from the heating coil. The pattern of the 60% sample was that of zirconium dioxide plus tungsten. Since no structures appeared other than those of the metal and the dioxide, it was assumed that no new compound formed in the 55 to 63% region. Thus that region was one of two immiscible solids, namely, zirconium and zirconium dioxide.

In Fig. 2 is given the phase diagram for the system as interpreted from the present results. Since the points represent the melting points of the samples, the curve is the solidus line for the system. The dotted lines drawn downward from the horizontal portion of the curve are included to indicate that a region of solid immiscibility exists and are not intended to mark the actual limits of solubility.

The diagram indicates that near the melting points only two solid phases are stable—those of zirconium metal and zirconium dioxide. The metal phase is capable of dissolving oxygen to form a solid solution of 55 atom per cent. oxygen, while the dioxide can form a solid solution with as much as 15 mole per cent. zirconium in zirconium dioxide.[15] In particular the diagram shows that no compound such as ZrO or Zr_2O_3 is stable at its melting point. The compound ZrO has been postulated to account for a number of phenomena,[16,17,18] however, in general it is possible to explain these on the basis of a solid solution of metal in the dioxide.

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[15] The value of 15 mole per cent. represents the mole fraction of Zr in ZrO_2. It is obtained by a simple calculation from the solubility limit of 63 atom per cent. oxygen in zirconium shown in Fig. 3.

[16] E. Friederich and L. Settig, *Z. anorg. Chem.*, **145**, 127 (1925).

[17] H. Jacobs, *J. Appl. Phys.*, **17**, 596 (1946).

[18] C. A. Zapffe, *J. Am. Ceramic Soc.*, **27**, 293 (1944).

CHICAGO 16, ILLINOIS RECEIVED NOVEMBER 1, 1950

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Studies in the Theory of the Polarographic Diffusion Current. V. Effects of Certain Variables on *m* and the Residual Current

BY LOUIS MEITES

Data are presented on the effects of pressure, supporting electrolyte, applied potential, temperature and gelatin concentration on *m* and the residual current.

Experimental

The apparatus and technique have been described in preceding papers.[1-3]

Data and Discussion

Factors Affecting *m*. The Effective Pressure.—The theory underlying the variation of *m* with the applied pressure has been discussed by Kolthoff and Lingane,[4] and has been tested by Maas.[5] Assuming $\sigma = 400$ dynes/cm.[4]

$$m = k_1\,(h_{\text{eff.}} - 3.1\,[mt]^{-1/3}) \qquad (1)$$

Table I summarizes the data for a typical capillary giving drop times between 1.8 and 7.6 sec. *Within these limits* equation (1) is satisfied with a mean error of ± 0.10%, and hence may be used with confidence so long as no better accuracy than this is required. However, the data clearly show small but significant deviations from the theory: k_1 is lower at both high and low pressures than at intermediate pressures. Over five hundred measurements of *m* with fourteen capillaries of widely varying characteristics, nearly all with more than one supporting electrolyte, indicate that k_1 increases about 2% as the drop time is increased from 0.5 to about 4 sec. and decreases about 1.5% from t = 6 to 19 sec. As most of these variations occur at drop times below 2 sec. and above 10 sec., it is plain that equation (1) cannot be relied on for capillaries with very short or very long drop times.

TABLE I

EFFECTS OF APPLIED PRESSURE AND SUPPORTING ELECTROLYTE ON *m*

Data for capillary C (marine barometer tubing) at $E_{\text{d.e.}} = -1.00$ v. *vs.* S.C.E. The value of the back pressure term in equation (2) was 1.57 ± 0.01 sec.$^{1/3}$mg.$^{-1/3}$; $T = \theta = 25.0°$

h, cm. of Hg	*m*, mg./sec. in 0.1 *F* KNO_3	*m*/(*h* − 1.57) × 10² in 0.1 *F* KNO_3	*m* in 0.1 *F* KCl	*m* in 0.1 *F* KCl–0.1 *F* HCl
107.78	4.2730	4.023	4.2432	4.2747
98.78	3.9133	4.025	3.8840	3.9129
89.78	3.5514	4.026	3.5291	3.5545
80.78	3.1837	4.019	3.1649	3.1830
71.78	2.8277	4.027	2.8052	2.8304
63.78	2.5062	4.028	2.4875	2.5032
57.78	2.2645	4.028	2.2468	2.2669
52.78	2.0640	4.030	2.0492	2.0653
47.78	1.8644	4.034	1.8524	1.8634
42.78	1.6625	4.033	1.6518	1.6602
38.78	1.5019	4.035	1.4896	1.5020
34.78	1.3357	4.021	1.3285	1.3347
31.78	1.2155	4.022	1.2098	1.2147
28.78	1.0952	4.024	1.0888	1.0958
26.78	1.0118	4.012	1.0064	1.0140

The Supporting Electrolyte.—Typical data for *m* of a single capillary in three supporting electrolytes are shown in Table I. The values of *m* in 0.1 *F* potassium nitrate and in 0.1 *F* potassium chloride–0.1 *F* hydrochloric acid are practically identical. In 0.1 *F* potassium chloride, however, *m* is appreciably lower: the difference varied somewhat among capillaries but was always between 0.4 and 0.9%. In ordinary polarographic work, therefore, it is justifiable to assume that *m* is independent of supporting electrolyte composi-

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

[2] L. Meites and T. Meites, *ibid.*, **73**, 395 (1951).

[3] L. Meites, *ibid.*, **73**, 1581 (1951).

[4] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 62–69.

[5] J. Maas, *Collection Czechoslov. Chem. Commun.*, **10**, 42 (1938).

tion, in agreement with the conclusion of Kolthoff and Lingane.[6] But in more precise work this assumption will not, in general, be permissible.

The Applied Potential.—According to equation (1) *m* should pass through a minimum at the potential of the electrocapillary maximum. This has been studied by Lingane and Kolthoff,[7] but their data are not sufficiently precise to confirm the theory conclusively. The data in Table II show that, in accordance with this prediction, *m* passes through a minimum at about −0.5 v., which is the potential at which *t* is greatest.

TABLE II

VARIATION OF CAPILLARY CHARACTERISTICS WITH APPLIED POTENTIAL

Capillary Q in 0.1 *F* KCl; $h = 30.1$ cm.; $T = 25.00 \pm 0.05°$

$E_{d.e.}$ *vs.* S.C.E., volt	*m*, mg./sec.	*t*, sec.	$m^{2/3}t^{1/6}$
0.00	3.4042	2.700	2.6703
−0.20	3.3948	2.883	2.6947
−0.40	3.3831	2.925	2.6950
−0.60	3.3831	2.927	2.6953
−0.80	3.3872	2.882	2.6906
−1.00	3.3891	2.740	2.6690
−1.20	3.3915	2.551	2.6386
−1.40	3.4039	2.337	2.6068
−1.70	3.4218	1.933	2.5344
−2.00	3.4487	1.435	2.4243

Temperature.—The effect of temperature on *m* has been discussed by Kolthoff and Lingane.[8] Their analysis involves two temperatures: that of the capillary and the mercury flowing through it, and that of the mercury column above the capillary. These temperatures, however, cannot be sharply demarcated in practice: usually the cell and a portion of the capillary are at one temperature, *T*, and the mercury in the stand tube above the capillary at another temperature, θ, and the form of the intervening temperature gradient is uncertain.

Values of *m* secured with capillary C-95 (10.0 cm. of marine barometer tubing, 5.8 mm. o.d., depth of immersion 3.0 cm. in 0.1 *F* potassium nitrate) are shown in Table III. The values of "*m*, calcd." were found from the empirical equation

$$m = 4.2730 + 0.00935(T - 25) + 0.00222(\theta - 25) \quad (2)$$

When $T = \theta$, as when *m* is measured in air, dm/dT is thus 0.0027/deg., which agrees well with the value 0.0031/deg. reported by Lingane.[9] The individual temperature coefficients from equation (2) have little general significance, but it is of interest that the sign of the coefficient of θ is opposite to that expected.[8]

TABLE III

TEMPERATURE COEFFICIENTS OF *m*

$E_{d.e.} = -1.00$ v. *vs.* S.C.E.

T	θ	*m*, obsd.	*m*, calcd.
25.0	25.0	4.2730	(4.2730)
26.0	27.7	4.2883	4.2883
28.0	28.7	4.3088	4.3093
30.0	30.6	4.3325	4.3322
31.7	27.2	4.3407	4.3405
31.8	31.8	4.3521	4.3517
34.8	27.8	4.3706	4.3708

The Gelatin Concentration.—The effect of gelatin on the interfacial tension at the electrode-solution interface (and hence on *t*) has been described elsewhere.[10] Some pertinent data are shown in Table IV, in which each value of *m* is the mean of four measurements. When the mean values of m/m^0 are plotted against the logarithm of the gelatin concentration, a discontinuity is found at approximately the polarographic critical concentration (5×10^{-3}% from drop time data). Because of the relatively low driving pressures used in these experiments, the error caused by the assumption that *m* in a solution containing up to 0.01% gelatin is identical with *m* in the absence of gelatin will usually be less than the value found here. Against this error one must set the lower precision attainable when *m* is measured in the presence of gelatin, which corresponds to an uncertainty of about 0.1%. Thus it is substantially immaterial whether *m* in a solution containing 0.01% gelatin is measured directly or is taken as equal to *m* in the same medium without gelatin.

TABLE IV

EFFECT OF GELATIN CONCENTRATION ON *m*

$E_{d.e.} = -1.00$ v. *vs.* S.C.E. in 0.1 *F* KCl. "Head" corrections were 7.1 cm. for capillary III and 8.7 cm. for capillary IV; $T = 25.00°$; $\theta = 25.5 \pm 0.2°$

Gelatin concn., $\times 10^{-3}$ %	*m*	m/m^0	*m*	m/m^0
	Capillary III-26		Capillary IV-25	
0	4.4045	1.0000	4.4259	1.0000
2.2	4.4009	0.9992	4.4251	0.9998
4.5	4.4018	.9994	4.4241	.9996
9.0	4.3948	.9978	4.4187	.9984
18.0	4.3910	.9969	4.4150	.9975
35.0	4.3869	.9960	4.4100	.9964

Factors Affecting i_r.—According to Kolthoff and Lingane,[11] and Lingane and Loveridge,[12] the residual current should be given by

$$i_r/m^{2/3}t^{1/6} = k_1 + 0.0085K(\Delta E)t^{-1/3}$$

where *K* is the capacity of the double layer (microfarads/cm.²) and ΔE is the difference between the potential at which the current is measured and the potential of the electrocapillary maximum. For a solution free from reducible impurities, k_1 is theoretically zero. Values of the other constants required are available from the work of Grahame[13] and Grahame, Larsen and Poth.[14] In 0.1 *F* potassium chloride, then

$$I_r = k_1 + 0.073t^{-1/3} \quad (E_{d.e.} = -1.00 \text{ v. } vs. \text{ S.C.E.})$$

and

$$I_r = k_1 + 0.159t^{-1/3} \quad (E_{d.e.} = -1.50 \text{ v. } vs. \text{ S.C.E.})$$

Figure 1 shows some typical results secured at these two potentials. The points fall on straight lines with, in each case, a mean deviation of slightly

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(6) I. M. Kolthoff and J. J. Lingane, *Chem. Revs.*, **24**, 1 (1939).

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

(8) Ref. 3, p. 75.

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

(10) L. Meites and T. Meites, THIS JOURNAL, **73**, 177 (1951).

(11) Ref. 3, pp. 108-110.

(12) J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **66**, 1425 (1944).

(13) D. C. Grahame, *ibid.*, **71**, 2975 (1949).

(14) D. C. Grahame, R. P. Larsen and M. A. Poth, *ibid.*, **71**, 2978 (1949).

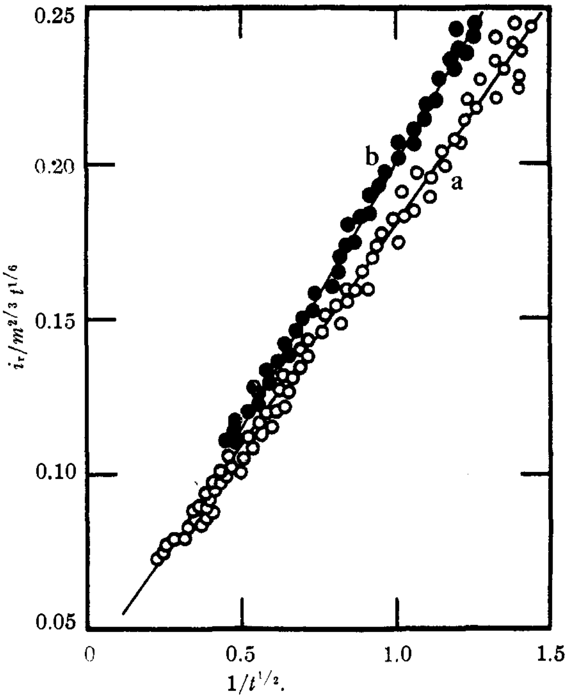

Fig. 1.—Residual currents in 0.1 *F* KCl at $E_{d.e.} = -1.000$ v. *vs.* S.C.E. (open circles, curve *a*) and −1.50 v. *vs.* S.C.E. (solid circles, curve *b*).

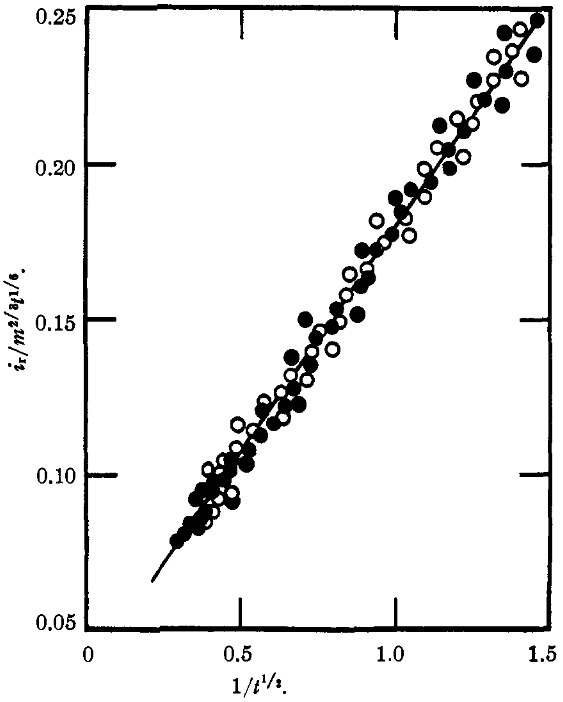

Fig. 2.—Residual currents at $E_{d.e.} = -1.00$ v. *vs.* S.C.E. in 0.1 *F* potassium nitrate (open circles) and in 0.1 *F* potassium chloride–0.1 *F* hydrochloric acid (solid circles). The line shown is the least-squares "best" line through the values in 0.1 *F* potassium chloride at this potential (*cf.* Fig. 1).

better than ±6%. About 550 measurements at −1.00 v. and about 80 at −1.50 v. give

$$I_r = 0.033 + 0.146t^{-1/2} \quad (E_{d.e.} = -1.00 \text{ v.})$$

and

$$I_r = 0.028 + 0.173t^{-1/2} \quad (E_{d.e.} = -1.50 \text{ v.})$$

At −1.5 v. the slope is in satisfactory agreement with the theoretical value, but at −1.0 v. the calculated slope is only half the experimental value. There is no evident explanation for this discrepancy. The agreement between the two values of k_1 is fortuitous and indicates merely that these solutions contained no detectable impurities reducible at −1.5 v. but not at −1.0 v.

At −1.0 v. *vs.* S.C.E. the residual current is the same, within the probable error of the measurements, in each of the three media used (Fig. 2); this shows that the values of $K(\Delta E)$ are nearly identical in these solutions at this potential. The residual current is also unaffected by the addition of 0.01% gelatin, in agreement with the fact that this concentration of gelatin does not appreciably change the shape of the electrocapillary curve.[10]

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