GALVANOSTATIC DISSOLUTION OF MERCURY FROM THE SURFACE OF GLASSY CARBON INTO THIOCYANATE SOLUTION

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The galvanostatic dissolution of mercury from the surface of glassy carbon into a thiocyanate solution proceeds in accord with theoretical assumptions, as manifested by the constant product of the dissolution current and transition time. Under certain relations between the amount of oxidised mercury and concentration of thiocyanate at the electrode surface, however, a small part of the mercury dissolves at more positive potentials than correspond to the Nernst equation. This dissolution can be accompanied by potential oscillations. The anomalous behaviour is elucidated by the concept about coverage of a certain part of mercury with a film of sparingly soluble compounds of SCN^- ions with mercury. This film is formed at the end of the galvanostatic dissolution on certain places of the electrode surface covered with mercury droplets, where SCN^- ions are much exhausted as a result of a high current density.

The galvanostatic dissolution in stripping analysis has been used rather rarely, even when it brings a marked advantage against classical potentiostatic methods, namely a much higher selectivity in determining trace amounts of depolarizer mixtures[1,2]. The determination of mercury by the galvanostatic stripping method has been done on glassy carbon electrodes[3-5]. Vydra and Luong[2,3] followed besides other analytically important factors also the dependence of the dissolution current on the transition time and found that at lower dissolution currents (10—100 μA) the dependence of the transition time on reciprocal current is nonlinear, *i.e.*, the product $I\tau$ changes with the current. This effect, which was observed with a number of metals, is at variance with the theory[1,6] of the galvanostatic dissolution of a substance deposited on an electrode.

In the case of mercury dissolved into a solution of HCl, a nonproportional increase of the transition time was observed at lower currents[3]. We therefore concentrated on the galvanostatic dissolution of mercury into a more suitable medium and chose a solution of thiocyanate, which has been reported to have favourable properties for the determination of mercury[7].

EXPERIMENTAL

Apparatus. For preliminary electrolysis at constant potential with following galvanostatic dissolution, we used a circuit enabling an instantaneous switching over from potentiostatic to galvanostatic regime of the electrode polarization[8]. The time sequence of the individual steps (bubbling with inert gas, duration of electrolysis, standing idle) was controlled automatically by a programator[9]. The curves were recorded on an XYt recorder of the type BRYANS 26000A3.

Electrode system. The rotating disc electrode (R.D.E.) from glassy carbon GC 20 (Tokay Electrode, Japan) had a geometric area of $6.42 \cdot 10^{-2}$ cm^2 and was pressed in a Teflon cylinder of 10 mm diameter. Some measurements were carried out with a ring-disc electrode whose disc was from glassy carbon and the ring from platinum; its parameters were: $r_1 = 2.54$ mm, $r_2 = 2.71$ mm, $r_3 = 2.85$ mm. The electrodes were cleaned only by polishing with a humid velvet. The potentials in this work are referred to S.C.E. (type K 401, Radiometer) separated from the measuring compartment by a salt bridge filled with saturated NaNO$_3$. The auxiliary electrode from a platinum spiral was separated from the solution by fritted glass. The cell with the electrodes contained 10 ml of solution whose ionic strength was maintained at 1M by the addition of NaNO$_3$. The solution was deaerated by bubbling nitrogen purified with a Cr(II) solution and with distilled water.

Chemicals. A stock solution of Hg(II) was prepared by dissolving a weighed amount of mercury in concentrated HNO$_3$ and the solution was made up with water redistilled from a quartz apparatus. The final concentration was $6.38 \cdot 10^{-3}$M-Hg in 0.1M-HNO$_3$. Other chemicals were of reagent grade. The concentration of NaSCN used was 10^{-3}—1M.

Method of measurement. Mercury was deposited potentiostatically from the prepared deaerated solution during rotation of the electrode ($\omega = 251.3$ rad/s) for a chosen time in the range 30—300 s. After 30 s idling, the circuit was switched over from the potentiostatic to the galvanostatic regime and a chronopotentiometric curve on stationary electrode was recorded at a dissolution current of 2—50 μA. If the dissolution curve was recorded during rotation, the idling period was left out. The measurement was carried out at room temperature (about 22°C).

RESULTS AND DISCUSSION

At optimum conditions, the quantity of deposited metal from a solution of concentration c_b at constant potential electrolysis in the region of limiting current I_{lim} is given as $Q = I_{lim}t_{el}$, where t_{el} is the time of electrolysis. When the deposition proceeds on a R.D.E., then[10]

$$Q = nFAD^{2/3}c_b t_{el} \sqrt{\omega}/1.61 v^{1/6} = B' t_{el} \sqrt{\omega} . \qquad (1)$$

The transition time during galvanostatic dissolution of this quantity of the deposited metal at a current I will be given as[1,6]

$$\tau = Q/I = B' t_{el} \sqrt{\omega}/I . \qquad (2)$$

Hence, the theoretical dependence of the transition time on the dissolution current can be determined for any metal if the constant B' is known. For mercury dissolution, the value of $B'/c_b = 7.07$ Acm^3 s$^{1/2}$ mol^{-1} was found from the slope of the linear dependence of limiting current for reduction of Hg^{2+} in a solution of NaSCN on the square root of the angular velocity of rotation of the electrode. The experimentally found dependence of τ on $1/I$ is linear in accord with the theoretical one. The charge consumed in the dissolution of the deposited mercury was determined also from

potentiostatic curves and an agreement was found between the theoretical and experimental dependence of the transition time on the duration of preliminary electrolysis.

However, during a galvanostatic study of mercury dissolution in the medium of thiocyanate, an anomalous course of E–t curves toward the end of the dissolution time was observed. In solutions of more than about 0.01M-SCN$^-$ and with a quantity of deposited mercury of the order of 10^{-3} C/cm^2, at least 90 percent Hg dissolved at a potential corresponding to

$$E = E' + (RT/2F)\ln\left\{[\mathrm{Hg(SCN)}_4^{2-}]_0/\beta_4[\mathrm{SCN}^-]_0^4\right\},$$

where β_4 denotes constant of complexity; this formula is in accord with the slope of the linear dependence of potential on the logarithm of thiocyanate concentration, namely 122 mV (Fig. 2, curve *1*). The potential was measured in the intersection of straight lines drawn through the charging and dissolution portions of the E–t curve. A certain portion of the mercury, however, dissolved at much more positive potentials, which was manifested by a short transition time on the descending part of the E–t curve. This transition time had to be added to the main one to obtain the theoretical value. That this anomalous transition time corresponds also to oxidation of mercury on the disc electrode was proved by measurement with a ring-disc electrode. The result is seen from Fig. 3 (curves *1* and *1'*), where the increase of the ring current corresponds to the instant when the anomalous transition time is recorded on the disc. The ring potential was chosen so as to lie in the region of the limiting current for reduction of Hg^{2+} on platinum electrode (-0.2 V in 0.05M-NaSCN).

A typical dissolution E–t curve is shown in Fig. 1 (curve *1*). With respect to literature data[7,11] it was assumed that the remainder of mercury dissolves from active centers on the electrode surface (so-called monolayer). It turned out, however, that the mercury dissolution from this "monolayer" is largely influenced not only by the potential of preelectrolysis and state of the electrode surface (its "history") but mainly by the actual concentration of SCN$^-$ ions at the electrode surface during dissolution.

Since mercury forms during dissolution in the studied medium complexes Hg(SCN)$_i^{2-i}$, the complexing agent in the vicinity of the electrode is exhausted and must be transported by diffusion. The degree of exhaustion of thiocyanate can be influenced by its analytical concentration, by the charge passed to dissolve the mercury (*i.e.*, by the duration of preliminary electrolysis), intensity of the dissolution current, and eventually by the solution temperature. According to these experimental conditions, the form of the E–t curves at the end of dissolution and the potential at which the remainder of mercury oxidises change.

In Fig. 1 is shown the course of the last portion of the E–t curves in dependence on the analytical concentration of SCN$^-$ ions for constant dissolution current and

constant quantity of deposited mercury. It is seen that at higher concentrations (about $1-0.5\text{M-SCN}^-$) the dissolution of the re mainder of mercury is manifested by a short transition time (curve *1*). This occurs generally at such experimental conditions which ensure a relatively high concentration of thiocyanate at the electrode with respect to the quantity of Hg^{2+} formed by oxidation. When the analytical concentration of SCN^- ions is lowered (from about 0.4 to 0.05M), potential oscillations appear on the $E-t$ curves (curves *2, 5,7*); when it is lowered further, the oscillations disappear and the dissolution of the remainder of mercury is again manifested by a transition time (curve *9*). In the presence of less than 0.005M-SCN^-, mercury dissolves in three steps (curve *10*). The dependence of the potential at which the remainder of mercury dissolves on the analytical concentration of SCN^- ions at various dissolution currents is shown in Fig. 2 (curves *2—5*).

Hence, the necessary condition for the potential oscillations is a certain concentration of thiocyanate at the electrode. Their formation depends also on the potential
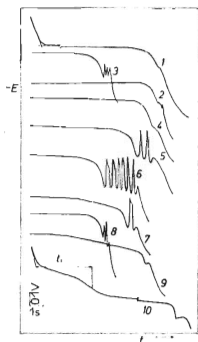

Fig. 1

Portions of $E-t$ Curves for Mercury Dissolution in SCN^- Solutions

$1.27 \cdot 10^{-5}\text{M-Hg}^{2+}$, 120 s electrolysis during rotation at -1.0 V, 30 s idling (mercury deposit of 170 µC), dissolution current 10 µA (except otherwise noted). $[SCN^-]_b$: *1* 1M; *2, 3* 0.4M; *4—6* 0.1M; *7* 0.07M; *8, 9* 0.05M; *10* 0.001M. *3* Dissolution current 50 µA; *4* electrolysis at -1.5 V; *6* at -0.7 V; *8* dissolution during rotation at 40 r.p.s.
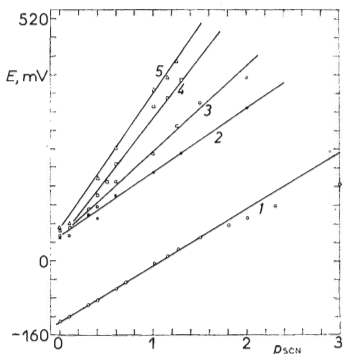
Fig. 2

Dependence of Potential of Mercury Dissolution on $[SCN^-]_b$

1 Potential of intersection of straight lines led through the charging and dissolution portions of the $E-t$ curve; dissolution current 10 µA. *2—5* Dissolution potential of remaining mercury at a current of: *2* 6 µA; *3* 10 µA; *4* 30 µA; *5* 50 µA. Electrolysis conditions see Fig. 1; $p_{SCN} = -\log_{10}$. $.[SCN^-]_b$.

of preliminary electrolysis and state of the electrode surface. At potentials more negative than -1.2 V, the oscillations practically do not appear. Between -1.2 and -1.0 V, the potential oscillations occur usually only after several deposition-dissolution cycles without mechanical polishing of the electrode. At potentials of preliminary electrolysis more positive than about -0.8 V, the oscillations are formed most easily. The influence of the electrolysis potential on their formation is seen from Fig. 1, curves $4-6$. The fact that Hg^{2+} ions are evolved from the disc electrode during the oscillations was proved by measurement with a ring-disc electrode (Fig. 3, curves 2 and $2'$).

In the given experimental arrangement and at dissolution currents $2-50\ \mu A$, oscillations were formed most easily in the presence of about $0.05-0.2M\text{-SCN}^-$ with a quantity of deposited mercury of about $0.008-0.08$ C/cm^2 and at a potential of preliminary electrolysis of -0.7 V.

A quantitative evaluation of the oscillation frequency is made difficult by the dependence of the character of the oscillations on the actual state of the electrode surface, which is difficult to determine. Moreover, the $E–t$ curves showed usually two or three potential oscillations with increasing duration of the period, often deformed by a slight formation of a transition time on the peak (Fig. 1, curve 7). The oscillation frequency increases with increasing dissolution current and concentration of SCN^- ions.

The described behaviour of mercury during galvanostatic dissolution was observed both in neutral ($NaNO_3$) and acidic ($HClO_4$) solutions of thiocyanate and it apparently specific for this medium, since in solutions of iodides, bromides, and chlorides none of the mentioned effects was observed. The specific behaviour of mercury during dissolution in thiocyanate medium is apparent also from the results of potentiostatic measurements[7,11,12].

To explain the observed facts, it is necessary to know the concentration of thiocyanate at the electrode surface during dissolution of mercury. It is known[15] that mercury forms following complexes in thiocyanate solutions of various concentrations: $Hg(SCN)_2$, $Hg(SCN)_3^-$, $Hg(SCN)_4^{2-}$, and $Hg_2(SCN)_2$ (Fig. 4).

The glassy carbon electrode covered with deposited mercury, most probably in the form of droplets,[11] is a very complicated system. The surface concentration $[\text{SCN}^-]_0$ can be roughly estimated as follows. Galvanostatic oxidation of the mercury deposit on a stationary planar electrode contributes to the surface analytical concentration of Hg(II) ions by the quantity[13]

$$[Hg^{2+}]_0 = 2I\ \sqrt{(t)}/nFA\ \sqrt{(\pi D)}. \tag{3}$$

If the complexing agent is present in solution, it is depleted at the electrode by the formation of mercury complexes. Assuming that their formation rate is large and

their relative proportion α_i as function of thiocyanate concentration is known, the surface concentration of thiocyanate can be estimated from the equation

$$[SCN^-]_0 = [SCN^-]_b - \left[\frac{2I\sqrt{t}}{nFA\sqrt{(\pi D)}} (2\alpha_2 + 3\alpha_3 + 4\alpha_4) \right], \qquad (4)$$

where

$$\alpha_i = \beta_i[SCN^-]_0^i \, \alpha_0 , \quad \alpha_0 = 1/(1 + \sum_{i=2}^{4} \beta_i[SCN^-]_0^i)$$

and β_i are complexity constants of the complexes $Hg(SCN)_i^{2-i}$ (see text to Fig. 4).

If we assume that mercury is present on the electrode surface in the form of droplets, then the true surface area through which the current passes is given by their surface area. To calculate the latter, we assume that during the deposition of mercury the geometric surface area, A_G, of the electrode becomes covered with P droplets per cm^2, which have a half-spherical form. From the quantity of mercury in coulombs,
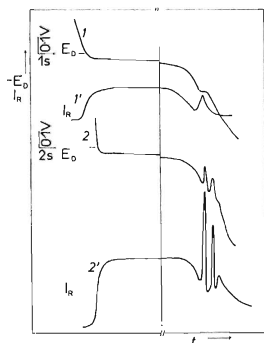

Fig. 3

E_D-t and I_R-t Curves for Mercury Dissolution on Ring-Disc Electrode

$1.27 \cdot 10^{-5}$M-Hg^{2+}, 0.05M-NaSCN, $E_R = -200$ mV. 1 60 s electrolysis at -700 mV during rotation, dissolution current $10\,\mu$A; 2 240 s electrolysis at -700 mV during rotation, dissolution current $20\,\mu$A. Electrolysis and dissolution during rotation at 40 r.p.s.
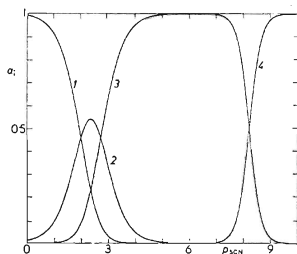

Fig. 4

Relative Content of Mercury Thiocyanate Complexes as Function of Thiocyanate Concentration

Complexity constants[15]: $\beta_2 = 2.7 \cdot 10^{16}$, $\beta_3 = 1.32 \cdot 10^{19}$, $\beta_4 = 1.32 \cdot 10^{21}$. 1 Hg(SCN)$_4^{2-}$; 2 Hg(SCN)$_3^-$; 3 Hg(SCN)$_2$; 4 Hg^{2+}.

molar mass 200·6 g/mol, density $\varrho = 13·6$ g/cm³, and geometric surface area $A_G = = 6·42 . 10^{-2}$ cm² the surface area of the droplets, A, as a function of time can be calculated:

$$A = 2(\pi P A_G)^{1/3} \left[\frac{3}{2} \frac{200 . 6I(\tau - t)}{2F\varrho} \right]^{2/3} . \qquad (5)$$

This equation was used in solving Eq. (4). The value of P was determined from the literature[11] as $P = 1·5 . 10^7$ droplets per cm².

Eq. (4) gives the dependence of the surface concentration of thiocyanate on the time of dissolution (or on the charge Q_t passed from the beginning of the dissolution) (Fig. 5). It is seen that the drop in the concentration of SCN^- ions is initially negligible; it is compensated by diffusion from the bulk of the solution, so that the soluble complex $Hg(SCN)_4^{2-}$ is formed preferentially (Fig. 4). With progressive dissolution, the surface area of the droplets diminishes and the current density on them increases resulting in a larger exhaustion of thiocyanate from their vicinity. This in turn leads to the formation of lower complexes of mercury. The region of thiocyanate concentrations between A and B in Fig. 5 corresponds in the distribution diagram of mercury complexes to the region of coexistence of all three complexes. Eventually only $Hg(SCN)_2$ is formed (region between B and C in Fig. 5). In the extreme case, SCN^- ions can be in the vicinity of mercury droplets so exhausted that no complex can be formed and mercury is oxidised to Hg_2^{2+} ions.

With respect to many simplifications used in deriving and solving Eq. (4) (neglection of charging current, diffusion was considered to a planar and not spherical electrode, neglection of diffusion in the space above the noncovered electrode surface) it can be expected that the true concentration of thiocyanate at the electrode will be higher than calculated. The model used does not involve also the possible formation of $Hg_2(SCN)_2$. Therefore, the E–t curves calculated for $[SCN^-]_b = 0·4M$ were found
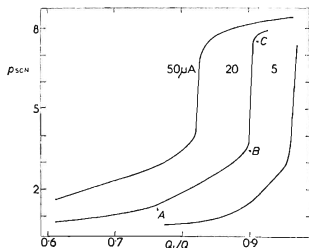

Fig. 5

Dependence of Surface Concentration $[SCN^-]_0$ on Charge Passed from the Beginning of Mercury Dissolution for Various Dissolution Currents

Calculated according to Eq. (4) for $[SCN^-]_b = 0·4M$; mercury deposit of 170 μC.

experimentally at $[SCN^-]_b < 0.07M$ (other experimental conditions being the same), which is seen from curves 7, 9, and 10 in Fig. 1. These show after some time of dissolution a break to more positive potentials, which probably indicates the formation of lower mercury complexes. Owing to their lower complexity constants, the concentration of Hg^{2+} ions at the electrode becomes higher resulting in an increase of the electrode potential.

Finally, for $[SCN^-]_b < 5 . 10^{-3}M$, the transition time is separated into three parts (curve 10 in Fig. 1). The time t_1 corresponding to the first part of this curve depends only on the analytical concentration of thiocyanate[14]. The second portion of mercury is oxidised at $+0.4$ V, i.e., at a potential corresponding to the dissolution of mercury in a solution of $NaNO_3$. The third portion is an anomalous dissolution of the remainder of mercury.

This anomalous dissolution can be elucidated on the basis of the preceding estimate of the time dependence of the surface concentration of SCN^- ions. The high current density toward the end of the dissolution causes such an exhaustion of thiocyanate in the vicinity of the mercury droplets that a layer of little soluble $Hg(SCN)_2$ or $Hg_2(SCN)_2$ is formed on their surface, whereby the ohmic resistance, R, in the system is increased. Accordingly, during passage of a constant dissolution current the potential increases by the value of IR. The resistence R depends on the film thickness and this in turn is governed by the difference between the rates of formation and dissolution or disintegration of the film. The rate of formation is a function of the current density and actual concentration of thiocyanate at the electrode surface. The rate of disintegration is due to a complex process of chemical $(Hg(SCN)_2 + 2 SCN^- = Hg(SCN)_4^{2-}$ and eventually $Hg_2(SCN)_2$ disproportionates) and physical dissolution; it is a function of thiocyanate concentration at the electrode.

The observed phenomena can be on the basis of this concept elucidated as follows:

a) Case of high concentration of complexing agent, small dissolution current — thiocyanate is exhausted from the vicinity of the electrode only after oxidizing nearly all mercury. Conditions for the formation of an insoluble film are fulfilled only on a very small remainder of mercury on the electrode thanks to high current density. The remainder of mercury, however, is oxidised before the film disintegrates even when this disintegration is relatively rapid. The oxidation of the remainder of mercury is manifested by a short transition time at a more positive potential (curve 1, Fig. 1).

b) Low concentration of the complexing agent, large dissolution current — thiocyanate is exhausted from the vicinity of a large portion of mercury droplets, which are covered with a film. With respect to low concentration of thiocyanate, the disintegration of the film proceeds very slowly and mercury is also oxidised before this film is dissolved. The oxidation of mercury covered with the film is manifested on the $E-t$ curve by a transition time at a more positive potential (curves 9 and 10 in Fig. 1).

c) Between these extreme cases such conditions can be realized at the electrode that the film covers a sufficient quantity of mercury so that the film is dissolved sooner than the mercury. At such conditions, oscillations of the potential take place between the value of E corresponding to normal dissolution of mercury and $E + IR$ (see also below) corresponding to dissolution of mercury covered with the film. The film dissolution is accelerated because the oxidation product of mercury remains partly under the film (diffusion of the product into the solution is hindered) and is set free only after its disintegration. This results in a large increase of the ring current during measurement with the ring-disc electrode above the value corresponding to the stationary state during dissolution with constant current (Fig. 3, curves 2 and 2'). In the moment when the film disintegrates, the undissolved droplets of mercury become naked and the potential drops. Due to a high current density, mercury is soon covered with a film again and the whole process is repeated till all mercury on the electrode surface is oxidised. The coverage of mercury with the film is accelerated because Hg^{2+} ions set free after the film disintegration consume a large portion of SCN^- ions transported by diffusion to form complexes (curves 5—7 in Fig. 1). Curve 3 in Fig. 1 illustrates the transition from the discussed case *a*) into the state where oscillations occur owing to a drop in the surface concentration of SCN^- ions caused by an increase of the dissolution current. Curve 8 illustrates the transition from the state discussed as case *b*) into the state where the oscillations are caused by an increase of thiocyanate concentration at the electrode due to rotation of the the electrode during dissolution. On the contrary, it is possible to pass from the situation where oscillations take place to case *a*) by increasing the solution temperature. Thus, when oscillations took place at the laboratory temperature, then by increasing the temperature to 60°C and *E*–*t* curve was obtained not only without oscillations but also without the anomalous transition time. The higher temperature apparently favoured the dissolution of the film relative to its formation rate.

Hence, the heterogeneity of the electrode surface covered with mercury droplets and the resulting inhomogenous current density on the electrode surface are principally responsible for the potential oscillations during mercury dissolution in a thiocyanate solution. This condition was even considered necessary for the formation of oscillations in electrochemical systems[16], although not in general[17].

Our results show further that the potential at which the remainder of mercury dissolves can be determined not only by the film resistance but also by the increased concentration of mercury ions at the electrode diffusing more slowly from places covered with the film. Finally, the potential value can be also controlled by the formed electrode of the second kind, $Hg \mid Hg(SCN)_2 \; Hg_2(SCN)_2 \mid SCN^-$. The potential will be in all these cases the more positive the lower is the surface concentration of thiocyanate, *i.e.*, the lower is its analytical concentration in solution and the higher is the dissolution current at the given quantity of deposited mercury on the electrode (Fig. 2).

The influence of the state of the electrode surface and potential of preliminary electrolysis can be elucidated by assuming that a favourable size distribution of mercury droplets on the electrode is necessary for the formation of oscillations; this is related to the distribution of energetically differentiated sites on the glassy carbon surface and this distribution can be influenced by the potential of the preliminary electrolysis[11].

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