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Abstract

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THE MECHANISM OF POLARIZATION IN THE POLAROGRAPHY OF SIMPLE NICKEL AND COBALT IONS

(Presented by Academician A. N. Frumkin, 15 IX 1956)

The mechanism of polarization in the polarography of simple ions Ni^{2+} and Co^{2+}, which give so-called irreversible waves, has been insufficiently studied. In the literature there are very few data also on the polarographic characteristics of simple Ni^{2+} and Co^{2+} ions in the presence of various "indifferent" electrolytes. This has led to a number of contradictory results. Thus, in some works (^{1,2}) $\varphi_{1/2,\mathrm{Co}^{2+}} = -1.23$ V, whereas in another (^{3}) it is -1.44 V (N.C.E.).

In work (^{4}) the polarization in the polarography of simple Ni^{2+} and Co^{2+} ions was investigated against a background of $0.1M$ KNO_3. Some data (^{4}), in particular the angular coefficient of the straight line $\varphi - \lg \frac{i}{i_d - i}$, indicated the suitability of the theory of slow discharge for explaining the polarization mechanism. For further verification of the theory of slow discharge it was very important to investigate the influence of the nature and concentration of the background, to which the present work is devoted.

The investigation* was carried out on a visual apparatus with a normal calomel reference electrode. The standard character of the reference electrode and of the measuring instruments was checked from polarograms of Tl^{+} in $1M$ KNO_3. The temperature of the measurements was 25±0.3°. The capillary characteristic in the investigation of Ni^{2+} was $m^{2/3}t^{1/6} = 1.60$ $\mathrm{mg}^{2/3}$ $\mathrm{sec}^{-1/2}$, and in the investigation of Co^{2+}, $m^{2/3}t^{1/6} = 1.02$ $\mathrm{mg}^{2/3}$ $\mathrm{sec}^{-1/2}$. The cell resistance was determined from polarograms of Cd^{2+}, which was introduced into the solution after recording the polarograms of Ni^{2+} or Co^{2+}. Polarography was carried out in the absence of any maximum suppressors. In order to exclude complex formation, nitrates, perchlorates, and sulfates were chosen as the backgrounds.

Nickel. The results obtained (Tables 1, 2, Figs. 1, 2) make it possible to explain the irreversibility of the polarographic wave of Ni^{2+} by the slowness of ion discharge. According to the theory of slow discharge developed by A. N. Frumkin (^{5,6}), the equation of an irreversible polarographic wave has the form:

$$\varphi = \text{const} - \frac{RT}{\alpha nF} \ln i_D - \frac{1-\alpha}{\alpha}\psi_1 - \frac{RT}{\alpha nF} \ln \frac{i}{i_d - i}, \tag{1}$$

whence the half-wave potential is:

$$\varphi_{1/2} = \text{const} - \frac{RT}{\alpha nF} \ln i_D - \frac{1-\alpha}{\alpha}\psi_1. \tag{2}$$

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* G. S. Koshkina and B. Sh. Pel’ tina took part in the experimental part of the work.

Table 1

Constants of the diffusion current and half-wave potential of simple nickel and cobalt ions in the presence of various “indifferent” electrolytes

Background	Ni^{2+} i_D, µA mM^{-1} $sec^{-1/2}$	Ni^{2+} $-\varphi_{1/2}$, V	Co^{2+} i_D, µA mM^{-1} $sec^{-1/2}$	Co^{2+} $\varphi_{1/2}$, V	Background	Ni^{2+} i_D, µA mM^{-1} $sec^{-1/2}$	Ni^{2+} $-\varphi_{1/2}$, V	Co^{2+} i_D, µA mM^{-1} $sec^{-1/2}$	Co^{2+} $\varphi_{1/2}$, V
$NaNO_3$					Na_2SO_4				
0.01 M	4.32	0.96			0.2 M	3.19	1.12	3.09	1.31
0.03 »	4.10	0.99			0.4 »	1.58	1.12	2.89	1.42
0.1 »	4.11	1.03			1 »	0.54	1.12	2.60	1.50
0.3 »	4.60	1.07			$Ca(ClO_4)_2$				
1 »	2.71	1.09			0.01 M	3.27	1.04		
$NaClO_4$					0.034 »	2.95	1.06	2.87	1.27
0.01 M	4.45	0.96			0.1 »	2.89	1.08	2.78	1.32
0.034 »	4.43	1.00	3.01	1.17	0.34 »	2.32	1.09	2.89	1.36
0.1 »	4.30	1.03	3.12	1.23	1 »	1.06	1.08		
0.34 »	4.52	1.06	3.27	1.26	$Ca(NO_3)_2$				
1 »	2.74	1.07	3.22	1.31	0.01 M	4.21	1.05		

Background	Ni^{2+} i_D, μA mM^{-1} $sec^{-1/2}$	Ni^{2+} $-\varphi_{1/2}$, V	Co^{2+} i_D, μA mM^{-1} $sec^{-1/2}$	Co^{2+} $\varphi_{1/2}$, V	Background	Ni^{2+} i_D, μA mM^{-1} $sec^{-1/2}$	Ni^{2+} $-\varphi_{1/2}$, V	Co^{2+} i_D, μA mM^{-1} $sec^{-1/2}$	Co^{2+} $\varphi_{1/2}$, V
Na_2SO_4					0.034 »	3.73	1.07		
0.034 M	4.02	1.04	3.25	1.21	0.1 »	3.08	1.09		
0.1 »	3.52	1.08	3.13	1.25	0.34 »	1.87	1.10		

Here i_D is the diffusion-current constant. The dependence of the negative ψ_1-potential on the concentration of a uni-univalent electrolyte is expressed by equation (6):

$$\psi_1 = \text{const}' + \frac{RT}{F} \ln c. \tag{3}$$

All these equations are well confirmed by the experimental data:

1. The dependence $\varphi - \lg \frac{i}{i_d - i}$ is linear (Fig. 1) (equation (1)), with a slope coefficient of 0.060–0.080. Taking the average slope coefficient as 0.070, we obtain the value $\alpha = 0.42$. This conclusion, which previously concerned (4) a 0.1 M KNO_3 solution, can be extended to perchlorate, sulfate, and nitrate solutions of various concentrations.

Table 2

Half-wave potentials of simple nickel and cobalt ions at various metal concentrations

Background 1 M $NaNO_3$	Background 1 M $NaNO_3$	Background 1 M $NaClO_4$	Background 1 M $NaClO_4$
$C_{Ni^{2+}}$, mM/l	$-\varphi_{1/2}$, V	$C_{Co^{2+}}$, mM/l	$-\varphi_{1/2}$, V
0.11	1.08	0.20	1.31
0.18	1.09	0.39	1.30
0.32	1.09	0.57	1.30
1.03	1.09	1.50	1.32

2. The half-wave potential does not depend on the concentration of Ni^{2+} (Table 2) (equation (2)).
3. Between $\varphi_{1/2}$ and the logarithm of the concentration of a uni-univalent background a linear dependence is observed (Fig. 2) (equations (2), (3)).

Fig. 1

Figure 1: Fig. 1

$\varphi_{1/2}$ shifts in the negative direction by 0.074 V when the background concentration is increased tenfold, which from equations (2) and (3) gives $\alpha = 0.44$—a value in good agreement with α from the slope of the straight lines $\varphi - \lg \frac{i}{i_d - i}$. The somewhat lowered value of $\varphi_{1/2}$ at $c = 1M$ (Fig. 2), as well as the passage of the curve $\varphi_{1/2} - \lg c$ through a maximum in the case of solutions of Na_2SO_4, $Ca(ClO_4)_2$, and $Ca(NO_3)_2$ (Fig. 2), is explained by the decrease in the diffusion-current constant with increasing background concentration (see Table 1). Indeed, the introduction of po

correction for the change in i_D (according to equation (2)) leads to an increase in the values of φ_1 with increasing background concentration.

4. The nature of the anion (NO_3^-, ClO_4^-) had practically no effect on the value of $\varphi_{1/2}Ni^{2+}$. In the presence of SO_4^{2-}, $\varphi_{1/2}$ shifted in the negative direction

Fig. 1. Dependence $\varphi - \lg \frac{i}{i_d - i}$. Ni^{2+}: *a*–0.1 *M* $NaClO_4$ ($\mathrm{tg}\,\alpha = 0.063$); –0.1 *M* $NaNO_3$ ($\mathrm{tg}\,\alpha = 0.064$), –0.1 *M* $Ca(ClO_4)_2$ ($\mathrm{tg}\,\alpha = 0.070$), –0.1 *M* Na_2SO_4 ($\mathrm{tg}\,\alpha = 0.072$; Co^{2+}: –0.1 *M* $NaNO_3$ ($\mathrm{tg}\,\alpha$ 0.106–0.080), –0.1 *M* $NaClO_4$ ($\mathrm{tg}\,\alpha = 0.096$–0.068), –0.1 *M* Na_2SO_4 ($\mathrm{tg}\,\alpha = 0.116$), –0.1 *M* $Ca(ClO_4)_2$ ($\mathrm{tg}\,\alpha = 0.128$–0.086). Metal concentration 0.1–0.2 mM/l

direction (Fig. 2), which is possibly caused by association of Ni^{2+} and SO_4^{2-} ions. A similar effect of sulfates on the deposition potential of Ni^{2+} on a solid cathode has already been observed by other authors ([7],[8]). It is interesting to note the considerable decrease in the diffusion-current constant with increasing sulfate concentration (see Table 1). Replacing the monovalent background cation (Na^+) by a divalent one (Ca^{2+}) led to a shift of $\varphi_{1/2}$ in the negative direction (Fig. 2), which is associated with a shift of the ψ_1-potential in the positive direction (equations (2) and (3)).

In conclusion, we note that in the study of the electrocrystallization of Ni on a solid cathode ([8]), it was also possible to explain the polarization mechanism by the slow discharge of ions.

Cobalt. A number of facts indicate the suitability of the theory of slow discharge also for explaining the irreversibility of the polarographic wave of simple cobalt ions.

1. The half-wave potential does not depend on the concentration of Co^{2+} (Table 2).

2. Between $\varphi_{1/2}$ and the logarithm of the concentration of a uni-univalent

Fig. 2

Figure 2: Fig. 2

background there is a linear dependence with a slope of 0.105 (Fig. 2), which gives $\alpha = 0.36$—somewhat smaller than for Ni^{2+}.

Fig. 2. Dependence of $\varphi_{1/2}Ni^{2+}$ and Co^{2+} on the logarithm of the concentration of the background cation: a—Ni^{2+}, —Co^{2+}, —$NaNO_3$, —$NaClO_4$, —Na_2SO_4, —$Ca(ClO_4)_2$, —$Ca(NO_3)_2$

3. As with Ni^{2+}, the use of a background with a polyvalent cation

(Ca^{2+}) led to a considerable shift of $\varphi_{1/2}$ in the negative direction (Fig. 2), owing to a shift of the ψ_1-potential in the positive direction. A supporting electrolyte with the SO_4^{2-} anion showed a more negative $\varphi_{1/2}$, especially at a high sulfate concentration, than a supporting electrolyte with the ClO_4^- anion (Fig. 2). Apparently, by analogy with Ni^{2+}, this is connected with the phenomenon of association.

There is also a difference in the polarographic behavior of Co^{2+} as compared with Ni^{2+}, namely: the wave of Co^{2+} in nitrate and perchlorate media is not symmetrical, and the dependence

$$\varphi - \lg \frac{i}{i_d - i}$$

has a break at the point $\varphi_{1/2}$ (see Fig. 1). The break in the straight lines was small in many experiments, especially in nitrate media, and therefore was not observed in the preceding work (^{4}). The cause of the asymmetry of the Co^{2+} wave is as yet unclear. In general, the Co^{2+} wave is more sloping than that of Ni^{2+}, which is in qualitative agreement with the smaller value of the coefficient α noted above.

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