[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Studies in the Theory of the Polarographic Diffusion Current. VII. The Effect of Drop Weight on the Relationship between the Diffusion Current Constant of Lead and the Drop Time[1]

BY LOUIS MEITES

The diffusion current constant of lead ion in 0.1 *F* potassium chloride–0.1 *F* hydrochloric acid, with and without 0.01% gelatin, has been studied as a function of drop time for capillaries producing drops whose weights varied from 0.3 to 65 mg. These data indicate that the Strehlow–von Stackelberg equation is incapable of representing the effect of drop weight on I, and that t is the true independent variable governing the changes in I.

Introduction

Since the publication by Lingane and Loveridge in 1945 of the first precise data on the variation of the diffusion current constant with drop time,[2] there has been much doubt about the effect of variations in drop weight on the I *versus* t curve. These authors found no detectable influence of drop weight between 4 and 9 mg., but Taylor and Molins,[3] who studied the variation of the "critical drop time"[4] of thallous and cadmium ions with drop weight and gelatin concentration, found large effects over the much wider range of 4–50 mg. Although the "critical drop time" has been shown[5] to be dependent on maximum formation and hence difficult to interpret in terms of the diffusion current alone, the results of Taylor and Molins would appear to indicate at least that the diffusion current at low drop times decreases with increasing drop weight. This, in fact, is fully confirmed by the data here reported. Their conclusion that, in solutions containing gelatin, the diffusion current constant is independent of drop time above this "critical drop time" is, however, untenable in the face of a number of more precise studies.[5–9]

The present investigation was undertaken in order to discover whether the conclusions earlier drawn concerning the validity of the Ilkovic equation in gelatin-free solutions[10] and of the Strehlow-von Stackelberg equation[7,8] in solutions containing 0.009% gelatin[5] was also applicable to drops of widely varying weights. Lead ion was selected to allow an estimation of the effect of supporting electrolyte by comparison with the data of Lingane and Loveridge.[2]

Experimental

The apparatus and technique have been described elsewhere.[5,9] Measurements were made at −1.00 v. *vs.* S.C.E.

Capillaries delivering 7–12 mg. drops were of two types. One was cut from Corning marine barometer tubing, of which three different lots were used. Results apparently identical with these were secured with capillaries drawn from thermometer tubing, cut near the center of the constricted portion, and used small end down; this is the conventional "hand-drawn capillary."

Very small drops, weighing 0.3–0.8 mg., can be secured by a simple modification of this second type. A capillary prepared as described above is bent at two right angles into a ⊔ shape. The small end of the capillary, which then points straight up, is again bent at a right angle a centimeter or so from the tip so that it projects horizontally into the solution. In this range, short drop times are best secured with an L-shaped capillary.

The 16–25 mg. drops were produced by capillaries made in the following manner: a suitable length of thermometer tubing is heated and drawn as for a conventional hand-drawn capillary, but it is then cut, not in the center of the constricted portion, but a few centimeters below it, in the unconstricted part of the tube. The resulting capillary is essentially two conventional capillaries joined at their tips. Occasionally a conventional capillary will give drop weights in this range (*e.g.*, capillaries H and J in the earlier work[9,10]) but in general this procedure is incomparably simpler and more reliable.

It was thought that still larger drops could be secured by further increasing the area of the capillary tip. A number of capillaries were made by sealing a length of 0.2–0.5 mm. capillary tubing to a piece of marine barometer tubing which was in turn attached to a stand tube. Such capillaries invariably gave unsatisfactory results, as did others which flared out just above the tip; this is conveniently done by cutting a thermometer a few tenths of a millimeter below the top of the bulb. Drops weighing 50–600 mg. are easily secured with such capillaries, but they are quite unsuited to the present purpose. The drop is approximately spherical during the first few instants of its life, but it becomes more and more cylindrical as it grows, and it (usually with the first type of capillary, and invariably with the second) breaks into two drops when it falls, leaving behind it a relatively large residual drop. As all diffusion current theory assumes that the drop is nearly spherical throughout its life, it is plain that data on drops as badly distorted as these would cast little light on the theory.

After many unsuccessful attempts, capillaries which gave large drops that appeared accurately spherical under 14 × optical magnification were finally secured by the following method. An intact thermometer was heated below the top of the mercury thread and slowly pulled out, thus giving, as a result of the thermal expansion of the mercury, a long uniform capillary with heavy walls and a relatively large bore. The thermometer was cut near the center of the constricted portion, and the piece terminating in the bulb was discarded. The other piece was heated some distance above the first constriction, then pulled out to a very small diameter. The second constriction was not near its center and the capillary was used with the larger lumen at the bottom. Such capillaries are extremely sensitive to vibration, but under optimum conditions the values of m and t are generally reproducible to ±0.05% and the drops appear entirely normal.

These procedures have been given in some detail because the construction of the capillary may exert considerable influence on the results. We spent much time on the design of these capillaries, and it is thought that an outline of the methods used will be of much help, not only in the interpretation of our results, but to anyone wishing to duplicate any part of the work.

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(1) Tables I–VIII, summarizing data on I as a function of m and t, and Table IX, listing height corrections for the sixteen capillaries used, are available as Document 3233 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.80 for photocopies (6 × 8 inches) readable without optical aid.

(2) J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **66**, 1425 (1945).

(3) J. K. Taylor and E. E. Molins, *Anales real soc. espan. fis. y quim.*, **45B**, 507 (1949); *C. A.*, **44**, 4349 (1950).

(4) F. Buckley and J. K. Taylor, *J. Research Natl. Bur. Standards*, **34**, 97 (1945).

(5) L. Meites and T. Meites, THIS JOURNAL, **72**, 3686 (1950).

(6) B. A. Loveridge, Ph.D. Thesis, Harvard University, 1947.

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

(8) H. Strehlow and M. v. Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

(9) L. Meites and T. Meites, THIS JOURNAL, **73**, 395 (1951).

(10) L. Meites, *ibid.*, **73**, 1581 (1951).

Lead nitrate was twice recrystallized from very dilute nitric acid and was dried at 120°. Recrystallized potassium chloride was used in the preparation of the 0.1 *F* potassium chloride–0.1 *F* hydrochloric acid used throughout as supporting electrolyte. The lead concentration was always between 0.5 and 1.2 millimolar. All measurements were made at 25 ± 0.02°.

Data and Discussion

mt = 7–12 mg.—Tables I and II[1] list data on i_d, m and t for capillaries giving drop weights between 7 and 12 mg. The values of the diffusion current constants calculated from these data are plotted against the drop time in Figs. 1 (no gelatin) and 2 (0.009% gelatin), respectively.

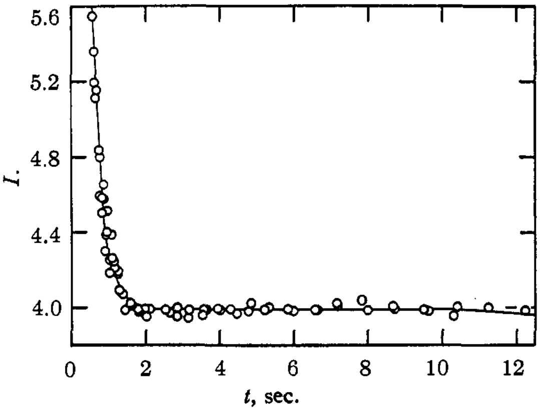

Fig. 1.—Variation with the drop time of the diffusion current constant of lead in 0.1 *F* potassium chloride–0.1 *F* hydrochloric acid with 7–12 mg. drops.

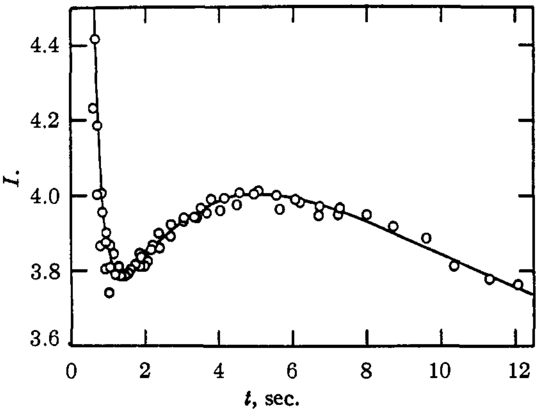

Fig. 2.—Variation with the drop time of the diffusion current constant of lead in 0.1 *F* potassium chloride–0.1 *F* hydrochloric acid–0.009% gelatin with 7–12 mg. drops.

In the absence of gelatin, the curve (Fig. 1) is substantially identical with that shown[10] to be typical for solutions containing no maximum suppressor. At drop times between 1.4 and 10.5 sec., I is constant and equal to 3.992 ± 0.013 (0.33%). For silver, cadmium, ferricyanide and iodate ions the corresponding limits of constancy of I with 7–12 mg. drops were 1.5–6.5, 1.5–6.5, 2.0–7.6 and 1.9–8.0 sec.[10]. It is apparent that the nature of the ion influences the limits of the region in which I is independent of t. The only safe generalization is that, *in the absence of gelatin, I may be expected to be independent of t between 2 and 6 sec.* for a substance whose I–t curve is normal (*i.e.*, if maximum formation does not persist up to abnormally high drop times, as it does with hydroquinone[6] and bismuth[5]). The three ions (cadmium, iodate and lead) thus far studied in this supporting electrolyte have given different values of these limits, showing that the nature of the medium is not the primary cause of these variations.

In the presence of 0.009% gelatin, the diffusion current constants in this medium are in excellent agreement with those found by Lingane and Loveridge[2] for lead ion in slightly acidic 1 *F* potassium chloride containing 0.01% gelatin. On the scale of Fig. 2 their values are nearly indistinguishable from ours, but they are shown on Fig. 3 (as solid circles), which is a Strehlow–von Stackelberg plot of I *versus* $t^{1/6}/m^{1/3}$. The data appear to conform to an equation of the form $I = k_1[1 + k_2 (t^{1/6}/m^{1/3})]$ for values of $t^{1/6}/m^{1/3}$ between 0.52 and 1.10, which are in fair agreement with the limits for other ions.[9] Within this range our data give 3.572 and 0.111 for k_1 and k_2: a similar recalculation of the data of Lingane and Loveridge gave[11] 3.596 and 0.094. The effect of supporting electrolyte is hence relatively small, and the agreement of these values lends additional weight to the pioneer work of Lingane and Loveridge.

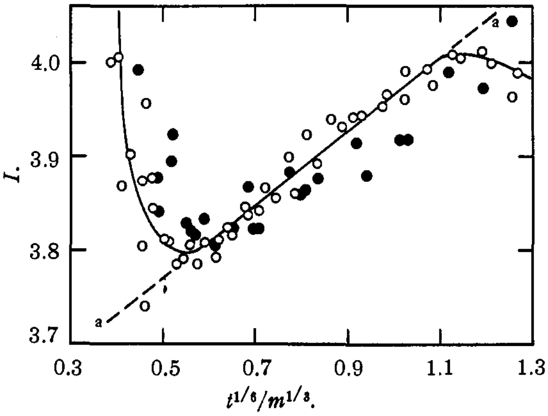

Fig. 3.—Variation with $t^{1/6}/m^{1/3}$ of the diffusion current constant of lead in 0.1 *F* potassium chloride–0.1 *F* hydrochloric acid–0.009% gelatin with 7–12 mg. drops. The data of Lingane and Loveridge[2] are plotted as solid circles.

The present data show that if, in the above equation, $k_1 = 607\ nD^{1/2}$ and $k_2 = AD^{1/2}$, D for lead ion in this medium is 8.66×10^{-6} cm.^{2}/sec. and A is 37.6. This value of A is, in accord with our earlier observation,[9] much more nearly equal to the figure 39 proposed by Lingane and Loveridge[7] than to the value 17 secured by Strehlow and von Stackelberg.[8]

mt = 16–25 mg.—Some incomplete data previously secured with two capillaries indicated that, at drop times above 6 sec., the rate of decrease of I with increasing t was abnormally small with drops weighing between 15 and 27 mg.[9,10] This is confirmed by the data in Tables III and IV, which are plotted in Figs. 4 and 5. The effect is especially marked in the presence of gelatin: I begins to fall off at 6.0 sec. with 7–12 mg. drops, but only at 11.5 sec. with 16–25 mg. drops.

At drop times above 2.0 sec., the average value of

[11] Ref. 9, footnote (11).

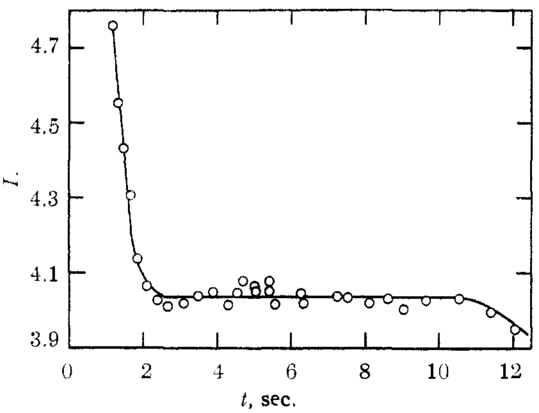

Fig. 4.—Variation with the drop time of the diffusion current constant of lead in 0.1 *F* potassium chloride-0.1 *F* hydrochloric acid with 16-25 mg. drops.

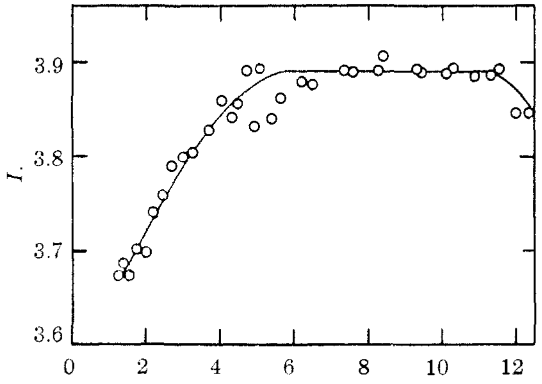

Fig. 5.—Variation with the drop time of the diffusion current constant of lead in 0.1 *F* potassium chloride-0.1 *F* hydrochloric acid-0.009% gelatin with 16-25 mg. drops.

I in the absence of gelatin is 4.039 ± 0.017 (0.43%). The small difference between this and the value secured with the smaller drops is in the direction that would be expected from the fact that the drops here must be slightly more pear-shaped and therefore must have larger areas than their smaller counterparts. However, a statistical test of the data shows that the difference is not significant on the 10% level of confidence.

The results in the presence of gelatin are somewhat more interesting from a theoretical point of view. Within the drop time range of most general practical interest (1.5-6 sec.), the diffusion current constant-drop time curve in Fig. 5 is roughly parallel with that in Fig. 2. Let us, however, consider points on the two curves with identical drops times of 9.0 sec. When $mt = 8$ mg., the value of $t^{1/6}/m^{1/3}$ will be about 1.51, which corresponds to a point well beyond the peak of a Strehlow-von Stackelberg plot (compare Fig. 3). But when $mt = 20$ mg., $t^{1/6}/m^{1/3}$ will be 1.11. This should give a point very near the peak of the curve, but in actuality it is found that the diffusion current constants in the two cases are nearly identical. Such a plot for the data of Fig. 5 gives a curve displaced considerably toward the left from that shown in Fig. 3, and in addition the slope of the relatively poorly defined straight-line portion is not in agreement with that given above. Therefore it would appear that the Strehlow-von Stackelberg equation is incapable of accounting for the effect of drop weight on the diffusion current, and the fact that the diffusion current constant-drop time curves are so nearly parallel for the two cases shown that it is indeed the drop time, and not $t^{1/6}/m^{1/3}$, which is the true independent variable governing the changes in *I*.

This is by no means a new conclusion: Loveridge years ago wrote[12] ". . . *t* is the controlling factor of the diffusion current constant variations." In the present case its validity depends on the assumption that the 8- and 20-mg. drops are geometrically similar, for otherwise these differences might be due to a lack of proportionality between the area of the drop and its volume. A comparison of the data in the presence of gelatin shows that the error introduced by this assumption must be small.

$mt = 60$–70 mg.—In the absence of gelatin, the diffusion current constant with 60-70 mg. drops (Table V) rises rapidly from 3.6 at $t = 0.9$ sec. to an average value of 3.995 between 3.8 and 5.8 sec., and then falls slowly to 3.95 at $t = 8$ sec. (Fig. 6). Although the maximum value of *I* is equal to that found in the same range with 7-12 mg. drops, the diffusion current constants with the larger drops are everywhere else lower than those

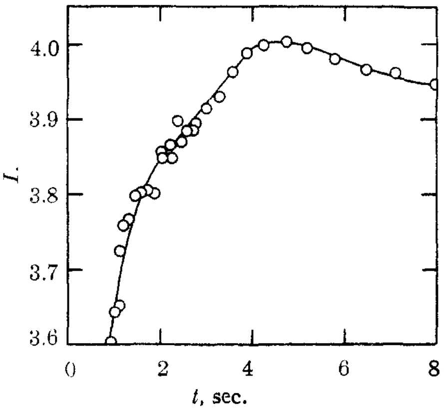

Fig. 6.—Variation with the drop time of the diffusion current constant of lead in 0.1 *F* potassium chloride-0.1 *F* hydrochloric acid with 60-70 mg. drops.

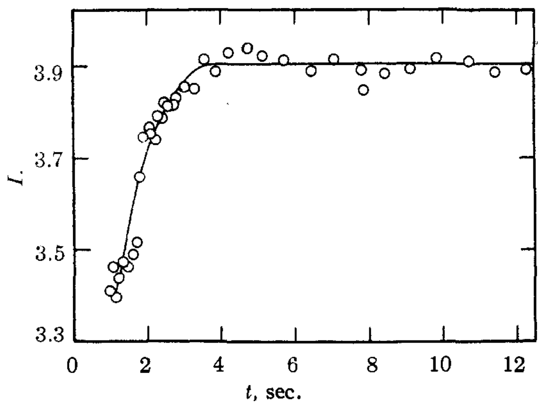

Fig. 7.—Variation with the drop time of the diffusion current constant of lead in 0.1 *F* potassium chloride-0.1 *F* hydrochloric acid-0.009% gelatin with 60-70 mg. drops.

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(12) Ref. 6, p. 110.

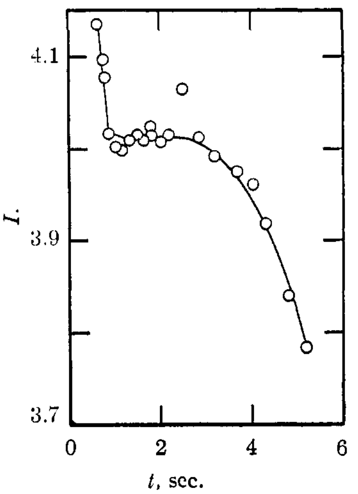

Fig. 8.—Variation with the drop time of the diffusion current constant of lead in 0.1 *F* potassium chloride–0.1 *F* hydrochloric acid with 0.3–0.8 mg. drops.

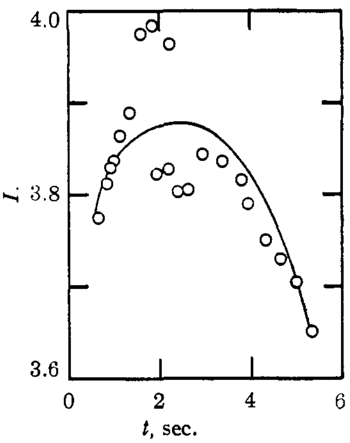

Fig. 9.—Variation with the drop time of the diffusion current constant of lead in 0.1 *F* potassium chloride–0.1 *F* hydrochloric acid–0.009% gelatin with 0.3–0.8 mg. drops.

found with normal capillaries: the maximum difference found is nearly 25%, at 0.9 sec. With 0.009% gelatin (Table VI and Fig. 7) the curve is almost identical with that for the 16–25 mg. drops, but no pronounced decrease of *I* is observed even at drop times as high as 14.7 sec. A comparison of Figs. 6 and 7 shows that *I* is always higher in the absence of gelatin, but that the difference decreases with increasing drop time. A reasonable extrapolation of the curve in Fig. 6 indicates that the values with and without gelatin may become identical at drop times above about 10 sec., but the evidence is not conclusive.

It would certainly be expected that both the pendulous shape, which must be more pronounced in drops of this size, and the extremely high rates of flow of mercury into the drop (as high as 77.5 mg./sec.), which must impart considerable turbulence to the drop–solution interface, would be responsible for higher diffusion current constants than those found with smaller drops. Why this expectation is not confirmed is very difficult to explain. Apparently the current corresponding to the normal value of *I* would require the reduction of more lead ion than is capable of diffusing up to the electrode surface in the relatively much shorter time available.

mt = **0.3–0.8 mg.**—In the absence (Table VII and Fig. 8) but not in the presence (Table VIII and Fig. 9) of gelatin, the diffusion current constants measured with capillaries producing very small drops are somewhat higher than with 7–12 mg. drops. Furthermore, although all the other evidence indicates that the position of the minimum in the *I–t* curve in the presence of gelatin shifts to longer drop times as *mt* decreases, there is no minimum in Fig. 9 down to a drop time of 0.66 sec. In the absence of any reasonable interpretation of these facts, they are presented here without further discussion.

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Polarographic Studies of Metal Complexes. V. The Cadmium(II), Zinc(II) and Iron(III) Citrates

BY LOUIS MEITES

Data are given on the effects of *p*H and supporting electrolyte concentration on the polarographic characteristics of cadmium, zinc and ferric iron in sodium, potassium and ammonium citrate solutions.

Introduction

The development of widely applicable methods of polarographic analysis requires a detailed knowledge of the characteristics of the waves of a large number of ions in numerous different supporting electrolytes. With the aid of such information, it should be possible, by employing suitable combinations of complexing ions, to secure well-defined waves for each of the ions of common interest in the presence of any impurities, and this with a minimum of preliminary chemical or other separations.

The present series was undertaken with the aim of securing a portion of the large mass of systematic data necessary to this end.

Experimental

The apparatus and experimental technique have been described previously.[1]

Data and Discussion

The Cadmium(II) Citrates.—In potassium or sodium citrate solutions at concentrations between 0.05 and 0.5 *F*,

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[1] L. Meites, THIS JOURNAL, **71**, 3249 (1949).