Polarographic Processes Involving Chemical Reaction of the Product of the Electron Transfer Reaction

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Using steady state and thermodynamical methods current-voltage equations have been derived for polarographic processes in which the product of the electron transfer reaction is involved in a subsequent chemical reaction.

The application of kinetics in the field of polarography has in recent years become increasingly popular. A better understanding of the conditions at the surface of the electrode, where the electron exchange reactions occur, has made it possible to attack problems concerning mechanisms of electrode reactions. For instance, the so-called irreversible polarographic processes, in which the electron transfer reaction is the slow step competing with the rate of diffusion, have been now thoroughly explained. Similarly, many catalytic processes that can occur at the surface of the microelectrode have been also clarified using kinetic considerations.

This investigation deals with a polarographic problem in which kinetics has been used to gain further insight into the phenomena in question. It is concerned with polarographic processes in which the product of the electron transfer reaction is involved in a subsequent chemical reaction¹. This type of process can be represented by the general scheme:

where A is the species undergoing reduction or oxidation and the various products of the electron transfer reaction are denoted by B, possible chemical reactants by C and the products of the chemical reaction by D. This investigation is restricted to cases where the products of the chemical reaction are not electrochemically active at the potential where A is reduced or oxidized. The so-called catalytic waves will thus be excluded from this study.

Comparatively few reports are found in the literature concerning polarographic processes involving a subsequent chemical reaction. Particularly this

is true for reduction waves, as pointed out by Tanford and Wawzonek². This type of polarographic wave was first reported by Smith, Kolthoff, Wawzonek and Ruoff³. They studied the oxidation of hydroxychromans and hydroxycoumarans at the dropping mercury electrode. Chemical or electrochemical oxidation of these compounds produces quinones. The quinones are reversibly reduced to the corresponding hydroquinones and not to the original hydroxychromans or coumarans. On the basis of an analysis of the oxidation waves, they concluded that the electrochemical oxidation involves a reversible step, but that the oxidation product formed is unstable and is irreversibly transformed to the corresponding quinone. The authors postulated that the potential is determined by the reversible reaction

whereas the irreversible step, the transformation of compound B into C

was pictured as an unimolecular reaction. In deriving the expression for the polarographic wave Smith *et al.* use a rather odd terminology in first considering α as a sort of equilibrium constant, $C_B = \alpha C_C$, but later calling it a rate constant, although it is given as a dimensionless quantity. Their equation has the form:

$$E_{d.c.} = \text{Const.} + \frac{RT}{2F} \ln \left[\frac{i}{i_d - i} \cdot \frac{k_A}{k'} \alpha \right] + \frac{RT}{2F} \ln [H^+] \quad (4)$$

where k_A is the Ilkovic constant for compound A and k' is that for compounds B and C (diffusion coefficients practically equal).

Vavrin⁴ studied a similar case in the polarographic oxidation of L-ascorbic acid. He derived an equation describing the current-voltage relationship assuming that the chemical decomposition of the oxidized form is a reversible monomolecular reaction:

where Ox_{rev} represents the form which can be reversibly reduced and Ox_{irr} that which cannot. The rate constant of the forward reaction is denoted by k_1 , that of the reverse reaction by k_2 . The derivation was based upon the Nernst relationship. In the customary way $(i_d - i) = k \text{ Red}$, where k is the Ilkovic constant for the reduced form. In trying to relate the current to the surface concentration of Ox_{rev} , Vavrin seems to have used an equation of doubtful validity, viz.,

$$i = k Ox_{rev} + k_1 Ox_{rev} - k_2 Ox_{irr} \quad (6)$$

where k again represents the Ilkovic constant, the same for both the oxidized and reduced forms, and Ox_{rev} and Ox_{irr} are the surface concentrations of the species involved. (The two last terms in the right hand side of equation (6) have the dimension of a rate: moles/liter/sec., whereas the term $k Ox_{rev}$ gives amperes). Solving for Red and Ox_{rev} and inserting these quantities into the Nernst relation gives

where the superscript ° refers to concentrations at the electrode surface. The various processes occurring at the electrode are considered as unimolecular rate processes. The rate constants are defined as the number of moles of substance reacting in unit time, per unit area, per unit concentration, the dimension being cm sec^{-1} . The heterogeneous rate constants may be related to conventional three-dimensional rate constants by considering the "thickness" of the reaction zone. Expressions for this have been derived by various authors^{8,10}. In scheme (8) the constants for the electron transfer reaction are denoted by k_1 (forward) and k_2 (backward), those for the chemical reactions by k_3 (forward) and k_4 (backward). The concentrations of the species involved are designated by A, B and C. The kinetic factors¹¹ which involve the activity coefficients, are here considered equal to unity for the sake of simplicity. The diffusion rate constants of the species are denoted by k_A , k_B and k_C , respectively. They are defined in the following manner:

The Ilkovic equation gives the mean diffusion current

$$i_d = \frac{6}{7} \sqrt{\frac{7}{3}} \cdot \frac{1}{\sqrt{\pi}} \left(\frac{36\pi}{d^2} \right)^{1/2} n F C D^{1/2} m^{1/2} t^{1/2} \quad (9)$$

in which the notations are the conventional ones. The expression of the mean diffusion current in the steady state treatment is given by (see below)

$$i_d = n F q C k_d \quad (10)$$

where q is the mean area of the mercury drop and k_d represents the diffusion rate constant. From equations (9) and (10) one obtains

$$k_d = \sqrt{\frac{7}{3}} \cdot \frac{1}{\sqrt{\pi}} \cdot \frac{5}{3} \cdot \frac{6}{7} \sqrt{\frac{D}{t}} = 1.231 \sqrt{\frac{D}{t}} \quad (11)$$

which is the expression for the diffusion rate constants.

The potential dependence of the rate constants of the electron transfer reaction is given by

$$k_1 = k_1^\circ \exp \frac{-\alpha n F E}{RT} \quad (12)$$

and

$$k_2 = k_2^\circ \exp \frac{(1-\alpha) n F E}{RT} \quad (13)$$

where k_1° and k_2° represent the values of the rate constants at zero applied potential¹². The transfer coefficient α is the fraction of the potential difference which effects the reduction, whereas $(1-\alpha)$ is the fraction which effects the oxidation^{2,12}. The sign of the exponent is to be taken negative for reductions (increasing k for more negative or less positive potential) and positive for oxidations.

The steady state treatment requires that the concentrations of the species involved, both in the bulk of the solution and at the electrode surface, are independent of time, i. e., the sum of moles brought to the electrode by diffu-

sion or reaction equals the sum of moles removed. Applying this condition to the above-mentioned scheme, the following equations are obtained:

$$Ak_A + B^{\circ}k_2 = A^{\circ}k_A + A^{\circ}k_1 \quad (14)$$

$$Bk_B + A^{\circ}k_1 + C^{\circ}k_4 = B^{\circ}(k_2 + k_3 + k_B) \quad (15)$$

$$Ck_C + B^{\circ}k_3 = C^{\circ}k_C + C^{\circ}k_4 \quad (16)$$

The mean cathodic current, i , is due to the difference in the rates of reduction and oxidation:

$$i = nFq(A^{\circ}k_1 - B^{\circ}k_2) \quad (17)$$

Using simple algebra the expression for the current can be derived from equations (14)–(17):

$$i = nFq \left[\frac{Ak_A k_1 (k_3 k_C + k_4 k_B + k_B k_C) - Bk_A k_B k_2 (k_4 + k_C) - Ck_A k_C k_2 k_4}{k_1 (k_3 k_C + k_4 k_B + k_B k_C) + k_A (k_2 k_4 + k_2 k_C + k_3 k_C + k_4 k_B + k_B k_C)} \right] \quad (18)$$

Considering potentials at which k_1 becomes very large, all the other terms except those containing k_1 are unimportant and equation (18) then takes the form

$$i_d = nFqAk_A \quad (19)$$

where i_d represents the diffusion limited mean current, *i. e.*, complete concentration polarization prevails. From equations (18) and (19) it is then possible to get

$$\frac{i_d - i}{i} = \frac{Ak_A (k_2 k_4 + k_2 k_C + k_3 k_C + k_4 k_B + k_B k_C) + Bk_B k_2 (k_4 + k_C) + Ck_C k_2 k_4}{Ak_1 (k_3 k_C + k_4 k_B + k_B k_C) - Bk_B k_2 (k_4 + k_C) - Ck_C k_2 k_4} \quad (20)$$

which reduces to

$$\frac{i_d - i}{i} = \frac{k_A (k_2 k_4 + k_2 k_C + k_3 k_C + k_4 k_B + k_B k_C)}{k_1 (k_3 k_C + k_4 k_B + k_B k_C)} \quad (21)$$

provided B and C, the concentrations of the products in the bulk of the solution, are equal to zero, which is usually the case.

Equation (21) has been derived without recourse to considerations of the relative magnitudes of the various velocity constants. It will, therefore, apply whether or not the reactions are reversible. It represents thus a general relationship from which current-voltage equations can be derived for polarographic processes coupled with a monomolecular chemical reaction.

Depending on relative magnitude of the various rate constants different situations are encountered.

If a case, where

$$k_1, k_2 \gg k_3, k_4, k_A, k_B, k_C \quad (22)$$

is at hand, equation (21) then takes the form

$$\frac{i_d - i}{i} = \frac{k_2}{k_1} \left[\frac{k_4 k_A + k_A k_C}{k_3 k_C + k_4 k_B + k_B k_C} \right] \quad (23)$$

since the terms in the nominator which do not contain k_2 can be neglected. Condition (22) actually represents the criterion of polarographic reversibility which requires that the rates of the electron transfer reactions are faster than the other processes involved ^{5, 13}. Accordingly, the current-voltage equation of this case should yield a "reversible" log plot slope.

If desired the activity coefficients can be introduced into equation (23) at this stage conveniently. They are associated with the reaction rate constants in scheme (8) as follows:

$$\begin{array}{l} \text{A} \dots \dots \dots f_1 k_1 \\ \text{B} \dots \dots \dots f_2 k_2, f_2 k_3 \\ \text{C} \dots \dots \dots f_3 k_4 \end{array}$$

The connection between the diffusion rate constants and the activity coefficients is of a different nature. The diffusion rate constants are derived on the basis of the Ilkovic equation which in turn is based upon Fick's laws which are valid only under ideal conditions. Therefore the change in the rates of diffusion with change in overall ionic strength must be referred to the variation of the diffusion coefficient D ^{14, 15}. Because of the lack of knowledge of values of D in various media, the usual practice is to consider it constant and equal to the value at infinite dilution. After inserting the activity coefficients into equation (23) it takes the form:

$$\frac{i_d - i}{i} = \frac{k_2 f_2}{k_1 f_1} \left[\frac{f_3 k_4 k_A + k_A k_C}{f_2 k_3 k_C + f_3 k_4 k_B + k_B k_C} \right] \quad (24)$$

Combining equations (12), (13) and (24) and taking logarithms, the following relation is obtained:

$$E = \frac{RT}{nF} \left[\ln \frac{k_1^\circ}{k_2^\circ} + \ln \frac{f_1}{f_2} + \ln \frac{f_2 k_3 k_C + f_3 k_4 k_B + k_B k_C}{f_3 k_4 k_A + k_A k_C} \right] + \frac{RT}{nF} \ln \frac{i_d - i}{i} \quad (25)$$

The three terms in the parenthesis of the right hand side of equation (25) are constant for a given solution and reference electrode and they represent the half-wave potential of the reaction. Thus

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} \ln \frac{i_d - i}{i} \quad (26)$$

which is the familiar equation for a reversible polarographic wave.

It has been shown that a first-order reversible chemical reaction which follows a reversible electron transfer reaction, does not alter the shape of the polarographic wave provided k_1 and k_2 are much larger than the other rate constants. The half-wave potential, however, is a function of the magnitude of the rate constants of the chemical reaction and of the diffusion rate constants.

When the first-order chemical reaction is very rapid fulfilling the condition

$$k_1, k_2, \gg k_3, k_4, \gg k_A, k_B, k_C \quad (27)$$

equation (21) then takes the form

$$\frac{i_d - i}{i} = \frac{k_2}{k_1} \cdot \frac{k_4 k_A}{k_3 k_C + k_4 k_B} \quad (28)$$

from which one obtains

$$E_{\frac{1}{2}} = \frac{RT}{nF} \left[\ln \frac{k_1^\circ}{k_2^\circ} + \ln \frac{f_1}{f_2} + \ln \frac{f_2 k_3 k_C + f_3 k_4 k_B}{f_3 k_4 k_A} \right] \quad (29)$$

That the same result is found whether the rate of the chemical reaction is faster or slower than the electron transfer reaction actually means that the system is in complete equilibrium. Again the wave is a reversible one. This is to be credited to the properties of a first-order reaction; under similar conditions, second-order reactions do not in general give reversible waves.

Thermodynamic consideration of case (27) results in an identical conclusion:

The Nernst relationship which presumes reversibility of the electrode reaction, is given by

$$E = E' + \frac{RT}{nF} \ln \frac{A^\circ}{B^\circ} \quad (30)$$

where E' denotes the standard potential of reaction

and the superscript $^\circ$ refers to surface concentrations. According to usual polarographic practice one has that $A^\circ = (i_d - i)/k'_A$. On the other hand, the current is proportional to the sum of the concentrations of the two forms of the reduction product, provided the diffusion coefficients are nearly equal:

$$i = k'_{B,C} (B^\circ + C^\circ) \quad (32)$$

Using homogeneous rate constants, one may write for the chemical reaction

$$\frac{C}{B} = \frac{k_3}{k_4} = K \quad (33)$$

Hence

$$B^\circ = \frac{i}{k'_{B,C} (1 + K)} \quad (34)$$

and inserting the expressions for A° and B° into equation (30) one has for the half-wave potential

$$E_{\frac{1}{2}} = E' + \frac{RT}{nF} \ln \frac{k'_{B,C} (k_3 + k_4)}{k'_A \cdot k_4} \quad (35)$$

which is identical with equation (29) save for the activity coefficients. The case studied by Vavrin⁴ falls under the category represented by condition (27). It is the opinion of the author that Vavrin should have used equation (32) rather than (6) to get the correct result.

When the first-order chemical reaction is irreversible the case can be that the following condition is fulfilled

$$k_1, k_2 \gg k_3 \gg k_A, k_B, k_C \quad (36)$$

From equation (21) it is then readily seen that

$$\frac{i_d - i}{i} = \frac{k_2}{k_1} \cdot \frac{k_A}{k_3} \quad (37)$$

and the expression for the half-wave potential becomes

$$E_{\frac{1}{2}} = \frac{RT}{nF} \left[\ln \frac{k_1^\circ}{k_2^\circ} + \ln \frac{f_1}{f_2} + \ln \frac{k_3}{k_A} \right] \quad (38)$$

Here the wave is reversible and the half-wave potential is a function of k_3 . Similarly, a reversible wave is obtained when

$$k_1, k_2 \gg k_3 \simeq k_A, k_B, k_C \quad (39)$$

viz.,

$$E_{\frac{1}{2}} = \frac{RT}{nF} \left[\ln \frac{k_1^\circ}{k_2^\circ} + \ln \frac{f_1}{f_2} + \ln \frac{k_3 + k_B}{k_A} \right] \quad (40)$$

If, on the other hand, k_3 is of the same order of magnitude or greater than k_2 , then the wave is irreversible, *e. g.*,

$$\frac{i_d - i}{i} = \frac{k_A}{k_1} \quad (41)$$

and thus

$$E = \frac{RT}{anF} \left[\ln k_1^\circ + \ln \frac{f_1}{k_A} \right] + \frac{RT}{anF} \ln \frac{i_d - i}{i} \quad (42)$$

which is the equation for an irreversible polarographic wave with an "irreversible" log plot slope of 0.0591 / an volt.

The case investigated by Smith *et al.*³ is one obeying condition (36). It is clear that when the rate of transformation is much faster than diffusion, k_3 will dominate and the half-wave potential will a function of it and not of the rate of diffusion. Considering $i = aC_B$ in the case of Smith *et al.* one arrives at the result given by equation (38).

Equation (38) is in agreement with the equation presented by Kern⁶ provided k_3 is replaced by μk_{hom} . The thickness of the reaction zone, μ , is equal to $\sqrt{D_B/k_{\text{hom}}}$ and k_{hom} is the homogeneous rate constant of the chemical decomposition. Note that Kern's case is an oxidation.

THE ELECTRODE REACTION COUPLED WITH A BIMOLECULAR CHEMICAL REACTION

Three different types of reaction are possible in this case. Firstly, the forward chemical reaction is of first order but the back-reaction is of second order, *viz.*,

Secondly, the forward chemical reaction is bimolecular, but the back-reaction is monomolecular which is illustrated by scheme (44):

The third possibility is at hand when both the forward and the reverse chemical reactions are bimolecular which, however, is a rare situation.

The steady state treatment of these schemes becomes hopelessly involved and hence only simplified cases will be considered below.

Employing Nernst relationship, the equation of the current-voltage curve for scheme (43) can be obtained in the following manner: As usual $\text{A}^\circ = (i_d - i)/k'_A$, and $i = k'_R (\text{B}^\circ + \text{C}^\circ)$. Assuming that the chemical reaction also is at all times in equilibrium and using homogeneous rate constants one has

$$i = k'_R (\text{B}^\circ + \sqrt{\text{B}^\circ k_3/k_4}) \quad (45)$$

from which, assuming further that $\text{B}^\circ \ll \sqrt{\text{B}^\circ k_3/k_4}$ it is found that

$$E = E' + \frac{RT}{nF} \ln \left[\frac{i_d - i}{i^2} \cdot \frac{(k'_R)^2}{k'_A} \cdot \frac{k_3}{k_4} \right] \quad (46)$$

In certain cases the concentration of D is approximately proportional to the current: $i = k'_R \text{D}^\circ$ and equation (46) can be written

$$E = E' + \frac{RT}{nF} \ln \left[\frac{i_d - i}{i} \cdot \frac{k'_R}{k'_A} \cdot \frac{k_3}{k_4} \right] - \frac{RT}{nF} \ln \text{D}^\circ \quad (47)$$

The constancy of the concentration of D at the surface of the electrode determines the wave form. Constant D° only gives a reversible wave, otherwise it will have irreversible characteristics, *i. e.*, owing to the proportionality between the current and D° the log plot slope will be non-linear. Scheme (43) represents a typical situation in which a metal complex is reduced to another oxidation state and the complexing agent is liberated.

Turning now to scheme (44) the current-voltage relationship is found in a similar fashion. Again $\text{A}^\circ = (i_d - i)/k'_A$ but now the current is proportional to the sum of the concentrations of B and D, *i. e.*, $i = k'_R (\text{B}^\circ + \text{D}^\circ)$. Assuming also here that the chemical equilibrium is attained instantaneously one has

$$\text{B}^\circ = \frac{i}{k'_R \left(1 + \frac{\text{C}^\circ k_3}{k_4} \right)} \quad (48)$$

and thus

$$E = E' + \frac{RT}{nF} \ln \left[\frac{i_d - i}{i} \cdot \frac{k'_R}{k'_A} \cdot \left(1 + C^\circ \frac{k_3}{k_4} \right) \right] \quad (49)$$

Depending on the relative magnitudes of k_3 , k_4 and the surface concentration of C, different waves are found. First of all, if k_4 is very large, i. e., B hardly decomposes at all, then the wave is reversible; $C^\circ k_3/k_4 = 0$. The case can be that $C^\circ k_3/k_4 \gg 1$, then depending upon the constance of C° during the electrolysis, the wave can show reversible characteristics (constant C° , high concentration of buffer or complexing agent) or can appear more or less irreversible (C° decreases on going up along the wave, e. g., inadequate buffer capacity or slow rate of proton splitting). The half-wave potential will thus be a function of $(1 + C^\circ k_3/k_4)$ giving a number of various situations.

When the bimolecular chemical reaction is irreversible, steady state treatment can be applied. Consider the following, somewhat simplified reaction scheme in terms of the heterogeneous rate constants:

Assuming a steady state to be attained, one has

$$Ak_A + B^\circ k_2 = A^\circ k_A + A^\circ k_1 \quad (51)$$

$$A^\circ k_1 = B^\circ (k_2 + k_3 + C^\circ k_3) \quad (52)$$

From equations (17), (51) and (52) then

$$\frac{i_d - i}{i} = \frac{k_A}{k_1} \left[\frac{k_2 + k_B + C^\circ k_3}{k_B + C^\circ k_3} \right] \quad (53)$$

It is readily seen that when $k_2 \gg k_B + C^\circ k_3$, a reversible polarographic wave is found, otherwise it will be irreversible. As to the effect of the variation of the surface concentration of C, the same applies as was said above in connection with the reversible cases.

Numerous polarographic processes belonging to the group involving a follow-up bimolecular chemical reaction have been reported in the literature. Especially organic reductions and oxidations coupled with hydrogen ion uptake have been analyzed. Reference is made to the section of organic polarography in the monograph on polarography by Kolthoff and Lingane¹⁶.

CONCLUSION

The results of the theoretical considerations in this paper can be summarized as follows:

1. Equation (20) represents a general relationship from which current-voltage equations can be derived for polarographic processes coupled with a

monomolecular chemical reaction. Equation (21) is valid under normal polarographic conditions and illustrates that E_1 will always be independent of the concentration of the reactant.

A *reversible* wave is found when

- a) the chemical reaction is *reversible* and either of conditions (22) or (27) is satisfied;
- b) the chemical reaction is *irreversible* and either of conditions (36) or (39) is fulfilled.

An *irreversible* wave is the result when

- c) the chemical reaction is *reversible* and $k_2 \sim k_3 \gg k_4$;
- d) the chemical reaction is *irreversible* and $k_2 \leq k_3$;
- e) in all cases where $k_1, k_2 \leq k_A, k_B, k_C$ or when $k_1 \gg k_2$.

2. Where a *bimolecular* chemical reaction affects the concentration of the product of the electron transfer reaction, the same general principles apply as in the previous case, except that here a situation corresponding to conditions (27) does not in general produce a reversible wave. This class is characterized by the fact that E_1 is a function of the concentration of either reactant A or C.

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