ELECTROCHEMICAL BEHAVIOUR OF SILVER COMPLEXES OF DITHIA-ALKANEDICARBOXYLIC ACIDS*

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INTRODUCTION

The Ag complexes of the following complex-forming acids were investigated : (I) 2,5-dithiahexane-1,6-dicarboxylic acid

COOH-CH2-S-CH2-CH2-S-CH2-COOH

(II) 3,6-dithiaoctane-1,8-dicarboxylic acid

COOH-CH2-CH2-S-CH2-CH2-S-CH2-CH2-COOH

(III) 4,7-dithiadecane-1,10-dicarboxylic acid

COOH-CH2-CH2-CH2-S-CH2-CH2-S-CH2-CH2-CH2-COOH

(IV) 2,2,7,7,-tetramethyl-3,6-dithiaoctane-1,8-dicarboxylacid

$$COOH-C-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-COOH -C-COOH -CH_2-S-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

The Ag complex of (I) was first prepared by Tiberg¹. He found that by electrolysis of a solution of this complex and sodium acetate, metallic Ag was deposited at the cathode. The current efficiency was about 9%.

Recently, Bellaart and Verbeek² reported the preparation of the complex of (II). The method of preparation of the Ag complexes of (III) and (IV) will be published later.

The electrochemical behaviour of these complexes was investigated as it was probable that this would give some insight into the influence of the structure of the complexes on cathodic metal deposition. In particular the effect of chain length might be deduced from a comparison of the behaviour of (I), (II) and (III) and steric effects from a comparison of (II) and (IV).

^{*} Dedicated to Professor J. Th. G. Overbeek on the occasion of the 25th anniversary of his appointment as a Professor of Physical Chemistry.

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2. EXPERIMENTAL

The thia-alkane-dicarboxylic acids and their Ag complexes were prepared by Bellaart in the laboratory of Organic Chemistry at the Eindhoven University of Technology, The Netherlands.

The pH was measured with a Radiometer pH meter (type 52A), using a glass electrode and a saturated calomel electrode.

The electrolytic cell used was divided into a cathodic and an anodic compartment, separated by a glass diaphragm. The volume of each compartment was about 50 cm³. The cell was thermostatted. A rotating (800 rev. min⁻¹) Ag wire with a diameter of 0.15 cm and a length of 2.25 cm served as cathode, its geometric surface area being 1.10 cm². A platinum electrode of 1 cm² surface area was used as anode. The reference electrode in the cathodic part was a saturated calomel electrode.

Supporting electrolytes used were 0.5 M NaHCO₃+0.5 M Na₂CO₃, and 1 M H₂SO₄. In the following these are termed the alkaline, and the acid electrolyte. Both electrolytes contained 0.005 M complex and 0.002 M of the complex-forming ligand, unless stated otherwise. In 1 M H₂SO₄ the complex and the complex-forming acid were dissolved at 90°C since they dissolved very slowly at room temperature. To remove oxygen, nitrogen was passed through the electrolyte for 20 min before measurements were started.

The ε/j relation was determined with a Wenking potentiostat. The potential difference between the Ag cathode and the calomel electrode was measured with a Philips vacuum-tube voltmeter (GM 6020); the potentials are given versus NHE. The potential ε was changed in steps of 50 mV from the reversible potential ε_r to a potential at which the limiting current of the deposition of Ag had been reached and then back again in steps of 50 mV to ε_r .

3. RESULTS

3.1 *The ionization constant*

A known quantity of Ag complex in about 50 cm³ water was titrated with 0.1 M NaOH. At the beginning of the titration the Ag complex was not completely dissolved.

The titration curves for the Ag complexes investigated were equivalent. Figure 1 shows the curve for the titration of 0.379 gAg (II)₂ at 40° C with 0.1 M NaOH. The equivalence point at pH 8.7 corresponds to 2.94 H⁺-ions per molecule Ag(II)₂.

TABLE 1

IONIZATION CONSTANTS CALCULATED FROM THE pH OF SOLUTIONS OF COMPLEXES

Complex	$(AgX_2)/mol \ l^{-1}$	pH	$K_z/mol \ l^{-1}$
Ag(I),	6.2×10^{-5}	3.92	6.5×10^{-4}
$Ag(II)_2$	1.62×10^{-3}	3.58	1.5×10^{-5}
Ag(III) ₂	7.2×10^{-4}	4.07	3.5×10^{-6}
$Ag(IV)_2$	2.8×10^{-5}	4.58	1.2×10^{-5}

The number of H^+ -ions per complex molecule for $Ag(I)_2$. $Ag(III)_2$ and $Ag(IV)_2$ is 2.90, 2.85 and 3.15, respectively. Allowing for a small inaccuracy in these values, it follows that for the complexes investigated, 3 H^+ -ions are formed at a dissolving ionization of a one-molecule complex. This agrees with the number of H^+ -ions of the complexes in the solid state. As the titration curves show only one equivalence point, it follows that the ionization constant is the same for the 3 H^+ -ions.

The ionization constant at 40° C was determined by measuring the pH of a solution containing a known quantity of dissolved complex. The concentration of complex, the pH and the ionization constant K_z are given in Table 1. Since the titration curve has only one step (Fig. 1), the ionization constant was calculated from :

$$K_{z} = \frac{[H^{+}]^{2}}{3[Ag(X)_{2}] - [H^{+}]}$$

Suzuki and Yamasaki³ have found $K_{z,I} = 6.99 \times 10^{-4} \text{ mol } 1^{-1}$ for acid (I). There is a good agreement with the value in Table 1. Isotachophoresis⁴ showed that the complex at pH 8.6 has a negative charge. As measurements at pH < 2 appeared not to be possible, the sign of charge in acid solution could not be determined.



Fig. 2. Potential ε of a soln. of a complex on titration with an alkaline soln. of the complex-forming acid.

3.2 Complex constant

The composition of the complex was determined by measuring the potential of the Ag wire *versus* the saturated calomel electrode, when titrating a solution containing $AgNO_3$ or complex with a solution of the complex-forming acid.

About 25 cm³ 1 M H₂SO₄ solution containing 0.126 mmol AgNO₃ and about 25 cm³ 0.5 M NaHCO₃+0.5 M Na₂CO₃ solution containing 0.141 mmol AgNO₃ were titrated with a solution of 0.0518 M (II) and 0.15 M NaOH at 60°C

and 20°C respectively. The titration curves are given in Fig. 2. At the beginning of the titration of the alkaline electrolyte, Ag_2CO_3 precipitated; it dissolved after the addition of the complex-forming acid (II). When titrating the acid solution at 20°C a precipitate of (II) was formed only after reaching the equivalence point. The titration curve was similar to the curve of Fig. 2.

The potentials at the equivalence points in the acid and the alkaline electrolyte are about 345 and 305 mV, respectively (Fig. 2). From these curves it follows that in both acid and alkaline electrolyte a complex is formed with an Ag^+ :(II) ratio of 1:2.

Solution of $Ag(II)_2$ in acid as well as alkaline electrolyte were titrated with an alkaline solution of (II). The potential was plotted *versus* the logarithm of the added quantity of the alkaline solution of (II). The curves obtained obey the Nernst equation if the Ag:(II) ratio of the complex of (II) is 1:2.

The curves obtained by titrating the other complexes were similar to that for $Ag(II)_2$. Consequently, all complexes investigated have an Ag:X ratio of 1:2.

For 0.005 *M* complex and 0.002 *M* complex-forming acid (X) in both acid and alkaline solution the reversible potential $\varepsilon_r vs$. NHE, log [Ag⁺] and log K_c are given in Table 2. The Nernst equation was used for the calculation of log [Ag⁺]:

$$\log\left[\mathrm{Ag^{+}}\right] = \frac{\varepsilon_{\mathrm{r}} - 0.799}{0.0592}$$

where 0.799 V is the standard potential of the Ag⁺ + $e \rightleftharpoons$ Ag reaction⁵. Log K_c was calculated from log $K_c = \log [Ag^+] + 2 \log [X] - \log [AgX_2]$.

TABLE 2

Solution	Complex	$\varepsilon_{\rm r}-\varepsilon_0/mV$	$-\log [Ag]$	$-\log K_c$
alkaline	(I)	464	7.83	10.93
	(II)	498	8.41	11.51
	(III)	510	8.61	11.71
	(IV)	509	8.59	11.69
acid	(I)	359	6.06	9.16
	(II)	437	7.38	10.48
	ÌIÍ)	464	7.83	10.93
	ÌV)	438	7.39	10.49

DISSOCIATION CONSTANTS, CALCULATED FROM THE ELECTRODEPOTENTIAL OF Ag IN SOLUTIONS OF COMPLEXES

3.3 Kinetic parameters and activation energy of Ag deposition

The shape of the ε/j curves for the complexes investigated in both acid and alkaline electrolyte is the same. Typical curves at 25°C are given in Fig. 3 for a solution containing 0.5 *M* NaHCO₃, 0.5 *M* Na₂CO₃, 0.005 *M* Ag(II)₂ and 0.002 *M* (II) and for a solution containing 1 *M* H₂SO₄, 0.005 *M* Ag(II)₂ and 0.002 *M* (II). The difference between the currents measured at decrease and increase of potential is small, *viz.* about 5%. The current densities given in Fig. 3 are the average values of both current densities. To obtain the kinetic parameters, the influence of the concentration polarization upon the ε/j relation was eliminated. For this, $\varepsilon/\log (jj_g/j_g-j)$ curves were derived from the experimental ε/j curves, where j_g is the limiting current of Ag



Fig. 3. Current density of Ag deposition as a function of potential.



Fig. 4. Potential as a function of log $[(j_g/(j_g-j))]$ for the determination of the reaction parameters.

deposition. We define $jj_g/(j_g-j) = k$ as the rate constant at a certain potential. If the anodic reaction is negligibly small with respect to the cathodic reaction, the $\varepsilon/\log k$ curve⁶ is linear and its slope $b=2.3RT/\alpha F$ where α = the transfer coefficient and the other symbols have their usual significance. In Fig. 4 log k is plotted versus ε for the electrolytes of which the ε/j curves are given in Fig. 3. For the complexes investigated the reversible potential ε_r , the slope b, the exchange current density $j_0(j_0=k \text{ at } \varepsilon_r)$ and k at $\varepsilon = 190 \text{ mV}$ are given in Table 3. The results tabulated in Table 3 are the mean values of 4–6 measurements.

The slope b for Ag deposition from the alkaline electrolyte containing only 0.005 $M \operatorname{Ag}(II)_2$ was also 110 mV. Thus the presence of an excess of complex-forming acid does not affect the slope b.

TABLE 3

Supporting electrolyte	Ligand	$j_{g}/mA \ cm^{-2}$	ε_r/mV	$j_0/mA \ cm^{-2}$	b/mV	α	$k/mA \ cm^{-2}$
alkaline	(I)	0.69	335	0.065	135	0.44	0.91
	(II)	0.53	301	0.026	110	0.54	0.28
	(III)	0.38	289	0.016	115	0.52	0.12
	(IV)	0.37	290	0.015	120	0.49	0.10
acid	(I)	1.16	440	0.056	75	0.79	78
	(II)	0.86	362	0.017	75	0.79	3.1
	ÌII)	0.96	335	0.022	90	0.66	0.78
	(IV)	0.65	361	0.010	80	0.74	1.2

REACTION PARAMETERS OF COMPLEXES

The ε/j curves were also determined at different temperatures. In the same supporting electrolyte the differences in the temperature coefficient of the transfer coefficient as well as the differences in the activation energy were so small that the accuracy of the measurements was not sufficient for their determination. However, it is certain that in the temperature range 15–55°C the transfer coefficient increases in the alkaline electrolyte by about 0.003 per °C and in the acid electrolyte by about 0.004 per °C increase of temperature.

To determine the activation energy, log k at $\varepsilon = 190$ mV was plotted vs. T^{-1} . From the slope h of this curve, $h = -E_A/2.3$ R, the activation energy E_A was calculated. The average value of the activation energy for Ag deposition in the alkaline electrolyte was found to be 15 ± 2 kcal mol⁻¹ and in the acid electrolyte 25 ± 3 kcal mol⁻¹.

3.4 Diffusion coefficient and activation energy of diffusion

First the limiting current density for the reduction of $Fe(CN)_6^{3-}$ at the rotating Ag electrode at 25°C was determined in an electrolyte containing 1 *M* KCl and 0.004 *M* K₃Fe(CN)₆; it was found to be 1.37 mA cm⁻². For Ag deposition, the limiting current density was determined at the same electrode with the same rotation speed. The limiting current density⁷ is proportional to $D^{2/3}v^{-0.34}$, where *D* is the diffusion coefficient and *v* the kinematic viscosity. The diffusion coefficient⁸ of Fe(CN)₆³⁻ is $D=7.63 \times 10^{-6}$ cm² s⁻¹ at 25°C. The kinematic viscosity⁹ *v* of 1 *M* KCl, of 1 *M* H₂SO₄ and of 1 *M* Na₂CO₃ at 25°C, respectively, is 0.89, 1.11 and 1.16 cP. These values enable the diffusion coefficient of the Ag complexes to be calculated. In Table 4 the resulting *D* values at 25°C are tabulated.

The activation energy of diffusion was determined from the limiting current densities at different temperatures. Since j_g is proportional to $D^{2/3}v^{-0.34}$ it follows that :

$$\frac{d \log j_g}{dT^{-1}} = -0.146 E_{A,D} - 0.34 \frac{d \log v}{dT^{-1}}$$

For 1 M H₂SO₄ and for 1 M Na₂CO₃, d logv/d T^{-1} is 620°K⁹; this factor was used in the calculation of $E_{A,D}$.

In the same supporting electrolyte the difference in activation energy of diffusion of the different complexes is of the same order of magnitude as the accuracy, so

TABLE 4

Supporting electrolyte	Acid	$10^6 D/cm^2 s^-$
alkaline	(I)	2.2
	(II)	1.45
	(III)	0.87
	(IV)	0.87
acid	(I)	4.4
	(II)	3.0 ^a
	(III)	3.5
	(IV)	1.95

DIFFUSION COEFFICIENTS OF COMPLEX	DIFFUSION	COEFFICIENTS	OF	COMPLEXES
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^a During the measurement the limiting current density decreased with polarization time.

that only approximate values can be given. In the alkaline electrolyte the activation energy of diffusion is about 9.2 kcal mol^{-1} and in the acid electrolyte 7.7 kcal mol^{-1} .

3.5. Properties of the Ag deposit

By electrolysis of an alkaline electrolyte (pH 10.5) containing 0.06 M Ag(II)₂, metallic Ag was deposited with a current efficiency of 100 %, the potentials being above + 50 mV vs. NHE.

To investigate the presence of sulphur in the deposited Ag, 0.6 g Ag was dissolved in hot concentrated HNO₃. The addition of $Ba(NO_3)_2$ to the diluted solution gave no precipitate of $BaSO_4$, showing that the quantity of sulphur in the deposited Ag is very small. The same solution was electrolyzed at room temperature in a Hull cell, using a silver anode. With a current density of 3.6 mA cm⁻² a bright, well adhering silver layer was formed; this was also true of solutions which were used repeatedly. The anode appeared to dissolve with 100% current efficiency.

4. DISCUSSION

4.1. Structure of the complexes

Bellaart and Verbeek² have suggested a structure for the complex of (II) in the solid state. X-ray investigations showed¹⁰ that the Ag^+ -ion is tetrahedrally surrounded by the sulphur atoms of two molecules of (II).

In 3.2 it is concluded that the Ag:X ratio of the complexes investigated is 1:2. It may be assumed that in aqueous solution the position of the Ag⁺-ion with respect to the four sulphur atoms is the same as that in solid state¹⁰. By ionization of one molecule of complex, 3 H⁺-ions are formed (3.1). It has already been concluded that the three H atoms attached to the carboxylic groups have the same ionization constant. For reasons of symmetry it is evident that there can be no difference between the character of the four carboxylic groups.

From the small values of K_z it follows that in the alkaline electrolyte (0.5 M NaHCO₃+0.5 M Na₂CO₃) the four carboxylic groups will be completely ionized. Although it could not be proved, the complex in 1 M H₂SO₄ will be positively charged by taking up a proton attached to the fourth carboxylic group. The structure of the complex in alkaline and acid solutions is given in Fig. 5.



Fig. 5. Structure of complexes in: (a) acid, (b) alkaline electrolyses.

4.2. Stability of complexes

The complexes will dissociate into Ag^+ and complex-forming anions in the alkaline electrolyte and into Ag^+ and unionized acids in the acid electrolyte. The complex constants K_c are tabulated in Table 2. From these values it follows that the stability of $Ag(I)_2$ is lower than that¹² of $Hg^{2+}(I)_2$. In both the alkaline and the acid electrolyte K_c decreases with increasing size of the molecule of the complex-forming acid. The complex constant in the acid electrolyte is a factor of 6–60 higher than in the alkaline electrolyte. This is qualitatively in agreement with the difference between the slopes of the curves of Fig. 2 at the equivalence point. The difference in K_cH is greatest for the smallest complex-forming ligand. This will be a result of the different behaviour of the carboxylic group in the alkaline and the acid electrolytes. The difference between K_c for the Ag complexes of (II) and (IV) is very small.

4.3 Electrochemical parameters of Ag deposition

The transfer coefficient of the complexes in the alkaline electrolyte varies from 0.44 to 0.54 (Table 3) and in acid solution from 0.66 to 0.79. The transfer coefficient appears to depend on pH and thus on the charge of the complex. It is noteworthy that this is in agreement with the results mentioned in the literature, *viz*. that for the discharge of a positive $Ag(H_2O)_x^+$ complex in 1 *M* HClO₄ the transfer coefficient¹³ $\alpha = 0.74$ and for the discharge of a negative $Ag(CN)_2^-$ complex in electrolyte¹⁴ with (CN) = 1 *M*, $\alpha = 0.5$. Also the activation energy of 15 kcal mol⁻¹ found for Ag deposition from alkaline solution is of the same magnitude as that given¹⁵ for deposition from the cyanidic complex, *viz*. 11 kcal mol⁻¹.

The activation energy of Ag deposition from the complexes in acid electrolyte is 25 kcal mol⁻¹ (3.3). This is a very high value, probably due to adsorption of the unionized acid at the Ag electrode.

The diffusion coefficients depend on the magnitude of the ligand, and also on pH and thus, since there is practically no difference in the viscosity of the supporting

electrolytes (3.4), on the charge of the complex (Table 4) (4.1). The activation energy of diffusion in both electrolytes is high, owing to the large dimensions of the complex molecule (3.4).

4.4 The mechanism of Ag deposition

From the shape of the curves of Fig. 3 and from 3.5. it follows that in both the alkaline and the acid electrolytes only one electrode reaction occurs, *viz*. Ag deposition.

The reversible potential ε_r in the alkaline electrolyte is lower than ε_r in acid electrolyte (Fig. 2), owing to the fact that the concentration of Ag⁺-ions in the alkaline electrolyte is a factor of 6-60 smaller than in the acid electrolyte (Table 2). Notwithstanding this, the values of j_0 in the alkaline and acid electrolytes differ only slightly (Table 3). Also taking into consideration that the concentration of Ag^+ is very low, viz. about 10^{-8} M (Table 2), the inference is that Ag is deposited directly from the complex and not from Ag⁺-ions formed by dissociation of the complex. This is in agreement with the general concept of deposition of metals from complexes. This conclusion implies that there must be a relation between rate constant and stability of the complex, as it must be supposed that the more stable the complex, the more difficult it will be to remove Ag⁺ from it. Therefore the two factors used here as a measure for stability and rate constant: K_c and k at one potential, viz. 190 mV and 25°, are plotted in Fig. 6 on a logarithmic scale. It is clear that this supposition is correct, not only in a qualitative sense but also in a quantitative relation since for those complexes which have a straight chain, a straight line is obtained. Its slope is approximately unity, which means that the rate constant is proportional to the "instability" of the complex, the calculated average proportion being $k = (9.00 \pm$ $(0.04) \times 10^{10} K_{c}$

From Fig. 6 it follows that the rate constant for complex (IV) with a branched chain is smaller than the rate constants for complexes with unbranched chains. This



Fig. 6. Relation between an electrode kinetic and a thermodynamic parameter for different complexes.

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might be a result of steric hindrance, e.g. the distance of Ag⁺ present in the adsorbed complex from the electrode is greater.

SUMMARY

The composition and electrochemical behaviour of the Ag-complexes of dithia-alkane-dicarboxylic acids, *viz.* 2,5-dithiahexane-1,6-dicarboxylic acid (I), 3,6-dithiaoctane-1,8-dicarboxylic acid(II), 4,7-dithiadecane-1,10-dicarboxylic acid (III) and 2,2,7,7,-tetramethyl-3,6-dithiaoctane-1,8-dicarboxylic acid(IV) were investigated. The Ag⁺:X ratio of all these complexes was found to be 1:2 in alkaline as well as in acid solution.

These complexes can ionise into H^+ -ions and a charged Ag complex ion. The ionisation constants were determined. The complex molecule can also dissociate into an Ag⁺-ion and two ionised or unionised molecules of the complex-forming acid. The complex constants were determined. The complexes are more stable in alkaline than in acid solution.

The diffusion coefficients of complexes are low; in acid solution a factor of 2 higher than in alkaline solution. The activation energy of diffusion in alkaline solution is 9.2 kcal mol⁻¹ and 7.7 kcal mol⁻¹ in acid solution. The activation energy of Ag deposition is 15 kcal mol⁻¹ in alkaline and 25 kcal mol⁻¹ in acid solution. The transfer coefficient also depends on pH and is 0.50 in alkaline and 0.75 in acid solution.

The rate constant in alkaline solution is a factor of 6-60 smaller than that in acid solution. For the complexes with unbranched chains ((I), (II), (III)) the rate constant, in alkaline as well as in acid solution, is proportional to the complex constant. For the branched complex (IV), a lower reaction rate is found.

A cathodic Ag deposit can be obtained from these complexes as a bright, well adhering layer. The cathodic as well as the anodic current efficiency is 100 %.

REFERENCES

- 1 A. Tiberg, Ber., 49 (1916) 2029.
- 2 A. C. Bellaart and J. L. Verbeek, Inorg. Nucl. Chem. Lett., 5 (1969) 1005.
- 3 K. Suzuki and K. Yamasaki, J. Inorg. Nucl. Chem., 24 (1962) 1093.
- 4 F. M. Everaerts, dissertation, Eindhoven, 1968.
- 5 W. M. Latimer, Oxidation Potentials, Prentice Hall, Inc., New York, 1952.
- 6 P. Delahay, New Instrumental Methods in Electrochemistry, Interscience, New York, 1954, p. 222.
- 7 R. N. Adams, Electrochemistry at Solid Electrodes, Marcel Dekker, New York, 1969, p. 104.
- 8 M. v. Stackelberg, M. Pilgram and V. Toome, Z. Elektrochem., 57 (1953) 346.
- 9 Landholt-Börstein, 5 Teilband, Teil 1, Springer Verlag, Berlin-Heidelberg-New York, 1969.
- 10 A. C. Bellaart, Private communication.
- 11 D. Sužujevic, J. Doležal and M. Kopanica, J. Electroanal. Chem., 20 (1969) 279.
- 12 H. Gerischer and R. P. Tischer, Z. Elektrochem., 61 (1957) 1159.
- 13 W. Vielstich and H. Gerischer, Z. Phys. Chem. (NF), 4 (1955) 10.
- 14 B. Lebednikas and A. Molcadskii, Mater. Respub. Konf. Elektrokhim. Litov. SSR, 8th, Vilnyus, 1966, p. 91; Chem. Abstr., 67 (1967) 87149.