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On the Instantaneous Polarographic Current

IV. Measurements of the Diffusion Controlled Current

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The instantaneous diffusion current has been measured by means of a special method which makes use of an externally controlled drop time of the dropping mercury electrode. The results are shown to be very reproducible. Attempts to correlate the experimental data with the revised Ilkovic relationship support the assumption this equation is inadequate in its present form.

It is well-known that the Ilkovic formula gives a relatively clear picture of the mathematical relationship between the fundamental polarographic variables. However, more quantitative attempts to correlate the empirical values of the diffusion current using the Ilkovic formula have lead to the addition of a correction term to this expression, based upon theoretical considerations neglected in the original formula. The nature of this correction term has been widely discussed in the literature. As there are few sufficiently accurate measurements of the instantaneous diffusion current, the different proposals cannot be rigorously checked.

Such precise diffusion current data can only be obtained from reliable measurements of the following polarographic quantities, *viz.* the instantaneous rate of flow of mercury from the capillary, the instantaneous residual current and the instantaneous limiting current.

Using a method, described by Wåhlin and Bresle [1], the rate of flow of mercury [2] and the residual current [3] have been investigated. The results obtained show that it is possible to measure values of these variables with an accuracy of the same order of magnitude as the accuracy of, *e. g.*, the temperature constancy and the measurements of the concentration of the depolarizer in the experiments.

The instantaneous limiting diffusion current of cadmium ions in potassium chloride solution has been determined with the techniques mentioned above. This paper gives results of these measurements together with some calculations of the diffusion current according to the revised Ilkovic formula. The results are compared with those obtained by other investigators.

EXPERIMENTAL

The measurements were made with the same apparatus and the same techniques as described earlier [3]. The depolarizer was cadmium sulphate of ANALAR quality. A stock solution of this reagent was made and standardized with the aid of an ion exchanger resin (Dowex 50). Potassium chloride and gelatine were added to known volumes of this solution which was then diluted to give the final solutions used in the experiments.

For the calculations the value of the diffusion constant of cadmium ions in 0.1 M potassium chloride was assumed to be 7.17×10^{-6} cm^2 sec^{-1}, a value determined experimentally by v. Stackelberg *et al* [4].

THE REPRODUCIBILITY OF THE MEASUREMENTS

In order to check the reproducibility of the measurements some experiments have been repeated under identical conditions. The values of the currents measured in three experiments are given under No. 1, No. 2, and No. 3 in Table 1. The two first experiments are made with an electronic polarograph and the last with a non-electronic instrument. The deviation from the calculated mean of these values of the current is about 0.2 % indicating that there is no significant difference in the results obtained using the two types of polarograph.

List of symbols

$i_{\lim}$ = instantaneous limiting current microamps
i_τ = instantaneous diffusion current microamps
τ = age of the drop, sec
n = number of electrons taking part in the electrode reaction
D = diffusion constant, $cm^2 \cdot sec^{-1}$
m = rate of flow of mercury from the capillary, $mg \cdot sec^{-1}$
C = concentration of the depolarizer, $millimoles \cdot liter^{-1}$
K, a = constants

THE RELATION BETWEEN i AND C

According to the fundamental polarographic law

$$i_\tau = a \cdot C \quad (1)$$

the ratio of the instantaneous diffusion current and the concentration of the depolarizer is a constant for fixed values of m and τ. Using values of the residual instantaneous current [3] published earlier and of the limiting instantaneous current, given in Tables 1 and 2 in this paper, this ratio has been calculated.

The results are given in Table 3, together with the mean value and the percentage deviation of the three measurements for every value of τ.

The divergence from the mean value is about 1 % up to the first second of the life of the drop; it gradually diminishes as the drop grows older and is only some tenths of a per cent at the later part of the life of the drop. There is a slight increase of the ratio a with increasing concentrations of the depolarizer; this is probably due to some contribution of the migration current in the total measured current in the experiments with the highest depolarizer concentration.

Table 1. Measured values of the instantaneous limiting current.

Sec	i_{lim} (μA)				Percentage error	i_{lim} (μA)			Percentage error
	No. 1	No. 2	No. 3	Mean value		No. 4	No. 5	Mean value	
1.038	3.1894	3.2012	3.2171	3.2026	0.5	7.9489	7.9693	7.9591	0.1
1.383	3.4542	3.4449	3.4460	3.4484	0.2	8.5814	8.5792	8.5803	0.1
1.729	3.6730	3.6815	3.6908	3.6818	0.3	9.1174	9.1494	9.1334	0.2
2.075	3.8418	3.8448	3.8585	3.8484	0.3	9.5462	9.5605	9.5534	0.1
2.421	3.9915	3.9867	3.9888	3.9890	0.1	9.9482	9.9384	9.9433	0.1
2.766	4.1335	4.1287	4.1325	4.1316	0.1	10.2590	10.2566	10.2578	0.0
3.112	4.2372	4.2351	4.2470	4.2398	0.2	10.5699	10.5417	10.5558	0.1
3.458	4.3446	4.3440	4.3454	4.3447	0.1	10.8058	10.7671	10.7865	0.2
3.804	4.4310	4.4386	4.4412	4.4369	0.1	11.0309	11.0058	11.0184	0.1
4.150	4.5173	4.5309	4.5317	4.5266	0.1	11.2453	11.2047	11.2250	0.2

No. 1: 0.5256 mM Cd^{2+}, LKB polarograph (electronic)
No. 2: 0.5256 mM Cd^{2+}, —»—
No. 3: 0.5256 mM Cd^{2+}, Heyrovsky type polarograph (non-electronic)
No. 4: 1.3152 mM Cd^{2+}, LKB polarograph
No. 5: 1.3152 mM Cd^{2+}, Heyrovsky type polarograph

Nos. 1—5: —0.93 volts *vs* the silver anode, m = 2.024 mg Hg pr sec, supporting electrolyte: 0.1 M KCl with 0.009 % gelatine, temperature: 25 °C

Table 2. Measured values of the instantaneous limiting current.

Sec	i_{lim} (μA)			
	No. 6	No. 7	No. 8	No. 9
1.038	0.7262	2.8382	2.5465	2.2798
1.383	0.7681	3.0838	2.7768	2.4985
1.729	0.8100	3.2661	2.9591	2.6674
2.075	0.8393	3.4273	3.1049	2.7979
2.421	0.8630	3.5655	3.2220	2.9073
2.766	0.8905	3.6883	3.3371	3.0071
3.112	0.9124	3.8035	3.4350	3.0973
3.458	0.9324	3.8994	3.5310	3.1779
3.804	0.9506	3.9954	3.6116	3.2604
4.150	0.9664	4.0587	3.6538	3.3160

No. 6: 0.1049 mM Cd^{2+}, m = 2.024 mg Hg pr sec
No. 7: 0.5256 mM Cd^{2+}, m = 1.716 mg Hg pr sec
No. 8: 0.5256 mM Cd^{2+}, m = 1.487 mg Hg pr sec
No. 9: 0.5256 mM Cd^{2+}, m = 1.280 mg Hg pr sec
Nos. 6—9: —0.93 volts *vs* the silver anode, upporting electrolyte: 0.1 M KCl with 0.009 % gelatine, temperature: 25 °C.

Table 3. Relation between instantaneous diffusion current and concentration.

Sec	$i_\tau/C = a$						Mean value	Percentage deviation
	No. 6	No. 1	No. 2	No. 3	No. 4	No. 5		
1.038	5.878	5.860	5.882	5.912	5.961	5.976	5.916	1.0
1.383	6.364	6.381	6.363	6.365	6.448	6.447	6.395	0.8
1.729	6.824	6.820	6.825	6.843	6.861	6.885	6.843	0.6
2.075	7.135	7.137	7.142	7.168	7.189	7.200	7.162	0.5
2.421	7.386	7.426	7.417	7.421	7.497	7.490	7.440	0.7
2.766	7.664	7.700	7.667	7.698	7.735	7.733	7.700	0.5
3.112	7.892	7.901	7.897	7.920	7.952	7.951	7.922	0.4
3.458	8.102	8.109	8.108	8.111	8.153	8.124	8.118	0.2
3.804	8.289	8.276	8.291	8.295	8.326	8.310	8.298	0.3
4.150	8.456	8.443	8.469	8.471	8.460	8.459	8.465	0.3

MATHEMATICAL INTERPRETATION OF THE MEASURED DIFFUSION CURRENT

The revised Ilkovic equation can be written according to v. Stackelberg-Strehlow [5], Lingane-Loveridge [6] and Kambara *et al.*[7]

$$i_\tau = 709\ n\ D^{\frac{1}{2}}\ C\ m^{2/3}\ \tau^{1/6} + KnDC\ m^{1/3}\ \tau^{1/3} \qquad (2)$$

where different values are given to the symbol K by the various investigators. Eqn. (2) may be rewritten in a form more easily handled and more suitable for studying the symbol K:

$$i_\tau - 709\ n\ D^{\frac{1}{2}}\ C\ m^{2/3}\ \tau^{1/6} = P = KnDCm^{1/3}\ \tau^{1/3} \qquad (3)$$

$$K = \frac{P}{nDC\ m^{1/3}\ \tau^{1/3}} \qquad (4)$$

Taking the available values of the diffusion current given by Taylor *et al.*[8], Khalafalla [9], Hans *et al.*[10] and in Table 3 in this paper, K has been calculated and the different values are presented in Table 4. The variation of K with time can be studied in Fig. 1. The agreement between the results obtained from the data of the different investigators shows the term K to be a function of τ. It has large negative values in the beginning of the life of the drop, passes through the value zero when the drop is about 1 second old and then increases, more and more slowly, until the maximum drop time is reached. This indicates that the revised Ilkovic equation in the form given in eqn. (2) does not describe the experimental data exactly. The variation of i_τ with m has been studied in experiments Nos. 1, 7, 8, and 9 given in Tables 1 and 2. According to eqn. (2) the diffusion current for fixed values of C and τ should depend on

Table 4. Comparison between different calculated values of the symbol K in the revised Ilkovic equation.

Taylor			Khalafalla			Hans			The author		
τ	i_τ	K	τ	i_τ	K	τ	i_τ	K	τ	i_τ	K
0.100	8.26	−200 300	0.4	5.50	−55 600	0.10	1.308	−201 000	1.038	5.916	−10 700
0.200	12.14	− 93 200	0.5	6.05	−32 100	0.40	2.867	− 46 200	1.383	6.395	− 740
0.384	15.59	− 34 200	1.0	7.25	− 6 500	0.60	3.350	− 20 200	1.729	6.843	+ 8 440
0.495	16.98	− 5 250	1.5	7.95	+ 2 600	0.80	3.718	− 4 600	2.075	7.162	13 060
0.719	19.06	+ 3 900	2.0	8.55	10 700	1.00	3.994	+ 4 700	2.421	7.442	16 340
1.062	21.17	17 700	2.5	9.03	16 200	1.50	4.428	13 600	2.766	7.700	19 630
1.468	23.02	27 100	3.0	9.40	19 100	2.00	4.794	21 000	3.112	7.922	21 990
2.014	24.64	38 000				3.00	5.320	29 000	3.458	8.118	23 500
2.410	25.85	36 100				4.00	5.720	33 400	3.804	8.298	25 050
2.990	26.98	36 800				4.60	5.902	34 900	4.150	8.465	26 100
3.488	27.70	36 400									

the rate of flow, m, raised to a power of between one third and two thirds, or mathematically expressed

$$\frac{1}{3} < \left(\frac{\delta \log i_\tau}{\delta \log m}\right)_{C,\tau} < \frac{2}{3} \tag{5}$$

The plot of log i_τ *vs* log m (not reproduced here) for values obtained in the experiments described above, shows that the individual points lie very well together, but, somewhat surprisingly on a straight line of slope 0.7 rather than

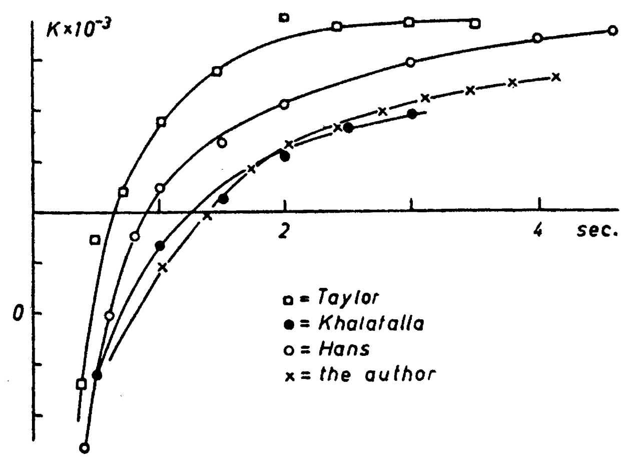

Fig. 1. The variation of the symbol K *in the revised Ilkovic equation.*

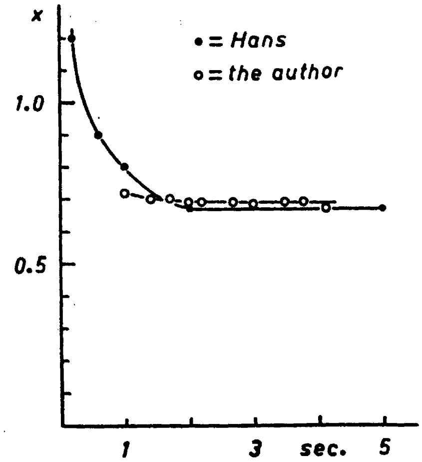

Fig. 2. The slope of the line $\log i_\tau = x \log \tau + \log A$ *for different values of the age of the drop.*

on a curve. For a comparison the corresponding values from the measurements of Hans *et al.*[10] have been studied, and the same result was obtained: for fixed values of C and τ, $\log i_\tau$ can be expressed as a linear function of $\log m$. In Fig. 2 the slopes of these lines are plotted *vs* the age of the drop. The result indicates that the diffusion current is a function of m raised to a power, not between 1/3 and 2/3, but greater than 2/3, or approaching it asymptotically. To explain this fact it is necessary to reconsider whether the best revision of the Ilkovic equation is to add a correction term as done by the authors cited above, or whether the theoretical principles underlying the original Ilkovic equation should be critically re-examined.

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