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On the Instantaneous Polarographic Current

II. Measurements of the Rate of Flow of Mercury

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The variation of the rate of flow of mercury from a polarographic capillary during the lifetime of a drop is given. The results are based upon measurements of the instantaneous rate of flow obtained by a special technique described earlier. The agreement between the experimental data and those calculated from the theoretical formula is shown, the deviation being about 0.3 %.

The polarographic diffusion current is a function of the age of the mercury drop, the rate of flow of mercury through the capillary and some characteristics of the electrolyzed solution, *i. e.* the concentration, the valency and the diffusion constant of the depolarizer. In ordinary polarographic work, for instance in analytical polarography where the mean diffusion current is measured, the mean value of the rate of flow of mercury is determined, but in investigations on the instantaneous current it is necessary to know the corresponding instantaneous value of the rate of flow.

As a part of an investigation on the instantaneous polarographic current data concerning the flow of mercury were collected and the theoretical and experimental results were compared.

List of symbols

m = instantaneous rate of mercury flow at the time τ ($\mathrm{mg \cdot sec^{-1}}$)
$\bar{m}$ = mean value of the rate of mercury flow, measured from the time zero to τ ($\mathrm{mg \cdot sec^{-1}}$)
M = constant rate of mercury flow obtained when the capillary tip is immersed in mercury ($\mathrm{mg \cdot sec^{-1}}$)
τ = age of the drop at a certain moment (sec)
r = radius of the drop at the time τ (cm)
r_c = inner radius of the capillary (cm)

l = length of the capillary (cm)
d = density of mercury ($g \cdot ml^{-1}$)
η = viscosity coefficient of mercury ($dynes \cdot sec \cdot cm^{-2}$)
σ = interfacial tension between mercury and the electrolyte ($dynes \cdot cm^{-1}$)
h = distance between the upper and lower mercury surfaces (cm)
P_{tot} = total applied pressure ($dynes \cdot cm^{-2}$)
P_{eff} = effective pressure ($dynes \cdot cm^{-2}$)
P_b = back pressure ($dynes \cdot cm^{-2}$)
ω = weight of the drop at the time τ
k_1, k_2, k_3, α, β = constants

THEORETICAL

When mercury flows through a capillary and forms a growing drop at the capillary tip, the rate of flow varies during the life of the drop. The relation between the dimensions of the drop and the variables m and τ is expressed by the equation

$$\frac{4}{3} \pi r^3 = \frac{\overline{m}\,\tau}{d} = \frac{\omega}{d} \tag{1}$$

or

$$r = k_1 \cdot (\overline{m}\,\tau)^{1/3} = k_1 \cdot \omega^{1/3} \tag{2}$$

and the rate of flow is given by the Poiseuille relation

$$m = \frac{\pi r_c^4 d\, P_{eff}}{8\, l\, \eta} = k_2\, P_{eff} \tag{3}$$

Owing to the back pressure, produced by the interfacial tension at the surface of the growing drop, the effective pressure varies during the life of the drop. The back pressure[1] is related to the geometry of the drop by the equation

$$P_b = \frac{2\,\sigma}{r} \tag{4}$$

and the effective pressure can be written

$$P_{eff} = P_{tot} - P_b \tag{5}$$

If eqns. (2), (3), (4), and (5) are combined the instantaneous rate of flow is given by

$$m = k_2 P_{tot} - \frac{2\, k_2\, \sigma}{k_1\, (\overline{m}\, \tau)^{1/3}} = M - \frac{k_3}{(\overline{m}\, \tau)^{1/3}} \tag{6}$$

This equation cannot be tested experimentally as the rate of flow is not explicitly expressed. It may, however, be transformed. The instantaneous and mean rates of flow are related to the weight of the drop by the equations

$$m = \frac{d\omega}{d\tau} \tag{7}$$

and

$$\bar{m} = \frac{\omega}{\tau} \tag{8}$$

After substituting these equations into eqn. (6) and solving for ω and differentiating the following expression is obtained [2]

$$m = M - \frac{2}{3} \cdot \frac{1.5\ M^{2/3}\ \delta\ \tau^{-1/3}}{172.7\ h} - \frac{1}{3} \cdot \frac{1.5\ M^{1/3}\ \sigma^2\ \tau^{-2/3}}{(172.7\ h)^2} \tag{9}$$

The corresponding formula of the mean rate of flow is

$$\bar{m} = M - \frac{1.5\ M^{2/3}\ \sigma\ \tau^{-1/3}}{172.7\ h} - \frac{1.5\ M^{1/3}\ \sigma^2\ \tau^{-2/3}}{(172.7\ h)^2} \tag{10}$$

In these equations the first term on the right hand side is equal to the rate of flow obtained when there is no back pressure. It can be measured by determining the rate of flow when the capillary tip is immersed in a pool of mercury [3]. The quantities M, σ, τ and h in the equations are known, or can easily be determined. With a technique described below the instantaneous rate of flow can be measured, thus making it possible to check eqn. (9) experimentally.

Table 1. Comparison between measured and calculated values of the instantaneous rate of flow of mercury.

Sec	Expt. a, −0.8 volts		Expt. b, −0.9 volts		Expt. c, −1.0 volts		Expt. d, −1.1 volts		Expt. e, −1.2 volts	
	m calc.	*m* meas.	*m* calc.	*m* meas.	*m* calc.	*m* meas.	*m* calc.	*m* meas.	*m* calc.	*m* meas.
0.432	1.648	1.652	1.649	1.655	1.651	1.647	1.655	1.663	1.659	1.658
0.864	1.675	1.669	1.676	1.681	1.678	1.665	1.681	1.682	1.684	1.687
1.296	1.688	1.681	1.689	1.698	1.691	1.685	1.694	1.695	1.696	1.697
1.723	1.696	1.694	1.697	1.698	1.699	1.700	1.701	1.702	1.703	1.701
2.592	1.707	1.705	1.708	1.713	1.709	1.710	1.711	1.712	1.713	1.712
3.447	1.713	1.714	1.714	1.717	1.715	1.719	1.717	1.717	1.718	1.720
3.889	1.716	1.709	1.716	1.719	1.717	1.723	1.719	1.717	1.721	1.723
5.160	1.721	1.720	1.722	1.724	1.723	1.720	1.724	1.724	1.726	1.726

EXPERIMENTAL

The method of determining the rate of flow is as follows.

For a given capillary and at a constant mercury pressure the weight of mercury droplets falling naturally from the dropping mercury electrode can be determined in a well-known manner. If now the individual droplets are disengaged from the capillary at a moment shortly before the natural drop time is reached, the difference between the weights of a natural and forced drop gives a mean value of the rate of flow during this last interval of the life of the drop. If this interval is chosen to be sufficiently short, the mean rate of flow can be taken as the instantaneous value during the interval.

This process is repeated for other selected intervals of the life of the drop, giving the instantaneous rate of flow of mercury from the capillary for any time.

The mercury drops are disengaged using an electromagnetically operated hammer described in a previous paper in this series [4]. The solution used in the experiments was 0.1 M potassium chloride with 0.009 % of gelatine, deaerated with purified nitrogen [5]. The anode consisted of a silver sheet and the applied potential, constant during each experiment, was varied from 0.8 to 1.2 volts *vs* the silver anode. The vessel and apparatus used for collecting the mercury drops has been described by Lingane and Kolthoff [6]. The temperature was held at 25 $\pm$ 0.1° C, the height of the upper mercury level above the capillary orifice was 57.0 cm and for M a value of 1.776 mg mercury per second was obtained.

With the technique described above a series of experiments has been carried out and the results are given in Table 1, where the measured values of m are listed together with those calculated according to eqn. (9). The values of the interfacial tension used in the calculations have been taken from Grahame [7].

The empirical results show a very good agreement with those calculated. The deviation of the measured value from the calculated value does not exceed 0.3 %, a figure that is of the same order of magnitude as for example the accuracy of the measurements of the age of the drop. Thus, eqn. (9) is shown to give a correct value of the instantaneous rate of flow of mercury from the measured data.

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