[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Studies in the Theory of the Polarographic Diffusion Current. IV. Diffusion Current Constants of Some Ions in the Absence of Gelatin[1]

BY LOUIS MEITES

Using capillaries producing 7–16 mg. drops, the diffusion current constants of four ions in various media in the absence of gelatin were found to be independent of drop time between about 2 and 7 sec. It is concluded that the relationship between diffusion current and capillary characteristics expressed by the Ilkovič equation is an accurate representation of the phenomena occurring at the dropping electrode under these conditions. Explanations are suggested for the different forms of the *I versus t* curve thus far observed.

Few precise data on the variation of the diffusion current constant with drop time in the absence of gelatin are available. In view of an earlier proof that gelatin causes an important change in the nature of this dependency,[1a] it appeared desirable to attempt to establish a characteristic *I versus t* curve in the absence of a maximum suppressor, as has been done in the presence of 0.01% gelatin.[2–4]

Experimental

The data here presented were secured concurrently with, and by the same technique as, those reported in an earlier paper.[4] All measurements were made at −1.00 v. *vs.* S.C.E., except those on silver ion, for which the applied potential was −1.50 v. Figure 1 demonstrates the necessity for selecting a potential considerably more negative than −1.00 v. for the silver measurements.

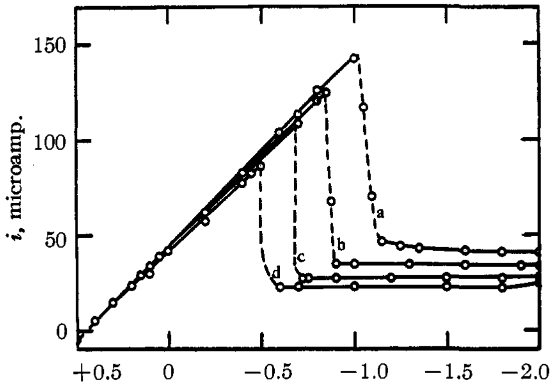

Fig. 1.—Polarograms of 4.5 millimolar silver in 0.1 *F* potassium nitrate. The drop time at −1.00 v. *vs.* S.C.E. was (a) 0.9, (b) 1.5, (c) 2.3 and (d) 3.7 sec.

Values of the "mercury 'head'" reported in this and preceding papers are the measured values of the elevation of the mercury meniscus above an arbitrary reference point. They are, therefore, less than the true applied pressures by an amount varying from 7.7 to 30.4 cm., depending on the length of the capillary. Dr. John K. Taylor[5] has kindly pointed out that this convention, used also by Lingane and Loveridge,[2] tends to confuse the relationship between the forward and back pressures acting on the drop. The appropriate corrections are listed in an accompanying table.[1]

Data and Discussion

Values of the diffusion current constants of silver and cadmium in 0.1 *F* potassium nitrate, ferricyanide in 0.1 *F* potassium chloride, and iodate in 0.1 *F* potassium chloride and 0.1 *F* hydrochloric acid are plotted as functions of *t* in Figs. 2–5. These curves are uniformly characterized by a rapid fall of *I* with increasing *t* at drop times below 1.5–2.0 sec., then a plateau extending to about 7 sec., followed by a much slower decrease as *t* is increased up to the highest values used in each case.

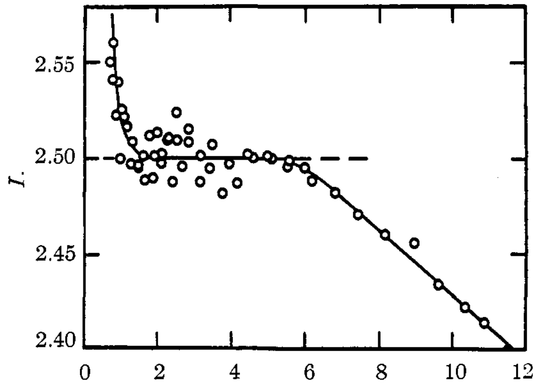

Fig. 2.—Diffusion current constant of silver in 0.1 *F* potassium nitrate as a function of drop time.

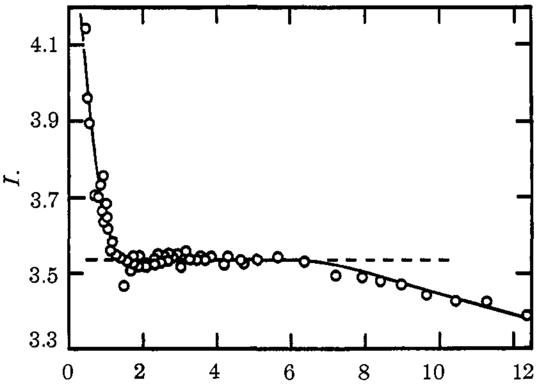

Fig. 3.—Diffusion current constant of cadmium in 0.1 *F* potassium nitrate as a function of drop time.

The initial portions of the curves, both in the presence and in the absence of gelatin, seem to be adequately explained by the stirring phenomenon invoked by Lingane and Loveridge[2] and recently termed the "rinse effect" by Strehlow and von Stackelberg.[6] This interpretation would indicate that the "diffusion" current in this region includes a

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[1] For tables listing values of the capillary characteristics and diffusion current constants for the four ions discussed in this paper order Document 3026 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $0.70 for photocopies (6 × 8 inches) readable without optical aid.

[1a] L. Meites and T. Meites, THIS JOURNAL, **72**, 3686 (1950).

[2] J. J. Lingane and B. A. Loveridge, *ibid.*, **66**, 1425 (1944).

[3] B. A. Loveridge, Ph.D. Thesis, Harvard University, 1947.

[4] L. Meites and T. Meites, THIS JOURNAL, **73**, 395 (1951).

[5] J. K. Taylor, private communication.

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

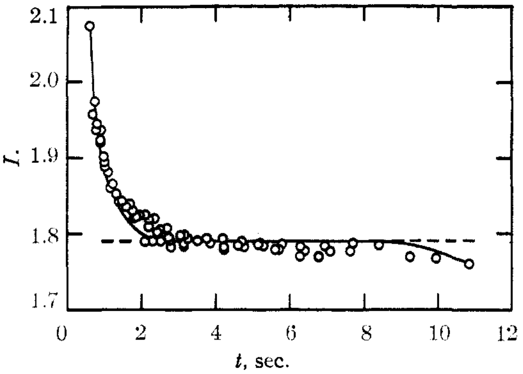

Fig. 4.—Diffusion current constant of ferricyanide in 0.1 F potassium chloride as a function of drop time.

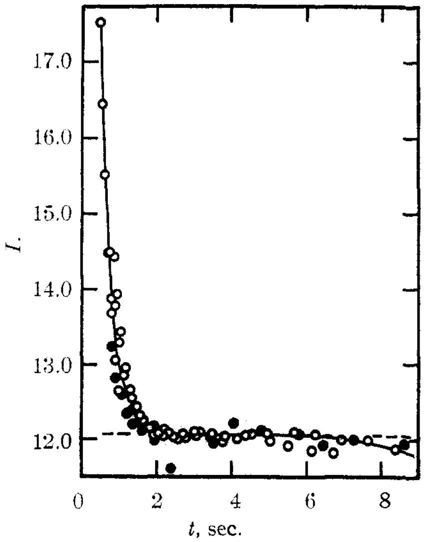

Fig. 5.—Diffusion current constant of iodate in 0.1 F potassium chloride and 0.1 F hydrochloric acid as a function of drop time. Solid circles represent data secured by Loveridge with 0.4163 mM iodate in 0.2 F sodium phosphate, pH 7.0.

contribution from an effect related to maximum formation.[1,7] In support of this, it is found that the lowering of I by gelatin depends very much on the nature of the reducible material. For example, at t = 0.6 sec. the addition of 0.01% gelatin lowers the diffusion current constant of ferricyanide about 4%, while at 0.5 sec. it lowers the diffusion current constant of iodate by 16%. It may be recalled that the diffusion current constant of bismuth in 1 F nitric acid at t = *ca.* 0.7 sec. is decreased nearly 70% by the addition of this concentration of gelatin.[1]

This is, of course, the behavior to be expected in view of the fact that maximum formation is principally dependent, not on the characteristics of the dropping electrode, but on the nature of the reducible ion and the supporting electrolyte used. Therefore no equation in terms of m and t alone can represent the behavior of all substances within this range of drop times.

The intermediate portion of the curve, in the presence of 0.01% gelatin, has been shown to be susceptible to treatment by an equation of the form recently derived by Strehlow and von Stackelberg[6] and by Lingane and Loveridge[8]

$$i_d/Cm^{2/3}t^{1/6} = k_1(1 + k_2(t^{1/6}/m^{1/3}))$$

This, however, is no longer the case in the absence of gelatin, for the present data show that in this region I is independent of capillary characteristics. In other words, within this range of drop times *diffusion to the dropping electrode in the absence of gelatin obeys the* $i_d/Cm^{2/3}t^{1/6} = k$ *prediction of the Ilkovič equation.*[9-12]

Thus, for silver I = 2.500 ± 0.007 (33 values) between 1.5 and 6.5 sec. For cadmium I = 3.535 ± 0.008 (33 values) between the same limits. For ferricyanide I = 1.789 ± 0.009 (47 values) between 2.0 and 9.5 sec., and for iodate $I = 12.03_5 \pm 0.04_5$ (30 values) between 1.9 and 8.0 sec. Loveridge[3] found 12.05 ± 0.08 for iodate in 0.2 F phosphate, pH 7.0, between 1.95 and 9.8 sec., rejecting one value of eleven (*cf.* Fig. 5). We believe that the average of these mean deviations, 0.35%, is a fair indication of the over-all precision of these measurements.

By comparison with curves secured in the presence of 0.01% gelatin, these plateaus can be divided into two portions: one, at shorter drop times, in which gelatin decreases the diffusion current constant, and another in which I is increased by the addition of gelatin. Thus there is a point at which I is unaffected by 0.01% gelatin, found at a drop time of 2.1 sec. for iodate or 3.6 sec. for ferricyanide and cadmium. (It has been reported to occur at t = 2.5 sec. for cadmium in another supporting electrolyte.[1])

At very high values of t the diffusion current constant again decreases. With cadmium the decrease from the plateau value is 4.1% at 12.4 sec., with silver it is 4.0% at 11.5 sec., and with iodate it is 3.2% at 13.1 sec. With ferricyanide the decrease is considerably less (1.6% at 10.9 sec.), but the values at the longest drop times were secured with a capillary delivering comparatively large (16-mg.) drops, and the lower rate of fall of I at high drop times is in accord with earlier observations on a capillary producing 26-mg. drops.[4]

Theoretical

From the measurements of Laitinen and Kolthoff[13] with a stationary plane platinum microelectrode, one can calculate diffusion coefficients for silver and ferricyanide ions under the conditions here employed. These, on substitution into the Ilkovič equation, give 2.533 and 1.761 for the diffusion current constants of silver and ferricyanide ions, respectively. Thus the diffusion current constant of silver is 1.3% lower than the calculated value, while that of ferricyanide is 1.6% higher than

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[7] F. Buckley and J. K. Taylor, *J. Res. National Bur. Standards*, **34**, 97 (1945).

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

[9] D. Ilkovič, *Collection Czechoslov. Chem. Communs.*, **6**, 498 (1934).

[10] D. Ilkovič, *J. chim. phys.*, **35**, 129 (1938).

[11] D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

[12] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 30-39.

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

the theoretical. These differences are nearly identical with those between the measured values of I in solutions containing gelatin and the values calculated from the modified Strehlow–von Stackelberg equation.[4] Consequently it would appear that the two equations as applied to their respective cases are either both valid or both invalid, and if the latter, that their errors are due to neglect of the same factors in their derivations.

It has been pointed out[14] that at relatively high ratios of reducible material to supporting electrolyte, such as were used with silver, cadmium, and ferricyanide, there may be an appreciable contribution from the migration current, and that the variation of this extraneous current with t might influence the shapes of the I *versus* t curves. Whether there is such a variation remains to be tested experimentally, but in any case it would not be expected to be subject to an appreciable gelatin effect and therefore the validity of comparisons made here between curves with and without gelatin should not be affected.

The Ilkovič equation has frequently been applied to the calculation of diffusion coefficients from diffusion current data. So far as these calculations are applied to data in the absence of a maximum suppressor, the present work would seem to confirm the validity of this procedure. This conclusion, however, based as it is on only two diffusion coefficients secured by a method evolved in a purely exploratory survey in which there was no attempt to secure very precise values, must remain tentative until much more information concerning the diffusion coefficients of ions under polarographic conditions becomes available.

The slow decrease in I at very long drop times, noted both in the presence and in the absence of gelatin, may be the result of an instrumental peculiarity rather than an inherent characteristic of the dropping electrode. Taylor, Smith and Cooter[15] have demonstrated that the average galvanometer deflection decreases when the galvanometer period becomes much less than the drop time. As the period of the galvanometer used in this study was approximately 8 sec., the measured current at drop times longer than this would be expected to fall below the true value. Data presented by Lingane and Loveridge[2] indicate that this error must become negligibly small at lower drop times.

There are now available data showing the existence of two characteristic types of I *versus* t curves. One, in the presence of gelatin, has a minimum at about 1.5 sec., followed by a rising portion which can be treated by a modified form of the Strehlow–von Stackelberg equation, and a maximum at about 6 sec. The other, in the absence of gelatin, is distinguished by an invariant I between about 2 and 7 sec. A variation of this second, also found only in the absence of gelatin, shows I decreasing nearly continuously as t is increased, with at most only a very short plateau.

The first of these types includes all of the ions studied in the presence of gelatin.[1,4,8] The second includes silver, ferricyanide and cadmium and iodate in two media; the variation mentioned above is illustrated by bismuth in 1 F nitric acid[1] and hydroquinone in 0.2 F phosphate, *p*H 7.0.[3]

In view of the close similarity between the bismuth and hydroquinone curves and the data secured for a variety of other ions by Buckley and Taylor[7] by a method of measurement which accentuated the influence of maximum formation,[1] it seems reasonable to attribute the abnormally high currents characteristic of this sub-group as including a contribution from a stirring effect even at rather high drop times. The decrease in I with increasing t therefore reflects a decrease in the importance of this extraneous stirring phenomenon rather than a change in a truly diffusion-controlled current.

This is substantially identical with the interpretation generally accepted, and supported by these data, for the portions of the two normal curves in the presence and absence of gelatin at drop times less than 1.5–2.0 sec. That is, at short drop times there is a transfer of material to the electrode surface in excess of that corresponding to true diffusion control, and this effect is decreased by increasing t or by adding a maximum suppressor.

Within the drop time range in which I is increased by the addition of gelatin, however, no such explanation is available. It seems highly probable that the diffusion current in this region is actually diffusion-controlled even in the absence of gelatin, and the effect of gelatin would seem to be due to some change in the mechanism of the diffusion process. This change is apparently such as to introduce the "wedge effect" responsible for the $t^{1/6}/m^{1/3}$ term in the Strehlow–von Stackelberg equation. This is difficult to justify quantitatively on geometrical grounds, and one suspects that the effect of gelatin is one of modifying the shape of the concentration gradient around the drop.

It does not appear that a wholly satisfactory explanation for the difference between these two types of behavior can be synthesized from data on the effect of t on the average current, but that information must be available on the effects of gelatin and of t on the instantaneous current during the growth of a drop before an adequate interpretation can be advanced.

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(14) J. J. Lingane, private communication.

(15) J. K. Taylor, R. E. Smith and I. L. Cooter, *J. Res. National Bur. Standards*, **42**, 387 (1949).