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Abstract

Full Text

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Ya. I. Turyan

Polarographic Study of the Mechanism of Electroreduction of Simple and Complex Nickel Ions

(Presented by Academician A. N. Frumkin, May 17, 1961)

On the basis of the theory of A. N. Frumkin (^{1}), we have shown (^{2}) that the overvoltage η of the process

$$\mathrm{Ni(H_2O)}_q^{2+} + 2e \rightarrow \mathrm{Ni(Hg)}^* \rightarrow \mathrm{Ni(Hg)} \tag{1}$$

I II

is due to the slowness of electrochemical stage I.

In the case of complexes of $\mathrm{Ni(H_2O)}_q^{2+}$ with pyridine Py (^{3}), rhodanide (^{4,5}), and other addends (X), the complex ion undergoes electroreduction:

$$\mathrm{Ni(H_2O)}_q + p\mathrm{X}^{-b} \rightarrow \mathrm{Ni(H_2O)}_{q-p} \cdot \mathrm{X}_p^{(2-pb)+} + 2e \rightarrow \mathrm{Ni(Hg)}^* \rightarrow \mathrm{Ni(Hg)}. \tag{2}$$

III IV II

It follows from (^{6}) that the larger the value of p, the lower η:

$$\mathrm{Ni(H_2O)}_{q-2} \cdot \mathrm{(CNS)}_2 < \mathrm{Ni(H_2O)}_{q-1}\mathrm{CNS}^+ < \mathrm{Ni(H_2O)}_q^{2+}.$$

We have also shown (^{3,4,6}) that at a low concentration of X ($\mathrm{Py}, \mathrm{CNS}^-$), the rate of stage III is comparable with the rate of diffusion (kinetic currents).

(Figure: Fig. 1. Oscillogram $1\,M$ $\mathrm{KNO_3} + 0.1\,M$ $\mathrm{Py} + 2 \cdot 10^{-3}\,M$ $\mathrm{NiSO_4}$.)

Fig. 1. Oscillogram $1\,M$ $\mathrm{KNO_3} + 0.1\,M$ $\mathrm{Py} + 2 \cdot 10^{-3}\,M$ $\mathrm{NiSO_4}$.

(Figure: Fig. 2. Oscillogram $1\,M$ $\mathrm{KCNS} + 2 \cdot 10^{-3}\,M$ $\mathrm{NiSO_4}$.)

Fig. 2. Oscillogram $1\,M$ $\mathrm{KCNS} + 2 \cdot 10^{-3}\,M$ $\mathrm{NiSO_4}$.

From the rate constants of stage III found in (^{6}), it follows that, as H_2O is displaced from the hydrate shell, the further attachment of X proceeds more rapidly.

With increasing C_X, the rate of process III becomes considerably greater than the rate of diffusion and, owing to the appearance of an appreciable concentration of a larger complex that is reduced with insignificant η, stage IV also becomes reversible ([3,4,7,8]).

At the same time, the following two facts indicate the presence of an irreversible process II (faster than stage I) of amalgam deactivation, analogous to the behavior of manganese ([9]).

First, the reversible quantities $(\varphi_{1/2})_s \mathrm{Ni(H_2O)}_q^{2+}$, found by us ([3,4]) by extrapolation to $C_X = 0$, had different values in KCNS and in $\mathrm{KNO_3} + \mathrm{Py}$. Second, an oscillographic study* showed absence of an anodic step (Figs. 1 and 2). The upper two steps in Fig. 1 appeared due to the capacitance effect of Py ([10]).

Taking stage II into account gives:

$$i = k_a[\mathrm{Ni(Hg)}^*] + k_r[\mathrm{Ni(Hg)}^*]. \tag{3}$$

On the basis of (3), with reversibility of stages III and IV and stepwise complex formation ([11]), we obtain

$$\varphi_c = (\varphi_0^*)_{\mathrm{Hg}} - \frac{RT}{2F} \ln \frac{k_c}{k_a + k_r}$$

$$-\frac{RT}{2F} \times \ln \left(1 + \frac{C_X}{K_1} + \frac{C_X^2}{K_2} + \ldots + \frac{C_X^p}{K_p}\right) - \frac{RT}{2F} \ln \frac{i}{i_d - i}; \tag{4}$$

$$(\varphi_{1/2})_c = (\varphi_0^*)_{\mathrm{Hg}} - \frac{RT}{2F} \ln \frac{k_c}{k_a + k_r} - \frac{RT}{2F} \ln \left(1 + \frac{C_X}{K_1} + \frac{C_X^2}{K_0} + \ldots + \frac{C_X^p}{K_p}\right); \tag{5}$$

$$(\varphi_{1/2})_s = (\varphi_0^*)_{\mathrm{Hg}} - \frac{RT}{2F} \ln \frac{k_s}{k_a + k_r}; \tag{6}$$

k_r is a quantity proportional to the rate constant of stage II; k_s is the diffusion-current constant of simple Ni ions; k_a is the same for Ni atoms in the amalgam; k_c is the same for complex Ni ions; C_X is the concentration of the addend; $K_1, K_2, \ldots$ are instability constants of the complexes.

Although stage II occurs, from (5) and (6) we obtain the De Ford and Hume equation ([11]):

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* Carried out with the participation of V. G. Ravdin.

$$(\varphi_{1/2})_c = (\varphi_{1/2})_s + \frac{RT}{2F}\ln\frac{k_s}{k_c} - \frac{RT}{2F}\ln\left(1 + \frac{C_X}{K_1} + \frac{C_X^2}{K_2} + \ldots + \frac{C_X^p}{K_p}\right). \qquad (7)$$

According to (4), the dependence of φ_c on $\lg\frac{i}{i_d - i}$ is a straight line with slope $\frac{RT}{2F}2.3$, which was also observed experimentally (see Table 1, φ relative to the normal calomel electrode).

Table 1

1 M KNO_3 + pyridine				0.15 M KNO_3 + imidazole + 0.05% gelatin (8)				KCNS			
C_{Py}, mmole/l	$-(\varphi_{1/2})_c$, mV	$b \cdot 10^3$*	$-(\varphi_{1/2})_s$ calc., mV	C_{Im}, mole/l	$-(\varphi_{1/2})_c$, mV	$b \cdot 10^3$	$-(\varphi_{1/2})_s$ calc., mV	C_{CNS^-}, mole/l	$-(\varphi_{1/2})_c$, mV	$b \cdot 10^3$	$-(\varphi_{1/2})_s$ calc., mV
12.7	780	28	771	0.962	1069	–	736	1.02	711	38	647
27.3	784	30	767	1.032	1073	37	736	1.30	716	–	643
53.1	791	29	765	1.038	1074	38	737	1.56	721	–	642
99.1	804	–	767	1.129	1082	37	737	1.81	726	–	644
124	808	27	763	1.236	1089	38	737	2.22	736	39	643
363	845	27	776				mean 737	3.11	746	36	639
604	862	30	776					3.48	751	–	640
			mean 769					3.86	756	–	640
								4.20	761	39	641
								4.60	766	–	642
											mean 642

* b is the angular coefficient of the straight lines $\varphi - \lg\frac{i}{i_d - i}$.

From the dependence of $(\varphi_{1/2})_c$ on $\lg C_{\mathrm{Py}}$ up to $C_{\mathrm{Py}} = 0.6\,M$ (12), on the basis of (13), as well as from spectrophotometric data up to $C_{\mathrm{Py}} = 0.5\,M$ (14), it follows that complexes with $p = 1, 2, 3$ are formed. The curve $(\varphi_{1/2})_c - \lg C_{\mathrm{CNS}^-}$ shows (Fig. 3) formation of complexes with $p = 1, 2, 3, 4$, while by spectrophotometry up to $C_{\mathrm{CNS}^-} = 0.5\,M$ (15) $p = 1, 2, 3$ was found, and at higher C_{CNS^-} (16) also $p = 4$. At $C_{\mathrm{Im}} \geq 1M$ (Im = imidazole), from polarographic potentiometric (pH) data (8), $p = 6$ was obtained.

Thus, comparison of the results on the composition of the complexes already confirms the applicability of equations (4)–(7) (cf. (11,13,17)).

Equation (7) is also confirmed by the constancy of $(\varphi_{1/2})_{s\,\mathrm{calc}}$ for different C_X (Table 1). In these calculations $k_c \simeq k_s$, and K_1, K_2, etc. were taken from spectrophotometric (14,15) and potentiometric (pH) (8) measurements, while $K_4(\mathrm{CNS}^-) = 5.34 \cdot 10^{-2}$ was taken from Fig. 3 and K_3 (15).

(Figure: Fig. 3. Dependence of $(\varphi_{1/2})_c$ on $\lg C_{\mathrm{CNS}^-}$)

Fig. 3. Dependence of $(\varphi_{1/2})_c$ on $\lg C_{\mathrm{CNS}^-}$

It is seen from Table 2 that $(\varphi_{1/2})_{s\,\mathrm{calc}}$ $(\mathrm{KNO_3} + \mathrm{Py})$ is in good agreement with that found by extrapolation (3). The difference in these values for KCNS is explained by the less accurate $(\varphi_{1/2})_s$ upon extrapolation, since at small C_{CNS^-} the irreversibility of the process becomes increasingly pronounced (4).

The difference in $(\varphi_{1/2})_{s\,\mathrm{calc}}$ in $\mathrm{KNO_3} + \mathrm{Py}$, $\mathrm{KNO_3} + \mathrm{Im}$ (gelatin), and KCNS is also explained by deactivation of the amalgam, since the nature and concentration of the addend adsorbed on Hg must affect the value of k_r (equation (6)). $(\varphi_{1/2})_{s\,\mathrm{calc}}$ shifts in the negative direction in the sequence $\mathrm{CNS}^- \to \mathrm{Im}$ (gelatin) $\to$ Py, i.e., in this same direction the inhibition of the deactivation process is intensified.

By analogy with (18), taking (6) and (8) into account, one may obtain:

$$(\varphi_{1/2})_s = \varphi^0 + E_s + \frac{RT}{2F}\ln C_{\mathrm{sat}} -$$

$$-\frac{RT}{2F}\ln\frac{k_s}{k_a + k_r} - \frac{RT}{2F}\ln(1 + K_{\mathrm{Hg}}), \tag{8}$$

where K_{Hg} is the equilibrium constant

$$\mathrm{Ni(Hg)^*} \rightleftarrows \mathrm{Ni(Hg)}.$$

Table 2

Solutions	$(\varphi_{1/2})s$ calc., mV	$(\varphi_{1/2})s$ extr., mV
$\mathrm{Ni^{2+}} + \mathrm{Py}$	769 ± 4	776
$\mathrm{Ni^{2+}} + \mathrm{Im}$	737 ± 0.4	–

Solutions	$(\varphi_{1/2})s$ calc., mV	$(\varphi_{1/2})s$ extr., mV
$Ni^{2+} + CNS^{-}$	642 ± 2	693

It is still impossible to calculate the normal potential of Ni, φ^0, from $(\varphi_{1/2})_s$, since the values k_r and K_{Hg} are unknown. Our calculations of φ^0 ([3,4]) included in φ^0 the last two terms, and therefore values were obtained that differed for different solutions.

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Lisichansk Branch
of the State Scientific-Research and
Design Institute of the Nitrogen Industry
and Products of Organic Synthesis

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