

## Complexing Equilibria and Redox Potentials of the Ag(II)/Ag(I) System in the Presence of 2,2':6',2''-Terpyridine in Water

Maksymilian Ignaczak\*, Andrzej Grzejdziak, and Barbara Olejniczak

Department of General and Inorganic Chemistry, University of Łódź, PL-90-136 Łódź, Poland

**Summary.** The conditional protonation constants ( $\mu = 0.1$ ) for 2,2':6',2''-terpyridine,  $\log K_1 = 4.93$ ,  $\log K_2 = 3.69$ , were determined by the *pH*-metric method. The compositions of complexes of  $\text{Ag}^{2+}$  and  $\text{Ag}^+$  ions with 2,2':6',2''-terpyridine (*tp*) were studied and equilibria of the complex formation process were described. The values of conditional complex formation constants are as follows: for  $\text{Ag}(tp)_2^+$ :  $\log \beta_{01} = 5.79$ ,  $\log \beta_{02} = 9.68$ , for  $\text{Ag}(tp)_2^{2+}$ :  $\log \beta_{02} = 25.31$ , while the conditional constant of the  $\text{Ag}(tp)\text{NO}_3$  precipitate formation is:  $K_{\text{SO}} = 2.45 \cdot 10^4$ . Using coulometric and chronovoltamperometric measurements, the redox systems being formed in the complex solutions of Ag(II) and Ag(I) were determined and described including their formal potentials.

**Keywords.** Chronovoltammetry; Formal potential; *pH*-metry; Redox systems with silver ions; Silver complexes.

### Komplexbildungsgleichgewichte und Redoxpotentiale des Systems Ag(II)/Ag(I) in Gegenwart von 2,2':6',2''-Terpyridin in Wasser

**Zusammenfassung.** Mit Hilfe der *pH*-metrischen Methode wurden die konditionalen Protonationskonstanten ( $\mu = 0.1$ ) von 2,2':6',2''-Terpyridin bestimmt:  $\log K_1 = 4.93$ ,  $\log K_2 = 3.69$ . Es wurde auch die Zusammensetzung der Komplexe von Ag(II) und Ag(I) mit 2,2':6',2''-Terpyridin (*tp*) bestimmt sowie die Gleichgewichte der Komplexbildung beschrieben. Die Werte der Konditionalkomplexbildungskonstanten sind: für  $\text{Ag}(tp)_2^+$ :  $\log \beta_{01} = 5.79$ ,  $\log \beta_{02} = 9.68$ , für  $\text{Ag}(tp)_2^{2+}$ :  $\log \beta_{02} = 25.31$  und für das Löslichkeitsprodukt  $\text{Ag}(tp)\text{NO}_3$ :  $K_{\text{SO}}^{-1} = 4.08 \cdot 10^{-5}$ . Die in Komplexlösungen von Ag(II) und Ag(I) vorliegenden Redoxsysteme wurden mittels cyclischer Voltammetrie und Coulometrie untersucht und die Formalpotentialwerte dieser Systeme in Wasser bestimmt.

### Introduction

The Ag(II)/Ag(I) system whose high standard potential  $E^0 = 1.98 \text{ V}$  [1] can be modified by complexing both silver ions, is of a considerable significance in non-conventional methods of organic synthesis. Therefore, numerous fundamental studies have been carried out on the Ag(II)/Ag(I) systems formed with heterocyclic nitrogen bases in water and nonaqueous solvents [2–8]. Studies carried out in our laboratory have allowed to characterize redox systems of this type with pyridine in water [9], with 2,2'-bipyridine in water and acetonitrile [10, 11], with 1,10-phenanthroline in water, acetonitrile and propylene carbonate [11–13] as well as to

characterize the complexes of Ag(II) with those ligands in the mentioned solvents [14].

The present study was aimed at the characteristics of the Ag(II)/Ag(I) system in the presence of 2,2':6',2''-terpyridine. There are only few data available concerning the complexing properties of this ligand. Protonation constants for terpyridine [15] and its complex formation constants with  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  [16] have been determined. The complexes of Ag(I) and Ag(II) ions with terpyridine are known [3, 17–19] and even a spectrophotometric method of quantitative determination of Ag(II) ions by complexing with the mentioned ligand has been reported [20]. The results given in papers [3, 17–19] are contradictory and give no clear information on the composition and stability of the complexes. Hence, we have considered it useful to characterize the complexing processes and to establish conditions and possibilities for the existence of the particular complexes. Knowing these equilibria, we were able to describe the redox systems in solutions by electroanalytical methods.

## Experimental

2,2':6',2''-Terpyridine was prepared by arylation of 2,2'-bipyridine with 2-lithopyridine according to the method of Kauffman [21]. The product was separated by the column chromatography (filler— $\text{Al}_2\text{O}_3$ , basic or neutral) and then crystallized from hexane. Melting point of the final product was 93–94°C.

$\text{AgNO}_3$ ,  $\text{KNO}_3$  and  $\text{HNO}_3$  were analytically pure products of POCh-Gliwice.

Silver(II)di(2,2':6',2''-terpyridine)nitrate— $\text{Ag}(tp)_2(\text{NO}_3)_2$  was obtained from AgO in the presence of excess terpyridine at molar ratio 1 : 3, in 2 M  $\text{HNO}_3$  at a temperature of 0°C according to Thorpe and Kochi [22]. A brown precipitate was filtered off, washed with a 0.1 M  $\text{KNO}_3$  solution and dried under vacuum over  $\text{CaCl}_2$ . Possible terpyridine impurities were washed off from the product with benzene [19] and the product was dried again. The Ag(II) ion content in the complex was determined by the amperometric method using  $\text{Na}_2\text{C}_2\text{O}_4$  in 2 M  $\text{HNO}_3$  according to the procedure described previously [12].

Silver(I)(2,2':6',2''-terpyridine)nitrate— $\text{Ag}(tp)\text{NO}_3$  was prepared from  $10^{-2}$  M  $\text{Htp}^+$  solutions by adding stoichiometric quantities of  $10^{-2}$  M  $\text{AgNO}_3$  solution.

The white amorphous precipitate obtained was synthesized directly with  $\text{AgNO}_3$  and 2,2':6',2''-terpyridine (molar ratio 1 : 1.1) in a 85% aqueous  $\text{C}_2\text{H}_5\text{OH}$  solution according to Morgan [17]. After crystallization, a precipitate in the form of white needles was obtained.

The apparatus used for coulometric, chronovoltamperometric and potentiometric measurements has been described previously [10, 12]. IR, UV and VIS spectra were taken with Specord 71 IR and Specord UV VIS spectrophotometers. Measurements of *pH* were carried out with an OP-211/1 *pH*-meter of Radelkis with an accuracy of  $\pm 0.01$  unit of *pH*.

## Results

### *Determination of the Composition of Complexes of Ag(II) with 2,2':6',2''-Terpyridine*

Quantitative analysis of the complex with 2,2':6',2''-terpyridine [synthesis at the molar ratio Ag(II) : L = 1 : 3] showed the following composition of the compound: Ag 15.3, C 50.5, N 15.5, H 3.4, O 15.3%; the theoretical composition of  $\text{Ag}(tp)_2(\text{NO}_3)_2$  is as follows: Ag 15.44, C 51.59, N 16.05, H 3.17, O 13.7%, the quantitative composition of  $\text{Ag}(tp)_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  is: Ag 15.05, C 50.30, N 15.64, H 3.38, O 15.63%. Thus, the analysis showed that it is a complex of the type  $\text{AgL}_2(\text{NO}_3)_2$ , and most certainly its hydrate:  $\text{Ag}(tp)_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ .

This is contrary to the results of Morgan and Burstall [17] who have stated that only the existence of the  $\text{Ag}(tp)(\text{NO}_3)_2$  complex is possible, in which the fourth ligand atom would be the atom of  $\text{NO}_3^-$  ion associated with  $\text{Ag}^{2+}$  by covalent bonds. The synthetic procedure of Morgan and Burstall, consisting of the oxidation of  $\text{AgNO}_3$  in the presence of terpyridil (molar ratio 1 : 1) with  $\text{Na}_2\text{S}_2\text{O}_8$  could not result in the formation of the  $\text{Ag}(tp)_2(\text{NO}_3)_2$  complex.

The IR spectra taken by us for the final product show a strong band at  $\nu = 1390\text{--}1400\text{ cm}^{-1}$  corresponding to the  $\text{NO}_3^-$  ion, a band at  $\nu = 3400\text{ cm}^{-1}$  characteristic for OH group, but there are no strong absorption bands within the ranges  $1250\text{--}1290\text{ cm}^{-1}$  and  $1480\text{--}1530\text{ cm}^{-1}$ , characteristic for covalently bonded nitrate ion [23].

The above results show that the product obtained by us is a complex of the type  $\text{AgL}_2\text{X}_2$  as the previously obtained compounds  $\text{Ag}(tp)_2\text{S}_2\text{O}_8$  [19],  $\text{Ag}(tp)_2(\text{ClO}_4)_2$  and  $\text{Ag}(tp)_2\text{ClO}_4\text{NO}_3$  [3] in which the  $\text{Ag}(\text{II})$  ion is surrounded by 6 coordinated nitrogen atoms and it probably assumes the structure of a deformed octahedron as in some complexes of  $\text{Cu}^{2+}$ .

A similar coordination number is revealed by the complex of  $\text{Ag}(\text{II})$  with pyridine-2,6-dicarboxylic acid and complexes with mixed ligands of nitrogen heterocyclic bases-pyridinecarboxylic acids [19, 24]. Our synthesis at the molar ratio  $\text{Ag}(\text{II}) : L = 1 : 1.1$  resulted in a compound with the quantitative composition: Ag 21.6, C 36.0, H 2.9, N 14.1, O 25.4%, which corresponds to the formula  $\text{Ag}(tp)(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ .

The VIS spectra of both compounds show different positions of the absorption bands: for  $\text{Ag}(tp)_2(\text{NO}_3)_2$  at  $\lambda = 460\text{ nm}$  ( $\epsilon = 1250$ ), and for  $\text{Ag}(tp)(\text{NO}_3)_2$  at  $\lambda = 480\text{ nm}$  ( $\epsilon = 900$ ) ( $10^{-3}\text{ M}$  solutions with ionic strength  $\mu = 0.1$  from  $\text{KNO}_3$ ).

#### Determination of Conditional Protonation Constants for 2,2':6',2'':Terpyridine

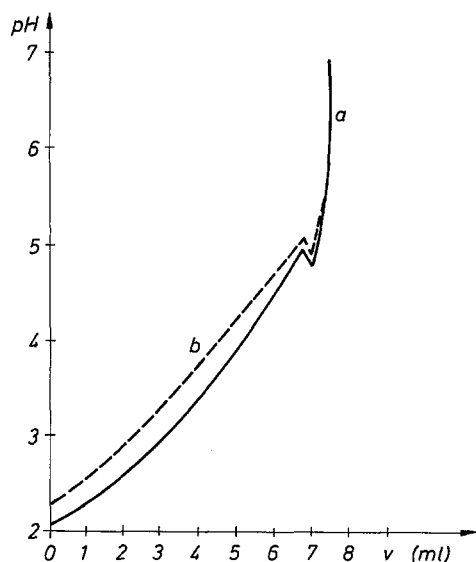
2,2':6',2'':terpyridine is a dibasic ligand. Its protonation constants, determined spectrophotometrically in solutions with ionic strength  $\mu = 0.01$ , are  $K_1 = 10^{4.7}$  and  $K_2 = 10^{3.3}$ . The constants for solutions with ionic strength  $\mu = 0.1$  ( $0.1\text{ M KNO}_3$ ) were determined by *pH*-metry.

Solutions with the composition:  $c\text{ M } tp + 3c\text{ M HNO}_3$  (where  $c$  is within  $10^{-2}\text{--}10^{-3}\text{ M}$ ) were titrated with a  $0.098\text{ M NaOH}$  solution. A typical titration curve is given in Fig. 1.

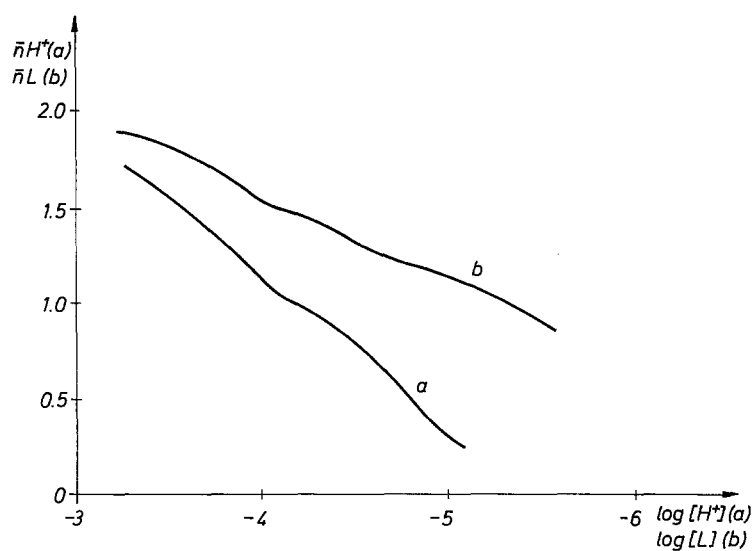
It follows from Fig. 1 a and the curve for the formation of protonated forms of terpyridine, calculated from the titration curves (Fig. 2 a) that the difference in the logarithms of the *tp* protonation constants is lower than 2.8 ( $\log K_1 \sim 4.8$ ,  $\log K_2 \sim 3.6$ ), thus the values of constants calculated from the equation

$$\log K_i = \log \frac{(1 - a + n - i)C_{\text{HnL}} - [\text{H}^+] + [\text{OH}^-]}{(a - n + i)C_{\text{HnL}} + [\text{H}^+] - [\text{OH}^-]} + pH$$

(where  $K_i$  is the  $i^{\text{th}}$  protonation constant of *L* and  $a$  is the degree of neutralization) would be inexact. Therefore, the method of Schwarzenbach was used to calculate  $K_1$  and  $K_2$  numerically:  $\log K_1 = 4.93 \pm 0.01$ ,  $\log K_2 = 3.69 \pm 0.01$ ,  $K_1 = (8.5 \pm 0.2) 10^4$ ,  $K_2 = (4.9 \pm 0.2) 10^3$ , the correlation coefficient being  $R = 0.997$ . The drop in curve 1 for  $pH \sim 5$  ( $pH > \log K_1$ ) is associated with precipitation of non-protonated terpyridine which is sparingly soluble in water.



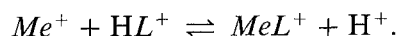
**Fig. 1.** Titration curves: (a) 50 cm<sup>3</sup> solution of  $5 \cdot 10^{-3} M$  2,2':6',2''-terpyridine +  $1.5 \cdot 10^{-2} M$  HNO<sub>3</sub> (—); (b) 50 cm<sup>3</sup> solution of  $5 \cdot 10^{-3} M$  2,2':6',2''-terpyridine +  $1.5 \cdot 10^{-2} M$  HNO<sub>3</sub> +  $1 \cdot 10^{-5} M$  AgNO<sub>3</sub> with a 0.098 M NaOH solution  $\mu = 0.1$  (0.1 M KNO<sub>3</sub>);  $T = 298 K$  (---)



**Fig. 2.** (a) Curve of formation of protonated forms 2,2':6',2''-terpyridine (calculated from the titration curve from Fig. 1 a); (b) Formation curve for the Ag(I) complexes with 2,2':6',2''-terpyridine (calculated from the titration curve from Fig. 1 b),  $\mu = 0.1$  (0.1 M KNO<sub>3</sub>);  $T = 298 K$

#### Determination of Conditional Complex Formation Constants $\beta_{01}$ and $\beta_{02}$ for Ag(I) Complexes with 2,2':6,2''-Terpyridine

The formation constants for the Ag(I) complexes with terpyridine were determined by *pH*-metry in solutions with  $\mu = 0.1$  (0.1 M KNO<sub>3</sub>). The complexing compound in the protonated form was titrated potentiometrically with a standard NaOH solution in the presence of AgNO<sub>3</sub>. During titration protons are released according to the reaction



In this case, change in  $pH$  of the solution allows to determine the equilibrium state of complexation.

Solutions with compositions:  $c M tp + 3 c M HNO_3 + 0.2 c M AgNO_3$  (where  $c = 10^{-2} M - 10^{-3} M$ ) were titrated with a  $0.098 M NaOH$  solution. A typical titration curve is given in Fig. 1 b.

The complexing compound under the measurement conditions is a diprotonated base, hence the concentration of "free" (non-protonated form) ligand is given by the equation

$$[L] = \frac{(2 - a)C_{H_2L^{2+}} - [H^+] + [OH^-]}{[H^+]K_1 + 2[H^+]^2K_1 \cdot K_2}.$$

The average number of ligands associated with one metal ion is described by the equation

$$\bar{\eta} = \frac{C_{H_2L^{2+}} - [L]\alpha_{L(H)}}{C_{Me}},$$

where  $\alpha_{L(H)}$  is a function of the ligand protonation.

The curve of  $Ag(I)$  complex formation with 2,2':6',2''-terpyridine (Fig. 2 b) shows that at  $C_{H_2L}:C_{Me} = 1:5$  within the investigated  $pH$  range, values of  $\bar{\eta}$  are higher than 0.8. This indicates the preponderance of the  $Ag(tp)_2^+$  form under the complexing conditions. Therefore, it was impossible to find the formation constants  $\beta_{01}$  and  $\beta_{02}$  by the graphic method of Bjerrum. They were calculated numerically [25] using the method of linear equations by means of the function

$$\bar{n} - \sum_1^N (\bar{n} - n) \beta_n [L]^n = 0,$$

where  $n$  and corresponding  $[L]$  values were taken from the curve in Fig. 2 b. The calculated complexation constants are:  $\log K_{C_1} = 5.79 \pm 0.03$ ,  $\log K_{C_2} = 3.89 \pm 0.02$ , with the correlation coefficient being  $R = 0.977$ . Hence, the total complex formation constants are

$$\log \beta_{01} = 5.79 \pm 0.03, \quad \log \beta_{02} = 9.68 \pm 0.03,$$

and

$$\beta_{01} = (6.16 \pm 0.4) \cdot 10^5, \quad \beta_{02} = (4.79 \pm 0.5) \cdot 10^9.$$

The present results prove that at a considerable molar excess of the ligand to the central ion (5:1) complex  $Ag(tp)_2^+$  is formed. If all the nitrogen atoms in two 2,2':6',2''-terpyridine molecules could form coordination bonds, the  $Ag(I)$  ion would be surrounded in the complex ion molecule by 6 nitrogen atoms, and the complex would possess a structure of an octahedron, which seems to be hardly probable. Presumably, in this case, the coordination bonds are formed by the two terminal nitrogen atoms of the three ones possessing ligand properties, and the complex possesses the structure of a flat square as in  $Ag(phen)_2^+$  and  $Ag(bipy)_2^+$  ions ( $phen$ —1,10-phenanthroline,  $bipy$ —bipyridine) [10, 12–14]. It is, however, difficult to verify this supposition due to the lack of possibility to isolate the complex  $Ag(tp)_2^+$ .

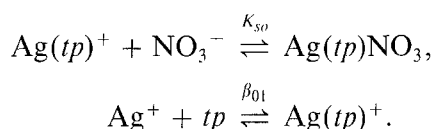
The existence of complex  $Ag(tp)_2^+$  is confirmed by potentiometric measurements with simultaneous measurements of  $pH$  and the  $Ag^+$  ion concentration

against Ag/0.01 M AgNO<sub>3</sub> + 0.1 M KNO<sub>3</sub> as a reference electrode. The values of  $\beta_{01}$  and  $\beta_{02}$  obtained by this method are in agreement with those obtained by *pH*-metry with an error of  $\pm 5\%$ .

#### Determination of Conditional Constant $K_{so}$ of the Ag(*tp*)NO<sub>3</sub> Precipitate Formation

As Ag<sup>+</sup> ions are added to Ag(*tp*)<sub>2</sub><sup>+</sup> solutions (at molar ratio  $L : Ag^+ \sim 1 : 1$ ), a white Ag(*tp*)NO<sub>3</sub> precipitate can be observed. To determine the precipitate formation constant, concentrations of Ag<sup>+</sup> ions in saturated solutions, being in equilibrium with the complex precipitate, were measured potentiometrically. All the solutions possessed an ionic strength of 0.1 established with NaClO<sub>4</sub> and NaNO<sub>3</sub>.

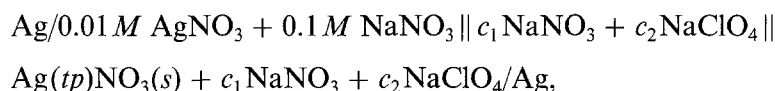
The equilibria taking place in the system under investigation may be given as follows:



The precipitate formation constant is described by the equation

$$K_{so}^{-1} = C_{exp}^2 \beta_{01} c_{NO_3^-},$$

where  $C_{exp}$  denotes the equilibrium concentration of Ag<sup>+</sup> ions in solution. The values of  $C_{exp}$  were determined by a measurement of EMF of the following cell



$c_1 + c_2 = 0.1 M$ , using variable concentrations of NO<sub>3</sub><sup>-</sup> ions. The results of measurements are given in Table 1.  $K_{so(0.1)} = (2.45 \pm 0.1) \cdot 10^4$ .

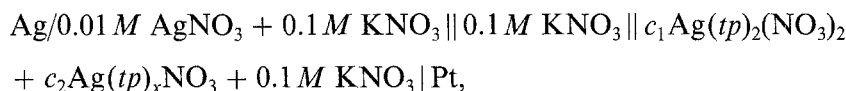
#### Coulometric Measurements

Coulometric measurements were carried out to determine the formal potentials of redox systems present in solutions of Ag(II) and Ag(I) complexes with 2,2':6',2''-terpyridine. Amperostatic coulometry was used to reduce solutions with variable

**Table 1.** Results of potentiometric determination of conditional constant  $K_{so(0.1)}$  of Ag(*tp*)NO<sub>3</sub> formation; values of EMF vs. Ag<sup>0</sup>/0.01 M AgNO<sub>3</sub> + 0.1 M NaNO<sub>3</sub>;  $\mu = 0.1$ ;  $T = 298 K$

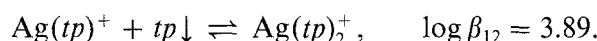
$c_{NO_3^-}$ mol/dm <sup>3</sup>	EMF mV	$c_{exp} \cdot 10^{-5}$ mol/dm <sup>3</sup>	$K_{so}^{-1} \cdot 10^{-5}$	$K_{so} \cdot 10^4$
$10^{-1}$	-148	2.59	4.14	2.42
$8 \cdot 10^{-2}$	-145	2.92	4.22	2.37
$6 \cdot 10^{-2}$	-142	3.30	4.03	2.48
$4 \cdot 10^{-2}$	-137	4.03	4.01	2.49
$2 \cdot 10^{-2}$	-128	5.79	4.13	2.42
$10^{-2}$	-120	8.00	3.94	2.54

concentrations of  $\text{Ag}(tp)_2(\text{NO}_3)_2$  and  $\mu = 0.1$ . The electrolysis and EMF measurement (currentless) were carried out in the system

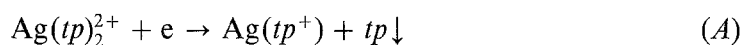


where  $c_1 + c_2 = c$  is the initial concentration of the complex  $\text{Ag}(tp)_2(\text{NO}_3)_2$ . The conditions for coulometric measurements are determined by the values of complexation constants for  $\text{Ag}^+$  ions:  $\beta_{01} = 6.16 \cdot 10^5$  and  $\beta_{02} = 4.79 \cdot 10^9$  and  $K_{\text{soAg}(tp)\text{NO}_3}^{-1} = 4.08 \cdot 10^{-5}$ .

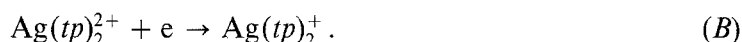
The  $\text{Ag}(tp)_2(\text{NO}_3)_2$  complex is a stable one and appears in solution only in the form of the  $\text{Ag}(tp)_2^{2+}$  ion. But in the case of  $\text{Ag(I)}$  we deal with  $\text{Ag}(tp)_2^+$  and  $\text{Ag}(tp)^+$  ions associated with each other within the equilibrium



The possible redox systems being formed during the reduction of  $\text{Ag}(tp)_2^{2+}$  in neutral solutions are:



and



The values of  $\beta_{01}$  and  $\beta_{02}$  show, in addition, that we would deal with system (B) at the initial concentration of the  $\text{Ag}(tp)_2^{2+}$  complex  $\sim 2 \cdot 10^{-2} M$ , while with system (A) for  $c_{\text{Ag}(tp)_2^{2+}} \sim 4 \cdot 10^{-5} M$ .

It is impossible to obtain a concentration of  $\text{Ag}(tp)_2^+$  of about  $2 \cdot 10^{-2} M$  due to its limited solubility. Therefore, the reduction was carried out for  $\text{Ag}(tp)_2(\text{NO}_3)_2$  solutions with  $c \leq 4 \cdot 10^{-5} M$ .

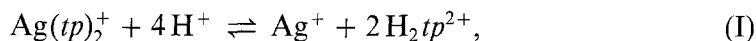
This allowed, at the same time, to maintain the concentration of  $\text{Ag}(tp)^+$  in the reduced solution at a lower level than that corresponding to the value of  $K_{\text{soAg}(tp)\text{NO}_3}^{-1}$ .

Another important factor in the coulometric measurements is the choice of  $pH$  of the solution being reduced. It is determined by the values of protonation constants  $K_1$  and  $K_2$  for 2,2':6',2''-terpyridine:  $K_1 = 8.5 \cdot 10^4$ ,  $K_2 = 4.17 \cdot 10^8$ . The course of the protonation function for the  $\alpha_{L(H)}$  ligand versus  $pH$  shows that at  $pH \geq 6$  protonated ligands will not be observed (Table 2).

**Table 2.** Participation of particular forms of 2,2':6',2''-terpyridine in solutions depending on  $pH$

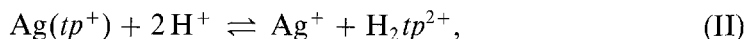
$pH$	% $tp$	% $Htp^+$	% $H_2tp^{2+}$
2	0	2.0	98.0
3	0.2	16.9	82.9
4	7.3	62.2	30.5
5	52.9	44.9	2.2
6	92.1	7.8	0.1

In solution with  $pH \leq 2$  the  $H_2tp^{2+}$  ion is the dominating form of the ligand. There will be a complete decomposition of  $Ag(tp)_2^+$  or  $Ag(tp)^+$  according to the equations



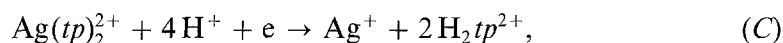
$$K_I = \frac{(K_1 \cdot K_2)^2}{\beta_{02}} = 3.63 \cdot 10^7$$

or



$$K_{II} = \frac{K_1 \cdot K_2}{\beta_{01}} = 676.$$

Under these conditions, we would deal with the system



$$\begin{aligned} E_{fc} &= E_{Ag(tp)_2^{2+}/Ag(tp)_2^+}^0 + 0.1182 \log K_1 K_2 - 0.0591 \log \beta_{02} \\ &= E_{Ag(tp)_2^{2+}/Ag(tp)_2^+}^0 + 0.446 \text{ V}, \end{aligned}$$

possessing a very high formal potential.

The  $Ag(tp)_2^{2+}$  complex would be, then, reduced chemically at a high rate resulting in water oxidation, and the measurements of coulometric reduction would lose their meaning.

The reduction of  $Ag(tp)_2^{2+}$  solutions within the  $pH$  range 3–5 resulted in the formation of all possible ligand forms in comparable quantities and consequently in the formation of redox systems with mixed potential, practically impossible to be measured. Hence, the coulometric measurements had to be carried out for  $Ag(tp)_2^{2+}$  concentrations  $\leq 4 \cdot 10^{-5} M$ , at  $pH \sim 6$ . The reduction comprised: (a) weighed portions of the  $Ag(II)$  complex directly after dissolving in water and (b) after previous anodic oxidation of the complex an EMF value as high as possible in the system. The EMF values of the system were measured versus the reduction time; the curves obtained were of the same shape as those of redox titration with a potential drop at  $c_1 Ag(II) = c_2 Ag(I)$ . In the vicinity of the end-point, a precipitate was observed (as in the acid-base titration curves) readily soluble in  $0.1 M HNO_3$ . Thus it was the ligand precipitate. Concentrations of  $Ag(tp)_2^{2+}$  were within the range  $1\text{--}4 \cdot 10^{-5} M$ ; oxidation and reduction were carried out at a current strength of 1 mA. The determined transition electronity (at an assumed yield 100%) was  $-1$  in all cases, while the value of formal potential was  $E_f^0 = 1.056 \text{ V}$  vs. NHE.

#### *Chronovoltamperometric Measurements*

Voltamperograms of the following solutions were made:

(a) Saturated solution of  $Ag(tp)NO_3$  complex ( $c = 4 \cdot 10^{-4} M$ ) +  $tp$  ( $c = 4 \cdot 10^{-4} M$ ).

(b) Solution of  $Ag(tp)_2(NO_3)_2$  with  $c = 4 \cdot 10^{-4} M$ .



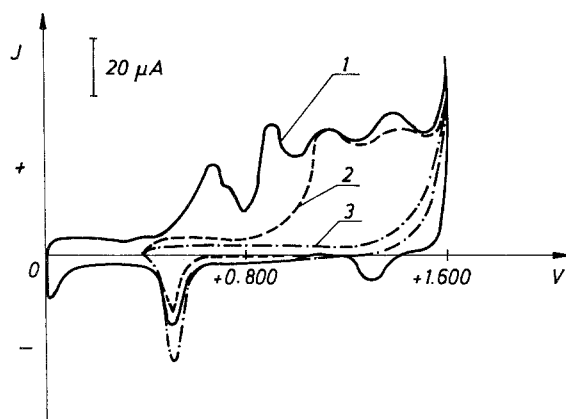
(c) Solution (b) anodically oxidized to as high EMF (values as possible in the system within the potential range + 600 to + 1 600 mV vs. NHE at  $pH = 5.3$  and 1.5.

(d) Solutions (a) and (b) within the potential range from 0 to + 1 600 mV vs. NHE at  $pH 5$ .

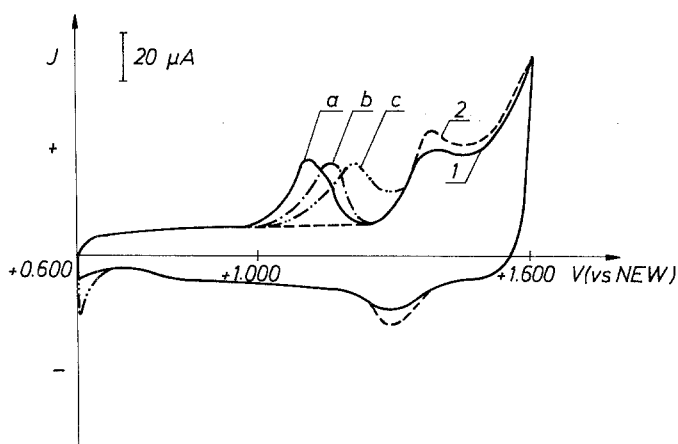
(e) Solutions (a) and (b) within the potential range from + 400 mV to + 1 600 mV vs. NHE at  $pH 5$ .

(f) Solution of  $2 \cdot 10^{-4} M$  2,2':6',2''-terpyridine in  $0.1 M KNO_3$ .

The ionic strength of all the solutions was  $\mu = 0.1$  ( $0.1 M KNO_3$ ). The curves were recorded against  $Ag/0.01 M AgNO_3 + 0.1 M KNO_3$  with a salt-bridge containing  $0.1 M KNO_3$ . The rate of potential sweep was 10–200 mV/s. Exemplary chronovoltamperometric curves are shown in Figs. 3 and 4.



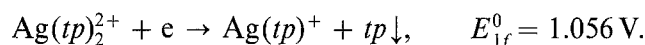
**Fig. 3.** Chronovoltamperometric curves: (1) solution of  $Ag(tp)_2(NO_3)_2$  ( $C = 4 \cdot 10^{-4} M$ ); (2) saturated solution of  $Ag(tp)NO_3$  ( $c = 4 \cdot 10^{-4} M + 4 \cdot 10^{-4} M tp$ ); (3) solution of  $0.1 M KNO_3 + 4 \cdot 10^{-4} M tp$ ;  $pH = 5$ ;  $\mu = 0.1$  ( $0.1 M KNO_3$ );  $T = 298 K$ ;  $V = 20 mV/s$



**Fig. 4.** Chronovoltamperometric curves: (1) saturated solution of  $Ag(tp)NO_3$  ( $c = 4 \cdot 10^{-4} M + 4 \cdot 10^{-4} M tp$ ); (a)  $pH = 5$ ; (b)  $pH = 3$ ; (c)  $pH = 1.5$ ; (2) oxidized solution of  $Ag(tp)_2(NO_3)_2$  ( $c = 4 \cdot 10^{-4} M$ )  $pH = 5$ , from + 600 to + 1 600 mV vs. NHE;  $\mu = 0.1$  ( $0.1 M KNO_3$ );  $T = 298 K$ ;  $V = 20 mV/s$

## Discussion

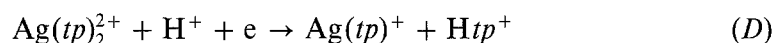
The course of the coulometric reduction curves for solutions of  $\text{Ag}(tp)_2(\text{NO}_3)_2$  at  $pH$  6 points to the presence of redox system associated with a single electron exchange and with a formal potential of  $E_{1f}^0 = 1.056$  V. The value of  $E_{1f}^0$  excludes the possibility of reduction of  $\text{Ag(II)}$  complex to metallic silver. The 2,2':6',2''-terpyridine precipitate appearing during reduction, together previous considerations, lead to the conclusion that the only possible system is the following one,



The existence of this system and the value of  $E_{1f}^0$  are confirmed by the anodic peaks in the region  $\varphi \sim 1100$  mV in chronovoltamperograms of the saturated  $\text{Ag}tp^+$  complex (Fig. 3, curve 2, Fig. 4, curve 1 a) at  $pH$  5 and of the  $\text{Ag}(tp)_2(\text{NO}_3)_2$  complex within the potential range from 0 to +1600 mV vs. NHE (Fig. 3, curve 1).

The voltamperograms point to the existence of an irreversible redox system. An ultimate identification of the system is impossible for lack of possible separation of the cathodic peak (the reduction takes place together with the reduction and desorption of oxygen from the electrode (Fig. 3)). The reduction curves of oxidized solutions of the  $\text{Ag(II)}$  complex gave the same value of  $E_{1f}^0$ , and their initial course (for  $\text{EMF} \geq +1300$  mV) shows that in solution of  $\text{Ag}(tp)_2^{2+}$  ions there is a system with higher potential than that of  $E_{1f}^0$ . However, the coulometric measurements failed to provide a second potential drop. The analysis of chronovoltamperometric curves (Figs. 3 and 4) has confirmed the above hypothesis. The curves suggest a single electron transition in the region from +1300 to +1400 mV vs. NHE. Under the measurement conditions (rates of potential sweep –10–200 mV/S)  $\Delta E_{\text{Peak}} \approx 60$  mV, thus it is a reversible redox system.

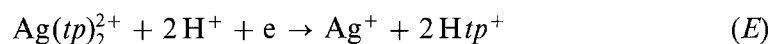
Possible systems with higher formal potential than  $E_{1f}^0$  are as follows:



with

$$E_{Df}^0 = E_{1f}^0 + 0.0591 \log K_1 = 1.347 \text{ V}$$

and

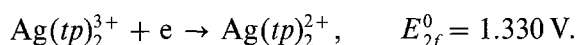


with

$$E_{Ef}^0 = E_{1f}^0 + 0.1182 \log K_2 - 0.0591 \log \beta_{01} = 1.296 \text{ V.}$$

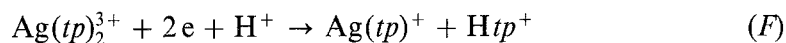
The potentials of anodic and cathodic peaks and the formal potential obtained for this system  $E_{2f}^0 = 1.330$  V do not depend, however, on the  $pH$  of solution (investigated  $pH$  range 1.5–6.0).

Therefore, the only possible one is the redox system containing  $\text{Ag(III)}$  ions:



The existence of this system is confirmed by the UV spectrum of the oxidized  $\text{Ag}(tp)_2(\text{NO}_3)_2$  complex, showing a weak absorption maximum at  $\lambda = 275$  nm [26, 27], pointing to the existence of  $\text{Ag}(tp)_2^{3+}$  ions (though in small quantities). The constancy of  $E_{2f}^0$  with variable  $pH$  and the single-electron transition eliminate also

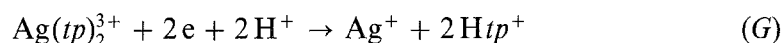
the possibility of existence for redox systems with  $\text{Ag}(tp)_2^{3+}$  with similar formal potential, such as



with

$$E_{Ff}^0 = \frac{E_{1f}^0 + E_{2f}^0}{2} + 0.03 \log K_1 = 1.339 \text{ V}$$

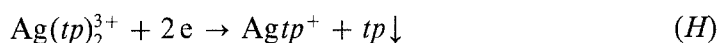
and



with

$$E_{Gf}^0 = \frac{E_{1f}^0 + E_{2f}^0}{2} + 0.0591 \log K_1 - 0.03 \log \beta_{01} = 1.313 \text{ V}$$

and also

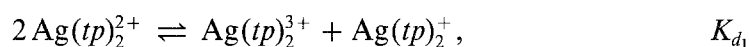


with

$$E_{Hf}^0 = \frac{E_{1f}^0 + E_{2f}^0}{2} = 1.193 \text{ V},$$

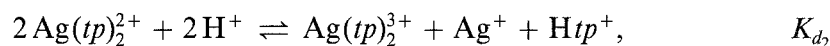
appearing usually in solutions of oxidized complexes of Ag(II) with nitrogen heterocyclic bases [10, 12] in which disproportionation takes place.

The calculated values of disproportionation equilibrium constants for  $\text{Ag}(tp)_2^{2+}$ :



$$\log K_{d_1} = \frac{E_{1f}^0 + E_{2f}^0}{0.0591}, \quad K_{d_1} = 1.3 \cdot 10^{-5},$$

and



$$K_{d_2} = K_{d_1} \frac{K_1^2}{\beta_{02}}, \quad K_{d_2} = 1.96 \cdot 10^{-5},$$

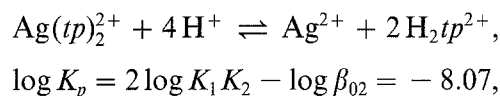
show that the disproportionation extent, both in neutral and acidic solutions, is small (not exceeding 1%) and excludes additionally the existence of systems (F), (G) and (H).

Known values of  $E_{1f}^0$ ,  $E_{\text{Ag}^{2+}/\text{Ag}^+}^0 = 1.98 \text{ V}$  and of  $\beta_{02} \text{Ag}(tp)_2^+$  allow to calculate the  $\text{Ag}(tp)_2^{2+}$  complex formation constant,

$$\log \beta_{02\text{Ag}(tp)_2^{2+}} = \frac{E_{\text{Ag}^{2+}/\text{Ag}^+}^0 + E_{1f}^0}{0.0591} + \log \beta_{02\text{Ag}(tp)_2^+} = 25.31,$$

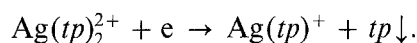
$$\beta_{02\text{Ag}(tp)_2^{2+}} = 2.06 \cdot 10^{25}.$$

The value of  $\beta_{02 \text{ Ag(II)}}$  and the calculated value of equilibrium constant of the process:



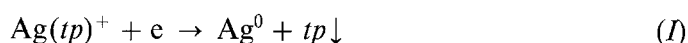
support the initial assumption concerning the stability of  $\text{Ag}(tp)_2^{2+}$  and lack of its protonation.

The chronovoltamperograms of the saturated  $\text{Ag}tp^+$  solution (Fig. 4) show a shift of the oxidation peak of the complex towards higher potential values with decreasing  $pH$ , while at  $pH 5$   $E_{pa}$  can be ascribed to the system



The shift of peaks may be relatively simply elucidated by the formation with increasing solution acidity of systems (D) and (E) with higher formal potentials than  $E_{1f}^0$ . It is, however, impossible in the voltamperometric measurements to determine more closely the content of these systems in electrodic layer.

Finally, the anodic peaks in the regions  $\sim 650$  mV and  $900$  mV, visible in the chronovoltamperometric curves, correspond to the systems



with

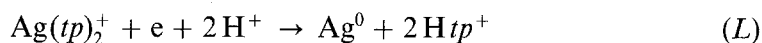
$$E_{1f}^0 = E_{\text{Ag}^+/\text{Ag}^0}^0 - 0.0591 \log \beta_{01} = 0.457 \text{ V},$$

$$\text{Ag}(tp)^+ + e + \text{H}^+ \rightarrow \text{Ag}^0 + \text{H}tp^+ \quad (K)$$

with

$$E_{Kf}^0 = E_{1f}^0 + 0.0591 \log K_1 = 0.748 \text{ V},$$

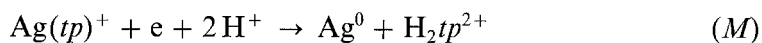
or



with

$$E_{Lf}^0 = E_{\text{Ag}^+/\text{Ag}^0}^0 + 0.1182 \log K_1 - 0.0591 \log \beta_{02} = 0.810 \text{ V},$$

or



with

$$E_{Mf}^0 = E_{\text{Ag}^+/\text{Ag}^0}^0 + 0.0591 \log K_1 K_2 - 0.0591 \log \beta_{01} = 0.969 \text{ V}.$$

The height of the first discussed peak drops with increasing rate of the potential sweep, which confirms the desorption of metallic silver atoms from the electrode and its oxidation associated with complexation.

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