MAXIMA IN PULSE POLAROGRAPHY

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Maxima may occur in pulse polarography under certain circumstances. They have been found in solutions of Zn^{2+} and Cd^{2+} ions with very dilute supporting electrolytes. The possibility of adsorption phenomena, which may cause another kind of maxima, has been excluded. Due to the fact that maxima have not yet been systematically studied with the present technique, it is premature to assign them to any particular kind, although they somewhat resemble to classical d.c. polarographic maxima of the first kind. It is shown that larger peak maxima are obtained at short pulse widths and, mainly, at short decay times and that they disappear by increasing either the decay time or the measuring time, or both; by shortening the delay time or by turning to the differential pulse polarographic technique. Some considerations are made on the influence of the double layer and of surface phenomena on the dropping mercury electrode.

Maxima in pulse polarography were first reported by Parker and the present author[1] who found that some peaks in the normal wave were due to the specific adsorption of the depolarizer, induced by the presence of certain anions. Solutions of Pb^{2+} ion with increasing concentrations of Br^- ion in strongly acid media were employed. Several years later Anson and coworkers[2] and Bresnahan and Elving[3] found similar effects. The first team studied solutions of Cd^{2+} ion with iodides and the second one studied the nicotinamide adenine dinucleotide with carbonate ions. In all these cases the concentration of the supporting electrolyte was medium to high.

A different situation may arise if the concentration of the supporting electrolyte is low, say, 10^{-2} to 10^{-3} mol l^{-1}. In these cases the conductivity of the solution is low and it is possible that maxima occur due to the streaming of the solution or the mercury surface. In this paper such maxima are studied and the possible influence of the electric double layer and of surface movements at the dropping mercury electrode are discussed.

EXPERIMENTAL

Solutions of $2·5 . 10^{-5}$ M-$ZnSO_4$ in $2·5 . 10^{-3}$ M-$NaNO_3$, $5 . 10^{-5}$ M-$ZnSO_4$ in $5 . 10^{-3}$ M-$NaNO_3$, $1 . 10^{-4}$ M-$ZnSO_4$ in $1 . 10^{-2}$ M-$NaNO_3$, and $1 . 10^{-4}$ M-$CdSO_4$ in $1 . 10^{-2}$ M-KCl were employed. In some experiments the concentration of the supporting electrolyte was increased to 0·05 or 0·1 mol l^{-1}, keeping constant the concentration of the metal ions. Temperature was 298·16 ±

0·02 K, controlled with a Bühler thermostatic bath. Water was triple distilled and mercury was purified by acid washing and vacuum distillation. Electrocapillary curves for all these solutions, for the supporting electrolytes alone, and for 0·1M-NaNO$_3$ and 0·1M-KCl were made by timing the life of about 50 drops as a function of potential between 0 and −1·6 V.

A Southern Analytical model A 3 100 pulse polarograph was employed in both normal and differential model with a two-electrode cell. The polarograph averages the cell current during the measuring time. Pulse width varied between 7 and 80 ms, divided in two lapses, hereinafter designated by digits linked by the + sign. The first number will indicate the lapse allowed for the discharge of the double layer current (decay time), the second, the phase for measuring the faradaic current ideally free from double layer current (measuring time). The delay time (from the mercury drop birth to the moment the pulse is applied) was 3·87 s. The decay of the cell current as a function of time was measured with a Nicolet oscilloscope and a Hewlett–Packard x-y recorder. Potentials were measured against an Ag/AgI reference electrode with a Solartron digital voltmeter.

RESULTS

Figures 1 to 4 show some typical results. Potential scale is 100 mV/cm and the current scale is in arbitrary units in all cases. Polarograms have been recorded from right to left and drawings have been traced from the actual recordings, ignoring the
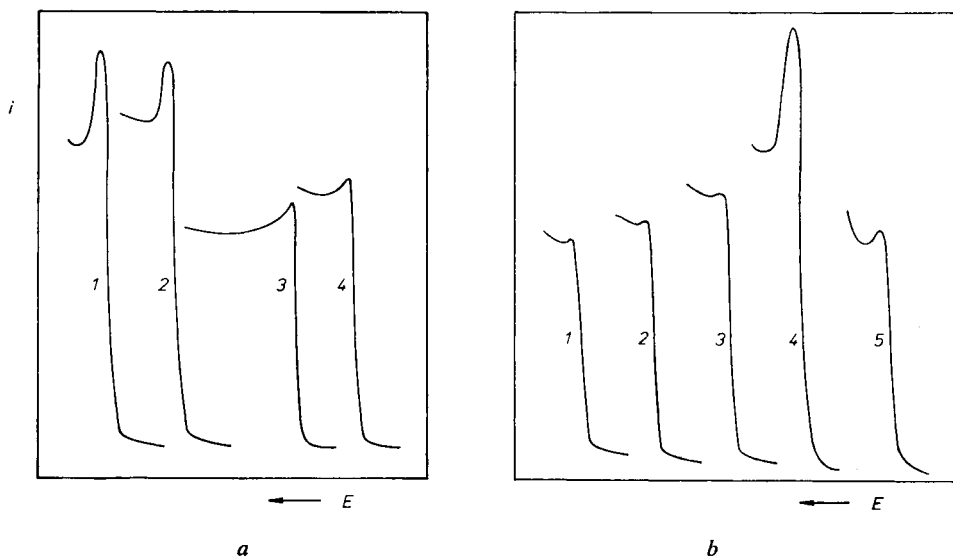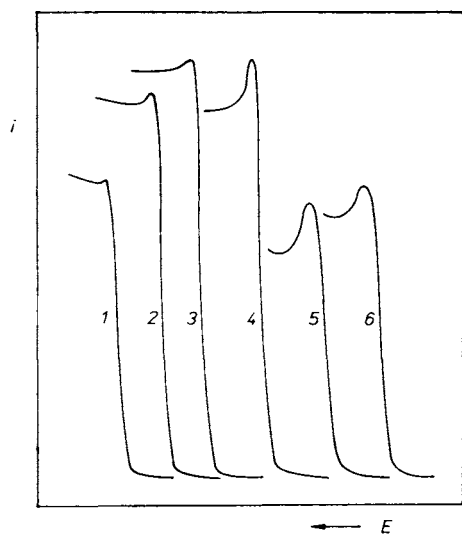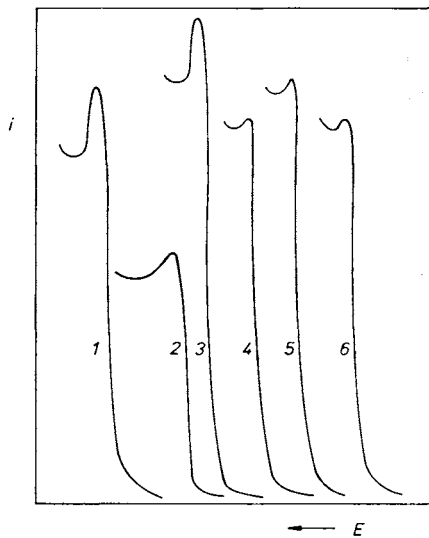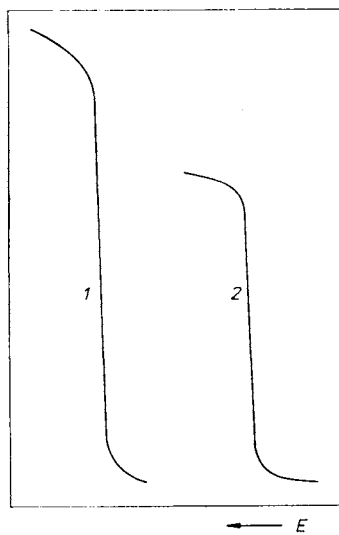

Fig. 1

2·5 . 10^{-5}M-ZnSO$_4$, 2·5 . 10^{-3}M-NaNO$_3$, starting potential −0·9 V. *a* Pulse width (ms), instrumental sensitivity: *1* 20 + 2, 1/4; *2* 20 + 20, 1/32; *3* 20 + 40, 1/64; *4* 30 + 2, 1/4. *b* Conditions as in *a*, pulse width (ms), instrumental sensitivity: *1* 30 + 20, 1/32; *2* 40 + 20, 1/32; *3* 40 + 10, 1/16; *4* 10 + 10, 1/32; *5* 10 + 20, 1/64

Fig. 2

$5 \cdot 10^{-5}$ M-ZnSO$_4$, $5 \cdot 10^{-3}$ M-NaNO$_3$, starting potential -0.9 V. Pulse width (ms), sensitivity: *1* $5 + 5$, $1/64$; *2* $5 + 40$, $1/256$; *3* $10 + 20$, $1/64$; *4* $10 + 40$, $1/128$; *5* $20 + 5$, $1/16$; *6* $20 + 10$, $1/32$

a

b

Fig. 3

a $1 \cdot 10^{-4}$ M-ZnSO$_4$, $1 \cdot 10^{-2}$ M-NaNO$_3$, starting potential -0.9 V. Pulse width (ms), sensitivity, *1* $20 + 20$, $1/256$; *2* $20 + 2$, $1/32$; *3* $10 + 40$, $1/256$; *4* $10 + 2$, $1/32$; *5* $5 + 5$, $1/256$; *6* $5 + 20$ $1/512$. *b* Disappearance of maxima by increasing the pulse width: *1* same solution as in Fig. 1, $40 + 40$, $1/32$; *2* same solution as in Fig. 3*a*, $30 + 2$, $1/32$

characteristic small steps. As a rule, polarograms were recorded at different instrumental sensitivities but, for comparative purposes, they were normalized in the calculations dividing the peak height between the top and the following valley by the height of the wave from the foot to the valley. It is appreciated from the figures that the relative peak height increases with smaller concencetrations of the supporting electrolyte (less conducting solutions). It also varies with the pulse width, increasing with the shorter decay and measuring times. Thus, for example, for the $2 \cdot 5 \cdot 10^{-5}$M-$ZnSO_4$ in $2 \cdot 5 \cdot 10^{-3}$M-$NaNO_3$ solution the sequence of pulse widths corresponding to gradually decreasing relative heights of maxima is (values expressed in ms):

$$10 + 10 > 10 + 20 > 10 + 40 > 20 + 2 > 20 + 10 > 20 + 20 >$$
$$> 20 + 40 > 30 + 2 > 30 + 10 > 30 + 20 > 40 + Y0 > 40 + 20$$

which deaggregates in four series:

$$10 + 10 > 10 + 20 > 10 + 40$$
$$20 + 2 > 20 + 10 > 20 + 20 > 20 + 40$$
$$30 + 2 > 30 + 10 > 30 + 20$$
$$40 + 10 > 40 + 20 \,.$$

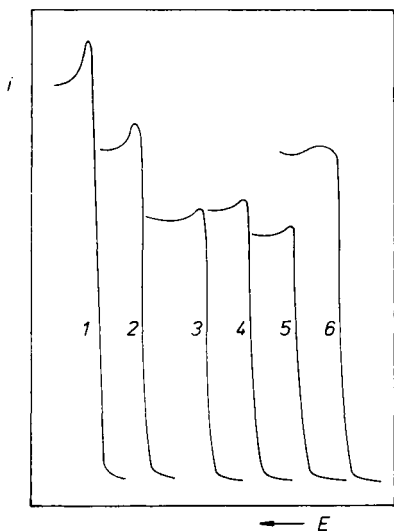No peaks are found when pulses are longer than $40 + 20$ ms.

FIG. 4

$1 \cdot 10^{-4}$M-$CdSO_4$, $1 \cdot 10^{-2}$M-KCl, starting potential $-0 \cdot 4$ V. Pulse width (ms), sensitivity: *1* $5 + 5$, $1/64$; *2* $5 + 10$, $1/128$; *3* $5 + 20$, $1/256$; *4* $10 + 5$, $1/64$; *5* $10 + 10$, $1/64$; *6* $10 + 40$, $1/256$

With the $5 . 10^{-5}$M-$ZnSO_4$ in $5 . 10^{-3}$M-$NaNO_3$ solution the following arrangement is found:

$$5 + 2 > 5 + 5 > 5 + 10 > 5 + 20 > 5 + 40 > 10 + 2 > .19 + 5 >$$
$$> 10 + 10 > 10 + 20 > 10 + 40 > 20 + 5 > 20 + 10$$

which deaggregates in three series:

$$5 + 2 > 5 + 5 > 5 + 10 > 5 + 20 > 5 + 40$$
$$10 + 2 > 10 + 5 > 10 + 10 > .10 + 20 > 10 + 40$$
$$20 + 5 > 20 + 10$$

No peaks appear with pulses longer than $20 + 10$ ms.

For the $1 . 10^{-4}$M-$ZnSO_4$ in $1 . 10^{-2}$M-$NaNO_3$ solution we have:

$$5 + 2 > 5 + 5 > 5 + 10 > 5 + 20 > 5 + 30 > 10 + 2 > 20 + 2 >$$
$$> 20 + 20 > 10 + 40$$

which deaggregates as follows:

$$5 + 2 > 5 + 5 > 5 + 10 > 5 + 20 > 5 + 30$$
$$10 + 2 > 10 + 40$$
$$20 + 2 > 20 + 20 .$$

No peaks exist with pulses longer than $20 + 20$ ms.

The Cd^{2+} ion solution gives these results:

$$5 + 5 > 5 + 10 > 5 + 20 > 5 + 30 > 5 + 40 > 10 + 5 > 10 + 10 >$$
$$> 10 + 20 > 10 + 30 > 10 + 40$$

deaggregated as

$$10 + 5 > 10 + 10 > 10 + 20 > 10 + 30 > 10 + 40 .$$

Results with pulses $20 + n$ ms wide are indecisive and definitely no peaks are found with pulses $30 + n$ ms wide.

It is seen that the first controlling factor is the decay time and the second is the measuring time. It is interesting to note that in some experiments at constant Zn^{2+} ion concentration the supporting electrolyte concentration was increased to 0·05 or 0·1 mol l^{-1}, resulting in a complete diappearance of the peak maxima.

DISCUSSION

First, a caveat is necessary. Since the basic theory of classical d.c. polarography and that of pulse polarography are different in several fundamental aspects (see, for example, ref.[4]) though similar in others, it is not possible, as a universal rule, to apply the old concepts to new phenomena, unless concepts those are demonstrated to be valid in the new case. Thus, until the theory is more fully developed, these maxima will not be assigned to any particular kind, though they are in some respects similar to classical d.c. polarographic maxima of the first kind.

It is well known that if the double layer current has not decayed enough to be negligible or null during the decay time, the remnant adds to the faradaic current in the measuring time, and a more or less large error is caused.

In the usual equivalent circuit of a polarographic cell the double layer current decays according to:

$$i = (E/R)\exp(-t/RC).\qquad(1)$$

RC values can be measured directly or the minimum decay time, required to ensure that the non-faradaic component does not affect the results, can be calculated[5].

Generally, with supporting electrolyte concentrations of $0.1\ mol\ l^{-1}$ or higher, for short decay times, the effect of the decay current which still has some finite value is seen in a sloping base line of the polarogram and/or in an abnormally high sloping plateau, but without peak maximum. This has been verified in this research. By increasing the concentration of the supporting electrolyte in a solution with a peak maximum the peak disappeared.

If the supporting electrolyte is very dilute, by making the decay time shorter and shorter, the fraction of the decay current still existing at the end of this lapse is in each case larger, and it may even be larger than the faradaic current. In cases like these, frequently peak maxima occur. It is then observed that by increasing the pulse width above some value, mainly if the decay time is increased, the peak disappears.

It should be remembered that the pulse height is about 0.5 to $-2\ V$ in the plateau, with a rising time of a few ms/V. Thus, only if the internal resistance of the cell is very low it can be expected that the potential will be uniformly distributed instantaneously on the drop surface. Otherwise, it is probable that polarographic maxima occur. Frumkin, Levich, and coworkers have discussed maxima in several classical papers[6,7]. According to the theory, in a less conducting solution the potential in the mercury drop surface may not be uniformly distributed. It follows that charges may not be uniformly distributed, too. Local inhomogeneities in electric charges produce differences in the surface tension between the neck and bottom of the drop, which is higher in the bottom when the potential is positive with respect to the potential of zero charge (positive maxima), or lowwer, for potentials more negative than the p.z.c. (negative maxima). The inhomogeneity in surface tension causes a strong

movement in the mass of mercury which induces the streaming of the solution. Thus, the well-known maxima of the first kind appear.

Now we will consider the pulse polarographic experiments. If the decay current contributes notably to the total current, the large number of charges may not be uniformly distributed and they could start the chain of events leading to the appearance of maxima. This assumption is supported by the observation that by reducing the width of the decay lapse (less time allowed for decaying, so more decay current added to the faradaic one) the relative height of the peak increases. It is also supported by a further observation: for a given decay lapse the relative peak height decreases with longer measuring times. Now, the charging current decays according to Eq. (*1*), while the faradaic current decays as:

$$i = kt^{-1/2} . \tag{2}$$

It is notorious, by comparing Eqs (*1*) and (*2*) that the double layer current decays much faster than the faradaic current. The comparison is also valid even though our polarograph measures average currents. For a short measuring time and a given decay time the fraction of non-faradaic current added to the faradaic one may be considerable. On the other side, by merely extending the decay or the measuring lapses or both, the non-faradaic fraction will diminish to such extent as to become negligible or null. Thus, peak maxima may be found or not according to the length of these lapses.

These considerations are also supported by another experimental evidence. Fig. 5 shows oscilloscopic recordings of the cell current in an experiment with $5 \cdot 10^{-5}$M--ZnSO$_4$ in a $5 \cdot 10^{-3}$M-NaNO$_3$ solution applying a single 10 ms pulse. According to the manner in which the pulse polarograh operates in this particular case, the total current decays freely between 0 and 5 ms and is measured between 5 and 10 ms. Curve *1* corresponds to a potential in the rising part of the polarographic wave before the peak maximum and shows no anomalies. Curve *2* corresponds to a potential in the peak maximum. There is a deformation in the curve rise before the peak (hardly noticeable in the figure, somewhat better defined in the actual recording), while the fall, instead of being smooth and continuous, shows three sections, the latter two with imprecise limits. From 5 ms on, when the measuring begins, curve *2* shows a current higher than curve *1*. This would be reasonable provided both curves were approximately parallel. This is not the case and curve *2* is obviously anomalous. Curve *3* corresponds to a potential in the valley after the peak maximum and falls without anomalies, being practically parallel to curve *1* in the region of measurement (5 – 10 ms); the shoulder near the peak is of no consequence, it is far from the measuring section. Fig. 6 shows curves due to a 45 ms width pulse in the same solution. In this case the polarograph can measure the current in a combination of times, either 5 + 40 ms or 40 + 5 ms. In the first case it is observed that from 5 ms

on, curve *2* (polarographic maximum) shows a notable anomaly with respect to curve *1* pertaining to a potential before the maximum. However, if the measuring begins at 40 ms both curves are parallel. This parallelism is obtained from 20 ms on, so if the measurement is made with any combination of times, provided the decay lapse is not shorter than 20 ms, the same result would be obtained, that is, a polarogram without a maximum. This is what occurs experimentally when the decay lapse is extended beyond certain minimum value. With these 45 ms curves we can reason in another way. Since the pulse width is fixed arbitrarily, we can imagine that we cut it abruptly at 10 ms, measuring the current between 5 and 10 ms. It is seen that all the anomaly in curve *2* is located in this space of time. We can then expect the appearance of a large peak maximum. On the other side, we can imagine that the pulse is longer, more than 20 ms in length. Now the curves have normal shapes, without anomalies, and the polarograms should show no maxima.

Figs 7 and 8 correspond to experiments with a $1 . 10^{-4}$M-$CdSO_4$ in $5 . 10^{-3}$M-KCl solution. In the former figure, with a 10 ms pulse, curve *1* pertains to a potential in the rising part of the polarogram. The shape is normal. Curve *2* corresponds to a potential in the maximum and shows some distortion, though less than in the case of Zn^{2+} ions. Precisely. the peak maxima of Cd^{2+} solutions are relatively smaller than those of Zn^{2+} solutions. Curve *3* was obtained at a potential in the following valley and is normal in shape. Fig. 8 shows curves obtained with a 54 ms pulse. Distortion is seen in curve *2* between 5 and 10 ms. From 20 ms on, curve *2* is parallel to curve *1*, overlapping curve *3*, which was obtained at a potential in the valley. The same consideration of the Zn^{2+} ion case apply here.
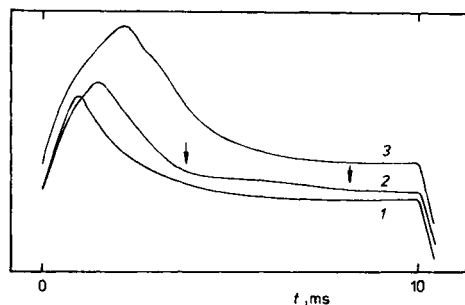

FIG. 5

$5 . 10^{-5}$M-$ZnSO_4$, $5 . 10^{-3}$M-$NaNO_3$. Pulse width, 10 ms. *E*, V: *1* $-1·042$; *2* $-1·313$; *3* $-1·673$
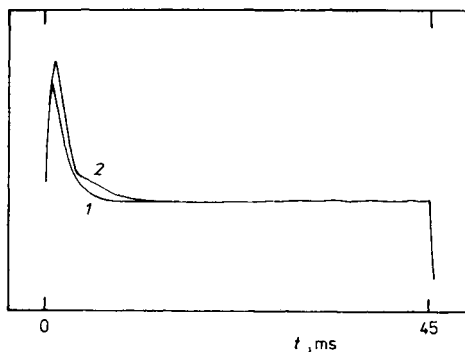

FIG. 6

Same solution as in Fig. 5. Pulse width, 45 ms. *E*, V: *1* $-1·042$; *2* $-1·313$

A semi-quantitative treatment can be attempted. Considering curve 2, Fig. 5, we assume that the final point, 10 ms, is sufficiently removed from the origin so that the current measured at this point is totally faradaic. Then the curve which meets Eq. (2) can be constructed. Fig. 9 contains calculated together with experimental values. Data are represented in arbitrary units equivalent to current units. At 3 ms the experimental current exceeds by 336% the teoretical one, at 5 ms by 150%, and at 7 ms the excess is only 76%. Though part of the excess may be non--faradaic, this figure gives an idea of how much above the theoretical value may lie the experimental ones when a polarographic maximum is present.

Anson and coworkers[2] also found that the peak height increases with a shorter pulse width but they studied an adsorption process and the explanation is different. In the present study solutions with no adsorption were purposely selected. The absence of adsorption was confirmed by the electrocapillary curves. All the curves except that of 0·1M-KCl — which gives values about 5−8% lower than the others in the negative side of the p.z.c. — are practically coincident, not differing by more than ±0·5% or less.

It is interesting to mention that some Zn^{2+} ion solutions were also studied by differential pulse polarography. In no case maxima were observed. As with this technique, the base potential increases slowly and the pulse height is small and so is the cell current; possibly electric charges can distribute homogeneously on the drop surface more easily. Thus, no differences in surface tension arise and no streaming occurs. Differential pulse polarography is one of the choices in order to avoid maxima.
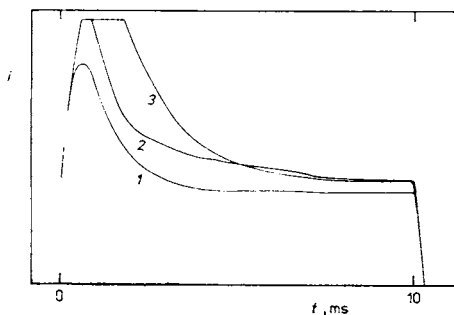

Fig. 7

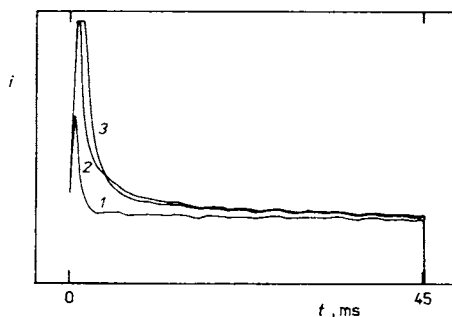1 . 10⁻⁴M-CdSO₄,   1 . 10⁻²M-KCl.   Pulse width,   10 ms. E, V: 1 −0·667; 2 −0·789; 3 −1·000

Fig. 8

Same solution as in Fig. 7. Pulse width, 45 ms. E, V: 1 −0·667; 2 −0·789; 3 −1·000

Some experiments with the Cd^{2+} ion solution were made with a delay time of 0·98 and 2·27 s, instead of the normal 3·78 s. At 2·27 s the relative size of the peak decreases and at 0·98 s the peak disappears altogether with any pulse width (see Fig. 10). Since with a shorter delay time the surface area and the currents, both faradaic and non-faradaic, diminish notably, the inhomogeneities in the distribution of the current charges and the possibility of the appearance of streaming should decrease in a similar fashion. It should be remembered that in pulse polarography the cell current varies faster by the power 4 with the delay time than it does in classical d.c. polarography with the life of the drop. In the first case[8] the ratio is $i = kt^{0.69}$ while in the second it is $i = kt^{1/6}$. Thus, when maxima occur in pulse polarography, shorter delay times may be chosen to suppress them.

The height of the peak maxima herein studied is not directly related to the concentration of the reducing species, so it offers no advantage from an analytical point of view.

In some circumstances very dilute supporting electrolytes are employed in pulse polarography. In such cases maxima may appear. A judicious selection of the pulse width and of its compounding times and of the delay time or, eventually, chanigng to differential pulse polarography is required to minimize or eliminate the undesirable peak.
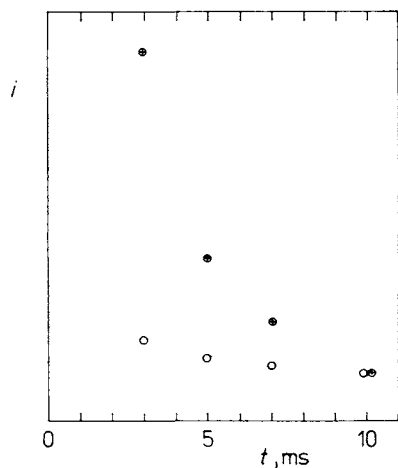

FIG. 9

Same solution as in Fig. 5, curve 2. ○, Theoretical values of the current calculated with Eq. (2); ⊕, experimental values (arbitrary units)
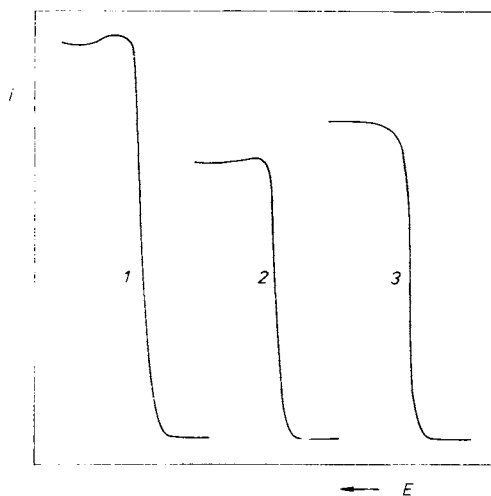
FIG. 10

Same solution as in Fig. 7. Effect of the area of the electrode. Pulse width, 10 + 40 ms. Delay time (s), sensitivity: 1 3·78, 1/256; 2 2·27, 1/256; 3 0·98, 1/128

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