[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Calibrated Cottrell Diffusion Measurements[1]

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Relative Cottrell measurements of the diffusion coefficients of eight ions in various supporting electrolytes are reported. A value of $0.70_0 \times 10^{-5}$ cm.²/sec. was adopted as the diffusion coefficient of cadmium ion in 0.1 *M* KCl. The Cottrell cell was calibrated by a cadmium run prior to each determination. This procedure obviated any necessity for using a physically measured electrode area in the calculations. A 13% difference between measured and effective electrode areas resulting in a 28% difference between "absolute" and "secondary" diffusion coefficients was found in the present study.

Introduction

In polarographic work the difference between the actual diffusion coefficients of m*M* test ions in the presence of excess supporting electrolyte and the calculable infinite dilution values is known to be large in many cases. But far too few reliable measured values have been reported to justify their use in testing equations of interest in polarographic theory.

The general validity of the form of Cottrell's relation for linear diffusion[2]

$$i_t = nFAC(D/\pi t)^{1/2} \qquad (1)$$

where i_t is the instantaneous current observed at any time t and at a plane electrode of area A whose potential is beyond the decomposition potential of an electroactive ion of concentration C and diffusion coefficient D, has been repeatedly confirmed.[3-5] But the agreement between workers on experimentally measured diffusion coefficients based on using the Cottrell technique as an absolute method employing physically measured electrode areas has been very poor. The method is attractive and convenient since electrical parameters are measured and the significant data are obtainable in 10 or 20 minutes. Unlike conductance measurements, the procedure is also applicable to the case of an electroactive ion in the presence of a large excess of indifferent electrolyte.

Cadmium ion is one of the very few ions for which a reasonable number of diffusion coefficient measurements are in good agreement. In the present study, cadmium has been selected as a calibration ion for the Cottrell technique used as a "secondary" measurement of other diffusion coefficients. To the extent, at least, that an "effective" electrode area at a given electrode may be the same for the electrolysis of different ions, any major general discrepancy between apparent and real areas should be overcome.

Experimental

The linear diffusion electrode was fashioned from "Plexiglas" rod in the manner described by von Stackelberg and co-workers.[4] The inside diameter of the diffusion column was 4.00 mm. giving an apparent electrode area of 0.126 cm.². The length of the diffusion column was about 3 cm. Electrical contact is made with a platinum electrode disk positioned at the top of the diffusion column. The entire "Plexiglas" cell is provided with an outer jacket of glass tubing to prevent leakage. After each determination the platinum surface was cleaned with one molar nitric acid and rinsed with distilled water.

The reference electrode was a large mercury pool which is connected to the linear diffusion cell with an agar bridge containing dissolved potassium chloride. A potassium nitrate agar bridge was substituted in the determinations with silver ion. All measurements were made at 25.00 ± 0.05° which temperature was maintained by immersion of the system in the bath of a Wilkens–Anderson Lo-Temp Bath.

The constant voltage applied to the cell was selected from polarograms of the electroactive ion and of the background solutions using a platinum microelectrode and the mercury pool reference electrode.

A Sargent Model III Manual Polarograph was used to supply the constant voltage. The instrument's galvanometer, with a maximum sensitivity of 0.005419 microampere per scale division was used to follow the current changes.

A procedure was devised which permitted the automatic recording of the current–time data by taking advantage of the fact that the galvanometer scale of the Model III is printed on a translucent material on which the galvanometer light image is projected as a bright vertical line. The instrument was rewired so that the galvanometer lamp is in series with a relay activated by a 1 r.p.m. synchronous motor; with each revolution of the motor the lamp circuit is closed and the lamp is on for about 0.5 sec. In subdued light a 1 cm. × 30 cm. strip of bromide paper is taped onto the outside of the galvanometer scale, emulsion side down and covered with a black cloth. Prior to a run the galvanometer scale is printed on the paper by a short exposure with a seven watt bulb placed inside the instrument. On development the current measurements stand out distinctly as a series of dark lines against the galvanometer scale background. Figure 1 is a diagram of the automatic recording circuit.

The solutions were deaerated for 15 minutes by bubbling with purified nitrogen gas presaturated with water vapor at 25° to prevent evaporation of the test solutions.

The solutions studied were Cd^{++}, Pb^{++}, Cu^{++}, Tl^{+}, $Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$ in 0.1 *M* KCl; Ag^{+} in 0.1 *M* KNO_3; Hg^{++} in 0.1 *M* HNO_3; and Bi^{+++} in 0.5 *M* HCl. These solutions were prepared from reagent grade chemicals and were millimolar in concentration of electroactive substances.

The potassium chloride solutions were prepared by weighing out the required amount of $CdCl_2$, $Pb(NO_3)_2$, TlCl and $K_4Fe(CN)_6$, and dissolving these in 0.1 *M* KCl solution and diluting to volume with the necessary 0.1 *M* KCl solution. The ferricyanide solution was prepared by diluting a standard stock solution of $K_3Fe(CN)_6$. The silver and bismuth solutions were prepared similarly from $AgNO_3$ and BiOCl except that these were dissolved in 0.1 *M* KNO_3 and 0.5 *M* HCl, respectively. The mercury solutions were prepared by dissolving the necessary amount of mercury metal in sufficient concentrated nitric acid to react completely with the mercury and yield a 0.1 *M* acid solution after diluting with distilled water.

Residual currents were carefully determined with each type of background solution at appropriate voltage settings. These corrections amounted to from 0.5 to 15% of the limiting currents. With ions having as negative reduction potentials as cadmium and thallium, residual current corrections determined on a clean platinum electrode were always too high and of inferior reproducibility due to hydrogen evolution. In these two cases a cadmium or thallium

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

[2] F. G. Cottrell, *Z. physik. Chem.*, **42**, 385 (1902).

[3] H. A. Laitinen and I. M. Kolthoff, THIS JOURNAL, **61**, 3344 (1939).

[4] M. von Stackelberg, M. Pilgram and V. Toome, *Z. Elekrochem.*, **57**, 342 (1953).

[5] H. Rubin and F. C. Collins, *J. Phys. Chem.*, **58**, 958 (1954).

plated electrode must be used to obtain a valid background correction since appreciable hydrogen overvoltages on the metals actually permits no hydrogen evolution during a run.

Diffusion current constants measured over a period of three months with a given platinum electrode, which was repeatedly cleaned but never disassembled from the Plexiglas cell, showed a standard deviation of about 1%.

Results and Discussion

The equation for linear diffusion to a plane electrode may be written as

$$\frac{i_d t^{1/2}}{C} = K\,NAF(D/\pi)^{1/2} \qquad (2)$$

where i_d is the corrected diffusion current, t the time and C, the concentration of reducible or oxidizable substance. K is a constant for a given ion, electrode, background solution and temperature, and has the units of microamperes × min.$^{1/2}$ × l./mole. K may be called the Cottrell linear diffusion current constant analogous to the Ilkovic diffusion current constant in polarography. The values of K are calculated from current data obtained from linear diffusion experiments after correction for the residual current has been made for each minute of measurement. The average of these values then yields the value for the diffusion current constant of the ion in question for a given electrode, medium and determination. Column 2 of Table I shows the average of the measured values for nine ions. From 5 to 20 runs were made per ion employing various concentrations within the range of 1 to 5 mM. The uncertainties shown represent the standard deviations of the mean.

TABLE I

CALCULATED VALUES OF DIFFUSION COEFFICIENTS AT 25°

Substance	(μa. min.$^{1/2}$ l./mole)	D(cm.^{2}/sec. × 10^5)
Cd^{++} in 0.1 M KCl	5.29 ± 0.001	(0.700 ± 0.005) std.
Pb^{++} in 0.1 M KCl	5.87 ± .024	.862 ± .010
Cu^{++} in 0.1 M KCl	5.01 ± .015	.628 ± .006
Tl^{+} in 0.1 M KCl	3.97 ± .035	1.58 ± .030
$Fe(CN)_6^{-4}$ in 0.1 M KCl	2.62 ± .010	0.687 ± .008
$Fe(CN)_6^{-3}$ in 0.1 M KCl	2.89 ± .020	0.836 ± .013
Ag^{+} in 0.1 M KNO_3	3.72 ± .012	1.384 ± .014
Bi^{+++} in 0.5 M HCl	7.99 ± .042	0.710 ± .009
Hg^{++} in 0.1 M HNO_3	5.59 ± .015	0.782 ± .008

The value $0.70_0 \pm 0.00_5 \times 10^{-5}$ cm.^{2}/sec. was selected as the best available value for the diffusion coefficient of cadmium ion in 0.1 M KCl at 25°. This value represents a weighted average derived from 0.693,[6] 0.700,[7] 0.717[4] and 0.720[8] which are values determined independently and by a variety of methods.

The individual ionic diffusion coefficients were calculated from the corresponding values of the measured linear diffusion current constants using the relation

$$D_{\text{ion}} = (n_{\text{Cd}}/n_{\text{ion}})^2\,(K_{\text{ion}}/K_{\text{Cd}})^2 D_{\text{Cd}}$$

The values obtained for the individual diffusion coefficients along with the estimated errors in each are listed in Table I. These errors were estimated from

$$(\mathrm{d}D/D)_{\text{ion}} = \pm\sqrt{(2\,\mathrm{d}K/K)^2_{\text{ion}} + (2\,\mathrm{d}K/K)^2_{\text{ion}} + (\mathrm{d}D/D)^2_{\text{Cd}}}$$

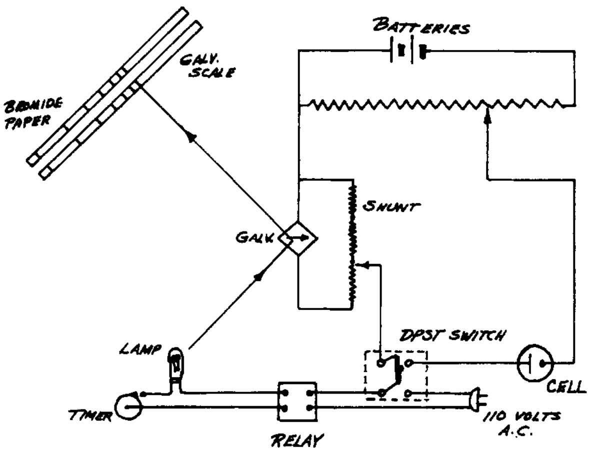

Fig. 1.—Electrolysis circuit and automatic recording apparatus.

where dD and dK refer to the standard deviations of the mean of the appropriate diffusion coefficients and diffusion current constants.

For comparison, values for the diffusion coefficients of each of the substances studies have been collected or calculated from available literature data and are presented in Table II. Also included are the values for the diffusion coefficient at infinite dilution which are calculated from the Nernst expression. No literature D values could

TABLE II

DIFFUSION COEFFICIENTS AT 25° COLLECTED FROM LITERATURE SOURCES

Substance	$D \times 10^5$	Ref.	Remarks
Ag^{+} in H_2O	1.69	Calcd.	
Ag^{+} in 0.1 M KNO_3	1.384	6	Cottrell-relative
	1.74	3	Cottrell-absolute
	1.510	4	Cottrell-absolute
	1.33	11	Pt wire-rel. to Pb
Cd^{++} in H_2O	0.72	Calcd.	
Cd^{++} in 0.1 M KCl	.700	6	Graham method-abs
	.700	7	Diaphragm cell-rel.
	.717	4	Cottrell-absolute
	.76	9	Spherical electrode
Cu^{++} in H_2O	.72	Calcd.	
Cu^{++} in 0.1 M KCl	.628	6	Cottrell-relative
	.617	11	Pt wire-rel. to Pb
$Fe(CN)_6^{-3}$ in H_2O	.89	Calcd.	
$Fe(CN)_6^{-3}$ in 0.1 M KCl	.836	6	Cottrell-relative
	.842	3	Cottrell-absolute
	.67	5	Cottrell-absolute
	.763	4	Cottrell-absolute
	.713	11	Pt wire-rel. to Pb
$Fe(CN)_6^{-4}$ in H_2O	.74	Calcd.	
$Fe(CN)_6^{-4}$ in 0.1 M KCl	.687	6	Cottrell-relative
	.650	3	Cottrell-absolute
	.80	5	Cottrell-absolute
	.717	4	Cottrell-absolute
	.638	11	Pt wire-rel. to Pb
Pb^{++} in H_2O	.98	Calcd.	
Pb^{++} in 0.1 M KCl	.862	6	Cottrell-relative
	.750	7	Diaphragm cell-rel.
	.869	4	Cottrell-absolute
	.970	12	Capillary cell-abs.
	.875	8	Chronopot.-relative
Tl^{+} in H_2O	2.00	Calcd.	
Tl^{+} in 0.1 M KCl	1.58	6	Cottrell-relative
	1.67	7	Diaphragm cell-rel.
	1.84	13	Capillary cell-abs.
	2.02	9	Spherical electrode
	1.67	11	Pt wire-rel. to Pb

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[6] Classical diffusion measurements by Graham's method described in thesis of D. J. Macero.

[7] C. L. Rulfs, THIS JOURNAL, **76**, 2071 (1954).

[8] Calculated from data of C. N. Reilley, G. W. Everett and R. H. Johns, *Anal. Chem.*, **27**, 483 (1955).

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's[9] 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 Laitinen[10] cited in Kolthoff and Lingane[11] 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 Johns[7] 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 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.

[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.

[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 Equation[1]

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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 $i_d = 607ncD^{1/2}m^{2/3}t^{1/6}(1 + 31.3D^{1/2}m^{-1/3}t^{1/6})$.

Introduction

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

$$i_d = 607nCD^{1/2}m^{2/3}t^{1/6}(1 + AD^{1/2}m^{-1/3}t^{1/6}) \quad (1)$$

has been the subject of considerable controversy. Values ranging from 17 to 39 have been derived from theoretical considerations by several investigators[2-6] with little conclusive agreement obtained 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 known[7] that in most cases a significant difference exists between the actual diffusion coefficient determined in the presence of excess sup-

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[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).

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