Polarography of Tris-ethylenediaminecobalt(III) Ion in the Absence of Excess of the Complexing Agent[1]

BY P. KIVALO[2]

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The polarographic reduction of tris-ethylenediaminecobalt(III) in the absence of excess of the complexing agent is polarographically irreversible. The product of the first reduction wave, the divalent complex, decomposes to lower amine complexes whereupon the half-wave potential and the wave form are altered. The decomposition reaction is reversible and very rapid and the successive divalent complexes attain equilibrium instantaneously. Theoretical current–voltage curves were computed for this case on the basis of known successive equilibrium constants of the divalent tris-ethylenediaminecobalt complexes. The experimental verification of the derived curves included oscillographic polarography for testing the reversibility of the electron transfer reaction and variation of the mercury head to confirm complete diffusion control of the entire wave. Furthermore, the effect of the variation of the concentration of the reductant upon the half-wave potential and the wave form was investigated. Inasmuch as the concentration of the free ethylenediamine and the aquated cobalt(II) ion both are dependent on the hydrogen ion concentration, also the effect of pH was studied. Satisfactory agreement between the results and the predictions was established.

In a recent paper[3] the author presented theoretical current–voltage equations for polarographic processes in which the product of the electron transfer reaction is involved in a subsequent chemical reaction. In order to be able to test experimentally these equations, the electron transfer reaction has to be reversible and fast and furthermore, the rate or equilibrium constants of the accompanying chemical reactions must be known. Very few reactions can satisfy both of these conditions and therefore the available material is scanty. The only suitable case found is that of the tris-ethylenediaminecobalt(III) reduction. It belongs to the category where the product of the electron transfer reaction decomposes rapidly, the forward reaction being of first order and the reverse of second order (actually, the system is somewhat more complicated in that a number of successive complexes are formed by the decomposition). The reaction attains equilibrium very rapidly which allows one to use the equilibrium constants in the calculations predicting the wave form and shift of the half-wave potential with concentration of the reductant.

Theoretical

A number of trivalent cobalt ammine complexes are reducible at the dropping mercury electrode. The reduction products of the first wave, the divalent complexes, differ from the trivalent forms in a characteristic way in the nature of the bonding. The trivalent forms have covalent bonds, d^2sp^3-hybridization and are distinctively inert[4] but the divalent forms are labile having ionic bonds, sp^3d^2-hybridization. The characteristic property of the ionic bond is that it allows very rapid exchange of ligands, i.e., the various states of the complex come to equilibrium with the ligand rapidly. The homogeneous consecutive complexity constants for a number of divalent metal ammines have been determined by Bjerrum.[5] Using these constants

one can calculate the extent to which the divalent complex will decompose and thus it is possible to predict the half-wave potential and the wave form.

A suitable compound for the present purpose seemed to be the tris-ethylenediaminecobalt(III) ion. Grieb[6] discovered that it is reversibly reduced to the divalent state at the dropping mercury electrode provided an excess of ethylenediamine is present but that the wave shows irreversible characteristics in the absence of the complexing agent. It is also known from Bjerrum's work that the couple

$$Coen_3^{+++} + e^- \rightleftarrows Coen_3^{++} \qquad (1)$$
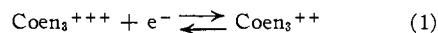
is potentiometrically reversible.[7] Ethylenediamine is here denoted by en. Lewis, Coryell and Irvine[8] used a radioactive tracer technique to study the rate of electron exchange between the two forms of the complex and found a remarkably high rate. This is equivalent to a large natural exchange current[9] which is confirmed by the polarographic reversibility. The cause for the irreversibility of the polarographic reduction in the absence of excess of ethylenediamine is thus clearly the chemical decomposition of the divalent tris-ethylenediaminecobalt to lower complexes.

The computation of the current-voltage curve for this case is based on the assumption that the Nernst relation is valid for reaction 1 at all times during the polarographic reduction. Inasmuch as the experiments to be described later were performed at constant ionic strength, the activity coefficients are considered constant and deviations from unity are ignored. One has then

$$E_{d.e.} = E' - \frac{RT}{F} \ln \left[\frac{i}{i_d - i} \times \frac{k'_{ox}}{k'_r} \times \alpha_{MA_s} \right] \quad (2)$$

where E' is the formal potential of reaction 1, k'_{ox} represents the Ilkovic constant for the oxidized form. The immediate product of the reduction of the trivalent cobalt complex is of course the divalent tris-ethylenediaminecobalt ion which yields lower complexes and a certain amount of ethylenediamine. The sum of the concentrations of the various

(1) A preliminary publication on the subject has appeared in THIS JOURNAL, **75**, 3286 (1953).

(2) Abstracted from the Doctoral Dissertation, Åbo, Finland, 1954. Present address, Åbo Akademi, Åbo, Finland.

(3) P. Kivalo, Acta Chem. Scand., **9**, 221 (1955).

(4) (a) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond." Interscience Publishers, Inc., New York, N. Y., 1950, p. 385. (b) H. Taube, Chem. Revs., **50**, 69 (1952).

(5) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, pp. 180, et seq.

(6) M. W. Grieb, Ph.D. Thesis, University of Illinois, Urbana, Ill. 1953.
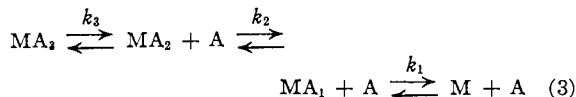
(7) Ref. 5, p. 219.

(8) W. Lewis, C. D. Corvell and J. W. Irvine, Jr., J. Chem. Soc. (Suppl. Issue No. 2), S 386 (1949).

(9) J. E. B. Randles, Trans. Faraday Soc., **48**, 828 (1952).

divalent forms is proportional to the current: k'_r represents the average Ilkovic constant for all the divalent forms. Finally, α_{MA_3} is the fraction of the total divalent cobalt which is in the tris-ethylenediamine form.

In calculating the current dependence of α_{MA_3} the following symbols for the surface concentrations will be used: M denotes Co^{++}, A denotes ethylenediamine, and the various divalent complexes are denoted by MA_{1-3}.

As is known from Bjerrum's work,[5] the divalent complexes form an equilibrium system, viz.

$$MA_3 \underset{k_3}{\overset{}{\rightleftarrows}} MA_2 + A \underset{k_2}{\overset{}{\rightleftarrows}}$$

$$MA_1 + A \underset{k_1}{\overset{}{\rightleftarrows}} M + A \quad (3)$$

The logarithms of the homogeneous consecutive complexity constants (determined in the same medium where the experiments later to be described were performed) are as follows: $\log k_1 = 5.89$; $\log k_2 = 4.83$; $\log k_3 = 3.10$.

The calculations are complicated somewhat by the fact that part of the aquated metal ions which are liberated, may, at sufficiently high hydroxyl ion concentration, precipitate in the form of metal hydroxide. This has been shown to occur in the case of the reduction of hexamminecobalt(III) ion in the absence of excess of ammonia.[10] Although the ethylenediamine complexes of the divalent cobalt are much more stable than the corresponding ammonia complexes, cobaltous hydroxide still might be formed in this case. However, it is assumed that no *solid* hydroxide is produced. This assumption is considered permissible for the following reasons. The incubation time for the formation of precipitate is a function of the degree of supersaturation. In the present case a calculation reveals that the solubility product of cobaltous hydroxide is not largely exceeded[11] when the tris-ethylenediamine complex decomposes. For instance, for a 2 mM Coen$_3^{++}$ solution: $Co^{++} \sim 10^{-8}$ M, $OH^- \sim 10^{-3}$ M, and the ion product for $M(OH)_2$ becomes 10^{-14} which is only 40 times larger than the solubility product (the corresponding product for the ammonia complex is 4×10^5 times larger). It has been shown[12] that the sole species that causes a slight solubility of cobaltous hydroxide between pH 10 and 12 is $Co(OH)_2$(aq.), the undissociated hydroxide molecule. Consequently, it is thought that in a situation where only as light supersaturation exists, the equilibrium

$$Co(OH)_2(aq.) \rightleftarrows Co^{++} + 2OH^- \quad (4)$$
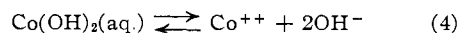
prevails and that the constant for it can be used. In other words, the incubation time is considered long enough so that no solid hydroxide is formed during the lifetime of a drop.

The expression for the sum of the concentrations of the various divalent forms of cobalt at equilibrium becomes thus

$$\Sigma MA_n = MA_3 + MA_2 + MA_1 + M + M(OH)_2 \quad (5)$$

The ethylenediamine set free by the decom-

position does not remain as such because it is able to react with hydrogen ions. The sum of the concentrations of the various forms of the non-complexed ethylenediamine is given by

$$\Sigma A_n = A + AH^+ + AH_2^{++} \quad (6)$$

According to Bjerrum's investigation[13] the acid-base constants of ethylenediamine in 1 molar potassium chloride solution and at 30° are $pk_{AH^+} = 10.05$ and $pk_{AH_2^{++}} = 7.31$. Using these values and introducing

$$\beta_A = \frac{A}{\Sigma A_n} = \frac{k_{AH^+} \times k_{AH_2^{++}}}{k_{AH^+} \times k_{AH_2^{++}} + k_{AH_2^{++}}[H^+] + [H^+]^2} \quad (7)$$

where β_A is the fraction of the total non-complexed ethylenediamine which is in the "free" form, A, one can calculate the effect of pH upon the system.

The concentration of the total ethylenediamine produced at the electrode surface by the decomposition can also be expressed in terms of the concentrations of the various divalent metal ions present

$$\Sigma A_n = MA_2 + 2MA_1 + 3M + 3M(OH)_2 \quad (8)$$

or combined with equation 7 and using the equilibrium constants for reaction 4[14] and reaction 3.

$$A = \beta_A M \left[k_2 k_1 A^2 + 2k_1 A + 3 \left(1 + \frac{4.0 \times 10^{-19}}{[H^+]^2} \right) \right] \quad (9)$$

Equation 5 is rearranged to give

$$\Sigma MA_n = M \left[k_3 k_2 k_1 A^3 + k_2 k_1 A^2 + k_1 A + 1 + \frac{4.0 \times 10^{-19}}{[H^+]^2} \right] \quad (10)$$

Dividing equation 10 by equation 9 one obtains

$$\beta_A \Sigma MA_n = \frac{K_3 A^4 + K_2 A^3 + K_1 A^2 + A \left(1 + \dfrac{4.0 \times 10^{-19}}{[H^+]^2} \right)}{K_2 A^2 + 2K_1 A + 3 \left(1 + \dfrac{4.0 \times 10^{-19}}{[H^+]^2} \right)} \quad (11)$$

where $K_3 = k_3 k_2 k_1$, $K_2 = k_2 k_1$ and $K_1 = k_1$. This equation enables one to calculate the amount of free ethylenediamine which is produced by the decomposition of a certain amount of the divalent tris-ethylenediaminecobalt complex. The solution of this equation is found graphically. Giving A a set of values and taking into account the effect of hydrogen ion concentration upon the formation of cobaltous hydroxide, corresponding values of $\beta_A \Sigma MA_n$ are obtained. This was done for a few pH values between 9 and 12.5. The other influence the hydrogen ion concentration exerts on the system, namely, the β_A-function, is obtained separately using equation 7. Now the corrected relation between ΣMA_n and A is found by sliding along the appropriate curve in the graphical representation of equation 11 to take into account the multiplication of ΣMA_n by β_A.

(10) H. A. Laitinen, A. J. Frank and P. Kivalo, THIS JOURNAL, **75**, 2865 (1953).

(11) K. H. Gayer and A. B. Garrett, *ibid.*, **72**, 3921 (1950).

(12) K. H. Gayer and L. Woontner, *ibid.*, **74**, 1436 (1952).

(13) Ref. 5, p. 204.

(14) The value 6×10^{-19}, given by Gayer and Garrett,[11] is valid at 25° although the other constants are valid at 30°. The effect of the temperature difference is, however, considered negligible. The value of the ion product for water at 30° is employed here: $pk_w = 13.81$.[15]

(15) N. Bjerrum and A. Unmack, *Kgl. Dansk. Videnskab. Selskab.*, **9**, 1 (1929).

In calculating α_{MA_3} as a function of ΣMA_n, the connecting link is the concentration of the non-complexed ethylenediamine, A. It is thus necessary to know α_{MA_3} as a function of A

$$\alpha_{MA_3} = \frac{MA_3}{\Sigma MA_n} = \frac{\Sigma MA_n - (MA_2 + MA_1 + M + M(OH)_2)}{\Sigma MA_n} \quad (12)$$

which reduces by algebraic manipulation to

$$\alpha_{MA_3} = \frac{K_3 A^3}{K_3 A^3 + K_2 A^2 + K_1 A + 1 + \dfrac{4.0 \times 10^{-19}}{[H^+]^2}} \quad (13)$$

This function has been calculated for the same pH values as equation 11 and was plotted against pA. Using these plots it is thus possible to evaluate α_{MA_3} as a function of ΣMA_n and also as a function of the current, i. Employing equation 2 it is then a simple matter to construct theoretical current-voltage curves for the reduction of the trivalent complex ion to the divalent state. Figure 1 shows a family of these curves calculated for pH 11.05 and a temperature of 30° and under the assumption that $k'_{ox} = k'_r$. A sliding scale of the ordinate has been used in order to make the presentation more illustrative. As can be seen, the half-wave potential shifts to more positive values and the shape of the wave becomes increasingly "irreversible" as the concentration of the reducible substance decreases. Curve 1 in Fig. 1 represents the limiting case where the divalent complex does not decompose, i.e., when a sufficient excess of ethylenediamine is present and $\alpha_{MA_3} = 1$. A plot of log $(i_d - i)/i$ versus the applied potential for curves 2-4 naturally does not yield a straight line.
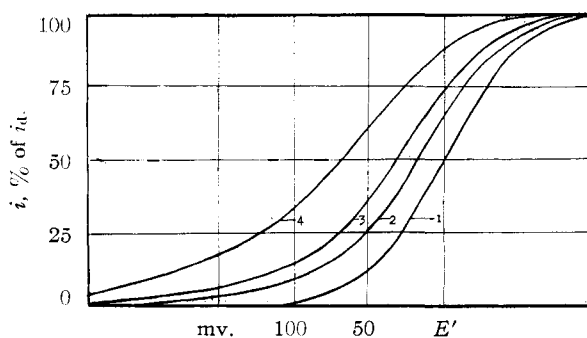

Fig. 1.—Theoretical current–voltage curves for polarographic reduction of various concentrations of tris-ethylenediaminecobalt(III) in the absence of the complexing agent; pH 11.05, temp. 30°. Curve 1 for $\alpha_{MA_3} = 1$ (excess ethylenediamine present): curve 2, 3×10^{-3} M; 3, 10^{-3} M; 4, 2×10^{-4} M.

Experimental

The polarographic apparatus employed has been described previously.[16] The set-up for the alternating current technique is shown in Figure 2 schematically. The manual polarograph (A) was of type "Ampot" manufactured by E. H. Sargent and Co. The oscillator (B) was a Hewlett-Packard type 202D audio oscillator capable of producing a 2–70,000 c.p.s. symmetrical sine wave signal with a maximum output voltage of 10 v. The cathode ray oscilloscope was a Du Mont oscillograph of type 304-H with a maximum Y-axis deflection of 1 in. per 28 millivolts d.c.

(16) P. Kivalo, K. B. Oldham and H. A. Laitinen, THIS JOURNAL, 75, 4148 (1953).

To this was attached a type 296 Oscillograph-record camera. The line voltage was stabilized by means of a Sorensen voltage regulator (E). The potentiometer (R₁) made it possible to vary the amplitude of the a.c. signal and the iR drop across the resistor (R₂) was fed to the oscillograph Y-input. By means of a two-pole double-throw switch, not shown in the figure, the wires were so connected that the oscillograph also served as a voltmeter. The horizontal deflection was synchronized with the Y-input (dotted line).
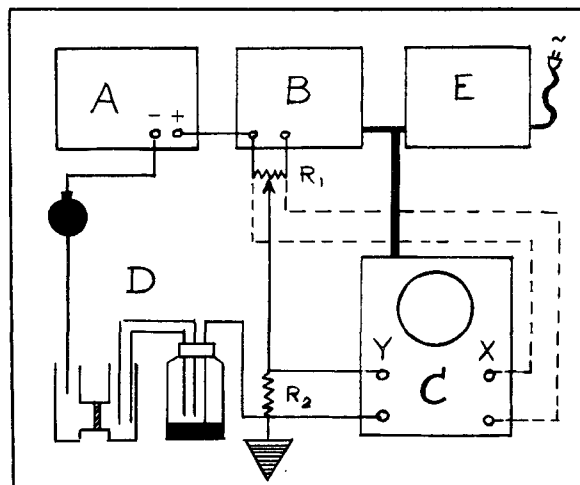

Fig. 2.—Block diagram of the a.c. polarography set-up: A, manual polarograph; B, oscillator; C, cathode-ray oscilloscope; D, dropping electrode assembly; E, line voltage regulator.

Results and Discussion

The Reversibility of the Electron Transfer Reaction.—Inasmuch as the theoretical calculations presented above are based upon the assumption that the electron transfer reaction is reversible in spite of the fact that the wave has "irreversible" characteristics, the reversibility was first tested. This was done using the a.c. technique. The sine wave voltage sweep generated by the audio oscillator served as the source of e.m.f. The signal had an amplitude of 1 volt, the biasing d.c. voltage applied by means of the manual polarograph, being also 1 volt. This arrangement gave the sweep a 2 volt span. The initial potential, i.e., the most positive potential of the sweep, could thus be adjusted according to need. The frequency used was 2 c.p.s. and the measuring resistor, R₂, was 200 ohms in these experiments. Figure 3 shows an oscillographic polarogram of a 2 millimolar $Coen_3Cl_3$ solution. The supporting electrolyte was 1 M KCl containing 0.005 M NaOH. One can clearly see that the half-wave potential of the divalent form practically coincides with the half-wave potential of the trivalent form. The condition of the reversibility of the electron transfer reaction is thus fulfilled. As expected, an almost identical oscillographic polarogram (save for the slightly more negative oxidation–reduction potential) was recorded when the supporting electrolyte also contained ethylenediamine (0.1 M). In this case the divalent complex does not decompose at all, and the system is perfectly reversible.

Diffusion Control of the Wave.—The established usage of determining the type of "control" of a polarographic process involves the variation of the
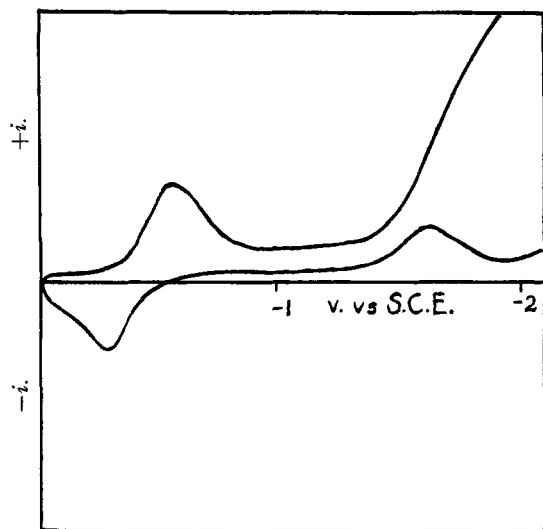
Fig. 3.—Oscillographic polarogram of a solution containing 2 mM Coen$_3$Cl$_3$, 1 M KCl and 0.005 M NaOH per liter; span 2 v., initial potential -0.1 v. *versus* S.C.E.

mercury head which affects the current in the plateau. In a typical diffusion controlled wave the current varies directly proportional to $\sqrt{h}$ where h is the effective mercury head (the actual reservoir height less a small correction term).[17] A kinetically controlled process is characterized by the fact that the current is more or less independent of the mercury head, whereas the adsorption waves vary linearly with h.

As mentioned, the tests have been made on the plateau only and until recently very little attention has been paid to the rising portion of the wave in this respect. The author, together with Oldham and Laitinen,[16,19] has recently studied the effect of variation of the mercury head in the rising portion of polarographic waves. In the irreversible waves (slow electron transfer), for instance, the plateau exhibits a diffusion control whereas, when going down along the wave, the process becomes increasingly kinetically controlled. Realizing this, it is necessary to test the reduction wave of tris-ethylenediaminecobalt(III) all along the rising portion to assure complete diffusion control, which assumption underlies the theoretical calculations. By this experiment it is ascertained whether the rates of the electron transfer reaction and the chemical reaction are faster than the rates of diffusion.

According to the theory for a case where the product is soluble in the solution, the variation of h for complete diffusion is characterized by

$$\frac{\mathrm{d}(i/i_0)_m}{\mathrm{d}\sqrt{h/h_0}} = \text{const.} \tag{14}$$

at every point of the wave.[19] The testing of this relationship was done using the Leeds and Northrup

(17) Strictly speaking $i_d/\sqrt{h}$ is not constant, but decreases slightly with increasing value of h.[18]

(18) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, pp. 78–86.

(19) K. B. Oldham, P. Kivalo and H. A. Laitinen, THIS JOURNAL, **75**, 5712 (1953).

Electrochemograph. The solution contained 2 millimoles Coen$_3$Cl$_3$, 1 M KCl and 0.005 M NaOH per liter. The results are given in the following table, where the maximal currents, i_m, are corrected for the residual value and the back-pressure correction for h used here is 1.5 cm.[18]

TABLE I

VARIATION OF MERCURY HEAD IN THE POLAROGRAPHIC REDUCTION OF TRIS-ETHYLENEDIAMINECOBALT(III)

E, v. vs. S.C.E.	-0.700	-0.500	-0.450	-0.400
$(i/i_d)_m$	1.0	0.73	0.37	0.13
h, cm.	i_m, μa.	i_m, μa.	i_m, μa.	i_m, μa.
73.5	7.56	5.50	2.79	0.97
58.5	6.80	4.95	2.48	.88
43.5	5.95	4.30	2.23	.76
33.5	5.25	3.81	1.95	.67

Taking as reference value the current at $h = 33.5$ cm., the plots of $(i/i_0)_m$ *versus* $\sqrt{h/h_0}$ give straight lines with the same slope. The results of the experiment confirm the diffusion control of the entire wave. There is another criterion for the diffusion control; this is the constancy of the ratio i/i_m, *viz.*, average current/maximal current. In the present case where the product is soluble in the solution and the diffusion coefficients of the oxidized and reduced forms are approximately equal, the ratio should be constant for the whole wave. This was tested with the same solution and the same apparatus and the results are shown in Fig. 4. For the sake of comparison, the same ratio for a case with large difference in diffusion coefficients (4 mM CdSO$_4$, 0.2 M KNO$_3$, 0.005% gelatine) has been plotted in the same graph. The result seems to be rather convincing.

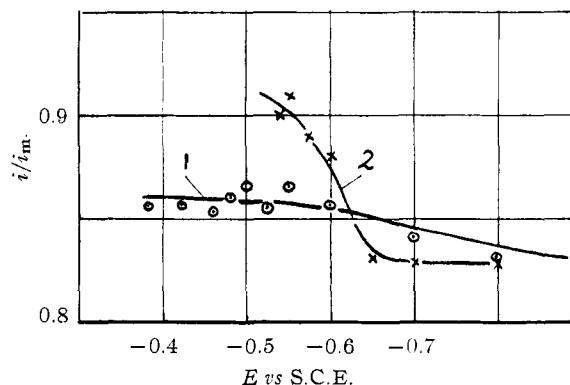Fig. 4.—The ratio average current/maximal current plotted against the applied potential: 1, Coen$_3$Cl$_3$; 2, CdSO$_4$.

The Half-wave Potential as a Function of the Complex and Hydrogen Ion Concentrations.—Using the plots of equations 11 and 13 and equation 2 one can easily calculate the shift of the half-wave potential to more positive values with decreasing concentration of the complex. As the reference point, the half-wave potential where $\alpha_{\mathrm{MA}_3} = 1$, *i.e.*, when a sufficient excess of the complexing agent is present, is taken. This was found to be equal to -0.489 v. *versus* S.C.E. with a supporting electrolyte consisting of 1 M KCl and 0.05 M

ethylenediamine per liter. An addition of 0.1 M NaOH per liter did not change the potential.

The shift of the half-wave potential was experimentally studied with the Sargent Model XXI polarograph using a number of concentrations ranging from 0.1 to 5 millimolar, the supporting electrolyte being 1 M KCl containing 0.005 M NaOH. Figure 5, curve 1 gives the experimentally observed shift. Maximal currents were used and
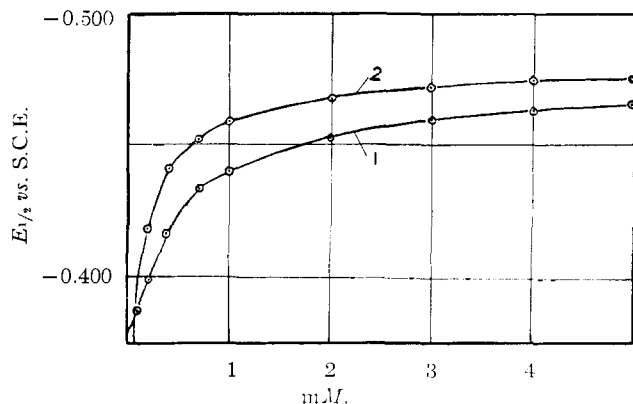

Fig. 5.—The half-wave potential of Coen$_3$Cl$_3$ as a function of its concentration: 1, experimental; 2, theoretical.

the potentials were corrected for the iR drop (cell resistance 335 ohms, minimum value at the instant of drop fall). Curve 2 in the same figure represents the theoretical shift calculated for the same concentrations and using the above-mentioned reference potential.

The agreement is not very good, but the discrepancy is attributed mostly to the difference in the diffusion coefficients of ethylenediamine and the divalent complexes. The theoretical calculations were made assuming that the coefficients are equal; however, the smaller sized, uncharged ethylenediamine molecule probably diffuses considerably faster, which results in a shift of the equilibrium of the divalent complex system to the right (reaction 3). The relative amount of MA$_3$ is then decreased and the corresponding potential is naturally more positive than expected. Lacking an accurate value of the diffusion coefficient of en, one can estimate the effect caused by $D_{en}/D_{MA_n} = 2$. This correction shifts the theoretical points (curve 2) to within 3–5 millivolts from the experimental curve. However, slight precipitation of cobaltous hydroxide also might interfere as well as lack of instantaneous attainment of the various equilibria, the latter especially at low concentrations of the complex.

The effect of pH on the half-wave potential (also measured at maximal current) was studied using an 1 mM concentration of the complex, the supporting electrolyte being the same except for the buffer used. The pH was adjusted by adding sodium hydroxide (pH>10) and using boric acid and phosphate buffers (pH<10) and was measured by means of a Beckman pH meter. The observed shift in the half-wave potential is given in Fig. 6, and it is seen to have a maximum, most negative potential, around pH 11. In a more acidic solution

the positive shift is caused by the decrease of β_A which in turn diminishes α_{MA_3}. On the other side of the maximum, the increased formation of cobaltous hydroxide will decrease α_{MA_3}. By means of equation 2 and the plots of equations 7, 11 and 13 one can easily calculate the theoretical curve shown in Fig. 6. Again it is seen that the experimental curve is located on the positive side of the theoretical one. In addition to the reasons for the discrepancy given above the increased concentration of the hydroxyl ion certainly will cause solid hydroxide to precipitate.

The Wave Form.—The form of the waves did not differ much from the "reversible" form at high concentrations of the complex, a circumstance which is to be expected. With decreasing concentration, however, the waves became drawn out, more and more "irreversible." The actual polarograms using various concentrations ranging from 0.1 to 5 millimolar of the complex were recorded with the Sargent Model XXI automatic polarograph. A number of points on the waves were theoretically calculated using the half-wave potentials as reference to "fit" the points to the curves. The agreement was found to be fairly good.

Conclusion.—The theory of the polarographic reduction of tris-ethylenediaminecobalt(III) in the absence of excess of the complexing agent has been tested experimentally. The electrode reaction was found to be reversible and the process diffusion controlled in spite of the "irreversible"
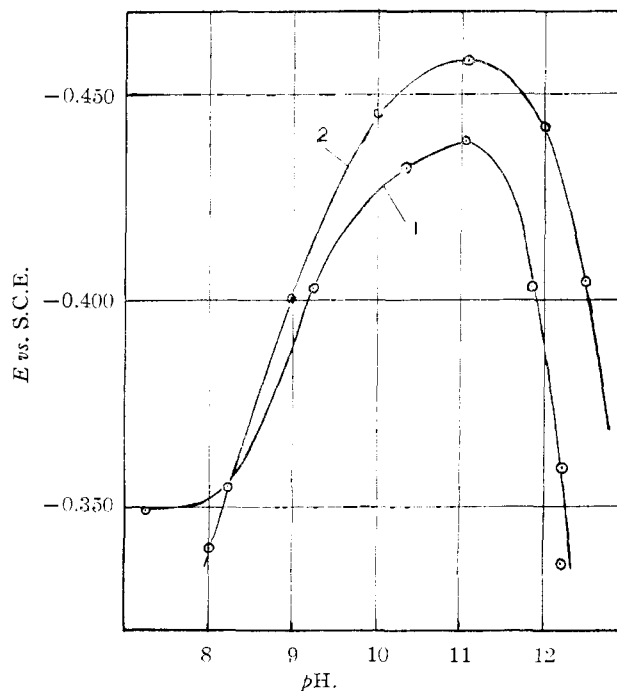

Fig. 6.—The pH dependence of the half-wave potential of Coen$_3$Cl$_3$: 1, experimental; 2, theoretical.

characteristics of the wave. As predicted the half-wave potential is a function of both the hydrogen ion and the complex ion concentrations. The shape of the wave follows the theoretical pattern.

It can thus be concluded that the polarographic irreversibility of the reduction of this complex in the absence of excess of the ligand is caused by the *chemical decomposition* of the divalent complex formed as the result of the electron transfer reaction.

Polarography in Anhydrous Ethylenediamine. I. The Mercury Pool Anode; Reduction of Some Heavy Metal Ions[1]

BY WARD B. SCHAAP, ARTHUR E. MESSNER AND FREDERIC C. SCHMIDT

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Reversible polarographic waves are obtained with the ions Tl^+, Cd^{++}, Pb^{++} and Cu^{++} in anhydrous ethylenediamine as a solvent. The mercury pool serves as a satisfactory reference electrode in spite of the absence of any depolarizing anion. The anodic reaction occurring at the pool appears to be $Hg \rightarrow Hg^{++} + 2e^-$. Diffusion coefficients for the ions studied in ethylenediamine are about 30–40% of the values in aqueous solution. The order of reduction (*i.e.*, of the half-wave potentials) of the metal ions in ethylenediamine is not the same as in aqueous solutions. The metal ions that form the more stable ethylenediamine complexes become relatively more difficult to reduce when the solvent is changed from water to ethylenediamine.

Introduction

A considerable amount of electrochemical research has been carried out in the solvent liquid ammonia. Polarographic studies,[2-8] electrode potential measurements,[9] solubility[10] and conductance[11,12] measurements have all been made in liquid ammonia as a solvent yielding results of considerable theoretical and practical significance.[13]

Electrochemical research in other amine solvents has been much more limited. For example, although ethylenediamine was isolated as a pure compound by A. W. Hoffman in 1853, it was not until 1935 that Wilson reported extensively on its physical properties.[14] Up to the present time, there have been a few reports on solubilities[15-18]

and conductance measurements[18,19-24] in anhydrous ethylenediamine along with several attempts to use the solvent as a medium from which to plate active metals.[20,24] Recently, there has been an increasing amount of interest in ethylenediamine, due to its basic character, as a solvent for the potentiometric titration of weakly acidic substances.[25-28]

An investigation of several phases of electrochemistry in anhydrous ethylenediamine as the solvent medium is under way in this Laboratory. This paper is the first on polarographic studies in this solvent. Ethylenediamine is quite convenient for use as a solvent medium because of its water-like physical properties (m.p. 11.0°, b.p. 116°). Moreover, salts of many metallic elements are sufficiently soluble in ethylenediamine for polarographic study.

Experimental

Apparatus.—A Sargent Model XXI Visible Recording Polarograph was used in these studies. A Rubicon Co. portable potentiometer was employed to accurately measure the applied potential at several points during the recording of each wave. The electrolysis cell used consisted

(1) Taken in part from a thesis submitted by Arthur E. Messner to the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Master of Arts, June, 1954. Presented in part before the 126th Meeting of the American Chemical Society, Division of Analytical Chemistry, New York, N. Y., September 16, 1954.

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