

be obtained for bismuth and mercuric ions for the conditions studied.

The values reported as "Cottrell-absolute"³⁻⁵ employing physically measured or apparent electrode areas show spreads of 14, 21 and 22%. Skobets and Kavetskii's⁹ assumption that equation 2 could be employed using a spherical electrode with diffusion times limited to 20 seconds, seems doubtful. The values marked "Pt wire rel. to Pb" have been calculated from data of Laitinen¹⁰ cited in Kolthoff and Lingane¹¹ for diffusion to a stationary platinum wire micro-electrode using the relation

$$i_d = knDC$$

These calculations were based on our measured value for lead ion, Table II, since data for cadmium ion were not given. Some doubt attends the validity of this procedure since the diameter of the platinum wire may not have adequately exceeded the effective diffusion layer thickness. The chronopotentiometric data of Reilley, Everett and Johns⁷ permits the calculation of a D -value for lead ion using cadmium as standard of reference. Three of the values cited are derived from diaphragm cell measurements where KCl was used for calibration.⁷ Two values are cited which are derived from an absolute method using a capillary cell

(9) E. M. Skobets and N. S. Kavetskii, *Zhur. Fiz. Khim.*, **24**, 1486 (1950); *C. A.*, **45**, 5541 (1951).

(10) H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, **45**, 1079 (1941).

(11) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Vol. I, Interscience Publishing Co., Inc., New York, N. Y., 1952, pp. 409-411.

technique with radiochemical tracers for measurement.^{12,13}

The measured diameter of the linear diffusion column in the Cottrell cell is 4.00 mm., giving a calculated exposed area of the platinum electrode of 0.1257 cm.². Recalculating the data of the present study in terms of this measured area yields diffusion coefficients which are 28% higher than those based on the cadmium calibration. Conversely, calculation of the "effective" electrode area from the data on cadmium ion gives 0.1427 cm.² which is 13% higher than the area defined by the diffusion cylinder. The large discrepancy between "measured" and "effective" areas could involve edge effects, curvature of the platinum foil, surface roughness factors, etc. The resulting amplified difference between "absolute" and "calibration" Cottrell diffusion coefficient measurements justifies the significance of the present study and merits further consideration. Tentatively, at least, the present "calibration" values seem to be reasonable in every case, and the evident magnitude of the variables involved in an absolute specification of area would seem to account for much of the existing poor agreement between absolute measurements.

One of the interesting and useful applications of a set of reliable diffusion coefficient data, of course, will be to permit an experimental test of the relative merits of the numerous proposed modifications of the Ilkovic equation.

(12) J. H. Wang, *THIS JOURNAL*, **76**, 1528 (1954).

(13) J. H. Wang and F. M. Polestra, *ibid.*, **76**, 1584 (1954).

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The Empirical Evaluation of the Constant in the Modified Ilkovic Equation¹

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A constant for the modified Ilkovic equation is evaluated from polarographic data obtained with the d.m.e. for a number of electroactive ions whose diffusion coefficients have been determined under actual polarographic conditions. The value of 31.3 ± 1.6 was obtained which compares favorably with those calculated in the same manner from existing polarographic data and with values recently derived from theoretical considerations. This favorable agreement suggests a modified Ilkovic equation for the average diffusion current of the form $i_d = 607nC D^{1/2} m^2 / t^{3/2} \epsilon (1 + 31.3 D^{1/2} m^{-1} / t^{1/2} \epsilon)$.

Introduction

The exact value of the constant A in the modified Ilkovic equation for the average diffusion current observed at the dropping mercury electrode

$$i_d = 607nCD^{1/2}m^2/t^{3/2}\epsilon(1 + AD^{1/2}m^{-1}/t^{1/2}\epsilon) \quad (1)$$

has been the subject of considerable controversy. Values ranging from 17 to 39 have been derived from theoretical considerations by several investigators²⁻⁶ with little conclusive agreement obtained

(1) Taken from the Ph.D. thesis by Daniel J. Macero, University of Michigan, 1958.

(2) J. J. Lingane and B. A. Loveridge, *THIS JOURNAL*, **72**, 438 (1950).

(3) H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

(4) T. Kambara and I. Tachi, *Bull. Chem. Soc. Japan*, **25**, 284 (1952).

(5) J. Koutecky, *Czechoslov. J. Phys.*, **2**, 50 (1953).

(6) H. Matsuda, *Bull. Chem. Soc. Japan*, **26**, 342 (1953).

between theory and observation for any one value. Since a rigorous derivation which would take into account all the conditions encountered at the d.m.e. would be so unwieldy as to be of little practical use and since the simplifying assumptions always required have thus far yielded inconclusive results, an empirical approach would seem to offer a practical method of resolving this dilemma. This would require the use of equation 1 and experimentally determined values for the average diffusion current i_d , the drop time t , the rate of mercury flow m , the concentration C , and the diffusion coefficient D , of polarographically active substances.

It is known⁷ that in most cases a significant difference exists between the actual diffusion coefficient determined in the presence of excess sup-

(7) See, for example, D. J. Macero and C. L. Rulfs, *THIS JOURNAL*, **81**, 2942 (1959).

porting electrolyte and the corresponding calculated infinite dilution value. Such differences could account for the failure of earlier empirical approaches based on infinite dilution D values to yield a conclusive value for A .

The present investigation is concerned with the evaluation of a constant for the modified Ilkovic equation using data for a number of polarographically active ions whose diffusion coefficients have been determined under actual polarographic conditions. With the aid of these D values and corresponding polarographic data gathered from various sources an "experimental" constant is obtained and is compared with those derived from theory.

Experimental

The preparation of standard solutions of Cd^{++} , Pb^{++} , Tl^+ , Cu^{++} and $\text{Fe}(\text{CN})_6^{-3}$ in 0.1 M KCl ; Ag^+ in 0.1 M KNO_3 ; Bi^{+++} in 0.5 M HCl , and Hg^{++} in 0.1 M HNO_3 is described in a previous article.⁸ All polarograms were taken with a Sargent Model III Polarograph. Residual current polarograms were also determined for each background solution. A mercury pool was used as the reference electrode in an H-type polarographic cell. All measurements were carried out at $25.00 \pm 0.05^\circ$. Nitrogen gas, presaturated with water vapor, was bubbled through each test solution to remove dissolved oxygen.

The d.m.e. used had an $m^2/t^{3/2}$ value of 2.182 $\text{mg.}^2/\text{sec.}^{-1/2}$ and an $m^{-1}/t^{1/2}$ value of 0.942 $\text{mg.}^{-1}/\text{sec.}^{1/2}$ at -0.50 volt vs. the mercury pool in 0.1 M KCl .

Results and Discussion

Table I gives the average values for the constant A for each substance studied. Those for cadmium, lead, silver, cupric and thallos ions are the average of five determinations each, that for bismuth, four, and those for ferricyanide and mercuric ions, one. In Table II are shown typical

TABLE I
EMPIRICAL VALUES OBTAINED FOR THE MODIFIED ILKOVIC CONSTANT

Substance	A
Cd^{++} in 0.1 M KCl	30.4
Pb^{++} in 0.1 M KCl	32.0
Cu^{++} in 0.1 M KCl	27.8
Tl^+ in 0.1 M KCl	34.5
Ag^+ in 0.1 M KNO_3	31.0
Bi^{+++} in 0.1 M HCl	32.0
Hg^{++} in 0.1 M HNO_3	(10.6)
$\text{Fe}(\text{CN})_6^{-3}$ in 0.1 M KCl	(8.2)
Av.	31.3 ^a

^a Excluding the values for Hg^{++} and $\text{Fe}(\text{CN})_6^{-3}$ which were based on single determinations.

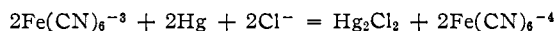
TABLE II
CALCULATION OF THE MODIFIED ILKOVIC EQUATION CONSTANT FROM POLAROGRAPHIC DATA

Substance	Exptl. D ($\text{cm.}^2/\text{sec.} \times 10^6$)	Concn. (mmol./l.)	Current ($\mu\text{a.}$)	A
Cd^{++} in 0.1 M KCl	0.700	1.398	10.41	29.9
Pb^{++} in 0.1 M KCl	.862	0.995	8.40	31.1
Cu^{++} in 0.1 M KCl	.628	1.906	13.57	30.8
Tl^+ in 0.1 M KCl	1.58	1.212	7.14	31.8
Ag^+ in 0.1 M KNO_3	1.38	1.426	7.78	31.1
Bi^{+++} in 0.5 M HCl	0.710	0.976	11.38	33.1
Hg^{++} in 0.1 M HNO_3	.778	1.380	10.48	(10.6)
$\text{Fe}(\text{CN})_6^{-3}$ in 0.1 M KCl	.832	1.575	6.15	(8.2)

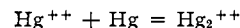
(8) J. J. Lingane and I. M. Kolthoff, *THIS JOURNAL*, **61**, 825 (1939); **62**, 852 (1940).

polarographic data for each substance and the corresponding calculated value of A .

The values obtained for cadmium, bismuth, lead, silver, cupric and thallos ions are in good internal agreement; all show an average deviation of only 5% from the value of 31.3. The poor agreement exhibited by ferricyanide and mercuric ions may possibly be due to reduction by the mercury, *i.e.*



and



A search of the literature yielded further data for the calculation of A . The values calculated from such data using the experimental diffusion coefficient values obtained by us are given in Table III. Included for comparison are the values of A obtained with the authors' own polarographic measurements.

TABLE III
VALUES OF THE CONSTANT A CALCULATED FROM AVAILABLE POLAROGRAPHIC DATA

Substance	A	Ref.	Remarks
Cd^{++} in 0.1 M KCl	30.4	1	Av. of 5 results
	42.0	8	One result
	16.4	3	Calcd. from I vs. $m^{-1}/t^{1/2}$ plot
Pb^{++} in 0.1 M KCl	24.8	3	Recalcd. by D.J.M. ¹
	32.3	1	Av. of 5 results
	32.8	9	Av. of 6 results
Tl^+ in 0.1 M KCl	18.3	3	From I vs. $m^{-1}/t^{1/2}$ plot
	32.1	3	Recalcd. by Meites ¹¹
	34.1	1	Av. of 5 results
$\text{Fe}(\text{CN})_6^{-3}$ in 0.1 M KCl	34.0	8	One result
	17.4	3	From I vs. $m^{-1}/t^{1/2}$ plot
	35.5	3	Recalcd. by D.J.M. ¹
Ag^+ in 0.1 M KNO_3	8.2	1	One result
	21.2	8	One result
	25.8	10	From I vs. $m^{-1}/t^{1/2}$ plot
Cu^{++} in 0.1 M KCl	31.5	1	Av. of 5 results
	39.5	10	From I vs. $m^{-1}/t^{1/2}$ plot
	27.3	1	Av. of 5 results
	25.2	11	One result

All the values show good agreement with that of 31.3. The A values for ferricyanide obtained from literature data are closer to this value than that calculated from our single run.

Some of the data in Table III were compiled from studies dealing with the variation of the quantity, $i_d C m^2/t^{3/2}$, with the ratio, $t^{1/2}/m^{1/2}$. This was done with the use of a large number of different capillaries with varying drop times and m values. Using the method of least squares each investigator summarized his data for each substance in an empirical equation of the form

$$I = k_1(1 + k_2 t^{1/2}/m^{-1/2}) \quad (2)$$

(9) J. J. Lingane and I. M. Kolthoff, *ibid.*, **61**, 830 (1939).

(10) L. Meites and T. Meites, *ibid.*, **73**, 395 (1951).

(11) I. M. Kolthoff and E. F. Orlemann, *ibid.*, **63**, 2085 (1941).

where

$$I = i_a / Cm^{2/3} t^{1/6}$$

and represents the diffusion current constant defined by the original Ilkovic equation.¹² The quantity, k_1 , corresponds to the intercept of a plot of the I and $t^{1/6} m^{-2/3}$ data and is given by

$$k_1 = 607nD^{1/2} \quad (3)$$

and k_2 by

$$k_2 = AD^{1/2} \quad (4)$$

The values of A were then calculated from the value of k_2 and the experimental diffusion coefficients obtained previously.

The data of Strehlow and von Stackelberg³ for cadmium, lead and thallos ions calculated in this manner all yield the value of approximately 17 for A which is in poor agreement with the value obtained in Table I. Meites and Meites,¹⁰ however, point out that in using Strehlow and von Stackelberg's data for lead ion, it is not possible to obtain the same empirical equation for the variation of I with $t^{1/6} m^{-2/3}$, reported by these authors, and on using the value of k_2 calculated for this ion by Meites and Meites an A value of 32.1 results (Table III). On recalculating the slopes from the data presented for cadmium and thallos ions by Strehlow and von Stackelberg, we also obtained A values more in accordance with the value of 31.3.

In connection with this value the results of Meites and Meites again are of interest. These investigators also obtained empirical equations in the form of (2) above for cadmium and silver ions in 0.1 M KNO_3 , and ferricyanide and iodate ions in 0.1 M KCl . The values of A calculated from their k_2 values for ferricyanide and silver ions and our experimental D values have already been considered in Table III. At the time, however, Meites and Meites estimated the diffusion coefficient in each case from the definition of k_1 given by (3) above and used this to calculate a value of the constant, A . In the same manner, from the results of a study by Lingane and Loveridge¹³ on the systems Pb^{++} in 1 M KCl , and $Zn-(NH_3)_4^{++}$ in 1 M NH_4Cl and 1 M NH_3 , they calculated a diffusion coefficient and an A value for each substance. The mean value of A for these six cases is 31.5 ± 4.6 which is in excellent agreement with the average value of 31.3 found in the present study.

Meites and Meites, however, expressed doubt as to the correctness of the coefficient, 607, in equation 1, since experimental D values available at the time from the work of Kolthoff and Laitinen¹⁴ for ferricyanide and silver ions led to empirical values of 575 and 544 for this constant and on this

(12) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 588 (1943).

(13) J. J. Lingane and B. A. Loveridge, *THIS JOURNAL*, **66**, 1425 (1944).

(14) I. M. Kolthoff and H. A. Laitinen, *ibid.*, **61**, 3344 (1939).

basis they concluded that a modified Ilkovic equation could be represented by

$$i_a = 560nCD^{1/2} m^{2/3} t^{1/6} (1 + 29D^{1/2} m^{-1/3} t^{1/6}) \quad (5)$$

However, the experimental D values obtained by us for silver, ferricyanide and lead ions are more in agreement with those values calculated from equation 4 using the coefficient 607 instead of 560.

Von Stackelberg's modification¹⁵ introduces the

$$i_a = 619nCD^{1/2} m^{2/3} t^{1/6} (1 + 17D^{1/2} m^{-1/3} t^{1/6}) \quad (6)$$

value of 619 to compensate for the "impoverishment effect" which refers to the decrease in current resulting from the lowered concentration of test ion found in the vicinity of successive drops relative to the bulk concentration in the solution. The factor 17 corrects for the "enrichment effect" which results from the fact that a drop does not grow with radial symmetry. This produces an unsymmetrical diffusion layer around the drop and gives rise to an increased current. The present investigation shows that the correction factor of 17 is much too low but cannot evaluate the correctness of any "impoverishment factor," nor clearly divide the relative magnitude of the two constants.

More recent derivations by Kambara and Tachi,⁴ Koutecky⁵ and Matsuda⁶ all retain the factor of 607 in the first term and give values of 29.3, 34, 31.7, respectively, for the second constant. Markowitz,¹⁶ who recently reviewed each derivation critically, concluded that Matsuda's treatment is the most reliable.

Comparison with the value of 31.3 obtained empirically in this study shows good agreement with all of these values, thus the question as to which of these theoretical equations actually represent the current at the d.m.e. must still remain unanswered. However, an equation with the original Ilkovic coefficient of 607 and a best-fit empirical value of 31.3 ($\pm 5\%$) for the constant in the second term is indicated, *i.e.*

$$i_a = 607nCD^{1/2} m^{2/3} t^{1/6} (1 + 31.3D^{1/2} m^{-1/3} t^{1/6})$$

Such an equation can only be recognized, of course, as representing an appropriate expression for the integrated average (or maximal, with minor changes) current flow observed in polarography. It is known to be seriously in error with respect to the instantaneous current flow early in the life of a drop. While considerations of "capillary shielding" seem to be unimportant,¹⁶ the "impoverishment effect" is significant and recent work^{17,18} suggests a dependence of the A factor on t (and thereby, on E) as well as other changes.

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(15) M. von Stackelberg, *Z. Elektrochem.*, **57**, 338 (1953).

(16) J. Markowitz, Ph.D. Thesis, University of Michigan, 1958. A related article with P. J. Elving will appear in *Chem. Revs.*

(17) Hans, Henne and Meurer, *Z. Elektrochem.*, **58**, 836 (1954).

(18) A. Bresle, *et al.*, *Acta Chem. Scand.*, **10**, 935 (1956).