Application of Polarographic Maxima to the Determination of Kinetic Parameters of Irreversible Reductions*

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Most methods hitherto used for the determination of the kinetic parameters of irreversible reductions (or oxidations) from polarographic data have the disadvantage that surface-active maximum suppressors must be present; these often change the kinetic parameters. In this paper it is suggested that use be made of the strong convection which accompanies a polarographic maximum of the first kind, occurring in the absence of maximum suppressors. For currents up to 15-30 % of the diffusion current, concentration polarization has been found to be negligible. For higher currents a simple empirical relation for the concentration polarization has been found, which made it possible to include these data (up to twice the diffusion current) in the determination of the kinetic parameters. In this way, the kinetic parameters for the reduction of bivalent cobalt and manganese in solutions containing lithium or magnesium perchlorate as supporting electrolyte have been determined.

Among the methods for the determination of the kinetic parameters of an irreversible oxidation or reduction, the analysis of polarographic data has found the widest application, because it gives accurate results while it requires only simple instrumentation. For a simple irreversible reduction, involving n electrons,

$$ox + ne \rightarrow red \tag{1}$$

the cathodic current i_c may be represented by

$$i_c = nFAk_0{}^\circ C \exp\left[\frac{-\alpha n_a F}{RT}(E_c - E_0)\right], \tag{2}$$

in which A is the area of the dropping mercury electrode, $^\circ C$ the concentration of ox at the electrode surface, α the transfer coefficient of the reduction, n_a the number of electrons involved in the rate-determining step ($n_a \leqq n$), E_c the cathode potential against, e.g., a 0·1 N calomel electrode, E_0 the standard potential of the redox system, against the same reference electrode, and k_0 the standard rate constant. The kinetic parameters αn_a and k_0 can be determined from the current-potential relation at constant electrode area, if the surface concentration $^\circ C$ is known. Due to the reduction, ox is depleted at the surface of the electrode, i.e., concentration polarization occurs. Therefore the reliability of the results depends largely on the accuracy with which $^\circ C$ can be estimated or predicted.

Generally, the kinetic parameters are determined from the diffusion-controlled polarographic wave; among the existing derivations, Koutecky's equations, derived from Fick's second law for semi-infinite diffusion to an expanding mercury drop, yield the most accurate results.[1, 2] The advantage of using the diffusion-controlled wave is that the whole rising part of the wave can be used, which benefits the accuracy of the results. The disadvantage is, however, that a maximum

suppressor must be added to the solution; these surface-active substances are known to change the kinetic parameters in most instances,[3-7] e.g., the transition from 0·001 to 0·1 % gelatin shifts αn_a for the nickel ion reduction from 0·56 to 0·32.[8]

Two methods for the determination of the kinetic parameters of irreversible reductions in the absence of surfactants have so far been published. Elving and Zemel[9] worked at very low ratios of ox concentration to supporting electrolyte concentration, at which no polarographic maxima of the first kind occur; this method is not very accurate, because at very low concentrations of ox the residual current is relatively large, while at concentrations of supporting electrolyte over 0·5 N the occurrence of a maximum of the second kind is possible. Laitinen and Subcasky[4] suggested to use such low current densities that depletion at the drop surface would be negligible; their claim, however, that this is true up to $i_c = 0\cdot10-0\cdot15$ i_d (i_d is the diffusion current) is not justified.

In this paper it is suggested that the occurrence of a polarographic maximum of the first kind in the absence of surfactants, which is usually considered troublesome, may be useful for the determination of kinetic parameters. During these maxima a very intensive convection takes place along the electrode surface; it is caused by a gradient in the surface tension along the drop surface, which results from non-uniform polarization due to the screening effect of the glass capillary. For the rate of streaming, values up to 5-10 cm/sec have been measured.[10] It will be shown that for currents up to 0·15-0·30 i_d, depending on the composition of the solution, concentration polarization can be considered negligible in most cases, i.e., causes a negative error in αn_a of less than 1 %. In addition to yielding more accurate results than the previous methods, the use of maxima also has the advantages that an accurate knowledge of the diffusion current is not necessary, and that the occurrence of streaming is a guarantee of the absence of surface-active impurities. If C is the concentration of ox in the bulk of the solution, one can derive from eqn. (2):

$$\log i_c = \log nFAk_0C - \log \frac{C}{{}^\circ C} - \frac{\alpha n_a}{0\cdot0591}(E_c - E_0). \tag{3}$$

The relation between $\log i_c$ and $(-E_c)$ is linear in the region in which concentration polarization is negligible (${}^\circ C = C$); its slope yields αn_a, while $\log k_0$ is obtained after extrapolation to $E_c = E_0$.

EXPERIMENTAL

The instantaneous current is measured as a function of applied potential difference and time for the circuit of fig. 1. A potential difference of slightly over 2 V is applied by a battery to a ten-turn Helipot potentiometer of 100 Ω, with a linearity tolerance of 0·1 % (Beckman Instruments, California, U.S.A.). This potential difference is adjusted to exactly 2 V with the aid of a 5 Ω variable resistance, a Weston cell and a sensitive galvanometer as null-point detector. By reversing a switch, the circuit containing the Weston cell can be replaced by the circuit containing the polarographic cell; a variable and known voltage can then be applied between the working electrodes of the polarographic cell. The current passing through the cell is measured as the potential difference across a resistance R_e in series with the cell. R_e is a precision decade box of 10-10,000 Ω±0·1 % (Bleeker, Zeist, Netherlands). The potential difference across R_e is measured by means of a Honeywell-Brown Electronik recorder with a full-scale response time of ¼ sec and a chart speed of 1 in./sec. The recorder has a range of 0-10 mV and works as a self-balancing potentiometer. The measured current must be corrected for the residual current i_r, which is determined for every solution in a separate experiment under identical conditions of drop formation.

The polarographic cell consists of two compartments, separated by a sintered-glass disc; one contains the test solution and the dropping mercury electrode, the other the counter electrode, being a Hg/Hg_2SO_4 electrode in contact with a sulphate solution of approximately the same conductance as the test solution. In each experiment the potential of this counter electrode is measured against a 0·1 N calomel electrode by means of a Philips potentiometer type GM 4491 (Philips, Netherlands). This potential difference is accurate to 0·1-0·2 mV, and independent of the current. Diffusion potentials have been neglected.
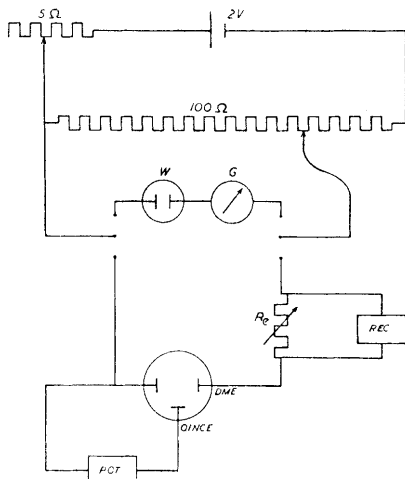

FIG. 1.—Measuring circuit; W = Weston cell, G = galvanometer, Rec = recorder, Pot = poten-
tiometer, DME = dropping mercury electrode, 0·1 NCE = 0·1 N calomel electrode.

The applied potential difference must be corrected for the ohmic potential drop in the cell circuit, which equals $(i_c + i_r)(R_e + R_t)$. R_t is the instantaneous cell resistance at the time t counted from the beginning of drop-life; it is determined with the aid of a Philo-scope bridge type GM 4249/01 (Philips, Netherlands) at 1000 c/sec. The time t, needed for bridge balance, is measured with a stopwatch for a number of set resistance values; one determines the instantaneous cell resistance at any time t from the linear plot of R_t against $t^{-\frac{1}{3}}$.

Since polarographic maxima are very sensitive towards surface-active impurities, extreme care has been taken to avoid contamination with organic matter. The polarographic cell is an all-glass apparatus with ground-glass joints. The nitrogen needed for removing dissolved air from the solution in the cell is freed from oxygen by an active copper compound (B.T.S. Katalysator, B.A.S.F., Germany), and from possible organic impurities by passing through silica gel and molecular sieves (Linde, Union Carbide, U.S.A.). The nitrogen passes through glass tubing and Teflon stopcocks only. Before entering the cell, it is saturated with the solvent of the test solution.

Water was twice distilled in an all-glass apparatus, first from permanganate and sulphuric acid, next from alkaline permanganate. Mercury was twice distilled. Stock solutions of $LiClO_4$ and $Mg(ClO_4)_2$ were prepared from A.R. 60 % perchloric acid and from lithium carbonate and magnesium carbonate, respectively. Cobaltous nitrate (A.R.) and manganous sulphate were reagent-grade chemicals.

RESULTS

Fig. 2 shows the plots of log i_c against $-E_c$ for the polarographic maxima during the reduction of cobaltous ions in seven different media, at a constant drop size (drop radius, $r = 0·0506$ cm). Fig. 3 shows similar plots for the reduction of manganous ions, in three different media, for a drop radius of 0·0437 cm. These
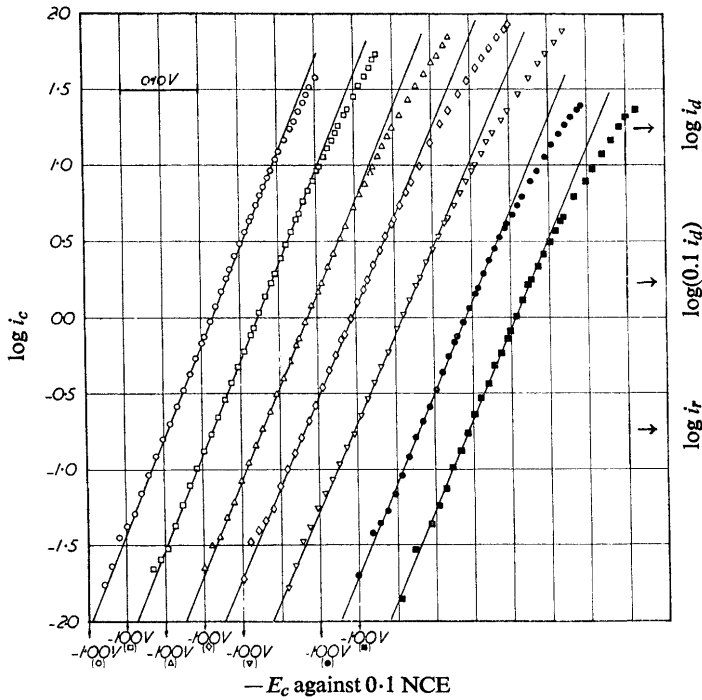
FIG. 2.—Plots of log i_c against $-E_c$ for the reduction of 0·002 M Co(NO₃)₂ ; $r = 0·0506$ cm, supporting electrolyte : ○, 0·02 M ; □, 0·04 M ; △, 0·08 M ; ◇, 0·12 M ; ▽, 0·20 M LiClO₄ and ●, 0·01 M ; ■, 0·02 M Mg (ClO₄)₂. i_c in μA.
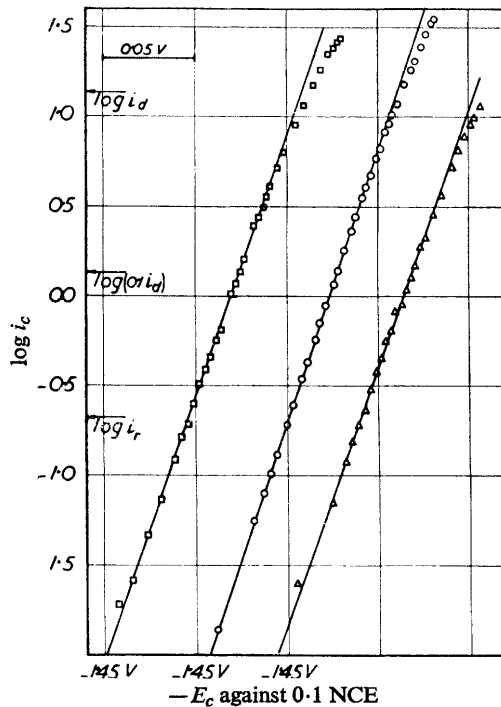

FIG. 3.—Plots of log i_c against $-E_c$ for the reduction of 0·002 M MnSO₄ ; $r = 0·0437$ cm, supporting electrolyte : □, 0·04 M ; ○, 0·08 M LiClO₄ ; and △, 0·02 M Mg(ClO₄)₂.

figures show that the relations are linear up to some value of $\log i_c$ between $\log (0{\cdot}1\ i_d)$ and $\log i_d$; above this value, the influence of concentration polarization begins to be apparent. At the foot of the maxima, where $\log i_c < \log i_r$, the measurements are not very accurate. Therefore the most probable straight line has been calculated from the linear part of the plot, with double weight given to the points between $\log i_r$ and $\log (0{\cdot}1\ i_d)$; the method of least squares has been employed. These straight lines have been inserted in fig. 2 and 3.

INFLUENCE OF CONCENTRATION POLARIZATION

It is as yet not possible to calculate theoretically the magnitude of the concentration polarization during a maximum of the first kind, due to the complicated stirring conditions. The approach by Frumkin and Levich,[11, 12] the best available at present, does not allow quantitative conclusions. For an estimation of the concentration polarization during polarographic maxima, one has to make use of empirical relations.

As a measure of the concentration polarization we have selected the quantity $\log (C/^{\circ}C)$, which is equal to the vertical distance between the experimental points and the continuation of the linear $\log i_c$ against $-E_c$ relation. In fig. 4, $\log (C/^{\circ}C)$ has been plotted against i_c/i_d for the reduction of cobaltous ions in six different
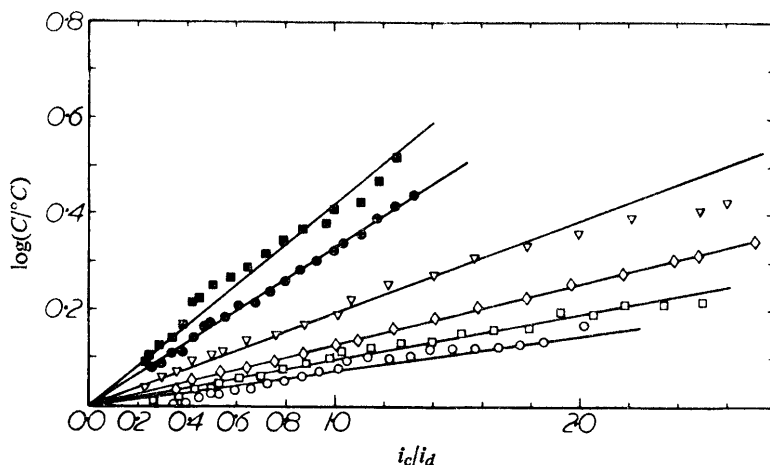

FIG. 4.—The influence of the concentration and type of supporting electrolyte on the concentration polarization; plots of $\log (C/^{\circ}C)$ against i_c/i_d for the reduction of $0{\cdot}002$ M $Co(NO_3)_2$; $r = 0{\cdot}0506$ cm; supporting electrolyte: $\bigcirc$, $0{\cdot}02$ M; $\square$, $0{\cdot}04$ M; $\diamondsuit$, $0{\cdot}12$ M; $\triangledown$, $0{\cdot}20$ M $LiClO_4$ and $\bullet$, $0{\cdot}01$ M; $\blacksquare$, $0{\cdot}02$ M $Mg(ClO_4)_2$.

media. Though the experimental error is fairly large, the relations are fairly well represented by straight lines, which must go through the origin because concentration polarization is absent when $i_c = 0$. It appears from fig. 4 that concentration polarization increases with increasing concentration of $LiClO_4$ or $Mg(ClO_4)_2$; moreover, the concentration polarization in solutions containing $Mg(ClO_4)_2$ is considerably larger than in solutions containing $LiClO_4$.

In a similar manner the concentration polarization has been determined for the maximum occurring with the reduction of manganous ions in $0{\cdot}08$ M $LiClO_4$; the result is shown in fig. 5 (circles; curve A). For comparison, we have drawn in the same figure (curve B) the relation between the concentration polarization and i_c/i_d

which would occur for the diffusion-controlled wave of this reduction, calculated according to Koutecky.[1, 2]

Using the empirical relation

$$\log (C/^{\circ}C) = ai_c, \tag{4}$$

eqn. (3) can be transformed into

$$\log i_c = \log nFAk_0C - ai_c - \frac{\alpha n_a}{0 \cdot 0591}(E_e - E_0) \tag{5}$$

$$= p - ai_c - qE_e, \tag{6}$$

where $p = \log nFAk_0C + \alpha n_a E_0/0 \cdot 0591$ and $q = \alpha n_a/0 \cdot 0591$.

For each series of experiments the best values of p, a and q have been determined with a least-squares programme for the best fit to eqn. (6), using all data between $i_c = i_r/4$, and $i_c = 2i_d$, and giving double weight to the points between $i_c = i_r$ and $i_c = 0 \cdot 1\ i_d$. Table 1 lists the values of αn_a and k_0 calculated from p and q, using for E_0 the values given in the table.
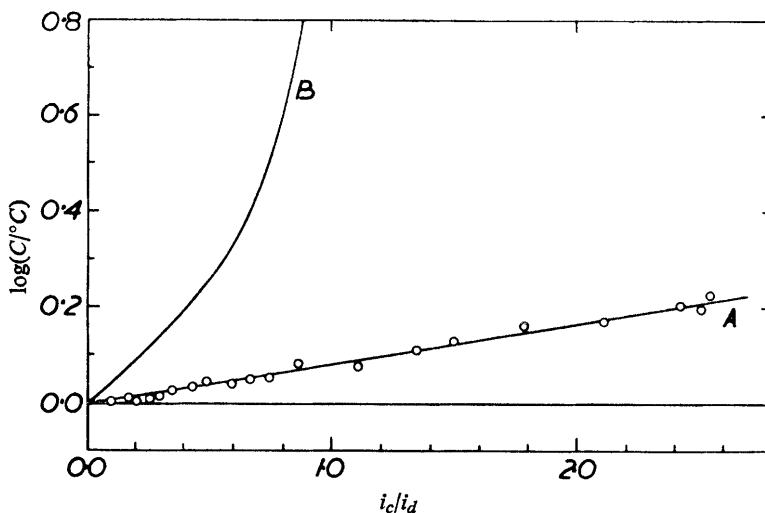

FIG. 5.—The relation between the concentration polarization factor $\log (C/^{\circ}C)$ and i_c/i_d for the reduction of Mn(II) in $0 \cdot 08$ M LiClO$_4$: A, for the polarographic maximum; B, calculated for the diffusion-controlled wave.

Values for a, which is a measure for the remaining concentration polarization have not been listed, but the following statements can be made about it: (i) concentration polarization increases with increasing concentration of supporting electrolyte and with increasing valency of the counter ions as is shown in fig. 4. (ii) It si virtually independent of the rate of drop formation. (iii) It increases slightly with nicreasing drop size. (iv) Concentration polarization, being proportional to the current (eqn. (4), (5)), acts as if there is an extra ohmic potential drop in the circuit.

CONCLUSION

The good internal consistence of the data of table 1 and of other data [13] not reproduced here, shows that the method of using polarographic maxima for the determination of kinetic parameters is capable of good accuracy. From fig. 4 and 5, at $i_c = 0 \cdot 2\ i_d$ the error in $\log i_c$, which is equal to $\log (C/^{\circ}C)$ varies between $0 \cdot 015$

and 0·035 for the LiClO4 solutions rising to about 0·08 for $Mg(ClO_4)_2$ as supporting electrolyte. If no correction for concentration polarization were applied, this would cause a maximum (negative) error in αn_a of 1-2 % for the LiClO4 solutions

TABLE 1.—THE KINETIC PARAMETERS

electroactive substance	supporting electrolyte	αn_a			$-\log k_0$, k_0 in cm/sec		
		$r = 0.0442$ cm	$r = 0.0506$ cm	average	$r = 0.0442$ cm	$r = 0.0506$ cm	average
0·002 M Co(NO3)2	0·02 M LiClO4	0·753	0·754	0·753₅	11·13	11·13₅	11·13
	0·04 M "	0·752	0·746	0·749	11·23	11·16	11·20
	0·08 M "	0·728	0·735	0·731₅	11·18	11·25	11·22
$E_0 = -0.277$ V against NHE *	0·12 M "	0·696	0·710	0·703	10·95	11·08	11·01
	0·20 M "	0·675₅	0·688₅	0·682	10·94	11·06	11·00
	0·01 M Mg(ClO4)2	0·727	0·733	0·730	11·24	11·27	11·26
	0·02 M "	0·682	0·708	0·695	10·99	11·21	11·10
		$r=0.0442$ cm	$r=0.0487$ cm	average	$r=0.0442$ cm	$r=0.0487$ cm	average
	0·02 M LiClO4	0·757	0·739	0·748	11·07	10·87	10·97
	0·04 M "	0·740	0·740	0·740	11·07	11·19	11·13
	0·08 M "	0·722	0·729₅	0·726	11·12	11·11	11·12
	0·12 M "	0·689	0·698	0·694	10·90	10·99	10·95
		$r=0.0437$ cm	$r=0.0480₅$ cm	average	$r=0.0437$ cm	$r=0.0480₅$ cm	average
0·002 M MnSO4	0·04 M LiCoO4	1·778	1·788	1·783	8·03	8·07	8·05
	0·08 M "	1·809	1·809	1·809	8·02	8·06	8·04
$E_0 = -1.050$ V against NHE *	0·02 M Mg(ClO4)2	1·763	1·784	1·774	7·83	7·89	7·86

* NHE = normal hydrogen electrode.

and 4 % for the $Mg(ClO_4)_2$ solutions.   With the corrections as outlined in eqn. (4) and (5), the accuracy of the αn_a values is estimated to better than 1 %.

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