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Characteristic of the Ag(II)/Ag(I) System in the Presence of Picolinic Acid in Water

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Summary. Using IR spectrophotometry, potentiometry, and quantitative analysis, it was ascertained that the process of complexing Ag(I) ions with picolinic acid (H*pic*) results in the formation of complexes such as $\mathrm{AgH}(pic)_2$ ($pH < 4$) and $\mathrm{Ag}(pic)_2^-$ ($pH \cong 7$). Complex Ag(II) occurs in the form $\mathrm{Ag}(pic)_2^\circ$ independently of the medium. The values of conditional complex stability constants ($\mu = 0.1$) for $\mathrm{Ag}(pic)^\circ$ and $\mathrm{Ag}(pic)_2^-$ found by potentiometry are as follows: $\beta_{01} = 3.4 \times 10^3$ and $\beta_{02} = 1.2 \times 10^6$. Redox systems formed in solutions were described and their formal potentials were determined by chronovoltamperometry:

$$\mathrm{Ag}(pic)_2^\circ + \mathrm{e} \rightleftarrows \mathrm{Ag}(pic)_2^- \qquad E_f^\circ = 1.388\ \mathrm{V\ vs.\ NHE}$$
$$\mathrm{Ag}(pic)_2^\circ + \mathrm{e} \rightleftarrows \mathrm{Ag}(pic)^\circ + pic^- \qquad E_f^\circ = 1.240\ \mathrm{V\ vs.\ NHE.}$$

Keywords. Chronovoltametry; Formal potential; IR spectrophotometry; pH-metry; Picolinic acid; Potentiometry; Redox systems with silver complexes.

Charakteristik des Ag(II)/Ag(I)-Systems in Gegenwart von Picolinsäure in Wasser

Zusammenfassung. Mittels IR-Spektroskopie, Potentiometrie und quantitativer Analyse wurde festgestellt, daß der Komplexierungsprozeß von Ag(I)-Ionen mit Picolinsäure (H*pic*) die Bildung von Komplexen $\mathrm{AgH}(pic)_2$ ($pH < 4$) und $\mathrm{Ag}(pic)_2^-$ ($pH \sim 7$) ergibt. Komplexiertes Ag(II) tritt unabhängig vom Medium als $\mathrm{Ag}(pic)_2^\circ$ auf. Die potentiometrisch gefundenen Stabilitätsparameter ($\mu = 0.1$) für $\mathrm{Ag}(pic)_2^\circ$ und $\mathrm{Ag}(pic)_2^-$ sind $\beta_{01} = 3.4 \times 10^3$ und $\beta_{02} = 1.2 \times 10^6$. Die Redoxsysteme in Lösung wurden mittels Chronovoltamperometrie bestimmt:

$$\mathrm{Ag}(pic)_2^\circ + \mathrm{e} \rightleftarrows \mathrm{Ag}(pic)_2^- \qquad E_f = 1.388\ \mathrm{V\ gegenüber\ NHE}$$
$$\mathrm{Ag}(pic)_2^\circ + \mathrm{e} \rightleftarrows \mathrm{Ag}(pic)^\circ + pic^- \qquad E_f = 1.240\ \mathrm{V\ gegenüber\ NHE.}$$

Introduction

In our previous studies [1–3], the stability constants of Ag(I) complexes with pyridine in water, acetonitrile, and propylene carbonate have been determined. α-Pyridinecarboxylic acid (picolinic acid), in addition to its pyridine ring, contains a carboxylic group capable to form a 5-membered ring with the coordination bond N–Ag and O–Ag. The literature data concerning the protonation constants of picolinic acid and its complexes with Ag(I) and Ag(II) ions are incomplete and often inconsistent [4–9].

The present study is aimed towards the synthesis and determination of Ag(I) and Ag(II) complexes formed with picolinic acid depending on the pH of the medium used, the effect of cyclization on the stability of the compounds, including description and determination of formal potentials of the redox systems formed in the solutions of Ag(I) and Ag(II) complexes with this ligand in aqueous solutions.

Experimental Part

Measurements of *pH* were carried out by means of an OP-211/1 *pH*-meter of Radelkis with an accuracy of ± 0.01 unit of *pH*.

Potentiometric measurements (determination of the Ag^+ ions concentration in the solutions) were performed with the use of a V-543 multimeter of Meratronik. A silver electrode $Ag^0/0.01\,M$ $AgNO_3 + 0.1\,M\ KNO_3$ was used as a reference electrode, while a silver-plated platinum wire was the indicator electrode.

Spectrophotometric examinations within the IR range were carried out by means of a IR Specord 75 spectrophotometer and those in UV and visible light with a Specord UV–VIS spectrophotometer. The procedure of coulometric and voltamperometric measurements have been described in [10–11]. Picolinic acid (Fluck AG), HNO_3, $AgNO_3$, KNO_3, and NaOH (POCh, Gliwice) were used without prior purification.

Results and Discussion

Determination of Conditional Protonation Constants for Picolinic Acid

The protonation constants of picolinic acid were found by *pH*-metric titration of solutions (50 cm^3) with the composition: $4 \times 10^{-3}\,M$ H*pic* + $5 \times 10^{-3}\,M$ HNO_3 and with a ionic strength of 0.1 ($0.1\,M$ KNO_3) maintained with $0.09828\,M$ NaOH solution. The protonation constants of picolinic acid were calculated from the data given in Table 1, using the equation:

$$\log K_i = \log \frac{(1 - a + n - i)c_{H_nL} - [H^+] + [OH^-]}{(a - n + 1)c_{H_nL} + [H^+] - [OH^-]} + pH,$$

where K_i is the i^{th} protonation constant and a the degree of neutralization. For the calculations the program given in [12] was used.

The average values found for conditional protonation constants of picolinic acid ($\mu = 0.1$) are as follows: $\log K_1 = 5.44 \pm 0.03$, $\log K_2 = 1.59 \pm 0.07$, $K_1 = (2.75 \pm 0.2) \times 10^5$, $K_2 = 38.9 \pm 2$, and $K_1 \times K_2 = (1.07 \pm 0.2) \times 10^7$, the mean square deviation being SD = 6×10^{-4} of *pH* unit. The obtained results are consistent with those of Takata [5] in $0.1\,M$ $NaClO_4$, and only slightly different from the values K_1 and K_2 obtained by Anderegg [7] and Eberle [6].

Synthesis and Analysis of Ag(I) *Complexes with Picolinic Acid*

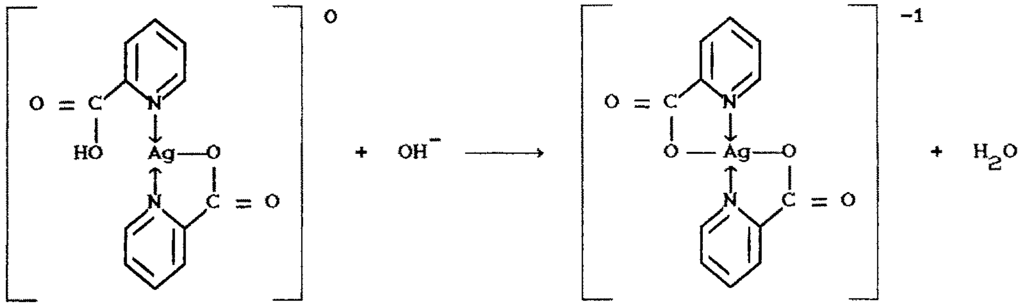
In order to prepare an AgL_2 complex, 0.01 mol of picolinic acid was mixed with 0.005 mol of $AgNO_3$ in 100 cm^3 of water. The resultant white precipitate was almost insoluble in water, methanol, ethanol, acetonitrile, and propylene carbonate. $pH < 4$ of the mixture ensured the existence of most ligand molecules in undissociated form. So, complexes such as $Ag(Hpic)_2NO_3$, $AgH(pic)_2^0$ or $AgHpic^0$ could be formed.

Table 1. Results of *pH*-metric titration of 50 cm^3 solution with the composition: $4 \times 10^{-3}\,M$ picolinic acid $+ 5 \times 10^{-3}\,M$ HNO$_3$; $\mu = 0.1$; (0.1 M KNO$_3$) by means of 0.09828 M NaOH solution

v_{red} [cm^3]	a	pH	v_{red} [cm^3]	a	pH
0.29	0.1422	2.51	2.39	1.1716	4.78
0.39	0.1912	2.54	2.44	1.1961	4.85
0.49	0.2402	2.57	2.49	1.2206	4.91
0.59	0.2892	2.60	2.59	1.2696	5.01
0.69	0.3382	2.63	2.69	1.3186	5.11
0.79	0.3873	2.67	2.79	1.3676	5.21
0.89	0.4363	2.71	2.89	1.4167	5.31
0.99	0.4853	2.75	2.99	1.4657	5.41
1.09	0.5343	2.80	3.09	1.5147	5.50
1.19	0.5833	2.86	3.19	1.5637	5.59
1.29	0.6324	2.92	3.29	1.6127	5.69
1.39	0.6814	2.98	3.39	1.6618	5.79
1.49	0.7304	3.07	3.49	1.7108	5.89
1.59	0.7794	3.16	3.59	1.7598	6.02
1.69	0.8284	3.28	3.69	1.8088	6.17
1.79	0.8529	3.35	3.74	1.8333	6.26

In order to identify the precipitate, IR spectra of the examined compound and picolinic acid were taken. The results show that the complex and ligand reveal vibration of the OH group included in the carboxylic group ($\nu = 3550\,\mathrm{cm}^{-1}$) with shifts of vibration bands of C=C and C=N in the complex ($\nu = 1570$ and $1590\,\mathrm{cm}^{-1}$) in relation to analogous bands in the ligand ($\nu = 1600$ and $1610\,\mathrm{cm}^{-1}$). The shifts suggest a coordination bond Ag–N.

Murta and Walton [8] named the complex obtained in this medium: "Ag(*pic*)-low *pH* form" without determination of its elementar formula. Their data ruled out a formula such as Ag(H*pic*)NO$_3$. The performed quantitative analysis of the compound brought the following results: H 2.60, C 40.70, N 8.00, O 18.20, Ag 30.50%, while the theoretical composition of AgH(*pic*)$_2^{\circ}$ is: H 2.57, C 40.80, N 7.94, O 18.14, Ag 30.55%. Thus, these results confirm undoubtedly that this compound is AgH(*pic*)$_2^{\circ}$. Then it should be soluble at $pH > 7$ (taking into account the protonation constants



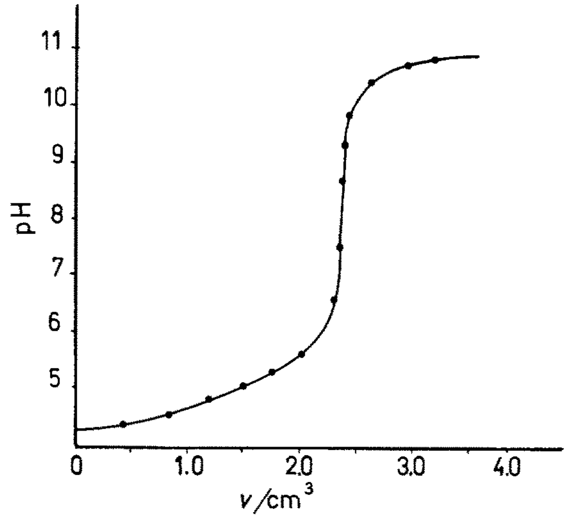


Fig. 1. The pH-metric titration curve of 40 cm^3 solution containing 2.36×10^{-4} mol of AgH(pic)$_2^\circ$ with 0.1003 M NaOH solutions; $T = 298$ K

of picolinic acid), giving a ionic form according to the reaction shown in the formula.

Therefore, weighed portions of the precipitate were titrated with a standard NaOH solution. An exemplary titration curve is shown in Fig. 1.

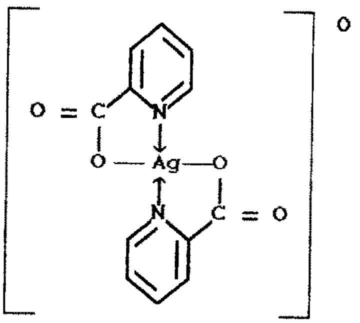
An abrupt change in the titration curves always corresponds to the quantity (mmol) of the tested compound, which confirms most certainly that this is the chelate AgH(pic)$_2^\circ$.

IR spectra of the Ag(I)L_2 complex, synthesized at $pH = 7.2$ (Ag(pic)-high pH form of Walton) was the same as in [8] and does not reveal a vibration of an –OH band in the carboxylic group ($\nu = 3550\,\mathrm{cm}^{-1}$).

The Ag(pic)$_2^-$ formula of the compound was proved by an elementar analysis. Thus the equilibrium between the "low" and "high-pH" forms may be described by the equation shown in the formula.

Synthesis of the Ag(II) *Complex with Picolinic Acid*

The complex was prepared by two methods: (a) from AgO in concentrated nitric acid with excessive ligand in an acetone-ice bath, and (b) by oxidation of AgH(pic)$_2^\circ$ with sodium peroxydisulphate. In both cases, the product obtained had the following composition: Ag 30.70, O 18.15, N 8.05, C 40.90, and H 2.20%, which



corresponds to $Ag(C_5H_4NCOO)_2$. The compound is sparingly soluble in water, *AN*, CH_3OH, C_2H_5OH, and PC. IR spectra of the Ag(II) complex with picolinic acid did not show an absorption band at $v = 3550\,cm^{-1}$ characteristic for an OH group. It is an inner chelate shown in the formula. This is consistent with the results of Bacon and Hanna [13].

Determination of Conditional Formation Constants of the Ag(I) Complexes with Picolinic Acid

In order to obtain precise values for the formation constants of Ag*L* and AgL_2 and to examine the mechanism of complexing the Ag(I) ion with picolinic acid, the process was examined by potentiometry depending on the *pH* of the ligand solution.

Complex formation equilibria were examined by titrating the ligand solutions ($40\,cm^3$) with a particular *pH*, using a standard solution of $AgNO_3$ to find out the electromotive force of the cell being formed:

$$Ag^o/0.01\,M\ AgNO_3 + 0.1\,M\ KNO_3 \,\|\, 0.1\,M\ KNO_3 \,\|\, c_L + c_{Ag^+} + 0.1\,M\ KNO_3/Ag^o.$$

The Nenst equation for Ag^+ ions was held within the range from 10^{-1} to $10^{-6}\,M$, when $\partial\,EMF/\partial \log c_{Ag^+} = 58.25\,mV$.

Measurements in Solutions with pH $\leqslant$ 4

The ligand concentration used was within the range from 4×10^{-2} to $10^{-3}\,M$ and that of $AgNO_3$ from 10^{-3} to $10^{-1}\,M$. The initial *pH* of the titrated solutions was dependent on the concentration of picolinic acid and was within the range 4.0–3.2. During potentiometric measurements, the concentration of Ag^+ ions and *pH* values of the titrated solutions were determined at the same time. A typical titration curve is shown in Fig. 2.

It can be seen in Fig. 2 that the hydrogen ion concentration increases with the advancement of the complex formation process, so the formation of coordination bond Ag–N is accompanied by the creation of an Ag–O bond.

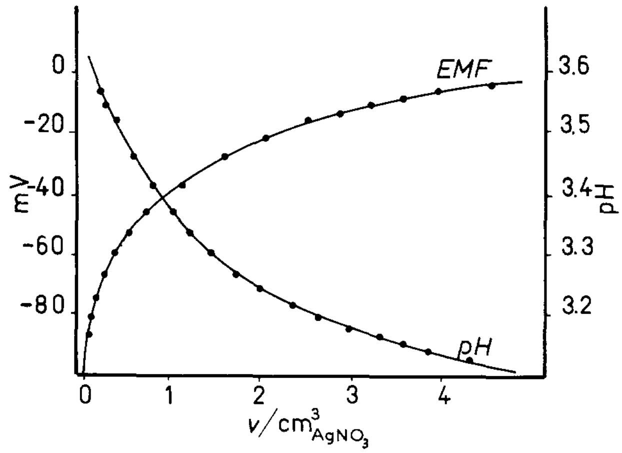


Fig. 2. Potentiometric titration curve for $40\,cm^3$ of $4 \times 10^{-2}\,M$ picolinic acid solution titrated with $0.1\,M$ $AgNO_3$; $\mu = 0.1$ ($0.1\,M$ KNO_3); $T = 298\,K$, (φ vs. $Ag/0.01\,M$ $AgNO_3 + 0.1\,M$ KNO_3)

The plateau in the titration curve is associated with the precipitation of a white deposit of the complex. The precipitate was separated and analysed as already described. The obtained spectra and elementary composition correspond to $\mathrm{AgH}(pic)_2^{\mathrm{o}}$. Thus the complexation of Ag^+ ion with picolinic acid can be described by the equations:

$$\mathrm{Ag}^+ + \mathrm{H}pic \rightleftarrows \mathrm{Ag}(pic) + \mathrm{H}^+ \qquad \beta_{01}$$

and

$$\mathrm{Ag}(pic) + \mathrm{H}pic \rightleftarrows \mathrm{AgH}(pic)_2 \qquad \beta_{12}$$

or

$$\mathrm{Ag}^+ + \mathrm{H}pic \rightleftarrows \mathrm{AgH}(pic)^+ \qquad \beta_{01}$$

and

$$\mathrm{AgH}pic^+ + \mathrm{H}pic \longrightarrow \mathrm{AgH}(pic)_2 + \mathrm{H}^+ \qquad \beta_{12}.$$

Of course, irrespective of the mechanism of chelate formation, the complex formation constants β_{01} and β_{12} should be identical since they describe the thermodynamic potential change concomitant with the formation of Ag–N and N–Ag–N bonds. On the other hand, it would be rather impossible that under the experiment conditions, in solutions with $pH \leqslant 4$, a coordination bond such as Ag–O could be formed without splitting off the hydrogen atom from carboxylic group. (The nitrogen atom of the ligand is not protonated under these conditions $-\log K_1 = 1.59$.)

Since during titration the chelate was precipitated, the measurement readings for the determination of the complexing equilibria constants were taken before the precipitation took place. The constants were determined numerically as previously [12]. The results of three measurement series are given in Table 2.

Table 2. Results of potentiometric measurements of the Ag(I) complexes formed with picolinic acid in solution with $pH < 4$; $T = 298$ K; (c_c-concentration of the complexed Ag^+ ions)

$c_L^{\mathrm{o}} \times 10^2$ mol/dm^3	$c_{\mathrm{Ag}^+}^{\mathrm{o}} \times 10^3$ mol/dm^3	EMF mV	$c_c \times 10^3$ mol/dm^3	$c_L^{\mathrm{o}} \times 10^2$ mol/dm^3	$c_{\mathrm{Ag}^+}^{\mathrm{o}} \times 10^5$ mol/dm^3	EMF mV	$c_c \times 10^6$ mol/dm^3
3.9801	0.4975	−103.8	0.3323	0.9926	0.7444	−73.8	0.2036
3.9604	0.9901	−84.8	0.6400	0.9913	0.8642	−69.8	0.2307
3.9409	1.4778	−73.8	0.9370	0.9901	0.9901	−66.3	0.2627
3.9216	1.9608	−66.3	1.2334	0.9889	1.1125	−63.3	0.2935
3.9024	2.4390	−60.3	1.5168	0.9876	1.2346	−60.3	0.3124
3.8835	2.9126	−56.3	1.8326	0.9852	1.4778	−55.3	0.3538
3.8647	3.3816	−52.8	2.1416	0.9828	1.7199	−51.3	0.4039
3.8462	3.8462	−50.3	2.4772	0.9804	1.9608	−47.8	0.4498
3.8278	4.3062	−47.8	2.7952	0.9913	0.8674	−162.3	2.666
3.8095	4.7619	−45.3	3.0939	0.9901	0.9901	−159.8	3.155
3.7645	5.8824	−40.8	3.8894	0.9889	1.1120	−157.3	3.545
3.7209	6.9767	−35.8	4.5477	0.9876	1.2351	−154.8	3.845
				0.9864	1.3563	−153.3	4.444
0.9950	0.4975	−83.3	0.1260	0.9852	1.4778	−151.8	5.003
0.9938	0.6211	−78.3	0.1684	0.9840	1.5998	−150.8	5.752

The numerical β-values are: $\log\beta_{01} = 3.51 \pm 0.2$, $\beta_{01} = (3.33 \pm 0.5) \times 10^3$, $\log\beta_{02} = 6.10 \pm 0.05$, $\beta_{02} = (1.26 \pm 0.15) \times 10^6$, with the mean deviation being $SD = 0.4\,mV$.

The values of complex formation constants are consistent with the results of Anderegg [7], but inconsistent with those of Batanero [14] according to which there are complexes such as Ag_2L ($\log\beta = 3.5$), AgL ($\log\beta = 3.46$) and $AgHL$ ($\log\beta = 4.1$). The procedure of investigation given in [14] arouses serious doubts, and the assumption that the ligand (picolinic acid) occurs in a protonated form irrespective of *pH* must be incorrect.

Measurements in Solution with pH = 7

In solutions with $pH > \log(K_1K_2)$ (K_1 and K_2 – protonation constants of picolinic acid, $\log K_1 = 5.44$, $\log K_2 = 1.59$), so with $pH \cong 7.03$ the ligand is present only as pic^- anion, and the complex formation process is described only by the equilibria:

$$Ag^+ + pic^- \rightleftarrows Ag(pic)^o \quad (A) \quad \beta_{01}$$

and

$$Ag(pic)^o + pic^- \rightleftarrows Ag(pic)_2^- \quad (B) \quad \beta_{12}.$$

The potentiometric measurements were carried out in the system given above at the same initial concentrations of the ligand and titrant ($AgNO_3$), bringing the initial solutions to $pH \cong 7.2$ with NaOH. In solutions with higher *pH*, Ag_2O was precipitated during the titration. On titration the values of EMF were settled within one hour on the average, which was most likely a result of the low rate of cyclization of the chelate in neutral medium. But no precipitate was observed even at relatively high concentrations of the complex, which excluded the formation of chelate $AgH(pic)_2^o$.

The results of two measurement series are given in Table 3. The numerically calculated values β_{01} and β_{02} are as follows: $\log\beta_{01} = 3.54 \pm 0.2$, $\beta_{01} = (3.4 \pm 0.5) \times$

Table 3. Results of potentiometric measurements of the Ag(I) complexes formed with picolinic acid in solution with $pH = 7.2$; $T = 298\,K$; (c_c-concentration of the complexed Ag^+ ions)

$c_L^o \times 10^3$ mol/dm^3	$c_{Ag^+}^o \times 10^3$ mol/dm^3	EMF mV	$c_c \times 10^3$ mol/dm^3	$c_L^o \times 10^3$ mol/dm^3	$c_{Ag^+}^o \times 10^3$ mol/dm^3	EMF mV	$c_c \times 10^3$ mol/dm^3
8.9286	0.2232	−198.2	0.2222	7.1048	2.2203	−101.2	2.1285
8.7336	0.4367	−177.7	0.4340	6.4516	0.3161	−170.6	0.3125
8.5470	0.6410	−165.6	0.6374	6.2500	0.6125	−148.7	0.6014
8.3682	0.8368	−155.5	0.8294	6.0606	0.8909	−136.7	0.8732
8.1967	1.0246	−146.4	1.0133	5.8824	1.1529	−125.2	1.1228
8.0321	1.2048	−138.9	1.1888	5.7143	1.4000	−113.0	1.3469
7.8740	1.3779	−132.2	1.3552	5.5556	1.6333	−103.6	1.5513
7.7220	1.5444	−126.0	1.5153	5.4054	1.8541	−96.3	1.7389
7.5614	1.7202	−119.4	1.6808	5.2632	2.0632	−89.0	1.9017
7.4349	1.8587	−114.2	1.8085	5.1282	2.2138	−84.7	2.0644
7.2993	2.0073	−108.9	1.9431	5.0000	2.4500	−80.8	2.2138
7.2333	2.0796	−106.4	2.0065	4.8781	2.6293	−77.8	2.3578
7.1685	2.1505	−104.1	2.0703	4.7619	2.8000	−75.3	2.4952

10^3, $\log \beta_{02} = 6.08 \pm 0.05$, $\beta_{02} = (1.20 \pm 0.15) \times 10^6$, with the mean deviation being SD = 1 mV.

Practically the same values of the complex formation constants described by equations (A) and (B) as those obtained in measurements at $pH \leqslant 4$ confirm the hypothesis that the complex formation and cyclization take place with simultaneously expelling hydrogen ion.

Determination of Formal Potentials of the Redox Systems of Ag(II)/Ag(I) in the Presence of Picolinic Acid

Oxidation of the Ag(I) complexes $Ag(pic)_2^-$ and $AgH(pic)_2^\circ$ with $Na_2S_2O_8$ results in the chelate of Ag(II), $Ag(pic)_2^\circ$, which is insoluble in water and organic solvents. Therefore, the determination of formal potentials of redox systems by means of amperostatic coulometry seemed to be impossible. Amperostatic oxidation was carried out in the system: Pt/0.01 *M* $AgNO_3$ + 0.1 *M* KNO_3 ‖ 0.1 *M* KNO_3 ‖ 3×10^{-3} *M* $Ag(pic)_2^-$ + 0.1 *M* KNO_3/Pt at $i = 2$ mA. During the anodic oxidation, once the chelate $Ag(pic)_2^\circ$ had appeared, the value of EMF of the system was practically constant and equal to about 600 mV vs. Ag/0.01 *M* $AgNO_3$ + 0.1 *M* KNO_3. At the same time a brown-red precipitate appeared in the cell, while the solution being oxidized showed only a slight change in colour. In the case of saturated $AgH(pic)_2^\circ$ solution in the same system, the formation of the chelate $Ag(pic)_2^\circ$ took place at potentials corresponding to the decomposition of the basic electrolyte ($\varphi > 2.0$ V vs. NHE).

Since the concentration of the Ag(II) complex in the examined solutions was very low, it was impossible to determine the formal potential of the system by means of coulometry. The only way to do this was through chronovoltamperometric measurements.

The complex formation constants ($\log \beta_{01} = 3.5$ and $\log \beta_{12} = 2.5$) point to the fact that within a wide range of concentrations of Ag^+ and pic^-, we deal with the following equilibria:

$$\begin{tikzcd} Ag(pic)_2^- \arrow[r, shift left, "\beta_{12}^{-1}"] & Ag(pic) + pic^- \arrow[l, shift left] \arrow[d, shift left, "\beta_{01}^{-1}"] \\ & Ag^+ + pic^-. \arrow[u, shift left] \end{tikzcd}$$

Table 4. The concentration values found for particular Ag(I) forms vs. concentration of the complex $Ag(pic)_2^-$

$C^\circ_{Ag(pic)_2^-}$ mol/dm^3	$C^\circ_{pic^-}$ mol/dm^3	$[AgL_2]$ mol/dm^3	$[AgL]$ mol/dm^3	$[Ag^+]$ mol/dm^3
1×10^{-4}	–	3.021×10^{-6}	3.275×10^{-5}	6.423×10^{-5}
5×10^{-4}	–	6.067×10^{-5}	2.864×10^{-4}	1.529×10^{-4}
1×10^{-3}	–	2.016×10^{-4}	6.053×10^{-4}	1.931×10^{-4}
5×10^{-3}	–	2.302×10^{-3}	2.437×10^{-3}	2.605×10^{-4}
5×10^{-3}	2.5×10^{-2}	4.449×10^{-3}	5.443×10^{-4}	6.7×10^{-6}

The concentrations of particular Ag(I) forms vs. concentration of the complex $\mathrm{Ag}(pic)_2^-$ are given in Table 4.

It follows from the results listed in Table 4 that the solutions of $\mathrm{Ag}(pic)_2^-$ with concentration above $10^{-3}\,M$ contain mostly the $\mathrm{Ag}L^-$ form and a considerable amount of Ag^+ ions. In the solution containing $10^{-4}\,M$ of $\mathrm{Ag}(pic)_2^-$, about 33% of Ag(I) is in the form of simple Ag^+ ions. The composition of this solution makes it possible to determine the formal potential of the redox system:

$$\mathrm{Ag}(pic)_2^{\circ} + \mathrm{e} \rightleftarrows \mathrm{Ag}(pic)^{\circ} + pic^- . \qquad \text{(A)}$$

A considerable predominance of $\mathrm{Ag}(pic)_2^-$ appears in the solutions with a concentration of about $5 \times 10^{-3}\,M$ and excessive concentration of the ligand $-2.5 \times 10^{-2}\,M$. At a fivefold excess of pic^- ions, 89% of Ag(I) forms were included in the complex $\mathrm{Ag}(pic)_2^-$, which made it possible to determine the formal potential of the system:

$$\mathrm{Ag}(pic)_2^{\circ} + \mathrm{e} \rightleftarrows \mathrm{Ag}(pic)_2^- . \qquad \text{(B)}$$

Chronovoltamperograms of the following solutions were made: (1) $10^{-3}\,M$ $\mathrm{AgNO_3}$; (2) $10^{-3}\,M$ 2-pyridinecarboxylic acid; (3) $10^{-3}\,M$ sodium salt of 2-pyridinecarboxylic acid; (4) saturated solution $\cong 10^{-4}\,M$ $\mathrm{AgH}(pic)_2^{\circ}$; (5) $10^{-4}\,M$ $\mathrm{Ag}(pic)_2^-$; (6) $5 \times 10^{-3}\,M\,\mathrm{Ag}(pic)_2^- + 5 \times 10^{-2}\,M\;pic^-$.

All the solutions had a ionic strength of $\mu = 0.1$ (0.1 M $\mathrm{KNO_3}$). Solutions (3), (5) and (6) had $pH = 7$, ensuring the existence of pyridinecarboxylic acid in the form of anions.

The voltamperograms of solutions (1)–(5) were taken within the potential range $\varphi = -500\,\mathrm{mV}$ to $+1000\,\mathrm{mV}$ and that of solution (6) within the range $\varphi = +100$ to $+1000\,\mathrm{mV}$ vs. Ag/0.01 M $\mathrm{AgNO_3}$ + 0.1 M $\mathrm{KNO_3}$ as a reference electrode. The rate of potential sweep was $v = 10 - 100\,\mathrm{mV/s}$.

The voltamperograms of solutions (1)–(3) did not show current peaks within the anodic part of the curves. The saturated $\mathrm{AgH}(pic)_2^{\circ}$ solution (solution 4) shows in the CVA curves (Fig. 3, curve 1) no system associated with the oxidation of the chelate to the Ag(II) complex:

$$\mathrm{AgH}(pic)_2^{\circ} - \mathrm{e} \rightleftarrows \mathrm{Ag}(pic)_2^{\circ} + \mathrm{H}^+ .$$

The Ag(II) complex is formed, as was shown in coulometric measurements, during

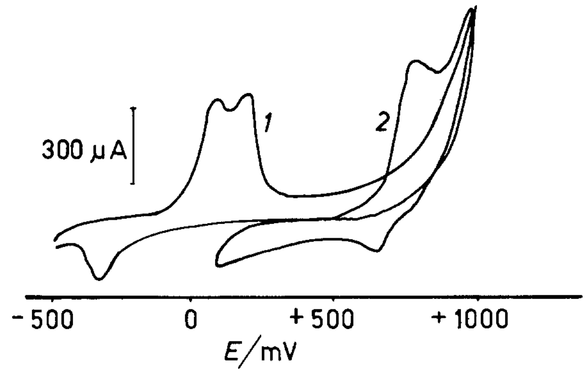


Fig. 3. Chronovoltamperometric curves of the solution: (1) $10^{-4}\,M$ $\mathrm{AgH}(pic)_2$ within the potential range $\varphi = -500$ to $+1000\,\mathrm{mV}$; (2) $5 \times 10^{-3}\,M$ $\mathrm{Ag}(pic)_2^- + 2.5 \times 10^{-2}\,M$ pic^- within the potential range -100 to $+1000\,\mathrm{mV}$ (φ vs. Ag/0.01 M $\mathrm{AgNO_3}$ + 0.1 M $\mathrm{KNO_3}$); $\mu = 0.1$; (0.1 M $\mathrm{KNO_3}$); $T = 298$ K; rate of potential sweep $v = 50\,\mathrm{mV/s}$

the electrolysis of solution (4) at $\varphi > 2.0\,\mathrm{V}$ vs. NHE. But comparing to analogous curve for solution (1), the voltamperogram of this solution shows a shift of the cathodic peak of the Ag^+ reduction and the adsorption anodic peak corresponding to dissolution of metallic silver. On the other hand, there appears an anodic peak with $\varphi = +200\,\mathrm{mV}$ corresponding to the system:

$$\mathrm{AgH}pic^+ + \mathrm{e} \rightleftarrows \mathrm{Ag}^\circ + \mathrm{H}pic. \qquad \text{(C)}$$

The reduction of Ag^+ and $\mathrm{AgH}pic^+$ ions takes place simultaneously, which results in a single cathodic peak observed. The electrodic processes shown in Fig. 3, curve 1 are irreversible, which makes it impossible to determine the formal potential of the system (C). The voltamperogram of solution (5), $10^{-4}\,M$ $\mathrm{Ag}(pic)_2^-$, does not show, besides the reduction of Ag^+ ions, any clearly shaped anodic and cathodic peaks for potentials $\varphi > 300\,\mathrm{mV}$ vs. Ag/0.01 M $AgNO_3$ + 0.1 M KNO_3, which makes it impossible to determine experimentally the formal potential of system (A).

During the CVA measurements of solutions (5) and (6), the working electrode is coated with a brown-red deposit of the complex $\mathrm{Ag}(pic)_2^\circ$, therefore, to obtain reproducible results, it was purified after each potential cycle, maintaining its constant surface.

The voltamperogram of solution (6) (Fig. 3, curve 2) shows the presence of redox system (B) being reversible at $v = 20\,\mathrm{mV/s}$ ($\Delta E_p = 50\,\mathrm{mV}$) and becoming quasi-reversible at higher values of v. The formal potential $E_f^\circ = 712 \pm 2\,\mathrm{mV}$, found from the CVA curves, corresponds to the value:

$$E_f^\circ = 712\,\mathrm{mV} + 678\,\mathrm{mV} = 1.388\,\mathrm{V}\ \text{vs. NHE.}$$

The value of E_f° found for the system:

$$\mathrm{Ag}(pic)_2^- - \mathrm{e} \rightleftarrows \mathrm{Ag}(pic)_2^\circ \qquad \text{(B)}$$

allows the determination of the complex formation constant β_{02} $\mathrm{Ag}(pic)_2^\circ$ and the formal potential of the system:

$$\mathrm{Ag}(pic) + pic^- - \mathrm{e} \rightleftarrows \mathrm{Ag}(pic)_2^\circ. \qquad \text{(A)}$$

The relationship between formal potentials of system (A) and (B) can be given by the equation:

$$E_f^\circ(\mathrm{A}) = E_f^\circ(\mathrm{B}) - 0.059 \log \beta_{12}(\mathrm{I})$$

hence

$$E_f^\circ(\mathrm{A}) = 1.388\,\mathrm{V} - 0.148\,\mathrm{V} = 1.240\,\mathrm{V}\ \text{vs. NHE.}$$

Then

$$E_f^\circ(\mathrm{B}) = E^\circ_{\mathrm{Ag}^{2+}/\mathrm{Ag}^+} - 0.059 \log \frac{\beta_{02}(\mathrm{II})}{\beta_{02}(\mathrm{I})}$$

hence β_{02} of the complex $\mathrm{Ag}(pic)_2^\circ$ is 1.26×10^{16}.

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