′,2″-terpyridine (*tp*) have been established. It has been found that the Ag^+ ion forms only one complex $Ag(tp)^+$ with *tp* in acetonitrile; its conditional formation constant: $\beta_{01} = 6.6 \cdot 10^4$ has been determined by the potentiometric method. Equilibria and redox systems formed in solutions due to the complexation of Ag^+ and Ag^{2+} and oxidation of Ag(II) complexes are described. Their formal potentials have been found by coulometric and voltamperometric examinations. The presence of the $Ag(tp)_2^{3+}$ ion in the anodic oxidized solutions of the complexes $Ag(tp)(NO_3)_2$ and $Ag(tp)_2(NO_3)_2$ has been proved. Properties of the system Ag(II)/Ag(I) in the presence of terpyridine in water and in acetonitrile have been compared.

Keywords. Acetonitrile; Chronovoltammetry; Coulometry; Formal potential; Redox systems; Silver complexes.

Charakteristik der Systeme Ag(II)/Ag(I) in Gegenwart von 2,2′:6′,2″-Terpyridin in Acetonitril

Zusammenfassung. Die Zusammensetzung der Komplexe von Ag(I)- und Ag(II)-Ionen mit 2,2′:6′,2″-Terpyridin (*tp*) wurde bestimmt. Das Ag^+-Ion bildet mit *tp* in Acetonitril nur einen Komplex-$Ag(tp)^+$. Seine Konditionalbildungskonstante $\beta_{01} = 6.6 \cdot 10^4$ wurde mit Hilfe der potentiometrischen Methode bestimmt. Es wurden die Gleichgewichte und Redoxsysteme als Resultat der Komplexbildung von Ag(II)- und Ag(I)-Ionen und der Ag(II)-Komplexoxidation charakterisiert und die Formalpotentiale mittels Voltametrie und Coulometrie bestimmt. Die Gegenwart der $Ag(tp)_2^{3+}$-Ionen wurde in anodisch oxydierten Lösungen der Komplexe $Ag(tp)(NO_3)_2$ und $Ag(tp)_2(NO_3)_2$ nachgewiesen. Die Eigenschaften des Systems Ag(II)/Ag(I) in Gegenwart von 2,2′:6′,2″-Terpyridin in Wasser und in Acetonitril wurden verglichen.

Introduction

In the last decade one can observe a considerable development of research concerning the properties of the Ag(II)/Ag(I) system in the presence of nitrogen heterocyclic bases which lower its standard potential by complexation of both ions [1–8]. Particular interest is arisen due to the possibility of using these systems for oxidation of organic compounds in non-aqueous solvents [9–14]. Our previous studies provided descriptions of the systems AgL_2^{2+}/AgL_2^+ (*L*-pyridine, 2,2′-bipyridine or 1,10-phenanthroline) in water, acetonitrile and propylene carbonate [5–8, 15–17]. Recently, complexation equilibria and potentials of this system in the presence of 2,2′:6′,2″-terpyridine in water have been also described [18].

The present paper was aimed at analogous studies on the above mentioned systems in acetonitrile and comparison of its properties in these two solvents.

Experimental

2,2′ : 6′,2″-Terpyridine was prepared according to the method of Kauffman [25] from 2,2′-bipyridine. The product purified by column chromatography, was crystallized from hexane. The melting point of final product was 93–94°C.

Silver(I) (2,2′ : 6′,2″-terpyridine)nitrate, Ag(*tp*)NO_3, was prepared directly from $AgNO_3$ and terpyridine (molar ratio 1 : 1) by their dissolution in 85% aqueous solution of C_2H_5OH. The product obtained in the form of white needles was crystallized twice from acetonitrile and dried under vacuum.

Silver(II) di(2,2′ : 6′,2″-terpyridine) nitrate, $Ag(tp)_2(NO_3)_2$, was prepared from AgO in the presence of terpyridine (molar ratio 1 : 3) in 2 *M* HNO_3 at 0°C according to the method of Thorpe and Kochi [2]. The precipitate, brown in colour, was filtered off and, after washing with 0.1 *M* KNO_3 solution, dried over $CaCl_2$. The excess of terpyridine was removed by washing the precipitate with benzene [19]. Then, the precipitate was crystallized twice from acetonitrile and dried under vacuum.

Quantitative analysis of the final product gave the following results: Ag 15.40, C 51.60, N 16.06, H 3.21, O 13.73%, which matches the formula $Ag(tp)_2(NO_3)_2$.

Silver(II) (2,2′ : 6′,2″-terpyridine) nitrate, $Ag(tp)(NO_3)_2$, was prepared analogously to $Ag(tp)_2(NO_3)_2$ at the molar ratio AgO to terpyridine 1 : 1.1. Quantitative analysis of the final product gave the following results: Ag 21.80, C 38.90, N 17.00, H 2.85, O 19.45%, the theoretical composition of $Ag(tp)(NO_3)_2$ being: Ag 23.19, C 38.73, N 15.06, H 2.38, O 20.64. This points to the existence of silver(II) (2,2′ : 6′,2″-terpyridine) nitrate in the form of solvate $Ag(tp)(NO_3)_2 \cdot CH_3CN$ in which the nitrogen atom in the acetonitrile molecule is probably bounded with Ag^{2+} ion by coordination. It could be accepted then that as in the case of AgL_2^{2+} complexes with 2,2′-bipyridine and 1,10-phenanthroline, the Ag^{2+} ion shows dsp^2 hybridization corresponding to the structure of a flat square complex.

$(C_2H_5)_4NClO_4$ was prepared according to the method of Kolthoff [20], and the final product was crystallized from acetonitrile three times and dried at room temperature under vacuum.

Acetonitrile, of VEB Laborchemie Apolda (GDR), was purified by the method of Coetzee [21] and distilled over P_2O_5. Detailed description of its preparation is given in [15].

Other reagents from POCh-Gliwice analar grade, were used without purification.

The apparatus used for coulometric, chronovoltamperometric and potentiometric measurements is described in [15, 18]. Visible and UV spectrophotometric examinations were carried out with a Specord UV VIS spectrophotometer.

Results

Potentiometric Measurements

Equilibria of complexation of Ag(I) ions with 2,2′ : 6′,2″-terpyridine in acetonitrile were examined potentiometrically in solutions with ionic strength $\mu = 0.1$ from $(C_2H_5)_4NClO_4$ measuring the EMF of following system:

$$\begin{gathered} Ag \,|\, AgNO_3(0.01\,M)(AN) + (C_2H_5)_4NClO_4(0.1\,M)(AN) \,\| \\ (C_2H_5)_4NClO_4(0.1\,M)(AN) \,\| \\ c^0_{AgNO_3}(AN) + c_{0_{tp}}(AN) + (C_2H_5)_4NClO_4(0.1\,M)(AN) \,|\, Ag \end{gathered}$$

where $c^0_{AgNO_3} - 10^{-5} - 10^{-3}\,M$, $c_{0_{tp}} - 10^{-2} - 10^{-3}\,M$.

The stability of the potential of the electrode $Ag \,|\, AgNO_3(0.01\,M)(AN) + (C_2H_5)_4NClO_4(0.1\,M)(AN)$ was occasionally verified in relation to the electrode Fc^+/Fc in acetonitrile. The Nernst equation for Ag^+ ions was satisfied with a good accuracy (± 0.5 mV) within the concentration range $10^{-7} - 10^{-2}\,M$,

$$\frac{\partial \, \mathrm{EMF}}{\partial \log c} = 58.5\,\mathrm{mV},$$

$$\left(\frac{\partial \, \mathrm{EMF}}{\partial \log c_{0_{tp}}}\right)_{c^0_{\mathrm{AgNO_3}}} = 60.2\,\mathrm{mV}.$$

This means that we deal with the formation of only one type of complex $\mathrm{Ag}(tp)^+$ (even at high excess of ligand).

$AgNO_3$ is partially associated in acetonitrile ($K_{as_{0.1}} = 75$) [15], hence the concentration of Ag^+ ions, c_{exp}, determined from the EMF value, describes the concentration of free Ag^+ ions (uncomplexed and non-associated).

The concentration of associated ions can be calculated using the value of $K_{as\mathrm{AgNO_3}}$:

$$c_{as} = \frac{c_{exp}\, K_{as}\, c^0_{\mathrm{AgNO_3}}}{1 + K_{as}\, c_{exp}}.$$

Under the experimental conditions at c_{exp} being within the range $10^{-5} - 10^{-7}$ and $K_{as} = 75$, $1 + K_{as}\, c_{exp} \cong 1$, hence the equation may assume a simple form:

$$c_{as} = c_{exp}\, K_{as}\, c^0_{\mathrm{Ag^+}}.$$

The concentration of Ag^+ ions resulting from the complexation equilibrium can

Table 1. Results of potentiometric determination of the conditional stability constant of the $\mathrm{Ag}(tp)^+$ complex in acetonitrile; $T = 298\,\mathrm{K}$, $\mu = 0.1 - (C_2H_5)_4NClO_4$; the values of EMF are given against the potential of the electrode: $\mathrm{Ag}\,|\,\mathrm{AgNO_3}(0.01\,M)(AN) + (C_2H_5)_4NClO_4(0.1\,M)(AN)$

$c^0_{\mathrm{Ag^+}} \cdot 10^4$ mol dm^3	$c_{0L} \cdot 10^3$ mol dm^3	$c_{0L}\, c^0_{\mathrm{Ag^+}}$	EMF mV	$c_{exp} \cdot 10^7$ mol dm^3	$\log \beta$
0.1247	9.9751	800	−338.1	0.167	4.87
0.2488	9.9502	400	−320.5	0.332	4.88
0.3722	9.9256	267	−308.0	0.543	4.84
0.4951	9.9010	200	−302.0	0.688	4.86
0.6173	9.8765	160	−295.0	0.906	4.84
0.7389	9.8522	134	−289.3	1.134	4.82
0.8599	9.8280	114	−284.7	1.359	4.81
1.1002	9.7800	89	−275.0	1.991	4.76
1.2195	9.7561	80	−273.1	2.146	4.77
0.1247	0.9975	80	−274.0	2.071	4.78
0.2488	0.9950	40	−261.2	3.428	4.87
0.3722	0.9926	27	−247.6	5.855	4.82
0.4951	0.9901	20	−239.5	8.053	4.81
0.6173	0.9876	16	−235.0	9.614	4.83
0.7389	0.9852	13	−230.1	11.659	4.83
0.8599	0.9828	11	−221.9	16.099	4.77
1.1002	0.9780	9	−216.8	19.679	4.80
1.2195	0.9756	8	−213.7	22.233	4.80

be described by the equation

$$c = c_{exp} + c_{as} = c_{exp}(1 + K_{as}c^0_{\mathrm{Ag}^+}).$$

Hence, the formation constant of the complex $\mathrm{Ag}(tp)^+$ can be described by the equation

$$\beta = \frac{c^0_{\mathrm{Ag}^+} - c_{exp}(1 + K_{as}c^0_{\mathrm{Ag}^+})}{c_{exp}(1 + K_{as}c^0_{\mathrm{Ag}^+})[c_{0_{tp}} - c^0_{\mathrm{Ag}^+} + c_{exp}(1 + K_{as}c^0_{\mathrm{Ag}^+})]}.$$

Results of measurements and values of the conditional formation constant of the complex are given in Table 1; $\log\bar{\beta} = 4.82 \pm 0.1$, $\bar{\beta} = (6.61 \pm 0.2) \cdot 10^4$.

Coulometric Measurements

Amperostatic coulometry was used to determine the formal potentials of redox systems formed by the complexes $\mathrm{Ag}(tp)_2^{2+}$, $\mathrm{Ag}(tp)^{2+}$ and $\mathrm{Ag}(tp)^+$ in acetonitrile.

The value of stability constant of $\mathrm{Ag}(tp)^+$, ($\beta = 6.61 \cdot 10^4$), shows that in solutions with concentrations above $10^{-3}\,M$ the degree of dissociation does not exceed 10%. In addition, the reduction of $\mathrm{Ag}(tp)_2^{2+}$ is accompanied by liberation of *tp* which suppresses additionally the dissociation of $\mathrm{Ag}(tp)^+$. Hence, the saturated solution of $\mathrm{Ag}(tp)_2(\mathrm{NO_3})_2$ ($c \sim 10^{-3}\,M$) and $10^{-3}\,M$ solution of $\mathrm{Ag}(tp)(\mathrm{NO_3})_2$ ensure the existence of $\mathrm{Ag}(tp)^+$ in the solution being reduced as practically the only one.

The following solutions were reduced:

(1) Saturated solution ($c \sim 10^{-3}\,M$) of $\mathrm{Ag}(tp)_2(\mathrm{NO_3})_2$.
(2) $10^{-3}\,M$ $\mathrm{Ag}(tp)(\mathrm{NO_3})_2$ solution. Solution (1) and (2) were prepared from weighed portions and were titrated directly after preparation.
(3) $10^{-3}\,M$ $\mathrm{Ag}(tp)(\mathrm{NO_3})_2$ solution $+$ $10^{-3}\,M$ *tp* after oxidation ($i = 1$ mA) to maximum EMF possible to obtain in the system under investigation.
(4) Solution (1) after the same oxidation.

Measurements of EMF (currentless) and reduction ($i = 2$ mA) were carried out in the system:

$$\mathrm{Ag}\,|\,\mathrm{AgNO_3}(0.01\,M)(AN) + (\mathrm{C_2H_5})_4\mathrm{NClO_4}(0.1\,M)(AN)\,\|$$

$$(\mathrm{C_2H_5})_4\mathrm{NClO_4}(0.1\,M)(AN)\,\|$$

$$x\mathrm{Ag}(tp)_n(\mathrm{NO_3})_2(AN) + y\,\mathrm{Ag}(tp)\,\mathrm{NO_3}\,(AN) + (\mathrm{C_2H_5})_4\mathrm{NClO_4}(0.1\,M)(AN)\,|\,\mathrm{Pt}$$

The curves of coulometric titration of solutions (1) and (2) showed the same shapes as the curves of redox titration with a potential drop at equal concentrations of oxidized and reduced forms. The values of formal potentials found by this method were: $E^0_{1f} = 0.810$ V and $E^0_{2f} = 0.900$ V for solutions (1) and (2), respectively (potential values vs. $\mathrm{Ag}\,|\,\mathrm{AgNO_3}(0.01\,M)(AN) + (\mathrm{C_2H_5})_4\mathrm{NClO_4}(0.1\,M)(AN)$ electrode). Assuming that the potential of the above mentioned electrode is equal to 0.532 V vs. NHE [22], we obtain: $E^0_{1f} = 1.342$ V and $E^0_{2f} = 1.432$ V vs. NHE.

In both cases the transition electronicity was 1. The curves of amperostatic reduction of solutions (3) and (4) show the same shapes with a drop at higher potential values ($E^0_f = 1.790$ V vs. NHE). The transition electronicity in both cases was 2. The solutions after oxidation to maximum EMF, unlike the brown solution (1) and (2), were colourless and during their reduction no characteristic colouration as that for Ag(II) complexes was observed.

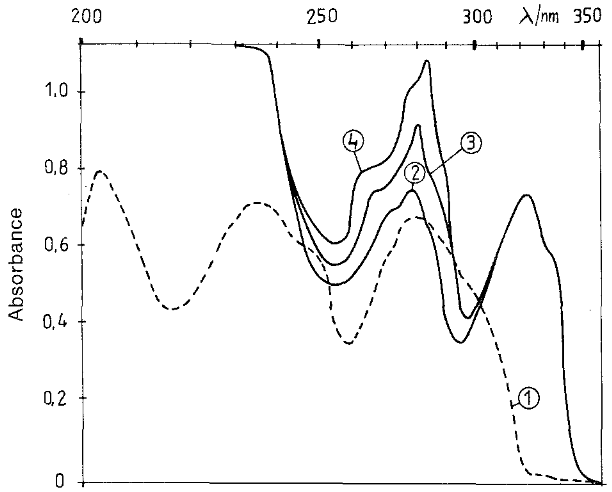

Fig. 1. UV spectra of acetonitrile solutions: ① $4 \cdot 10^{-5}$ *M tp*, ② $2 \cdot 10^{-5}$ *M* Ag(*tp*)$_2$(NO$_3$)$_2$, ③ solution ② after 1 h oxidation ($i = 1$ mA), ④ solution ② with maximum EMF; the spectra were taken against 0.1 *M* (C$_2$H$_5$)$_4$NClO$_4$ (*AN*), $T = 298$ K, $\mu = 0.1$

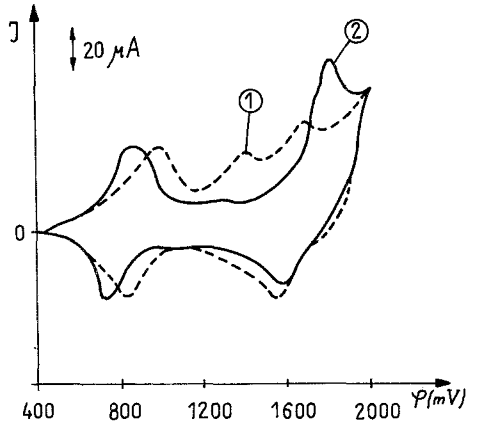

Fig. 2. Chronovoltamperometric curves of acetonitriles solutions: ① 10^{-3} *M* Ag(*tp*)NO$_3$, ② 10^{-3} *M* Ag(*tp*)NO$_3$ + $5 \cdot 10^{-3}$ *M tp*. $v = 50$ mV/s, $T = 298$ K, $\mu = 0.1 - (C_2H_5)_4NClO_4$; the values of φ are given against the potential of the electrode: Ag | AgNO$_3$ (0.01 *M*) (*AN*) + (C$_2$H$_5$)$_4$ NClO$_4$ (0.1 *M*) (*AN*)

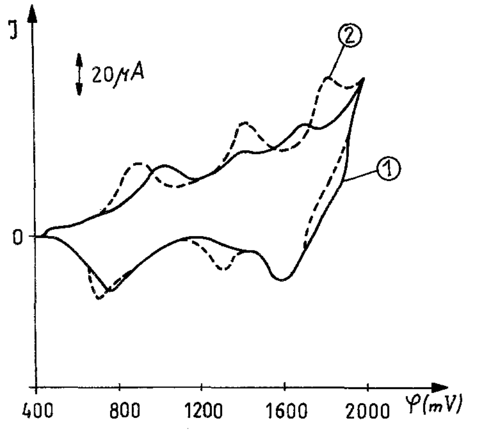

Fig. 3. Chronovoltamperometric curves of acetonitrile solutions: ① 10^{-4} *M* Ag(*tp*)$_2$(NO$_3$)$_2$, ② 10^{-4} *M* Ag(*tp*)$_2$(NO$_3$)$_2$ + $5 \cdot 10^{-4}$ *M tp*. $v = 20$ mV/s, $T = 298$ K, $\mu = 0.1 - (C_2H_5)_4NClO_4$; the values of φ are given against the potential of the electrode: Ag | AgNO$_3$ (0.01 *M*) (*AN*) + (C$_2$H$_5$)$_4$NClO$_4$ (0.1 *M*) (*AN*)

Spectrophotometric Measurements

The VIS spectra taken for $10^{-4}\,M$ Ag(*tp*)$_2$(NO$_3$)$_2$ and Ag(*tp*)(NO$_3$)$_2$ solutions show absorption maxima at $\lambda = 450\,\mathrm{nm}$ ($\varepsilon = 1\,500$) and $\lambda = 500\,\mathrm{nm}$ ($\varepsilon = 960$), respectively.

UV spectra were taken for the solutions: (a) $4 \cdot 10^{-5}\,M$ *tp*, (b) $2 \cdot 10^{-5}\,M$ Ag(*tp*)$_2$(NO$_3$)$_2$, (c) solution (b) after oxidation for 1 h with a current $i = 1\,\mathrm{mA}$, (d) solution (b) with maximum EMF.

The results are illustrated in Fig. 1.

Chronovoltamperometric Measurements

Voltamperograms for the following solutions were recorded: (1) $10^{-3}\,M$ Ag(*tp*)NO$_3$, (2) $10^{-3}\,M$ Ag(*tp*)NO$_3$ + $5 \cdot 10^{-3}\,M$ *tp*, (3) $10^{-4}\,M$ Ag(*tp*)$_2$(NO$_3$)$_2$, (4) solution (3) + $5 \cdot 10^{-4}\,M$ *tp*, (5) $10^{-3}\,M$ Ag(*tp*)(NO$_3$)$_2$, (6) $2 \cdot 10^{-3}\,M$ *tp*.

All the solutions had ionic strength $\mu = 0.1$ (tetraethylammonium perchlorate). The voltamperograms were made within the potential range +400 − +2000 mV vs. Ag | AgNO$_3$(0.01 *M*)(*AN*) + (C$_2$H$_5$)$_4$NClO$_4$(0.1 *M*)(*AN*) with the rate of potential sweep 10–200 mV s.

The voltamperograms of solutions (1) and (5) were the same. Solution (6) showed no peaks at the used sensitivities. Examples are given in Figs. 2 and 3.

Discussion

The amperostatic reduction curves of $10^{-3}\,M$ Ag(*tp*)$_2$(NO$_3$)$_2$ and $10^{-3}\,M$ Ag(*tp*)(NO$_3$)$_2$ solutions gave the formal potential values of systems $E^0_{1f} = 1.342\,\mathrm{V}$ and $E^0_{2f} = 1.432\,\mathrm{V}$ vs. NHE. These values and the transition electronicity exclude the presence of systems in which the reduced form would be metallic silver. The number of exchanged electrons points clearly to the formation of systems:

$$\mathrm{Ag(II)} + \mathrm{e} \rightleftharpoons \mathrm{Ag(I)}\,.$$

In addition, as follows from the previous considerations, the following system is also excluded:

$$\mathrm{Ag}(tp)_2^{2+} + \mathrm{e} \rightleftharpoons \mathrm{Ag}^+ + 2\,tp$$

or

$$\mathrm{Ag}(tp)^{2+} + \mathrm{e} \rightleftharpoons \mathrm{Ag}^+ + tp\,.$$

Thus, we shall have the systems:

$$\mathrm{Ag}(tp)_2^{2+} + \mathrm{e} \rightleftharpoons \mathrm{Ag}(tp)^+ + tp\,, \qquad E^0_{1f} = 1.342\,\mathrm{V}\,,$$

and

$$\mathrm{Ag}(tp)^{2+} + \mathrm{e} \rightleftharpoons \mathrm{Ag}(tp)^+\,, \qquad E^0_{2f} = 1.432\,\mathrm{V}\,.$$

There is a simple relationship between the formal potentials E^0_{1f} and E^0_{2f},

$$E^0_{2f} = E^0_{1f} + 0.059 \log \beta_{12}(\mathrm{II}).$$

Hence, the value of $\beta_{12}(\mathrm{II})$ can be found as

$$\log \beta_{12}(\mathrm{II}) = \frac{E^0_{2f} - E^0_{1f}}{0.059} = 1.525, \qquad \beta_{12}(\mathrm{II}) = 33.5.$$

In the voltamperogram of $10^{-3}\,M$ $\mathrm{Ag}(tp)\mathrm{NO_3}$ solution (Fig. 2, ①), one can observe a pair of peaks with a formal potential $E^0 = 1.428\,\mathrm{V}$. $\Delta E_{p_{ac}} = 90\,\mathrm{mV}$ points to quasireversibility (under the measurements conditions) of the electrode process. This confirms the value of the formal potential found from coulometric measurements, $E^0_{2f} = 1.432\,\mathrm{V}$.

A similar pair of peaks, which seems strange, can be observed in the voltamperogram of $10^{-4}\,M$ $\mathrm{Ag}(tp)_2(\mathrm{NO_3})_2$ solution (Fig. 3, ①). However, taking into account the concentration of Ag(II) complex and the value of $\beta_{12}(\mathrm{II})$, one should consider here an advanced dissociation process (under the experimental conditions more than 90%):

$$\mathrm{Ag}(tp)_2^{2+} \rightleftharpoons \mathrm{Ag}(tp)^{2+} + tp\,.$$

The existence of the system

$$\mathrm{Ag}(tp)_2^{2+} + \mathrm{e} \rightleftharpoons \mathrm{Ag}(tp)^{+} + tp$$

is confirmed by the voltamperograms of $10^{-3}\,M$ $\mathrm{Ag}(tp)\mathrm{NO_3} + 5\cdot 10^{-3}\,M$ tp and $10^{-4}\,M$ $\mathrm{Ag}(tp)_2(\mathrm{NO_3})_2 + 5\cdot 10^{-4}\,M$ tp solutions shown in Figs. 2, ② and 3, ②. There can be observed shifts of anodic and cathodic peaks towards the cathodic side and decrease in the formal potential value $E^0_f = 1.344\,\mathrm{V}$. $\Delta E_{p_{ac}} = 150\,\mathrm{mV}$ points also to the quasireversibility of the above system under the measurement conditions.

Another pair of peaks within the range 1 500–1 800 mV vs. $\mathrm{Ag}\,|\,\mathrm{AgNO_3}(0.01\,M)(AN) + (\mathrm{C_2H_5})_4\mathrm{NClO_4}(0.1\,M)(AN)$ can be clearly seen also in Figs. 2 and 3. The formal potential determined from them are as follows: $E^0_f = 2.140\,\mathrm{V}$ vs. NHE for $10^{-3}\,M$ $\mathrm{Ag}(tp)\mathrm{NO_3}$ solution (Fig. 2, ①) and $E^0_f = 2.232\,\mathrm{V}$ vs. NHE for $10^{-3}\,M$ $\mathrm{Ag}(tp)\mathrm{NO_3}$ + $5\cdot 10^{-3}\,M$ tp and $10^{-4}\,M$ $\mathrm{Ag}(tp)_2(\mathrm{NO_3})_2$ + $5\cdot 10^{-4}\,M\,tp$. For all solutions $\Delta E_{p_{ac}} = 100\,\mathrm{mV}$, showing the quasireversibility of the corresponding electrode processes. The electronicity of the processes found on the basis of non-cyclic chronovoltamperometric curves equals 1. The above facts show that we deal with the following redox systems:

$$\mathrm{Ag}(tp)_2^{3+} + \mathrm{e} \rightleftharpoons \mathrm{Ag}(tp)^{2+} + tp, \qquad E^0_{3f} = 2.140\,\mathrm{V\,vs.\,NHE},$$

and

$$\mathrm{Ag}(tp)_2^{3+} + \mathrm{e} \rightleftharpoons \mathrm{Ag}(tp)_2^{2+}, \qquad E^0_{4f} = 2.232\,\mathrm{V\,vs.\,NHE}.$$

The potentials E^0_{3f} and E^0_{4f} are associated with each other with the following relation:

$$E^0_{3f} = E^0_{4f} - 0.059 \log \beta_{12}(\mathrm{II}).$$

The difference in their values $\Delta(E^0_{4f} - E^0_{3f}) = 92\,\mathrm{mV}$ corresponds with good approximation to the value $\beta_{12}(\mathrm{II})$ found previously, therefore confirming our considerations.

The formal potential determined for the system existing within this region in $10^{-4}\,M$ $Ag(tp)_2(NO_3)_2$ solution is equal to 2.190 V, which points to the existence of $Ag(tp)_2^{2+}$ and $Ag(tp)^{2+} + tp$ in reduced forms. This is associated with the low value of $\beta_{12}(II)$.

The curves of amperostatic reduction of the following solutions, oxidized to maximum EMF possible in the system (a) $10^{-3}\,M$ $Ag(tp)(NO_3)_2$ + $10^{-3}\,M\,tp$ and (b) $10^{-3}\,M$ $Ag(tp)_2(NO_3)_2$, show a potential drop at higher values than the solutions without previous oxidation. The value of E_f^0 found is identical for both solutions, $E_f^0 = 1.790$ V vs. NHE. Also the chronovoltamperogram of the oxidized solution $10^{-4}\,M$ $Ag(tp)_2(NO_3)_2$ + $5 \cdot 10^{-4}\,M\,tp$ (Fig. 3, ②) suggests the presence of a system with $E_f^0 = 1.785$ V vs. NHE and with well developed two electron peaks. In the case of other solutions investigated, the voltamperograms (Figs. 2 and 3, ②) show an anodic peak at $\varphi \sim 1.820$ V without a clearly developed corresponding cathodic peak.

Taking into account the exchange of two electrons, which is shown by coulometric and voltamperometric measurements, and the fact that the reduction process does not proceed with simultaneous formation of Ag(II) complex, it can be assumed that we deal with the Ag(III)/Ag(I) redox system:

$$Ag(tp)_2^{3+} + 2e \rightleftharpoons Ag(tp)^{+} + tp \qquad \text{with} \qquad E_{5f}^0 = 1.790\,\text{V}.$$

This system would have a formal potential described according to the principle of Luther:

$$E_{5f}^0 = \frac{E_{1f}^0 + E_{4f}^0}{2} = \frac{E_{2f}^0 + E_{3f}^0}{2}.$$

Calculated average values $(1/2)(E_{1f}^0 + E_{4f}^0) = 1.787$ V and $(1/2)(E_{2f}^0 + E_{3f}^0) = 1.786$ V (vs. NHE), consistent with the approximation contained within the error limits, confirm the existence of these systems in the oxidized solutions of Ag(II) complexes.

They also explain the identical values of E_f^0 obtained in coulometric measurements for oxidized solutions (3) and (1). Independently of the reduction mechanism, both systems have identical ox and red forms.

A clear proof for the appearance and growing concentration of Ag(III) ions are the UV spectra (Fig. 1) showing the increasing absorption value of solutions during oxidation at the wavelength $\lambda = 260$–265 nm characteristic for complexes of Ag(III) ions [23–24].

The absence of cathodic peaks in Figs. 2 and 3, ① testifies that in the anodically unoxidized solutions of Ag(I) and Ag(II) complexes, the Ag(III) ions are consumed in the subsequent chemical reaction, which most likely is the following one:

$$Ag(tp)_2^{3+} + Ag(tp)^{+} + tp \rightleftharpoons 2\,Ag(tp)_2^{2+}.$$

The equilibrium constant of this reaction may be described by the equation

$$\log K = \frac{E_{4f}^0 - E_{1f}^0}{0.059}, \qquad K = 8.2 \cdot 10^{14}.$$

The value of K clearly shows a shift of equilibrium towards the formation of $Ag(tp)_2^{2+}$ ions.

The comparison of $Ag(tp)_2^{2+}/Ag(tp)^+$ and $Ag(tp)_2^{3+}/Ag(tp)_2^{2+}$ systems in water and in acetonitrile shows distinctly that the formal potential values of analogous systems are considerably higher in acetonitrile.

In addition, the $Ag(tp)_2^+$ complex, identified in aqueous solutions, is not formed in acetonitrile.

The comparison of values for $Ag(tp)^+$ complexes in H_2O ($\log \beta = 5.79$) and in *AN* ($\log \beta = 4.82$) points to its lower stability in acetonitrile, and $\Delta \log \beta = 0.97$ according to previous reasoning [16]) suggests incomplete screening of the central ion charge by 3 atoms of nitrogen ligand.

As in the case of $Ag(py)_2^+$ (*py* – pyridine) we deal most likely here with outer-spheric $Ag(tp)^+ \cdot n\,H_2O$ and $Ag(tp)^+ \cdot n\,AN$ complexes, the latter one being more stable (interactions soft acid – soft Pearson base).

This explains to some extent the higher formal potential values of analogous redox systems in acetonitrile.

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