THE DIFFUSION CURRENT/DROP AREA RELATIONSHIP IN PULSE POLAROGRAPHY

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In the case of pulse polarography theoretical considerations show that the diffusion current, either instantaneous or average, is proportional to the drop area, which in turn is a function of time to the 0·691 power. Experimental evidence collected from successive drops in the plateaus is presented. The depletion in the vicinity of the drop which prevents the use of others than the first drop in classical polarography does not seem to occur in pulse polarography to any noticeable extension because of the short electrolysis time inherent to this technique.

Pulse polarography due to Barker and coworkers is now a well-established technique for analytical purposes as well as for studies of electrode processes[1,2]. A comprehensive equation for this technique which accounts for the sphericity of the electrode and for the shielding effect has been formulated and tested by Fonds, Brinkman and Los (FBL equation)[3]. This equation in the form presented by these authors does not show at first sight the relationship between the diffusion current and the drop area, although this is implicitly included. The purpose of this work is to demonstrate that relationship and offer experimental evidence supporting it. From the start, it must be born in mind that any comparison later made between classical and pulse polarography will not be made on quantitative terms since the potential perturbation at the electrode surface is different in each case. Such comparisons will serve only for qualitative purposes.

THEORETICAL

The FBL equation for the average diffusion current is:

$$\bar{i}_\mathrm{d} = 6{\cdot}05 \,.\, 10^4 n D^{1/2} \frac{c m^{2/3} t^{1/6}}{\theta'' - \theta'} \{[(1 + \theta)^{7/3} - 1]^{1/2} + \\ + 1{\cdot}1 D^{1/2} m^{-1/3} t^{1/6} (1 + \theta)^{7/3}\}\Big|_{\theta'}^{\theta''} . \qquad (1)$$

The first terms in the numerator are similar to those of the Ilkovic equation, while the remaining terms are specific for pulse polarography, being corrections for the sphericity of the drop and for the shielding effect. For a detailed derivation of this equation the original paper must be consulted[4]. In the equation, t_1 is the delay time, *i.e.*, the time elapsed from the start of the drop till the moment the pulse is applied, while in the Ilkovic equation the analogous time is the whole life of the mercury drop. Other terms have their usual meaning. θ is a reduced time obtained from the quotient t/t_1, between the pulse width and the delay time. When average currents are measured, two values of θ limit the interval of the measurement.

It is well known that the diffusion current is a function of the drop area, the latter being in turn a function of the drop life[5]. This is represented by the t time in classical polarography and by the t_1 time in pulse polarography. Then, by presenting the FBL equation as above, the diffusion current seems to be proportional to the 1/6th power of the delay time. Experimental results, when represented in the usual log i *vs* log t_1 plot, do not support this premise, the observed exponent of time deduced from the slope of the straight lines being between 2/3 to 3/4. The apparent anomaly is easily resolved if, in deducing the FBL equation, the starting equation for the plane, non-expanding electrode is modified. Thus, recalling that the area is given by[6]:

$$A = 4\pi \left(\frac{3m}{4\pi d}\right)^{2/3} (t_1 + t)^{2/3}\,, \tag{2}$$

where m is the flow rate of mercury and d its density, the starting equation can be written in the form:

$$i_d = 0{\cdot}479nFD^{1/2}m^{2/3}(t_1 + t)^{2/3}\,t^{-1/2}\,. \tag{3}$$

Thereafter, the numerous steps leading to the final expression for the expanding spherical electrode, which are omitted here for the sake of brevity, are deduced without recourse to the non-dimensional transformation, $\theta = t/t_1$. The latter, if employed, transforms *inter alia*, the $(t_1 + t)^{2/3}$ term into $t_1^{1/6}$.

The assumption that the drop area is a function of time to the 2/3rd power, although generally accepted and made use of, is no more than a convenient approximation, as was pointed out by Heyrovský[7]. A rigorous treatment of the flow of mercury during the drop growth has been made by Smith[8]. He showed that for the last seven eights of the drop life the weight of the drop at a given time is a function of the form:

$$w = \alpha t_i^{\beta}\,, \tag{4}$$

where t_i is the drop life and $\alpha = W/T^{\beta}$, W and T being experimental values of the weight and life of the drop. β is found to be 1·036, so that the drop weight is a parabolic rather than a linear function of time. In consequence, the area of an admittedly spherical drop of mercury is:

$$A = 4\pi\left(\frac{3m}{4\pi d}\,t_i^{1.036}\right)^{2/3} \tag{5}$$

$$A = 0{\cdot}849m^{2/3}(t_i + t)^{0.691}\,. \tag{6}$$

Generally, in pulse polarography, t_1 is equated to t_i, but in Eq. (6) t_i has been taken equal to $t_1 + t$ since the drop also grows, although not very significantly, during the time the pulse is being applied. In conclusion, the diffusion current can be expected to be proportional to the term $(t_i + t)$ to the 0·691 power or, to a good approximation, well within experimental error, to t_1 to the same power.

EXPERIMENTAL

Chemicals. Solutions of 10^{-4}M cadmium sulphate in 0·1M potassium chloride and 10^{-4}M zinc chloride in 0·1 M potassium sulphate were employed. Chemicals were of analytical reagent quality, the solids dried in vacuum, and solutions were prepared whenever possible by weighing. Water was triply distilled. Mercury for the dropping electrode was purified by washing with dilute nitric acid and aeration, followed by double distillation at reduced pressure, filtration through a fine-grade fritted glass funnel and final lixiviation of very fine particles with a pure nitrogen stream.

Apparatus. A Southern Analytical pulse polarograph model A3100, based on the original Barker's design was used. The apparatus measures the average current in the second part of the pulse width (sampling time) which, like the first (for the discharge of the DL), is chosen at will within the limits imposed by the instrument. Values of the experimental parameters were: delay time, 0·93; 2·3; 3·9; 5·5 and 6·7 s; total pulse width, 10 to 80 ms, the first and second halves having been chosen from 5 to 40 ms in several combinations. Exact values were used in the calculations, having been determined with a Tektronix oscilloscope which in turn had been calibrated in the time axis with an electronic timer to a precision of 0·01 ms. The blunt-tip capillary was placed vertically and the current due to successive drops was recorded. The temperature was controlled with a Buhler thermostat to 0·02°C. Each polarogram was recorded at least three times and several solutions of each depolarizer were prepared in order to minimize experimental errors.

RESULTS AND DISCUSSION

Experimental log–log plots of the $i_d - t_1$ curves are shown in Figs 1 to 5. The slopes vary between 0·66 and 0·72 depending on the solutions employed. The agreement between experimental and theoretical results is good. In several cases the slope is 0·69, as it was expected, in strict accord which theory. In some cases there is a small discrepancy which may be attributed to the experimental error, due most probably to slight but unavoidable electronic noise.

As stated above, the Southern polarograph measured the average current in the second part of the pulse width. For a rigorous comparison between theory based on equation (6) and experiment, a point in the decay curve should be located where

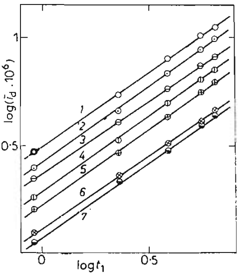

FIG. 1

Solutions of 1 . 10^{-4} mol/l $CdSO_4$ in 0·1 mol/l KCl. Discharge time (ms^{-1}), sampling time (ms^{-1}), slope: *1* 5, 40, 0·70; *2* 5, 30, 0·71; *3* 10, 30, 0·68; *4* 5, 20, 0·71; *5* 10, 20, 0·70; *6* 40, 30, 0·68; *7* 5, 10, 0·69

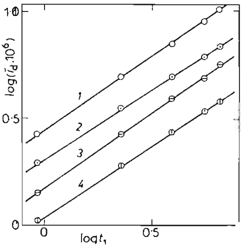

FIG. 2

Solutions see Fig. 1. Discharge time (ms^{-1}), sampling time (ms^{-1}), slope: *1* 10, 40, 0·70; *2* 30, 40, 0·67; *3* 20, 30, 0·71; *4* 30, 20, 0·67

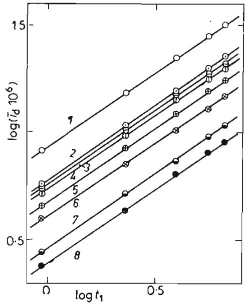

FIG. 3

Solutions see Fig. 1. Discharge time (ms^{-1}), sampling time (ms^{-1}), slope: *1* 40, 20, 0·69; *2* 20, 10, 0·70; *3* 30, 10, 0·69; *4* 10, 5, 0·69; *5* 40, 10, 0·69; *6* 20, 5, 0·69; *7* 30, 5, 0·71; *8* 40, 5, 0·69

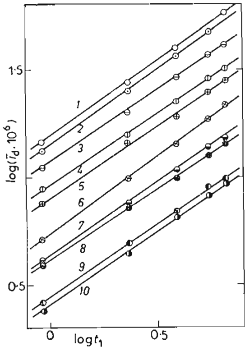

FIG. 4

Solutions of 1 . 10^{-4} mol/l $ZnCl_2$ in 0·1 mol/l KCl. Discharge time (ms^{-1}), sampling time (ms^{-1}), slope: *1* 10, 30, 0·70; *2* 5, 20, 0·70; *3* 10, 20, 0·68; *4* 20, 20, 0·68; *5* 30, 20, 0·69; *6* 5, 5, 0·72; *7* 30, 10, 0·69; *8* 10, 5, 0·66; *9* 20, 5, 0·68; *10* 40, 5, 0·68 the average and the instantaneous currents would be equal and the pulse time elapsed till then added to the delay time for the purpose of calculating the electrode area. However since the pulse width is small compared with the delay time, by using the whole pulse width the error is negligible. It is even permissible to use only the t_1 figure instead of $(t_1 + t)$, provided $t_1 \gg t$, as the case is usually.

Equation (*6*) and the present results show that the diffusion current in pulse polarography is proportional to $(t_1 + t)^y$, with y slightly greater than 2/3, and equal to 0·691. A similar time dependency is valid in classic polarography using the Ilkovich equation, but here this fact is obscured because the polarization time is equal to the drop life and since the time for the drop area is normally taken as $t^{2/3}$, the consequence is that the quotient $t^{2/3}/t^{1/2}$, disregarding momentarily the correction suggested by Smith, results in an overall power of 1/6. Pulse polarography shows a different case, in which the drop life to the end of the pulse and the polarization time (pulse width) are two different magnitudes and can therefore be distinguished in the equation. This dissimilar behaviour accounts for one of the factors that make pulse polarography a more sensitive technique than classical polarography since the respective diffusion currents, regarded only from this point of view and omitting other considerations, are in the ratio $(t_1 + t)^{2/3}/t^{1/6} = t^2$ for a given drop area, in a particular case in which the pulse polarography delay time plus pulse width and the classical polarography drop life (t_d) have the same value.

On the basis of the reasoning here presented it is obvious that although the experimental results supporting these views were obtained with an apparatus measuring average currents, the same principles must be valid for a pulse polarograph measuring instantaneous currents.

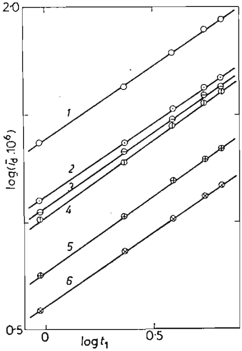

FIG. 5

Solutions see Fig. 4. Discharge time (ms^{-1}), sampling time (ms^{-1}), slope: *1* 5, 30, 0·68; *2* 20, 30, 0·68; *3* 30, 30, 0·69; *4* 5, 10, 0·71; *5* 20, 10, 0·69; *6* 40, 10, 0·69

It is interesting to note that these experiments have been made by measuring the current at successive drops in the plateaus. In classical polarography a linear log i–log t_d relationship is obtained only when the current due to the first drop in the diffusion region is measured. Otherwise, at short drop times, a curve slowly approaching the theoretical slope from below results. Numerous authors found such unexpected results until Airey and Smales[9] suggested that the cause of this anomaly was the depletion of the solution in the vicinity of the drop, due to the electrolysis at the preceding drop, its effects being transferred to the next one, and so on. To overcome this difficulty, Hans and Henne[10] then proposed the use of only the first drop. The results so obtained were in a somewhat better agreement with theory, although the experimental slopes differred sensibly from the theoretical one. In the present case no such problem arises and this can be attributed to the fact that the electrolysis time is so short that depletion of the depolariser seems not to be transferred from drop to drop to any significant extent.

As to the correction suggested by Smith for the t_i time, it is also interesting to note that in classical polarography the theoretical slope, as stated above for the first drop, is 0·167. However, the experimental values are always about 0·19 and this discrepancy has not been satisfactorily explained. It must be pointed out that at least part of it is due to overlooking the aforementioned correction, since the product 0·167 times 1·036 equals 0·173, which is higher than the 1/6th power and nearer to the 0·19 exponent observed experimentally. Obviously, this does not account for the whole difference and suggests that there are also other factors in classical polarography yet to be considered.

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