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Polarographic Behaviour of Cobalt(II), Nickel(II), and Iron(II)

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The kinetics and mechanism of reduction of bivalent metals of the iron group at a mercury dropping electrode are examined. The effect of the pH, organic solvent, structure of the double layer, and adsorption of the depolariser on the half-wave potential and limiting currents of the wave for the reduction of cobalt (II), nickel (II), and iron (II) complexes is described. The role of complex formation in depressing the overpotential for the discharge of these metals is considered in detail. Various viewpoints are presented on the mechanism of formation of the catalytic waves of hydrogen, which appear when doubly-charged ions of these metals and various organic substances are present in the solution simultaneously.
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I. INTRODUCTION

Despite many papers dealing with the mechanism of the reduction of ions of metals of the iron group at a mercury dropping electrode (MDE), there is not a sufficiently detailed and systematic review of these studies. We have tried to fill this gap to some extent.

From the point of view of polarography, the most noticeable general feature is that cobalt, nickel, and iron are almost insoluble in mercury, and the redox potentials of these metals are very similar; there is also much in common in the mechanism of the polarographic behaviour of these metals.

In this review we have examined only certain (we think the most important) aspects of the electrochemical release of cobalt, nickel, and iron from their bivalent state at a mercury dropping electrode.

2. EFFECT OF THE pH OF THE SOLUTION ON THE POLAROGRAPHIC BEHAVIOUR OF COBALT, NICKEL, AND IRON

Brdička[1] was the first to observe that $E_{\frac{1}{2}}$ of the cobalt wave is shifted to more negative potentials when the pH of the solution is decreased. A similar relation between the shift in the discharge potential of cobalt or nickel ions and the pH of the solution was found at a solid cobalt electrode[2] and was also noted in earlier studies[3-5].

Since in aqueous solution the cobalt ion exists as a complex with six water molecules, Brdička[1] explained the decrease in the negative values of $E_{\frac{1}{2}}$ of cobalt when the pH of the solution was increased by the partial dehydration of the hexahydrate with the replacement of one water molecule by an OH^- ion:

$$\underset{(I)}{[Co(H_2O)_6]^{2+}} + H_2O \rightleftarrows H^+ + \underset{(II)}{[Co(H_2O)_5OH]^+}. \qquad (1)$$

He thought that such a complex would be reduced more readily than the hexahydrate.

The polarograms of Fig. 1, taken from Brdička's work[1] show clearly how the wave for the reduction of Co^{2+} is displaced to more negative potentials as the solution is acidified, and finally merges with the background. As the result of the selection of definite values of Co^{2+} concentration, pH of the medium, and temperature, in the absence of strong complex-forming substances splitting of the cobalt wave could be observed. Fig. 2[1] shows the appearance and increase of the wave for the reduction of complexes II (reaction 1) as the temperature is raised.

In certain instances the splitting of the wave could not be observed but semilogarithmic plots of the waves for the reduction of Co^{2+} showed inflections[6-8]; the explanation could be that the observed wave really describes two processes in which two types of complex participate—cf. Eqn. (1).

Our results[8] mainly agree with Brdička's observations[1]: as the pH is increased from 2.9 to 4.0 $E_{\frac{1}{2}}$ for Co^{2+} in a solution of 0.1 N KCl + HCl varies from −1.380 to −1.345 V. In the pH range 4.0–4.5 $E_{\frac{1}{2}}$ hardly alters. We were unable to investigate the variation of $E_{\frac{1}{2}}$ with pH for cobalt in the range pH < 2.9 owing to the superimposition of the hydrogen discharge wave on the cobalt wave.

Interestingly, the transfer coefficient (α), determined from the slope of the graph constructed on coordinates of $\lg i$ against E at the potentials of the start of the cobalt wave, also shows a decrease in the rate of the electrochemical process for the reduction of the cobalt ion in the acidic range of pH (< 4.0).[8] Fig. 3 shows the change in α as the pH of the solution is varied.

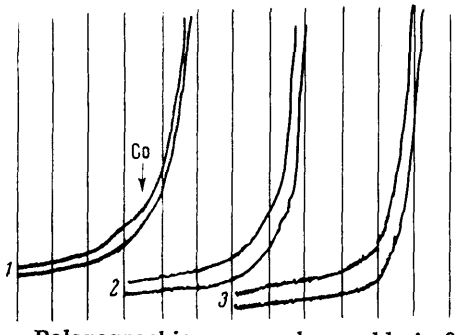


Figure 1. Polarographic curves observable in 0.01 N $CoCl_2$ + 0.01 N KCl solutions at various HCl concentrations: 1) without addition of HCl; 2) 10^{-5} N HCl; 3) 10^{-4} N HCl. The curves start at −0.6 V.

Zytner and Rotinyan[9] used the method of recording electrostatic partial polarisation curves to study the discharge of Co^{2+} ions at a cobalt electrode in 0.6 M cobalt sulphate solution at 56°C in the pH range 2.55–3.80. They found that the cathodic potential for the discharge of cobalt ions shifts in the negative direction as the pH is reduced. The order of the cathodic reaction with respect to Co^{2+} and OH^- ions is 1.1 and 0.9 respectively, that is, close to 1. In explaining the mechanism of the reaction Zytner and Rotinyan[9] started from ideas on the participation of the OH^- ion in a potential-determining stage. Kravtsov and Lokshtanova[10] also noted that in the electrodeposition of cobalt at a cobalt electrode (from 1 N $CoSO_4$ + H_3BO_3) the rate of the process increased as the pH was raised from 3.5 to 4.2, showing that the rate-determining stage of the cathodic process is the transfer of the first electron to Co^{2+}.

An analogous relation between $E_{\frac{1}{2}}$ and pH is also observed for iron[11,12]. $E_{\frac{1}{2}}$ hardly alters as the pH is changed from 4.5 to 5.0 but at pH below 4.5–5.0 it is shifted rather significantly in the negative direction (Fig. 4). However, Dahms[13] did not observe a change in the $E_{\frac{1}{2}}$ of the iron wave.

A variation of $E_{\frac{1}{2}}$ with pH was also noted for all the metals of the iron group in the presence of a complex-forming substance (pyridine).[14]

A variation of $E_{\frac{1}{2}}$ for the nickel ion with the pH at the mercury dropping electrode in the absence of a complex-forming substance could not be observed[23].

At first glance the formation of a complex of a metal with an OH^- ion according to reaction (1) in a solution where the concentration of free hydroxyl ions is negligibly small ($\sim 10^{-11}$–10^{-10} g-ion litre^{-1}) seems improbable. However, allowance must be made for the fact that the process leading to the formation of a complex in which one molecule of water is replaced by a hydroxyl ion is kinetic in nature. Water, the concentration of which is ~ 55 M, participates in this process as a donor of hydroxyl ions. The kinetic nature of the wave for the discharge of the hydroxo-complex is shown by the large temperature coefficient of the limiting current of this wave (cf. Fig. 2). It can also be postulated that the hydroxo-complex is formed as a result of the slow deprotonisation of the hexa-aquo-complex of cobalt.

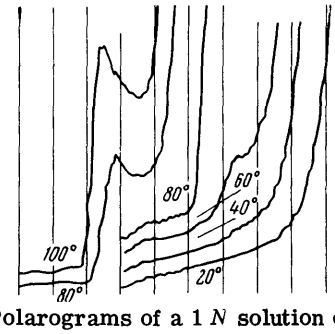


Figure 2. Polarograms of a 1 N solution of $CoCl_2$ at various temperatures. The sensitivity of the galvanometer decreased on going from 60° to 80° and 100°C.

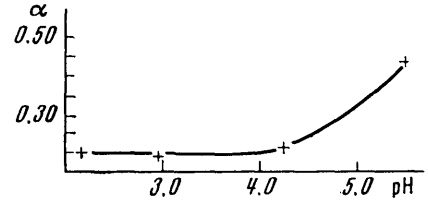


Figure 3. Variation of the transport coefficient α for waves of cobalt (0.64×10^{-3} M) with the pH of 0.1 N KCl + xHCl solution[8].

The decrease in the negative values of the half-wave potential as the pH of the solution is increased evidently reflects the fact that the observable wave is obtained as a result of the superimposition of two waves (the $E_{\frac{1}{2}}$ of which are different), which correspond with the discharge of complexes II (first wave) and I (second wave), according to reaction (1). As the pH is raised there is an increase in the wavelength corresponding to complex II, the $E_{\frac{1}{2}}$ of which is less negative than the $E_{\frac{1}{2}}$ of the hexahydrate wave. This also leads to a shift in the $E_{\frac{1}{2}}$ of the overall wave to less negative values as the pH is raised.

The mixed nature of the waves causes inflections on the curves on the semilogarithmic graphs[6–8] and the lower part of the curve is found by some[1,7,8] to be steeper than the upper, whereas another study[6] shows the lower part of the curve to be the less steep. The differences in the slopes of the initial parts observed by different authors are evidently due to differences in the experimental conditions.

As mentioned above, by choice of the experimental conditions (concentration of the cobalt salt, temperature of the solution, pH) Brdička succeeded in distinguishing the pure wave corresponding to the discharge of complex II (reaction 1). The value of αn_a which we found from the initial part of the graph plotted in coordinates of $\lg i$ against E for this wave is ~ 50 mV. The first wave is appreciably steeper than the main wave. Evidently the process which corresponds to the transfer of an electron to the complex $[Co(OH)(H_2O)_5]^+$ is rather close to reversible under these conditions.

Cosowic and Branica[15] found a charge of $Z = +2$ for the cobalt complex which exists in a phosphate buffer in the presence of 0.5 M $NaClO_4$ and consider the existence of the complex $[Co(OH)(H_2O)_5]^+$ improbable. However, it must be borne in mind that the equilibrium of reaction (1) is evidently shifted to the left, since the wave which corresponds to the reduction of this complex cannot exceed 10 to 20% of the total wave[1,7]; therefore the calculation of the kinetic parameters of the overall wave, despite the existence of a complex with $Z = +1$, can lead to a value of Z close to +2. In addition, as noted by Cosowic and Branica[15] they have been investigated only in a narrow range of pH (6.5–8.14).

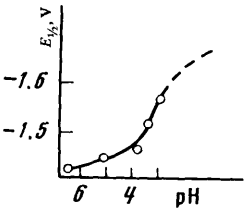


Figure 4. Variation of $E_{\frac{1}{2}}$ for the Fe^{II} reduction wave with the pH.[11]

We have calculated the number Z from Turyan's results[6] with the aid of an equation taken from Mairanovskii[16]:

$$\Delta E_{1/2} = \Delta\psi_1 \frac{\alpha n_a - Z}{\alpha n_a}, \qquad (2)$$

where Z is the charge of the species participating in the electrochemical reaction, α the transfer coefficient, n the number of electrons which is transferred in the potential-determining stages, and $\Delta\psi_1$ the potential jump in the diffusion part of the double layer. For a solution[6] of cobalt in 0.04–0.1 M Na_2SO_4 $Z = +1.25$, which evidently reflects the mixed nature of the wave in which both species with charge +1 and species with charge +2 participate.

We think it unusual that a species with one positive charge less should be discharged more readily than an analogous species carrying two positive charges. However, such a phenomenon is also observed when the concentration of the chlorides is increased (see below), when species with a smaller positive or even a negative charge are formed from a hexahydrate with charge +2. The drop in polarisation when water molecules are replaced by a hydroxyl ion is evidently due to several reasons. One of them, discussed below in most detail, is the acceleration of the dehydration on the introduction into the inner coordination sphere of a foreign ligand. In addition, it is necessary to take into account that the presence of an OH^- ion in the composition of a complex firstly allows the reaction centre of the complex—the metal ion—to approach nearer the surface, since the OH^- ion is smaller than H_2O; secondly, the transfer of one electron to the M^{2+} ion using the "relay" nature of the transfer (the OH^- ion transfers its electron to a metal ion, exchanging one electron with the electrode surface). It must be taken into account that a non-symmetric coordination sphere is deformed more readily (with subsequent dehydration) in the field of the double layer than is a symmetric one consisting of six water molecules.

3. ROLE OF COMPLEX FORMATION

Cobalt(II) and nickel(II) are known to exist in an aqueous solution in the absence of other complex-forming agents as the hexahydrates which have a stable octahedral configuration[17]. It has been shown recently[18] that iron(II) exists in aqueous solution also in the form of the hexahydrate. Such a structure for the complex is one of the reasons for the high overpotential of the reduction of the ions of the metals of the iron group. However, only the hydrate of the doubly-charged metal ion is stable in aqueous solution. The complex of the singly-charged ion, which should be formed after the transfer of the first electron (see, for example, Molodov and Losev[19]) in aqueous solutions of perchlorates, sulphates, nitrates, and other anions which do not form stable complexes with this ion, is unstable and immediately acquires a second electron; therefore in aqueous solutions the salts of these ions of cobalt, nickel, and iron give one two-electron (irreversible) wave with diffusion control[6-8,17,20].

According to Gierst and Hurwitz[21-24] the hexahydrate complexes of nickel and cobalt are partly dehydrated before the electrode reaction proper. The rate constant of the dehydration increases with the negative values of the ψ_1-potential (discussed in more detail below).

Attempts were made to determine the number of water molecules detached in stages which precede the transfer of electrons[25,26]. The polarographic curves were used to determine the activation energy of the dehydration of nickel hexahydrate[5,25], the value of which agrees satisfactorily with the activation energy of the isotopic exchange of one molecule of water between the solvent and the first sphere of hydration of nickel hexahydrate, determined by the NMR method[27] to be 11.6 kcal $mole^{-1}$. Hence it is concluded that in the stage which precedes the transfer of electrons into $NaClO_4$ solutions either one water molecule is detached[25] or another molecule of water[26] is introduced into the inner coordination sphere. In either instance the complex loses the stable octahedral configuration, which facilitates the deformation of the inner sphere and the transfer of an electron to the central atom.

The number of waves on the polarogram and their position on the potential axis depends on the nature and concentration of the ligand. The complex-forming substances, which give extremely stable complexes with our metals, for example, various compounds which contain $-NH_2$ or $\geqslant NH$ groups[28], have a greater tendency to form two waves. Halide ions are weaker complex-forming substances than amines; therefore they bring about only a decrease in $E_{\frac{1}{2}}$.

A similar effect was observed on raising the concentration of LiCl or LiBr (from 1 to 20 M) in a cobalt,

nickel, or iron solution[30,31], on increasing the concentration of calcium chloride in a solution of iron salt, and also in the partial replacement of saturated calcium perchlorate solution by calcium chloride in a solution of cobalt, nickel, or iron salts[11,31,32]; increasing the chloride concentration to 0.25 M reduces the half-wave potential of cobalt from −0.9 to −0.7 V. The graph in Fig. 5, constructed from Aylward and coworkers' results[30], shows the variation of $E_{\frac{1}{2}}$ for cobalt with the lithium chloride and bromide concentrations. It is necessary to bear in mind that when there is a considerable increase in the concentration of electrolytes such as lithium[30] or calcium[31] halides an additional shift in $E_{\frac{1}{2}}$ for the waves of the hydrated metal ions can appear due to the dehydrating action at high concentrations of the supporting electrolytes. Since there are six water molecules in the inner coordination sphere of complexes of iron group metals and another 26 molecules in the second sphere (the heat of formation of the second sphere is 240 kcal g-ion^{-1}—almost equal to the heat of formation of the first sphere)[18], the introduction, for example, of electrolytes such as LiCl and $CaCl_2$[30,31] should lead to an acceleration of the dehydration of the hexahydrate and consequently to a shift of $E_{\frac{1}{2}}$ to less negative potentials.

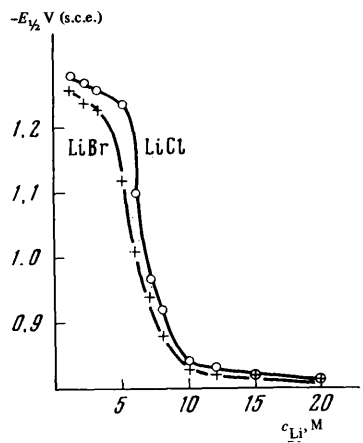


Figure 5. Variation of $E_{\frac{1}{2}}$ of the cobalt wave with the molal concentration of lithium chloride and bromide.[30]

When the concentration of halide ions is increased there is a gradual conversion of the octahedral hexahydrate into the tetrahedral tetrahalide[18,30]. For example, in LiCl and LiBr the transitional region corresponds to 8–14 M. The change from hexahydrate to tetrahalide affects the form of the polarogram: a graph constructed in semilogarithmic coordinates consists of two straight-line portions, the lower of which is the steeper[30]. A CN^- ion in a solution of nickel salt also forms (when its concentration is increased) a doubly-charged complex of tetrahedral structure $[Ni(CN)_4]^{2-}$.[33-37]

It is interesting that despite the anionic nature of the MX_4^{2-} complex (where X = Cl, Br, I, CN, or NCS) which exists in sufficiently concentrated solutions, the half-wave potential of the halogeno-complex is less negative than the half-wave potential of the hexahydrate, which has a charge of +2.

When the solution contains a ligand capable of forming a sufficiently stable bond with a metal ion, the water molecule that has been detached in the inner coordination sphere is replaced by a corresponding molecule or ion which is introduced into the inner coordination sphere. The introduction of the foreign ligand increases the rate constant of the exchange (k_{H_2O}) for the subsequent water molecules[27-29]. For example, for $[Ni(H_2O)_6]^{2+}$ $k_{H_2O} = 2.74 \times 10^4$ s^{-1},[27] and for the complex in which one water molecule is replaced by glycine $[Ni(Glyc)(H_2O)_5]^{2+}$ k_{H_2O} is 1.2×10^5 s^{-1}.[29] Some investigators think[25,29] that the increase in the rate constant for the exchange of the second and subsequent water molecules is the reason for the decrease in the polarisation in the introduction into aqueous solution of a complex-forming substance (leading in certain instances not only to a shift in the main wave but also to the appearance of new waves in a less negative range of potentials).

On reaching a certain concentration of the ligand the half-wave potential of the ionic complex can reach a limiting value and when the concentration of the ligands is increased further it starts to shift to the side of more negative potentials. However, this shift in the negative direction is small, since $E_{\frac{1}{2}}$ usually remains smaller in magnitude than $E_{\frac{1}{2}}$ of the hexahydrate (see Table, which is constructed from results of Refs. 11 and 31). Despite some shift in the negative direction the degree of reversibility is usually unaltered.

Some electrochemical characteristics of the reduction of doubly-charged ions of iron-group metals.

Compn. of the supporting electrolyte	Ni^{2+}			Co^{2+}			Fe^{2+}			Comparison electrode
	$E_{\frac{1}{2}}$	$\Delta E_{\frac{1}{2}}$	α	$E_{\frac{1}{2}}$	$\Delta E_{\frac{1}{2}}$	α	$E_{\frac{1}{2}}$	$\Delta E_{\frac{1}{2}}$	α	
0.1 M $NaClO_4$	−1.09	—	—	−1.22	—	—	−1.33	—	—	s.c.e.
saturated solution of $Ca(ClO_4)_2$	−0.712	0.378	0.43	−0.873	0.347	0.30	−0.981	0.349	0.50	ditto
saturated solution of $Ca(ClO_4)_2$ +0.25 M $CaCl_2$	−0.317	0.773	0.52	−0.674	0.546	0.62	−0.936	0.394	0.71	»
saturated solution of LiCl	−0.410	0.680	1.02	−0.800	0.420	0.88	−1.060	0.270	0.91	»
10*N* $CaCl_2$	−0.48	—	—	−0.9	—	—	−1.125	—	—	S.C.E.

The limiting current can also depend upon the ligand concentration. Thus, when acetylacetone (HAcac) is added[15] to a 5×10^{-4} M cobalt nitrate solution (in a phosphate buffer + 0.5 M $NaClO_4$) the cobalt wave decreases until the concentration of the free ligand reaches 10^{-4} M. The observed regularity is explained by the competition between the water and acetylacetone. A polarographically inactive complex $CoAcac_2$ is formed. The limiting current is kinetic in nature since the kinetics of formation of $CoAcac^+$ from this complex also determines the height of the wave that is observed[15]:

$$\begin{array}{ccccc} Co(H_2O)_6^{2+} & \rightleftarrows & CoAcac^+ & \rightleftarrows & CoAcac_2 \\ \alpha n_\alpha = 0.6 \downarrow\uparrow & & \downarrow\uparrow \alpha n_\alpha = 1.3 & & \\ Co\,(Hg) & & Co\,(Hg) & & \end{array}$$

For ligands which form stable complexes with the metal ion the dependence of $E_{\frac{1}{2}}$ and the limiting currents

upon the ligand concentration is more complex; a low concentration of the ligand leads to a reconstruction of the hydrate sheath of the ion. The influence of the concentration of diaminopropane[25] on $E_{\frac{1}{2}}$ and the number and form of the nickel waves has been studied in detail[25]. In the range of ligand concentrations where $\lg C_X < -8.1$ (in an acid solution of $NaClO_4 + HClO_4$, $I = 0.5$) a single wave is observed (as in the absence of the ligand), the $E_{\frac{1}{2}}$ of which does not change as the ligand concentration is altered ($E_{\frac{1}{2}} = -1.603$ V). This wave corresponds to the discharge of the hexa-aquo-complex of nickel. In the range $-8.1 < \lg C_X < -7.6$ there are two waves on the polarogram (see Fig. 6), the half-wave potentials of which hardly alter as the concentration of the complex-forming agent is increased. The first wave (that is, the wave at less negative potentials) on the polarogram obtained under the conditions described corresponds to the reduction of the complex with diaminopropane. When the diaminopropane concentration is increased ($\lg C_X > -7.6$) the first wave is displaced to less negative potentials. In the range $\lg C_X > -5.25$ the first wave merges with the second and with a further increase in the ligand concentration this combined wave again starts to shift to more negative potentials.

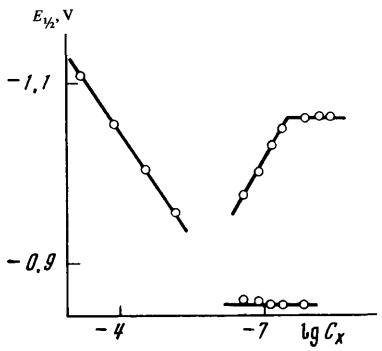


Figure 6. Change in the number of waves and half-wave potentials of nickel ion (1×10^{-4} M) with the logarithm of the ligand concentration (diaminopropane) in a solution of lithium perchlorate[25].

A similar picture is observed in the presence of pyridine. In the polarography of a solution of a nickel salt in the presence of $< 10^{-4}$ M pyridine a single wave with $E_{\frac{1}{2}} = -1.025$ V is observed[38]. An increase in the pyridine concentration by an order of magnitude leads to the appearance of two new waves, the $E_{\frac{1}{2}}$ of which are −0.76 V and −0.86 V respectively. When the pyridine concentration is raised further (to 0.1 M) two of the waves on the polarogram disappear and there remains only the wave observed in the less negative range of potentials; this wave shifts slightly in the negative direction when the pyridine concentration is increased further. Fig. 7, constructed from the results of Kemula and coworkers[38] shows the change in the number of waves and the $E_{\frac{1}{2}}$ of the nickel waves as the pyridine concentration is varied.

However, in several instances only a displacement of the wave along the potential axis is observed. Thus, when a ligand such as the hypophosphite ion ($H_2PO_2^-$) is introduced into a cobalt solution with pH 5.5 only a shift of the wave towards more negative potentials is observed[8].

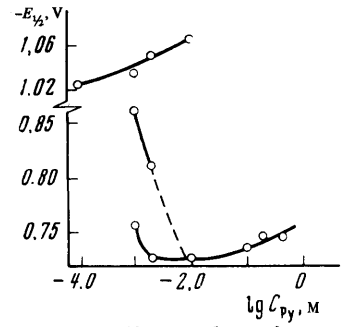


Figure 7. Variation of the number of waves and half-wave potentials in the reduction of a nickel ion with the pyridine concentration[38].

Calculation of the number of hypophosphite ions entering into the complex[8] under the condition that $\alpha = 0.5$ gives a value of 1. The semilogarithmic graph of Fig. 8 shows the change in $E_{\frac{1}{2}}$ of the cobalt wave as the sodium hypophosphite concentration (C_{HPP}) is raised. The curve for a solution with pH 4.5 has an inflection due to the appearance of the polarographic activity of the hypophosphite in a sufficiently acid medium in the presence of cobalt ions[8]; this will be discussed in greater detail below.

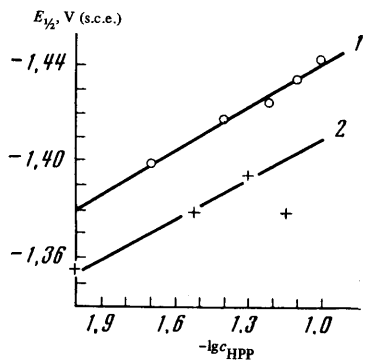


Figure 8. Variation of the half-wave potential of the cobalt ion with the concentration of sodium hypophosphite in solutions with pH 5.5 (curve *1*) and pH 4.25 (curve *2*).[8]

4. INFLUENCE OF ORGANIC SOLVENT

The partial or complete replacement of water by an organic solvent leads to a significant change in the polarographic conditions. On the addition of an organic solvent in a concentration comparable with that of the ion being studied or greater by about an order of magnitude, the organic solvent can be regarded as an ordinary ligand, the introduction of which into the solution leads usually to the

partial dehydration of the hexa-aquo-complex of the metal, and the replacement of even a single water molecule in the inner coordination sphere by a foreign ligand facilitates reduction, that is, leads to a shift in the $E_{\frac{1}{2}}$ of the wave of the complex to more positive potentials. In this nickel shows the greatest tendency towards the formation of complexes, so that $\Delta E_{\frac{1}{2}}$ for nickel ($\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}}^{H_2O} - E_{\frac{1}{2}}^{L}$) has the greatest absolute value. At a higher concentration of the organic solvent [39,40] the polarogram includes a wave having an $E_{\frac{1}{2}}$ several tenths of a volt less negative than the half-wave potential of the hexahydrates of these metals.

Interestingly, the completely solvated ion, like the completely hydrated one, is more difficult to reduce than an ion with a solvate sheath in which there are ligands of two or more kinds. Thus the addition of 8×10^{-4} M xanthate to a 4×10^{-4} M solution of a nickel salt (in a supporting electrolyte of 0.2 M $LiClO_4$) in absolute ethanol shifts $E_{\frac{1}{2}}$ from −0.840 to −0.667 V. [39] In ethanol solution (in the presence of small quantities of 1,10-phenanthroline) the wave corresponding to the transfer of an electron with the formation of a complex of cobalt(I) is irreversible: its $E_{\frac{1}{2}} = -1.02$ V, but when the 1,10-phenanthroline concentration is increased the $E_{\frac{1}{2}}$ is appreciably shifted in the positive direction and the wave acquires a quasireversible nature [40-42].

The introduction into an aqueous solution of an organic solvent capable of the formation of a stable complex, in the presence of other ligands can lead to the appearance of two waves corresponding to complexes of different composition. Thus in 1 M KCNS, taken as supporting electrolyte, nickel gives a single sharp wave with $E_{\frac{1}{2}} = -0.695$ V (s.c.e.), but when acetamide is added there are two waves on the polarogram [43]. The first wave was thought [43] to be due to the reduction of the thiocyanato-complex of the nickel ion, the second wave, which appears at more negative potentials, corresponds to the reduction of the complex of nickel with acetamide. Both waves are irreversible. When the acetamide concentration is increased $E_{\frac{1}{2}}$ of the second nickel wave is shifted monotonically to more negative potentials, from −1.562 V (5% acetamide) to −1.648 V (30% acetamide); there is also an increase in the irreversibility of the electrochemical process.

The opposite behaviour has also been observed [44]: the introduction of an organic solvent (ethanol, ethylene glycol, and especially propanol) leads to the merging of the two waves on the polarogram of nickel in 1–1.5 M solutions of HCOONa, Na_2SO_4, and NaI into a single wave [44].

In anhydrous dimethylformamide (DMF) in the presence of the Cl^- ion nickel also gives two waves [45], the first of which increases as the concentration of Cl^- ion in the solution is increased.

As regards the reversibility of the waves for the reduction of our metals in non-aqueous solvents it is usually considerably higher in comparison with the waves observable in water. Thus it has been noted that the waves of all three metal ions under consideration are reversible in DMF [45]; the cobalt wave is reversible in isobutyronitrile (the slope of the wave is 34 mV, $E_{\frac{1}{2}} = -0.60$ V relative to the s.c.e.) [46], but in this solvent it is not strange that the nickel wave is irreversible, though this has been attributed [46] to the possible presence of traces of water.

Allowance must also be made for the organic solvent exerting a specific action, since when its concentration is increased there is a decrease in the adsorbability of the organic ligands or of the complexes with these ligands, which should lead to an increase in polarisation.

Furthermore, when the concentration of the organic solvent is increased there is a decrease in the dielectric permeability of the medium, in consequence of which the association of our cations with the anions of the indifferent electrolyte is possible.

5. INFLUENCE OF THE STRUCTURE OF THE ELECTRICAL DOUBLE LAYER

In the reduction of cations at a negatively charged surface, the electrostatic action of the field facilitates their approach to the electrode surface [16,47]. On the other hand, on the positively charged surface of the electrode the electrostatic action of the field retards the electrode processes involving the cations and accelerates the processes involving the anions.

The reduction of cobalt, nickel, and iron complexes usually obeys these rules because the complexes of these metals (in a bivalent state) usually have a charge $Z \geqslant 0$ and at the same time the waves of these complexes lie on the negative branch of the electrocapillary curve. An exception is the complex of nickel in solutions of ligands such as Cl^-; for example, $E_{\frac{1}{2}}$ for nickel in a saturated $Ca(ClO_4)_2$ solution +0.25 M in $CaCl_2$ is −0.317 V (s.c.e.). [31]

On the above basis it is easy to explain the fact that when the concentration of the indifferent electrolyte is increased (within certain limits) $E_{\frac{1}{2}}$ for the waves of cobalt, nickel, and iron are shifted to the side of more negative potentials. For example, when the concentration of $CaCl_2$ (taken as supporting electrolyte) is raised to 1 N, the Fe^{2+} wave is shifted by ~ 300 mV in the negative direction. This is accompanied by a decrease in the limiting current, which the investigators attributed to an increase in the viscosity of the solution and a corresponding change in the diffusion coefficient of the iron [48]. A shift in $E_{\frac{1}{2}}$ in a negative direction when the ionic strength is increased is also observed in the reduction of cobalt complexes with cysteine [16] and for the "simple" ions of cobalt [8] and nickel [6].

As regards nickel complexes, the influence of the double layer is somewhat peculiar [49]. The reduction of nickel hexahydrate in dilute solutions is accompanied by the appearance of a single wave [49] with a sharply expressed limiting current plateau. However, as the concentration of the electrolyte is raised the limiting current of the wave falls completely and starts to depend upon the potential [49,50], increasing with increase in the negative potential. At the same time, $E_{\frac{1}{2}}$ for this wave hardly alters (Fig. 9); when the KCl concentration is increased above 0.8 M a second wave also appears, lying in a more negative range of potentials [8]. Splitting of the nickel wave was also observed at high concentrations (1–1.5 M) of sodium formate, sulphate, and iodide, used as supporting electrolyte [44]. In concentrated solutions of the supporting electrolyte the limiting current for the reduction of Ni^{2+} acquires a kinetic nature [49,50], and the magnitude of the kinetic current increases with the cathode potential (cf. Fig. 9). Gierst [21-24] assumes that hydrated nickel ions are partly dehydrated in the field of the double layer before the electrochemical stage proper:

$$[Ni(H_2O)_6]^{2+} \underset{k_b}{\overset{k_f}{\rightleftarrows}} [Ni(H_2O)_x]^{2+} + (6-x)H_2O$$

and the rate of dehydration increases with the absolute magnitude of the negative ψ_1-potential; hence the increase in the limiting current with increase in the cathodic potential is due to an increase in the negative value of the ψ_1-potential. The limiting current for the discharge of nickel

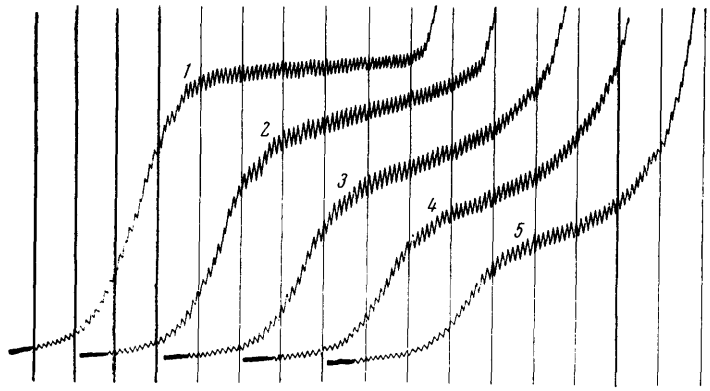


Figure 9. Effect of the concentration of an indifferent electrolyte (NaCl) on the wave for the reduction of 10^{-3} M $NiSO_4$ in the presence of 0.005% gelatin[49]. NaCl concentration, M: 1) 0.1; 2) 0.5; 3) 1.0; 4) 1.5; 5) 2. Each curve starts at −0.7 V (s.c.e.); the distances between the abscissae are 0.2 V.

ions in dilute solutions of an indifferent electrolyte (for example, in 0.1 *N* NaCl) is limited by diffusion, since at low concentrations of the electrolyte the negative value of the ψ_1-potential is so high that the increase in the rate of the preceding reaction brought about by the influence of the double layer has the result that the diffusion of the nickel ionic complex towards the electrode becomes the slowest stage of the process.

Even adsorption of the anion on the mercury surface can occur at a sufficiently high concentration of the indifferent electrolyte. This effect is opposite in sign to the effect of the cation; therefore, for example, when the concentration of chlorides is increased to more than 1–2 M there is a shift in $E_{\frac{1}{2}}$ for iron(II)[48] and cobalt(II)[31] to less negative potentials.

Fig. 10 shows the change in $E_{\frac{1}{2}}$ for iron(II) (curve *1*) as the $CaCl_2$ concentration is varied. Increasing the $CaCl_2$ concentration above 2 *N* shifts $E_{\frac{1}{2}}$ to less negative potentials. However, it is necessary to take into account the complexing action of the anion, which it is difficult to separate from the influence of the double layer during the change in the concentration of the anion[31].

6. INFLUENCE OF THE ADSORPTION OF THE DEPOLARISER

It is also necessary to consider the influence of the adsorption of the complex itself on the kinetics of the electroreduction of the metals concerned. This is especially so in those instances when the ligand is an organic molecule or an organic ion, since organic compounds (especially those which have a sufficiently high molecular weight) are readily adsorbed on the surface of mercury.

Olson[29] observed an increase in the reversibility of the wave for the reduction of the complex of nickel with triethylenetetramine. Since the rate constant for the exchange of the second water molecule is here lower than the rate constant for the exchange of the first water molecule, Olson considers that the reversibility of the wave for the reduction of the complex is due not to the labilisation of the complex but to its specific adsorption at the surface of the electrode. In this instance the reaction centre of the complex is located in the inner Helmholtz plane, where there is a much higher potential gradient, as a result of which the reduction is facilitated.

The influence of the adsorption of pyridine, thiourea[51–53], and diaminopropane[25] on the nickel wave, and of 2,2′-bipyridyl on the cobalt and iron waves[54] has also been noted. Results on the influence of adsorption of complexes of nickel with pyridine are especially numerous[38,51–53].

When 1,10-phenanthroline is present in a Co^{2+} solution a small prewave has been observed[28,29,55,56], which is attributed to the adsorption of the complex $CoPh_n^+$, where $n = 2$ or 3.

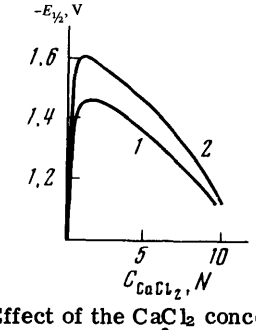


Figure 10. Effect of the $CaCl_2$ concentration on $E_{\frac{1}{2}}$ of the wave for the discharge of Fe^{2+} (1) and hydrogen ions (2); $[Fe^{2+}] = 2 \times 10^{-3}$ *N*, $[H^+] = 1 \times 10^{-3}$ *N*.[48]

7. STEPWISE NATURE OF THE REDUCTION OF COBALT, NICKEL, AND IRON

Two-electron waves are usually observed for the reduction of cobalt(II), nickel(II), and iron(II). However, Losev and Molodov[19] have shown that the transfer of the second electron is not simultaneous with the transfer of

the first, and under certain conditions the successive stepwise reduction of doubly- and multiply-charged cations can be observed.

In the presence of 1,10-phenanthroline two reduction waves are obtained[40-42,55,56] in solutions of Co^{2+} salts, these correspond to the successive transfer of a single electron in each stage. It has been suggested that under these conditions not only a Co^0 complex but also a Co^+ complex is stabilised. The waves have been shown to be irreversible and the limiting current of the first wave is diffusional in nature[40,56].

Single-electron waves were also observed in the investigation of complexes of iron with 2,2'-bipyridyl (Bipy) in an acetonitrile solution with rotating platinum and dropping mercury electrodes in tetraethylammonium perchlorate supporting electrolytes. Three waves are observed, which correspond to the reduction: to Fe^+ ($E_{\frac{1}{2}}^{I} = -1.45$ V) and then to Fe^0 ($E_{\frac{1}{2}}^{II} = -1.70$ V; s.c.e.); as Tanaka and Sato have shown[54], the third wave ($E_{\frac{1}{2}}^{III} = -2.0$ V) corresponds to the reduction of an uncharged complex with the formation of $[Fe(Bipy)_2]^-$.

The formation of a rather stable complex with a metal in a zerovalent state during the reduction of iron-group metals has been advanced repeatedly as a more or less substantiated hypothesis (see, for example, Refs. 25 and 57). The existence of such a complex has been proved[58] unambiguously with the aid of radiopolarography, in the investigation of the cyano-complexes of nickel labelled with ^{63}Ni. As has been shown[58], the ordinary polarogram and radiopolarogram of a solution of 1×10^{-3} M $NiCl_2$ in 0.1 M KCl are almost identical (Fig. 11). However, when 2.5×10^{-3} KCN is added to the solution, instead of a single wave on the ordinary polarogram three waves are observed, whereas on the radiopolarogram there is only one wave with $E_{\frac{1}{2}}$, which almost coincides with the $E_{\frac{1}{2}}$ of the main (second in order) wave. An increase in the concentration of KCN in the solution led to a decrease in the diffusion current of the first wave and to a decrease in the corresponding amount of radioactive nickel in the mercury drop. A further increase in the KCN concentration (to 10^{-2} M) leads to the disappearance of the first and second waves; on the polarogram there is only one wave with $E_{\frac{1}{2}} \simeq -1.5$ V, and the radioactive nickel is completely absent from the mercury drop (Fig. 12). On this basis it was concluded[58] that a stable complex with Ni^0 is formed (at sufficiently high KCN concentrations).

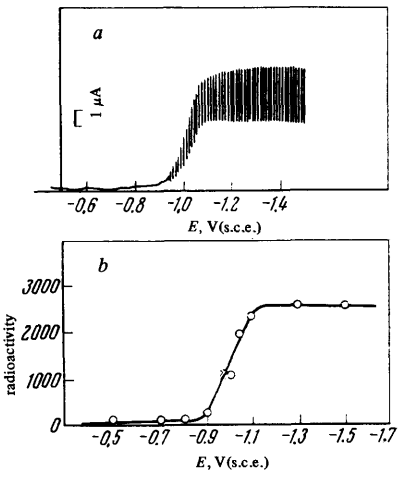


Figure 11. Comparison of the classical polarograms of nickel (a) and radiopolarograms (b); nickel chloride concentration 1×10^{-3} M, supporting electrolyte 0.1 M KCl.[58]

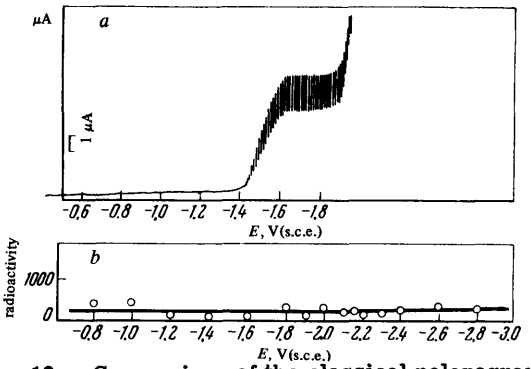


Figure 12. Comparison of the classical polarograms of nickel (a) and of radiopolarograms (b); nickel chloride concentration 1×10^{-3} M, supporting electrolyte 0.1 M KCl + 1×10^{-2} M KCN.[58]

8. FORMATION OF WAVES WHICH ARE CATALYTIC IN NATURE

Catalytic waves which are observed in the polarography of solutions containing cobalt and nickel salts with addition of sulphur-containing amino-acids have been considered sufficiently fully in Mairanovskii's review[59] and also in his monograph[60]. These publications systematised almost the entire literature up to 1965. Consequently, we will only briefly consider the catalytic waves of cobalt in the presence of organic additives. During the period that has elapsed since these two publications there have been no significant changes in opinions on the mechanism of the formation of catalytic hydrogen waves produced by certain organic compounds in the presence of cobalt salts; the mechanism for the production of such waves is still not fully explained.

Brdička[61] was the first to describe (in 1933) the unusual waves observable in the polarography of solutions which contain a cobalt salt and certain compounds with a mercapto-group. Since the wave for the reduction of Co^{2+} precedes the catalytic wave for the release of hydrogen, Brdička[62] and other investigators (see, for example, Ref. 63) have proposed that catalytically active centres form metallic cobalt, which is released at the surface of the mercury drop. To verify this point of view, Brdička[64] made a preliminary electrolysis of a solution at a stationary mercury cathode at a potential at which Co^{2+} is discharged but there is still no catalytic release of hydrogen. In the opinion of Brdička, under these conditions metallic cobalt will accumulate on the surface of the mercury drop. The catalytic wave should rise sharply if the metallic cobalt participates in this reaction. If the preliminary electrolysis were to have no effect on the height and form of the catalytic wave it would indicate that the metallic cobalt is not formed at the surface of the mercury drop. In Brdička's experiments the preliminary electrolysis did not alter the characteristics of the catalytic wave. This work has a definite effect on the formulation of ideas about the mechanism of the catalytic wave formed by certain organic molecules in the presence of cobalt and nickel ions. Most

investigators assume that a complex of the cobalt ion with the organic molecule acts as a catalyst.

Substances which contain a mercapto-group are known [60] to show catalytic activity in the absence of Co^{2+} or Ni^{2+} ions from the solution, but in the presence of the latter the catalytic activity of thiols increases sharply. The increase in the catalytic activity of thiols in their formation of complexes with Co^{2+} is linked, according to Mairanovskii [60], with the increase of the charge of the catalyst by two units, which from the point of view of the influence of the electrical double layer should facilitate the transfer of an electron to these species.

The greatest catalytic activity in the presence of Co^{2+} and Ni^{2+} is exhibited by compounds which simultaneously contain amino- and mercapto-groups. The catalytic effect observable in solutions of such compounds is determined by the action of all the active groups in the molecule. Using the example of the waves produced by cysteine and its derivatives, in which either amino-groups (*NN*-diacetylcysteine) or carboxyl groups (diethyl ester of cysteine) are blocked, Sunahara [65] has shown that blocking of the amino-groups leads to the complete loss of the catalytic activity of the cysteine whereas esterification of the carboxyls has hardly any effect on the characteristics of the catalytic wave. Mairanovskii therefore suggested that in catalysts containing both amino- and mercapto-groups the catalytic activity is due mainly to the amino-groups, whereas the adsorbability of the catalyst is determined mainly by the mercapto-groups. From this point of view, Mairanovskii [66] explains the observed parallelism between the ability of the catalysts to suppress the polarographic maximum, that is, their adsorbability and the height of the catalytic wave they produce. The adsorbability of the catalysts, which under strictly equal conditions determines the limiting catalytic currents is increased (in general) as the size of the catalyst molecule or the number of mercapto-groups in the molecule is increased. As Mairanovskii noted [60], this circumstance is evidently explained by Ito's observation [67] of the approximately proportionate increase in catalytic activity with increase in the number of cysteine residues in the composition of the protein-catalysts.

The height of the catalytic wave increases with the catalyst concentration and the curve for the dependence of the height of the wave on the concentration of the catalytically active substance is reminiscent of a Langmuir adsorption isotherm [60].

The influence of the pH on the catalytic waves due to complexes of cobalt or nickel with thiols is extremely complex. Maximal height of the waves is observed at some definite pH of the solution, as was noted by Březina and Gultjaj [68].

The catalytic activity of cobalt and nickel is usually regarded as an example of complexes with thiols; however, it is known that cobalt and nickel also increase the catalytic activity of pyridine [69], moreover the catalytic activity of pyridine is appreciably higher in the presence of Co^{2+} than in that of Ni^{2+} at the same concentration. It is especially high when both cobalt and nickel are present together in the solution. The catalytic wave which appears in the polarography of solutions of a complex of cobalt or nickel with pyridine has a surface nature. This is shown, for example, by the temperature dependence: as the temperature is raised the height of the catalytic wave falls rapidly and at a temperature above 35°C (in a solution with 0.1 *N* pyridine, 0.1 *N* pyridinium chloride, and 5×10^{-4} M cobalt and nickel salts) the wave is no longer observed [69].

Several new examples of organic compounds (including some which do not contain sulphur) which give catalytic waves in the presence of cobalt or nickel in the solution have recently been observed, e.g. 1,2-pyridylazoresorcinol dimethylglyoxime [70]. In this instance the height of the wave is several orders of magnitude greater than the diffusion current according to the metal ion. This allowed Vinogradova and coworkers [70] to use the catalytic wave of the complex with dimethylglyoxime for the analytical determination of nickel and cobalt in the negligibly small concentration of 2×10^{-8} M.

In certain instances in the presence of organic catalysts nickel gives catalytic waves or prewaves not connected with the release of hydrogen. For example, Tur'yan and coworkers [51,71-74] investigated in detail the nature of the similar catalytic waves observable in the polarography of thiocyanato-, pyridine, and thiourea complexes of nickel. The polarographic catalytic prewaves of nickel in the presence of various organic compounds, which although they contain sulphur in their molecule belong to several different classes of organic compounds, have been investigated [75]. In this study [75] the influence of additions of thioacetamide (Ta), thiourea (Tu), ethylthiourea (TuEt), diethylthiourea ($TuEt_2$), phenylthiourea (TuPh), thiosemicarbazide (Ts), rubeanic acid (dithiooxamide, DTO), unithiol (Ut), and thiocyanate (SCN^-) on the polarographic behaviour of Ni^{2+} (1 M $NaClO_4$; pH 6.25) was investigated. In every instance two catalytic prewaves were observed in the range $E = -0.6$ to -1.0 V (s.c.e.), not connected with the catalytic release of hydrogen. The following sequence of catalytic activity of the sulphur-containing compounds was observed: $Tu \simeq Ta < TuEt < TuEt_2 < TuPh < SCN^- < Ut < Ts < DTK$, which with the exception of SCN^- (Ut and DTO were not investigated in this plan) correlate with the adsorbability of these compounds at the mercury electrode. It was suggested that the catalytic prewaves investigated were due to chemical retardation in the stage of formation of polarographically active complexes, evidently with participation of the adsorbed ligand in most instances.

Calusaru [76] found that Co^{2+} forms a complex with nitrohydroxylamine (in an ammoniacal buffer solution). This leads to some decrease in the Co^{2+} wave and to the appearance of a catalytic wave of hydrogen with a characteristic maximum (in ammoniacal solution and in veronal acetate buffer solutions, starting from pH 6.12). Its height is maximal at pH 8.35 and is independent of the ionic strength of the solution. Nickel also forms a complex with nitrohydroxylamine but this leads only to splitting of the nickel wave [77].

It has been suggested [76,77] that catalytic waves are formed in the reduction of complexes of cobalt with substances which exhibit at least two chelate-forming functional groups. One of them is adsorbed on the mercury and the other shows a donor–acceptor function in relation to hydrogen ions.

Mark and Reilley [78] reported that in the presence of many amines which do not contain sulphur in their molecules Ni^{2+} gives a catalytic wave which appears at more positive potentials than the wave for the discharge of $[Ni(H_2O)_6]^{2+}$. Having studied in detail the mechanism of the electrode process with participation of *o*-phenylenediamine, Mark [79] concluded that the catalytic wave is due to the reduction of a complex formed on the surface of the electrode.

Hence catalytic waves of the most varied nature are formed in solutions of Co^{2+} and Ni^{2+} not only in the presence of thioamino-acids but also in the presence of various

classes of organic and inorganic compounds. The conclusion that the presence of groups which contain sulphur is a necessary condition for the appearance of a catalytic effect[80] is incorrect in the light of recent results.

It must be stated that Brdečka's work[64], in which he carried out a preliminary electrolysis, cannot serve as proof that metallic cobalt does not participate in the formation of a catalytic wave. The fact is that when a solution is electrolysed at a mercury surface the nature of the release of the iron-group metals is more complex than appears at first glance.

Two versions of the formation of a metallic phase in the discharge of ions on mercury can be proposed. In the first, the discharge of the ions is accompanied by the diffusion of metal atoms or their aggregates into the bulk of the mercury, where the cobalt or iron subsequently crystallise, or intermetallic compounds are formed, as happens for nickel.

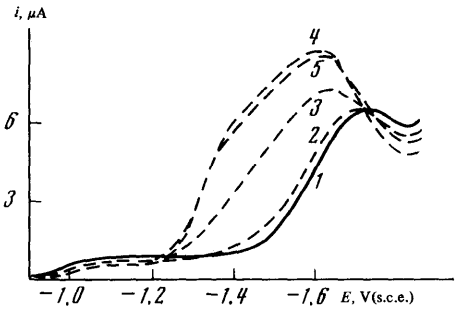


Figure 13. Polarograms of 4×10^{-4} M $CoCl_2$ + 2.3×10^{-4} M cysteine in a borate buffer (pH 9.2) in the presence of various amounts of surface-active substance—poly(vinyl acetate), 10^{-3}%: 1) 0; 2) 1; 3) 2; 4) 3; 5) 4.8.[57]

In the second, the formation of the metallic phase takes place on the surface of the mercury drop. This can be facilitated by the presence of adsorbed layers on the surface of the mercury drop. Owing to the local increase in current density on the mercury, crystallites of the metal will be produced (including nickel; nickel intermetallic compounds are subsequently produced as a result of the reaction of nickel crystals with the mercury).

The existence of a metallic phase on the mercury drop is also a complex phenomenon. The crystallites of the metallic phase are known to "sink" in mercury[81]. It is natural to assume that this process should depend upon the charge at the surface, the nature of the adsorbed layers, and other factors which influence the surface tension of the mercury. At a certain moment of time the nuclei break away from the surface and diffuse inside the mercury drop. Therefore there are no grounds for expecting the accumulation of the solid phase on a suspended mercury drop, as Brdečka[60] did. Under the conditions of his experiment a stationary process was established and the concentration of the metallic phase on the mercury remained constant (it did not depend on the period of electrolysis).

Evidently, when the solution contains a substance which is strongly adsorbed on the mercury it can inhibit the mixing of the solid (cobalt) and liquid (mercury) phases. When at the surface of the mercury there is a solid phase of a metal at which the hydrogen overpotential is considerably less (as happens, for example, for cobalt) than on mercury, then one may expect the discharge of hydrogen ions to be facilitated.

What has been stated above is supported by the fact that the catalytic effect for cobalt is appreciably greater than that for nickel. Cobalt has just as low a solubility in mercury as has nickel, but unlike nickel it does not form intermetallic compounds with mercury[82-85]. Nickel does not exhibit the ability to form compounds with mercury, which hinders the release of nickel on the mercury as an individual phase[82-85].

The recent work of Kolthoff and Mader[57] is extremely interesting in this connection. They recorded a cobalt wave for an insignificant concentration of it in the solution (4×10^{-4} M) in the presence of a little cysteine (2×10^{-4} M), that is, when the catalytic wave of hydrogen is absent from the polarogram. Then a surface-active substance which does not exhibit catalytic properties—poly(vinyl acetate) (PVA)—was added to the cell and a catalytic wave appeared and increased in height (as the PVA concentration was increased) (Fig. 13).

The addition of PVA to a solution which gives catalytic waves when polarographed increases the height of the catalytic wave and shifts this wave to less negative potentials (Fig. 13). However, these investigators start from the determinative role of a complex with zerovalent cobalt. They think[57] that the complex is stabilised in the presence of PVA.

It is noteworthy that iron behaves like cobalt in relation to mercury and consequently if the reason for the appearance of hydrogen waves is the formation of a phase which reduces the hydrogen overpotential, then in the presence of iron salts waves of this type should also be observed.

Ivanov and Ioffe observed this type of wave[48] on polarographing a solution of an Fe^{2+} salt in the presence of a surface active tetrabutylammonium (TBA) cation under conditions when the adsorption of this cation is greatly increased—in concentrated salt solutions (10 *N* $CaCl_2$). A sharp maximum is formed, the height of which is about 50 times that of the limiting diffusion current for iron (Fig. 14, curves *4* and *5*).

On the photomicrographs of a hanging mercury drop obtained[48] at the potential of the peak copious evolution of hydrogen is evident. At a potential more negative than that of the peak the liberation of hydrogen gradually ceases. It must be emphasised that the descending branch of the maximum is in the range of the negative peak of TBA adsorption.

We have also observed waves which are reminiscent in properties of the catalytic waves of hydrogen in solutions of cobalt and iron on the addition of a solution of sodium hypophosphite (curve *3* in Fig. 15); in the absence of these metals sodium hypophosphite is polarographically inactive[86]. The introduction of hypophosphite leads to the formation of the alloy Co_xP_y, insoluble in mercury, playing the part of a new solid phase on the mercury and it was noted earlier[87] that on an alloy of Co and P of a certain composition the overpotential of hydrogen liberation is lower than on cobalt. In every instance a film is formed on the mercury surface and has such a high surface activity that when hypophosphite is introduced into the solution the period of oscillation of the capillary is increased about tenfold, which leads to a change in the form of the wave and an increase in the limiting current (cf. Fig. 15, curves *4* and *5*). The formation of a similar wave for nickel is observed only at high concentrations of

hypophosphite but then the wave mentioned is insufficiently sharp: it almost merges with the background.

In support of the formation of a solid phase on mercury in the discharge of the ions of the Group VIII metals there is the recent work of Astley and Harrison[88]. By combining the method of superimposition of a triangular-wave potential with the impedance method they showed that on an electrode in the form of a hanging mercury drop the cobalt released from a 1×10^{-2} *N* $Co(NO_3)_2$ solution in the presence of KSCN (1–4 M) is formed either as an amalgam or as a phase surface layer of solid cobalt; in the latter instance the process is limited by the rate of nucleation and growth of the cobalt crystals.

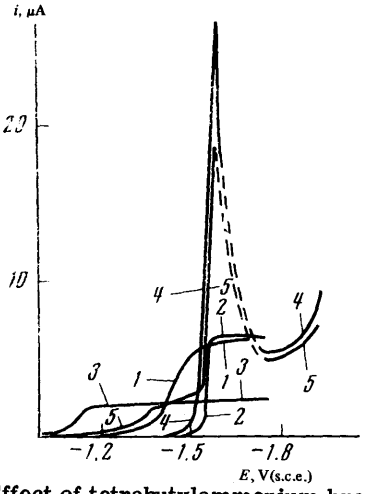


Figure 14. Effect of tetrabutylammonium bromide (TBA) on the kinetics of reduction of Fe^{2+} ions: 1) 1.0 *N* KCl, pH 5.5; 2) 1.0 *N* KCl, 1×10^{-3} *N* TBA; 3) 10.0 *N* $CaCl_2$, pH 5; 4) 10 *N* $CaCl_2$, 0.3×10^{-3} *N* TBA; 5) 10 *N* $CaCl_2$, 0.3×10^{-3} *N* TBA, pH ≃ 3. In every instance $[Fe^{2+}]$ is 2×10^{-3} *N*.[48]

The waves for the release of hydrogen, which resemble in properties the catalytic waves which are also observed in the polarography of solutions of metals of the platinum subgroup[49,89,90], and the heights of these waves are to the first approximation inversely proportional to the solubility of the metal in mercury or its ability to form intermetallic compounds with the mercury. For example, palladium, which is capable of forming intermetallic compounds with mercury, does not give such waves, despite the fact that the overpotential of hydrogen on palladium is appreciably less than that on mercury. The waves for the release of hydrogen in the presence of rhodium chloride[8], which have properties reminiscent of those of catalytic waves, were also observed on the addition of hypophosphite and certain aldehydes and ketones.

Hence it can be assumed that in at least several instances the waves are of a catalytic nature, observable in the presence of metals of Group VIII, due to the depression of the overpotential for the discharge of hydrogen on Group VIII metals, formed on mercury as a result of the discharge of the metallic phase. This conclusion does not contradict Gul'tyai and Mairanovskii's conclusion[91] that Co^{2+} accelerates only those catalytic processes which proceed either on the surface of an electrode with participation of an adsorbed catalyst or in a very thin layer adjacent to the electrode.

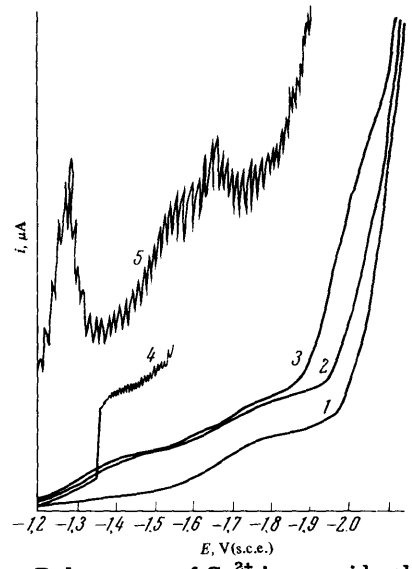


Figure 15. Polarogram of Co^{2+} in an acid solution (pH 2.97) on the addition of sodium hypophosphite. Curves: 1) supporting electrolyte 0.1 *N* KCl + HCl; 2) ditto + Co^{2+} (0.64×10^{-3} M); 3) as for 2 but + 1×10^{-2} M HPP; 4) and 5) as for 3, but the capillary drop period was arbitrarily increased and consequently also the wave height.[8]

There are also results[92,93] on the formation of catalytic hydrogen waves in the presence of chromium(III) (with bipyridyl) so that this property is intrinsic not only for Group VIII metals, but also for all metals, the hydrogen liberation overpotential (or that of other reactions with the participation of a proton) on the surface of which is lower than on mercury. In this instance the presence in the solution of PVA, which forms some similar "grids" which hinder the penetration of the microcrystal inside the mercury drop, is necessary for the appearance of a catalytic current. The magnitude of the effect should depend on the stability of this grid, in addition to other factors.

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The ions of our metals lie in the following order of the increase in the negative values of the half-wave potentials: Ni, Co, Fe.

In dilute aqueous solutions, most often used as a saline supporting electrolyte (alkali metal halides and perchlorates), each ion gives one two-electron wave; the $E_{\frac{1}{2}}$ for these ions lie in a rather narrow region of potentials, from −1.1 to −1.4 V (s.c.e.). Under these conditions the electrochemical process is irreversible. The nickel, cobalt, and iron ions exist in the solution as the hexahydrates.

An increase in the concentration of an indifferent electrolyte usually has a marked effect on the half-wave potential and limiting currents; this influence is mainly symbathic for all the three cations considered. In studying the influence of an indifferent electrolyte, it is essential to take into account the following effects which frequently act simultaneously:

1. A decrease in the negative values of the ψ_1-potentials as the concentration of the cation of the indifferent electrolyte is increased leads to a shift in the $E_{\frac{1}{2}}$ of the wave of our ions to more negative potentials; this effect is appreciably noticeable when the cations of the indifferent electrolyte have a charge of +2 or more, as, for example, in using calcium chloride. The limiting currents in concentrated solutions of the supporting electrolyte are lower than in dilute solutions.

2. The adsorption of ions of an indifferent electrolyte, of a foreign ligand, or of a complex formed by the metal ion concerned. As regards the specific adsorption of the ions of an indifferent electrolyte, in the instances we have considered it is usually necessary to take into account the specific adsorption of only the anions on the electrode surface, which occurs despite the negative charge of the electrode surface. This phenomenon is usually encountered in using rather concentrated solutions of halide ions and the specific adsorption increases very markedly in the order F^-, Cl^-, Br^-, I^-. This effect leads to an increase in the negative values of the ψ_1-potential, which in turn causes a shift in $E_{\frac{1}{2}}$ along the potential axis to more positive values.

A shift in $E_{\frac{1}{2}}$ also results from the reconstruction of the hydrate sheath of the ion, the introduction into the inner coordination sphere of a foreign ligand, such as the halide ions, OH^-, CN^-, CNS^-, and also a series of organic and inorganic ligands (those negatively charged and those without a charge), which are capable of forming a rather stable complex with the cation. The introduction of a foreign ligand into the hydrate sheath is facilitated by dehydration, which leads to a decrease in the negative values of the half-wave potential and an increase in the reversibility of the electrochemical process. Usually on the polarogram there appears a second wave at potentials more positive than the $E_{\frac{1}{2}}$ of the wave for the discharge of the completely hydrated ion.

On reaching a certain concentration of the complex-forming substance (the organic ligand or the anion of the supporting electrolyte) the complex formed is more stable than the hexahydrate. This leads to a shift in $E_{\frac{1}{2}}$ in the negative direction along the potential axis and frequently to a decrease in the limiting currents of the corresponding waves.

The influence of the above effects is mainly analogous for all three of the metals being considered. The influence of the composition of the supporting electrolyte is maximal for Ni and gradually falls in the order Ni, Co, Fe, and the reduction of the nickel complexes in sufficiently concentrated chloride solutions takes place in the positive range of the electrocapillary curve. This can facilitate the discharge of the complex of composition $[NiX_4]^{2-}$, whereas reduction of the negatively charged complexes of cobalt and especially iron, which takes place on the negative branch of the electrocapillary curve will experience some retardation. The addition to the solution of a ligand which forms a stable complex with the metal ion can so increase the stability of the intermediate complex with a singly-charged ion that is formed that the two-electron wave is split into individual waves corresponding to the transfer of a single electron. Here there is observed a rise in stability and the complex with the metal is found in the zerovalent state.

The replacement of water by an organic solvent significantly affects $E_{\frac{1}{2}}$, the limiting currents, and the degree of reversibility of the waves for the discharge of iron-group metals. The organic solvent plays the part of a ligand and then its influence obeys the rules listed above. In addition, in the presence of an organic solvent there is a decrease in the adsorbability of the organic ligands or complexes with such ligands, which usually leads to an increase in the polarisation.

Under certain conditions (the presence of surface-active substances, optimal conditions of electrolysis) the release of Group VIII metals at the surface of a mercury drop leads to the formation of a new phase which adopts the role of an electrode with greatly different characteristics from a liquid mercury electrode. The formation of a solid phase leads to the appearance of new waves on the polarogram—catalytic waves for the discharge of hydrogen. The appearance of a new phase also affects the reversibility of the discharge of the metal ion.

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