

A SIMPLE METHOD FOR THE OPTIMIZATION OF THE DECAY TIME IN PULSE POLAROGRAPHY

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A simple method for optimization of the minimum decay time, previous to the sampling time of the polarographic current, is described. The former should make compatible two requisites: it should be short enough for obtaining the maximum value of the faradaic current and long enough for the minimum or null value of the double layer decay current. The method is performed with the pulse polarograph only, without ancillary instruments, is fast and its accuracy is fairly comparable with earlier methods, which were more accurate but by far more involved to perform.

In an earlier publication¹ the need for the optimization of the pulse width and the concomitant current decay and sampling times in pulse polarography was discussed, and an accurate method for establishing the correct values of these parameters under different working conditions was given. Rather sophisticated instrumentation was required, comprising a computer for data processing, for such method. However, in many cases it is enough to ascertain the minimum value of the decay time which ensures that the current to be sampled is purely faradaic. Once such time is known, one can take any convenient sampling time to complement the value of the chosen pulse width. Recently a simple method has been developed for this purpose. Though it is perhaps less accurate than the previous one, it gives reliable results for most cases and it has the advantage of being performed in regular practice with only the pulse polarograph. It is easier to perform and it is time-saving, too.

EXPERIMENTAL

Solutions of cadmium sulphate (concentration about 10^{-4} mol l⁻¹) were employed. This ion was selected on account of its well-known "good behaviour" in the electrochemical sense. Supporting electrolytes were 0.1 and 1M-KCl and 4.5M-NaNO₃. A Southern Analytical pulse polarograph model A3100 was employed. Its electrical sensibility was $2.07 \cdot 10^{-1}$ A/mm. This apparatus monitors the current over an interval, consisting of two parts. During the first, called the decay time, t_d , the cell current decays freely and its non-faradaic current, due to the double layer, reaches a negligible value. During the second, which is the sampling time, t_s , the faradaic component, due to the electrochemical process, is averaged and measured. Each part can be selected

between 2 and 40 ms, in any combination. The whole pulse width is the sum of t_d plus t_s and is designated in this paper by two figures joined by a + sign. Normal and differential pulse polarograms were recorded with a Leeds & Northrup x-t recorder. Decay curves were recorded with a Nicolet digital oscilloscope and a Hewlett-Packard x-y recorder. Temperature was 298.16 ± 0.02 K, controlled with a Bühler thermostatic bath. Electrode characteristics were: flow in air, 0.4290 mg/s at 298.16 K; delay time, 0.98, 2.27, 3.78, 5.48, and 6.35 s, fixed as instrumental parameters and calibrated with an electronic timer². Potentials were measured with an Ag/AgI reference electrode and a Solartron digital voltmeter.

To perform this method, polarograms with different decay times, 5 to 40 ms, and small sampling times, mostly 2 or 5 ms, in some cases longer but not exceeding the value of the decay time, are recorded and the limiting or peak current according to the technique employed, is measured. Both normal (NPP) and differential (DPP) pulse polarographic techniques have been employed. Further experimental details are given in the tables.

RESULTS AND DISCUSSION

The observed current, i_{obs} , was calculated from the limiting (NPP) or peak (DPP) currents measured on the recorded polarograms and the electrical sensitivity of the polarograph. The theoretical current, i_{teor} , was calculated for the other pulse widths on the basis of the observed current value for the widest pulse, applying Eq. (2). Deviation was calculated as $100[(i_{\text{obs}}/i_{\text{teor}}) - 1]$ per cent.

When a potential pulse is applied to a polarographic cell a two-component current is generated. One of them is due to the charging of the electrical double layer (EDL), which decays approximately as³

$$i_{\text{DL}} = (E/R) \exp(-t/RC), \quad (1)$$

where E is the applied potential measured with respect to the p.z.c., R is the inner ohmic resistance of the cell, C is the double layer capacity and t is the pulse duration. The second component, the faradaic current, decays more slowly⁴:

$$i_{\text{F}} = kt^{-1/2}. \quad (2)$$

In Eqs (1) and (2) i is the instantaneous value of the current at time t . When a polarograph which measures the average current is used, as in the present case, those equations are still valid provided that the following conditions are fulfilled, according to Matsuda⁵:

$$t = t_d + \frac{1}{2}t_s \quad (3)$$

with:

$$t_d \geq \frac{3}{2}t_s. \quad (4)$$

Under these restrictions the theoretical average current equivalent to the instantaneous value is calculated with Eq. (2), taking k as the value of the average current for the

widest pulse multiplied by the square root of this lapse, as a starting point. Fig. 1 shows the validity of Eq. (2) when conditions (3) and (4) are enforced. This method is based on the fact that the double layer decay current is practically null after a few milliseconds. Thus, the measured current is essentially faradaic if t_d is long enough. The shortest length of the decay time for which this condition is fulfilled is ascertained by applying the present method.

In most of the experiments included in this research condition (4) was obeyed. However, in some cases the condition was stretched to $t_d = t_s$, since even so the error is small, less than 1%. At any rate, the sampling time should preferably be small, to be on the safe side when using equations valid for instantaneous currents for the calculation of average currents⁶. The error is then minimized. However, the sampling time should not be chosen smaller than necessary, since the measured current is proportional to its length⁷. Unnecessarily short sampling times afford unwanted accuracy when using Eq. (2), sacrificing at the same time analytical sensitivity. A balanced choice is then indispensable.

In comparing observed and theoretical currents, those of the first type which do not deviate more than 1% from the theoretical value are regarded as good, and this means that the corresponding pulse widths are acceptable for further measurements in other solutions of the same or approximate composition.

Table I shows that, in general, decay times longer than 10 ms are sufficient to ensure a deviation of about 1% or less, and even zero for much longer decay times, in the observed currents.

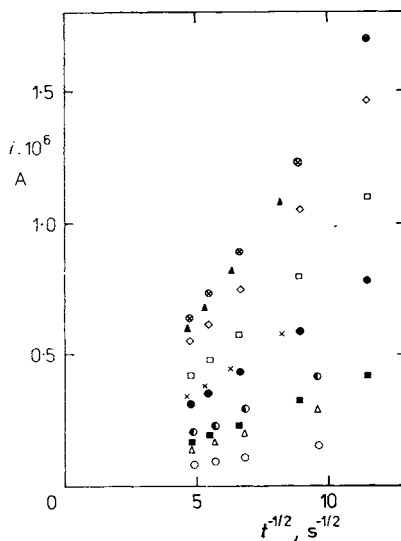


FIG. 1

Eq. (2) with conditions (3) and (4). Values of the observed current from the tables. \circ Table I, delay 0.98 s; \triangle I, 2.27 s; \blacksquare III, $t_s = 5$ ms; \bullet I, 3.78 s; \bullet II, $t_s = 5$ ms; \times , III, $t_s = 10$ ms; \square I, 3.78 s; \diamond I, 5.48 s; \blacktriangle II, $t_s = 10$ ms; \otimes I, 6.35 s

Larger deviations are encountered when the decay time is short. Table I shows deviations up to 13.4% for pulses of 5 + 5 ms. At short decay times any spurious component of even a short time constant might not have decayed enough and could be measured together with the faradaic component in the following sampling time. In consequence, the observed current may comprise an undesirable component. Data of this table correspond to a solution containing 1M-KCl. This is a high conductivity and low internal ohmic resistance solution (specific resistance about 10 ohm). Moreover, the differential capacity of the electrode/solution interface is about 20–40 $\mu\text{F cm}^{-2}$ (ref.⁸). Therefore, in less than 1 ms the EDL current should decay, according to Eq. (1), to a negligible value. In practice it may not always be so. One should remember that the rise-time of the pulse generator of the polarograph is not infinitely small. In fact, the rise-time is 3 ms/V in this instrument, and the actual time depends then on the pulse amplitude, which, in turn, depends on the starting potential of each polarogram. It is well to recall that the pulse amplitude is the difference between the fixed starting potential at the beginning of the potential sweep, and the linearly increasing potential of the pulse at every step of the polarogram. Then, the leading flank of the pulse takes 3 ms per volt to reach 90% of its maximum amplitude and some more to reach its top value. Since the going-up of the potential pulse is not instantaneous, the concomitant current should behave likewise and its falling-down should take a time longer than that calculated, for the EDL current, solely on the basis of the ohmic resistance of the cell and the differential

TABLE I

Theoretical and observed currents for various conditions. $1 \cdot 10^{-4}\text{M-CdSO}_4$ in 1M-KCl. NPP; d.t. — delay time

Pulse ms	i_{obs} μA	i_{teor} μA	dev. %	i_{obs} μA	i_{teor} μA	dev. %	i_{obs} μA	i_{teor} μA	dev. %
d.t. 0.98 s				d.t. 2.27 s			d.t. 3.78 s		
10 + 2	0.156	0.152	+2.6	0.300	0.282	+6.4	0.415	0.392	+5.8
20 + 2	0.111	0.110	+1.0	0.206	0.204	+1.0	0.286	0.284	+0.7
30 + 2	0.091	0.091	0	0.168	0.168	0	0.233	0.233	0
40 + 2	0.079	0.079	0	0.146	0.146	0	0.203	0.203	0
d.t. 3.78 s				d.t. 5.48 s			d.t. 6.35 s		
5 + 5	1.095	0.995	+10.0	1.472	1.297	+13.4	1.696	1.528	+11.0
10 + 5	0.795	0.770	+3.2	1.048	1.005	+4.3	1.225	1.184	+3.5
20 + 5	0.577	0.574	+0.5	0.754	0.749	+0.7	0.886	0.882	+0.4
30 + 5	0.478	0.478	0	0.623	0.623	0	0.734	0.734	0
40 + 5	0.418	0.418	0	0.545	0.545	0	0.642	0.642	0

capacity of the interface, and for the faradaic current, as a $t^{-1/2}$ function. The shape of the composite current is distorted for some time though finally, after the EDL component is null, it obeys the time function. This can be appreciated, qualitatively, in Fig. 2, which shows the composite cell current shape recorded with an auxiliary oscilloscope and an x-y recorder in a $1 \cdot 10^{-4}\text{M-CdSO}_4$ in 1M-KCl solution for a -0.6 volt pulse amplitude. The theoretical curve is the faradaic component drawn as a time function from 1 to 10 ms. The zero to 1 ms lapse is the theoretical time for the complete decay of the EDL current in this solution. It is assumed that the current at 10 ms is purely faradaic, a supposition which may not be necessarily true but is useful for this reasoning. It is seen that the theoretical current differs from the actual recording between 1 and 7 ms. This means that in this lapse the current is not purely faradaic. The current does not reach its top value until about 2 ms after the pulse application, though it should have reached the top instantaneously if the pulse rise-time were negligibly small. The current starts to decay not at zero time, but at 2 ms time and at this moment its value is quite different from the value of its faradaic component. Then, the composite current still contains a high contribution of the EDL current (at a time when calculation shows that it should be null) and since the latter decays faster than the faradaic component, the total cell current approaches the theoretical curve rapidly, though does not join it before 7 ms. From 5 ms on the current is averaged and recorded, but its value is higher than the theoretical one. This explains the somewhat large errors encountered with short decay times.

Data also show that it is permissible to enlarge the t_s lapse, making it equal to t_d . This means a greater sensitivity with small or even null deviation. As to the delay time, it is found that it does not influence the deviations much, as seen from Table I,

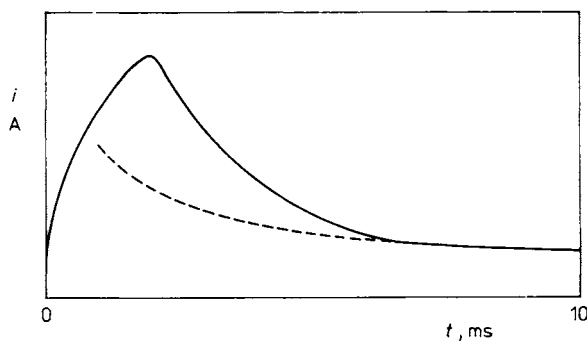


FIG. 2

$1 \cdot 10^{-4}\text{M-CdSO}_4$ in 1M-KCl . Decay current vs time curve. Pulse amplitude -0.6 V, width 10 ms. Dashed line, theoretical curve calculated with Eq. (2) assuming no double layer decay current contribution after the first millisecond; full line, actual recording

if figures for five different delay times are compared. On the other side, the width of the sampling time exerts some influence, and the wider ones tend to reduce the errors. Taking, for example, data of Table II and III for 20 + 5, 20 + 10, and 20 + 20 ms, that is, with varying t_s at constant t_d , it is seen that deviations tend to become smaller at wider sampling times. This is the logic sequence since with the longer sampling times, the averaged current is less influenced by any non-faradaic component remaining at the end of the decay time, as already found⁷.

Higher concentrations of the supporting electrolytes are also beneficial. Comparing data from Tables I and II, for 5 + 5 to 40 + 5 ms at 3.78 s delay time, they show that at a 4.5 mol l⁻¹ concentration of the supporting electrolyte the errors are smaller than at 1 mol l⁻¹ concentration. This should be expected on account of the

TABLE II

Theoretical and observed currents for various conditions. $1 \cdot 10^{-4}$ M-CdSO₄ in 4.5 M-NaNO₃; NPP, delay time 3.78 s

Pulse ms	i_{obs} μA	i_{teor} μA	dev. %	Pulse ms	i_{obs} μA	i_{teor} μA	dev. %
5 + 5	0.788	0.735	+7.2	20 + 10	0.820	0.820	0
10 + 5	0.584	0.570	+2.4	30 + 10	0.693	0.693	0
20 + 5	0.426	0.425	+0.2	40 + 10	0.611	0.611	0
30 + 5	0.353	0.353	0	20 + 20	1.380	1.380	0
40 + 5	0.309	0.309	0	30 + 20	1.195	1.195	0
10 + 10	1.078	1.058	+1.9	40 + 20	1.069	1.069	0

TABLE III

Theoretical and observed currents for various conditions. $1 \cdot 10^{-4}$ M-CdSO₄ in 0.1 M-KCl. DPP, delay time 3.78 s

Pulse ms	i_{obs} μA	i_{teor} μA	dev. %	Pulse ms	i_{obs} μA	i_{teor} μA	dev. %
5 + 5	0.416	0.402	+3.5	20 + 10	0.442	0.440	+0.5
10 + 5	0.320	0.312	+2.6	30 + 10	0.372	0.372	0
20 + 5	0.234	0.232	+0.9	40 + 10	0.328	0.328	0
30 + 5	0.193	0.193	0	20 + 20	0.775	0.772	+0.4
40 + 5	0.169	0.169	0	30 + 20	0.669	0.669	0
10 + 10	0.575	0.568	+1.2	40 + 20	0.598	0.598	0

smaller internal ohmic resistance of the more concentrated solution. The already mentioned problem of the pulse rise-time should not be forgotten but at any rate a shorter time constant for the decay of the non-faradaic current means a total cell current reaching the theoretical value somewhat earlier in the pulse life. Table III corresponds to a less concentrated solution but is excluded from this comparison since it contains data for an electronically different technique.

Data obtained with differential pulse polarography are assembled in Table III. They show deviations of the same order of magnitude as the data obtained with the normal technique.

The present method makes possible to choose the minimal decay time for the analysis of an unknown solution by performing some half a dozen polarograms with either NPP or DPP and a simple calculation, in a matter of less than half an hour. Ideally such minimum corresponds to the shortest decay time for which the theoretical and observed currents are equal, that is, for zero deviation. However, one can purposely choose a shorter value with a tolerable small deviation, for the sake of obtaining a larger current and in consequence a better sensitivity. Once the decay time is fixed, any convenient sampling time can be chosen. If operating with theoretical equations for the instantaneous current, the sampling time should not exceed $2/3$ of the decay time. If the purpose is purely analytical such restriction may be waived, provided that a calibration curve or the standard addition method is employed. Then a longer sampling time will afford better sensibility.

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