

reason, this particular section of the line is shown dotted. The data show that the activation energy E_k for the oxidation of carbon monoxide on a platinum surface is 45 000 cal mole⁻¹; the corresponding value of k_0 is 10¹⁵. The kinetic equation is thus

$$\frac{d[\text{CO}_2]}{dt} = 10^{15}[\text{CO}] \exp(-45\,000/RT) \text{ moles cm}^{-3} \text{ sec}^{-1},$$

where $[\text{CO}]$ is the molar concentration of carbon monoxide.

The Combustion of Carbon Monoxide in a Copper Tube

The experiments were conducted at 450°–730°, with flow rates of 6–15 m sec⁻¹ and initial concentrations of carbon monoxide of 3–5%. Otherwise conditions were the same as for the experiments with a platinum tube.

The results, presented in Fig. 5, show that at low rates of flow the oxidation of carbon monoxide in a copper capillary begins at 440°; at 660°–700° its extent reaches 80%. At a higher temperature (800°) the walls of the tube became covered with a layer of copper oxide, which reduced markedly the degree of oxidation. For instance, at 760° the extent of oxidation was 40%.

The experimental data are shown in Fig. 3. Using the previously described method of allowing for the spatial combustion and calculating k^* , it is possible to evaluate the role of the homogeneous reaction and of diffusion of reactants to the walls and to determine the value of k for the whole temperature range. The results of such calculations are shown in Fig. 5. The data show that the activation energy E_k for a copper tube is 22 000 cal mole⁻¹ and $k_0 = 10^6$. The diffusional limit lies in a temperature region around 900°. The kinetic equation takes the form

$$\frac{d[\text{CO}_2]}{dt} = 10^6[\text{CO}] \exp(-22\,000/RT) \text{ moles cm}^{-3} \text{ sec}^{-1}.$$

The author acknowledges the assistance of Corresponding Member of the Academy of Sciences L. N. Khitrin and thanks Prof. M. V. Ravich and senior colleague O. A. Tsukhanova for valuable advice.

SUMMARY

1. Using a platinum tube, a heterogeneous reaction on platinum has been studied at 320°–650°, and the diffusion constant measured. The combustion of carbon monoxide on platinum has been shown to have a high activation energy (about 45 000 cal mole⁻¹) and a high pre-exponential factor. Even in the narrow tube studied, the heterogeneous oxidation of carbon monoxide becomes limited by diffusion in the region of temperatures as low as 400° and is therefore only slightly dependent on temperature.
2. From the constant for the spatial combustion of CO, obtained with a quartz tube, and the values of the diffusion constants, it was possible to determine the characteristics of the combustion of carbon monoxide on platinum and copper surfaces.

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POLAROGRAPHIC MAXIMA OF THE FIRST ORDER. DEPENDENCE OF MAXIMUM CURRENT ON CONCENTRATION OF REDUCIBLE SUBSTANCE AND CONDUCTIVITY OF SOLUTION

T. I. Popova and T. A. Kryukova

The reason for the appearance of first-order maxima on polarographic current vs. potential curves was established by Frumkin and Bruns¹ as early as 1934, and since then such maxima have been studied both experimentally and theoretically by many investigators^{2–10}. Until recently, however, the complex dependence of the first-order maximum current on the concentration of reducible substance and on the conductivity of the solution has remained unexplained. The causes of the arrest of movement with growth in the negative charge on the surface and the shape of the negative maximum, which differs markedly from that of the positive maximum, have also remained obscure.

Great differences of opinion exist about the dependence of the first-order maximum current on concentration. Several workers^{11–14} consider this dependence to be linear; others^{15,16} assume the height of the maximum to be proportional to the concentration of reducible substance raised to a power greater than unity. According to Herasymenko et al.¹⁷ the exponent is 1.5; the value calculated from the data of Kolthoff and Lingane¹⁸ is almost 2 (if their extrapolated current values are accepted as correct).

Frumkin and Levich¹⁹ have shown theoretically that the maximum current should be, within certain limits, proportional to the square of the concentration and inversely proportional to the square root of the conductivity of the solution. With regard to the latter, it was observed long ago that the height of the maximum for a given concentration of reducible substance is greatly affected by change in the conductivity of the solution, all investigators having noted the existence of certain optimum conditions (concentration of supporting electrolyte), under which the maximum has its highest value. Different electrolyte concentrations have been indicated: 0.001N KCl in the case of the reduction of oxygen^{11,17,20}; and equal to the concentration of the reducible substance itself²¹.

All the investigations show that the maximum is absent with a very low concentration of supporting electrolyte, increases as the concentration rises to a certain limit, then falls, disappearing completely in concentrated solutions. Later investigations^{22–24} showed the incorrectness of this last statement, and gave examples of first-order maxima

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4. G. K. Sobolev, ibid., **1**, No. 5, 34 (1958).

in 1–6*N* solutions of supporting electrolytes, thus demonstrating that it is not the absolute magnitude of the concentration of supporting electrolyte which is important, but the ratio between this concentration and that of the reducible substance.

The cause of the marked discrepancies between the results of different investigators lies in differences in experimental conditions and in factors which they disregarded — presence of traces of surface-active substances in the form of so-called "natural" polarographic contamination and in the presence of tangential motion of the mercury surface as it runs out — both of which can strongly distort the results.

The aim of this work was to study the dependence of the first-order maximum on the concentrations of reducible substance and supporting electrolyte under conditions which avoided the appearance of second-order maxima in the almost complete absence of surface-active substances.

EXPERIMENTAL

Measurements with the dropping electrode were carried out in the apparatus described previously²⁵. The apparatus depicted in Fig. 1 was made for experiments in which radial movement of the surface of the drop, due to its growth, was also eliminated.

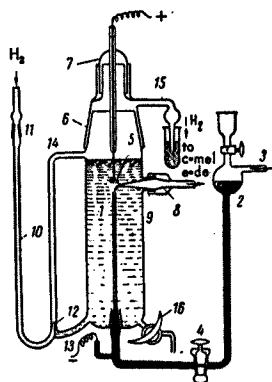


Fig. 1. Vessel for measurements with fixed mercury drop.

The cathode 1 is fixed at the centre of the apparatus by means of a ground joint, and consists of a capillary of internal diameter 1 mm which connects through a tap with the mercury reservoir 2, which itself connects through the side tube 3 with a bulb for producing pressure. With tap 4 open, mercury was forced out of the capillary, and as soon as a drop of the required size has been formed the tap was closed. The anode was a platinum disc 5 1 cm in diameter, which could be introduced into the electrolytic cell through the cover 6 provided with a mercury seal 7. Polarisation of the fixed mercury electrode and measurement of the current were accomplished in the same way as with the usual dropping electrode. The cathode potential was measured by means of a 0.01*N* calomel electrode, the siphon 8 of which was brought through the ground-in side outlet 9 to a

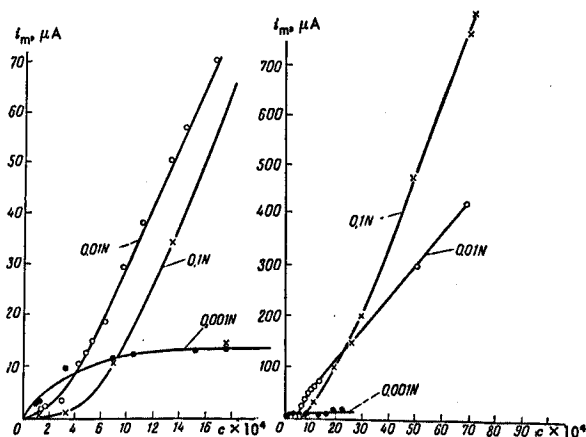


Fig. 2. Variation of maximum current with concentration of mercury in KCl solutions of different concentrations (dropping electrode).

distance of 0.1 mm from the surface of the drop. By rotating the ground joint 9 the tip of the siphon could be turned away from the mercury drop while the current was being measured.

Solution was run into the apparatus through the cover 6. The apparatus was connected to a supply of pure hydrogen via the U-tube 10 and the ground joint 11. A capillary 12 was sealed inside the U-tube, and to it was sealed the outlet tube 13 from the bottom of the vessel. Solution from the lower part of the apparatus was transferred to the upper part through the tube 14, and in this way mixing of the solution was achieved. The hydrogen emerged from the apparatus through the tube 15, which was provided with a water seal. Solution was run out of the apparatus through the tube 16.

The size of the drop was not the same from experiment to experiment, and therefore in the case of the fixed drop current densities in A/cm² are always given instead of the total current through the drop, as with the dropping electrode.

Three quite different concentrations of supporting electrolyte (0.1, 0.01, and 0.001*N* KCl or KClO₄) were chosen to study the dependence of the maximum current on the concentration of reducible substance. The curves in Fig. 2, obtained with a dropping electrode, show that no maximum arises at low concentrations of mercury ions. As the mercury concentration rises, a maximum develops, appearing at a lower concentration the lower the conductivity of the solution.

A similar relation between maximum current and concentration of reducible substance is observed with the negative maximum for zinc (dropping electrode, Fig. 3). The i_m vs. c curves for different electrolyte conductivities intersect in this case also.

Experiments with the fixed mercury drop show that the relation between maximum current and concentration remains of the same character as with the dropping electrode (Fig. 4).

Fig. 5 shows curves obtained for the change in maximum current with conductivity of the solution for a dropping

Concentration of mercury and zinc ions and corresponding optimum conductivities of solution (dropping electrode).

Concn. of mercury ions, N	Optimum conductivity, $\Omega^{-1}\text{cm}^{-1}$	Concn. of zinc ions, N	Optimum conductivity, $\Omega^{-1}\text{cm}^{-1}$
$1.0 \cdot 10^{-4}$	$1.94 \cdot 10^{-4}$	$9.4 \cdot 10^{-4}$	$1.35 \cdot 10^{-3}$
$2.17 \cdot 10^{-4}$	$2.81 \cdot 10^{-4}$	$4.3 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$
$1.09 \cdot 10^{-3}$	$1.55 \cdot 10^{-3}$	$8.3 \cdot 10^{-3}$	$1.3 \cdot 10^{-2}$
$1.74 \cdot 10^{-3}$	$2.55 \cdot 10^{-3}$		

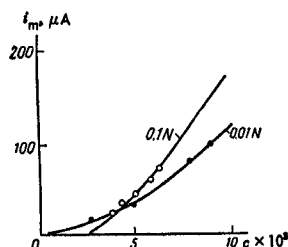


Fig. 3. Variation of maximum current with concentration of zinc in KCl solutions of different concentrations (dropping electrode).

electrode in KClO_4 solutions with constant concentrations (10^{-4} and $10^{-3}N$) of mercury. When the conductivity is very low there is no maximum, but as it increases a sharp maximum appears, itself increasing to a certain maximum value; with further increase in conductivity, the maximum becomes more and more rounded, and gradually decreases, until finally it vanishes altogether at a definite concentration of supporting electrolyte, which exceeds that of the reducible substance by a factor of about 200–250. A typical curve for the change in maximum current with conductivity of the solution is shown in Fig. 6. It follows from the above data that a definite conductivity of the solution exists at which the maximum has its greatest value, and this will be

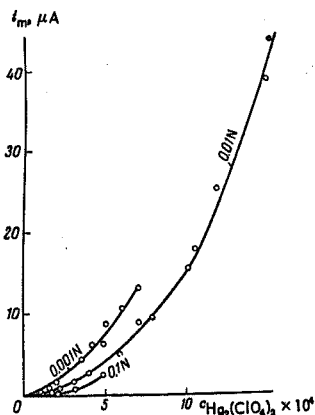


Fig. 4. Variation of maximum current with concentration of mercury $[\text{Hg}_2(\text{ClO}_4)_2]$ in KClO_4 solutions of different concentrations (fixed mercury drop).

subsequently termed the "optimum conductivity". The accompanying Table gives values of the optimum conductivity both for mercury ions and for zinc ions.

Over the concentration range investigated, the optimum conductivity varies linearly with the concentration of reducible ion:

$$\kappa_{\text{opt}} = 1.5c,$$

where c is measured in equiv. litre $^{-1}$ and κ in $\Omega^{-1}\text{cm}^{-1}$.

In the case of the fixed mercury electrode the optimum conductivity varies in a different way with concentration, e.g.:

Concentration of mercury ions, N	Optimum conductivity, $\Omega^{-1}\text{cm}^{-1} \times 10^{-4}$
1.0×10^{-4}	0.98
4.9×10^{-4}	2.41
1.2×10^{-3}	2.6

The shape of the negative maxima, obtained, for example, during the discharge of zinc ions, differs markedly from that of the positive maxima (e.g. those of mercury). A negative maximum is most developed at the half-wave potential, and the fall in current begins at potentials at which the limiting current has not yet been reached (Fig. 7). This is especially clearly shown in i vs. ϕ curves obtained with the fixed drop electrode, but can also be observed with the usual dropping electrode when the applied voltage is varied slowly (the automatic recording of polarisation curves generally makes it impossible to observe this feature). Such maxima can be found in the literature^{26,27}.

DISCUSSION

The rate of tangential motion of the surface, v_t , which governs the appearance of first-order maxima on the i vs. ϕ curve, is determined, according to the theory of Frumkin and Levich¹⁹, by, other conditions being the same, the potential difference $\Delta\Phi$ along the drop and the surface charge ϵ :

$$v_t = \frac{1}{2} \frac{\Delta\Phi\epsilon}{2\mu + 3\mu^1 + (\epsilon^2/\kappa)}, \quad (1)$$

where $\Delta\Phi$ is proportional to the intensity of the electric field E and the radius of the drop a :

$$\Delta\Phi = 3aE = 3a \frac{i_m}{\kappa}. \quad (2)$$

The magnitude of ϵ^2/κ , which has the dimensions of viscosity, is in Eqn. (1) a measure of the retardation of the tangential motion. The magnitude of the current, increased by the tangential motion of the surface of the mercury drop, can be represented as a function of the ratio of the speed of movement to the field strength with a drop of unit radius, i.e. of the quantity Z , termed by Frumkin and Levich the "specific surface mobility":

$$Z = \frac{\epsilon}{2\mu + 3\mu^1 + (\epsilon^2/\kappa)}. \quad (3)$$

It can be shown, from a theoretical consideration of the variation of the first-order maximum current with the conductivity of the solution, that

$$i_m = k\kappa^{-0.5}. \quad (4)$$

Experiment shows that the decrease in peak current with increase in conductivity can be represented, at values of

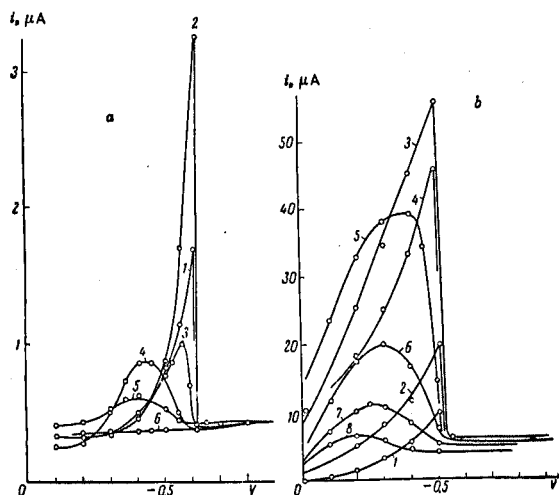


Fig. 5. Polarisation curves obtained in various solutions: a) $10^{-4} N \text{ Hg}_2(\text{ClO}_4)_2 + \text{KClO}_4$ of the following concentrations, N : 1) 2×10^{-4} ; 2) 10^{-3} ; 3) 4×10^{-3} ; 4) 6×10^{-3} ; 5) 10^{-2} ; 6) 1.5×10^{-2} ; b) $10^{-3} N \text{ Hg}_2(\text{ClO}_4)_2 + \text{KClO}_4$ of the following concentrations, N : 1) 2×10^{-4} ; 2) 10^{-3} ; 3) 10^{-2} ; 4) 5×10^{-2} ; 5) 10^{-1} ; 6) 5×10^{-1} ; 7) 1; 8) 2.

$\kappa > \kappa_{\text{opt}}$, by the equation

$$i_m = k\kappa^{-\beta}, \quad (5)$$

where $-0.6 > \beta > -0.7$.

This formula expresses the variation of the maximum current with the conductivity of the solution for both the dropping and the fixed electrodes. The data, which have been cited, show that at conductivities greater than the optimum experimental results agree approximately with theoretical deductions in the case of positive first-order maxima. With negative first-order maxima, the decrease in current with increase in conductivity above the optimum value is more rapid than that shown by Eqn. (5).

The decrease in maximum current when the conductivity is diminished to low values and the existence of an optimum conductivity do not follow directly from the above theory. The existence of an optimum conductivity can be explained by examining the variation of $\Delta\Phi$ with conductivity and of Z with potential.

At conductivities below the optimum, a considerable potential difference is still produced along the surface, which might lead to motion, but the mobility of the surface changes abruptly with potential²⁸. As a result, vigorous movement occurs only over a very limited portion of the surface of the drop, over which the potential is close to the value for maximum mobility. At the remaining portions of the surface of the drop, at which vigorous movement could be produced by a high value of $\Delta\Phi$, it is not developed, since the surface is practically immobile, any movement being strongly opposed by the charge on the electrical double layer. For example, on a drop of surface $S = 4 \times 10^{-2} \text{ cm}^2$, at a current of $2 \times 10^{-6} \text{ A}$, and $\kappa = 5 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$,

$$\Delta\Phi = \frac{3.6 \times 10^{-2} \times 2 \times 10^{-6}}{5 \times 10^{-5} \times 4 \times 10^{-2}} = 0.18 \text{ V}. \quad (6)$$

The mobility of the surface can change more than four-fold over this range of potentials.

Visual observations of the movement of solution near the mercury drop have shown that in fact a very small proportion of the surface of the drop is in motion in this case: the moving zone has a width of about 0.1 mm with a drop of 1 mm diameter. When the conductivity is increased, with the potential difference along the drop kept the same, the width of the surface of the mercury drop which is in motion is greatly increased, as can be seen from Fig. 8.

The variation in the maximum current with the concentration of reducible substance can be represented by the empirical equations

$$i_m = 2.8c_0^{0.6} \quad (\text{for } 0.01 N \text{ KCl}), \quad (7)$$

$$i_m = 4.0c_0^{0.7} \quad (\text{for } 0.1 N \text{ KCl}), \quad (8)$$

when i_m is measured in microamperes and c_0 in equiv. litre⁻¹.

The curves for the variation in maximum current with concentration can be satisfactorily represented by these equations only within a comparatively narrow range of concentrations of mercury ions, from 4.0×10^{-4} to $4 \times 10^{-3} N$ in the first case, and from 5×10^{-4} to $5 \times 10^{-3} N$ in the second. The reason for this is that, when the concentration of reducible substance is altered, the optimum conductivity

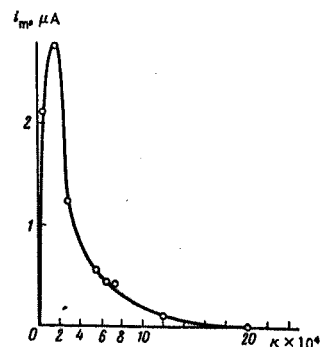


Fig. 6. Variation of maximum current with conductivity for a mercury concentration of $10^{-4} N \text{ Hg}_2(\text{ClO}_4)_2$.

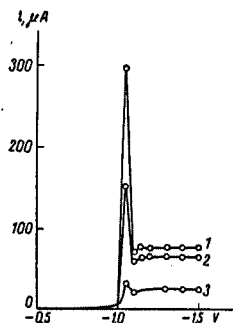


Fig. 7. Polarisation curves obtained in $0.1 N \text{ KCl} + \text{ZnCl}_2$ of the following concentrations, N : 1) 10^{-2} ; 2) 8×10^{-3} ; 3) 3.44×10^{-3} (dropping electrode).

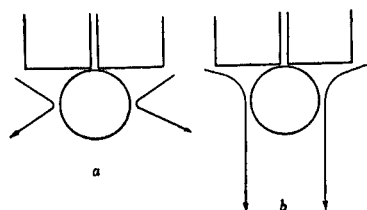


Fig. 8. Visual observations of motion of solution close to surface of dropping mercury electrode:
a) conductivity of solution less than optimum;
b) at optimum conductivity of solution.

is also changed. This is one of the causes of the divergence between the results of different investigators on the dependence of the size of the maximum on the concentration. For a constant conductivity, the corresponding equation represents the variation of maximum current with concentration of reducible substance only between concentrations which differ by a factor of at most 10.

The above relationship can be expressed in a similar manner in the case of the reduction of mercury ions at a fixed drop:

$$i_m = 1.5c_0^{1.6} \quad (\text{for } 0.001N \text{ KCl}); \quad (9)$$

$$i_m = 7.0c_0^{1.9} \quad (\text{for } 0.01N \text{ KCl}); \quad (10)$$

$$i_m = 7.8c_0^2 \quad (\text{for } 0.1N \text{ KCl}). \quad (11)$$

These experiments, especially with 0.01 and 0.1N KCl solutions, demonstrate the applicability, within a certain range of concentrations of reducible substance, of the approximate formula of Frumkin and Levich¹⁰:

$$j_m = kD\kappa^{-1/2}(2\mu + 3\mu')^{1/2}(nFc_0)^2, \quad (12)$$

where j_m denotes the current density.

In the derivation of this equation it was assumed that the potential differences along the drop are small. Experiment shows that, under conditions such that this requirement is met, the maximum current is in fact proportional to the concentration raised to a power which is close to 2.

In studying the dependence of the size of negative maxima on the concentration of reducible substance, experiments were carried out only with 0.01 and 0.1N KCl solutions (dropping electrode); negative maxima for zinc appear only at concentrations which are considerably greater than those at which positive maxima appear, and 0.001N solutions of supporting electrolyte cannot be used.

The variation of maximum current with concentration of zinc ions (dropping electrode) can be represented by the following equations:

$$i_m = 0.3c_0^{1.7} \quad (\text{for } 0.01N \text{ KCl}); \quad (13)$$

$$i_m = 0.65c_0^2 \quad (\text{for } 0.1N \text{ KCl}). \quad (14)$$

With zinc ions the variation of maximum current with concentration is characterised by smaller values of the coefficients. The rate of movement of the surface of the

mercury electrode is usually one-twentieth of that in analogous cases with positive maxima. It is known also from practical polarography that negative maxima are usually smaller than positive maxima. The causes of this phenomenon have been analysed in the work of Frumkin and Levich¹⁰.

SUMMARY

1. An explanation is given for the existence of an optimum conductivity, at which the current maximum has its greatest value.
2. The variation of the magnitude of the first-order positive maximum with the conductivity of the solution, as the latter increases beyond its optimum value, is represented by an equation in κ raised to a power between -0.6 and -0.7, close to the theoretical value of -0.5
3. The variation of the magnitude of the current maximum with concentration of reducible substance is represented by an equation in which the exponent of the concentration is 1.6-1.8 with a dropping electrode under normal conditions of polarography, and the exponent is 2, corresponding to the theoretical value, with a fixed mercury drop.

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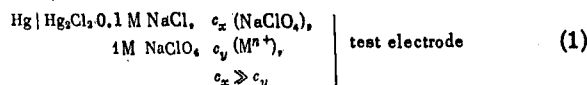
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POLAROGRAPHIC DETERMINATION OF THE ACTIVITY COEFFICIENT OF THE CADMIUM ION

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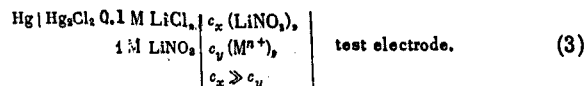
In the electrochemical determination of the activity coefficients of individual ions over a wide range of ionic strengths, it is necessary to allow for the liquid-junction or diffusion potential at the boundary with the reference electrode. This problem can be solved with sufficient accuracy by means of the following voltaic cell¹



employed² for the polarographic determination of the activity coefficient of the lead ion. The diffusion potential at the boundary with this reference electrode is calculated from the equation

$$-\varphi_d = 0.059 \frac{U-V}{U+V} \log \frac{1}{c_x} \quad (2)$$

In our polarographic research, in addition to (1) we have used also the cell



In contrast to NaClO_4 solutions, in which only simple Cd^{2+} ions are present, the formation of $[\text{Cd}(\text{NO}_3)]^+$ is possible in LiNO_3 solution³, and should be allowed for in calculations of the activity coefficient $f_{\text{Cd}^{2+}}$.

To find $f_{\text{Cd}^{2+}}$ in NaClO_4 at different ionic strengths μ the equation²

$$\log (f_{\text{Cd}^{2+}})_\mu = \frac{[(\varphi_{1/2})_\mu - (\varphi_{1/2})_{\mu=0}]}{0.0295} + \log \frac{(i_s)_\mu}{(i_s)_{\mu=0}}, \quad (4)$$

obtained from the well-known Heyrovský-Ilkovič formula, was employed. Here $[(\varphi_{1/2})_\mu]$ is the half-wave potential of Cd^{2+} at ionic strength μ , $[(\varphi_{1/2})_{\mu=0}]$ is the corresponding value at $\mu = 0$, $(i_s)_\mu$ is the diffusion current of Cd^{2+} at ionic

strength μ , $(i_s)_{\mu=0}$ is the corresponding current at $\mu = 0$.

In determining $f_{\text{Cd}^{2+}}$ in LiNO_3 solution use was made of the equation

$$\log \frac{(f_{\text{Cd}^{2+}})_\mu}{1 + K_1^0 (f_{\text{Cd}^{2+}})_\mu c_{\text{NO}_3^-}} = \frac{[(\varphi_{1/2})_\mu - (\varphi_{1/2})_{\mu=0}]}{0.0295} + \log \frac{(i_s)_\mu}{(i_s)_{\mu=0}}, \quad (5)$$

which we have obtained from the equation of DeFord and Hume⁴ by allowing for the occurrence of $[\text{Cd}(\text{NO}_3)]^+$ in addition to Cd^{2+} ions and assuming that $f_{\text{NO}_3^-} = f_{[\text{Cd}(\text{NO}_3)]^+}$; K_1^0 is the thermodynamic stability constant of $[\text{Cd}(\text{NO}_3)]^+$, equal to 2.54^5 , and $c_{\text{NO}_3^-}$ is the molar concentration of LiNO_3 .

The remaining quantities have the same significance as in Eqn. (4), but relate to LiNO_3 solution.

The polarographic constants of cadmium and the calculated values of $f_{\text{Cd}^{2+}}$ for different concentrations of NaClO_4 and LiNO_3 are set out in the Table ($m^{1/2}t^{1/4} = 1.35 \text{ mg}^{1/2}\text{sec}^{-1/4}$, $c_{\text{Cd}^{2+}} \approx 10^{-4} \text{ M}$, $t = 25^\circ$). Values of $\varphi_{1/2}$ are given relative to the appropriate reference electrode, (1) or (3), and are corrected for the ohmic voltage drop and also for the diffusion potential.

Values of $(i_s)_{\mu=0}$ and $(i_c)_{\mu=0}$ were found by extrapolation of the $(i_s)_\mu$ vs. μ curve to $\mu = 0$ (Fig. 1). The value of $(i_s)_\mu$ in LiNO_3 varies insignificantly with the concentration of the supporting electrolyte (Fig. 1), which made it possible also to determine $(i_s)_{\mu=0}$ (NaClO_4) with sufficient accuracy, since $(i_s)_{\mu=0} = (i_c)_{\mu=0}$. The quantities $[(\varphi_{1/2})_{\mu=0}]$ and $[(\varphi_{1/2})_{\mu=0}]$.

μ, M	NaClO_4				LiNO_3			
	$-\varphi_{1/2}, \text{V}$	$i_d, \mu\text{A}$	$f_{\text{Cd}^{2+}}$	$f_{\text{Cd}^{2+}}^{10}$	$-\varphi_{1/2}, \text{V}$	$i_d, \mu\text{A}$	$f_{\text{Cd}^{2+}}^{10}$ no allowance for complex	$f_{\text{Cd}^{2+}}^{10}$ complex allowed for
0.000	0.6345	0.62	1	1	0.6505	0.61	1	1
0.010	0.6430	0.74	0.615	0.657*	—	—	—	—
0.020	—	—	—	—	0.6596	0.62	0.500	0.513
0.025	0.6454	0.78	0.537	—	—	—	—	—
0.030	—	—	—	0.549	0.6607	0.64	0.473	0.492
0.035	0.6484	0.80	0.434	—	0.6605	0.64	—	—
0.050	0.6496	0.76	0.376	—	—	—	—	—
0.060	—	—	—	0.473	—	—	—	—
0.100	0.6547	0.77	0.256	0.417	0.6680	0.64	0.267	0.286
0.200	0.6561	0.77	0.230	—	—	—	—	—
0.300	0.6564	0.79	0.230	0.352	0.6719	0.65	0.197	0.232
0.600	0.6570	0.76	0.211	0.304	0.6753	0.67	0.156	0.205
1.000	0.6524	0.72	0.286	—	0.6755	0.63	0.147	0.235
2.000	0.6452	0.68	0.475	—	0.6707	0.59	0.200	—
3.000	0.6374	0.66	0.850	—	0.6625	0.55	0.354	—
5.000	0.6151	0.53	3.89	—	0.6501	0.50	0.849	—

* $\mu = 0.012$.

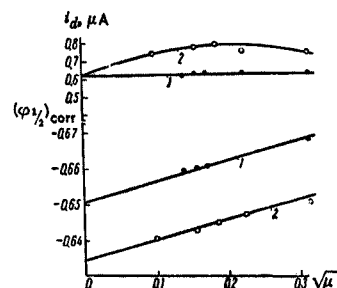


Fig. 1. Variation of i_d and of $(\varphi_{1/2})_{\text{corr}}$ with $\sqrt{\mu}$: 1) LiNO_3 ; 2) NaClO_4 .