THE OPTIMIZATION OF THE CURRENT SAMPLING TIME IN PULSE POLAROGRAPHY

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A method for computing the approximate value of the non-faradayic component of the total decay current in a pulse polarographic experiment is described. Undesirable effects of such component are discussed. The method employed is simpler than computing the non-faradayic current from *RC* measurements and has the advantage of being applied under actual polarographic working conditions.

Pulse polarography is a powerful technique in analytical chemistry and electrochemistry, following the fundamental researches of Barker and coworkers[1,2]. Theoretical equations for the current in the normal operation mode have been derived[3,4]. Instrumental factors affect some parameters of the equations and they must be optimized to obtain accurate results. Their undesirable effects are not sometimes apparent, if the wave shape is not manifestly distorted. However, under certain circumstances, an erroneous current may be recorded if those factors are not adequately fixed. This paper deals with criteria for the optimization of the current sampling time.

EXPERIMENTAL

Chemicals. Solutions of potassium chromate in sodium hydroxide, cadmium sulphate in potassium chloride, nickel sulphate in potassium thiocyanate and zinc sulphate in potassium chloride were employed. The concentration of the reducible species was 10^{-4} mol l^{-1} and that of supporting electrolytes varied between 0·1 and 1 mol l^{-1}. Mercury was bidistilled under reduced pressure and water was tridistilled. Nitrogen was 99·995% pure.

Instrumentation. A Southern Analytical model A3100 pulse polarograph was employed. This apparatus measures the average of the current along a lapse in the second part of the decay curve. The width of the voltage pulse applied to the cell can be selected in the range from 10 to 80 ms. The width of the pulse comprises first part (the "integrator discharge time", for this instrument, that is, the lapse allotted for the non-faradayic current becoming null) and a second part (the "integrator signal gate time", for this instrument, which is the lapse, when, in principle, only the faradayic current is measured). Each part can be selected at either 5, 10, 20, 30 or 40 ms, and it is possible to make any combination. For this research the full decay current curves at different potentials along the polarographic wave have been recorded with a Tektronix model 543B oscilloscope fitted with a 35 mm photographic camera attachment. Temperature was $25 \pm 0·01°C$,

controlled with a Bühler thermostatic bath. The drop electrode characteristics were: flow in air, 0·7860 mg/s at 25°C; drop delay, 3·78 s, fixed as an instrumental factor and calibrated with an electronic timer[5]. The electrode area was regarded as constant during the measurements, as usual in pulse polarography, since the drop growth is negligibly small during a short polarization pulse. Potentials were measured *vs* the mercury pool. Mathematical calculations were made with programme WOIYC fed into a Hewlett–Packard HO1000/45 computer.

RESULTS

Table I and II contain typical data for some of about 200 experiments made. In practice, currents were measured in milimeters on the photographs taken from the oscilloscope screen (after blowing them up to an exactly 1 : 1 ratio), relative to the zero base line, and no attempt to convert the data to the true magnitude was deemed necessary, since it was of no consequence for the subsequent evaluations. The basic sensitivity of the polarograph is $2·05 . 10^{-11}$ A/mm.

Theoretically, all points should fit a negative slope straight line in an i *vs* $t^{1/2}$ plot. However, as a result of the additive capacitive component existing during the first part of the decay process, the current is enhanced in this region. To find the error consequent to an inadequate choice of the "integrator discharge time", curves were integrated all along, and the extra areas resulting from points not fitting a straight line were computed as an added capacitive charge, and the percentage error was then evaluated. Tables I and II contain data for the first part of the curves, where errors were computed. Obviously, points beyond the last ones mentioned in the Tables are free from any contribution from the capacitive decay current.

DISCUSSION

There are two types of pulse polarographs, the one that measures the instantaneous current and the type that measures the average current in a definite part of the current––time curve. The first type has the advantage that, in principle, the current at any given time may be recorded, and this is generally made just before the end of the pulse life. The second type overcomes the possibility of measuring, by chance or for unexpected reasons, erroneous instantaneous values, by averaging the current along a finite interval. This is a valid and commendable approach, provided that only the faradayic current is sampled.

When a potential pulse is applied to an electrochemical cell a two-component current is generated. The well-known equivalent circuit of such a cell consists of a generator and a resistance in series with a capacitance, the former being the internal resistance of the cell and the latter consisting of the capacitance of the electrical double layer, the more significant component, and the capacitance of the bulk of the solution, both in parallel with the faradayic impedance. A part of the current is purely faradayic, as a result of the electrochemical reaction, but another part

is non-faradayic, due to the charge of the double layer, the latter process generating a high, short-lived current which decays according to the following equation[6]:

$$i_{DL} = -\frac{E}{R} e^{-(t/RC)} . \qquad (1)$$

As it is well known, RC is called the time constant, and it causes that after a lapse $t = RC$, the current decays to 36·8% of its original value. For all practical purposes, for $t = 5RC$, the capacitive current is almost null. Other factors remaining constant, the larger the conductance of the solution, the shorter RC. This desirable effect can be achieved by increasing the concentration of the supporting electrolyte, since

TABLE I
Computed errors along experimental $i - t$ curves in measuring diffusion-controlled faradayic currents. $1 . 10^{-4}$M K_2CrO_4, 1M NaOH. Pulse width, W, and sensitivity, S, as indicated

Time, ms	W 60 ms, S 1/1280, E —1·02 V		W 45 ms, S 1/2560, E —1·02 V	
	Current, mm	Error, %	Current, mm	Error, %
5	—	—	48·0	20·1
10	55·0	7·6	25·5	6·0
15	—	—	20·0	1·8
20	34·5	2·5	17·0	0·9
25	—	—	15·0	0·1
30	27·5	0·5	—	—
40	24·0	0·0	—	—

TABLE II
Computed errors along experimental $i - t$ curves in measuring diffusion-controlled faradayic currents. $1 . 10^{-4}$M $NiSO_4$, 0·6M KCNS; in both experiments $W = 40$ ms, $S = 1/1280$

Time, ms	$E = -0·75$ V		$E = -0·93$ V	
	Current, mm	Error, %	Current, mm	Error, %
5	72·0	9·9	—	—
10	54·0	2·7	65·0	3·5
15	43·0	1·3	50·0	1·7
20	37·0	0·1	41·0	0·0

the latter, besides carrying almost all the migration current of the cell, reduces its internal resistance.

For a reversible reaction, the faradayic current resulting from the pulse decays as a function of time, as follows[7]:

$$i = nFAC \sqrt{\left(\frac{D}{\pi t}\right)} \left[1 + \exp\left\{\frac{nF}{RT}(E - E_{1/2})\right\}\right]^{-1}. \tag{2}$$

For an irreversible reaction, equation (2) becomes:

$$i = nFAC \sqrt{\left(\frac{D}{\pi t}\right)} \left[1 + \sqrt{\left(\frac{D}{D'}\right)} \exp\left\{\frac{nF}{RT}(E - E_{1/2})\right\}\right]^{-1} \Phi(\lambda), \tag{3}$$

where

$$\Phi(\lambda) = \sqrt{(\pi)} \lambda \exp \lambda^2 \, \text{erfc} \, \lambda \tag{4}$$

and

$$\lambda = k_s \sqrt{\left(\frac{t}{D}\right)} \exp\left\{-\frac{\alpha nF}{RT}(E - E_s)\right\} \left[1 + \sqrt{\left(\frac{D}{D'}\right)} \exp\left\{\frac{nF}{RT}(E - E_s)\right\}\right]^{-1}. \tag{5}$$

All symbols have their usual meaning. It is evident that in both cases the current decays as a function of $t^{-1/2}$. In the reversible case a proportionality is found along the whole polarographic wave, while in the irreversible case it is found only in the plateau and the region immediately before.

As a result of Eqs (2) and (3), a plot of the diffusion current i_a vs $t^{1/2}$ will give, ideally, a straight line of negative slope. In practice, curves slope upwards, out of alignment, during the early part of the pulse, because in this region faradayic and non-faradayic currents add together.

Whatever type of pulse polarograph is employed, it is essential to sample the current when the non-faradayic component is practically null. This is automatically done if the instantaneous current is measured near the end of the pulse life, but if it is done early in the pulse life or by averaging a large part of the current decay curve, a non--faradayic component may enhance spuriously the measured current. This can introduce serious errors in the results, even in analytical work employing a calibration standard; when errors can be made to cancel each other only on condition that a blank is also recorded.

The pulse polarograph used in this work can be set to measure only that part of the curve which follows the theoretical equation. However, unless the optimum conditions have been determined experimentally, it well might be that an anjudicious selection of the "integrator discharge time" results in an error in the current measured.

From approximate values of the differential capacity of the double layer obtained with a special built-in circuit of the pulse polarograph[8], of the drop area at the time of sampling, and with known data of the specific conductance of the supporting electrolytes, a value for RC of the order of $0·001$ s is estimated for all the solutions here employed. In consequence, an "integrator discharge time" of no less than 5 ms should be chosen. An analysis of the $i - t$ curves reveals that even longer "discharge times" must be chosen in definite cases, to be on the "safe" sided.

Table I shows, for example, that if the pulse width of 45 ms is chosen as $5 + 40$ ms ("integrator discharge time" + "integrator signal gate time"), the error in measuring the faradayic current is very large, while by reversing the selection of times, *i.e.*, $40 + 5$ ms, the error is nil, since after the first 20 ms the capacitive current is almost null, the 60 ms width can be chosen either as $20 + 40$ ms, $30 + 30$ ms, or $40 + 20$ ms. In the first case the error is not negligible; in the second, only $0·5\%$ and in the third, there is no measurable error at all.

In Table II, in both experiments the pulse width can be chosen either as $10 + 30$ ms, $20 + 20$ ms, or $30 + 10$ ms. The first choice introduces a significant error in the faradayic current, while since at 20 ms the error is almost non-existing, either the second or the third combination of times give good results.

It is, of course, possible, in order to establish the initial time to compute accurate values of R and C by careful measurements of these parameters, but, mainly in the case of C, the experimental technique is involved and laborious. On the other hand, the technique here employed is straightforward, requires common laboratory instruments and yields results obtainable under actual polarographic working conditions.

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