Studies on the Equilibria in Ag(I) – 1,4,8,11-Tetraazacyclotetradecane and Ag(I) – 1,4,8,11-Tetramethyl-1,4,8,11-Tetraazacyclotetradecane Systems in Water

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Summary. Protonation constants of 1,4,8,11-tetraazacyclotetradecane ($TACT$) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane ($TMTACT$) ($\mu = 0.1$) were determined by pH-metry. The values are $\log K_1 = 10.922$, $\log K_2 = 10.511$, $\log K_3 = 2.646$, $\log K_4 = 1.620$ for $TACT$, and $\log K_1 = 9.387$, $\log K_2 = 9.050$, $\log K_3 = 2.491$, $\log K_4 = 1.380$ for $TMTACT$. Absorption maxima of the complexes $AgTACT(NO_3)_2$ and $AgTMTACT(NO_3)_2$ were found to be $\lambda_1 = 280\,nm$, $\lambda_2 = 350\,nm$, and $\lambda_1 = 290\,nm$, $\lambda_2 = 400\,nm$, respectively. The disproportionation constants of Ag(I) ions in the presence of the amines were determined by potentiometry: for $TACT$ $\log K_d = 12.778$, and for $TMTACT$ $\log K_d = 11.778$. The mechanisms of the electrode processes taking place in solutions of the complexes under investigation were examined by means of chronovoltamperometric and coulometric measurements. The formal potential, E_f^0, of the system: $AgTMTACT^{2+} + e \rightleftharpoons AgTMTACT^+$ is $+0.450\,V$ vs. NHE.

Keywords. Chronovoltammetry; Coulometry; Formal potential; Redox systems; Silver complexes; Tetraazamacrocyclic amines; Water.

Untersuchungen zu den Gleichgewichten Ag(I) – 1,4,8,11-Tetraazacyclotetradekan und Ag(I) – 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradekan in Wasser

Zusammenfassung. Die Protonierungskonstanten von 1,4,8,11-Tetraazacyclotetradekan ($TACT$) und 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradekan ($TMTACT$) wurden pH-metrisch bei $\mu = 0.1$ bestimmt. Folgende Werte wurden ermittelt: $\log K_1 = 10.922$, $\log K_2 = 10.511$, $\log K_3 = 2.646$, $\log K_4 = 1.620$ für $TACT$ und $\log K_1 = 9.387$, $\log K_2 = 9.050$, $\log K_3 = 2.491$, $\log K_4 = 1.380$ für $TMTACT$. Die Absorptionsmaxima der Komplexe $AgTACT(NO_3)_2$ und $AgTMTACT(NO_3)_2$ waren $\lambda_1 = 280\,nm$, $\lambda_2 = 350\,nm$, bzw. $\lambda_1 = 290\,nm$, $\lambda_2 = 400\,nm$. Die Disproportionierungskonstanten der Ag(I)-Ionen in Gegenwart der Amine wurden potentiometrisch bestimmt: $\log K_d = 12.778$ für $TACT$ und $\log K_d = 11.778$ für $TMTACT$. Der Mechanismus des Elektrodenprozesses in den Komplexlösungen wurde mittels Chronovoltamperometrie und Coulometrie überprüft. Das formale Potential E_f^0 des Systems $AgTMTACT^{2+} + e \rightleftharpoons AgTMTACT^+$ ist $+0.450\,V$ gegenüber NHE.

Introduction

Protolytic and complexing properties of tetraazamacrocyclic amines have been widely investigated in recent years [1–5]. These compounds arouse interest mainly

due to the high thermodynamic stability of their complexes in aqueous solutions. The basic properties of tetraazamacrocyclic compounds have been examined by various methods to show often quite different results [2, 5–8] and the same concerns their complexes with metal ions. Ag(I) ions in the presence of tetraazamacrocyclic amines with a ring size of 14 and 15 atoms are disproportionated and form stable Ag(II) complexes in aqueous solutions [9–10]. The electrochemical redox properties of these complexes have been examined only in acetonitrile [10, 11], since in the case of water, even a qualitative interpretation of chronovoltamperometric measurements was impossible.

In this connecion the present study was aimed at the determination of protonation constants of 1,4,8,11-tetraazacyclotetradecane (*TACT*) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (*TMTACT*), quantitative examination of equilibria in the Ag(I)-*TACT* and Ag(I)-*TMTACT* systems, characteristics of the resultant Ag(II) complexes and description of their electrochemical properties in aqueous solutions with ionic strength $\mu = 0.1$.

Experimental Part and Results

1,4,8,11-Tetraazacyclotetradecane, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane of Aldrich and other analytical grade reagents of POCh-Gliwice were used without initial purification.

Potentiometric, coulometric and voltamperometric procedures have been described in details in [12–13]. Measurements of pH were carried out with an OP-211/1 pH-meter of RADELKIS, using an OP-0808P combined electrode, the accuracy being $\pm 0.01 pH$ unit. Spectra of the compounds under investigation were taken with a Philips UV-VIS spectrometer.

The ionic strength of all the investigated solutions was $\mu = 0.1$ ($0.1M$ KNO_3).

pH-Metric Measurements

TACT and *TMTACT* are water-soluble tetrabasic ligands. Their protonation constants were determined by titration of solutions with a composition of $c_L + 5cHNO_3$, with standard KOH solutions. Ligand concentrations from 10^{-2} to $10^{-3}M$ were used. Drops in the titration curves were observed at the second degree of neutralization of all the solutions investigated. Curves of the titration of $2 \times 10^{-3} M L + 1 \times 10^{-2}M$ HNO_3 solutions with a $9.72 \times 10^{-2} M$ KOH solution are given in Fig. 1.

Protonation constants were calculated numerically using a TURBO-BASIC programme based on PKAS [14] and MINIGLASS [15] algorithms. Values of the constants were determined for 5 measurement series and for 15 points in the titration curves from each titration interval. An average square error of measurements did not exceed $0.02 pH$ unit. The protonation constants of the ligands are given in Table 1.

Characteristic of the Ag Complexes

The investigated cyclic tetraamines in aqueous solutions, in accordance with previous results [9, 10], reacted with Ag(I) ions to form Ag(II) complexes with
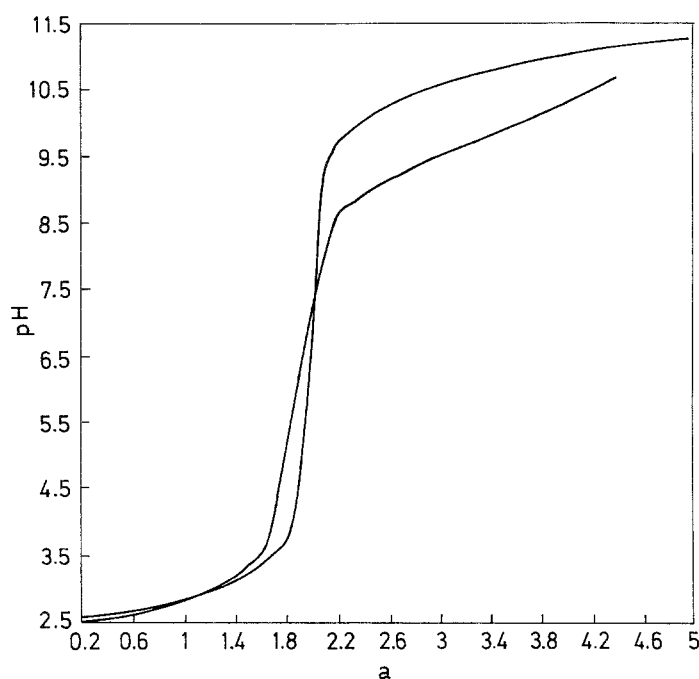
Fig. 1. pH-metric titration curves of the solutions (40 ccm): **1**: $2 \times 10^{-3}\,M$ $TACT + 1 \times 10^{-2}\,M\,HNO_3$, **2**: $2 \times 10^{-3}\,M$ $TMTACT + 1 \times 10^{-2}\,M\,HNO_3$ with $0.0972\,M\,KOH$ solution; $T = 298\,K$, $\mu = 0.1$ $(0.1\,M\,KNO_3)$

Table 1. Values of protonation constants of $TACT$ and $TMTACT$; $T = 298\,K$, $\mu = 0.1$

Ligand	$TACT$	$TMTACT$
$\log K_1$	10.922 ± 0.005	9.387 ± 0.005
$\log K_2$	10.511 ± 0.005	9.050 ± 0.005
$\log K_3$	2.646 ± 0.01	2.491 ± 0.01
$\log K_4$	1.620 ± 0.01	1.380 ± 0.02
$\log K_{04}$	25.699 ± 0.01	22.308 ± 0.02

precipitation of metallic silver:

$$2\,AgNO_3 + L \rightleftharpoons AgL(NO_3)_2 + Ag^0.$$

The resultant complexes in the form of nitrate salts were separated and their compositions were determined by elementary analysis. In the case of $TACT$, the composition was: %Ag $= 24.94$, %C $= 27.81$, %N $= 19.42$, %H $= 5.60$, %O $= 22.23$, and in the case of $TMTACT$: %Ag $= 22.10$, %C $= 34.41$, %H $= 6.59$, %N $= 17.20$, %O $= 19.70$. Both complexes, similarly as in the case of perchlorate ions, form compounds with the composition $AgL(NO_3)_2$.
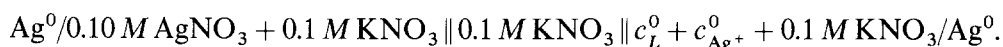
VIS and UV spectra of these compounds were taken. For $AgTACT(NO_3)_2$, the absorption maxima were found at $\lambda_1 = 280\,nm$ and $\lambda_2 = 350\,nm$, while those of $AgTMTACT(NO_3)_2$ at $\lambda_1 = 290\,nm$ and $\lambda_2 = 400\,nm$. The values of λ_2 correspond to the absorption maximum characteristic for Ag(II) complexes and corresponding to the transition: $b_{2g} \rightarrow b_{1g}$ in fields with a symmetry of D_{4h}. The value of λ_{2max} can

be used to find approximate values of the crystalline field splitting energy, $10\,\text{Dq}$, assuming that the Ag–N bond is ionic in nature. $\Delta_{TACT} = 331.4\,\text{kJ/mol}$, $\Delta_{TMTACT} = 299.0\,\text{kJ/mol}$.

The maxima at $\lambda_1 = 280\,\text{nm}$ for $TACT$ and $\lambda_2 = 290\,\text{nm}$ for $TMTACT$ (near ultraviolet) correspond to ligand $-\,\text{Ag}^{2+}$ charge transfer [16].

Potentiometric Measurements

The equilibria of Ag(I) disproportionation in ligand solutions were examined potentiometrically in the system

$$\text{Ag}^0/0.10\,M\,\text{AgNO}_3 + 0.1\,M\,\text{KNO}_3 \,\|\, 0.1\,M\,\text{KNO}_3 \,\|\, c_L^0 + c_{\text{Ag}^+}^0 + 0.1\,M\,\text{KNO}_3/\text{Ag}^0.$$

The EMF of the cell was determined and hence the equilibrium concentration of Ag^+ ions in solutions. Within the concentration range used, the equation of Nernst with the slope $\partial\text{EMF}/\partial\log c_{\text{Ag}^+} = 58.9 \pm 0.1\,\text{mV}$ was satisfied. The disproportionation process was very slowly, therefore values of EMF of the cell were stabilized after 24–30 hours.

The disproportionation equilibrium constant

$$2\text{AgNO}_3 + L \rightleftharpoons \text{AgL(NO}_3)_2 + \text{Ag}^0$$
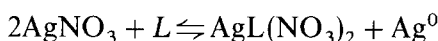
can be described by the equation

$$K_d = \frac{c_k}{c_{exp}^2[L]},$$

where c_k is the equilibrium concentration of the $\text{Ag}L^{2+}$ complex, $[L]$ the equilibrium concentration of the ligand, and c_{exp} the equilibrium concentration of Ag^+ ions;

$$c_k = \frac{c_{\text{Ag}^+}^0 - c_{exp}}{2},$$

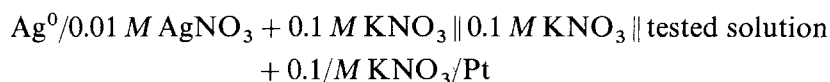$$[L] = c_L^0 - c_k = c_L^0 - \frac{c_{\text{Ag}^+}^0 - c_{exp}}{2},$$

hence

$$K_d = \frac{c_{\text{Ag}^+}^0 - c_{exp}}{c_{exp}^2(2c_L^0 - c_{\text{Ag}^+}^0 + c_{exp})}.$$

Results of the measurements and the determined disproportionation constants are given in Tables 2 and 3.

Average values of the constants are: for $TACT$ $\log K_d = 12.778 \pm 0.05$, and for $TMTACT$ $\log K_d = 11.778 \pm 0.03$.

Chronovoltamperometric and Coulometric Measurements

In order to determine redox systems n the Ag(II) complex solutions and to examine the mechanisms of electrode processes involved, chronovoltamperomeric measurements were carried out in the system

$$\text{Ag}^0/0.01\,M\,\text{AgNO}_3 + 0.1\,M\,\text{KNO}_3 \,\|\, 0.1\,M\,\text{KNO}_3 \,\|\, \text{tested solution}$$
$$+ 0.1/M\,\text{KNO}_3/\text{Pt}$$

Table 2. Results of potentiometric measurements of disproportionation of Ag(I) ions in the presence of $TACT$; $\partial\text{EMF}/\partial\log c_{\text{Ag}^+} = 58.9\,\text{mV}$, $T = 298\,\text{K}$, $\mu = 0.1$

$c_L^0 \times 10^3\,M$	$c_{\text{Ag}^+}^0 \times 10^3\,M$	EMF [mV]	$\log c_{exp}$	$\log K_d$
4.0000	4.0000	−258.1	−6.3820	12.7639
4.1667	3.3333	−263.4	−6.4720	12.7678
4.3478	2.6087	−268.0	−6.5501	12.7320
4.4776	2.0895	−273.7	−6.6469	12.7771
4.6154	1.5385	−279.9	−6.7521	12.8052
6.6667	6.6667	−258.5	−6.3888	12.7776
6.8182	6.3636	−259.9	−6.4126	12.7672
6.9767	6.0465	−262.3	−6.4533	12.7901
7.1429	5.7143	−263.8	−6.4788	12.7815
7.3171	5.3659	−265.9	−6.5144	12.7915
7.5000	5.0000	−267.1	−6.5348	12.7685
7.6923	4.6154	−269.7	−6.5789	12.7899
7.8947	4.2105	−270.9	−6.5993	12.7593
8.1081	3.7838	−274.1	−6.6537	12.7908
8.3333	3.3333	−276.9	−6.7012	12.8003
8.5714	2.8571	−279.2	−6.7402	12.7814

Table 3. Results of potentiometric measurements of disproportionation of Ag(I) ions in the presence of $TMTACT$; $\partial\text{EMF}/\partial\log c_{\text{Ag}^+} = 58.9\,\text{mV}$, $T = 298\,\text{K}$, $\mu = 0.1$

$c_L^0 \times 10^3\,M$	$c_{\text{Ag}^+}^0 \times 10^3\,M$	EMF [mV]	$\log c_{exp}$	$\log K_d$
4.0000	4.0000	−228.8	−5.8818	11.7608
4.1209	3.5165	−232.9	−5.9542	11.7797
4.1667	3.3333	−234.3	−5.9779	11.7796
4.2857	2.8571	−238.3	−6.0458	11.7905
4.3478	2.6087	−239.6	−6.0679	11.7677
4.4118	2.3529	−242.6	−6.1188	11.7980
4.4776	2.0895	−244.0	−6.1426	11.7684
4.5455	1.8182	−246.6	−6.1868	11.7713
4.6154	1.5385	−249.8	−6.2411	11.7830
6.6667	6.6667	−229.1	−5.8896	11.7790
6.8182	6.3636	−230.5	−5.9134	11.7688
6.9767	6.0465	−232.6	−5.9491	11.7816
7.1429	5.7143	−234.3	−5.9779	11.7798
7.3171	5.3659	−235.8	−6.0034	11.7694
7.5000	5.0000	−238.5	−6.0492	11.7975
7.6923	4.6154	−239.6	−6.0679	11.7678
8.1081	3.7838	−244.3	−6.1477	11.7788
8.5714	2.8571	−250.0	−6.2445	11.7900

at potential rates $v = 10\text{–}100\,\text{mV/s}$. the same system was used for coulometric measurements. The solutions were additionally oxidized at $i = 1\,\text{mA}$ until maximum EMF was obtained, and then they were reduced amperostatically.

Examination of $\text{Ag}TACT(\text{NO}_3)_2$ Solutions

The following chronovoltamperograms were made:

1) $5 \times 10^{-3}\,M\,TACT$ solution within the potential range $\varphi = -1200\text{–}+1000\,\text{mV}$,

2) $5 \times 10^{-3}\,M\,\text{Ag}TACT(\text{NO}_3)_2$ solution within the potential range $\varphi = -1200\text{–}+1200\,\text{mV}$,

3) $5 \times 10^{-3}\,M\text{Ag}TACT(\text{NO}_3)_2$ solution within the potential range $\varphi = -400\text{–}+200\,\text{mV}$.

All the solutions had ionic strength $\mu = 0.1$ ($0.1\,M$ KNO$_3$). Potential values vs. $\text{Ag}^0/0.01\,M$ AgNO$_3$ + $0.1\,M$ KNO$_3$ electrode.

The voltamperogram of $5 \times 10^{-3}M\,TACT$ solution (Fig. 2, curve 1) shows in the region $\varphi < -200\,\text{mV}$ cathodic reduction peaks of NO$_3^-$ ions ($\varphi_1 \cong -750\,\text{mV}$, $\varphi_2 \cong -360\,\text{mV}$) while corresponding anodic peaks are considerably lower and their position confirms that the process is irreversible. At $\varphi > +600\,\text{mV}$ the CVA curve shows no oxidation of the ligand. The chronovoltamperogram of $5 \times 10^{-3}M$ $\text{Ag}TACT(\text{NO}_3)_2$ solution, made within similar potential range, shows a shift of the NO$_3^-$ reduction peaks towards the cathodic side. There is (Fig. 2, curve 2) an evident pair of peaks associated with oxidation of metallic silver: $\text{Ag}^0 - e \rightarrow \text{Ag}^0$ ($\varphi_{a1} \cong 0\,\text{mV}$, $\varphi_{a2} \cong +70\,\text{mV}$) and a peak associated with the process

$$\text{Ag}TACT^+ + e \rightarrow \text{Ag}TACT^{2+}$$
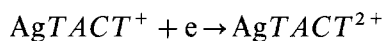
($\varphi \cong +150\,\text{mV}$ for $v = 50\,\text{mV/s}$). A corresponding peak is observed at $\varphi = -300\,\text{mV}$, with its slope comprising the first reduction peak of NO$_3^-$ ($\varphi \cong -480\,\text{mV}$). These assumptions were confirmed by confining the potential range to $\varphi_c = -400\,\text{mV}$. The voltamperogram made within this range shows no bulge in the anodic part ($\varphi \cong -150\,\text{mV}$) corresponding to oxidation of the reduced form of NO$_3^-$ ion. The
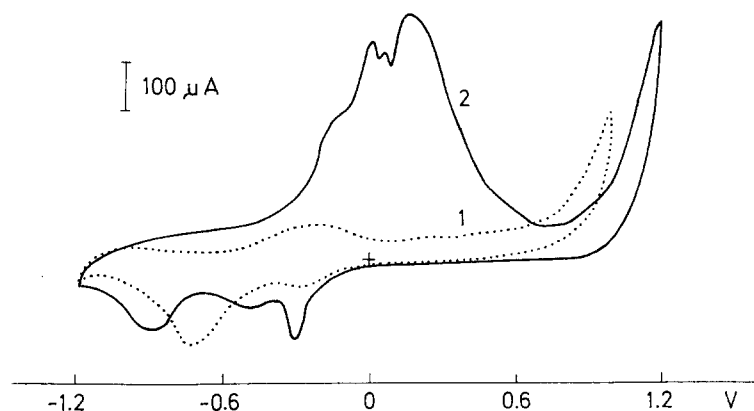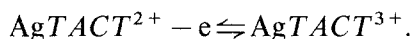

Fig. 2. Chronovoltamperograms: 1: $5 \times 10^{-3}\,M\,TACT$, 2: $5 \times 10^{-3}\,M\,\text{Ag}TACT(\text{NO}_3)_2$. φ vs. $\text{Ag}^0/$ $0.01\,M$ AgNO$_3$ + $0.1\,M$ KNO$_3$; $T = 298\,\text{K}$, $\mu = 0.1$ ($0.1\,M$ KNO$_3$)

system

$$\text{Ag}TACT^+ - \text{e} \rightleftharpoons \text{Ag}TACT^{2+}$$
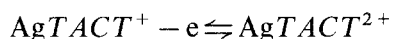
is an electrode irreversible system ($\Delta E_{pac} \cong 460\,\text{mV}$ for $v = 50\,\text{mV/s}$). Moreover, no reduction peaks of the Ag(I) and Ag(II) complexes or of reduction of Ag^+ to Ag^0 are observed and there are no characteristic peaks for the system

$$\text{Ag}TACT^{2+} - \text{e} \rightleftharpoons \text{Ag}TACT^{3+}.$$

Narrowing the potential range in the anodic part to $\varphi = +200\,\text{mV}$ does not change the character of the CVA curve.

Amperostatic reduction of the $1 \times 10^{-3}\,M\,\text{Ag}TACT(\text{NO}_3)_2$ solution (previously additionally oxidized to maximum EMF, $i = 1\,\text{mA}$) was carried out and the relationship $\varphi = f(t) = f(Q)$ is shown in Fig. 3. The curve is considerably different from common curves of this type due to the presence of a potential minimum and increase in potentials of the system with advancing reduction processes. It is noteworthy that at $\varphi \leqslant 0\,\text{mV}$ vs. $\text{Ag}^0/0.01\,M\,\text{AgNO}_3 + 0.1\,M\,\text{KNO}_3$, metallic silver has been deposited on the Pt electrode. The obtained relationship distinctly point to the presence of two redox systems. Taking into consideration the CVA curves which point to the potential regions of the occurring processes, one can conclude with a high probability that we deal with reduction of the $\text{Ag}TACT^{2+}$ complex in the descending part of coulometric curves and in the ascending part with oxidation of metallic silver resulted from disproportionation of $\text{Ag}TACT^+$ complex.
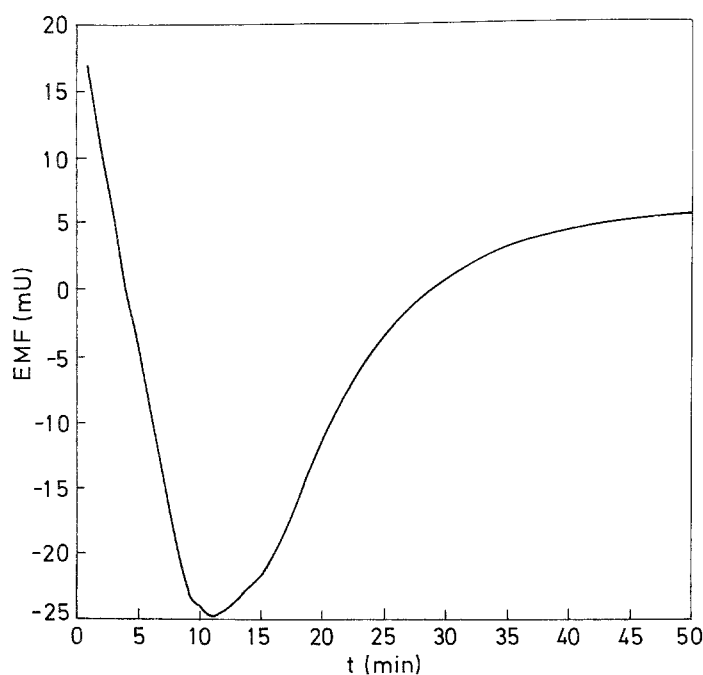

Fig. 3. Amperostatic reduction curve of the $1 \times 10^{-3}\,M\,\text{Ag}TACT(\text{NO}_3)_2$ solution oxidized to the maximum EMF, ($i = 1\,\text{mA}$). φ vs. $\text{Ag}^0/0.01\,M\,\text{AgNO}_3 + 0.1\,M\,\text{KNO}_3$; $T = 298\,\text{K}$, $\mu = 0.1$

Examination of Ag$TMTACT$(NO$_3$)$_2$ Solutions

The chronovoltamperograms of the $5 \times 10^{-3}\,M$ Ag$TMTACT$(NO$_3$)$_2$ solutions within the potential ranges: (a) $\varphi = -1200-+1000$ mV, (b) $-600-$ OmV vs. Ag^0/0.01 M AgNO$_3$ + 0.1 M KNO$_3$ are shown in Figs. 4 and 5. Voltamperogram (a) (Fig. 4) in the cathodic region $\varphi \leqslant -200$ mV shows, as in the case of
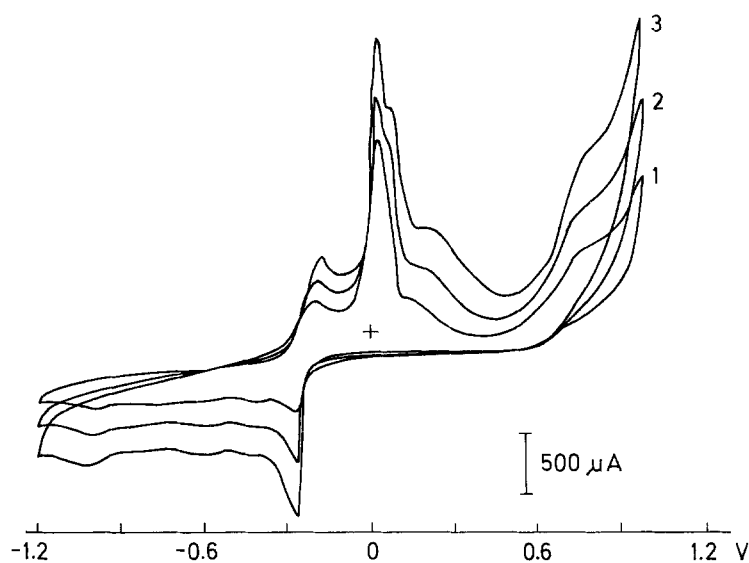

Fig. 4. Voltamperometric curves of the $5 \times 10^{-3}\,M$ Ag$TMTACT$(NO$_3$)$_2$ solution versus the increasing rate of potential sweep: **1**: $v = 20$ mV/s, **2**: 50 mV/s, **3**: 100 mV/s. φ within the range from $-1200-+1000$ mV vs. Ag^0/0.01 M AgNO$_3$ + 0.1 M KNO$_3$; $T = 298$ K, $\mu = 0.1$
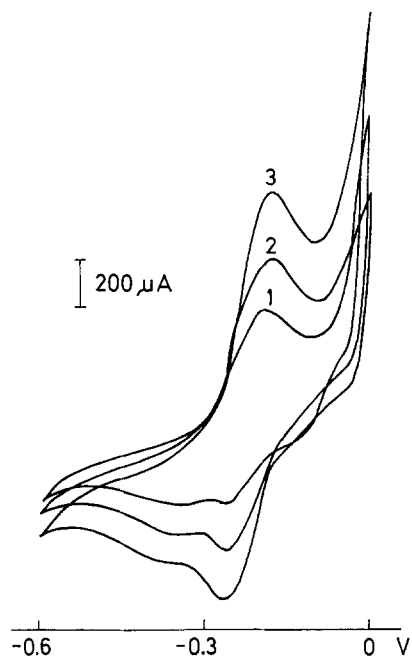
Fig. 5. Chronovoltamperograms of the redox system Ag(II)/Ag(I) $- TMTACT$, being formed in the $5 \times 10^{-3}M$ Ag$TMTACT$(NO$_3$)$_2$ solution versus the increasing rate of potential sweep: **1**: $v = 20$ mV/s, **2**: 50 mV/s, **3**: 100 mV/s. φ vs. Ag^0/0.01 M AgNO$_3$ + 0.1 M KNO$_3$; $T = 298$ K, $\mu = 0.1$

$AgTACT(NO_3)_2$, reduction peaks of the nitrate ions. In the anodic region this curve shows, however, quite a different character. The oxidation peak potential of $AgTMTACT^+$ ($\varphi \cong -200\,mV$) is lower than the desorption oxidation peak potentials of metallic silver ($\varphi \cong +60\,mV$). It is easy to notice the electrode reversible redox system

$$AgTMTACT^+ - e \rightleftharpoons AgTMTACT^{2+}$$
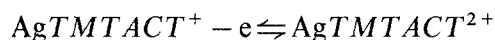
as well as the irreversible oxidation process ($\varphi \cong +780\,mV$). The presence of an identical anodic wave ($\varphi \cong +800\,mV$) in the CVA curve of the $5 \times 10^{-3}\,M\,TMTACT$ solution allows to conclude that this is a process of ligand oxidation.

The formal potential of the system

$$AgTMTACT^{2+} + e \rightleftharpoons AgTMTACT^+$$
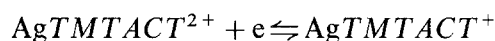
was determined; it can be easily noticed within the narrowed potential range (Fig. 5), while the current peaks ratio $i_c/i_a = 1.5$, is, of course, a result of disproportionation of the complex $AgTMTACT^+$. The value of formal potential of this redox system for 5 independent series measurement is $-226 \pm 2\,mV$ vs. $Ag^0/0.01\,M\,AgNO_3 + 0.1\,M\,KNO_3$ electrode $= +450\,mV$ vs. NHE.
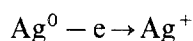
Discussion

The obtained protonation constants, as expected, point to a higher basicity of $TACT$ (a secondary amine) than that of $TMTACT$ (a tertiary amine). $TACT$ shows also higher splitting energy of ligand field for the Ag(II) ion (d^9). With the same spatial structure, this is synonymous with higher thermodynamic stability of the complex $AgTACT^{2+}$. This fact has found its confirmation in potentiometric measurements; the Ag(I) complex with $TACT$ is disproportionated easier ($\log K_{dTACT} = 12.778$, $\log K_{dTMTACT} = 11.778$).
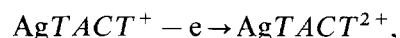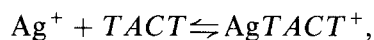
The voltamperometric and coulometric measurements allow to explain the electrochemical processes taking place in the Ag(II) complex solutions. In connecion with the fact that the potential region of the system

$$AgTACT^+ - e \rightleftharpoons AgTACT^{2+}$$

and of the process

$$Ag^0 - e \rightarrow Ag^+$$
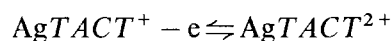
penetrate one another, while only one cumulative anodic peak is observed in the CVA curves at $v = 100\,mV/s$, it is impossible to carry out a quantitative discussion of the Ag(II)/Ag(I) system. Nevertheless, we can clearly state that we are dealing with the following processes,

$$AgTACT^{2+} + e \rightarrow AgTACT^+, \tag{A}$$

$$2AgTACT^+ \rightleftharpoons Ag^0 + AgTACT^{2+} + TACT, \tag{B}$$

$$Ag^0 - e \rightarrow Ag^+, \tag{C}$$

$$Ag^+ + TACT \rightleftharpoons AgTACT^+,$$

$$AgTACT^+ - e \rightarrow AgTACT^{2+},$$

which is confirmed by the presence of desorption oxidation peaks of Ag^0 in voltamperograms without a corresponding reduction peak of Ag(I).

The coulometric curves of the $1 \times 10^{-3} M \, AgTACT^{2+}$ solution allow to describe the relationships qualitatively. The electrode process (A) taking place within the range of lower potentials leads to the formation of $AgTACT^+$ which, undergoing disproportionation in process (B), gives metallic silver on the electrode and system (C) with a higher formal potential, which consequently leads to a rapid oxidation of Ag^0. Thus, the formal potential $E^0_{f(A)}$ is lower than $E^0_{f(C)}$, which is not clearly visible in the presented CVA curves, and the disproportionation process (B) is thermodynamically reasonable. Theoretical determination of K_d for (B) is impossible due to he lack of $E^0_{f(A)}$ and $E^0_{f(C)}$.

Also in the case of $TMTACT$ the formal potential of the system

$$AgTMTACT^{2+} + e \rightleftharpoons AgTMTACT^+$$
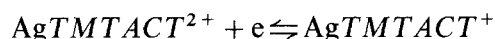
is lower than that of the system: $Ag^+ + e \rightleftharpoons Ag^0$, which is an oxidation process observed in CVA curves.

Hence, we are dealing with a similar mechanism of the reduction of Ag(II) to Ag(I) with a simultaneous process of disproportionation of $AgTMTACT^+$ and with the presence of oxidation peaks of Ag^0 in the CVA curves without prior reduction of the complexes to metallic silver.

The $1 \times 10^{-3} M \, AgTMTACT^{2+}$ solutions, additionally oxidized by amperostatic mode, show the maximum EMF $= + 700 \, mV$ vs. $Ag^0/0.01 \, M$ $AgNO_3 + 0.1 \, M$ KNO_3 electrode. This value drops rapidly to EMF $\cong - 100 \, mV$, most likely due to the fast chemical reduction of the formed ligand radicals. The curves of amperostatic reduction have similar shapes as in Fig. 3 and confirm the above given mechanism. The rate of the relatively slow process of reduction of the Ag(II) complex during coulometric measurements is comparable with that of the chemical disproportionation process, hence in measurements of this type there is no chance for "pure" redox systems to exist in solutions and to determine their formal potentials.

The peak corresponding to the process
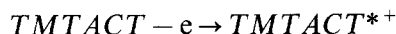
$$TMTACT - e \rightarrow TMTACT^{*+}$$

present in CVA curves, as opposed to analogous curves made in the presence of $TACT$, points to an easier oxidation of $TMTACT$ (a tertiary amine) and is consistent with the above obtained values of wavelength of charge-transfer spectra of Ag(II) complexes ($\lambda_{1TACT} = 280 \, nm < \lambda_{1TMTACT} = 290 \, nm$).

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