

The Evaluation of Complexity Constants from Polarographic Data

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The possibility of studying the equilibria of complex compounds polarographically was recognized by Heyrovsky and Ilkovic¹ as early as 1935. Since then several polarographic determinations of equilibrium constants of various systems have been reported in the literature.

Hitherto essentially the last complexity product of a system has been measured, whereas little attention has been paid to the consecutive constants illustrating the stepwise formation of complex compounds. Some authors even seem to deny the possibility of measuring these constants polarographically.

In 1950 the present authors² suggested the use of the polarographic method for the investigation of the stepwise formation of complexes, and recently de Ford and Hume³ have presented a method of calculating the consecutive constants from polarographic data. Furthermore Hume, de Ford and Cave⁴ have reported their results on the equilibrium constants of the cadmium thiocyanate system.

De Ford and Hume³ assume that the ligand concentration at the drop surface is the same as the concentration in the body of the solution, and their calculations refer to the case where the central metal ion is reversibly reducible at the electrode. In this article we intend to show that the polarographic method is capable of still wider application. It can be used when the ligand concentrations at the drop surface and in the body of the solution are not the same and even when the central metal ion is not reversibly reducible. In the last case, however, it is necessary to use an indirect method based on the behaviour of an „indicator ion”.

DIRECT POLAROGRAPHIC METHOD

The method generally used for the determination of the last complexity product is based on the following principle:

Let M be the central atom and A the ligand of a complex compound MA_n . If E_1 is the half-wave potential of a solution containing no ligand — *e.g.*

a metal perchlorate solution — and E_2 is the half-wave potential in the presence of a large excess of ligand, the following equation is valid:

$$\Delta E_{\frac{1}{2}} = E_2 - E_1 = -\frac{RT}{mF} \cdot \ln(\beta_n \cdot A^n) \quad (1)$$

It is assumed that the m -valent metal is reduced to the metallic state. β_n is the last complexity product of the following system of equilibria:

$$\frac{MA}{M \cdot A} = \beta_1; \frac{MA_2}{M \cdot A^2} = \beta_2; \dots; \frac{MA_n}{M \cdot A^n} = \beta_n \quad (2)$$

The letters denote concentrations of different species. For the sake of convenience, activity coefficients have not been taken into consideration. The relationship between the complexity products and the individual complexity constants is

$$b_1 \cdot b_2 \cdot \dots \cdot b_n = \beta_n \quad (3)$$

where

$$b_n = \frac{MA_n}{MA_{n-1} \cdot A} \quad (4)$$

Equation (1) is based on the assumption that the concentration of the ligand at the electrode is the same as in the bulk of the solution and that only the last of the consecutive complex compounds needs to be taken in account. In other words, the equation cannot be used unless the final complex is strong and there is a large excess of ligand in the solution.

If a more generally valid equation is required all the complexity equilibria must be taken in consideration, and it is further necessary to pay attention to the fact that the concentrations at the electrode surface and in the solution are not the same. Polarographic equilibrium calculations must always be made on the basis of the concentrations at the surface. According to general principles of polarography we can write:

	Solution	Electrode surface
Total concentration of ligand	c_A	c_A
Total concentration of metal	c_M	$\frac{i_d - i}{i_d} \cdot c_M$
Concentration of free ligand	A	A_o
Concentration of free metal ion	M	M_o

The concentrations at the electrode surface are designated by the subscript o , i is the measured current, i_d is the diffusion current. The total concentration of the ligand at the electrode surface is known, and the total concentration of the metal can be calculated if i and i_d are also known. A_o will be discussed later. M_o can be calculated from the equation

$$\Delta E = -\frac{RT}{mF} \cdot \ln \frac{\frac{i_d - i}{i_d} \cdot c_M}{M_o} \quad (5)$$

ΔE is the difference between the potential of a metal perchlorate solution with ligand present and without any ligand at a defined current value. If $i = \frac{1}{2} i_d$, then $\Delta E = \Delta E_{1/2}$, the difference between half-wave potentials. Also other current values can be employed if the small corrections for the change in the residual current and the diffusion current (due to the changes in the diffusion coefficients) are taken into account.

If weak complexes are formed, the slope of the curve will usually be the theoretical one, but if the complex formed is strong and if only small amounts of the ligand are present, the slope, especially in the upper part of the curve, will be smaller. This is because A_o increases when metal is removed from the solution. Consequently M_o decreases as the current increases, and the curve shifts towards more negative values. Of course, the change in the slope is no indication of any irreversible reaction.

If consecutive complexity products are to be determined, ΔE must be measured at different ligand concentrations c_A . For the calculations, ΔE and c_A must be expressed as functions of the equilibrium constants. This is easily done, since the total concentration equals the sum of the concentrations of all the components. In other words:

$$\frac{i_d - i}{i_d} \cdot c_M = M_o \cdot (1 + \beta_1 \cdot A_o + \beta_2 \cdot A_o^2 + \dots + \beta_n \cdot A_o^n) \quad (6)$$

From (5) and (6) we obtain

$$\Delta E = - \frac{RT}{mF} \cdot \ln(1 + \beta_1 \cdot A_o + \beta_2 \cdot A_o^2 + \dots + \beta_n \cdot A_o^n) \quad (7)$$

Furthermore

$$c_A = A_o + M_o \cdot (\beta_1 \cdot A_o + 2 \cdot \beta_2 \cdot A_o^2 + \dots + n \cdot \beta_n \cdot A_o^n) \quad (8)$$

The problem of computing individual complexity constants is hereby reduced to a purely mathematical problem. One simply conducts a series of c_A and ΔE measurements and calculates A_o and the β constants from equations (5), (7) and (8). If $n = 1$ or 2, the calculations are very simple. If n is larger than 2, equations of higher order are obtained, and their solution is not quite simple. An approximate value for β_1 can be obtained from measurements at a low ligand concentration by assuming that only the first complex is formed. In an analogous way an approximate value for the last complexity product β_n can be obtained — if the complex is strong enough — from measurements at high ligand concentrations. Equation (7) will then be transformed into

$$\Delta E = - \frac{RT}{mF} \cdot \ln(\beta_n \cdot A_o^n) \quad (9)$$

This equation is identical with the previous equation (1), which neglects all the complexes with less than n ligands.

Correct values for the other constants can be obtained by successive approximations. Leden ⁵, in a potentiometric study of the cadmium complexes,

was the first to determine consecutive complexity constants by measuring the concentration of the central metal ion. He used a partly graphical method. Fronaeus⁶ has later modified this method. De Ford and Hume³ used a method similar to Leden's. For details one must refer to the original papers and to a following paper by Eriksson⁷.

De Ford and Hume assume that the ligand concentration at the drop surface is the same as in the body of the solution. It may be remarked that this assumption is not essential. According to equations (5)–(8) it is possible to determine all concentrations in question at the drop surface.

It may some time be of advantage to measure the potential shift at a smaller current than $\frac{1}{2} i_d$.

In the following paper⁷, the polarographic determinations of the complexity constants of cadmium chloride and bromide will be described.

If the central metal ion is not reversibly reducible or oxidizable but the ligand is, the consecutive complexity constants can be determined polarographically in an analogous way. The calculation will then be simpler and can be made according to the method of J. Bjerrum⁸.

INDIRECT POLAROGRAPHIC METHOD

Even if polarography offers a possibility of determining individual complexity constants, the method seems at first sight to be of only limited value as the application of polarographic methods to equilibrium problems presupposes a reversible reaction at the electrode surface. Unfortunately, only a few metals — *e.g.* Cd, Pb, Tl — are reversibly reducible at the mercury electrode.

It may be noted, however, that a non-reducible metal can be titrated amperometrically after adding a suitable indicator ion, as shown by Ringbom and Wilkman⁹, and in an analogous way it is possible to determine the concentration of a non-reducible metal ion by using another ion as an indicator.

As an example we may take the case in which the equilibrium constants of the compounds of a metal M and the ligand A are to be determined. If cadmium, for example, forms complexes of known strength with the same ligand, the cadmium ion can be used as an indicator, provided that the cadmium wave appears before the M-wave.

Applying the equation (7) to cadmium we get

$$\Delta E = - \frac{RT}{2F} \cdot \ln(1 + \beta_1 \cdot A_0 + \beta_2 \cdot A_0^2 + \dots + \beta_n \cdot A_0^n) \quad (10)$$

If all the β constants are known, the equation (10) represents a quite general method for the determination of anion (or molecule) concentrations. One merely adds a little indicator, in this case cadmium perchlorate, to the metal solution and measures the half-wave potential with reference to the half-wave potential of a cadmium perchlorate polarogram. From a graph showing the relation between ΔE and A_0 the ligand concentration can be immediately obtained.

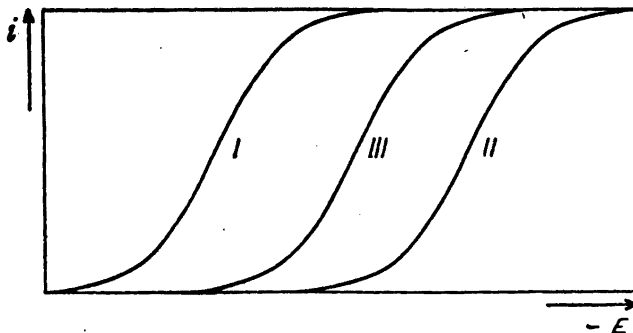


Fig. 1. Polarograms illustrating the indicator method of measuring ligand concentrations.

- I. Indicator ion.
 II. Indicator ion + ligand.
 III. Indicator ion + metal ion + ligand.

It is clear that when M ions are added to a solution containing Cd ions and A ligands, they will react with part of the ligands; in other words, A_o will decrease. In Fig. 1 three polarograms are plotted: curve I has been recorded in a cadmium perchlorate solution, curve II has been taken in a solution containing cadmium and the ligand, and curve III in the same solution as II after adding M ions in a known concentration.

It may be emphasized that the mathematical calculation of the complexity constants by the indirect method is simpler than in the direct determination of the central ion. It is suitable to use the average ligand number \bar{n} introduced by J. Bjerrum⁸ *i.e.*

$$\bar{n} = \frac{\text{number of bound ligands}}{\text{total number of metal atoms}} \quad (11)$$

The average ligand number of cadmium at the electrode surface can be calculated from the equation

$$\bar{n}_{\text{Cd}} = \frac{\beta_1 \cdot A_o + 2 \cdot \beta_2 \cdot A_o^2 + \dots + n \cdot \beta_n \cdot A_o^n}{1 + \beta_1 \cdot A_o + \beta_2 \cdot A_o^2 + \dots + \beta_n \cdot A_o^n} \quad (12)$$

It is convenient to plot \bar{n}_{Cd} as a function of $\log A_o$. If only mononuclear complexes are formed, \bar{n}_{Cd} does not depend on c_{Cd} and \bar{n}_{OM} can then be computed from the equation

$$\bar{n}_{\text{OM}} = \frac{c_A \cdot A_o - \bar{n}_{\text{Cd}} \cdot \frac{i_d - i}{i_d} \cdot c_{\text{Cd}}}{c_M} \quad (13)$$

For the complexity constants of the M—A-complexes the following method suggested by J. Bjerrum⁸ can be used:

Equation (12) is written as follows

$$\bar{n}_{oM} + (\bar{n}_o - 1) \cdot A_o \cdot \beta_1 + (\bar{n}_o - 2) \cdot A_o^2 \cdot \beta_2 + \dots + (\bar{n}_o - n) \cdot A_o^n \cdot \beta_n = 0 \quad (14)$$

From the $\log A_o$ versus \bar{n}_{oM} curve, A_o values corresponding to $\bar{n}_{oM} = 0.5, 1.5, 2.5$ etc. are taken. The constants are then calculated from these values by means of equation (14). Some approximations can usually be made.

When cadmium is used as an indicator, it seems probable that the concentrations of the following ligands can be determined: chloride, bromide, iodide, nitrite, thiocyanate, azide, acetate, several organic anions, ammonia. Cyanide ions form a strong complex with cadmium, but according to Kolthoff and Lingane¹⁰, the wave is not perfectly reversible. The complexes with nitrate, chlorate, bromate and fluoride seem to be too weak for the purpose in question.

In the indirect method suggested above there is one weak point. If the metal M is not reversibly reducible, the reaction between M and the ligand does not occur instantaneously. Consequently, even if it is possible to calculate all the concentrations at the electrode surface, it is not certain that the M ions are in equilibrium with the ligands liberated at the surface.

If A and A_o do not differ very much, *i.e.* if the slope of the curve is the theoretical one, the error caused by the unattained equilibrium can be neglected. All the cadmium complexes mentioned above, except the cyanide complex, seem to be so weak that no considerable differences between A and A_o exist if $i = \frac{1}{2} i_a$ or less. But if there is a marked decrease in the slope, then it is better to measure potential differences using a lower current strength than the half-wave current, or to measure ΔE at various current strengths and to extrapolate the values to $i = 0$. In this way the concentration in the bulk of the solution is obtained, and the polarographic method is similar to a potentiometric method, the indicator system representing an electrode of the second order.

The accuracy of the method described above is of course dependent on the strength of the indicator complex. If the indicator complex is a very weak one, the accuracy is low, but if the complex is strong, the attainable accuracy can be surprisingly high. A simple calculation illustrates this.

In direct measurements of cadmium potentials, the error at 25° is

$$\frac{dE}{dCd} = \frac{RT}{2F} = 12.3 \text{ mV} \quad (15)$$

This means that ± 1 mV corresponds to an error about $\pm 8\%$. If on the other hand, the concentration of ligand A is measured by means of cadmium potentials, the error is given by the equation

$$\frac{dE}{dA} = - \frac{\bar{n}_{Cd}}{A} \cdot \frac{RT}{2F} \quad (16)$$

This means that if the average ligand number \bar{n}_{Cd} is larger than 1, the theoretical accuracy is greater than in the direct measurement of cadmium concentrations. If cadmium forms a strong complex, so that \bar{n}_{Cd} approaches the value 4, then ± 1 mV will correspond to an error of only $\pm 2\%$. Of course, other factors can affect the results, which largely depend on the accuracy of the determination of the indicator complexity constants. It may also be mentioned that if the M-complexes are weak, the accuracy in determining \bar{n}_{M} and hence the equilibrium constants according to equation (13) is essentially dependent on the accuracy of the determination of the difference $c_{\text{A}} - A_0$. Consequently, it is necessary to have a rather high concentration of M in order to decrease A_0 sufficiently.

The influence of activity coefficients has not been considered above. If possible, it is advantageous to make all the measurements in a concentrated sodium perchlorate solution, as is usual in potentiometric measurements.

The polarographic method is probably in some instances superior to the potentiometric method, since the dropping mercury electrode is more convenient than amalgam electrodes, which demand great care. Moreover, when low concentrations are measured, the polarographic method gives no polarization troubles. Which of the two methods can be used depends on the case in question; this aspect will not be discussed here. It seems, however, worth while to emphasize that polarography as well as potentiometry offer possibilities for the measurement of the concentrations of anions or molecule groups that form complexes with a reversibly reducible metal. It also appears to be theoretically possible to determine consecutive complexity constants of other metal complex compounds, even when neither the central ion nor the ligand can be determined polarographically.

SUMMARY

The possibility of determining consecutive complexity constants from polarographic data are discussed.

An indicator method is proposed for the determination of ligand concentrations. Complexity constants can be determined polarographically by this method even if neither the metal nor the ligand of the complex is reduced at the electrode.

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