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Fundamental Studies with the Dropping Mercury Electrode.[1] III. Influence of Capillary Characteristics on the Diffusion Current and Residual Current

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From theoretical considerations presented originally by Ilkovič,[2] which have been discussed in detail elsewhere,[1,3] a diffusion controlled limiting current observed with the dropping electrode should obey the equation

$$i_d = knD^{1/2}Cm^{2/3}t^{1/6} = ICm^{2/3}t^{1/6} \qquad (1)$$

in which i_d is expressed in microamperes, k is a constant whose theoretical value is 605 at 25°, n is the number of electron equivalents per molar unit of the electrode reaction, D is the diffusion coefficient (cm.^{2}/sec.) of the reducible or oxidizable substance, C is its concentration (millimoles per liter), m is the rate of mercury flow (mg./sec.) from the dropping electrode capillary, and t is the drop time (sec.). The quantity I, which theoretically is equal to $knD^{1/2}$, and which is experimentally determinable as $i_d/(Cm^{2/3}t^{1/6})$, is the "diffusion current constant."[4]

Recently it was pointed out[4] that the performance of practical polarographic analyses can be simplified and greatly expedited when the I-value of the substance being determined is already known in a particular supporting electrolyte, because it is then only necessary to determine i_d in an unknown case, measure the m and t values of the particular dropping electrode that is used, and then apply equation 1 to calculate C. Thus, calibration of each dropping electrode with known concentrations of the substance being determined can be dispensed with. Obviously, this method will be reliable only if i_d is strictly proportional to C and to $m^{2/3}t^{1/6}$, that is, if I is independent of these quantities, as predicted by eq. 1. Results obtained by numerous investigators demonstrate conclusively that i_d is exactly proportional to C in every case in which the limiting current is known to be diffusion controlled, and when proper correction is made for the residual current,[1,3] but the reliability of the predicted linear relation between i_d and $m^{2/3}t^{1/6}$ has not been demonstrated satisfactorily over a large range of m and t values.

The only previous systematic study of the relation between i_d and $m^{2/3}t^{1/6}$ was carried out some years ago by Maas,[5] who obtained data for the diffusion current of cadmium ion in 0.1 N potassium chloride with about thirty different dropping electrode capillaries. The corresponding diffusion current constants of cadmium ion computed from Maas' data show no definite trend when plotted against $m^{2/3}t^{1/6}$ (compare Fig. 1), but the precision of these data is too poor (*ca.* ± 2%), and the range of $m^{2/3}t^{1/6}$ values too limited (from about 0.6 to 1.5 mg.$^{2/3}$ sec.$^{-1/2}$) to constitute a very rigorous test of eq. 1.

These facts prompted us to investigate more carefully the relation between i_d and $m^{2/3}t^{1/6}$ over as large a range of m and t values as possible. The results obtained demonstrate conclusively that i_d is not an exact linear function of $m^{2/3}t^{1/6}$, but that I varies significantly in a regular manner with $m^{2/3}t^{1/6}$. Over the range of capillary characteristics normally employed in polarographic measurements the deviation from linearity is not large enough to invalidate the use of diffusion current constants in practical analytical work, but with very rapidly dropping capillaries (drop time less than about 1 sec.) the deviation becomes quite large.

This paper also presents data showing the relation between the residual current and capillary

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(1) For papers I and II of this series see, J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825, 1045 (1939).

(2) D. Ilkovič, *Coll. Czechoslov. Chem. Commun.*, **6**, 498 (1934); *J. chim. phys.*, **35**, 129 (1938).

(3) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

(4) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

(5) J. Maas, "De Polarografische methode met de druppelende Kwikelectrode ten dienste van het Pharmaceutisch Onderzoek," Dissertation, Amsterdam, 1937.

characteristics, and the effect of the medium in which the mercury drops form on the rate of flow of mercury from the dropping electrode.

Experimental

In order to determine if the diffusion current observed with the dropping electrode is influenced by the type of measuring instrument three different sets of apparatus were used, embodying two different principles, which we shall refer to as the "resistance-potentiometer" and "galvanometric" methods. In the resistance-potentiometer method a standard 10,000 ohm resistance was placed in series with the polarographic cell, the potential drop across this resistance was measured with a potentiometer and the current was computed by applying Ohm's law. The e. m. f. applied across the polarographic cell was measured directly with the same potentiometer used to measure the current. The apparatus used was essentially the same as that described previously.[1,3]

In the "galvanometric" method the current was measured from the deflection of a calibrated galvanometer in series with the polarographic cell. Two sets of apparatus were used in this method; one was the manual apparatus used in the resistance-potentiometer method with the standard resistance replaced by a Leeds and Northrup Type HS galvanometer, and the other was a Sargent–Heyrovsky Polarograph. The Leeds and Northrup galvanometer had a natural period of 3 sec., which is too short for polarographic measurements, and to adapt it to these measurements it was over-damped by means of a parallel resistance so that its half-period was increased to 11 sec.; *i. e.*, starting from rest 11 sec. were required for the deflection to attain 95% of its final value. The instrument was provided with an Ayrton-type shunt for regulating the sensitivity, and to minimize errors it was calibrated at each setting of the Ayrton shunt and at each time of use by a method that has already been described.[3] We believe that the precision and accuracy of these calibrations was about ±0.1%. The maximum sensitivity of this instrument was 0.02002 ± 2 microamp. per mm.

In the measurements with the Sargent–Heyrovsky Polarograph readings were taken on the visual scale of the instrument, which was calibrated at each time of use as described elsewhere.[3] The galvanometer in this instrument had a half-period of 8 sec., and its maximum sensitivity was 0.00329 ± 1 microamp. per mm. Since the visual scale on the Polarograph is only 15 cm. long the measurements made with it were somewhat less precise than those made on the 50-cm. scale that was used with the Leeds and Northrup galvanometer, but, from the agreement of replicate calibration data, we believe that the precision was about ±0.3% when the deflection was 100 mm. or greater.

The dropping electrode assembly comprised a stand-tube connected to a mercury reservoir by rubber pressure tubing, with the dropping electrode capillary connected to the stand-tube by a short length of rubber tubing, as described by Lingane and Laitinen.[6]

To determine whether the type of capillary had any effect on the diffusion current, experiments were made with capillaries that were hand drawn from Pyrex capillary tubing and also with capillaries consisting of 6 to 10 cm. lengths of "marine barometer" tubing from the Corning Glass Works.[3] With each capillary, measurements were made at several values of the pressure over a range from about 20 to 70 cm. to obtain as many different values as possible of the drop time and rate of mercury flow.

The rate of mercury flow, *m*, was determined by collecting mercury from the electrodes over a measured time interval and weighing it. The method used to collect the mercury and prepare it for weighing was the same as that previously described,[1] and duplicate determinations usually agreed to ±0.1%.

An H-type cell similar to that already described[6] was used, with a saturated calomel electrode as a working anode. For the measurements made by the resistance-potentiometer method, and with the Leeds and Northrup galvanometer, electrolytic hydrogen, purified by passage over copper gauze at about 400°, was used to free the solutions from dissolved air, whereas purified nitrogen was used for this purpose during the measurements with the polarograph. In both cases the gas was passed through the solution until the residual current became constant (*ca.* 30 min.), and it was then deflected over the surface of the solution while the diffusion currents were measured. All measurements were made with the cell in a water thermostat at 25.00 ± 0.05°.

Lead ion was chosen as the test substance because its diffusion current is excellently developed. Standard solutions of lead nitrate were prepared directly by dissolving the requisite amount of the pure, dried salt in water and diluting to known volume. The concentrations of these standard solutions and the test solutions prepared from them were known to within ±0.2%. One molar potassium chloride, containing 0.01% gelatin as a maximum suppressor, was used as the supporting electrolyte.

Results and Discussion

Diffusion Current Constant as a Function of $m^{2/3}t^{1/6}$.—The diffusion current constant of lead ion in 1 *N* potassium chloride containing 0.01% gelatin was determined at 25° with a number of different capillaries, which were selected to cover as large a range of *m* and *t* values as possible. Some of the capillaries were hand drawn from Pyrex capillary tubing and others consisted of Corning "marine barometer tubing" whose internal diameter is of the order of 0.05 mm. As shown in Tables I and II, the values of *m* ranged from less than 1 to almost 16 mg./sec., and the drop times varied from about 9 to less than 0.6 sec.

Table I contains data that were obtained by the resistance-potentiometer method of measuring the diffusion current and by the galvanometric method with the Leeds and Northrup galvanometer. Table II presents the results obtained with the Sargent–Heyrovsky Polarograph. The diffusion currents and the values of *m* and *t* were measured at −0.75 v. *vs.* the S.C.E., which value is well onto the diffusion current plateau of the lead wave. In all cases *m* and *t* were determined at the same time that the diffusion current was measured, so that the three quantities would be strictly comparable. The residual current of the 1 *N* potassium chloride supporting electrolyte was determined at −0.75 v. separately for each experiment, and it was subtracted from the observed diffusion current to obtain the corrected values of i_d given in Tables I and II. With 2.000 millimolar lead ion this correction never exceeded 2.5%, and in most cases it was much smaller. With each capillary measurements were made at several values of the applied pressure, *h*, which was measured from the tip of the dropping electrode to the mercury level in the reservoir.

The diffusion currents given in Tables I and II were measured as the average of the galvanometer oscillations, since it was believed that this would correspond more closely to the true average current to which the Ilkovič equation refers than either the maximal or minimal deflection.[3]

The diffusion current constants from Tables I

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[6] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, 11, 504 (1939).

TABLE I

DATA OBTAINED BY THE RESISTANCE-POTENTIOMETER METHOD AND BY GALVANOMETRIC MEASUREMENT WITH THE LEEDS AND NORTHRUP GALVANOMETER

All measurements were made at −0.75 v. *vs.* the S.C.E. at 25.00° with 1.995 millimolar lead ion in 1 *N* potassium chloride containing 0.01% gelatin. Capillary I consisted of "marine barometer tubing," and capillaries J and K were hand drawn. The diffusion current values have been corrected for the residual current.

Capillary	h, cm.	m, mg./sec.	t, sec.	$m^{2/3}t^{1/6}$ mg.$^{2/3}$ sec.$^{-1/2}$	i_d, microamperes Res.-Pot.	Galv.	$\frac{i_d}{Cm^{2/3}t^{1/6}}$ Res.-Pot.	Galv.
I	20	0.9026	8.86	1.344	10.66	10.68	3.976	3.984
	30	1.408	5.67	1.678	13.38	13.23	3.996	3.952
	40	1.902	4.30	1.958	15.33	15.28	3.925	3.912
	50	2.385	3.40	2.189	17.17	17.01	3.932	3.895
	60	2.881	2.86	2.412	18.69	18.62	3.884	3.870
	70	3.373	2.45	2.611	20.26	20.20	3.889	3.878
J	20	3.392	2.90	2.696	20.84	20.66	3.875	3.841
	30	5.239	1.96	3.375	25.79	25.68	3.835	3.814
	40	7.090	1.41	3.908	29.90	29.74	3.843	3.815
	50	8.889	1.11	4.366	33.53	33.40	3.850	3.834
	60	10.71	0.925	4.797	37.65	37.56	3.934	3.925
	70	12.54	0.765	5.162	43.23	43.28	4.198	4.203
K	20	4.269	2.28	3.019	23.10	22.96	3.835	3.812
	30	6.577	1.46	3.739	28.59	28.36	3.833	3.802
	40	8.895	1.05	4.328	33.41	33.57	3.869	3.887
	50	11.14	0.803	4.809	39.19	39.52	4.084	4.119
	60	13.40	0.667	5.276	47.34	47.50	4.497	4.513
	70	15.74	0.567	5.714	56.69	57.03	4.973	5.003

TABLE II

DATA OBTAINED WITH THE SARGENT–HEYROVSKY POLAROGRAPH

All measurements made at −0.75 v. *vs.* the saturated calomel electrode at 25.00°, with 2.000 millimolar lead ion in 1 *N* potassium chloride. Capillaries F, G, and H were hand-drawn. The diffusion current values have been corrected for the residual current

Capillary	h, cm.	m, mg./sec.$^{-1}$	t, sec.	$m^{2/3}t^{1/6}$, sec.$^{-1/2}$ mg.$^{2/3}$	i_d, microamp. (cor.)	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
F	40.0	1.072	4.49	1.345	10.88	4.045
	50.0	1.354	3.60	1.515	12.09	3.990
	60.0	1.642	2.92	1.664	13.04	3.918
	70.0	1.922	2.56	1.804	14.00	3.880
G	30.0	2.988	2.50	2.417	18.68	3.864
	40.0	4.050	1.82	2.807	21.46	3.823
	50.0	5.113	1.41	3.143	23.93	3.807
	60.0	6.174	1.18	3.460	26.44	3.821
	70.0	7.245	1.02	3.757	29.26	3.895
H	30.0	4.146	1.79	2.844	22.00	3.868
	40.0	5.617	1.31	3.305	25.34	3.834
	50.0	7.101	1.02	3.707	29.09	3.924
	60.0	8.543	0.870	4.083	33.84	4.144

and II are shown plotted against $m^{2/3}t^{1/6}$ in Fig. 1, which should simply produce a straight horizontal line if eq. 1 were strictly correct. Actually, however, it is seen that I first decreases, then passes through a flat minimum, and finally increases very rapidly as $m^{2/3}t^{1/6}$ increases.

By reference to Tables I and II and Fig. 1, it is seen that up to a value of $m^{2/3}t^{1/6}$ of about 3.2 all three methods of measurement yield agreeing values of the diffusion current constant; the average agreement is about ±0.3%, which is about the limit of precision of the measurements. Furthermore, identical results are obtained with the hand drawn and with the "marine barometer tubing" capillaries. Therefore, the variation of I with $m^{2/3}t^{1/6}$ is evidently a real effect, and is not due to peculiarities in the measuring instruments nor to the type of capillary used.

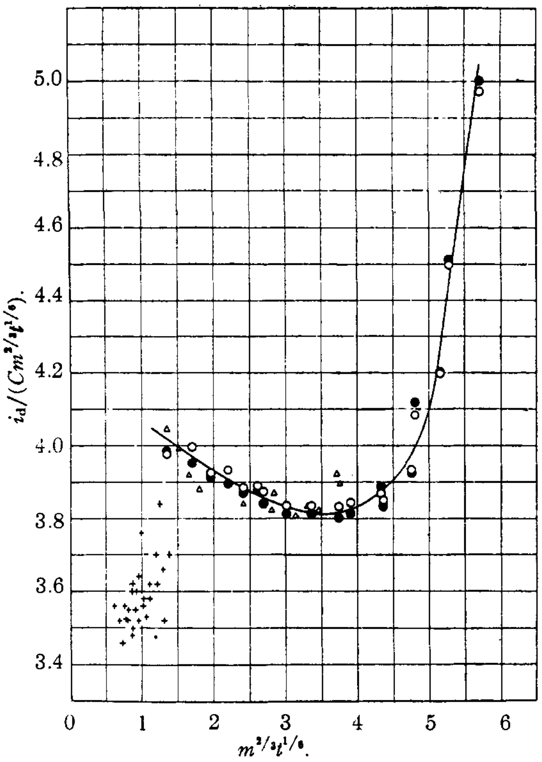

Fig. 1.—Diffusion current constant as a function of capillary characteristics. Open circles represent data obtained by the resistance–potentiometer method. Solid circles represent data obtained by galvanometric method with the Leeds and Northrup galvanometer. Triangles represent data obtained by galvanometric measurement with the Sargent–Heyrovsky Polarograph. Crosses denote data obtained by Maas with cadmium ion in 0.1 *N* potassium chloride.

The only noticeable effect of the type of measuring instrument is that the minimum in the data obtained with the Sargent–Heyrovsky Polarograph occurs at a slightly smaller value of $m^{2/3}t^{1/6}$ than with the other two methods of measurement. With all three methods of measurement the minimum occurs when the drop time is in the neighborhood of 1 sec., and with smaller values of t the ratio $i_d/(Cm^{2/3}t^{1/6})$ increases very rapidly. These results demonstrate clearly the unsuitability of rapidly dropping capillaries.

For the sake of comparison, diffusion current constants of cadmium ion in 0.1 *N* potassium chloride at 25°, computed from data obtained by Maas,[5] are also shown in Fig. 1 (points denoted by crosses). Although Maas employed about thirty different capillaries the range of $m^{2/3}t^{1/6}$ values is too limited, and the precision of the data is too poor, to demonstrate any variation of I with capillary characteristics.

The shape of the curve in Fig. 1, and the occurrence of a minimum, indicates that two opposing factors are involved in the variation of I with capillary characteristics. The rapid increase of I at large values of $m^{2/3}t^{1/6}$, and correspondingly small drop times, is understandable, because a very rapid drop rate promotes stirring of the solution in the vicinity of the drops. Since stirring disturbs the establishment of a normal diffusion layer, and thus accelerates the transfer of the reducible substance from the body of the solution up to the mercury surface, the current becomes abnormally large.

We are unable to offer any plausible explanation for the negative slope of the left-hand branch of the curve in Fig. 1. From the fact that the values of I obtained with the three different sets of measuring apparatus agree very well it seems unlikely that instrumental peculiarities could be responsible for the negative slope. However, it is conceivable that the current observed by the galvanometric method might be influenced by the relative period of the galvanometer, that is, by the ratio of galvanometer period to drop time, and hence an experiment was carried out with the Leeds and Northrup galvanometer to test this possibility. By changing the damping resistance the half-period of the galvanometer was varied from 3.1 to 11.2 sec., and the diffusion current at -0.75 v. of a 2.06 millimolar solution of lead ion in 1 N potassium chloride was measured with the same capillary under identical conditions. The galvanometer was calibrated at each new setting of the period, immediately before the diffusion current was measured. The results are shown in Table III, in which $i_{\text{min.}}$ and $i_{\text{max.}}$ refer to the minimum and maximum values of the galvanometer oscillations.

TABLE III

INDEPENDENCE OF OBSERVED DIFFUSION CURRENT ON GALVANOMETER PERIOD

$m = 2.87$ mg./sec., $t = 2.91 \pm 0.02$ sec.

Half-period, sec.	Half-period/drop time	i, microamp.			
		Min.	Max.	Diff.	Av.
3.1	1.06	17.66	20.14	2.48	18.90
5.0	1.71	17.93	19.85	1.92	18.89
7.0	2.42	18.24	19.66	1.42	18.95
9.5	3.28	18.30	19.46	1.16	18.88
11.2	3.84	18.35	19.35	1.00	18.85
				Av.	18.89 ± 0.03

Although the ratio of half-period to drop time varied about fourfold, and the amplitude of the oscillations decreased correspondingly from about 13 to 5% of the average value, the average current was constant to better than 0.2%. It is evident that the average current observed with a normal capillary is not influenced by the period of the galvanometer when the ratio of half-period to drop time is 1 or larger.

The capillaries normally used in polarographic measurements usually have values of $m^{2/3}t^{1/6}$ between about 1.5 and 3.0 mg.$^{2/3}$ sec.$^{-1/2}$, corresponding to the middle section of the left-hand branch of the curve in Fig. 1, and over this range I changes by about 4%. Therefore, the use of standardized diffusion current constants in practical analytical work, as previously recommended,[4] may lead to an error of a few per cent. when the $m^{2/3}t^{1/6}$ value of the capillary used in an analysis differs greatly from that of the capillary originally used to obtain the diffusion current constant. However, it is a simple matter to fabricate capillaries whose $m^{2/3}t^{1/6}$ values lie well within a range of ± 0.5 unit in the neighborhood of 2.5 mg.$^{2/3}$ sec.$^{-1/2}$, and with such capillaries the use of standardized diffusion current constants should give results reliable to within about ± 1 per cent.

Dependence of Residual Current on Capillary Characteristics.—It has previously been postulated[3] that the residual current observed with the dropping electrode is the cumulative result of a small faradic current from the reduction of traces of reducible impurities (*e. g.*, oxygen) and a "charging current" or "condenser current." The latter is assumed to result from the orientation of charges in the electrical double layer at the surface of the mercury drops as each freshly forming element of the surface assumes a charge sufficient to counteract the applied potential, somewhat analogous to the current which flows when an ordinary condenser is charged. It has been shown that this simple assumption accounts for the order of magnitude of observed residual currents.[3] On the basis of these postulates the residual current may be expressed by

$$i_r = i_f + i_c \qquad (2)$$

and from this equation a relation between the residual current and capillary characteristics can be predicted.

The faradic component of the residual current obeys the Ilkovič equation, and may be expressed by $i_f = k_1 m^{2/3}t^{1/6}$. On the assumption that the electrical double layer behaves as a perfect condenser, which admittedly is an oversimplification, Kolthoff and Lingane[3] concluded that the *average* value of the charging current during the life of a drop should obey the equation

$$i_c = (3/2)\kappa \Delta E\ (\mathrm{d}A/\mathrm{d}t) = 0.0085\kappa(\Delta E)m^{2/3}t^{-1/3} \qquad (3)$$

where κ is the capacity of the double layer (microfarad./cm.^{2}), ΔE is the difference (volts) between the potential of the dropping electrode at which i_c is measured and the potential at the maximum in the electrocapillary curve of mercury, A is the area (sq. cm.) of the drop surface, and the other symbols have their usual significance. In any given supporting electrolyte, and at a given value of the potential, eq. 3 has the form $i_c = k_2 m^{2/3}\cdot$

$t^{-1/3}$. When these relations are combined we obtain

$$i_r = k_1 m^{2/3} t^{1/6} + k_2 m^{2/3} t^{-1/3} \qquad (4)$$

from which

$$i_r/(m^{2/3}t^{1/6}) = k_1 + (k_2/t^{1/2}) \qquad (5)$$

Therefore, a plot of $i_r/(m^{2/3}t^{1/6})$ against $1/t^{1/2}$ should produce a straight line with slope equal to k_2 and intercept equal to k_1. Furthermore, the same values of k_1 and k_2 should be observed with different capillaries if measurements are made with the same solution at the same potential.

Some representative residual current data that we have obtained with three different capillaries are presented in Table IV, and values of $i_r/(m^{2/3}t^{1/6})$ for each capillary are plotted against $1/t^{1/2}$ in Fig. 2. Note that a different ordinate scale is used for curve F than for curves G and H.

TABLE IV

RESIDUAL CURRENT AS A FUNCTION OF CAPILLARY CHARACTERISTICS

All measurements at 25° in 1 N potassium chloride at −0.75 v. *vs.* the saturated calomel electrode. Air removed from the solutions with purified nitrogen.

Capillary	h, cm.	m, mg. sec.$^{-1}$	t, sec.	$1/t^{1/2}$	i_r, microamp.	$m^{2/3}t^{1/6}$	$\frac{i_r}{m^{2/3}t^{1/6}}$
F	40	1.072	4.49	0.47	0.220	1.35	0.163
	50	1.354	3.60	.53	.250	1.52	.164
	60	1.642	2.92	.59	.280	1.66	.169
	70	1.922	2.56	.63	.310	1.80	.172
G	30	2.988	2.50	.63	.223	2.42	.092
	40	4.050	1.82	.74	.272	2.81	.097
	50	5.113	1.41	.84	.322	3.14	.102
	60	6.174	1.18	.92	.372	3.46	.108
	70	7.245	1.02	.99	.418	3.76	.111
H	30	4.146	1.79	.75	.207	2.84	.073
	40	5.617	1.31	.87	.263	3.31	.079
	50	7.101	1.02	.99	.321	3.71	.087
	60	8.543	0.870	1.07	.382	4.08	.094

It is seen from Fig. 2 that the points pertaining to the different capillaries do fall very well on straight lines as predicted by eq. 5. In further agreement with eq. 5, the lines have identical slopes. The intercepts (k_1) of the lines from the different capillaries are not the same, but, since k_1 is proportional to the concentration of reducible impurity (very probably oxygen), this simply indicates that the amount of residual oxygen remaining in the three separate solutions was not the same.

The theoretical slope predicted by eq. 3 is shown as the dashed line in Fig. 2, and the agreement of the observed slopes with the theoretical value is surprisingly good. In calculating the theoretical slope ($0.0085\kappa\ \Delta E$) the value of κ was taken to be 22 microfarad./sq. cm. at −0.75 v., as found experimentally by Philpot,[7] and the maximum in the electrocapillary curve was assumed to be at −0.52 v. *vs.* S.C.E. in 1 N potassium chloride,[3] so that ΔE = 0.23 v. From these data the theoretical slope is 0.04, with a probable uncertainty of ±0.01, whereas the average observed slope is 0.054.

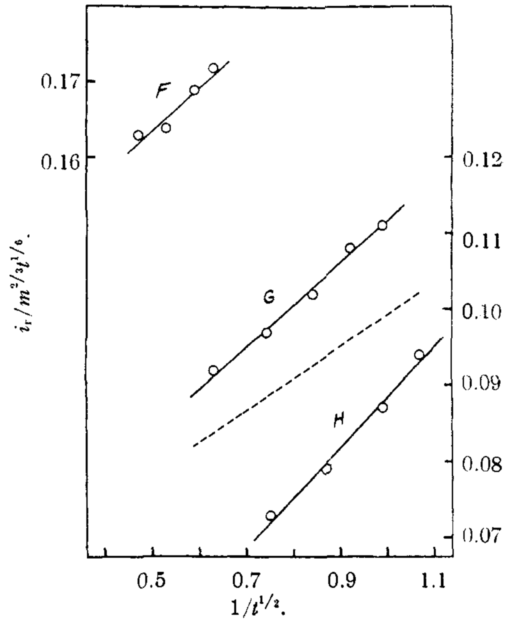

Fig. 2.—Residual current as a function of capillary characteristics.

In view of the fact that the simple "condenser" theory of the charging current cannot be more than a very crude approximation to the truth, we hesitate to ascribe very much theoretical significance to these data. However, they do indicate that the simple theory is at least a step in the right direction.

Influence of the Medium on *m*.—On the basis of a relatively few experiments, with dropping electrodes in air and in various aqueous solutions, Kolthoff and Lingane,[3] and Müller,[8] concluded that the medium in which the mercury drops form has very little effect on the rate of flow of mercury from a dropping electrode. However, the former authors also pointed out that m should not be entirely independent of the medium because the interfacial tension at the surface of the growing drops, which depends on the medium, creates a "back pressure" which opposes the applied pressure. In order to obtain more precise information on the magnitude of this effect m-values were determined with four different capillaries in air and in 1 N potassium chloride containing 0.01% gelatin, with the results shown in Table V.

Capillaries A and D were hand drawn, whereas B and C were made from Corning "marine barometer tubing." The characteristics of capillaries B and C correspond closely to those normally used in polarographic measurements. Several values of m and drop time t were obtained with each capillary at various values of the applied pressure h,

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(7) Y. St. L. Philpot, *Phil. Mag.*, (7) **13**, 775 (1932).

(8) O. H. Müller, "The Polarographic Method of Analysis," Journal of Chemical Education, Easton, Pa., 1941.

TABLE V

COMPARISON OF DROP TIMES AND m-VALUES IN AIR AND IN 1 N POTASSIUM CHLORIDE AT 25°

Capillary	h, cm.	t, sec. air	t, sec. soln.	$t_{\text{air}}/t_{\text{soln.}}$	m, mg./sec. air	m, mg./sec. soln.	Δm, % Obs.	Δm, % Calcd.
A	41.7	95.1	6.52	14.6	0.982	0.959	2.3	2.1
	51.7	66.5	5.16	12.9	1.214	1.203	0.9	1.6
	61.5	59.0	4.36	13.5	1.454	1.439	1.0	1.4
B	23.3	49.8	6.00	8.3	1.285	1.239	3.6	2.9
	33.3	35.3	4.09	8.6	1.875	1.824	2.7	2.0
	43.1	27.4	3.19	8.6	2.454	2.409	1.8	1.6
	53.1	23.0	2.56	9.0	3.040	2.983	1.9	1.3
C	24.7	42.7	4.52	9.5	2.062	2.004	2.8	2.7
	34.7	29.5	3.04	9.7	3.033	2.983	1.7	1.9
	44.7	17.8	2.36	7.5	3.964	3.927	0.9	1.3
	54.5	14.0	1.92	7.3	4.868	4.842	0.5	1.0
D	29.6	10.4	1.37	7.6	7.095	6.960	1.9	2.0
	39.6	7.76	1.01	7.7	9.454	9.372	0.9	1.5
	49.6	6.24	0.79	7.9	11.90	11.84	0.5	1.2

which was measured from the tip of the dropping electrode to the level of mercury in the stand-tube.

It was necessary to determine the value of m in air at ambient room temperature, which ranged from 25 to 29°, but the values of m_{air} given in Table V have been corrected to 25°. In applying this correction the temperature coefficient of m was taken as $+0.0031$ deg.$^{-1}$, which is an experimentally determined value previously reported.[9] The values of $m_{\text{soln.}}$ were measured with the capillaries immersed to known depths in the solution at 25°. Since the hydrostatic pressure between the tip of the dropping electrode and the solution level opposes the applied pressure, the measured values of $m_{\text{soln.}}$ were corrected back to zero immersion to obtain the values given in Table V. In applying this correction, it was assumed that m is directly proportional to h and that each 13.5 mm. of immersion corresponds to a decrease of 1 mm. in the effective value of h. Although the first of these assumptions is not strictly exact (see eq. 6) it is amply correct for the purpose of applying the correction which never amounted to more than 1% and usually was considerably less.

With all of the capillaries $m_{\text{soln.}}$ is considerably smaller than m_{air}, the maximum observed difference being 3.6% and the minimum 0.5%. Furthermore, in every case Δm decreases with increasing values of h.

The data in Table V confirm predictions previously made by Kolthoff and Lingane,[3] who have shown that when the Poiseuille equation for the flow of liquid from a capillary tube is applied to the dropping electrode, with allowance for the back pressure due to the interfacial tension at the surface of the mercury drops, m at 25° should be given by

$$m = 4.64 \times 10^{9} \frac{r_c^4}{l}\left[h - \frac{7.73 \times 10^{-3}\,\sigma}{(mt)^{1/3}}\right] \qquad (6)$$

In this equation r_c is the radius of the bore of the capillary (cm.), l is its length (cm.), σ is the interfacial tension (dyne/cm.) at the mercury-medium interface, h is the vertical distance (cm.) between the tip of the dropping electrode and the mercury level in the reservoir or stand-tube, and m and t have their usual significance. The numerical terms are combinations of universal constants. The second term in parentheses is the back pressure in terms of cm. of mercury.

When eq. 6 is applied to the same capillary dropping into air and then into solution at the same temperature and at the same value of h, and using the subscripts a and s for quantities in air and in solution, respectively, we have

$$\Delta m\% = \left(\frac{m_a - m_s}{m_s}\right)100 = \frac{0.77\left[\frac{\sigma_s}{(m_s t_s)^{1/3}} - \frac{\sigma_a}{(m_a t_a)^{1/3}}\right]}{h - \frac{7.7 \times 10^{-3}}{(m_s t_s)^{1/3}}} \qquad (7)$$

Since the second term in the denominator is the back pressure term in solution which is very much smaller than h, it is amply accurate to rewrite eq. 7 as

$$\Delta m\% \cong \frac{0.77}{h}\left[\frac{\sigma_s}{(m_s t_s)^{1/3}} - \frac{\sigma_a}{(m_a t_a)^{1/3}}\right] \qquad (8)$$

This equation predicts that Δm should be inversely proportional to h, and, since t_a is seven to fifteen times larger than t_s, whereas σ_a is of the same order of magnitude as σ_s, it predicts that m_a should be larger than m_s. Both of these predictions are in agreement with the experimental results in Table V.

The values under $\Delta m_{\text{calcd.}}$ in the last column of Table V were computed from eq. 8 with the aid of the experimentally determined values of $m_s t_s$ and $m_a t_a$, and with the assumption that $\sigma_a = 473$ and $\sigma_s = 400$ dyne/cm. The chief uncertainty in this calculation is the value of the drop time in air. If the drops formed normally in air the ratio of the drop time in air to that in solution at a constant value of h would be determined solely by the values of σ_a and σ_s, and hence $t_{\text{air}}/t_{\text{soln.}}$ should have the same value for all the different capillaries. However, it will be noted that the observed values of this ratio in the fifth column of Table V are only roughly constant for a particular capillary, and they differ considerably with the different capillaries. This is due to the fact that when the mercury drops form in air they adhere to the glass at the tip of the dropping electrode, and therefore become much larger than if they remained suspended freely from the end of the mercury thread. Consequently the back pressure deviates from the value for a freely hanging drop. In view of this uncertainty the values of $\Delta m_{\text{calcd.}}$ agree as well as can reasonably be expected with $\Delta m_{\text{obs.}}$ The agreement is certainly sufficiently good to confirm the hypothesis that it is the difference in back pressure which is responsible for the observed differences in m_a and m_s.

It is evident from these results that m should be measured directly in the solution concerned when maximal accuracy is desired in polarographic measurements. The practice of measuring m in air, as previously recommended,[3,9] is per-

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(9) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **14**, 655 (1942).

missible only when an error that may amount to as much as 2 or 3% is tolerable.

Summary

The diffusion current constant $i_d/(Cm^{2/3}t^{1/6})$ of lead ion in 1 N potassium chloride was determined over a range of $m^{2/3}t^{1/6}$ values from about 1 to 6 mg.$^{2/3}$ sec.$^{-1/2}$. The ratio $i_d/(Cm^{2/3}t^{1/6})$ decreased by about 3.0 per cent. per unit increases in $m^{2/3}t^{1/6}$ between 1 and about 3.2 mg.$^{2/3}$ sec.$^{-1/2}$, but with larger values of $m^{2/3}t^{1/6}$ the ratio $i_d/(Cm^{2/3}t^{1/6})$ increased rapidly.

Diffusion currents measured from the potential drop across a standard resistance agreed within about 0.5%, on the average, with value obtained by direct measurement with calibrated galvanometers.

Identical results were obtained with hand drawn capillaries and with those made from commercial capillary tubing.

The observed value of the diffusion current (average of the galvanometer oscillations) was independent of the relative galvanometer period when the ratio of half-period to drop time was varied from 1 to 4.

An equation relating the residual current to capillary characteristics has been presented and shown to be in harmony with experimental residual current data.

Experimental data obtained with several different capillaries demonstrate that the rate of mercury flow from the dropping electrode, with all other conditions constant, is smaller in 1 N potassium chloride solution than in air; the difference is inversely proportional to the pressure on the dropping electrode, and, depending on the characteristics of the capillary, it varies from about 0.5 to 3.6%.

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Polarographic Behavior of Alkaline Earth Metals. I. Barium and Strontium

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Few polarographic studies on alkaline earth metals have been made. Heyrovsky and Berezičky[1b] found that both barium and strontium produce well-defined waves in 0.1 N lithium chloride with half-wave potentials of about -1.9 volts and -2.1 volts, respectively (*vs.* S. C. E. = saturated calomel electrode). They found that the diffusion currents were no longer proportional to the concentration of barium ions when the latter was less than 5×10^{-4} molar. The observed discrepancy probably is due[2] to the fact that the authors failed to correct the measured diffusion currents for the residual current of the supporting electrolyte. With properly corrected values we found a satisfactory proportionality at dilutions far beyond the above limit. Furthermore, because of its more positive half-wave potential, barium could be determined in the presence of large amounts of strontium. However, when dealing with mixtures of both cations containing a large excess of barium, the determination of strontium became inaccurate.

Experiments conducted by Kimura[3] indicated that calcium produces a wave at about -2.2 v. (*vs.* S. C. E.) in the presence of tetraethylammonium salts as supporting electrolytes. However in view of the fact that the waves displayed very pronounced maxima, which could not be eliminated and which were suppressed with difficulty by the usual maximum suppressors, they were not suitable for analytical purposes. No suitable procedure is available for the polarographic determination of calcium.

In the present study we have determined the polarographic behavior of barium and strontium separately and in mixtures. In a subsequent paper the polarography of calcium alone and in mixtures with barium and strontium will be presented.

Experimental

The current–voltage curves were measured with a manual apparatus described elsewhere.[4] Although this method is not as convenient as the use of an automatic polarograph, it has the advantage of greater precision and accuracy, which is particularly important for determining the diffusion coefficients of alkaline earth metal ions in various media. The electrolytic cells used in this work and the method of measurement of the cell resistance were described in detail in a previous paper.[5] The reported values of the cathode potential refer to the saturated calomel electrode and were properly corrected for iR drop. All electrolyses were carried out in a thermostat at 25°. Except for the measurements carried out in studying the effect of the mercury drop time upon the diffusion current, the initial free dropping time of the dropping mercury electrode in all of the experiments was 3 ± 0.2 sec.

Kahlbaum reagent tetraethylammonium iodide, purified by repeated recrystallizations from ethanol–water mixtures, was used as supporting electrolyte in this work. In order to get the true diffusion currents, the residual current of the supporting electrolyte solution determined in a blank experiment was subtracted from the measured values of all diffusion currents. For all solutions of the alkaline earth metal salts, Merck reagent chlorides were used. The ethanol for alcohol–water mixtures was redistilled azeotropically and kept in a vacuum.

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(1b) J. Heyrovsky and S. Berezičky, *Coll. Czechoslov. Chem. Commun.*, **1**, 19 (1929).

(2) *Cf.* I. Zlotowski and I. M. Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 473 (1942).

(3) G. Kimura, *Coll. Czechoslov. Chem. Commun.*, **4**, 492 (1932).

(4) J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).

(5) I. Zlotowski and I. M. Kolthoff, *ibid.*, **64**, 1297 (1942).