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On the Instantaneous Polarographic Current

III. Accurate Measurements of the Residual Current

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With an apparatus described by Wåhlin and Bresle the instantaneous residual polarographic current has been measured. Data from these measurements are presented in this paper. The measured values show that the residual current can quantitatively be divided into a condenser and a faradaic current. From the condenser current the capacity constant is calculated giving the value of 19.7 $\pm$ 0.2 microfarads $\cdot$ cm^{-2}.

The instantaneous diffusion current is not a primary quantity found experimentally, but is a calculated difference between the measured limiting current and the measured residual current. The accuracy of the calculated diffusion current, as a consequence, depends on the accuracy of measurement of these quantities. Several theoretical considerations on the form of the mathematical expression for the diffusion current are to be found in the literature, but there are few accurate experimental data on the instantaneous currents.

This paper gives experimental data and calculations on the instantaneous residual current obtained in a common electrolyte under ordinary polarographic conditions. The measurements are intended to be used later in presenting instantaneous values of the diffusion current from measurements of the limiting current.

THEORETICAL

The instantaneous condenser current produced by the dropping mercury electrode can be written [1]

$$i_c = k \cdot \frac{dF}{d\tau} \cdot \Delta E \qquad (1)$$

where F is the area of the drop at the time τ, ΔE the potential difference between the electrocapillary maximum and the actual constant potential for the experiment, τ the age of the drop, and k the capacity constant. If the drop is assumed to be spherical [2,3], the area can be expressed using the symbols m (the rate of flow of mercury from the capillary in mg per sec) and τ, eqn. (1) being transformed to

$$i_c = k \cdot 0.0057 \cdot m^{2/3}\ \tau^{-1/3} \Delta E \tag{2}$$

As it is very difficult to remove the last traces of oxygen and mercury ions from the solution [4] the current obtained is always a sum of the condenser current and a faradaic current, i_F, caused by the reduction of the above-mentioned elements and sometimes of other impurities. Thus the measured current i_{res} can be written

$$i_{res} = i_c + i_F \tag{3}$$

or, as the condenser current is proportional to $\tau^{-1/3}$ and the faradaic current is proportional to $\tau^{1/6}$

$$i_{res} = A\tau^{-1/3} + B\tau^{1/6} \tag{4}$$

This can be transformed to

$$\frac{i_{res}}{\tau^{1/6}} = A\tau^{-\frac{1}{2}} + B \tag{5}$$

The value of the true condenser current is obtained graphically if the experimental data, $i_{res}/\tau^{1/6}$, are plotted against $\tau^{-\frac{1}{2}}$ and the constant A is evaluated.

EXPERIMENTAL

The apparatus used in the experiments was Polarograph Type 3266 B, LKB-Produkter Fabriks AB, Sweden, furnished with a device for knocking the mercury drop off the capillary, described earlier by Wåhlin and Bresle [5].

The solution was 0.1 M potassium chloride with 0.09 % of gelatine in ion-free water. Deaeration was carried out for two hours with oxygen-free nitrogen gas, purified according to Meyer and Ronge [6]. The chemicals used, mercury, potassium chloride, and gelatine, were of Polaritan reagent grade in all experiments. The temperature was 25 ± 0.1 °C. The mean rate of flow of mercury from the capillary was measured and the corresponding instantaneous value was calculated as described in a previous paper in this series [7]. The calculations justified the use of a constant value of m for the last 2/3 of the life of the drop without any great error. The potential at the electrocapillary maximum was obtained by evaluating the maximum drop time from observed values of the drop time at different potentials. The value thus obtained was −0.45 ± 0.02 volts *vs* the silver anode. The potential in all the experiments was −0.94 volts *vs* the silver anode.

The rates of flow of mercury in the experiments are given in Table 1 and corresponding values of time and residual current in Table 2. With the aid of eqn. (5) the constants A and B are calculated [8] and listed in Table 3 together with the values of the capacity constant, calculated according to eqn. (2). Table 4, finally, gives a comparison between the residual current measured directly, and the calculated as the sum of a condenser and a faradaic current using Table 3 and eqn. (4).

CONCLUSIONS

The reproducibility of the measurements can be studied in Table 2. The experiments number 1 and 2 listed in this table are made under the same conditions. The values of the residual current differs somewhat, those in expt. 1

Table 1. Values of the rate of flow of mercury.

Expt.	m mg / sec
1	2.024
2	2.024
3	1.716
4	1.487
5	1.280

Table 2. Instantaneous values of the residual current.

Sec	i_{res} measured				
	No. 1	No. 2	No. 3	No. 4	No. 5
1.383	0.1005	0.0967	0.0855	0.0784	0.0703
1.729	0.0942	0.0917 *	0.0811 *	0.0745 *	0.0669 *
2.075	0.0908	0.0867	0.0774	0.0701	0.0630
2.421	0.0882	0.0852 *	0.0753 *	0.0687 *	0.0614 *
2.766	0.0865	0.0829	0.0730	0.0663	0.0594
3.112	0.0845	0.0807 *	0.0715 *	0.0646 *	0.0580 *
3.458	0.0825	0.0792	0.0694	0.0632	0.0566
3.804	0.0811	0.0776 *	0.0682 *	0.0615 *	0.0550 *
4.150	0.0794	0.0764	0.0672	0.0606	0.0542

* interpolated

Table 3. The capacity constant for different parameters.

Expt.	A	B	k
1	0.0873	0.0200	19.9
2	0.0872	0.0175	19.9
3	0.0748	0.0164	19.1
4	0.0705	0.0133	19.5
5	0.0647	0.0111	20.1

always exceeding those in expt. 2 by about 4 %. The explanation for this difference is given in Table 3, where it can be seen that the condenser current part in these two experiments is the same, as the values of A are practically identical. The different values of the constant B, however, indicate that the faradaic component, due to impurities, is somewhat smaller in the latter experiment.

The capacity constant of the expanding mercury drop calculated from values of the current for different rates of flow assumes the value of 19.7 ± 0.2 microfarads · cm^{-2}. The value given by other authors obtained by different methods are: Philpot [9], 21.8 microfarads · cm^{-2}; Ilkovic [1], 22.3 microfarads · cm^{-2}.

There is good agreement between the measured residual current, and that calculated on the assumption that this current can be divided into a condenser part and a faradaic part. The deviation is about 1 % at the beginning of the life of the drop, but is then diminished to some tenths of a per cent, as can be seen from Table 4.

Table 4. Comparison between calculated and measured values of the instantaneous residual current obtained in experiment No 1.

Sec	i_c calc.	i_F calc.	$i_c + i_F$ calc.	$i_c + i_F$ meas.
1.383	0.0784	0.0211	0.0995	0.1005
1.729	0.0727	0.0219	0.0946	0.0942
2.075	0.0684	0.0226	0.0910	0.0908
2.421	0.0650	0.0232	0.0882	0.0882
2.766	0.0622	0.0237	0.0859	0.0865
3.112	0.0598	0.0242	0.0840	0.0845
3.458	0.0578	0.0246	0.0824	0.0825
3.804	0.0560	0.0250	0.0810	0.0811
4.150	0.0544	0.0254	0.0798	0.0794

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