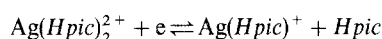


Characteristic of the Ag(II)/Ag(I) System in the Presence of 2-Pyridinecarboxylic Acid in Acetonitrile

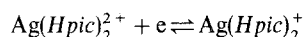
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Summary. Formation constants of the complexes of Ag(I) with 2-pyridine-carboxylic acid (*Hpic*) were determined by the potentiometric method: $\beta_{01} = 36$, $\beta_{02} = 537$. It was shown by IR spectroscopy that the complexation of Ag(I) ions in acetonitrile proceeds without the formation of Ag–O bond and the complexes have the following forms: AgHpic^+ and $\text{Ag}(\text{Hpic})_2^+$. Oxidation of $\text{Ag}(\text{Hpic})_2^+$ at the potential $\varphi = 1850$ mV vs. NHE resulted in the complex $\text{Ag}(\text{Hpic})_2^{2+}$. The formal potential $E_f^0 = 1.772$ V vs. NHE of the system



was determined by chronovoltamperometry, while the formal potential $E_f^0 = 1.841$ V vs. NHE of the system



was calculated. Properties of the system in water and acetonitrile were compared.

Keywords. Acetonitrile; Chronovoltammetry; Formal potential; IR spectrophotometry; Picolinic acid; Potentiometry; Redox systems; Silver complexes.

Charakteristik des Ag(II)/Ag(I)-Systems in Gegenwart von 2-Pyridincarbonsäure in Acetonitril

Zusammenfassung. Es wurden die Bildungskonstanten der Komplexe von Ag(I) mit 2-Pyridincarbonsäure (*Hpic*) mittels Potentiometrie bestimmt: $\beta_{01} = 36$, $\beta_{02} = 537$. Die IR-Spektren bewiesen, daß die Komplexierung von Ag(I)-Ionen über die Ausbildung einer Ag–O-Bindung verläuft, wobei die Komplexe die folgenden Formeln besitzen: AgHpic^+ und $\text{Ag}(\text{Hpic})_2^+$. Die Oxidation von $\text{Ag}(\text{Hpic})_2^+$ beim Potential $\varphi = 1850$ mV gegenüber NHE ergab den Komplex $\text{Ag}(\text{Hpic})_2^{2+}$. Das formale Potential $E_f^0 = 1.772$ V (gegenüber NHE) des Systems $\text{Ag}(\text{Hpic})_2^{2+} + e \rightleftharpoons \text{Ag}(\text{Hpic})^+ + \text{Hpic}$ wurde mittels Chronovoltamperometrie ermittelt, während das formale Potential $E_f^0 = 1.841$ V (gegenüber NHE) des Systems $\text{Ag}(\text{Hpic})_2^{2+} + e \rightleftharpoons \text{Ag}(\text{Hpic})_2^+$ berechnet wurde. Außerdem wurden die Eigenschaften der Systeme in Wasser und Acetonitril verglichen.

Introduction

In our previous studies on the system Ag(II)/Ag(I) in water and non-aqueous solvents we have used ligands in the form of heterocyclic compounds containing only donor nitrogen atoms [1–4]. 2-Pyridinecarboxylic acid, in addition to the

pyridine ring, possesses a carboxylic group which is able to form, in aqueous solutions, a five-membered ring showing sometimes a stabilizing influence on the complex through the entropy effect [5].

In water, depending on the pH value of the medium, there are two forms of AgL_2 complex: $Ag(Hpic)_2^0$ and $Ag(pic)_2^-$.

Acetonitrile is a solvent of less basicity than that of water, therefore the complex formation mechanism and the complex composition may be different. The redox systems $Ag(II)/Ag(I)$ may also have different forms.

Hence the present study was aimed at the examination of complexation processes and characteristics of the system in the presence of 2-pyridinecarboxylic acid.

Experimental Part

Potentiometric measurements were carried out by means of a V-543 multimeter of Meratronik. A silver electrode $Ag^0/0.01 M AgNO_3 + 0.1 M (C_2H_5)_4NClO_4$ in acetonitrile was used a reference electrode [7]. IR spectrophotometric examinations were performed with a IR Specord 75 spectrophotometer. The methods of coulometric and chronovoltamperometric measurements are described in [8]. Acetonitrile solvate $(C_2H_5)_4NClO_4$ was prepared by the method of Kolthoff [9]. Acetonitrile was purified according to the procedure of Coetzee [10]. The obtained acetonitrile had its "cut off" at 210 nm and specific conductivity of $2 \times 10^{-7} \Omega^{-1} cm^{-1}$. $AgNO_3/POCh$ –Gliwice/of analar grade was crystallized three times from acetonitrile and dried in vacuum at a temperature of 120 °C to a constant weight.

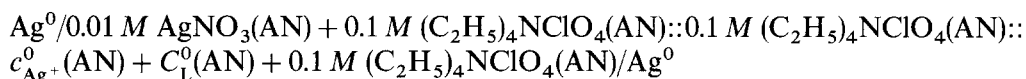
Results and Discussion

Determination of Stability Constants of the Complexes of Ag(I) with 2-Pyridinecarboxylic Acid

In order to examine the equilibria of Ag^+ complexation with 2-pyridinecarboxylic acid in acetonitrile, the procedure described in [6] was used. The Nernst equation for Ag^+ ions was satisfied within the concentration range of $AgNO_3$ from 10^{-6} to $10^{-2} M$ with the slope

$$\frac{\partial(EMF)}{\partial(\log c_{Ag^+}^0)} = 53.67 \text{ mV}$$

at the temperature of 298 K. The complexation equilibria were examined by measuring the EMF of the system

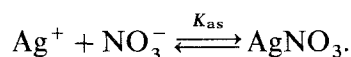
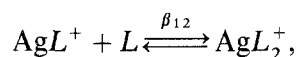
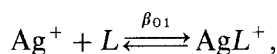


where $c_{Ag^+}^0$ is the initial concentration of $AgNO_3$ from 10^{-5} to $10^{-3} M$ and c_L^0 is the initial concentration of 2-pyridinecarboxylic acid from 10^{-3} to $10^{-2} M$.

Having the value of EMF of the system, the experimental concentration c_{exp} describing the concentration of free Ag^+ ions was found. Since under the measurements conditions, $AgNO_3$ is partly associated ($K_{as} = 75.1$) [6], the obtained value of c_{exp} represents in this case the concentration of Ag^+ ions which are uncomplexed and non-associated.

The equilibria established in the examined solutions can be described by the

following equations,



To calculate the constants of complexation equilibria, one should find the concentration of “free” Ag^+ ions which have been associated. It can be calculated using the value of association constant K_{as} ,

$$c_{\text{as}} = \frac{c_{\text{exp}} K_{\text{as}} c_{\text{Ag}^+}^0}{1 + K_{\text{as}} c_{\text{exp}}},$$

where $c_{\text{Ag}^+}^0$ is the initial concentration of AgNO_3 .

The concentration of Ag^+ ions resulting from the complexation equilibria will be described by the equation

$$c_{\text{eq}} = c_{\text{exp}} + c_{\text{as}} = c_{\text{exp}} \left[1 + \frac{K_{\text{as}} c_{\text{Ag}^+}^0}{1 + K_{\text{as}} c_{\text{exp}}} \right].$$

Table 1. Results of examination of the dependence of EMF of the system $\text{Ag}^0/0.01 \text{ M AgNO}_3(\text{AN}) + 0.1 \text{ M } (\text{C}_2\text{H}_5)_4\text{NClO}_4(\text{AN})::0.1 \text{ M } (\text{C}_2\text{H}_5)_4\text{NClO}_4(\text{AN}):c_{\text{Ag}^+}^0(\text{AN}) + c_{\text{L}}^0(\text{AN}) + 0.1 \text{ M } (\text{C}_2\text{H}_5)_4\text{NClO}_4(\text{AN})/\text{Ag}^0$ on the Ag^+ ions concentration, taking into account association $c_{\text{L}}^0 = 0.01 \text{ M}$ ($\log \beta_{01} = 1.55$, $\log \beta_{12} = 1.14$)

$c_{\text{L}}^0 \times 10^3$ mol/dm ³	$c_{\text{Ag}^+}^0 \times 10^4$ mol/dm ³	EMF mV	$c_{\text{exp}} \times 10^4$ mol/dm ³	c_{as} mol/dm ³	EMF' mV
9.975	0.249	-150.5	0.157	2.932×10^{-8}	-150.45
9.950	0.498	-133.0	0.333	1.241×10^{-7}	-132.91
9.926	0.744	-123.5	0.500	2.783×10^{-7}	-123.37
9.901	0.990	-116.5	0.675	4.994×10^{-7}	-116.33
9.877	1.235	-111.0	0.855	7.877×10^{-7}	-110.79
9.852	1.478	-106.5	1.037	1.142×10^{-6}	-106.24
9.828	1.720	-103.0	1.205	1.542×10^{-6}	-102.70
9.804	1.961	-99.5	1.400	2.040×10^{-6}	-99.16
9.780	2.200	-96.5	1.592	2.599×10^{-6}	-96.12
9.756	2.439	-94.0	1.772	3.204×10^{-6}	-93.59
9.709	2.913	-89.5	2.150	4.628×10^{-6}	-89.00
9.662	3.382	-86.0	2.498	6.228×10^{-6}	-85.43
9.615	3.846	-83.0	2.841	8.035×10^{-6}	-82.35
9.569	4.306	-80.0	3.232	1.020×10^{-5}	-79.27
9.524	4.762	-77.5	3.597	1.253×10^{-5}	-76.70
9.479	5.213	-75.0	4.005	1.522×10^{-5}	-74.13
9.434	5.660	-73.0	4.364	1.796×10^{-5}	-72.06
9.390	6.103	-71.0	4.754	2.104×10^{-5}	-69.99
9.346	6.542	-69.5	5.070	2.400×10^{-5}	-68.42
9.302	6.977	-68.0	5.408	2.723×10^{-5}	-66.85

The complex formation constants were calculated numerically (Turbo Basic program [11]). The results of measurements and calculated values of β_{01} and β_{12} are given in Tables 1 and 2.

The values of EMF' given in Tables 1 and 2 correspond to EMF which would be found in the system if only the complexes were formed in solutions without the association of Ag^+ ions.

The average value of the determined data are as follows:

$$\begin{aligned}\log \beta_{01} &= 1.56 \pm 0.02, & \beta_{01} &= 36.3 \pm 0.6, \\ \log \beta_{12} &= 1.17 \pm 0.03, & \beta_{12} &= 14.8 \pm 1.0, \\ \log \beta_{02} &= 2.73 \pm 0.02, & \beta_{02} &= 537.0 \pm 2.0,\end{aligned}$$

at an average square deviation $\text{SD} = 0.14 \text{ mV}$.

Examination of the Composition and Structure of the $\text{Ag}(I)$ Complexes with 2-Pyridinecarboxylic Acid

The values of complex formation constants of the complexes AgL_2 and AgL in water [5] $\beta_{01} = 3.23 \times 10^3$, $\beta_{02} = 1.26 \times 10^6$ and in acetonitrile $\beta_{01} = 36$, $\beta_{02} = 537$ show that these compounds have considerably lower stabilities in acetonitrile.

Table 2. Results of examination of the dependence of EMF of the system $\text{Ag}^0/0.01 \text{ M AgNO}_3(\text{AN}) + 0.1 \text{ M } (\text{C}_2\text{H}_5)_4\text{NClO}_4(\text{AN})::0.1 \text{ M } (\text{C}_2\text{H}_5)_4\text{NClO}_4(\text{AN}):c_{\text{Ag}^+}^0(\text{AN}) + c_{\text{L}}^0(\text{AN}) + 0.1 \text{ M } (\text{C}_2\text{H}_5)_4\text{NClO}_4(\text{AN})/\text{Ag}^0$ on the Ag^+ ions concentration, taking into account association $c_{\text{L}}^0 = 4 \times 10^{-3} \text{ M}$ ($\log \beta_{01} = 1.57$, $\log \beta_{12} = 1.20$)

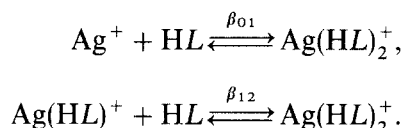
$c_{\text{L}}^0 \times 10^3$ mol/dm ³	$c_{\text{Ag}^+}^0 \times 10^4$ mol/dm ³	EMF mV	$c_{\text{exp}} \times 10^4$ mol/dm ³	c_{as} mol/dm ³	EMF' mV
3.980	0.498	-131.0	0.362	1.352×10^{-7}	-130.91
3.960	0.990	-114.0	0.752	5.556×10^{-7}	-113.83
3.941	1.478	-104.0	1.154	1.270×10^{-6}	-103.75
3.922	1.961	-97.0	1.558	2.268×10^{-6}	-96.67
3.902	2.439	-91.5	1.973	3.561×10^{-6}	-91.08
3.883	2.913	-87.0	2.393	5.143×10^{-6}	-86.51
3.865	3.382	-83.5	2.781	6.919×10^{-6}	-82.93
3.846	3.846	-80.5	3.163	8.924×10^{-6}	-79.85
3.828	4.306	-77.5	3.597	1.133×10^{-5}	-76.78
3.810	4.762	-75.0	4.005	1.390×10^{-5}	-74.20
3.765	5.882	-70.0	4.963	2.114×10^{-5}	-69.03
3.721	6.977	-65.5	6.020	3.018×10^{-5}	-64.36
3.678	8.046	-62.5	6.847	3.935×10^{-5}	-61.20
3.636	9.091	-59.5	7.787	5.023×10^{-5}	-58.04
3.596	10.110	-57.0	8.669	6.180×10^{-5}	-55.39
3.556	11.111	-54.5	9.650	7.508×10^{-5}	-52.75
3.516	12.088	-52.5	10.515	8.847×10^{-5}	-50.62
3.478	13.043	-50.5	11.457	1.033×10^{-4}	-48.49
3.441	13.978	-48.5	12.483	1.198×10^{-4}	-46.36
3.404	14.894	-47.0	13.313	1.354×10^{-4}	-44.74

Acetonitrile is a solvent of lower basicity compared to water. This is shown by the parameters of its basicity – the donor number of Guttmann and standardized numbers of Reichardt:

	DN	B _{MeOH}	B' _{phenol}
Acetonitrile	14.1	101	160
Water	18.0(33.0)	123	166

Moreover, acetonitrile is a softer Pearson base than water, and the process of addition of a hard acid (H⁺ ion) should proceed easier in water. In addition, these solvents have different dielectric constants: $\epsilon_{\text{H}_2\text{O}} = 78.1$, $\epsilon_{\text{AN}} = 33.1$.

All these parameters show that the dissociation of 2-pyridinecarboxylic acid in acetonitrile proceeds to a considerably lower extent. Therefore, one can assume that the complexation of Ag⁺ ions takes place through the addition of the ligand in the form HL to the central ion,



In order to confirm this hypothesis, IR spectra were taken of 0.1 M solution of picolinic acid, 0.05 M AgL₂ and 0.02 M solution of AgL₂ in acetonitrile. In both spectra of the complex two vibration bands were observed ($\nu = 3540 \text{ cm}^{-1}$ and $\nu = 3620 \text{ cm}^{-1}$), which are independent of concentration and can be described to the stretching vibration of the OH group conjugated with carbonyl group. This band is absent in the spectrum of picolinic acid which is completely associated in solution. The double peak in the spectrum of the complex is most likely connected with the Fermi resonance brought about by the presence of the carbonyl group band ($\nu = 1770 \text{ cm}^{-1}$).

An additional confirmation of the complex structure was obtained by the replacement of hydrogen atoms in the AgL₂⁺ complex by deuterium atoms. The spectrum of the Ag(Hpic)₂⁺ complex containing deuterium in acetonitrile shows a single peak at $\nu = 2270 \text{ cm}^{-1}$ as characteristic for the O–D bond; at the same time, the double band of vibration at $\nu = 3540 \text{ cm}^{-1}$ and 3620 cm^{-1} disappears.

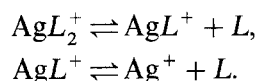
Thus, the formation of the coordination bond N→Ag in these complexes proceeds without simultaneous creation of chelates which would stabilize the ions being formed through the entropy effect.

The absence of cyclization and entropy effect should considerably lower the values of complex formation constants, which is actually confirmed by the values of β_{01} and β_{12} obtained for the solutions in acetonitrile.

An additional decrease in the values of complex stability constants of the complexes Ag⁺-Hpic in acetonitrile results from the strong Debay – London interaction Ag⁺-AN: soft acid – soft Pearson base [1].

Examination of the Redox Systems Ag(II)/Ag(I) in the Presence of 2-Pyridinecarboxylic Acid in Acetonitrile

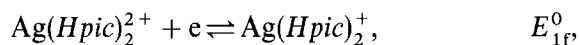
The formation constants of the complexes AgL and AgL_2 , $\beta_{01} = 36.3$, $\beta_{02} = 537.0$, determined by potentiometric measurements show that the stability of these compounds is rather very low. The small difference in the successive constants indicates that within the wide range of concentration of the AgL_2 complex there are three forms of Ag(I) originating from dissociation of complexes



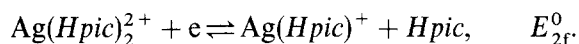
The content of particular forms of Ag(I) versus initial concentration of AgL_2^+ is given in Table 3.

Chronovoltamperometric Measurements

The chronovoltamperometric measurements were intended to determine formal potentials of the redox systems



and



The relationship between formal potentials of E_{1f}^0 and E_{2f}^0 is given by the equation

$$E_{1f}^0 = E_{2f}^0 + 0.059 \log \beta_{12}.$$

The value of β_{12} as found from the potentiometric measurements is 14.8, hence the potential difference

$$E_{1f}^0 - E_{2f}^0 \cong 68 \text{ mV}.$$

This difference indicates that in the case of comparable concentration of the complexes AgL_2^+ and AgL^+ , these compounds will be oxidized and the products of their oxidation will be reduced at similar potentials.

Table 3. Content of various forms of Ag(I), depending on the concentration of the $\text{Ag}(\text{Hpic})_2^+$ complex

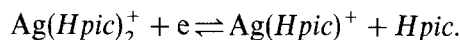
$c_{0\text{AgL}_2^+}$ mol/dm ³	c_L^0 mol/dm ³	$[\text{AgL}_2^+]$ mol/dm ³	$[\text{AgL}^+]$ mol/dm ³	$[\text{Ag}^+]$ mol/dm ³
10^{-3}	—	1.44×10^{-5}	6.38×10^{-5}	9.18×10^{-4}
5×10^{-3}	—	3.23×10^{-4}	1.08×10^{-3}	3.60×10^{-3}
10^{-2}	—	1.16×10^{-3}	3.07×10^{-3}	5.77×10^{-3}
10^{-2}	10^{-2}	2.09×10^{-3}	3.54×10^{-3}	4.37×10^{-3}
10^{-2}	5×10^{-2}	4.51×10^{-3}	2.23×10^{-3}	3.26×10^{-3}
10^{-2}	10^{-1}	6.06×10^{-3}	3.12×10^{-3}	8.20×10^{-4}
5×10^{-2}	—	1.65×10^{-2}	2.09×10^{-2}	1.26×10^{-3}
5×10^{-2}	5×10^{-2}	2.61×10^{-2}	1.78×10^{-2}	6.10×10^{-3}
5×10^{-2}	10^{-1}	3.18×10^{-2}	1.48×10^{-2}	3.40×10^{-3}
5×10^{-2}	0.5	4.41×10^{-2}	5.59×10^{-3}	3.04×10^{-4}

In the voltamperometric curves, one can observe a broad anodic and a similar cathodic peak; the formal potential determined would be a potential of a mixed system.

Hence the chronovoltamperometric measurements have sense only for solutions of AgL_2^+ with maximum concentrations and negligible quantities of AgL^+ or vice versa. According to the results given in Table 3, such conditions are satisfied by two solutions:

- (a) $5 \times 10^{-3} M$ solution of AgL_2^+ in which the complexes concentration ratio $\text{AgL}_2^+/\text{AgL}^+ = 1:4.5$ with considerable concentration of free Ag^+ ions being higher than that of both compounds,
- (b) $5 \times 10^{-2} M$ solution of AgL_2^+ with excess ligand $-0.5 M L$ for which the ratio $\text{AgL}_2^+/\text{AgL}^+ = 8:1$.

It is impossible to prepare solution (b) due to limited solubility of the complex of AgL_2^+ with 2-pyridinecarboxylic acid in acetonitrile. The composition of 50 cm^3 of solution (b) would be 0.4245 g AgNO_3 , 3.69 g 2-pyridinecarboxylic acid and 1.1475 g $(\text{C}_2\text{H}_5)_4\text{NClO}_4$. So, the formal potential can be determined only for solution (a); in this case one can assume with a high probability that the following redox system is involved:



Chronovoltamperograms of the following solutions in acetonitrile were taken:

- (1) $0.1 M (\text{C}_2\text{H}_5)_4\text{NClO}_4$,
- (2) $10^{-3} M \text{ AgNO}_3$ ($\mu = 0.1 - (\text{C}_2\text{H}_5)_4\text{NClO}_4$),
- (3) $10^{-2} M \text{ Hpic}$ ($\mu = 0.1 - (\text{C}_2\text{H}_5)_4\text{NClO}_4$),
- (4) $5 \times 10^{-3} M \text{ Ag}(\text{Hpic})_2^+$ ($\mu = 0.1 - (\text{C}_2\text{H}_5)_4\text{NClO}_4$).

Curves were made within the potential range from $+600$ to 1600 mV vs. $\text{Ag}^0/0.01 M \text{ AgNO}_3(\text{AN}) + 0.1 M (\text{C}_2\text{H}_5)_4\text{NClO}_4(\text{AN})$ electrode, where no reduction of Ag^+ ions and no further oxidation of metallic silver to Ag^+ ions and $\text{Ag}(\text{Hpic})^+$ complex take place. The indicator electrode in the measurements was a Pt wire. The potential sweep was from 10 to 100 mV/s . Solutions (1), (2), and (3) showed no electrode activity under the measurements conditions. The voltamperogram of solution (4) is shown in Fig. 1.

The potential values of anodic and cathodic peaks and the values of formal potentials are given in Table 4.

Table 4. Dependence of the formal potentials for various rates of potential sweep

v [mV/s]	E_a [mV]	E_c [mV]	$\Delta E_{p_{ac}}$ [mV]	E_f^0 [mV]
10	1280	1200	80	1240
20	1304	1176	128	1240
50	1348	1160	188	1254
100	1400	1144	256	1272

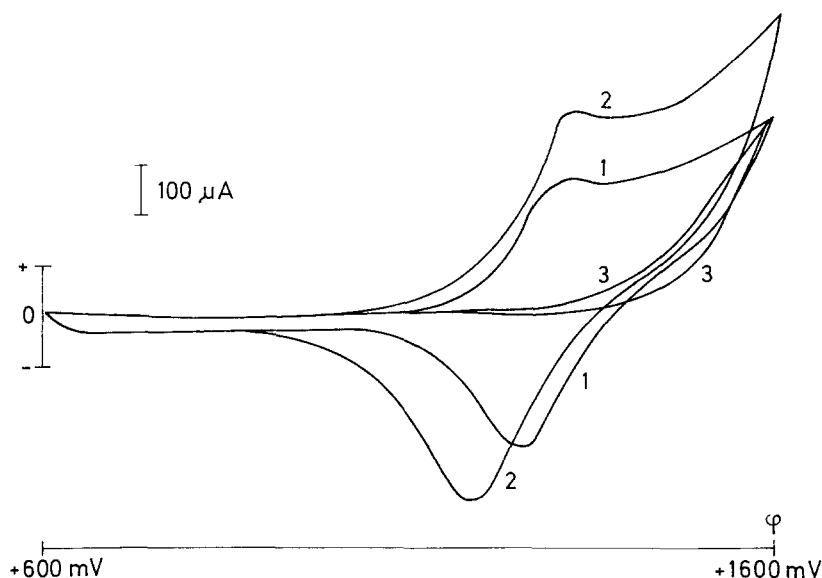
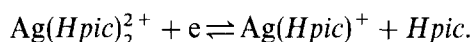


Fig. 1. Chronovoltamperometric curves of acetonitrile solution $5 \times 10^{-3} M AgL_2$ for scanning potential rates: 1: $v = 10 mV/s$, 2: $v = 20 mV/s$, and acetonitrile solution $10^{-2} M Hpic$ scanning potential rate $v = 20 mV/s$, $T = 293 K$

The values of ΔE_{pak} for $v \geq 50 mV/s$ indicate an increasing irreversibility of the electrode process, while the oxidation and reduction peaks become more broadened and less developed. For $v < 50 mV/s$ the redox system is quasi-reversible, which allows to determine the value of formal potential,



$E_{2f}^0 = 1240 mV$ vs. $Ag^0/0.01 M AgNO_3(AN) + 0.1 M (C_2H_5)_4NClO_4(AN) = 1772 mV$ vs. NHE.

The determined value of E_{2f}^0 allows to calculate E_{1f}^0 from the equation

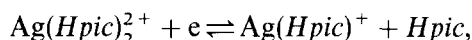
$$E_{1f}^0 = E_{2f}^0 + 59.1 \log \beta_{12} = 1772 + 69 = 1841 mV \text{ vs. NHE.}$$

Potentiometric Oxidation of the Complex $Ag(Hpic)_2^+$

In order to verify the form of $Ag(II)$ complex with picolinic acid, a solution of $10^{-2} M Ag(Hpic)_2ClO_4 + 0.1 M (C_2H_5)_4ClO_4$ in acetonitrile was potentiometrically oxidized at the potential $\varphi = 1850 mV$ vs. NHE in the above given system [12]. The brickred-brown crystals formed during the electrolysis were washed with acetone and dried at a temperature of $40^\circ C$ under vacuum. The obtained product has the following composition: $Ag = 19.6\%$, $O = 34.6\%$, $Cl = 12.8\%$, $N = 5.0\%$, $H = 1.8\%$, which corresponds to the compound: $Ag(Hpic)_2(ClO_4)_2$. So, as expected $Ag(Hpic)_2^{2+}$ is the oxidized form of the redox systems under investigation.

Coulometric Measurements

In order to confirm the value of formal potential of the system



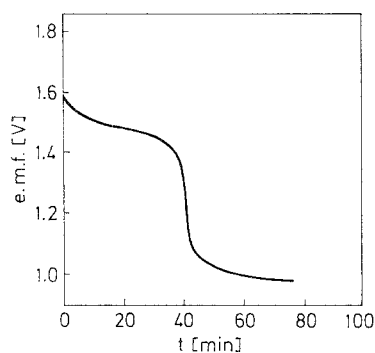
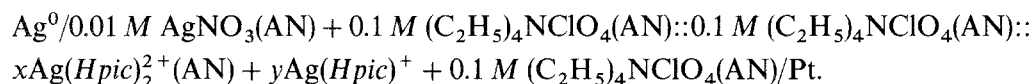


Fig. 2. Curve of the amperostatic reduction of anodically oxidized solution of $2 \times 10^{-3} M \text{Ag}(\text{Hpic})_2^+$ ($i = 2 \text{ mA}$). Values of potentials vs. Ag^0 : $0.01 M \text{AgNO}_3 + 0.1 M (\text{C}_2\text{H}_5)_4\text{NClO}_4$ electrode, $T = 298 \text{ K}$

oxidation of $2 \times 10^{-3} M \text{Ag}(\text{Hpic})_2^+$ ($i = 1 \text{ mA}$) was carried out until maximum EMF was obtained and then the formed $\text{Ag}(\text{Hpic})_2^{2+}$ was reduced ($i = 2 \text{ mA}$). It was also assumed that the complex AgL_2^{2+} , similarly to other complexes of Ag(II), is very stable and appears in solution only in the form $\text{Ag}(\text{Hpic})_2^{2+}$.

The measurements were carried out in the system:



A typical reduction curve given in Fig. 2 shows a potential drop for $c_{\text{Ag(II)}} = c_{\text{Ag(I)}}$; during the measurement no silver was deposited on Pt electrode.

The value of formal potential of the examined redox system corresponds to the maximum of the relationship

$$\frac{\partial \text{EMF}}{\partial Q} = \frac{\partial \text{EMF}}{\partial t},$$

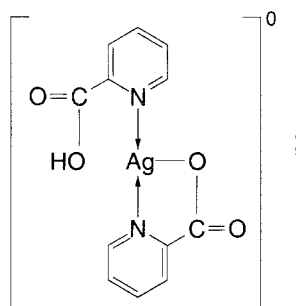
and for a series of 3 measurements $E_f^0 = 1774 \pm 3 \text{ mV}$ vs. NHE.

The obtained value is consistent with the results of chronovoltamperometric measurements.

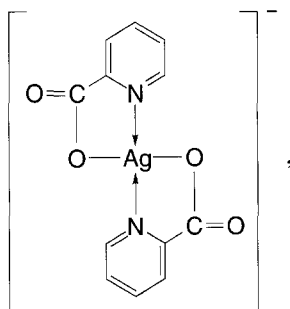
Conclusion

The results of examinations of the aqueous solutions indicate that two forms of complexes can be formed depending on pH :

(a) $pH < 4$:

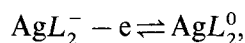


(b) $pH \cong 7$:

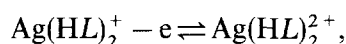


and the complex of Ag(II) with picolinic acid is a neutral chelate with a formula of $Ag(pic)_2^0$.

On the other hand, in acetonitrile solutions we deal with the complexes: $Ag(Hpic)_2^{2+}$ and $Ag(Hpic)_2^+$. Therefore, the redox system formed in water



has a different form than that in acetonitrile,



hence the comparison of their formal potential values is purposeless.

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