Precise Measurement of Ionic Diffusion Coefficients with a Hanging Mercury Drop Electrode

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(Received April 19, 1976)

The diffusion coefficient and the product of the charge number of electrode reaction n and the concentration of depolarizer c can be determined simultaneously from the time dependence of the diffusion limiting current observed at a spherical electrode of known size. Nearly ideal spherical diffusion was realized by means of a mercury drop electrode hanging from the tip of a fine glass capillary (0.2 mm, outer diameter) which was kept at constant size by adjusting the mercury head. The diffusion coefficients of thallium(I), cadmium(II), bismuth(III), and hexamminecobalt(III) ions in 0.1 mol dm^{-3} potassium nitrate aqueous solutions were determined at 25 °C. The experimental nc values agreed with the corresponding known values within 3%.

The present paper deals with a method for determining the diffusion coefficients of ions by using a mercury drop electrode hanging from a thin-walled capillary.

The dropping mercury electrode (DME) has been widely used for measuring the ionic diffusion coefficients in solutions containing excess indifferent electrolytes.[1-6] Ikeuchi[4] measured the diffusion coefficients of amminenitrocobalt(III) complexes in potassium nitrate solutions by means of the instantaneous diffusion current observed at the first drops.[7] The diffusion coefficients in the same systems were measured also by the diaphragm cell method.[8] The two sets of data did not agree with each other except for triamminetrinitrocobalt(III). Similar disagreement has been reported in the cases of hydrogen ion[6] and cadmium ion.[9] Since the reason for such a discrepancy was not clear, further investigation was required to know whether the discrepancy reflected a mere experimental artefact or an essential difference in the physical nature of the diffusion processes in the electrochemical and non-electrochemical methods.

For this purpose, the mass transfer process at DME is not simple enough.[10] The effects of depletion[11] and shielding[12] can be circumvented or reduced by the first-drop method[13,7] and by the use of a thin-walled capillary,[3,7] respectively; but streaming of solution caused by the continuously falling drops is inevitable. The polarographic maximum often interferes and necessitates the addition of surfactants, which may alter the diffusion current in an unpredictable way.[1] Besides these experimental complications, the convective diffusion to DME itself is an involved mathematical problem. In spite of considerable theoretical and experimental work devoted to the subject, no general agreement on the details of the mathematical expression for the diffusion current-time relationship of DME has yet been established[10]; different values of diffusion coefficients may be calculated from the same experimental data by using different equations.

With a stationary, hanging mercury drop electrode (HMDE) the situation is much less complicated: the ideal diffusion current-time relationship is strictly described by a simple equation, no polarographic maximum interferes, no streaming of the bulk of solution is caused, and HMDE is as reproducible as DME. A planar electrode may be simpler and, when properly positioned, more stable than HMDE against disturbance due to the convection caused by the density gradient developed in the diffusion layer. However, the spherical electrode has an interesting feature, described below, which is not shared by the planar electrode.

Laitinen and Kolthoff[14] first examined the diffusion current at a spherical platinum electrode. The theoretical equation for spherical diffusion was verified by Shain and Martin[15] with a Gerischer type HMDE. They pointed out the influence of shielding by the glass tip supporting the mercury drop. Kao and Chang[16] made an extensive study on the diffusion at a mercury drop electrode hanging from a fine support and showed that the equation was followed for as long as 20 min in certain particular systems in which the convection due to the density change was expected to be very small. Recently Kojima and Bard[17] also used a fine-tipped Gerischer type HMDE in a.c. polarographic study.

The magnitude of the current $|I_d|$ at time t controlled by the ideal spherical diffusion is given by the following equation:[18,10]

$$|I_d| = FSncD[r^{-1} + (\pi Dt)^{-1/2}] \quad (1)$$

with

$$S = 4\pi r^2, \quad (2)$$

where r is the radius of the electrode; F, the Faraday constant; n, the charge number of the electrode reaction; c and D, the bulk concentration and diffusion coefficient of the depolarizer, respectively. The plot of $|I_d|$ against $t^{-1/2}$ results in a straight line whose intercept A and slope B are given by

$$A = 4\pi FrncD \quad (3)$$

and

$$B = 4\pi^{1/2}Fr^2ncD^{1/2}. \quad (4)$$

If r is known, D and nc can be determined from a single $|I_d|-t$ curve by solving Eqs. 3 and 4. This situation, essentially different from that in the case of the diffusion at DME and planar electrode where these quantities appear always as product $ncD^{1/2}$, implies an interesting application of HMDE.

When n is known or estimated, c and D can be obtained. Hence, the measurement of an $|I_d|-t$ curve

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at HMDE of known size enables one to determine the diffusion coefficient of the species whose concentration is uncertain, or to determine its concentration without referring to any standard solution. Alternatively, n and D can be obtained when c is known, thereby offering a method for evaluating the n values under polarographic conditions. This will be particularly useful in those cases in which the conventional coulometric method fails because of complications due to reactions subsequent to the charge transfer.

The values of n and D can be determined independently by a suitable combination of electrochemical methods; *e.g.*, rotating disk voltammetry and chronopotentiometry,[19] and/or chronoamperometry and stationary electrode voltammetry.[20] However, such a procedure is technically complicated or often limited by the reversibility of the system.

Simultaneous determination of n and D is possible by using a hemispherical[21] or a cylindrical[22] electrode. These methods, however, involve the difficulties inherent to construction of a solid electrode of precise geometry with known surface area. Furthermore, the diffusion current-time relationship at a cylindrical electrode of finite length is too complicated to be described by any simple equation. The usefulness of these electrodes for the accurate determination of diffusion coefficients seems questionable.

In order to realize the ideal spherical diffusion at HMDE, the mercury drop must be small enough to remain practically spherical, and the disturbance of the diffusion layer due to convection and to the shielding by the drop support must be minimized. In other words, the support should be as fine as possible, and the diffusion current should be measured within a relatively short time before the diffusion layer becomes disturbed. These conditions can be satisfied approximately by adequate experimental arrangement.

In the present experiment, the $|I_d|-t$ curves of depolarizer of known n and c were measured, and r was determined from the mass of the mercury drop. By means of Eqs. 3 and 4, D and $(nc)_{obsd}$ were calculated. The value of $(nc)_{obsd}$ should agree with the product of the known n and c. This fact, together with the linearity of the experimental $|I_d|-t^{-1/2}$ plot, provides a test of the extent to which the data are consistent with Eq. 1.

Experimental

Electrode System and Electrolytic Cell. The HMDE and the electrolytic cell system are shown schematically in Fig. 1. The electrode capillary was constructed from a glass capillary, 0.3 mm and 7 mm in inner and outer diameters, respectively. A piece of the capillary was drawn so that a fine capillary tip was formed at one end. The tip was cut at a suitable length. The cut end must be sharp and rectangular when examined under a microscope. A length of the bore of the upper part was constricted in order to provide a suitable slow flow of mercury.[23] A glass sheath with several holes was placed around the fine part. The sheath not only protected the fragile fine tip but also served to reduce mechanical disturbance of the solution in the vicinity of the mercury drop.[3] The mercury reservoir was held by a clamp which could move smoothly between two adjustable stoppers of a heavy stand column. When the electrode was not in use, a minimum

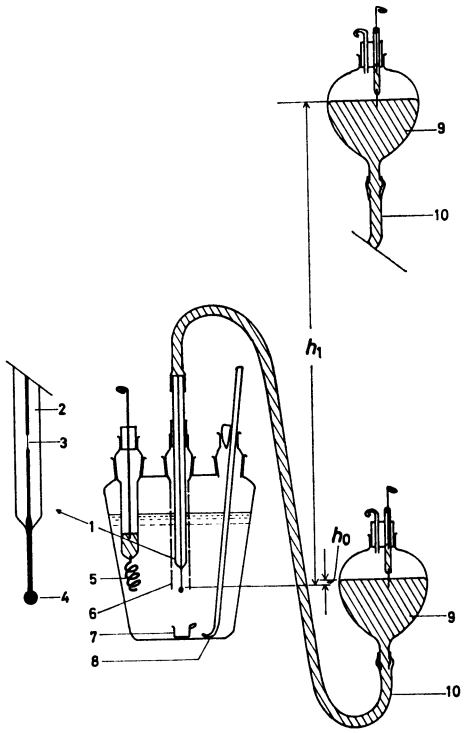

Fig. 1. HMDE and electrolytic cell.
(Reference electrode and nitrogen gas inlet and outlet are not shown.)
1: HMDE, 2: glass capillary, 3: constriction, 4: mercury drop, 5: Pt-spiral counter electrode, 6: glass sheath, 7: glass cup, 8: glass rod, 9: mercury reservoir, 10: Tygon tubing.

mercury head was applied to keep mercury flowing in order to avoid possible clogging. The characteristics of a typical capillary were as follows: radii of the capillary tip, 0.12 mm (outer) and 0.05 mm (inner); mercury flow rate, 6×10^{-2} mg·s^{-1} at mercury head of 40 cm.

The electrolytic cell (capacity, about 100 cm^3) was all of Pyrex. The counter electrode was a spiral of platinum wire, and the reference electrode was a saturated calomel electrode (SCE), which was connected to the electrolytic solution by means of a potassium nitrate bridge with an agar plug. The cell was placed in a thermostated water bath, the temperature of which was checked with a standard mecury thermometer. The temperature fluctuation in the cell solution was about $\pm$0.01 °C.

Instrumental. A potentiostat with a current follower was used. The output signal of the current follower was recorded by a high speed pen recorder (Riken Denshi Co. Ltd., SP-G3; response time, 0.2 s for full scale of 25 cm with auxiliary pen for recording reference time signal). The chart speed (16 mm s^{-1}) was checked by recording a reference signal (1 Hz) generated from a quartz crystal oscillator. The triangular wave generator for linear-sweep voltammetry was constructed according to Tsuji and Takahashi.[24]

Reagents. The purity of mercury was essential: traces of impurity tended to deposit on the constricted part of the capillary and eventually cause clogging. Mercury for polarographic use was repeatedly washed with 3—5% nitric acid and then with distilled water. After being dried, it was distilled under reduced pressure in an all-quartz distillator: the first two thirds of distillate was collected for use.

Thallium(I) nitrate (>99%: Yamada Kagaku Yakuhin, K. K.) was recrystallized from distilled water and dried in a

vacuum oven at 50 °C. Hexamminecobalt(III) nitrate was prepared according to the usual method,[25] recrystallized from dilute acetic acid, and dried over silica gel. The stock solution was prepared by dissolving a weighed amount of the nitrate. Cadmium(II) nitrate stock solution (10.59_3 mol m^{-3}) was prepared by dissolving 0.5953_5 g of the metal (99.999 % Wako Pure Chemical Industries, Ltd.) in reagent grade nitric acid and by diluting the solution to 500 cm^3. Bismuth-(III) nitrate stock solution (5.117_2 mol m^{-3}) was prepared similarly, from 0.5347_0 g of the metal (99.999%, Wako Pure Chemical Industries, Ltd.); but it contained about 0.7 mol dm^{-3} nitric acid in order to prevent hydrolysis. Potassium nitrate (reagent grade) was recrystallized from distilled water. The water used throughout was deionized water distilled in an all glass apparatus (Kinoshita Rikakogyo Co., Ltd., Model KR-70-AN). All the volumetric operations were performed in a water bath controlled at (25±0.1) °C.

Procedures. The hanging mercury drop was formed by letting a new drop grow at a fixed mercury head h_1 for a certain duration of time and then decreasing the head to h_0, the head necessary to balance the back pressure of the mercury drop. The mercury head h_1 was so chosen that a mercury drop 0.4—0.8 mm in diameter was produced in 5—10 min. The value of h_0 was determined for each capillary. The flow rates of mercury m were measured at several different mercury heads. By extrapolating the m-h plot to $m=0$, h_0 was estimated approximately. Then it was adjusted until the peak current of the linear-sweep voltammogram remained constant for 30 min. Once h_1 and h_0 were determined, the two stoppers on the supporting stand were fixed to these positions so that h_1 and h_0 were reproduced.

The cell solution was deoxygenated with nitrogen gas which had been passed through vanadium(II) sulfate solution and then distilled water; during the measurement nitrogen gas was flushed over the cell solution.

The diffusion current was recorded as follows. After a new mercury drop was formed, the lowest positive potential at which practically no electrolysis occurred was applied on it. Then the potential was switched to that at which the diffusion current was measured. These potentials were found by inspecting the d.c. polarogram of the depolarizer in question. After the current-time curve was recorded, the mercury drop was detached and taken out by means of a glass cup and rod (Figs. 1, 7, and 8). After rinsing and drying, it was weighed on a semimicro-balance. The radius r of the drop was calculated by assuming sphericity. The recorded current-time curve was corrected for the residual current, which was measured by repeating the above procedure with the corresponding supporting electrolyte solution.

The value of $|I_d|$ was plotted against $t^{-1/2}$, and A and B were calculated by the least squares method from the linear portion of the plot; deviating points (*vide infra*) were omitted. By inserting the value of r into Eqs. 3 and 4, D and $(nc)_{obs}$ were determined.

Results and Discussion

Some typical $|I_d|-t$ curves and the corresponding $|I_d|-t^{-1/2}$ plots are shown in Figs. 2 and 3, respectively. Two types of deviation are seen: one at shorter times and the other at longer times. The former, observed at $t<1.5$ s in all cases, was caused by the delay in response of the current measuring system, mainly of the recorder. The latter was dependent on the kind and temperature of the sample solution; for example, at 25 °C it began to appear at about 10 s for thallium ion

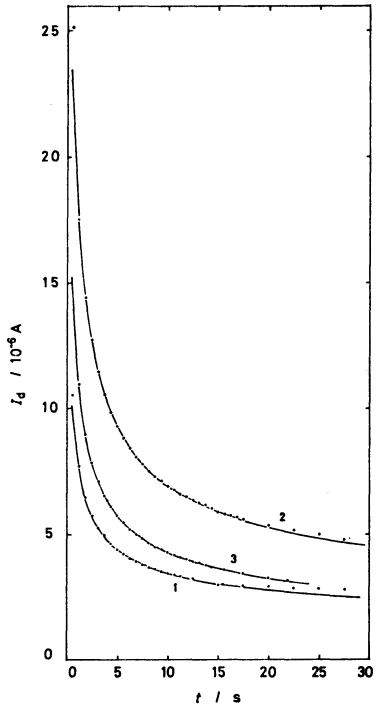

Fig. 2. Typical $|I_d|-t$ curves. In 0.1 mol dm^{-3} KNO_3 solution, at 25 °C.
Points represent observed $|I_d|$ values. Solid lines were calculated by Eq. 1 with A and B obtained from the straight lines in Fig. 3.
1) 1.000_0 mol m^{-3} Tl^+, −0.7 V *vs.* SCE, $r=0.484$ mm.
2) 1.059_3 mol m^{-3} Cd^{2+}, −0.7 V *vs.* SCE, $r=0.674$ mm.
3) 0.5117_2 mol m^{-3} Bi^{3+}, −0.2 V *vs.* SCE, $r=0.646$ mm.

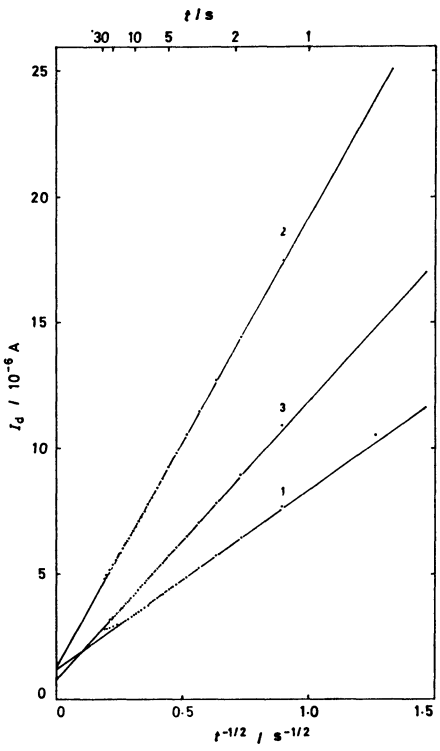

Fig. 3. $|I_d|-t^{-1/2}$ plots.
Conditions, the same as in Fig. 2.

Table 1. Diffusion coefficients in 0.1 mol dm^{-3} KNO_3 at 25 °C determined by thin-walled HMDE

Ion	Number of runs	Applied potential *vs.* SCE / V	r / mm	$(nc)_{calcd}$ / mol m^{-3}	$(nc)_{obsd}/(nc)_{calcd}$	$10^{10}D$ / $m^2\ s^{-1}$	Experimenter	Other data	$10^{10}D$ / $m^2\ s^{-1}$
Tl^+	3	−0.8, −0.9	0.6069	2.000	1.00	19.5	Y.F. (1970)	18.19[a]	
	6	−0.6, −0.7, −0.8, −0.9	0.6053	1.000	1.03 ±0.03	19.1 ±0.8	Y.F. (1970)	18.59[b] 19.9[c]	
	9	−0.7, −1.0, −1.3,	0.6406	1.000	0.997 ±0.024	19.3 ±0.7	H.I. (1971)	18.7[d]	
	7	−0.7, −1.0, −1.3	0.4853	1.000	1.01 ±0.02	19.7 ±0.6	H.I. (1972)		
	2	−1.0	0.4507	1.000	1.02	19.3	H.I. (1972)		
	5	−0.7, −1.0, −1.3	0.6307	1.001	0.999 ±0.028	19.6 ±0.9	K.I. (1972)		
	5	−0.6, −0.7, −0.8	0.6019	0.5000	0.984 ±0.021	20.7 ±1.0	Y.F. (1970)		
average	37				1.00 ±0.01	19.6 ±0.5			
$[Co(NH_3)_6]^{3+}$	2	−0.5, −0.6	0.6064	2.000	0.994	8.19	Y.F. (1970)	7.70[e]	
	3	−0.5, −0.7	0.6035	1.000	0.999	8.00	Y.F. (1970)	8.70[d]	
	1	−0.5	0.6071	0.5000	0.999	8.12	Y.F. (1970)		
average	6				0.997 ±0.031	8.08 ±0.34			
Cd^{2+}	4	−0.7	0.6720	2.119	0.990 ±0.032	7.41 ±0.04	H.I. (1974)	6.90[a], 6.87[b] 7.07[c], 7.24[d]	
Bi^{3+}	7	−0.1, −0.2, −0.4, −0.6	0.6469	1.540	1.01 ±0.01	6.32 ±0.12	H.I. (1974)		

The estimated uncertainty is 95% confidence limit.

a) von Stackelberg, Pilgram, and Toome,[1] with blunt DME, successive drops. b) Štráfelda and Šťastný,[3] with thin-walled DME, successive drops. c) Ikeuchi,[9] with blunt DME, first drop. d) Hashitani, Tanaka, and Tamamushi,[8] with glass diaphragm cell. e) Ikeuchi[4], with blunt DME, first drop.

(1 mol m^{-3}) and at about 17 s for cadmium and bismuth ions. The values for the thickness of the Nernst diffusion layer** at these time points fell around 0.15 mm, suggesting that the deviation was due to convection of the solution around the electrode: as the electrolysis proceeds, the diffusion layer thickens so that the density gradient in the thickening layer causes convection more easily.[14,1,26] Consequently, this deviation was strongly influenced by the concentration of the depolarizer, temperature fluctuation, and mechanical disturbance.

Apart from the above-mentioned deviations, the linearity of the $|I_d|-t^{-1/2}$ plots (Fig. 3) and the agreement between $(nc)_{obsd}$ and the corresponding known value $(nc)_{calcd}$ (Table 1) were satisfactory. The values of D and $(nc)_{obsd}/(nc)_{calcd}$ are independent of the concentration of the depolarizers at less than 2 mol m^{-3}, as shown for thallium(I) and hexamminecobalt(III) ions. Except for cadmium(II) ion, the values of D and $(nc)_{obsd}/(nc)_{calcd}$ are also independent of the potential at which the diffusion current was measured (at some potentials listed in Table 1, the diffusion current was accompanied by large polarographic maxima when DME was used in the absence of maximum suppressor). For cadmium(II) ion, the measurement was successful only at or near −0.7 V *vs.* SCE. At other potentials the current was not reproducible and in many cases $|I_d|-t^{-1/2}$ plot was not linear; if the plot happened to be linear, the value of $(nc)_{obsd}$ did not agree with $(nc)_{calcd}$. The cause of such behavior is not yet clear.

For the sake of comparison, Table 1 includes some D values in 0.1 mol dm^{-3} potassium nitrate solutions obtained by other methods.

Any actual hanging mercury drop cannot be strictly spherical; it is more or less pear-shaped and shielded by the capillary tip. For a small mercury drop hanging from a thin-walled capillary, however, the error due to these factors is not large. For example, microscopic observation[27] of a mercury drop 0.56 mm in radius hanging from a capillary 0.05 mm in inner radius with a wall thickness of 0.07 mm showed that the actual surface exposed to the solution was larger by 1.0% than that of a perfectly spherical drop of the same mass; the increase in surface area due to distortion of the drop shape outweighed the decrease in surface area due to the fact that a mercury thread is attached to the drop. The capillary tip, in this case, occupied 0.9% of the volume of the solution layer which was 0.15 mm thick. The increase in surface area and the shielding by the capillary tip influence the diffusion current in opposite directions and partially compensate each other. The effect of the change in curvature will be smaller, because the curvature is larger at the bottom of the drop and smaller at the top than that of the ideal sphere. Although quantitative analysis of the total effect of these factors on $(nc)_{obsd}$ and D values was too difficult, the

** The thickness of the Nernst diffusion layer δ for spherical diffusion was calculated by the equation:

$$\delta = \frac{SncFD}{|I_d|} = (\pi Dt)^{1/2} - \frac{\pi Dt}{r+(\pi Dt)^{1/2}}.$$

resultant error might scarecely amount to 1%.

Table 1 shows that the error in $(nc)_{obsd}$ is less than 3%. In view of this value the application of the present method to analytical purposes seems hopeful. The error involved in the D values will likely be of the same order of magnitude.

The data for thallium ion in Table 1 show remarkable agreement among the sets of measurements which were carried out by different experimenters on different solutions with different HMDE's over a long period of time. This fact confirms the validity of the present method.

The research was supported in part by a grant from the Ministry of Education. The financial support granted to H. I. by Matsunaga Science Foundation for the present work is gratefully acknowledged. The authors' thanks are due to Sr. Jean Michalec for correcting the manuscript.

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