[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Controlled Current Polarography at the Dropping Mercury Electrode[1]

BY I. M. KOLTHOFF AND Y. OKINAKA

RECEIVED MARCH 13, 1958

The known principle of voltammetry at controlled current recently has been recommended as a general polarographic procedure which has the advantage that no maxima are observed on the current–potential curves. The method has interesting features; however, there are various reasons why it cannot be recommended for general analytical purposes. The "apparent" diffusion current is different from the maximum diffusion current measured in the conventional method and dependent upon the nature of the supporting electrolyte or the second constituent reduced at the electrode. This difference is accounted for by (1) the effect of potential on drop time, (2) a negative condenser current which occurs during the period when the potential drops from that of the second to that of the first constituent, and (3) an anodic current resulting from the reoxidation of the supporting electrolyte or the second constituent when the reduction of these substances is reversible. It was confirmed that maxima do not appear, but streaming was found to take place around the mercury drop in the absence of surface active substances, causing irregular fluctuations of potential during the drop life. The controlled current method at the DME appears to be more promising for chronopotentiometric purposes.

Controlled current polarography (or current scanning polarography) was first recommended by Adams, Reilley and Furman[2] as a simple means to obtain polarograms at solid electrodes. Constant currents are applied to the electrolysis cell from a high voltage source through a variable series resistance, and the potential of the working electrode is measured against a reference electrode. They found no advantage in applying this method to the DME. Ishibashi and Fujinaga,[3] on the other hand, showed experimentally that the method offers an advantage over conventional polarography because of the absence of maxima. They found that the diffusion current is proportional to the concentration of electroactive species, and that the current–potential curve constructed from potential values at the maximum size of the mercury drop has characteristics similar to that in conventional polarography. A study of the principles underlying controlled current polarography led us to believe that the characteristics of a polarogram should differ in many respects from those in conventional polarography.

In Fig. 1 the situation is considered for a reducible compound O which gives a diffusion current at -0.5 volt *vs.* SCE in a solution of potassium chloride as supporting electrolyte. The curve represents the current–time curve obtained at -0.5 volt of the substance O during the life period of a mercury drop. We do not consider the condenser current for the moment. This current–time curve remains unchanged at potentials more negative than -0.5 volt up to the time when the drop falls. As long as the current is solely determined by diffusion, its maximum value should be given by this curve, regardless of whether the current-controlled or potential-controlled method is used. When a constant current i_2 which is smaller than the maximum current $i_{\max}$ is applied, the situation at time t_1 is such that the fraction QR ($= i_1$) serves for the reduction of the substance O, while the fraction PQ ($= i_2 - i_1$) is used in the reduction of potassium ions. This simultaneous reduction of two constituents continues until time t_2 is reached. At this point, the situation becomes such that enough of the substance O is present at the surface of the electrode that the entire applied current is used for the reduction of O, and hence no more potassium amalgam is formed. It is clear that the potential of the mercury drop between time zero and t_2 corresponds to that of the potassium amalgam (of the order of -2 volts), while at time t_2, the potential drops to that of the O system (in our example, approximately -0.5 volt). With increase of t only the substance O is reduced and the potentials correspond to those of the O system at varying ratios of O and its reduced form.

First we consider the diffusion current in the controlled current method, denoted as the "apparent" diffusion current to distinguish from the maximum and the average diffusion currents in conventional polarography, for a simple hypothetical case in which (1) the drop time is not affected by the potential, (2) the potassium amalgam formed is not oxidizable and (3) there is no condenser current. With an applied current even slightly smaller than $i_{\max}$, the potential would fall abruptly to that of the system O at the moment when the instantaneous diffusion current of the substance O becomes equal to the applied current. At applied currents greater than $i_{\max}$, the potential should stay at the value of the potassium amalgam during the entire drop life. Thus, the apparent diffusion current would be equal to the maximum diffusion current measured in the conventional method. This conclusion does not agree with the theoretical equation for the apparent diffusion current which has been derived recently by Senda, Kambara and Takemori.[4] They derived the following equation without taking account of any of the above three factors

$$I_d = 635nCD^{1/2}m^{2/3}t_{\max}^{1/6} \qquad (1)^5$$

where I_d is the apparent diffusion current in μa., n the number of electrons involved in the electrode reaction, C the concentration of electroactive species in mM, D the diffusion coefficient in cm.^{2}/sec., m the rate of flow of mercury in mg./sec. and $t_{\max}$ the drop time in sec. This equation is identical

---

[1] This investigation was supported by a research grant from the National Science Foundation.

[2] R. N. Adams, C. N. Reilley and N. H. Furman, *Anal. Chem.*, **25**, 1160 (1953).

[3] M. Ishibashi and T. Fujinaga, *J. Electrochem. Soc. Japan*, **24**, 375, 525 (1956); paper presented at Symposium on Modern Electrical Methods of Analysis, Paris, July, 1957; *Anal. Chim. Acta*, **18**, 112 (1958).

[4] M. Senda, T. Kambara and Y. Takemori, *J. Phys. Chem.*, **61**, 965 (1957).

[5] Apparently the numerical constant given in the original paper, 63.5, should read 635.

in form with the Ilkovic equation for the maximum diffusion current, but the numerical constant in the latter is 706.[6] Ignoring the approximate character of the Ilkovic equation, the numerical constant in equation 1 must be incorrect. This is shown to be the case in the Experimental section.

Actually, the above hypothetical conditions are never fulfilled; and, accordingly, the apparent diffusion current must be different from the maximum diffusion current. This is made clear by considering separately each of the three factors mentioned above.

(1) **Effect of Variation of Drop Time with Potential.**—If the drop time is 5 sec. at −0.5 volt (Fig. 1), it will be about 3 sec. at −2 volts. If a current i_3 which is equal to the maximum diffusion current at −2 volts is applied, the simultaneous reduction of potassium ions and the substance O continues until at $t = 3$ sec. the mercury drop falls. Therefore, the apparent diffusion current will be equal to i_3, which is smaller than $i_{\max}$ at −0.5 volt. If the second constituent or the supporting electrolyte is reduced at potentials more positive than that where potassium ions are reduced, the drop time is larger than 3 sec. but still smaller than 5 sec., and the difference between the apparent diffusion current and the maximum diffusion current $i_{\max}$ at −0.5 volt becomes smaller. Thus, the value of the apparent diffusion current depends on the potential where the supporting electrolyte or the second constituent is being reduced.

(2) **Effect of Reversibility of Reduction of the Second Constituent or the Supporting Electrolyte.**—According to the simple picture we have considered thus far, the potential should drop abruptly from −2 volts to −0.5 volt at the very moment when the applied current becomes equal to the instantaneous diffusion current of the substance O, for example, at time t_2 at the applied current of i_2 (Fig. 1). Actually, however, such a sharp potential shift does not take place because of the anodic dissolution of potassium when the potential becomes less negative than −2 volts. This anodic current must be compensated by an additional cathodic current of the substance O, which is the mirror image of the anodic current. As a result, the situation becomes similar to that of a "mixed potential"[7]; *i.e.*, the potential stays near the potassium potential for some time and then it is gradually shifted to that of the O system. This situation will arise when the applied current is slightly less than i_3, *e.g.*, i_4. After the point of intersection S with the current–time curve, the anodic potassium current is compensated by a total reduction current which is greater than i_4. This accounts for the fact that the apparent diffusion current is considerably smaller than i_3. If a supporting electrolyte which is irreversibly reduced is employed instead of potassium chloride and if its reduction occurs at the same potential as the reduction of potassium ions, the apparent diffusion current should be equal to i_3. Thus the apparent diffusion current depends on whether the supporting electrolyte or the second constituent is reversibly reduced or irreversibly reduced. The actual situation is even more involved because of the effect of condenser current, as discussed below.

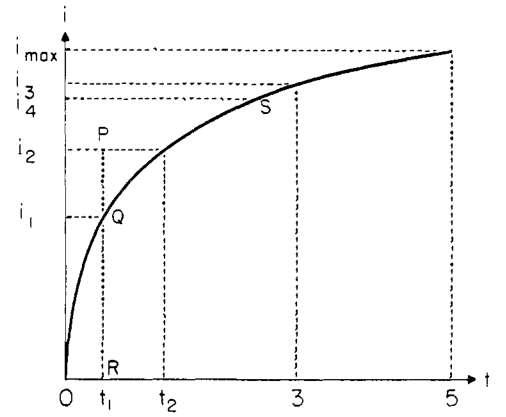

Fig. 1.—Diffusion current–time curve in conventional polarography.

(3) **Condenser Current Effect.**—The variation of potential from a negative to a less negative value in a short time should give rise to a significant negative condenser current. The quantity of electricity involved in the charge of the electrical double layer of capacity c at a potential E is given by

$$q = c(E_{\mathrm{m}} - E) \qquad (2)$$

where E_{m} is the potential at the electrocapillary maximum. The capacity c at the DME is a function of time t and given by

$$c = c_0A = c_0(4\pi(3m/4\pi d)^{2/3}t^{2/3}) \qquad (3)$$

where c_0 is the capacity per unit area, A the surface area of a growing mercury drop and d the density of mercury. By definition, the condenser current is given by differentiating equation 2 with respect to time

$$\begin{aligned} i_c &= \frac{\mathrm{d}q}{\mathrm{d}t} = \frac{\mathrm{d}c}{\mathrm{d}t}(E_{\mathrm{m}} - E) - c\frac{\mathrm{d}E}{\mathrm{d}t} \\ &= 4\pi\left(\frac{3m}{4\pi d}\right)^{2/3} c_0 \left\{\frac{2}{3}(E_{\mathrm{m}} - E)t^{-1/3} - \frac{\mathrm{d}E}{\mathrm{d}t}t^{2/3}\right\} \qquad (4)^{8} \end{aligned}$$

In conventional polarography, the potential of the DME is constant during the drop life, and the term dE/dt is equal to zero. In the controlled current method, however, this term cannot be neglected. It is easily calculated that during the period when the potential is shifted from the value of the supporting electrolyte to that of the substance to be electrolyzed, the second term in the brackets of equation 4 is much greater than the first term, and a negative value of i_c results.[9] Qualitatively this effect is similar to that of the "mixed potential," and is responsible for the fact that the apparent diffusion current is smaller than the maximum diffusion current even when the supporting electrolyte or the second constituent is irreversibly reduced.

---

(6) For example, I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1952, p. 41.

(7) Ref. 6, p. 116.

(8) P. Delahay, "Intrumental Analysis," The Macmillan Co., New York, N. Y., 1957, p. 86.

(9) For example, the condenser current calculated from potential-time curve A in Fig. 3 is approximately −0.4 μa. at −0.85 volt at 1.25 sec. (a point on the sharply descending part of the curve), while the values at −1.25 volt (0.65 sec.) and at −0.50 volt (3.00 sec.) are +0.08 and −0.002 μa., respectively. In these calculations, the capacity per unit area was assumed to be 20 microfarads per cm.^{2}.

Various experimental results shown in this paper substantiate the above interpretation. In practical applications, a difficulty is encountered in measuring the apparent diffusion current accurately and in making a proper correction for the residual current because of the complications mentioned above. Also, for this reason, controlled current polarography would be objectionable from the analytical viewpoint, even though the apparent diffusion current is proportional to concentration (see Experimental part). However, by virtue of the fact that maxima do not appear on polarograms, the method could be of advantage when it is of interest to obtain polarographic characteristics of substances whose maxima cannot be suppressed in the conventional method. This situation is often encountered in non-aqueous media.

Experimental

Materials.—C.P. thallous chloride and potassium chloride were used after recrystallization. All other chemicals were C.P. grade and used without further purification. Polyacrylamide used as a maximum suppressor was a product of American Cyanamid Co. (PAM 75), which was found to be an excellent maximum suppressor for general polarographic purposes.[10] Deaeration was done by passing 99.99% pure Linde nitrogen without further purification. Experiments were carried out at 25 ± 0.1°, except those to observe streaming, in which the cell was not immersed in the thermostat.

Observation of Streaming.—Streaming around the mercury drop was observed with a low power microscope, the solution containing a suspension of fine active charcoal powder (Norit A).

Electrode.—The DME had the characteristics in 0.1 M potassium chloride: $m = 1.307$ mg./sec., t (open circuit) $= 5.54$ sec. at $h = 51.5$ cm.

Circuit to Apply Constant Current.—Two circuits were employed. Circuit I was composed of a voltage source of 360 volts (four 90-volt "B" batteries), a variable resistance made by attaching several of each of 10, 5, 1, 0.5, 0.1 megohm carbon resistors to rotary switches, a microammeter or a galvanometer and the polarographic cell, all being connected in series. Circuit II was composed of a 90-volt "B" battery, a variable wire wound resistance of 25,000 ohms as the potential divider and a fixed carbon resistance of 10 megohms which was inserted in series with the cell. Since the potential of the DME acts as a source of back e.m.f. which varies during the drop growth, it is better to keep the voltage of the current source sufficiently large compared to the cell potential in order for the current fluctuation to be negligible. In this respect, circuit I is, in general, more suitable than circuit II which is similar in principle to the one employed by Ishibashi and Fujinaga.[3] This also was pointed out in a footnote in the paper by Senda, Kambara and Takemori.[4] We used both circuits and found that they gave substantially the same results in the range of our experiments, but only results obtained with circuit I are reported.

Recording of Potential–Time Curves.—Potential–time curves were recorded by using a combined system composed of a Keithley DC Indicating Amplifier Model 303 and the Sanborn system, which consists of a Single Channel Recorder Model 151-100A, a Stabilized DC Preamplifier Model 151-1800 and a Driver Amplifier and a Power Supply Model 150-200B/400. The electrodes were connected to the input terminals of the Keithley amplifier, which has an input resistance of 10^{12} ohms and allows measurements at frequencies of DC to 100 kc. at a full scale of 2 volts. By inserting proper resistances, the output voltage of this amplifier was fed into the input of the Sanborn Preamplifier, the potential variation during the drop life being recorded by the recorder. The response of the Sanborn system is 0.03 sec. in terms of the rise time when a square wave whose voltage corresponds to a deflection of 10 mm. is applied. At the maximum chart speed one millimeter of the time axis corresponds to 0.01 sec.

The use of the Keithley amplifier of such a high input resistance was necessary in order to prevent current from flowing through the instrument. If, for example, the latter should be smaller than 0.01 μa. at a cell potential of 2 volts, the input resistance of the instrument must be greater than $2/0.01 \times 10^{-6} = 2 \times 10^{8}$ ohms. Obviously, therefore, ordinary cathode-ray oscilloscopes or oscillographs cannot be used directly for the present purposes. Nor can the manual potentiometer be used because even if the potentiometer is adjusted so that no current flows at the maximum size of mercury drops, a considerable current flows through the potentiometer during the rest of the drop life. Experimentally it was found that these devices give entirely different results, which are not described because of the complications resulting from the current drawn by the instruments.

The potential at the maximum size of mercury drops can be estimated roughly from the predetermined electrocapillary curve by simply measuring the drop time. Although this is not an accurate means for measuring values of potential, it permits detection of a sudden potential shift at the maximum size of the drop. It was found that in favorable cases the apparent diffusion current can be determined by this method with the same precision as by the method with the Keithley amplifier.

Recording of Current–Time Curves.—Current–time curves at constant applied potential were recorded by using the Sanborn system described above in terms of a potential drop across a 1000-ohm resistance inserted in series with the cell circuit. The potential was applied manually.

Experimental Results and Discussion

Presence of Polyacrylamide.—Potential–time and diffusion current–time curves obtained with a solution of 1.52×10^{-3} M thallium chloride, 0.1 M potassium chloride and 0.01% polyacrylamide are shown in Fig. 2. Polyacrylamide was added to eliminate streaming (*vide infra*). The current–time curve was obtained at −1.0 volt. The delayed and slow shift of potential is accounted for by the anodic current due partly to the oxidation of the potassium amalgam and partly to the condenser current. At applied currents between 7.18 and 7.34 μa., the drop time was not constant and the potential at the end of the drop life was either −1.95 volts or −0.55 volt (curve C). When the Keithley–Sanborn instrument was disconnected, irregular drop times varying between 5.6 and 2.9 seconds were observed when the current was varied between 7.06 and 7.20 μa. This agreement in current values indicates that the potential measuring instrument did not affect the current actually flowing through the cell.

Figure 3 shows potential–time and current–time curves obtained when 0.1 M hydrochloric acid was used instead of potassium chloride. The applied current for curve A in this figure was the same as that for curve A in Fig. 2. Clearly the potential shift was sharper in the hydrochloric acid solution than in the potassium chloride solution, as is to be expected from the fact that the reduction of hydrogen ions is irreversible. The condenser current effect accounts for the result that the potential drop is not instantaneous even when the supporting electrolyte is irreversibly reduced. The peculiar large slope of the potential–time curves between −1.5 volts and −1.0 volt must be attributed to the greater hydrogen overpotential at the larger current density, *i.e.*, at the smaller t. Irregular potentials at the end of the drop growth were observed between 8.53 and 8.62 μa. (curve C, Fig. 3),

---

(10) I. M. Kolthoff, Y. Okinaka and T. Fujinaga, *Anal. Chim. Acta*, **18**, 295 (1958).

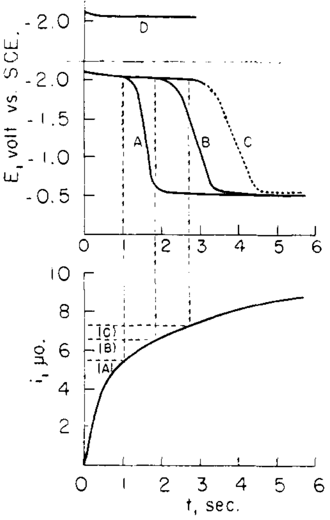

Fig. 2.—Potential-time and diffusion current-time curves of 1.52 × 10^{-3} *M* thallium chloride, 0.1 *M* potassium chloride and 0.01% polyacrylamide. Current applied: A, 5.52 μa.; B, 6.55 μa.; C, 7.18–7.34 μa.; D, 7.80 μa.

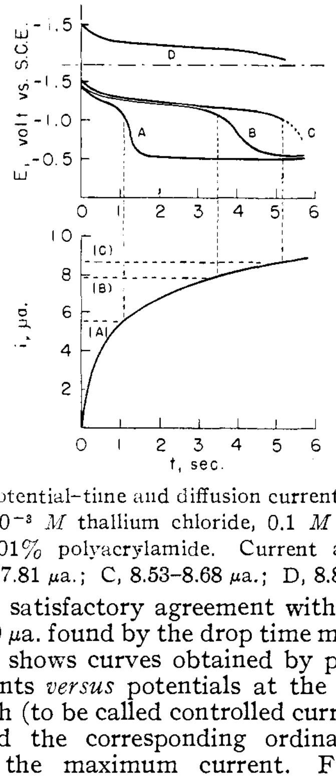

Fig. 3.—Potential-time and diffusion current-time curves of 1.52 × 10^{-3} *M* thallium chloride, 0.1 *M* hydrochloric acid and 0.01% polyacrylamide. Current applied: A, 5.59 μa.; B, 7.81 μa.; C, 8.53–8.68 μa.; D, 8.82 μa.

which is in satisfactory agreement with the values 8.60 to 8.70 μa. found by the drop time method.

Figure 4 shows curves obtained by plotting applied currents *versus* potentials at the end of the drop growth (to be called controlled current polarograms) and the corresponding ordinary polarograms of the maximum current. For reasons given in the discussion, the curves are not corrected for the residual current. The much smaller apparent diffusion current in potassium chloride than in hydrochloric acid medium should be ascribed to both the smaller drop time at the potassium potential and the anodic oxidation of the potassium amalgam. The effect of the anodic oxidation is much greater than that of the drop time. This was proved by adding zinc sulfate (0.001 *M*) to the thallium solution in 0.1 *M* potassium chloride. In this solution zinc is the second constituent to be reduced. The apparent diffusion current of the thallium in the zinc containing solution was 7.6 μa. as compared to 8.6 μa. in the zinc-free 0.1 *N* hydrochloric acid solution. The difference is entirely due to the oxidation of zinc amalgam as the reduction potentials of zinc and hydrogen are of the same order of magnitude. Instead of making use of the irreversible reduction of hydrogen ions, experiments were run in the potassium chloride solution which was buffered with acetic acid and sodium acetate (*p*H 4.5) and saturated with acetophenone. This compound is reduced before potassium and its reduction is irreversible. The apparent diffusion current of thallium was now 8.4 μa., which, as expected, was almost the same as the value of 8.6 μa. in 0.1 *N* hydrochloric acid solution.

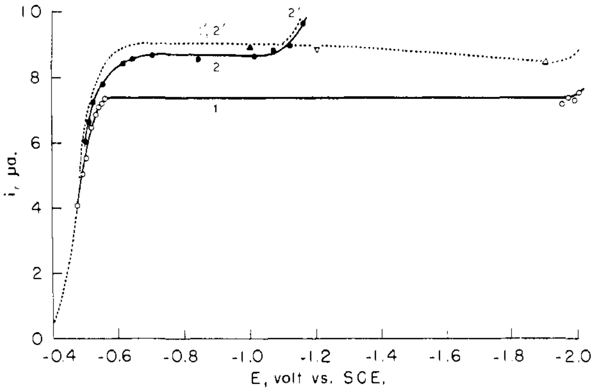

Fig. 4.—Current-potential curves of 1.52 × 10^{-3} *M* thallium chloride in (1,1') 0.1 *M* potassium chloride and in (2,2') 0.1 *M* hydrochloric acid, both in the presence of 0.01% polyacrylamide. Broken lines, ordinary polarograms (maximum current); solid lines, controlled current polarograms; open triangles, maximum diffusion currents in potassium chloride solution; solid triangle, in hydrochloric acid solution; no correction for i_r.

Another set of experiments was carried out with solutions of 1.06 × 10^{-3} *M* mercuric chloride (instead of thallous chloride) in 0.1 *M* potassium chloride plus 10^{-3} *M* zinc sulfate and in 0.1 *M* hydrochloric acid (Fig. 5). The effect of the reversible

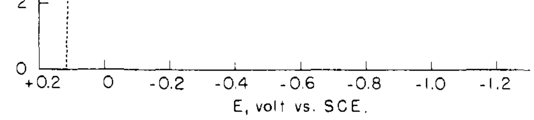

Fig. 5.—Current-potential curves of 1.06 × 10^{-3} *M* mercuric chloride in (1,1') 0.1 *M* potassium chloride plus 10^{-3} *M* zinc sulfate and in (2,2') 0.1 *M* hydrochloric acid, both in the presence of polyacrylamide. Broken lines, ordinary polarograms (maximum current); solid lines, controlled current polarograms; open triangles, maximum diffusion currents in the potassium chloride and zinc sulfate solution; solid triangles, in the hydrochloric acid solution.

reduction of zinc ions again is evident, the apparent diffusion current at −0.8 volt in the zinc-containing solution being about 0.9 μa. smaller than in hydrochloric acid medium. It is of interest to note that the slope of controlled current polarograms is much greater than the slope of the diffusion current line in the ordinary polarograms. This difference must be attributed to the large negative condenser current which occurs during the period when the potential is shifted from that of hydrogen or zinc to that of mercury. This effect was not observed in the experiments in Fig. 4, because the drop time at the thallium ion discharge potential (5.7 sec. at −0.5 volt) is greater than that at any other potentials on the polarograms. Consequently, neglecting irregularities, mercury drops fell either at the thallium potential or at the potential of the supporting electrolyte or the second constituent but not in between. In the examples in Fig. 5, on the other hand, the drop time at the mercury potential (4.8 sec.) is smaller than that at the potential of zinc or hydrogen (5.4 sec. at −1.0 volt), and actually mercury drops fell in the region where the potential was shifting from that of hydrogen or zinc to that of mercury. Therefore, the negative condenser current at the end of the drop life must have been significant.

As can be seen from Fig. 4, the apparent diffusion current of thallium in the hydrochloric acid solution is only slightly smaller than the maximum diffusion current (*ca.* 3% at −1.0 volt). The difference was small in all cases where the supporting electrolyte or the second constituent was irreversibly reduced; *e.g.*, for thallium in the presence of acetophenone and for mercury in the hydrochloric acid solution (curve 2 in Fig. 5). It is apparent from these results that equation 1 is inadequate, for this equation predicts that the apparent diffusion current should be (706 − 635)/706 = 10% smaller than the maximum diffusion current.

Absence of Polyacrylamide.—In the absence of a maximum suppressor maxima were absent in controlled current polarograms of 1.52×10^{-3} *M* thallium in 0.1 *M* potassium chloride and in 0.1 *M* hydrochloric acid, but both drop time and potential variation were irregular over a wider range of applied current than in the presence of polyacrylamide. For example, in potassium chloride as supporting electrolyte, the drop time and the potential at the end of the drop life were irregular at applied currents between 5.85 and 7.30 μa. Examples of the irregularities in potential–time curves are shown in Fig. 6. These irregularities are attributed to streaming, which was clearly observed around the mercury drop during its growth. The streaming which takes place at the ordinary polarographic maximum is a continuous motion of the solution, while the streaming observed here was not continuous but intermittent; the motion stopped a few times during the growth of the drop and then the direction of the motion changed. For example, when the applied current was 5.56 μa. in the solution of thallium and potassium chloride (curve A in Fig. 6), no streaming occurred until at approximately 2 sec. when the thallium potential was nearly attained. At this moment, a sudden brief pulsation (fraction of a second) of the drop accompanied by an upward streaming—typical of a "negative" maximum—was observed. The drop then grew quietly for about a second when another sudden brief pulsation was observed, but now accompanied by downward streaming of the liquid—typical of a "positive" maximum.[11] One or more pulsations were sometimes noticeable before the drop fell. The pulsation and the streaming were eliminated completely by addition of 0.01% polyacrylamide.

The enormous maxima observed on ordinary polarograms in glacial acetic acid solutions of mercuric acetate and of cupric acetate were absent on controlled current polarograms, but potential variations again were found to be irregular.

Proportionality between Apparent Diffusion Current and Concentration.—Ishibashi and Fujinaga[3] found proportionality between the apparent diffusion current and concentration, but they did not mention how to correct for the residual current. Since part of the applied current is consumed for charging the electrical double layer and for reducing impurities, if any, a proper correction must be made for the residual current resulting from these factors. Unfortunately, it is not possible to determine the residual current experimentally at any given time during the drop growth, because the condenser current is a function of the rate of potential variation dE/dt (see eq. 4) and this rate in the supporting electrolyte solution is entirely different from that in the solution containing the substance to be determined.

The ordinary instantaneous condenser current at potential E is given by

$$i_c = 3.22d^{-2/3}c_0m^{2/3}t^{-1/3}(E_m - E) \qquad (5)$$

which is derived from equation 4 by putting dE/dt = 0. If a constant current i_a is applied, the potential should vary according to

$$E_m - E = Ki_at^{1/3} \qquad (6)$$

where $K = (3.22d^{-2/3}\ c_0m^{2/3})^{-1}$. This equation implies that at $t = 0$, $E = E_m$, regardless of the values of i_a and K and that the direction of potential variation is from E_m to more negative (positive) values when i_a is positive (negative). Experimentally, this interpretation was found to be correct. Obviously the residual current of the supporting electrolyte determined by the controlled current method does not take into account that part of the condenser current which occurs in the solution containing the electroactive constituent to be determined during the period when the potential is shifted from that of the supporting electrolyte to that of the constituent. Consequently, the true residual current to be applied for correcting the apparent diffusion current cannot be determined exactly, but it can be found approximately.

At a potential very close to that where the reduction of the supporting electrolyte or the second constituent begins, the residual current in the constant current method is approximately equal to the ordinary residual current found at the end of the drop life at this potential in the supporting electrolyte alone, because the rate of potential variation

---

(11) Ref. 6, p. 173.

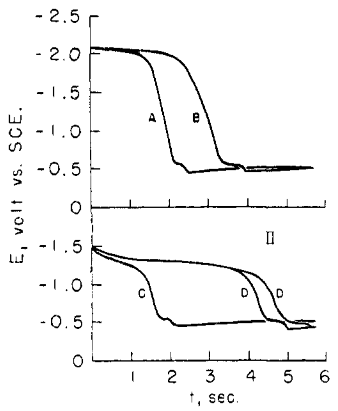

Fig. 6.—Potential-time curves of 1.52 × 10^{-3} *M* thallium chloride in 0.1 *M* potassium chloride (I) and in 0.1 *M* hydrochloric acid (II), both in the absence of polyacrylamide. Current applied: A, 5.56 μa.; B, 5.64 μa.; C, 5.55 μa.; D, 6.66 μa.

during the period when the supporting electrolyte or the second constituent is being reduced is small. For example, the residual current to be applied to curve 2 in Fig. 4 at −1.0 volt is assumed to be equal to the instantaneous residual current at the end of the drop life, as indicated on the residual current-time curve at −1.0 volt. Examples in Table I show that the proportionality between current and concentration is satisfactory when the proper correction is made for the residual current.

TABLE I

PROPORTIONALITY BETWEEN APPARENT DIFFUSION CURRENT AND CONCENTRATION

Supporting electrolyte[a]	Polyacrylamide, %	Concentration of thallium (*M*) 2.53 × 10^{-3} i_d (μa.)	i_d/C (μa./m*M*)	1.52 × 10^{-3} i_d (μa.)	i_d/C (μa./m*M*)	0.506 × 10^{-3} i_d (μa.)	i_d/C (μa./m*M*)
(Not corrected for the residual current)							
KCl	0.01	11.8	4.66	7.34	4.83	2.60	5.14
	0	11.5	4.55	7.30	4.80	..	..
HCl	0.01	14.3	5.65	8.62	5.67	2.93	5.79
	0	13.8	5.46	8.46	5.57	2.90	5.73
(Corrected for the residual current)[b]							
KCl	0.01	11.5	4.55	7.09	4.66	2.35	4.64
	0	11.2	4.43	7.05	4.64	..	..
HCl	0.01	14.2	5.61	8.50	5.59	2.81	5.55
	0	13.7	5.42	8.34	5.45	2.78	5.49

[a] 0.2 *M* for 2.53 × 10^{-3} *M* thallium, 0.1 *M* for 1.52 and 0.506 × 10^{-3} *M* thallium. [b] Residual currents: 0.25 μa. at −1.9 volts in KCl; 0.12 μa. at −1.0 volt in HCl.

Chronopotentiometric Analysis of Potential–Time Curves.—Consider current–time curves of (1) mercuric ions, (2) thallous ions and (3) a mixture of these ions in a hydrochloric acid solution at a potential on the diffusion current region of thallium, *e.g.*, at −0.8 volt *vs.* SCE (see Fig. 7). When a current i_a which is smaller than the maximum current of the mixture is applied, relationship (7) should hold at time t_a on the basis of the Ilkovic equation

$$i_a = i_{Tl} + i_{Hg} = 706n_1C_1D_1^{1/2}m^{2/3}t_a^{1/6} + 706n_2C_2D_2^{1/2}m^{2/3}t_a^{1/6} \quad (7)$$

where subscripts 1 and 2 denote thallium and mercury, respectively. It follows that

$$C_1 = \left(\frac{i_a}{706n_1D_1^{1/2}m^{2/3}}\right)\frac{1}{t_a^{1/6}} - \left(\frac{n_2D_2^{1/2}}{n_1D_1^{1/2}}\right)C_2 = A(1/t_a)^{1/6} - B \quad (8)$$

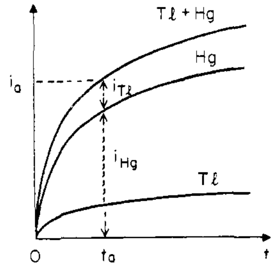

Fig. 7.—Current-time curves of thallium, mercury and their mixture.

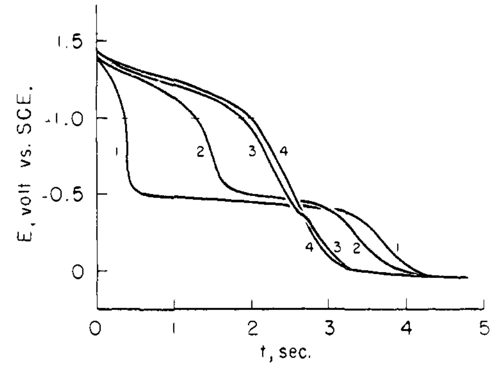

Fig. 8.—Potential-time curves of mixtures of thallium chloride and 1.06 × 10^{-3} *M* mercuric chloride in 0.5 *M* hydrochloric acid and 0.01 % polyacrylamide; concentration of thallium: (1) 1.01 × 10^{-3} *M*; (2) 2.02 × 10^{-4} *M*; (3) 2.02 × 10^{-5} *M*; (4) 0 *M*; applied current, 6.80 μa.

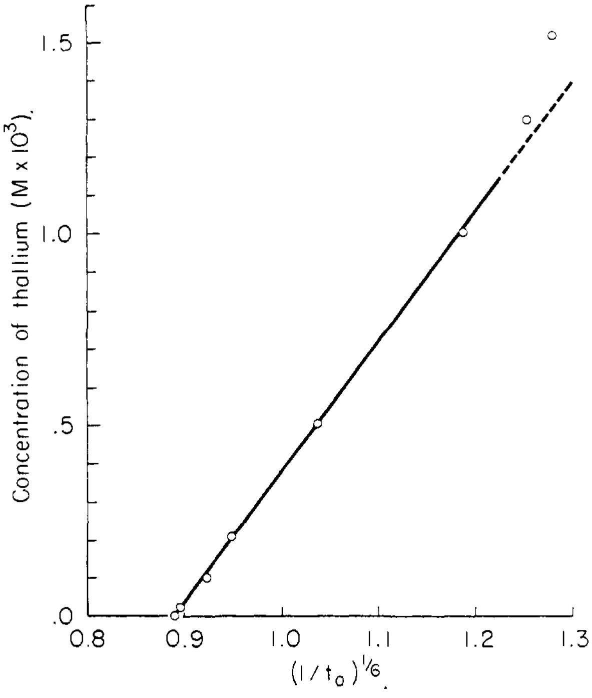

Fig. 9.—Concentration of thallium *vs.* $(1/t_a)^{1/6}$ (see text).

where A is a constant at a given applied current, while B is also a constant when the concentration of mercury is kept constant. Under these conditions Equation 8 predicts a linear relationship between the concentration of thallium and $(1/t_a)^{1/6}$.

A series of experiments was carried out to check this relationship with solutions of various concentrations of thallium, 1.06×10^{-3} M in mercuric chloride, 0.5 M in hydrochloric acid and 0.01% in polyacrylamide. Time t_a was measured on potential–time curves at −0.98 volt, where the hydrogen wave began to rise under the experimental condition. Some potential–time curves are reproduced in Fig. 8. The experimental relation between the concentration of thallium and $(1/t_a)^{1/6}$ is shown in Fig. 9, which indicates that the relationship represented by equation 8 holds when $(1/t_a)^{1/6}$ is not large, that is, when t_a is not too small. Apparently the deviation at small t_a values is related to the known fact that the Ilkovic relation does not hold at the beginning of the drop formation. A larger condenser current at small t may also be responsible for the deviation. It is worth mentioning that under the experimental conditions, thallium in a concentration as little as 10^{-5} M could be detected and determined in the presence of 10^{-3} M mercury. In such a mixture the detection of thallium in a concentration less than 2×10^{-5} M is not possible in the conventional polarographic method. The chronopotentiograms of thallium in Fig. 8 indicate that the chronopotentiometric method promises to be a sensitive means for the detection and determination of a second constituent in the presence of a large excess of another constituent which is reduced at a less negative potential. Note that the chronopotentiogram of thallium is clearly visible in curve 3 of Fig. 9. The possibilities of the chronopotentiometric method at the dropping mercury electrode are being studied in this Laboratory by Dr. S. Bruckenstein.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY]

The Preparation and Properties of Nitrosyl Azide

BY HAROLD W. LUCIEN

RECEIVED OCTOBER 4, 1957

Evidence for the formation of nitrosyl azide from reaction of sodium azide and hydrazoic acid with nitrosyl chloride, nitrosyl hydrogen sulfate and nitric acid at temperatures below −30° has been obtained. This evidence includes physical properties, decomposition studies and inferences made from infrared absorption spectra. Nitrosyl azide is an unstable yellow compound which decomposes even at temperatures as low as −50° to form nitrous oxide and nitrogen.

Since the initial preparation of hydrazoic acid in which Curtius[1] treated hydrazine with acidified nitrite solutions, several attempts have been made to verify the hypothesis that nitrosyl azide is an unstable by-product of the reaction. When these reagents are combined, the products are nitrous oxide, nitrogen, hydrazoic acid and ammonia. The nature of the products obtained and their relative amounts depend on the reaction conditions.[2-4] It was speculated that the hydrazoic acid which forms undergoes reaction with nitrous acid to form nitrosyl azide. The nitrosyl azide is unstable and immediately decomposes to form nitrous oxide and nitrogen. All attempts to prepare nitrosyl azide have resulted in the formation of equimolar quantities of nitrous ozide and nitrogen.[2,5-9]

The present approach to the synthesis of nitrosyl azide was to operate at lower temperatures than those which have been previously used and to select reagents suitable for use under these conditions. This study involved an investigation of the products which resulted from the reactions between sodium azide and nitrosyl chloride, sodium azide and nitric acid, sodium azide and nitrosyl hydrogen sulfate and nitrosyl hydrogen sulfate and hydrazoic acid at temperatures below −30°.

Experimental

Materials.—Nitrosyl chloride (Matheson) was fractionated twice on a vacuum line at −60 to −55° and the middle three-fifths fraction was used in these experiments. Sodium azide was obtained from the Matheson Co., Inc. Nitrosyl hydrogen sulfate and hydrazoic acid were prepared by standard procedures.[10]

Apparatus.—Experiments were conducted in a vacuum system located behind 5/8 inch Plexiglas shields in a well ventilated hood. Among other necessary components, the vacuum system consisted of a reaction vessel, six low-temperature U-tubes for fractionation, apparatus for measuring exact volumes, a gas density balance and melting point apparatus.

Analyses.—Molecular weights were determined with a gas density balance as well as from the mass of a given volume at a known temperature and pressure. Calibrated copper–constantan thermocouples were used with a potentiometer to measure the temperature, and melting points were observed by a technique described by Stock.[11] Infrared spectra were obtained on a recording spectrophotometer using a cell with sodium chloride prisms. The light path was 6.75 cm.

It was necessary to exercise due precaution against explosions in all the reactions investigated. Successful preparations were obtained only when the reagents were slowly mixed at the lowest practical temperature and gradually allowed to warm to the desired reaction temperature. Gradual and sudden pressure increases as well as explosions were encountered during fractionation procedures and the

---

(1) T. Curtius, *Ber.*, **26**, 1263 (1893).

(2) H. Thiele, *ibid.*, **41**, 2681 (1908).

(3) F. Sommer and H. Pincas, *ibid.*, **49**, 259 (1916).

(4) A. Seel and T. Schwabel, *Z. anorg. allgem. Chem.*, **274**, 169 (1953).

(5) F. Sommer, *Ber.*, **48**, 1884 (1915).

(6) E. Oliveri-Mandala, *Gazz. chim. ital.*, **51**, **I**, 138 (1921).

(7) T. Werner, *Proc. Roy. Soc.* (*London*), **28**, 257 (1911).

(8) E. Oliveri-Mandala, *Gazz. chim. ital.*, **51**, **I**, 101 (1922).

(9) T. Goyal, *Agra Univ. J. Research*, **4**, 17 (1955).

(10) H. S. Booth, Editor-in-Chief, "Inorganic Syntheses," Vol. I, 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1939, pp. 55, 78.

(11) A. Stock, *Ber.*, **50**, 156 (1917).