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Polarographic Study of Complex Formation Equilibria in Solutions

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Methods for the calculation of the coordination numbers and stability constants of complexes formed in solution from polarographic data are examined and methods for the determination of the parameters governing the formation of a single complex and stepwise complex formation as well as the formation of mixed and polynuclear complexes and complexonates are described. It is shown how kinetic and catalytic waves, the waves of the ligand, and the waves due to irreversible processes can be used for this purpose. Attention is drawn to the necessity to take into account the adsorption of the components of a system involving complex formation.
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I. INTRODUCTION

The use of polarography for the study of the compositions, equilibrium formation constants, and dissociation constants of complexes in solution is based on the simple principles first formulated in 1935 by Heyrovský and Ilkovič[1]. The electrode reduction or oxidation of any depolariser at a mercury electrode is reflected in the polarogram by the corresponding wave whose principal parameters are the half-wave potential $E_{1/2}$ and the limiting current i_d. Heyrovský and Ilkovič introduced the equation of the wave $E = f(i)$ for a reversible electrode process with participation of n electrons and showed that the potential $E_{1/2}$ is in this case close to the normal value (E^0):

$$E_{1/2} = E^0 - \frac{RT}{nF} \ln \left(\frac{D_o}{D_r}\right)^{1/2},$$

where D_o and D_r are the diffusion coefficients of the oxidised and reduced forms of the depolariser ($cm^2\ s^{-1}$). According to the Nernst equation,

$$E = E^0 - \frac{RT}{nF} \ln \frac{[O]}{[B]},$$

the electrode potential is determined by the ratio of the concentrations (more precisely activities) of the components of the oxidation-reduction system. Complex formation leads to a decrease of the concentration of a particular form of the depolariser, which influences the position of the polarographic wave: it shifts along the potential axis. The direction and magnitude of the shift of the wave depend on which component of the redox system forms a more stable complex, the composition of the complex, and its equilibrium formation constant. This fact is in fact used in polarography to determine the complex formation parameters in solution enumerated above.

Thus the polarographic method for the study of complex formation equilibria is in essence close to the potentiometric method. In both cases one uses the dependence of the potential on the concentrations of the components of the redox system. The difference consists in the fact that in potentiometry the ratio of the concentrations of the system components is varied by altering the composition of the solution, while in polarography it is varied by electrolysis at a mercury dropping indicator electrode, which is technically much simpler. The polarographic method is somewhat inferior to the potentiometric method as regards accuracy, but an enormous amount of experimental data on complex formation in solutions has been obtained by the former method[2]. This was promoted by the fact that polarography makes it possible to obtain information not only about the equilibrium properties of the complexes but also about the mechanisms and kinetics of electrode processes involving them, the kinetics of the dissociation of the complexes, and their electrochemical activity as a function of structures.

In the course of the study of equilibria in solutions by the polarographic method, instances of simple and stepwise complex formation, the formation of mixed-ligand and polynuclear complexes, the formation of complexes by metal ions with ligands involved in complex acid–base interactions (for example, with complexones), and the formation of molecular organic complexes and ion pairs have been examined. Methods of calculation from experimental data, including computer calculations, have been greatly improved and methods have been proposed for the investigation of electrochemically inactive complexes with the aid of indicator ions; it has become possible to use kinetic and catalytic waves as well as waves due to irreversible processes. One may conclude that, overall, the level of development of the polarographic method in this field is high.

This review describes the present state of the methods for the investigation of complex formation equilibria in solution with the aid of polarography. The original literature was surveyed inadequately in previous reviews[3-12] and many important studies have been published only in recent years.

II. REVERSIBLE ELECTRODE PROCESSES

Reversible electrode processes involving complexes are more favourable for the study of the compositions of the complexes and their equilibrium formation constants, because it is possible to derive definite useful relations even for very complex systems. It is therefore desirable to select as far as possible experimental conditions which lead to the attainment of reversibility in electrode process. Naturally, before using the relations derived for a reversible process, it is necessary to make sure that the process is indeed reversible. If the process is fully or partly irreversible, the shift of the wave in consequence of complex formation is added to the shift due to the retardation of one of the stages of the electrode process, i.e. to the overvoltage, and the calculation leads to unduly high equilibrium formation constants for the complexes.

In polarography there are a number of criteria which are normally employed to test the reversibility of the process.

1. The equation of the wave of a reversible process is

$$E = E_{1/4} - \frac{2.3RT}{nF} \lg \frac{i}{(i_d - i)} \cdot \quad (1)$$

A linear relation is obtained by plotting $\lg [i/(i_d - i)]$ against E, whose slope is $\partial E/\partial \lg [i/(i_d - i)] = 2.3RT/nF$. At 25 °C the latter is $2.3RT/nF \cong 0.06(V)/n$. According to Tomeš's criterion, which is readily obtained from Eqn.(1), we have

$$E_{3/4} - E_{1/4},\ \mathrm{V} = -\frac{0.06}{n} \lg 9 = -\frac{0.058}{n}.$$

2. The values of $E_{1/2}$ for the waves corresponding to the forward and reverse processes in reversible systems are equal. Cathodic and the corresponding anodic waves with humps of equal height arise on the cyclic voltamperogram for such a system when a stationary electrode is used, the peak potentials differing by $0.058/n$ volts.

3. For reversible processes the diffusion of the depolariser species to the electrode is the slowest stage at all points in the wave. The instantaneous diffusion current at any point in the wave is described by the Ilkovič equation:

$$i,\ \mu\mathrm{A} = 706nD^{1/2}m^{2/3}t^{1/6}(c - c_0),$$

where m (mg s^{-1}) is the rate of flow of mercury from the capillary, t(s) the time elapsed from the start of the growth of the drop, and c and c_0 (10^{-3} M) are the concentrations of the depolariser in the bulk of the solution and at the electrode respectively. According to the Ilkovič equation, $i = kt^{1/6}$, along the rising section of the wave, which can be tested experimentally with the aid of an oscillographic polarograph (for irreversible processes, this equation is valid only for the upper part of the wave).

4. A distinct symmetric peak, the potential at the vertex of which consists only of the value of $E_{1/2}$ for the wave on a classical polarogram, arises on an a.c. polarogram for a reversible system. The peak width at half its height is $0.088/n$ volts. In phase-selective a.c. polarography such peaks have the same shapes and heights: $[(i_p)_R = (i_p)_C]$ are obtained on the curves relating the potentials to the active (i_R) and reactive (i_C) components of the alternating current.

To test the reversibility of this process, it is of course not necessary to employ all the criteria enumerated, which is laborious; however, the reliability of the conclusions is naturally higher the greater the number of criteria used.

In a system with complex formation a series of species are present simultaneously at equilibrium: free metal ions, complex species of various compositions, and the free ligand. In principle, not only free metal ions are discharged at the electrode, which is usually assumed for simplicity in the derivation of the quations, but also the complex species. However, if the process is reversible, and its overall rate is determined solely by diffusion, then experiment does not yield information about which particular species is reduced or oxidised at the electrode; the disappearance of an electrochemically active species at the electrode leads to a change in the concentrations of species of all types at the electrode owing to rapid equilibration.

On the basis of the accumulated experimental data, it is in some cases possible to predict the reversibility of the process involving complexes[5,9]. If a labile metal complex is reduced with preliminary dissociation and the free metal ions are discharged at the electrode, then the process as a whole will be reversible, provided that the metal ions are reduced reversibly[9]. The Tl^+/Tl, Hg^{2+}/Hg, Cu^+/Cu, Cu^{2+}/Cu, Cd^{2+}/Cd, and Pb^{2+}/Pb systems are reversible. Under certain conditions, the Sn^{2+}/Sn, Bi^{3+}/Bi, Sb^{3+}/Sb, and In^{3+}/In systems are also reversible. The labile complexes of these metals are likewise reduced reversibly. We may note that the metals enumerated form amalgams[5]

Sometimes free hydrated metal ions are reduced irreversibly, while in a system with complex formation the process becomes reversible. For example, the hydrated In^{3+} and Ni^{2+} ions are reduced irreversibly, while many of their complexes are reduced reversibly. In such cases one can apparently postulate that complex species and not free metal ions are reduced directly at the electrode.

If the complex is not reduced to the metallic state and the process involves merely a change in the valence of the central complex-forming ion, then it proceeds as a rule reversibly with participation of a single electron[5]. The Fe^{3+}/Fe^{2+}, Cu^{2+}/Cu^+, V^{3+}/V^{2+}, Ti^{4+}/Ti^{3+}, U(VI)/U(V), U^{4+}/U^{3+}, Eu^{3+}/Eu^{2+} and more rarely Cr^{3+}/Cr^{2+}, Mn^{3+}/Mn^{2+}, Co^{3+}/Co^{2+}, Ru^{3+}/Ru^{2+}, Nb(V)/Nb(IV), and Np^{4+}/Np^{3+} are reversible.

Reversibility is particularly characteristic of the reduction of inert complexes, whose oxidised and reduced forms have the same compositions. Thus the hexacyanoferrate(III)/hexacyanoferrate(II), ferrocenium cation/ferrocene, $Cr(CN)_6^{3-}/Cr(CN)_6^{4-}$, etc. systems are reversible. On the other hand, if the oxidised and reduced forms have different structures, then the system is in most cases irreversible. The simple empirical rules enumerated above are useful for the approximate assessment of the reversibility of the system investigated.

Solutions to which a large excess of an indifferent electrolyte has been added are used in polarography. A fairly high electrical conductivity of this solution is attained in this way and the ohmic potential losses can be neglected. At the same time one excludes the migration component of the current, whose presence would constitute an additional complication. Finally, the electrolyte is added also to maintain a constant ionic strength in the solution, ensuring thereby the constancy of the activity coefficients, which are usually difficult to meaure. This is why concentration equilibrium formation constants of the complexes and not their thermodynamic values are found by the polarographic method. The thermodynamic constant can also be estimated by extrapolating the relation between the concentration constant and ionic strength to zero value of the latter.

1. Systems with a Single Complex

The equations of the waves for this case were derived by von Stackelberg and von Freyhold in 1940 [13] and by Lingane in 1941.[14]

(a) Reduction of the complex with formation of an amalgam. In the derivation of the equations of the reduction wave of the complex by the Lingane method[14], one uses the equation for the equilibrium formation or dissociation constant of the complex, the Nernst equation, and the Ilkovič equation, whereby one converts the concentrations into the currents.

The reduction of the complex with formation of an amalgam

$$MX^{(n-pb)+} + ne + Hg \rightleftarrows M(Hg) + pX^{b-}$$

can be conveniently regarded as the sum of two partial reactions:

$$M^{n+} + pX^{b-} \rightleftarrows MX_p^{(n-pb)+}$$

and

$$M^{n+} + ne + Hg \rightleftarrows M(Hg)$$

(here X^{b-} is the ligand). If these reactions are fast and the process as a whole is reversible, then the potential of the indicator electrode will be described by the Nernst equation

for an amalgam electrode, which includes the concentrations at the surface of the electrode of the amalgam formed $[M(Hg)]_0$ and free metal ions $[M]_0$, their activity coefficients $f_{M(Hg)}$ and f_M, and the activity of mercury in the surface layer of the electrode a_{Hg}. Since a very dilute amalgam is formed on the mercury electrode, the activity of the mercury in the amalgam differs little from that of pure mercury and can be regarded as a constant.

The concentration of metal ions in terms of the complex formation equilibrium constant can be substituted in the Nernst equation. The concentration of the complex in solution and of the metal in the amalgam near the interface are found with the aid of the Ilkovič equations for the diffusion of the complex in the solution and of the metal in the amalgam. Since the ligand is liberated in the reduction of the complex, the concentration of the former at the surface of the electrode does not remain constant as the potential of the latter varies along the wave:

$$[X]_0=[X]+pi/\varkappa_X, \qquad (2)$$

where $\varkappa_X = 605nD_X^{1/2}m^{2/3}\tau^{1/6}$, D_X is the diffusion coefficient of the ligand, and τ is the drop time.

Allowance for the change in the ligand concentration at the electrode greatly complicates the equation of the wave. The ligand concentration in the bulk of the solution is therefore made considerably greater than that of the metal ions, whereupon the term $pi/\varkappa_X$ in Eqn.(2) can be neglected and one can assume that $[X]_0 = [X]$.

Ultimately we obtain

$$E = E_{1/2} - \frac{2.3RT}{nF}\lg\frac{i}{i_d - i} \qquad (3)$$

and

$$(E_{1/2})_c = E^0 - \frac{2.3RT}{nF}\lg\frac{K_p f_{M(Hg)}}{f_{MX_p}} - \frac{2.3RT}{2nF}\lg\frac{D_c}{D_a} - p\frac{2.3RT}{nF}\lg[X]f_X. \qquad (4)$$

In the derivation of Eqns.(3) and (4) account was taken of the diffusion to the electrode of complex species alone. If the diffusion of free ions M^{n+} is also taken into account, then instead of Eqn.(4) we obtain[5]:

$$(E_{1/2})_c = E^0 - \frac{2.3RT}{nF}\lg\frac{K_p f_{M(Hg)}}{f_{MX_p}} - \frac{2.3RT}{2nF}\lg\frac{D_c}{D_a} - \frac{2.3RT}{nF}\lg(1+K_p[X]^p f_X^p).$$

For stable complexes, the diffusion of M^{n+} ions to the electrode can be neglected.

Inspection of Eqn.(3) shows that the equation of the wave for the reversible reduction of the complex in no way differs from the equation of the wave for any reversible process. Consequently all the polarographic criteria of reversibility are applicable to the reduction of the complex.

Eqn.(4) does not include the concentration of the complex, so that $E_{1/2}$ is independent of the concentration of the depolariser, as should be the case for the wave corresponding to a reversible process.

It can be readily shown that the following equation is valid for the wave due to the discharge of simple ions:

$$(E_{1/2})_s = E^0 - \frac{2.3RT}{nF}\lg\frac{f_{M(Hg)}}{f_M} - \frac{2.3RT}{2nF}\lg\frac{D_M}{D_a}. \qquad (5)$$

From Eqns.(4) and (5), we obtain the difference between the half-wave potentials of the complex and the simple ion:

$$(E_{1/2})_c - (E_{1/2})_s = \frac{2.3RT}{nF}\lg\frac{f_{MX_p}}{K_p f_{M^{n+}}} + \frac{2.3RT}{2nF}\lg\frac{D_M}{D_c} - p\frac{2.3RT}{nF}\lg[X]f_X.$$

If the experiment is carried out under the conditions of a constant ionic strength, then the contribution of the activity coefficients is usually disregarded. The contribution of the term including the ratio of the diffusion coefficients is also rarely taken into account, although the latter can be readily determined experimentally as the ratio of the limiting currents. The final form of the equation for the shift of $E_{1/2}$ on complex formation is as follows:

$$(E_{1/2})_c - (E_{1/2})_s = \frac{2.3RT}{nF}\lg\frac{(i_d)_M}{(i_d)_c} - \frac{2.3RT}{nF}\lg K_p - p\frac{2.3RT}{nF}\lg[X]. \qquad (6)$$

According to Eqn.(6), the dependence of $\Delta E_{1/2}$ on $\lg[X]$ is represented by a straight line with a slope $2.3pRT/nF$; the coordination number of the complex p can be found from the slope. The straight line makes an intercept $(2.3RT/nF)\lg(1/K_p)(i_d)_M/i_d)_c$ on the ordinate axis, i.e. at $[X]=1$; hence it is easy to find the equilibrium formation constant for the complex K_p.

Lingane[14] used Eqn.(6) in the study of the hydroxo-complex of lead and established that, in the concentration range of alkali 0.01–1 *N*, the coordination number $p = 3$. The electrode process

$$HPbO_2^- + 2e + H_2O + Hg \rightleftarrows Pb(Hg)_f + 3OH^-$$

corresponds to the lead wave.

(b) The reduction of a complex involving the transition from one oxidation state of the complex-forming metal to another. We shall now consider the case of a reversible electrode process as a result of which the complex is not reduced to the metal but gives rise to a valence state of the complex-forming metal differing from the initial state:

$$MX_p^{(n-pb)+} + (n-m)e = MX_q^{(m-qb)+} + (p-q)X^{b-}.$$

Suppose that only one of two complexes, for example $MX_p^{(n-pb)+}$, is present in the bulk of the solution. Both complexes are labile and are involved in a mobile equilibrium with the metal ions in the ligand:

$$M^{n+} + pX^{b-} \overset{K_p}{\rightleftarrows} MX_p^{(n-pb)+}, \qquad (I)$$

$$M^{m+} + qX^{b-} \overset{K_q}{\rightleftarrows} MX_q^{(m-qb)+}. \qquad (II)$$

The ligand is taken in excess, so that $[X]_0 = [X]$.

Using the Nernst equation, the equations for the equilibrium constants of reactions (I) and (II), and the Ilkovič equations for the diffusion of the complexes $MX_p^{(n-pb)+}$ and $MX_q^{(m-qb)+}$, we obtain

$$E = E^0 - \frac{RT}{(n-m)F}\ln\frac{K_p}{K_q} - \frac{RT}{(n-m)F}\ln\frac{i}{i_d - i} - \frac{RT}{(n-m)F}\lg\frac{\varkappa_p}{\varkappa_q} - \frac{(p-q)}{(n-m)}\frac{RT}{F}\ln[X], \qquad (7)$$

$$(E_{1/2})_c = E^0 - \frac{RT}{(n-m)F}\ln\frac{K_p}{K_q} - \frac{RT}{(n-m)F}\ln\frac{\varkappa_p}{\varkappa_q} - \frac{(p-q)}{(n-m)}\frac{RT}{F}\ln[X] \qquad (8)$$

and

$$(E_{1/2})_c - (E_{1/2})_s = \frac{2.3RT}{(n-m)F}\lg\frac{\varkappa_{M^{n+}}+\varkappa_q}{\varkappa_{M^{m+}}+\varkappa_p} - \frac{2.3RT}{(n-m)F}\lg\frac{K_p}{K_q} - 2.3\frac{(p-q)}{(n-m)}\frac{RT}{F}\lg[X]. \qquad (9)$$

If both complexes are present in solution, then the term involving the currents in Eqn.(7) assumes the following form:

$$\frac{RT}{(n-m)F}\ln\frac{i-(i_d)_q}{(i_d)_p - i}$$

where $(i_d)_p$ is the limiting current of the complex $MX_p^{(n-pb)+}$ and $(i_d)_q$ is the limiting current of the complex $MX_q^{(m-qb)+}$; Eqns.(8) and (9) retain their previous form. A single

anodic–cathodic wave arises on the polarogram, its anodic component corresponding to the oxidation of the complex $MX_q^{(m-qb)+}$ and the cathodic component corresponding to the reduction of the complex $MX_p^{(n-pb)+}$.

Eqns.(8) and (9) show that, by studying the dependence of $E_{1/2}$ on lg [X], it is possible to find in this instance only the difference between the coordination numbers and the ratio of the stability constants of the two complexes in the system. In particular, if the composition of the complex does not change on reduction, i.e. $p-q=0$, then the potential $E_{1/2}$ will be independent of the ligand concentration; at the same time it will not be equal to $E_{1/2}$ for the reduction of the simple ion M^{n+}. On the other hand, following the addition of the first portion of the ligand in excess with respect to the M^{n+} ions, the reduction wave of the latter shifts in the cathodic or anodic direction depending on which complex is more stable, but a further change in ligand concentration does not entail a shift.

If the composition and the formation constant of one of the complexes are known, then it is possible to determine by Eqns.(8) and (9) the corresponding parameters for the other complex. As an illustration, we shall consider a system consisting of the oxalate complexes of bivalent and tervalent iron[13,14]:

$$Fe(C_2O_4)_3^{3-} + e \rightleftarrows Fe(C_2O_4)_q^{(3-2q)+} + (3-q)\,C_2O_4^{2-}.$$

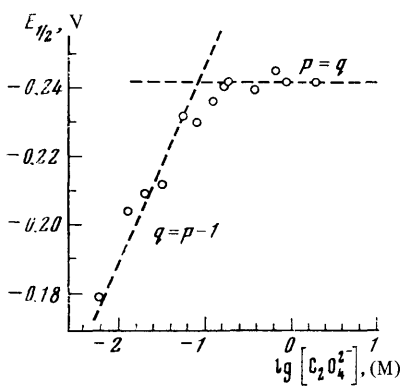


Figure 1. Dependence of the half-wave potential for the reduction of the complex $Fe(C_2O_4)_3^{3-}$ on the logarithm of the concentration of oxalate ions. Reference electrode—saturated calomel half-cell[14].

This system was investigated at 25 °C and an Fe^{3+} concentration of $(1–2)\times10^{-3}$ M. The $K_2C_2O_4$ concentration was varied[14] in the range 6.1×10^{-3}–1.76 M. The solutions also contained 0.3–0.6 M KCl. The dependence of $E_{1/2}$ of the reduction wave of the iron(III) oxalate complex on the logarithm of the oxalate concentration is illustrated in Fig.1. The plot consists of two sections. At an oxalate concentration in excess of ~0.15 M the half-wave potential $E_{1/2}$ is independent of $[C_2O_4^{2-}]$; consequently $p-q=0$ and the iron(II) and iron iron(III) complexes have the same compositions:

$$Fe(C_2O_4)_3^{3-} + e \rightleftarrows Fe(C_2O_4)_3^{4-}.$$

For $[C_2O_4^{2-}] < 0.15$ M, $E_{1/2}$ does depend on $[C_2O_4^{2-}]$ and $\partial E_{1/2}/\partial \lg [C_2O_4^{2-}] = 58$ mV, which corresponds to $p-q=1$ for $n-m=1$. Consequently, under these conditions, the reduction of the complex $Fe(C_2O_4)_3^{3-}$ leads to the formation of the complex $Fe(C_2O_4)_2^{2-}$:

$$Fe(C_2O_4)_3^{3-} + e \rightleftarrows Fe(C_2O_4)_3^{3-} + C_2O_4^{2-}.$$

The independence of $E_{1/2}$ of the ligand concentration for partial reduction of the complex is characteristic of the polarographic behaviour of metal complexonates which as a rule have the simplest composition, 1:1.

If the complex $MX_q^{(m-qb)+}$ is reduced with formation of an amalgam of the complex-forming metal at more negative potentials,

$$MX_q^{(m-qb)+} + m\,e + Hg \rightleftarrows M(Hg) + q\,X^{b-}$$

and a separate second wave arises on the polarogram, then both the composition and the stability constants of the two complexes can be determined by analysing the properties of the two waves. The properties of the first wave are fully consistent with Eqns.(7)–(9); those of the second wave are described by Eqns.(3), (4), and (6), but a number of corrections must be applied to them. Firstly, at the potentials of the second wave the current is determined by the rate of diffusion of the complex $MX_p^{(n-pb)+}$ and not $MX_q^{(m-qb)+}$ although its concentration does in fact fall almost to zero at the potentials of the first wave. Secondly, m electrons are involved in the process. Thirdly, at the potentials of the first and second waves the characteristics of the capillary differ owing to the influence of the potential on the drop time. Taking into account the above corrections, the following equations were obtained[13]

$$E'' = E''_{1/2} - \frac{2.3RT}{mF}\lg\frac{i''}{i''_d - i''},$$

$$(E''_{1/2})_c = E_2^0 - \frac{2.3RT}{mF}\lg K_q - \frac{2.3RT}{mF}\lg\frac{(n-m)}{m}\frac{\varkappa_q}{\varkappa_a} - q\frac{2.3RT}{mF}\lg[X],$$

and

$$(E''_{1/2})_c - (E''_{1/2})_s = \frac{2.3RT}{mF}\lg\frac{m}{(n-m)}\frac{\varkappa_{M^{m+}}}{\varkappa_q} - \frac{2.3RT}{mF}\lg K_q - q\frac{2.3RT}{mF}\lg[X].$$

In these equations E'' and $E''_{1/2}$ are respectively the potential of any point in the second wave and its half-wave potential, E_2^0 the normal potential for the process

$$M^m + me + Hg \rightleftarrows M(Hg);$$

i'' and i''_d are the current and the limiting current of the second wave reckoned from the limiting current of the first wave, K_q is the stability constant of the complex $MX_q^{(m-qb)+}$, $\varkappa_q$ the constant of the Ilkovič equation for the complex, $\varkappa_a$ the corresponding constant for the amalgam of M at the limiting current potential of the second wave, and $\varkappa_{M^{m+}}$ the corresponding parameter for the ion M^{m+} also at the limiting current potential of the second wave.

The reduction of certain copper complexes, particularly ammine complexes, serves as a striking example of a stepwise reduction process. Free copper(II) ions are reduced in one stage with formation of an amalgam, so that the normal potential for the process

$$Cu^+ + e + Hg \rightleftarrows Cu(Hg)$$

is more positive than that (and hence also $E_{1/2}$) for the process

$$Cu^{2+} + e \rightleftarrows Cu^+.$$

Ammine complexes of bivalent and univalent copper are formed in ammonia-containing solutions but the copper(I) complexes are more stable. The copper waves move apart; for this reason, at a fairly high ammonia concentration two waves arise on the polarogram of bivalent copper and can be used to investigate the composition and stabilities of the complexes of copper in both valence states. This system has been investigated by von Stackelberg and von Freyhold[13]; the experimental and calculated data obtained are illustrated in Fig.2. Evidently the stepwise reduction of the copper(II) ammine complex is observed at an ammonia concentration of 0.001 M and above. Fig.2 shows that the slopes of the plots of $E_{1/2}$ against lg $[NH_3]$ correspond to the complexes having this composition. In the reduction of the copper(II) complex this relation (curve *1*) has an anomalous form: along the initial section the increase of the ammonia concentration causes a shift of the wave in the positive direction. This is because at a very low ammonia concentration mainly complexes of Cu^{2+} with one or two ammonia molecules are formed, while copper(I) forms mostly a complex with two ammonia molecules under the same conditions. The ratio $K_p/K_q \ll 0$ and $\lg(K_p/K_q) < 0$, but this term has the minus sign in Eqn.(9). Furthermore, $p-q$ is either −1 or 0. As a result of the influence of these two parameters, the initial shift of the wave in the positive direction is observed. In the presence of ammonia the process

$$Cu^{2+} + 2e + Hg \rightleftarrows Cu(Hg)$$

does not occur (curve *2*).

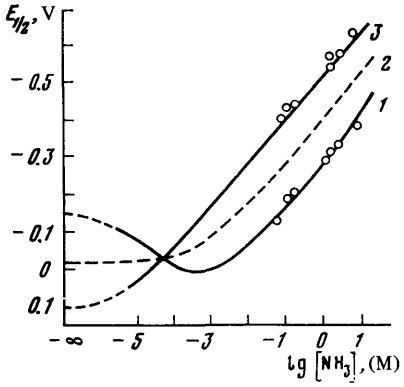


Figure 2. The influence of the concentration of ammonia on the half-wave potentials for different processes: 1) Cu^{2+}/Cu^{+} $[Cu(NH_3)_4^{2+}/Cu(NH_3)_2^{+}]$; 2) $Cu^{2+}/Cu(Hg)$; 3) Cu^{+}/Cu $[Cu(NH_3)_2^{+}/Cu(Hg)]$. Lines—calculations; circles—experimental data. Reference electrode—saturated calomel half-cell[13].

In the derivation of the equations of the reduction wave of the complex it was assumed that the ligand is present in solution in a fairly large excess. On the other hand, it is desirable to vary the concentration of the ligand within the widest possible limits. It is therefore necessary to know what excess is adequate. The change in the ligand concentration at the electrode as a result of the reduction of the complex is responsible for the undesirable shift of the wave. The excess of the ligand N, for which the error of the measurement of $E_{1/2}$ does not exceed $\Delta E_{1/2}$ for the reason discussed above, can be calculated by the equation (Heyrovský and Kuta[15], p.137)

$$N = \frac{p^2}{2} \cdot \frac{RT}{nF} \cdot \left(\frac{D_c}{D_X}\right)^{1/2} \cdot \frac{2}{\Delta E_{1/2}} .$$

Here $RT/F = 25$ mV at 25 °C. Thus, when $E_{1/2}$ is measured to within 2 mV, the excess of the ligand should be at least by a factor of 100 if $p = 4$ and $n = 1$ and a factor of 12 if $p = 2$, subject to the condition that $(D_C/D_X)^{1/2} = 1$. It follows from these calculations that a smaller excess of the ligand is required the smaller the value of p and the larger the value of n.

(c) Mercury complexes. The reduction waves of mercury complexes or the oxidation waves of metallic mercury involving the formation of a complex have an unusual form and properties. The explanation is that one of the components of the oxidation-reduction system is metallic mercury, whose activity is always constant. For this reason, the initial Nernst equation has a simpler form:

$$E = E^0 + \frac{RT}{2F} \ln [Hg^{2+}]_0.$$

Simple relations are also obtained where there is no excess of the ligand in solution.

The reasoning followed in the derivation of the equation of the wave is of the usual kind: the concentration of mercury ions is found from the equation for the stability constant of the complex and is substituted in the Nernst equation The concentrations are converted into the currented with the aid of the Ilkovič equation. It is therefore desirable to quote and discuss only the final equation in this instance (Heyrovský and Kuta, Ref.15, p.151).

The reduction of the mercury complexes will be considered in relation to the electrode process

$$Hg^{2+} + 2CN^- \overset{K}{\rightleftarrows} Hg(CN)_2,$$
$$Hg^{2+} + 2e \rightleftarrows Hg.$$

The equation of the wave is

$$E = E^0_{Hg^{2+}} - \frac{RT}{2F} \ln \frac{i^2}{(i_d - i)} \frac{\varkappa_c}{(\varkappa_X)^2} K, \qquad (10)$$

$$(E_{1/2})_c = E^0_{Hg^{2+}} - \frac{RT}{2F} \ln \frac{i_d}{2} \frac{\varkappa_c}{(\varkappa_X)^2} K. \qquad (11)$$

Eqns.(10) and (11) show that the wave of the mercury complex can be expressed in a linear form by plotting E against lg $[i^2(i_d - i)]$, the straight line intersecting the potential axis not at $E_{1/2}$ but at the potential

$$E^* = E^0_{Hg^{2+}} - \frac{2.3RT}{2F} \lg \frac{\varkappa_c}{(\varkappa_X)^2} - \frac{2.3RT}{2F} \lg K,$$

which depends on the characteristics of the capillary and the stability constant of the complex. The half-wave potential is a function of the concentration of the complex.

In the general case we have for the reduction of the complex HgX_p

$$E = E^0_{Hg^{2+}} - \frac{RT}{2F} \ln \frac{i^p}{(i_d - i)} \frac{\varkappa_c}{(\varkappa_X)^p} K_p$$

and

$$E_{1/2} = E^0_{Hg^{2+}} - \frac{RT}{2F} \ln \left(\frac{i_d}{2}\right)^{p-1} \frac{\varkappa_c}{(\varkappa_X)^p} K_p.$$

In the example under consideration CN^- is the anion of a weak acid, $K_a = [CN^-][H^+]/[HCN] = 7.2 \times 10^{-10}$. Taking this factor into account, we obtain somewhat different equations of the wave:

$$E = E^0_{Hg^{2+}} - \frac{RT}{2F} \ln \frac{i^2}{(i_d - i)} \frac{\varkappa_c}{(\varkappa_X)^2} K - \frac{RT}{F} \ln \frac{K_a}{K_a + [H^+]} .$$

When $[H^+] \gg K_a$ (i.e. at pH < 8) and a constant concentration of the complex $Hg(CN)_2$, we obtain

$$E_{1/2} = E^0_{Hg^{2+}} + \frac{RT}{F} \ln [H^+] + \text{const.}$$

Consequently at $[H^+] \gg K_a$ the half-wave potential $E_{1/2}$ is a function of the pH. On the other hand, if $[H^+] \ll K_a$ (i.e. at pH > 10), then $E_{1/2}$ is independent of the pH.

The principles governing the allowance for the acid–base equilibrium involving the ligand in simple complex formation equilibria without taking into account the participation of the protonated ligand in the complex formation reaction have been demonstrated in relation to the reduction of the complex $Hg(CN)_2$. More complicated cases will be considered below.

The equilibria in the formation of mercury complexes can be investigated also on the basis of the influence of the ligands on the anodic dissolution of mercury. Suppose that metallic mercury undergoes anodic dissolution in the presence of a small amount of CN^- ions;

$$Hg \rightleftarrows Hg^{2+} + 2e,$$
$$Hg^{2+} + 2CN^- \overset{K}{\rightleftarrows} Hg(CN)_2.$$

The CN^- ions bind the Hg^{2+} ions formed in a complex and the concentration of mercury ions at the electrode falls. As a result, an anodic wave arises on the polarogram, its height being determined by the diffusion of CN^- ions to the electrode and its position being related mainly to the stability constant of the mercury complex formed: the more stable the complex the more cathodic are the potentials at which the wave is located.

The equation of the anodic wave is

$$E = E^0_{Hg^{2+}} + \frac{RT}{2F} \ln \frac{i}{(i_d - i)^2} \frac{(\varkappa_X)^2}{\varkappa_c K} , \quad (12)$$

$$(E_{1/2})_c = E^0_{Hg^{2+}} + \frac{RT}{2F} \ln \frac{(\varkappa_X)^2}{\varkappa_c \cdot 0{,}5 i_d K} , \quad (13)$$

or

$$(E_{1/2})_c = E^0_{Hg^{2+}} + \frac{RT}{2F} \ln \left(\frac{D_X}{D_c}\right)^{1/2} \frac{2}{K[CN^-]} ,$$

since $i_d = \varkappa_X [CN^-]$. Comparison of Eqns.(10) and (11), on the one hand, and Eqns.(12) and (13), on the other, shows that the anodic wave for the formation of the mercury complex and the cathodic wave for its reduction have similar properties. This is understandable: the waves correspond to the forward and reverse processes of a single system.

The anodic waves of mercury are convenient for the investigation of mercury complexes. They have been used to study the equilibria in the formation of mercury complexes with the anions CN^-, SO_3^{2-}, $S_2O_3^{2-}$, SCN^- as well as complexones and ethylenediamine. In the presence of an excess of the ligand in solution, we obtain for the reduction wave of the mercury complex[15]

$$E = E^0 + \frac{RT}{2F} \ln (i_d - i) - \frac{RT}{2F} \ln \varkappa_c - \frac{RT}{2F} \ln K_p - p \frac{RT}{2F} \ln [X], \quad (14)$$

$$E_{1/2} = E^0 + \frac{RT}{2F} \ln \frac{i_d}{2} - \frac{RT}{2F} \ln \varkappa_c - \frac{RT}{2F} \ln K_p - p \frac{RT}{2F} \ln [X] \quad (15)$$

or

$$E_{1/2} = E^0 + \frac{RT}{2F} \ln \frac{[HgX_p]}{2} - \frac{RT}{2F} \ln K_p - p \frac{RT}{2F} \ln [X]. \quad (16)$$

Evidently the wave in this case is even more asymmetric, beginning from a sharp break at the potential

$$E_{i=0} = E^0 + \frac{RT}{2F} \ln [HgX_p] - \frac{RT}{2F} \ln K_p - p \frac{RT}{2F} \ln [X]. \quad (17)$$

The wave represents, as it were, the upper half of the normal reduction wave of a complex involving the formation of an amalgam. The half-wave potential is a function of the concentration of the complex, but is independent of the characteristics of the capillary; the equation can be expressed in a linear form by plotting E against $\lg (i_d - i)$.

If the complex is reduced with formation of a metal insoluble in mercury, then the wave has exactly the same shape and Eqns.(14)–(17) are valid for it.

(d) The displacement method[16]. If the solution contains only one ligand X and the two metal ions M and N, then the equilibrium mixture should contain the free ions M and N and the complexes MX and NX:

$$MX + N \rightleftarrows NX + M, \qquad K_{III} = [NX][M]/[MX][N] = K_{NX}/K_{MX} . \quad (III)$$

The additional unknowns in this equation are eliminated with the aid of the material balance equations

$$c_M = [M] + [MX],$$
$$c_N = [N] + [NX],$$
$$c_X = [MX] + [NX].$$

The relation is particularly simple if the experiment is carried out in such a way that $c_M = c_N = c_X = c$. Then

$$K_{III} = [M]^2/(c - [M])^2 = K_{NX}/K_{MX}.$$

[M] is determined polarographically and the ratio of the stability constants of the complexes NX and MX is calculated. If one of the constants is known, the other can be obtained from the ratio.

The experiment is carried out as follows[16]. A solution containing the complex MX, which is reduced with formation of a single wave on the polarogram, is treated with a salt containing the cation N. After the establishment of the new equilibrium, the reduction wave of the complex MX is preceded by the wave of the displaced free ions M. One of the conditions for the application of the displacement method is the slowness of the attainment of equilibrium (III). Only then is the reduction wave of the ions M of a purely diffusional type and its height characterises the equilibrium concentration of these ions. It is also necessary that the cation N and the complex NX are electrochemically more active than the ions M.

This procedure has been widely used[16] in the polarographic study of the formation of metal complexonates.

2. Stepwise Complex Formation

If several complexes are formed in solution, the dependence of the half-wave potential for the reduction of the complex-forming metal on the logarithm of the activity of the ligand will no longer be linear. In this case the plot of $E_{1/2}$ against lg [X] consists either of several linear sections (in accordance with the number of complexes formed, whose formation constants differ fairly appreciably) or of a smooth curve which is convex with respect to the abscissa axis, (with increase of the activity of the ligand, complexes with a larger coordination number are formed and the slope of the plot increases). The smooth curve is obtained when the stability constants of the complexes do not differ very markedly and the regions of

their existence overlap. In the former case the equations derived in the preceding section are applicable to the individual linear sections and it is possible to determine with their aid both the coordination number p and the formation constant K for each complex. The second case requires a more complicated analysis.

(a) Method based on the logarithmic Yatsimirskii plot[17-20]. We shall assume that at any ligand concentration not more than two complexes are formed in solution and these are in equilibrium:

$$MX_p + X \rightleftarrows MX_{p+1},$$
$$\beta_{p+1} = [MX_{p+1}]_0/[MX_p]_0[X].$$

(β_{p+1} is the successive formation constant of the complex MX_{p+1}). The ligand is again present in solution in a fairly large excess.

An expression for $[MX_{p+1}]_0$ and then for $[M]_0$ can be obtained from the equation for β_{p+1}. Having substituted $[M]_0$ in the Nernst equation and having replaced the concentrations by the currents with the aid of the Ilkovič equation, we arrive at the following equations for the wave, $E_{1/2}$, and $\Delta E_{1/2}$:

$$E = E^0 - \frac{RT}{nF}\ln\frac{i}{(i_d - i)} - \frac{RT}{nF}\ln\frac{\varkappa_c}{\varkappa_a} - \frac{RT}{nF}\ln[X]^p(1 + \beta_{p+1}[X]),$$

$$E_{1/2} = E^0 - \frac{RT}{nF}\ln\frac{\varkappa_c}{\varkappa_a} - \frac{RT}{nF}\ln K_p - \frac{RT}{nF}\ln[X]^p(1 + \beta_{p+1}[X]),$$

$$(E_{1/2})_s - (E_{1/2})_c = \Delta E_{1/2} = \frac{RT}{nF}\ln[X]^p(1 + \beta_{p+1}[X]) + \frac{RT}{nF}\ln K_p + \frac{RT}{nF}\ln\frac{\varkappa_c}{\varkappa_M}. \quad (18)$$

According to Eqn.(18), the function $\Delta E_{1/2} = f\{\ln[X]\}$ is represented by a curve whose slope at any point is determined by the derivative

$$\frac{\partial \Delta E_{1/2}}{\partial \ln[X]} = \frac{RT}{nF}\left(p + \frac{[X]}{\beta_{p+1}^{-1} + [X]}\right).$$

When $[X] \gg \beta_{p+1}^{-1}$, we have $\partial \Delta E_{1/2}/\partial \ln[X] = RT(p+1)/nF$ and Eqn.(18) is converted into Eqn.(6); the complex MX_{p+1} predominates in the solution. When $[X] \ll \beta_{p+1}^{-1}$, we have $\partial \Delta E_{1/2}/\partial \ln[X] = RTp/nF$ and Eqn.(18) is again transformed into Eqn.(6); the complex MX_p predominates in the solution.

When the concentrations of the two complexes are equal, i.e. $[X] = \beta_{p+1}^{-1}$, we have

$$\Delta E_{1/2} = \frac{RT}{nF}\ln[X]^p + \frac{RT}{nF}\ln K_p - \frac{RT}{nF}\ln\frac{\varkappa_M}{\varkappa_c} + \frac{RT}{nF}\ln 2, \quad (19)$$

$$\frac{\partial \Delta E_{1/2}}{\partial \lg[X]} = \frac{2.3RT}{nF}\left(p + \frac{1}{2}\right). \quad (20)$$

In conformity with these derivations, the experimental data are represented by a plot of $\Delta E_{1/2}$ against $\lg[X]$ and a series of tangents are drawn; their slopes are defined by Eqn.(20) in which integral values of p are substituted (1, 2, 3, etc.). The tangential points correspond to the equality of the concentrations of the complexes MX_p and MX_{p+1}, while the ligand concentrations at these points are numerically equal to β^{-1}. Knowing p and the corresponding values of $[X]$, it is possible to calculate the constants K_p by Eqn.(19). Yatsimirskii called this method the logarithmic plot method.

If a tangent is drawn having put $p = 0$, then the tangential point will correspond to the equality of the concentrations of the free ions M^{n+} and the complex MX, while the concentration of the ligand at this point is equal to the instability constant of the complex MX.[21]

Adamovich and Novakovskii[22] and also Tur'yan[23] considered the conditions under which the logarithmic plot method is applicable. According to these workers, the method can be used to determine the parameters p, K, and β even for non-existent complexes in those cases where for some reason ligands do not add to the metal ion solely one by one. Adamovich and Novakovskii therefore recommend that the method be used only for complexes whose existence has been demonstrated independently. However, real complex formation is reflected in the form of the relation between $E_{1/2}$ and $\lg[X]$ and for a non-existent complex the Yatsimirskii method should in principle yield the corresponding successive formation constants.

Tur'yan[23] pointed out that the logarithmic plot method is an approximation, so that the hypothesis that two adjacent complexes predominate when their concentrations are equal does not correspond exactly to reality. Sometimes it is altogether invalid and the situation depends on the ratio of the formation constants of the complexes. For this reason, the stability constants of the complexes determined by the logarithmic plot method are approximate. Nevertheless the method merits attention in view of its simplicity.

The method of tangents[9] is similar to the logarithmic plot method. In this procedure tangents are also drawn to the $\Delta E_{1/2} = f\{\lg[X]\}$ curve, but with the slope defined by Eqn.(6), i.e. $\partial \Delta E_{1/2}/\partial \lg[X] = 2.3RTp/nF$ with integral values of p. The tangential points correspond to the ligand concentrations at which a single complex MX_p predominates in the solution. The method of tangents is also approximate and practice has shown[9] that it leads to less accurate stability constants than the logarithmic plot method. The explanation is that the condition governing the predominance of two adjacent complexes usually holds better than the condition governing the predominance of a single complex.

(b) The graphical method of De Ford and Hume[24]. If n complexes are formed in solution, then each causes a shift of $E_{1/2}$ in accordance with Eqns.(6). The overall shift of $E_{1/2}$ can therefore be determined by adding together the shifts of $E_{1/2}$ corresponding to all the complexes:

$$(E_{1/2})_s - (E_{1/2})_c = \frac{RT}{nF}\lg\sum_{p=0}^{p=n} K_p[X]^p + \frac{RT}{nF}\ln\frac{\varkappa_c}{\varkappa_M},$$

$$\sum_{p=0}^{p=n} K_p[X]^p = F_0([X]) = \text{anti lg}\left\{\frac{nF}{2.3RT}[(E_{1/2})_s - (E_{1/2})_k] + \lg\frac{(i_d)_M}{(i_d)_c}\right\}, \quad (21)$$

$$F_0([X]) = 1 + K_1[X] + K_2[X]^2 + \ldots + K_n[X]^n. \quad (22)$$

The right-hand side of Eqn.(21) contains quantities which are determined experimentally. If $F_0\{[X]\}$ is plotted against $[X]$ then, according to Eqn.(22), one obtains a curve whose extrapolation to $[X] = 0$ yields unity, i.e. the formation constant of the zeroth complex.

In order to find K_1, we introduce the function $F_1\{[X]\}$:

$$E_1([X]) = \frac{F_0([X]) - 1}{[X]} = K_1 + K_2[X] + \ldots + K_n[X]^{n-1} \quad (23)$$

The plot of this function is also curved and its extrapolation to $[X] = 0$ yields K_1.

The plot of the function

$$F_2([X]) = \frac{F_1([X]) - K_1}{[X]} = K_2 + K_3[X] + \ldots + K_n[X]^{n-2} \quad (24)$$

and its extrapolation to $[X] = 0$ yield K_2, etc. The plot of the penultimate function against $[X]$ consists of an inclined straight line and that for the last function is represented by a straight line parallel to the abscissa axis.

It follows from Eqns.(22)–(24) that the slope of the plot of the function is initially equal to the next stability constant of the complex:

$$\left(\frac{\partial F_0([X])}{\partial [X]}\right)_{[X]\to 0} = K_1;\ \left(\frac{\partial F_1([X])}{\partial [X]}\right)_{[X]\to 0} = K_2, \text{ etc.}$$

Graphical analysis of the Leden functions $F\{[X]\}$ by the method of De Ford and Hume makes it possible to determine how many and what complexes are formed in the solution and to determine their formation constants.

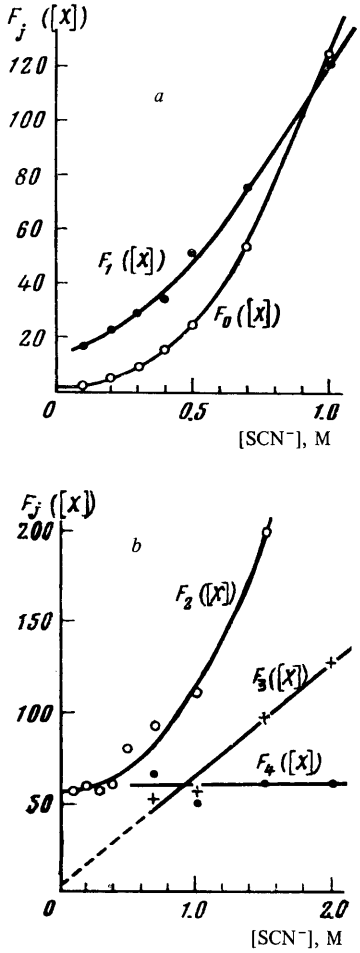


Figure 3. The De Ford and Hume analysis of the functions $F_j\{[X]\}$ for the Cd^{2+}/SCN^- system at an ionic strength $I = 2$ (established by the addition of KNO_3).[25]

Fig.3 illustrates plots of the functions $F\{[X]\}$ for the Cd^{2+}/SCN^- system at a constant ionic strength of 2. Evidently four complexes are formed in this system: $CdSCN^+$, $Cd(SCN)_2$, $Cd(SCN)_3^-$, and $Cd(SCN)_4^{2-}$, with the stability constants $K_1 = 11 \pm 0.5$, $K_2 = 56 \pm 2$, $K_3 = 6 \pm 5$, and $K_4 = 60 \pm 10$. This example demonstrates the fruitfulness of the method of graphical analysis, but at the same time it reveals its weak aspect, namely the increase of the error with increasing complexity of the complex. The existence of the complex $Cd(SCN)_3^-$ is doubtful. It is noteworthy that the reliability of the conclusions arrived at is greater the more stable the complex.

Hume et al.[25] determined $E_{1/2}$ to within 1 mV. A significant improvement of the accuracy of the measurements can be achieved by improving the experimental technique. Piljac et al.[26] prepared the solutions directly in the cell and introduced the ligand-containing solution with the aid of an accurate microburette. The potential was applied to the cell by means of a polarograph and the potential of the mercury dropping electrode relative to the reference electrode was measured by a precision pH-meter. The current was measured at the instant of separation of the drop with the aid of an undamped mirror galvanometer. All the measurements were made by hand and not automatically. The reproducibility of the measurement of the potential in these experiments was to within 0.2 mV.

More accurate stability constants are obtained by calculation and not by the graphical analysis of the Leden function. The problem reduces to the solution of a system of linear equations of type (22), the number of equations equal to the number of measurements of $F_0\{[X]\}$ exceeding the number of unknowns, i.e. the formation constants of the complexes:

$$1 + K_1[X]_1 + K_2[X]_1^2 + \ldots + K_n[X]_1^n - F_0([X])_1 = 0, \quad (25)$$

$$1 + K_1[X]_2 + K_2[X]_2^2 + \ldots + K_n[X]_2^n - F_0([X])_2 = 0, \quad (26)$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$1 + K_1[X]_m + K_2[X]_m^2 + \ldots + K_n[X]_m^n - F_0([X])_m = 0 \quad (27)$$

$(m > n)$. The calculations are performed mainly by the method of least squares[27–29], whereby the number of equations is reduced to the number of unknowns. The system of equations obtained is then solved by matrix algebra.

If the experiment has been formulated in such a way that

$$[X]_2 - [X]_1 = [X]_3 - [X]_2 = [X]_4 - [X]_3 = \ldots = [X]_m - [X]_{m-1},$$

i.e. $\Delta[X] = \text{const.}$, then calculations by the method of least squares are less laborious[28,29].

When the method of least squares is used, one must make an assumption about the number of complexes formed in solution. If the assumption is wrong, some of the calculated formation constants of the complexes are negative, which lacks physical significance. Calculations are therefore repeated for another postulated number of complexes and this is continued until all the constants obtained are positive. It is therefore desirable to combine calculations by the method of least squares with a graphical method whereby one determines initially the number of complexes and the approximate values of the constants.

Calculations using iterative or successive approximation methods, particularly the relaxation method, are much less laborious[30]. In the last method Eqns.(25)–(27) are solved by trying different values of the constants K_1–K_n until the left-hand sides of all the equations differ from zero by fairly small amounts. Computers are used successfully in the calculation of the stability constants for stepwise complex formation processes[26,31].

3. Mixed Complexes

If only one mixed complex is formed in solution,

$$M^{n+} + pX + qY \rightleftarrows MX_pY_q,$$

we obtain from the shift of the half-wave potential[32] $E_{1/2}$

$$(E_{1/2})_c - (E_{1/2})_s = \frac{RT}{nF}\ln\frac{\varkappa_M}{\varkappa_c} - \frac{RT}{nF}\ln K_{pq} - p\frac{RT}{nF}\ln[X] - q\frac{RT}{nF}\ln[Y].$$

The coordination numbers p and q can be determined by measuring experimentally the dependence of $\Delta E_{1/2}$ on lg [X] for [Y] = const., and on lg [Y] for [X] = const.:

$$\left(\frac{\partial \Delta E_{1/2}}{\partial \lg [X]}\right)_{[Y]=\text{const}} = -p\frac{2.3RT}{nF},$$

$$\left(\frac{\partial \Delta E_{1/2}}{\partial \lg [Y]}\right)_{[X]=\text{const}} = -q\frac{2.3RT}{nF}.$$

In the general case, involving the stepwise formation of simple and mixed complexes, Leden functions can also be used to analyse the data[33,34]:

$$F_{00}([X][Y]) = \sum_{p=0}^{p=m}\sum_{q=0}^{q=n} K_{pq}[X]^p[Y]^q.$$

The functions can be analysed by the graphical method of De Ford and Hume. For this purpose, one finds the dependence of $E_{1/2}$ on the concentration of one ligand corresponding to the constant concentration of the other and conversely, and it is necessary to consider series of constant concentrations of each ligand in order to investigate the system fully.

4. Metal Complexonates

A characteristic feature of complexones is their polydentate nature, so that more than one ligand only comparatively rarely interacts with a single metal ion. On the other hand, the complexones are polybasic acids which are characterised by the formation of protonated complexes, the number of protons attached to them increasing with increasing acidity of the medium.

In order to determine the stability constants of normal and protonated complexes of complexones, Gorelov[35] suggested a procedure based on the analysis of the dependence of $E_{1/2}$ on pH at constant metal and complexone concentrations.

When 1 : 1 complexes are formed, the following equilibria obtain in solution:

$$M + H_pX \overset{K_p}{\rightleftarrows} MH_pX.$$

Using the expressions for the equilibrium constants, one can obtain:

$$[M] = \frac{\sum_{p=0}^{p=n}[MH_pX]}{[X]\sum_{p=0}^{p=n} K_p[H]^p/k_nk_{n-1}\cdots k_{n-p+1}},$$

where K_p is the formation constant of the complex, MH_pX and

$$k_n = \frac{[H][X]}{[HX]},$$

$$k_{n-1} = \frac{[H][HX]}{[H_2X]} = \frac{[H]^2[X]}{k_n[H_2X]},$$

$$k_{n-2} = \frac{[H][H_2X]}{[H_3X]} = \frac{[H]^3[X]}{k_nk_{n-1}[H_3X]},$$

etc. are the successive dissociation constants of the complexone. The sum $\sum_{p=0}^{p=n} K_p[H]^p/k_nk_{n-1}\cdots k_{n-p+1}$ will be denoted by $F_0\{[H]\}$:

$$F_0([H]) = K_0 + K_1\frac{[H]}{k_n} + K_2\frac{[H]^2}{k_nk_{n-1}} + \ldots + K_n\frac{[H]^n}{k_nk_{n-1}\cdots k_1}.$$

Having substituted the expression for [M] in the Nernst equation and having carried out the usual transformations (the complexonate is reduced with formation of an amalgam), we obtain

$$F_0([H]) = \text{anti lg}\left\{\frac{nF}{2.3RT}\Delta E_{1/2} + \lg\frac{\varkappa_M}{\varkappa_c} - \lg(c_X - c_M) + \lg\alpha\right\}, \quad (28)$$

where c_X and c_M are the analytical concentrations of the complexone and the metal ions, while

$$\alpha = 1 + \frac{[H]}{k_n} + \frac{[H]^2}{k_nk_{n-1}} + \ldots + \frac{[H]^n}{k_n\ldots k_1}. \quad (29)$$

Eqns. (28) and (29) make it possible to determine $F_0\{[H]\}$ at a given hydrogen ion concentration. The formation constants of the complexes are found graphically: $F_0\{[H]\}$ is plotted against [H] and K_0 is found by extrapolating the plot to [H] = 0.

The new function

$$F_1([H]) = \frac{\{F_0([H]) - K_0\}k_n}{[H]} = K_1 + K_2\frac{[H]}{k_{n-1}} + K_3\frac{[H]^2}{k_{n-1}k_{n-2}} + \ldots.$$

is then calculated. The extrapolation of the plot of $F_1\{[H]\}$ to [H] = 0 yields K_1. By calculating the successive functions, it is possible to find the formation constants of all the protonated complexes.

If the species H_pX forms a 1 : 2 complex, i.e.

$$M + 2H_pX \overset{K_p}{\rightleftarrows} M(H_pX)_2,$$

then analogous reasoning[36] shows that one must calculate the functions $F_j\{[H]^2\}$:

$$F_0([H]^2) = K_0 + K_1\frac{[H]^2}{k_n^2} + K_2\frac{[H]^4}{k_n^2k_{n-1}^2} + \ldots + K_n\frac{[H]^{2n}}{k_n^2\ldots k_1^2}.$$

The final expression for $F_0\{[H]^2\}$ is

$$F_0([H]^2) = \text{antilg}\left[\frac{nF}{2.3RT}\Delta E_{1/2} + \lg\frac{\varkappa_M}{\varkappa_c} - 2\lg(c_X - 0.5c_M) + 2\lg\alpha\right].$$

When 2 : 1 complexes are formed,

$$2M + H_pX \overset{K_p}{\rightleftarrows} M_2H_pX$$

one analyses the same function $F_0\{[H]\}$ as in the formation of 1 : 1 complex but the final expression for $F_0\{[H]\}$ assumes a somewhat different form[36]:

$$F_0([H]) = \text{antilg}\left[0.903 + \frac{2nF}{RT}\Delta E_{1/2} + \lg\frac{D_M}{D_c} - 2\lg c_M - \lg(c_X - 2c_M) + \lg\alpha\right].$$

The composition of the complex is again found from the dependence of $E_{1/2}$ on the logarithm of the analytical concentration of the ligand.

Using the method described, Gorelov[35] investigated the formation of thallium complexes of ethylenediaminetetraacetic and ethylenediamine-*N*,*N*'-disuccinic acids. Only normal and monoprotonated complexes are formed in these systems. More complex phenomena are observed[36] in the Cd^{2+}–hydroxyethylidenediphosphonic acid (HEDPA) system. 1 : 1 complexes are formed in this system at concentrations in the range 10^{-3}–10^{-2} M HEDPA and 1 : 2 complexes are formed at higher concentrations. Fig. 4 presents the functions $F_j\{[H]\}$ for the 1 : 1 complex. Evidently Cd^{2+} ions form not only the normal complex but also four protonated complexes with HEDPA (HEDPA is a pentabasic acid). Furthermore, Fig. 4 shows that each specific complex must have its own extrapolation region of the function $F_j\{[H]\}$ closely adjoining the pH range corresponding to the existence of the given ligand. If the metal ion has a high affinity for hydroxide ions, then the region of high pH values becomes inaccessible to measurements. In this case the constants of certain protonated

complexes can nevertheless be determined by analysing the incomplete function $F_j\{[H]\}$.

5. Polynuclear Complexes

The formation of polynuclear complexes, for example M_mX_p, can be investigated polarographically:

$$m\,M + p\,X \underset{}{\overset{K_{mp}}{\rightleftarrows}} M_mX_p,$$

$$\Delta E_{1/2} = -\frac{2.3RT}{mnF}\lg\frac{mK_{mp}}{2^{m-1}} - \left(1-\frac{1}{m}\right)\frac{2.3RT}{nF}\lg[M] - \frac{p}{m}\frac{2.3RT}{nF}\lg[X],$$

$$\frac{\partial\Delta E_{1/2}}{\partial \lg[M]} = -\frac{2.3RT}{nF}\left(1-\frac{1}{m}\right).$$

These relations were obtained by Souchay and Faucherre[32], who identified with their aid polymeric copper complexes of tartaric acid in alkaline media. The stepwise formation of polymeric complexes can be also examined in principle.

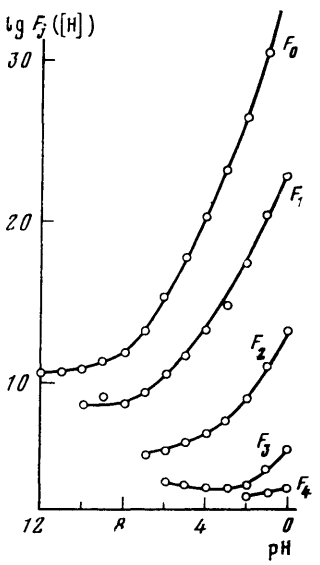


Figure 4. Dependence of the functions $\lg F_j\{[H]\}$ on the pH for the Cd^{2+}–hydroxyethylidenediphosphonic acid system at a complexone concentration of 0.004 M. Cd^{2+} concentration 1×10^{-4} M.[36]

6. Kinetic Waves

Hitherto we have considered cases where the complex species and the metal ions are involved in a rapid equilibrium. However, systems are encountered in which one of the dissociation stages is slow and a kinetic wave arises on the polarogram. The limiting current of the kinetic wave i_c is smaller than the limiting current of the usual diffusion wave i_d. Koryta[37] solved this problem under the condition where free metal ions are reduced reversibly with formation of an amalgam and the ligand is present in excess. The equation for the difference between the half-wave potentials $E_{1/2}$ is as follows:

$$(E_{1/2})_c - (E_{1/2})_s = \frac{RT}{nF}\ln\frac{i_d}{i_c} - \frac{RT}{nF}\ln\sum_{p=0}^{p=n} K_p[X]^p. \qquad (30)$$

In this equation $(E_{1/2})_c$ is the half-wave potential of the kinetic wave. Eqn.(30) is common to diffusion and kinetic waves for the reduction of complexes with formation of an amalgam in stepwise complex formation. It differs from the equation of De Ford and Hume only by the correction term $\ln(i_d/i_c)$, which corrects $E_{1/2}$ for the kinetic wave:

$$(E_{1/2})_d = (E_{1/2})_c - \frac{RT}{nF}\ln\frac{i_d}{i_c}.$$

When $i_c = i_d$, Eqn.(30) is transformed into the equation of De Ford and Hume.

7. Catalytic Waves

Yatsimirskii and Budarin[38–40] showed that the complex formation reaction can be identified and investigated from the decrease of the catalytic activity of metals in polarography. For example, molybdenum in acid solutions catalyses the reduction of hydrogen peroxide, but the introduction of phosphoric acid lowers the limiting current of the catalytic wave.

The catalytic activity of molybdenum is explained by the fact that the product of its interaction with hydrogen peroxide is reduced more readily than free hydrogen peroxide:

$$H_2MoO_4 + H_2O_2 \rightleftarrows H_2MoO_5 + H_2O,$$
$$H_2MoO_5 + 2H^+ + 2e \rightarrow H_2MoO_4 + H_2O. \qquad (IV)$$

In the presence of phosphoric acid, the complex interacts with hydrogen peroxide:

$$H_2MoO_4 + H_3PO_4 \rightleftarrows MoO_2HPO_4 + 2H_2O, \qquad (V)$$
$$MoO_2HPO_4 + H_2O_2 \rightleftarrows H_2O_2MoO_2HPO_4,$$
$$H_2O_2MoO_2HPO_4 + 2e + 2H^+ \rightarrow MoO_2HPO_4 + 2H_2O, \qquad (VI)$$

reaction (VI) being slower than reaction (IV). With increase of phosphoric acid concentration, the limiting current of the catalytic wave therefore diminishes, but not to zero, reaching a limiting value. Hence it follows that the complex $MnO_2.HPO_4$ also exhibits a catalytic activity, albeit smaller than that of free molybdic acid.

In the presence of a large excess of H_2O_2 and in the absence of H_3PO_4, we have

$$(i_c)_1 = A_1 c_{H_2O_2}[Mo].$$

In the presence of a sufficiently large excess of H_3PO_4 (for example 0.113 M at a hydrogen ion concentration of 0.444 M and an H_2MoO_4 concentration of 5.95×10^{-6} M), when the reduction of H_2O_2 is catalysed solely by the complex MoO_2. $.HPO_4$ (designated by convention as MoP), we have

$$(i_c)_2 = A_2 c_{H_2O_2}[MoP].$$

If the amount of phosphoric acid is insufficient to bind the entire molybdenum in a complex, then

$$i_c = c_{H_2O_2}(A_1[Mo] + A_2[MoP]).$$

Furthermore,

$$[MoP] = \alpha_1 c_{Mo},$$
$$[Mo] = (1-\alpha_1)c_{Mo}$$

where [Mo] and [MoP] are the equilibrium concentrations, c_{Mo} is the analytical concentration of H_2MoO_4, and α_1 is the fraction of complex formed:

$$i_c = c_{H_2O_2}c_{Mo}[\alpha_1 A_2 + (1-\alpha_1)A_1].$$

Hence

$$\alpha_1 = [(i_c)_1 - i_c]/[(i_c)_1 - (i_c)_2].$$

Having determined α_1, it is possible to calculate the equilibrium constant for reaction (V):

$$K = \alpha_1/(1-\alpha_1)(c_{H_3PO_4} - \alpha_1 c_{MoO_3}).$$

At still higher phosphoric acid concentration the catalytic wave again begins to fall and ultimately vanishes completely. This means that a more complex compound is produced:

$$MoO_2HPO_4 + H_3PO_4 \rightleftarrows H_4MoO_2(PO_4)_2,$$

which no longer exhibits a catalytic activity. By repeating the above reasoning, we obtain

$$\alpha_2 = [(i_c)_2 - i_c]/(i_c)_2.$$

In the general case, in the presence of stepwise complex formation, there should be a relation between the catalytic current and the ligand concentration[40]:

$$i_c = \frac{(i_c)_0 + (i_c)_1 K_1[X] + (i_c)_2 K_2[X]^2 + \ldots}{1 + K_1[X] + K_2[X]^2 + \ldots}, \quad (31)$$

where $(i_c)_0$ is the catalytic current and $[X] = 0$, $(i_c)_1$ and $(i_c)_2$, ... are the catalytic activities of the complexes MX_1, MX_2, ... The stability constants of the complexes and their catalytic activities can be determined from the relation between i_c and [X]. For this purpose, Eqn.(31) is transformed into an equation of the type

$$i_c = (i_c)_1 + \varphi_1/K_1 + [(i_c)_2 - i_c]\beta_2[X] + [(i_c)_3 - i_c]\beta_2\beta_3[X]^2 + \ldots$$

$$i_c = (i_c)_2 + \varphi_2/\beta_2 + [(i_c)_3 - i_c]\beta_3[X] + \ldots,$$

where β are successive stability constants:

$$\varphi_1 = [(i_c)_0 - i_c]/[X],$$

$$\varphi_2 = [(i_c)_0 - i_c]/K_1[X]^2 + [(i_c)_1 - i_c]/[X].$$

The quantities $(i_c)_1$ and K_1 can be determined graphically from the relation between i_c and ϕ_1 by extrapolation to $[X] \to 0$ and $(i_c)_2$ and β_2 can be determined from the relation between i_c and ϕ_2. $(i_c)_3$ and β_3 can be calculated analogously, etc. The quantities $(i_c)_1$, $(i_c)_2$, β_1, β_2, ... can also be found by another procedure. For this purpose, Eqn.(31) is transformed by substituting $y = [X]^{-1}$:

$$i_c = \frac{(i_c)_n K_n + (i_c)_{n-1} K_{n-1} y + (i_c)_{n-2} K_{n-2} y^2 + \ldots + (i_c)_0 y^n}{K_n + K_{n-1} y + K_{n-2} y^2 + \ldots + y^n}. \quad (32)$$

By extrapolating the relation between i_c and y to $y \to 0\{[X] \to \infty\}$, we find $(i_c)_n$.

Eqn.(32) can be put in the form

$$i_c = (i_c)_{n-1} + \psi_1\beta_n + [(i_c)_{n-2} - i_c]\frac{y}{\beta_{n-1}} + \ldots,$$

$$i_c = (i_c)_{n-2} + \psi_2\beta_{n-1}[(i_c)_{n-3} - i_c]\frac{y}{\beta_{n-2}} + \ldots,$$

where $\psi_1 = [(i_c)_n - i_c]/y$ and $\psi_2 = [(i_c)_{n-1} - i_c]/y - [i_c - (i_c)_n] \cdot \beta_n/y^2$. $(i_c)_{n-1}$ and β_n are determined graphically from the relation between i_c and ψ_1 and $(i_c)_{n-2}$ and β_{n-1} are found from the relation between i_c and ψ_2. All the quantities $(i_c)_i$ and β_i can be obtained similarly.

8. Determination of the Characteristics of the Complex from the Shift of the Ligand Wave

If the ligand, particularly an organic compound, is reduced more readily than the central metal ion, then inferences about complex formation can be drawn from the shift of the ligand wave. An equation has been derived[41] for the shift of the ligand wave subject to the condition that the ligand is reduced reversibly, that the complexes are dissociated rapidly, that metal ions are present in large excess, and that the ligand reduction product does not form complexes with the metal ions:

$$F_0([M]) = \text{antilg}\left(\frac{nF}{2.3RT}\Delta E_{1/2} - \lg\frac{(i_d)_c}{(i_d)_s}\right),$$

$$F_0([M]) = 1 + K_1[M] + K_{1/2}[M]^{1/2} + K_{1/3}[M]^{1/3} + \ldots.$$

In these equations $(i_d)_s$ and $(i_d)_c$ are the limiting currents of the ligand reduction waves in the absence of a metal ion and in its presence respectively and K_1, $K_{1/2}$, $K_{1/3}$, ... are the equilibrium constants of the complex formation reaction

$$X + pM \overset{K_p}{\rightleftarrows} M_pX.$$

($p = 1$, 1/2, 1/3, ...). The formation constants of the complexes are found by the graphical analysis of the relation between $\Delta E_{1/2}$ and [X] or by computational methods. This case is of limited applicability because only the 1:1 complex is formed as a rule in the presence of an excess of metal ions.

9. Organic Molecular Charge Transfer Complexes and Ionic Associated Species

The formation of organic molecular complexes and ionic associated species has been studied successfully by the polarographic method[42-45]. These phenomena are more distinctive in solvents with a low dielectric constant. Furthermore, the solvent must be aprotic in order that the reduction of the organic compound proceeds reversibly. The formation of molecular complexes was therefore studied in chloroform and methylene chloride.

Aromatic compounds are reduced reversibly in an aprotic medium:

$$A + e \rightleftarrows A^{\cdot-}.$$

The initial molecule A is a much stronger electron acceptor than the radical-anion $A^{\cdot-}$. After the addition of an electron donor, a complex is therefore formed with A and not with $A^{\cdot-}$ and the overall mechanism of the electrode process is as follows:

$$DA \overset{K}{\rightleftarrows} D + A \overset{e}{\rightleftarrows} D + A^{\cdot-}.$$

Complex formation shifts the wave of A in the cathodic direction and the composition and stability constant of the complex can be determined from the dependence of $E_{1/2}$ on the concentration of D either by calculation or graphically. The shift of the wave of the acceptor A can be due in principle not only to complex formation but also to a change in the potential of the liquid compound as well as a change in solvation. However, since experiment has shown that $E_{1/2}$ of the second wave of A does not change following the introduction of D, these effects must be insignificant. Studies have shown[44] that, in methylene chloride in the presence of 0.5 M $(C_4H_9)_4NClO_4$ as the supporting electrolyte, 2,3-dichloro-5,6-dicyanoquinone forms two complexes, 1:1 and 1:2, with hexamethylbenzene; 7,7',8,8'-tetracyanoquinodimethane also forms two complexes with pyrene. Only one complex is formed in each of the systems tetracyanoethylene/hexamethylbenzene, 7,7',8,8'-tetracyanoquinodimethane/hexamethylbenzene, chloranil/hexamethylbenzene, chloranil/pyrene, 1,2,4,5-tetracyanobenzene/hexamethylbenzene, and 1,2,4,5-tetracyanobenzene/pyrene. The stability constants as a rule differ significantly from the spectroscopic values. It has been noted in the literature that the spectroscopic determination of the equilibrium formation constants of charge-transfer

complexes is difficult, since the situation is complicated by the energy levels of the molecules of complex formation. In polarography this complication does not exist, since the acceptor molecule is reduced in a free state. It is therefore postulated that the stability constants of charge-transfer complexes found by the polarographic method are closer to the true values than the constant determined spectroscopically.

In aprotic solvents the radical-anions $A^{\cdot-}$, generated on reduction of the organic compound, interact with the counterions of the indifferent electrolyte, forming ionic associated species. As a result, the reduction wave shifts towards less negative potentials. Experiment shows[44] that the cations with a smaller crystallographic radius and with a larger charge are more effective. In dimethylformamide tetraalkylammonium cations do not interact with the radical-anions of quinones, while the anthraquinone radical-anion interacts with the lithium cation to form a 1:1 associated species having $K = 39$ litre mol^{-1}. Dianions interact with cations more strongly. For example, the anthraquinone dianion forms an associated species with three lithium ions. Very large effects are observed when polyvalent cations are introduced into the solution. Thus the addition of neodymium at a concentration of 0.002 M shifts the first wave of the quinone at a concentration of 0.003 M by 550 mV and the second wave by 950 mV (in acetonitrile). These equilibria have also been studied successfully by the polarographic method[44].

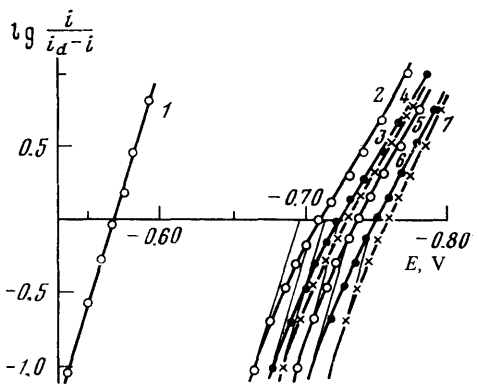


Figure 5. Logarithmic analysis of the waves of the Cd^{2+} ion and of its 2,2'-bipyridyl complex in aqueous solutions; molar concentration of 2,2'-bipyridyl: 1) 0; 2) 0.005; 3) 0.0063; 4) 0.00795; 5) 0.01; 6) 0.0126; 7) 0.02. Cd^{2+} concentration 1×10^{-4} M.[46]

10. The Influence of Adsorption

Organic ligands and complexes are adsorbed on mercury from aqueous solutions. It is therefore to be expected that the reduction waves of the complexes will in certain cases be complicated by the autoinhibition of the electrode process. Insufficient attention has been devoted to this problem in the literature. Autoinhibition is responsible for the additional shift of the wave of the complex in the cathodic direction and, if it is disregarded, the calculation leads to an unduly high stability constant of the complex. Autoinhibition is fully or partly eliminated by the addition of an organic solvent, since organic substances are adsorbed on mercury much less strongly from organic and mixed solvents. However, one should bear in mind that the addition of non-aqueous solvents influences the complex formation equilibrium.

If the autoinhibition phenomenon is not too pronounced, then in certain cases it is nevertheless possible to find the true stability constants. For example, the reduction wave of the trisbipyridylcadmium complex is only partly deformed and its lower part retains its original shape. The semilogarithmic plot of the wave is curved, but its lower part has a slope which approaches asymptotically the theoretical value $2.3RT/2F \cong 0.03$ V (Fig.5). This makes it possible to determine, by drawing tangents to the lower sections of the $\lg [i/(i_d - i)] - E$ plot, the values of $E_{1/2}$ unaltered by autoinhibition and to calculate the true stability constant[46]. A.c. measurements showed that 2,2'-bipyridyl exhibits a higher surface activity than its cadmium complexes. On this basis, it was concluded that the autoinhibition is due to the adsorption of free 2,2'-bipyridyl and the 2,2'-bipyridyl liberated on reduction of the complex[47].

Bond and Hefter observed[48] that the stability constants of the lead iodide and bromide complexes found by the polarographic method are significantly greater than the values obtained by other procedures. The authors suggested that, owing to the adsorption of the anions on mercury, the phenomenon of "additional complex formation" in the electrical double layer, where the ligand concentration is higher than in the bulk of the solution, is observed in this case. However, the experimental justification of this conclusion is open to objection. Thus it follows from a number of studies[49,50,51] that lead complexes and not free halide ions exhibit a higher surface activity in the Pb^{2+}/Br^- and Pb^{2+}/I^- systems. The additional complex formation effect could not therefore occur. It is more likely that the discrepancy between the stability constants observed by Bond and Hefter is in fact due to autoinhibition (the adsorption of the complex). It has been shown[52] that the phenomenon of "additional complex formation" postulated by Bond and Hefter is ruled out by its incompatibility with the thermodynamics of reversible processes.

III. IRREVERSIBLE ELECTRODE PROCESSES

In those cases where the criteria of reversibility enumerated in section II show that the reduction of the complex is irreversible overall, the use of the equations derived for reversible processes becomes impossible: the position of the wave is influenced not only by the equilibrium properties of the complexes but also by the kinetics of electrode processes. Kinetic analysis of irreversible waves yields very interesting information about the nature of the species which are reduced directly at the electrode[53-58]. This leads to the possibility of studying the relation between the reactivity of complexes and their structure.

Several approaches, permitting the study also of the equilibrium properties of complexes which are reduced irreversibly at the dropping mercury electrode, have been developed.

1. Determination of the Characteristics of the Complex from the Shift of the Half-Wave Potential

The principles of the study of the equilibria in the formation of complexes under conditions where the reduction is fully irreversible have been examined in detail[59]. Equations

have been derived for the current at any point in the polarographic wave and for the half-wave potential under the following conditions: (1) only mononuclear complexes are formed in solution; (2) the complex formation is rapid; (3) each complex can be reduced at the electrode independently with formation of an amalgam; (4) there is no specific adsorption in the experimental range of potentials.

The initial equation is that of the fully irreversible wave:

$$\frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}} = \frac{0.886 k^0 \tau^{1/2}}{D^{1/2}} \exp\left[-\frac{\alpha nF}{RT}(E - E^0)\right]. \qquad (33)$$

where k^0 is the rate constant at the normal potential E^0, τ the drop time, and i_{irrev} the current at the potential E of the irreversible wave.

The rate of the process $v = kc$ is equal to the sum of the rates of reduction of each complex:

$$kc = k_0[\text{M}] + k_1[\text{MX}] + k_2[\text{MX}_2] + \ldots + k_n[\text{MX}_n],$$

whence, taking into account the complex formation equilibria, we have

$$k = \frac{k_0 + k_1 K_1 [\text{X}] + k_2 K_2 [\text{X}]^2 + \ldots + k_n K_n [\text{X}]^n}{1 + K_1 [\text{X}] + K_2 [\text{X}]^2 + \ldots + K_n [\text{X}]^n}.$$

Since

$$k_p = k_p^0 \exp\left[-\frac{\alpha_p nF}{RT}(E - E^0)\right],$$

it follows that

$$k = \frac{\sum_{p=0}^{p=n} k_p^0 K_p [\text{X}]^p \exp\left[-\frac{\alpha_p nF}{RT}(E - E^0)\right]}{\sum_{p=0}^{p=n} K_p [\text{X}]^p}.$$

On substituting the expression for k in the initial Eqn.(33), we obtain

$$\frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}} = 0.886 \left(\frac{\tau}{D_c}\right)^{1/2} \frac{\sum_{p=0}^{p=n} k_p^0 K_p [\text{X}]^p \exp\left[-\frac{\alpha_p nF}{RT}(E - E^0)\right]}{\sum_{p=0}^{p=n} K_p [\text{X}]^p}, \qquad (34)$$

where D_c is the average diffusion coefficient of the complex.

The partial derivatives A, B, and C can be used conveniently for the analysis of experimental data:

$$A = \left(\frac{\partial}{\partial E} \ln \frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}}\right)_{[\text{X}]=\text{const}} = -\frac{\alpha nF}{RT},$$

where α is the average transfer coefficient. If the number of electrons is known (and this is frequently the case), α can be found from the derivative A. This quantity is useful for the elucidation of the mechanism of the electrode process: if it is independent of E and [X], then, on changing the ligand concentration and the potential along the wave, the mechanism remains unaltered, i.e. the same species is reduced, and the calculations are simplified. On the other hand, if α does depend on E, the implication is that two reactions with different α take place at the electrode.

The derivative B is of the form

$$B = \left(\partial \frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}} / \partial \ln [\text{X}]\right)_{E=\text{const}} = p_{\text{el}} - p,$$

where p_{el} is the average coordination number of the complexes being reduced and p is the average coordination number of the complexes formed in solution. If the difference $p - p_{\text{el}}$ for the maximum [X] is equal to the maximum coordination number for the given cation, then free cations are reduced at the electrode. At any rate, if p can be found independently, it is possible to discover from the derivative B which complex is reduced at the electrode.

The derivative C is

$$C = -\left(\frac{\partial E}{\partial \ln [\text{X}]}\right)_{i_{\text{irrev}}=\text{const}} = p - p_{\text{el}}.$$

If the difference $p - p_{\text{el}}$ over a range of values of [X] remains constant, then presumably only one complex predominates in solution and only one complex is reduced.

The overall equation of the wave for the fully irreversible reduction of the complexes is extremely involved. However, in reality frequently simpler cases are encountered where only one of the species involved in the equilibrium is reduced at the electrode.

If it has been established by studying A, B, and C that free cations are reduced at the electrode, then Eqn.(34) simplifies:

$$\frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}} = 0.886 \left(\frac{\tau}{D_c}\right)^{1/2} k_0^0 \frac{\exp\left[-\frac{\alpha nF}{RT}(E - E^0)\right]}{\sum_{p=0}^{p=n} K_p [\text{X}]^p}.$$

Hence

$$(E_{1/2})_c = E^0 + \frac{RT}{\alpha nF} \ln\left(0.886 \left(\frac{\tau}{D_c}\right)^{1/2} k_0^0\right) - \frac{RT}{\alpha nF} \ln \sum_{p=0}^{p=n} K_p [\text{X}]^p,$$

$$(E_{1/2})_s - (E_{1/2})_c = \Delta E_{1/2} = \frac{RT}{\alpha nF} \ln \sum_{p=0}^{p=n} K_p [\text{X}]^p - \frac{RT}{\alpha nF} \ln \frac{(i_d)_s}{(i_d)_c}.$$

This expression is similar to the equation for $\Delta E_{1/2}$ in the case of the reversible reduction of complexes and can be analysed in exactly the same way, i.e. by the graphical De Ford and Hume analysis, by computational methods, or by the method based on the Yatsimirskii logarithmic plot.

On the other hand, if the analysis of the derivatives A, B, and C shows that one of the complexes MX_i and not free cations, is reduced, then Eqn.(34) becomes

$$\frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}} = 0.886 \left(\frac{\tau}{D_c}\right)^{1/2} k_i^0 \frac{\exp\left[-\frac{\alpha_i nF}{RT}(E - E^0)\right]}{\sum_{0}^{n} K_j K_i^{-1} [\text{X}]^{(j-i)}}. \qquad (35)$$

The sum in Eqn.(35) is of the following form:

$$\sum_{0}^{n} \frac{K_j}{K_i} [\text{X}]^{(j-i)} = \frac{1}{\beta_1 \beta_2 \ldots \beta_i [\text{X}]} + \frac{1}{\beta_2 \beta_3 \ldots \beta_i [\text{X}]^{(i-1)}} + \ldots +$$

$$+ \frac{1}{\beta_i [\text{X}]} + 1 + \beta_{i+1} [\text{X}] + \beta_{i+1} \beta_{i+2} [\text{X}]^2 + \ldots + \beta_{i+1} \beta_{i+2} \ldots \beta_{n-1} [\text{X}]^{(n-i)},$$

where β_i are the successive stability constants of the complexes. The sum can be significantly simplified by making the reasonable assumption that the concentrations of complexes simpler than the complex MX_i being reduced at the electrode are negligible. Then

$$\frac{i_{\text{irrev}}}{i_d - i_{\text{irrev}}} = 0.886 \left(\frac{\tau}{D_c}\right)^{1/2} k_i^0 \frac{\exp\left[-\frac{\alpha nF}{RT}(E - E^0)\right]}{\sum_{i}^{n} [\text{X}]^{(j-i)} \prod_{i+1}^{j} \beta_m},$$

$$(E_{1/2})_c = E_i^0 + \frac{RT}{\alpha nF} \ln\left(0.886 \left(\frac{\tau}{D_c}\right)^{1/2} k_i^0\right) - \frac{RT}{\alpha nF} \ln \sum_{i}^{n} [\text{X}]^{(j-i)} \prod_{i+1}^{n} \beta_m$$

and

$$\Delta E_{1/2} = \frac{RT}{\alpha nF} \ln \sum_{i}^{n} [\text{X}]^{(j-i)} \prod_{i+1}^{j} \beta_m - \frac{RT}{\alpha nF} \ln \frac{(i_d)_i}{(i_d)_c}. \qquad (36)$$

Eqn.(36) can be solved particularly simply if the difference between the maximum coordination number and the coordination number of the complex being reduced $(n - i)$ does not exceed 2 {in this case the dependence of $\Delta E_{1/2}$ on ln [X] is linear}. When a mixture of complexes with $(n - i) > 2$ is present in solution, the logarithmic plot method can be used.

2. The Study of Complex Formation on the Basis of Limiting Diffusion Currents

The limiting diffusion current is the second source of information about complex formation in classical polarography. In fact, complex formation leads to a significant change in the size of the species; one must then bear in mind not only the dimensions of the central ions and the ligands but also those of the solvation shell around the complex species. This alters the diffusion coefficient of the species. The dependence of the limiting current on the ligand concentration is frequently of the expected type and can be used to determine the stability constants of the complexes[60,61]. Thus, when only one complex MX_1 is formed in solution, the average diffusion coefficient D is

$$D = (D_M + D_{MX}K_{MX}[X])/(1 + K_{MX}[X]).$$

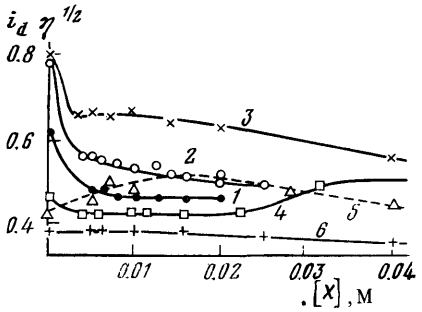


Figure 6. Dependence of the Cd^{2+} limiting current corrected for the viscosity of the medium ($i_d\eta^{1/2}$) on the 2,2'-bipyridyl concentration; ethanol content (vol.%): 1) 0; 2) 20; 3) 40; 4) 60; 5) 80; 6) ~100.[46]

The average diffusion coefficient is determined from the limiting current at the given ligand concentration, the diffusion coefficient of the free metal ions D_M can be found from the limiting current in the absence of the ligand, and the diffusion coefficient of the complex D_{MX} can be found from the limiting current in the presence of a large excess of the ligand, whereupon virtually only one complex is present in solution. The transition from the case involving the formation of only one complex to the more general case of stepwise complex formation does not give rise to fundamental difficulties.

The use of limiting diffusion currents for the calculation of equilibrium constants has an advantage over methods based on the measurement of half-wave potentials, which consists in the fact that it is applicable to all processes regardless of their reversibility. Instances of the successful application of this method in the study of the equilibria in the formation of ionic associated species have been described in a review[12].

However, when calculations based on limiting diffusion currents are used, caution must be exercised because there are frequent instances of anomalous relations between the diffusion coefficients and the ligand concentration. For example, an unusual type of influence of the ligand concentration has been observed in the Cd^{2+}–2,2'-bipyridyl system in a mixed aqueous alcoholic solvent (Fig.6) and the employment of the given method becomes difficult[46].

3. The Indicator Method

An indicator method has been proposed[62] for the determination of the stability constants, which is suitable when the complex is reduced irreversibly or is altogether electrochemically inactive. Its essential feature is as follows. One selects an indicator ion whose complexes with the given ligand are reduced reversibly and at less negative potentials than the complex investigated. The dependence of $E_{1/2}$ for the indicator ion on the ligand concentration is plotted on the basis of experimental or calculated (if the stability constants are known) data, and then the test cation is introduced into the solution and the change in $E_{1/2}$ for the indicator ion, occurring as a result of the formation of a complex by the test ion with the given ligand, is measured. The concentration of the free ligand is found from the plot of $E_{1/2} = f\{[X]\}$ for the indicator ion. Knowing the equilibrium concentration of the ligand [X] and the analytical concentrations of the ligand (c_X) and the test metal (c_M), it is possible to calculate the formation function for the given metal at the half-wave potential:

$$\bar{n} = \left(c_X - [X] - \frac{1}{2}n_i c_i\right)/c_M,$$

where $\bar{n}_i$ is the formation function of the indicator ion and c_i the analytical concentration of the latter. The stability constants can be determined from the formation functions of the test ion by the Bjerrum or Fronaeus methods[20]. The indicator ion method has been frequently tested[61,63,64].

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Thus, a survey of the literature shows that a wide variety of problems, associated with the equilibria in the formation of complexes and ionic associated species in solution, can be studied by the method of classical polarography virtually without limitations arising from the complexity of the equilibria and the reversibility of the electrode processes. One must note that many relations derived for classical polarography are applicable (without modifications or with certain non-fundamental changes) also when other varieties of polarography are used (oscillographic and a.c. polarography, chronopotentiometry, etc.)[12].

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