Voltammetric Investigations on Mercury(II) and Silver(I) Polyamine Complexes in Dimethyl Sulphoxide Solution

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The formation of mercury(II) and silver(I) complexes with polyamines in dimethyl sulphoxide solvent has been studied by anodic dissolution of mercury and silver electrodes in the presence of ethylenediamine, *sym*-dimethylethylenediamine, *NNN'N'*-tetramethylethylenediamine, propane-1,3-diamine, and triethylenetetramine. D.c. polarography at a dropping mercury electrode, d.c. voltammetry at a solid electrode with periodical renewal of the diffusion layer, cyclic voltammetry, and controlled-potential coulometry has allowed a determination of electrode reaction orders, the complexation steps, and the stability constants of the complex species arising at the electrode surface. Short-lived species have been detected by cyclic voltammetry and the species formed in the bulk of the solution have been identified by coulometry.

THE anodic oxidation of mercury in solutions containing compounds which can form stable species with mercury(II) has been already investigated in aqueous media in the presence of ligands such as thiosulphate, sulphite, cyanide, thiocyanate, chloride, bromide, iodide, and sulphide,[1-3] ethylenediamine (en),[4] propane-1,2-diamine and diethylenetriamine,[4b] ethylenediaminetetra-acetate (edta), and cyclohexanediaminetetra-acetate (cdta).[5-7] In non-aqueous media similar studies have been carried out in the presence of halides,[8-10] ammonia, methyl-, dimethyl-, and trimethyl-amine, en, propane-1,2-diamine, aniline, β-naphthylamine,[11] and diethyldithiocarbamate.[12]

In aqueous solvents, the anodic behaviour of silver electrodes has been investigated in the presence of amino-compounds,[13] while in nitromethane the dissolution of silver has been studied in the presence of some ligands.[14]

The present paper deals with the anodic dissolution of mercury and silver electrodes in dimethyl sulphoxide (dmso) in the presence of polyamines. The aim of the work is to study the formation of the amino-complexes of Hg^{II} and Ag^{I}. The electroanalytical techniques employed were d.c. polarography, voltammetry with periodical renewal of diffusion layer, linear-sweep and cyclic voltammetry, and controlled-potential coulometry.

EXPERIMENTAL

Chemicals.—Reagent grade ethylenediamine (en), propane-1,3-diamine (pd), *sym*-dimethylethylenediamine (dmen), *NNN'N'*-tetramethylethylenediamine (tmen), triethylenetetramine (trien), hexane-1,6-diamine, and hexamethylenetetramine were used as received (Aldrich) without further purification. *Pro analysi* Merck dimethyl sulphoxide was purified by distillation under reduced pressure. The $Na[ClO_4]$ supporting electrolyte was prepared by neutralizing $Na_2[CO_3]$ with $HClO_4$ and dried in a vacuum oven.

Apparatus.—Voltammetric experiments were carried out in three-electrode cells of suitable geometry.[15,16] The coulometric tests were performed in a H-shaped cell with anodic and cathodic compartments separated by a sintered glass disc. The mercury working microelectrodes were a dropping mercury electrode (d.m.e.), with mechanical control of the drop time in the polarographic experiments, and a gold sphere freshly covered with mercury in the cyclic-voltammetric tests. The silver working microelectrode was a silver sphere. In the coulometric experiments a mercury pool or a silver gauze was employed as working electrode. An aqueous saturated calomel electrode (s.c.e.) was used as reference. The auxiliary electrode was a platinum spiral in the voltammetric tests and a mercury pool in the coulometric ones.

All the voltammetric measurements were carried out with a PAR 170 Electrochemical System as polarizing unit; care was devoted to the *iR* drop compensation. Curves of current against potential (*i vs. E*) were recorded either on a Houston Instruments model 2000 XY recorder or, for potential scan rates higher than 0.5 V s^{-1}, on a Hewlett-Packard model 1123 A storage oscilloscope. In the controlled-potential coulometric tests an Amel model 551 potentiostat and an associated model 558 coulometer integrator were used. All measurements were performed at 25 ± 0.1 °C; concentration of the supporting electrolyte was 0.1 mol dm^{-3}.

RESULTS AND DISCUSSION

Mercury Electrode.—The addition of en, dmen, tmen, pd, or trien to dmso solutions caused the appearance of a well formed anodic wave at the d.m.e., attributable to the formation of a mercury(II) complex; it is known that in the presence of complex-forming species mercury is oxidized to Hg^{II}.[17] Within the amine concentration ranges employed, the limiting current of the wave was linearly dependent on the amine concentration. By analysing the polarographic data on the basis of suitable equations it was possible to determine both the number of ligand molecules co-ordinated to one Hg^{2+} ion at the electrode surface and the stability constant for the complex formed at the electrode.

The data were manipulated by use of equation (1),[18]

$$E_{\frac{1}{2}} = E^0(\mathrm{Hg}^{2+}/\mathrm{Hg}) + \frac{RT}{2F}\ln\frac{2^{m-1}D_L^{\frac{1}{2}}}{mD_C^{\frac{1}{2}}\beta_m[X]^{m-1}} \quad (1)$$

where $\beta_m = [HgX_m^{2+}]_0/[Hg^{2+}]_0[X]_0^m$, the subscripts L and C refer to ligand and complex, the subscript 0 indicates a concentration at the electrode surface, [X] is the polyamine concentration, and m is the number of polyamine molecules linked to one Hg^{2+} ion at the electrode surface. The value of m can be calculated from a plot of $E_{\frac{1}{2}}$ against log [X]; when m = 1 the halfwave potential is constant, independent of the ligand concentration.

The overall stability constants of the complexes formed at the electrode can be evaluated if $E^0(\mathrm{Hg^{2+}/Hg})$ in dmso is known. This has been calculated on the basis of $E^0(\mathrm{Hg^{2+}/Hg})$ in water [+0.854 V *versus* normal hydrogen electrode (n.h.e.)] and of the transfer activity coefficient from water to dmso [$\log \gamma(\mathrm{t,w} \longrightarrow \mathrm{dmso}) = -13.9$] [19] as +0.216 V *versus* s.c.e. The diffusion coefficients, D, of the ligand and of the complex have been assumed to be equal.

TABLE 1

Results obtained from polarography

Amine	Concentration range $\mathrm{dm^3\ mol^{-1}}$	$\partial E_{\frac{1}{2}}/\partial \log [\mathrm{X}]$ mV	m_1 [a]	$-\partial E/\partial \log[(i_d - i)^m/i]$ mV	m_2 [b]	β_m
en	1.18×10^{-4}—4.48×10^{-3}	32	2	30 ± 3	2	$1 \times 10^{14}\ \mathrm{dm^6\ mol^{-2}}$
dmen	7.43×10^{-5}—3.61×10^{-3}	26	2	32 ± 2	2	$6 \times 10^{11}\ \mathrm{dm^6\ mol^{-2}}$
tmen	8.41×10^{-5}—4.80×10^{-4}	0	1	29 ± 2	1	$4 \times 10^{2}\ \mathrm{dm^3\ mol^{-1}}$
	4.80×10^{-4}—3.53×10^{-3}	29	2	29 ± 2	2	$9 \times 10^{5}\ \mathrm{dm^6\ mol^{-2}}$
pd	9.40×10^{-5}—3.60×10^{-3}	25	2	30 ± 2	2	$7 \times 10^{11}\ \mathrm{dm^6\ mol^{-2}}$
trien	8.50×10^{-5}—1.20×10^{-3}	25	2	32 ± 3	2	$1 \times 10^{18}\ \mathrm{dm^6\ mol^{-2}}$

[a] Values of m calculated from $\partial E_{\frac{1}{2}}/\partial \log [\mathrm{X}]$. [b] Value obtained from logarithmic analyses of the waves.

The equation of the curve of current against potential in the rising portion of the wave [18] [$E = \text{constant} - (RT/2F) \ln (i_d - i)^m/i$, where i_d is the limiting current] allows one to treat the experimental data according to a logarithmic plot; thus a plot of E against $\log(i_d - i)^m/i$ gives a straight line with the theoretical gradient of 29 mV only if the correct value of m is used.

Table 1 summarizes the polarographic data obtained for the cited polyamines, together with the numbers of complexing molecules involved in the oxidation process and the relative stability constants. It can be noted that, unlike other amines, the stoicheiometry of the tmen complexes is a function of the amine concentration.

Since cyclic voltammetry is a suitable technique for studying the processes occurring primarily at the electrode, cyclic voltammograms were recorded at potential scan rates ranging from 0.02 to 50 V $\mathrm{s^{-1}}$ for solutions of en, dmen, tmen, pd, or trien. The solutions of en, dmen, tmen, and trien exhibited an anodic peak with an associated cathodic peak. The quotient of the anodic peak current and the square root of the scan rate [$(i_p)_a/v^{\frac{1}{2}}$] was strictly constant for all the polyamines; moreover, the anodic peak potentials [$(E_p)_a$] were constant at any scan rate, indicating the diffusive character of the process. The most interesting features of the cyclic voltammograms were the difference between the values of the peak potential and the half-peak potential [$(E_p)_a - (E_{p/2})_a$], the difference between the values of the anodic and cathodic peak potentials [$(E_p)_a - (E_p)_c$], and the quotients of the cathodic and the anodic peak currents [$(i_p)_c/(i_p)_a$], calculated according to Nicholson.[20]

Table 2 summarizes the cyclic-voltammetric results. The experimental data are consistent with the theoretical values relative to the reversible anodic dissolution of mercury in complexing solutions *via* either a first- or a second-order [21] electrode process [equation (2)], where $m = 1$ or 2. The calculated m values are in good

$$\mathrm{Hg} + m\mathrm{X} \rightleftharpoons [\mathrm{HgX}_m]^{2+} + 2\mathrm{e}^- \qquad (2)$$

agreement with those obtained from the polarographic responses.

Exhaustive controlled-potential coulometric experiments carried out at potentials corresponding to the limiting current of the anodic waves allowed a determination of the stoicheiometry of the final complex species formed in the electrolyzed solutions. Cyclic-voltammetric tests carried out during the electrolyses did not reveal the presence of free mercury ions in the solution; in contrast, if the mercury pool was anodized after the completion of the electrolyses, as long as a few Coulombs were consumed, the presence in the solution of free mercury ions could be revealed by cyclic voltammetry.

TABLE 2

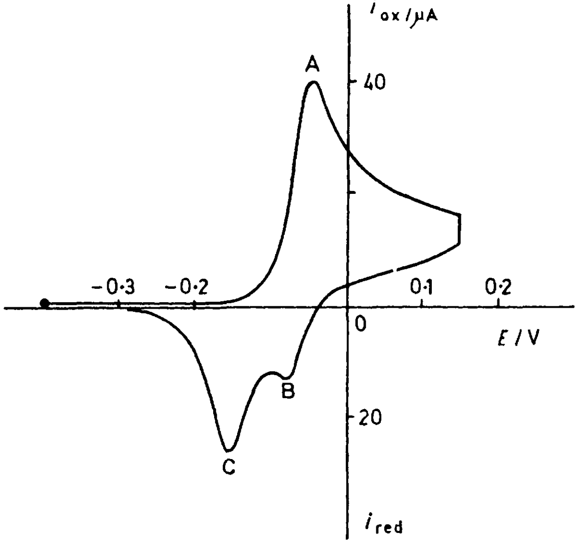
Cyclic-voltammetric results obtained at the mercury electrode; potential scan rate = 200 mV $\mathrm{s^{-1}}$

Amine	$(E_p)_a - (E_{p/2})_a$/mV	$(E_p)_a - (E_p)_c$/mV	$(i_p)_c/(i_p)_a$	m
en	42 ± 5	47 ± 5	1.10 ± 0.02	2
dmen	40 ± 4	46 ± 4	1.05 ± 0.03	2
tmen	59 ± 3 [a]	29 ± 4 [a]	1.01 ± 0.01 [a]	1 [a]
	43 ± 4 [b]	48 ± 5 [b]	1.09 ± 0.04 [b]	2 [b]
trien	40 ± 3	45 ± 5	1.09 ± 0.02	2

[a] At low tmen concentrations. [b] At high tmen concentrations.

Cyclic-voltammetric tests performed on pd solutions gave data somewhat different from those from polarography, in that at potential scan rates lower than 0.2 V $\mathrm{s^{-1}}$ two cathodic peaks could be detected after traversing the anodic peak (Figure). The difference between the values of the two cathodic peak potentials ranged from 80 to 130 mV, depending on the potential scan rate and on the switching potential; moreover $(i_p)_B/(i_p)_A$ was less than unity. At higher scan rates only the less cathodic peak B was detectable and the catho-anodic system exhibited the typical feature for a two-electron reversible process involving a unity electrode reaction order. Two cathodic peaks could be again detected at scan rates higher than 0.2 V $\mathrm{s^{-1}}$ if the sweep was stopped beyond the anodic peak A and the electrode potential was held constant for a few seconds before the start of the reverse scan. In the coulometric experiments, one electron per molecule of pd was consumed, suggesting that $[Hg(pd)_2]^{2+}$ is formed as final product. Cyclic-voltammetric curves recorded on the electrolyzed solution showed a cathodic peak located at the same potential as peak C in the Figure with an associated anodic peak corresponding to peak A in the Figure. On the basis of both cyclic-voltammetric and coulometric results, it can be concluded that, in correspondence with peak A, the species $[Hg(pd)]^{2+}$ arises at higher scan rates, while both the $[Hg(pd)]^{2+}$ and $[Hg(pd)_2]^{2+}$ species form at lower scan rates; $[Hg(pd)]^{2+}$ is reduced at peak B and $[Hg(pd)_2]^{2+}$ at peak C.

From the voltammetric response at higher scan rates it is possible to calculate the stability constant of the $[Hg(pd)]^{2+}$ species taking into account that, for a



Cyclic-voltammetric curve recorded for a dmso solution containing 3.8×10^{-3} mol dm^{-3} pd and 0.1 mol dm^{-3} $Na[ClO_4]$. Mercury working microelectrode: scan rate 0.1 V s^{-1}; anodic scan; (●) starting potential

surface, as deduced from the polarographic and cyclic-voltammetric data.

Silver Electrode.—Dimethyl sulphoxide solutions containing increasing amounts of en, dmen, pd, or trien exhibited an anodic wave at a silver electrode with periodical renewal of the diffusion layer. The limiting current was linearly dependent on the polyamine concentration; however, only a rather narrow concentration range (*ca.* 5×10^{-5}—8×10^{-4} mol dm^{-3}) could be explored since at higher concentrations the anodic wave was complicated by the occurrence of adsorption phenomena.

The voltammetric data were treated in a similar way to those obtained in the case of the mercury working electrode. In order to calculate the values of m and β relative to the complexation reaction occurring at the electrode surface equations (4) and (5) were employed. In fact the process occurring at the electrode is (6).

$$E_{\frac{1}{2}} = E^0(\mathrm{Ag^+/Ag}) + \frac{RT}{F}\ln\frac{D_\mathrm{L}^{\frac{1}{2}}}{mD_\mathrm{C}^{\frac{1}{2}}\beta_m[\mathrm{X}]^{m-1}} \qquad (4)$$

$$E = \text{constant} - \frac{RT}{F}\ln\frac{(i_\mathrm{d} - i)^m}{i} \qquad (5)$$

$$\mathrm{Ag} + m\mathrm{X} \rightleftharpoons [\mathrm{AgX}_m]^+ + \mathrm{e}^- \qquad (6)$$

The value of $E^0(Ag^+/Ag)$ in dmso was taken from ref. 23. The resulting m and β values are collected in Table 4. For all the polyamines, m was equal to one, suggesting that the complex species reported in Table 4

TABLE 4

Voltammetric and coulometric results for silver(I) complex species (m = 1)

Amine	Complex species arising at the electrode surface	β_1/ dm^3 mol^{-1}	Complex species formed by exhaustive electrolysis
en	$[Ag(en)]^+$	2×10^3	$[Ag(en)_2]^+$
dmen	$[Ag(dmen)]^+$	1×10^2	$[Ag(dmen)_4]^+$
pd	$[Ag(pd)]^+$	1×10^2	$[Ag(pd)]^+$

1 : 2 mercury(II)–ligand and 1 : 1 silver(I)–ligand species {except for $[Hg(tmen)]^{2+}$, detected at low diamine concentrations}. These conclusions are also supported by the constancy of the ratio between the limiting current and ligand concentration, independent of the nature of the ligand, both with mercury and silver electrodes.

Cyclic voltammetry confirms the polarographic data and gives additional useful information about the complexation steps, enabling the calculation of stability constants for short-lived complex species undetectable by conventional polarography.

It can be noted that ethylenediamine and its derivatives (en, dmen, tmen) form, both with Hg^{II} and Ag^{I}, complexes of decreasing stability from primary to tertiary amine groups. In addition, the stability constant of $[Hg(pd)_2]^{2+}$ is noticeably lower than that of $[Hg(en)_2]^{2}$; this result can be attributed to the known higher stability of five- compared to six-membered chelate rings.

The stability constant of $[Hg(trien)_2]^{2+}$, higher than that of the other amine complexes, could be explained by taking into account the fact that the tetramine can behave as a bidentate ligand, leading to a complex containing two stable five-membered chelate rings, similar to that of en and its derivatives, but with a more marked entropy gain in the complex formation. The same arguments hold in the case of similar complexes of Cu^{II}, Ni^{II}, and Zn^{II}.[24]

It is also noteworthy that the electrogenerated dmen and tmen complexes, for which a lower β_2 value than that of en has been found, undergo subsequent complexation steps in the bulk of the solution. In the final complex species the diamine can also act as a unidentate ligand; the higher the steric hindrance the larger becomes the number of unidentate ligand molecules. In this connection it can be hypothesized that the chelate effect plays a fundamental role in the stabilization of the primary polyamine complexes; molecules which almost always act as unidentate ligands, such as the long-chain hexane-1,6-diamine, are unable to form mercury(II) complexes stable enough to be revealed in polarography (see Results section). This is not surprising since Hg^{II}, like Ag^{I}, is a typically 'soft' acceptor, while diamines are relatively 'hard' donors.

The relative β_2 values and steric hindrance accounts for the final formulae of the mercury(II) complexes with pd and trien.

Similar conclusions can be drawn for the silver(I) complexes; however, it must be emphasized that the complexation step following the first one is noticeably slower than with the corresponding mercury(II) complexes. In all cases, d.c. voltammetry indicated a unity electrode reaction order with respect to the ligand. Accordingly, the pd ligand, which slowly reacts with Hg^{II} in the second complexation step, forms a 1 : 1 complex with Ag^{I} as final product of the electrolysis.

As regards the stability constants of mercury(II)–polyamine complexes in aqueous and non-aqueous media, the en ligand can be taken for comparison purposes. The β_2 value of $[Hg(en)_2]^{2+}$ in dimethylformamide (dmf) (3.2×10^{23} dm^6 mol^{-2}) [11] is very close to that calculated in water (2.6×10^{23} and 1.5×10^{23} dm^6 mol^{-2}),[4] and can be justified on the basis that the solvent has little effect on the complex stability. However, our data in dmso (β_2 10^{14} dm^6 mol^{-2}) clearly indicate that $[Hg(en)_2]^{2+}$ is notably less stable in this solvent than in water. This result is supported by the stronger solvation of the mercury(II) ion in dmso than in water,[25] which is reflected in $\log \gamma(\text{t,w} \longrightarrow \text{dmso}) = -13.9$ and consequently in $E^0(Hg^{2+}/Hg)$ in dmso. From $\log \gamma(\text{t,w} \longrightarrow \text{dmf}) = -11.25$,[26] it is possible to calculate a thermodynamic E^0 value which is noticeably lower than that used by Matsui *et al.*,[11] obtained from polarographic data.[8]

The reported stability constant of the $[Ag(en)]^{+}$ complex in nitromethane [14] is 6.3×10^9 dm^3 mol^{-1}. Our value in dmso (2×10^3 dm^3 mol^{-1}) is much lower and can be explained by taking into account the higher coordination ability of dimethyl sulphoxide compared to nitromethane, according to the 'donor numbers' listed by Guttmann,[27] which can be considered as a guide to the solvating properties of the solvent.

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