On the Application of the Dropping Mercury Electrode to the Measurement of Overvoltage

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Within the past few years the dropping mercury electrode has found wide application in various electrochemical investigations[1] owing to the simplicity of its make-up and its ideally clean surface obtained as a result of constant renewal. In particular the dropping electrode has found especially large application in the polarographic method[2].

Heyrovsky and his co-workers[3] attribute certain characteristic properties to the dropping mercury electrode. In the opinion of these authors the hydrogen overvoltage on a dropping mercury electrode is considerably higher and closer to the true value than that on a stationary one. Only on a dropping mercury cathode may one detect, with great sensitivity, insignificant amounts of mpurities in the electrolyte by a decrease in the hydrogen overvoltage[4].

It is necessary to note, however, that no careful and exac experimental investigations dealing with a comparison of the values for the hydrogen overvoltage on a dropping and a stationary mercury electrode have as yet appeared in the literature. Furthermore,

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[1] Kolthoff and Lingane, Chem. Rev., 24, 1 (1939).
[2] Heyrovsky, Phil. Mag., 45, 303 (1923). Heyrovsky, "The Polarographic Method and its Practical Application", ONTI, 1937.
[3] Emeljanova and Herasymenko, Trans. Farad Soc., 84, 257 (1928).
[4] Herasymenko and Slendyk, Coll. Czech. Chem. Com., 5, 479 (1933).

as has already been pointed out[5], the experimental data of different authors for the hydrogen overvoltage on a stationary mercury cathode, which have appeared in the literature up to now, markedly differ from one another and therefore cannot serve as a standard for comparison.

If we set aside for the present the question of the deviation of the values of the overvoltage and turn our attention to the dependence of this quantity upon various factors, for example, upon the current density or the temperature, we find that contradictions also exist in the quantitative estimation of their effect by these two methods. The most essential point in these contradictions concerns the dependence of the overvoltage upon the current density, $\frac{d\eta}{d \lg i} = b$. In the earlier papers dealing with the dropping mercury electrode, the values for the coefficient b markedly differ from one another: for instance, Bowden[6] gives the value 0.220; Lloyd[7], from 0.066 to 0.162 (depending upon the concentration and the nature of the electrolyte); and Herasymenko[8], 0.087. On a stationary electrode, however, according to the data of many authors, $b = 0.116 - 0.120$ (at 20° C) over a wide range of current densities.

In more recent investigations, Heyrovsky[9] points out that the coefficient b depends on the one hand upon the rate of formation of a drop of the mercury electrode and on the other, upon the current strength. In Heyrovsky's opinion this result, obtained from polarographic data[10], follows from the equation for the hydrogen overvoltage which he derived taking into account the saturation of the electrode surface with hydrogen molecules. From these considerations, at large rates of formation of the drops or at very small currents, the coefficient b should approach $2.30 \times \frac{RT}{F}$ (*i. e.*, 0.058). With a decrease in the rate of formation of a drop, the coefficient

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5 Jofa and Kabanov, Acta Physicochimica URSS, **10**, 317 (1939).
6 Bowden, Trans. Farad. Soc., **24**, 12, (1930).
7 Lloyd, Trans. Farad. Soc., **26**, 12 (1930).
8 Herasymenko, Z. Elektrochem., **34**, 129 (1928).
9 Heyrovsky, Coll. Czech. Chem. Com., 9, 273 (1937); Chem. Rev., **24**, 125 (1939).
10 Novak, Coll. Czech. Chem. Com., 9, 207 (1937).

increases and, in the limit, on a stationary mercury surface it should be equal to $2.30 \times \frac{2RT}{F}$ (*i. e.*, 0.116). Under the conditions when the dropping mercury electrode is usually employed this coefficient should lie between $2.30 \times \frac{RT}{F}$ and $2.30 \times \frac{2RT}{F}$, *i. e.*, it should be equal to approximately $2.30 \times \frac{3}{2}\frac{RT}{F}$ (*i. e.*, 0.087).

As regards the temperature effect, Heyrovsky points out that with an increase in temperature the coefficient b for the dropping mercury electrode increases slower than is required by the linear dependence upon T [9, 10], while for a stationary electrode, according to Bowden's data [11] and those of one of the authors of this communication, it is very close to $2.30 \times \frac{2RT}{F}$ within the temperature range from 0 to 80° C.

Recently some papers dealing with the dropping mercury electrode have appeared which are devoted to other problems. These problems are of considerable theoretical interest: for example, the question regarding the shift in the potential of a polarographic half-wave as a function of the hydrogen ion concentration in the solution [12].

The data of this investigation also lead to a conclusion which contradicts other experimental data obtained with a mercury cathode.

Upon comparing the data obtained with the aid of the dropping and stationary electrodes, the chief difficulty should be an exact determination of the current density on the dropping electrode, since the working area of the electrode changes with the rate of formation and the growth of each drop. This area, therefore, will not be equal to that which may be found from the weight of a drop that detaches itself from the capillary.

Upon a more thorough investigation of this problem it turned out that in calculating the true current density, as is shown in this paper, difficulties are encountered connected with a number of other factors also.

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[11] Bowden, Proc. Roy. Soc., (A) 126, 107 (1929).
[12] Tomeš, Coll. Czech. Chem. Com., 9, 150 (1937). Heyrovsky. Chem. Rev., 24, 125 (1939).

Experimental data and their discussion

The present investigation of the dropping mercury electrode was carried out in a specially constructed apparatus in which the electrolyte was first carefully freed from dissolved air by bubbling pure hydrogen through it, and then, by prolonged cathodic polarization on a large auxiliary mercury cathode, from traces of various kinds of depolarizers. The mercury drops issued from the capillary under a pressure of about 50 cm. of mercury. The constricted portion of the capillary was about 3 cm. long. This ensured a constant rate of flow of mercury, independent of the polarization. The potential measurements were made against a hydrogen electrode in the same electrolytic solution.

In order to determine the weight of the falling drops, a stopcock was sealed into the lower part of the cathode cell. Thus a definite number of drops could be removed for weighing without disturbing the established regime of electrolysis[13]. The rate of formation of the drops in most of the experiments was one drop in two seconds, while in individual experiments, one drop in one or four seconds. The results of the measurements obtained with the dropping electrode were compared with the data obtained with a large mercury cathode and with a small mercury drop renewed from time to time. Both of the latter methods of measuring the overvoltage with stationary cathodes have already been described in a preceding communication[5].

The comparison was made in solutions of hydrochloric and hydrobromic acids.

The results of the measurements are given in Figs. 1 and 2 in the form of η, lg i curves, where η is the overvoltage and i is the current density.

For a first approximate calculation of the current density, the effective area of the dropping electrode was determined from the weight of a definite number of falling drops in the given solution at a constant small current strength (about 10^{-6} A), according to equation (1).

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[13] For a diagram and description of the apparatus see the Russian ext in the Journal of Physical Chemistry (Russ.).

As we have already shown[5] the curves obtained by both stationary methods pointed out above give perfectly coinciding results. As regards the dropping mercury electrode method, it may be seen from Figs. 1 and 2 (solid lines 3 and 4) that the curves differ both in their form and in their position on the graph. For medium values of the current density the dropping mercury electrode method gives a curve almost parallel to the curve η, lg i obtained by the stationary method for the corresponding solution. However, it lies 40 mV higher.

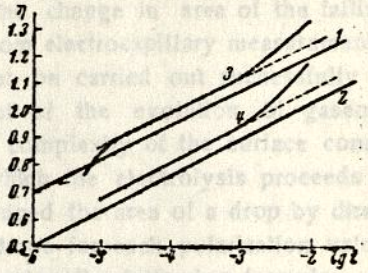

Fig. 1. Dependence of η upon lg i for HCl solutions. *1* — stationary method, 1 *N* HCl, *2* — the same method, 6.5 *N* HCl, *3* — dropping mercury method, 1 *N* HCl, *4* — the same method, 6.5 *N* HCl.

At large and small current densities, the η, lg i curve noticeably deviates from its normal course. At current densities larger than 5.10^{-4} A/cm.^{2} the curve bends upward in the direction of large values of the overvoltage; while at low current densities, 10^{-5} A/cm.^{2}, it exhibits just the opposite course, bending downward. The apparent increase of the overvoltage at large values of the current density is caused by a decrease in the size of the drops due to a decrease in the surface tension of mercury at its boundary with the solution, under the influence of polarization.

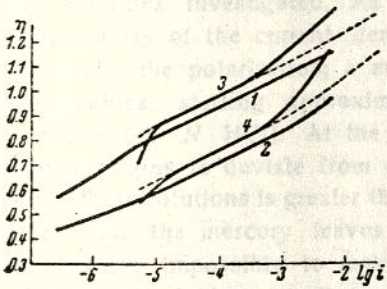

Fig. 2. Dependence of η upon lg i for HBr solutions. *1* — stationary method, 1 *N* HBr. *2* — the same method 5.5 *N* HBr, *3* — dropping mercury method, 1 *N* HBr, *4* — the same method, 5.5 *N* HBr.

A decrease in the size of the drops with an increase in the potential was noted by Ilkovič[14], and also by Lingane and Kolthoff[15], while testing an equation for the diffusion current. However, the

[14] Ilkovič, Coll. Czech. Chem. Com., 6, 498 (1934).
[15] Lingane and Kolthoff, J. Am. Chem. Soc., 61, 825 (1939).

experiments which they carried out cannot give a complete picture of the effect of polarization on the size of a drop, since in the latter paper the surface tension of mercury was known to have been lowered by the addition of a surface active substance to the solution.

It is impossible to calculate the change in area of the falling drops theoretically, for example, from electrocapillary measurements, because such measurements cannot be carried out successfully in the overvoltage region on account of the evolution of gaseous hydrogen, and also because of the complexity of the surface conditions that exist while a drop on which the electrolysis proceeds is being formed. Therefore, we determined the area of a drop by direct weighing of a definite number of drops for each polarization value, and then calculated its value employing the following formula:

$$S = 4\pi \left(\frac{3}{4\pi D}\right)^{2/3} \left(\frac{m}{n}\right)^{2/3} = 0.850 \left(\frac{m}{n}\right)^{2/3}, \qquad (1)$$

where n is the number of drops, m — their weight and D — the density of mercury.

The dependence of the area of a drop calculated by formula (1) upon the logarithm of the current strength i' is given in Fig. 3 for all the solutions investigated. As can be seen from these curves, for small values of the current density the area of a drop changes but little with the polarization; a marked decrease sets in, however, at large values, starting approximately from $i = 6 \times 10^{-4}$ A/cm.^{2} (in 1 N and 6.5 N HCl). At the same time the shape of the η, lg i curves begins to deviate from a straight line. When the current density in these solutions is greater than 10^{-1} A/cm.^{2}, the drops become so small that the mercury leaves the capillary as a fine spray, and it becomes impossible to make measurements. In more dilute solutions the effect of polarization upon the area of a drop decreases markedly and, in accordance with this, the current density region within which a drop electrode may be used is extended.

From the curves in Fig. 3 one may find the area of the electrode for any polarization value. The area of the electrode thus found is employed for correcting the η, lg i curves given in Figs. 1 and 2. The corrected curves are shown in the same figures by dotted lines. It is seen that these latter curves approach straight lines in the region of large current densities also.

The deviation of the η, lg i curves from straight lines at small current strengths is connected with the appearance of a non-faradaic current of charging of the double layer that appears on the newly formed surface of the electrode. If we subtract the value of the non-

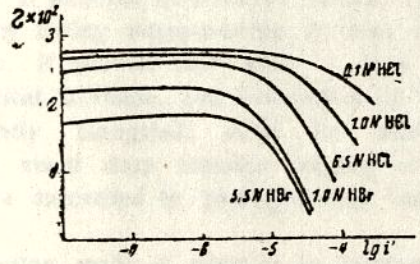

Fig. 3. Dependence of the area of a drop (S) upon the logarithm of the current strength (lg i').

faradaic charging current which may be found, *e. g.*, from the corresponding electrocapillary curves, from the current readings we may find the actual polarization current and, in accordance with this, correct the lower part of the η, lg i curves in Figs. 1 and 2. When this correction is made, these curves straighten out considerably in this region of current densities also.

Thus, after the corrections mentioned are made, the entire course of the curve approaches a straight line which is parallel to the curve obtained employing the stationary method; however, it still lies some 35—40 mV above the latter. This difference between the results obtained when the dropping and stationary electrodes are used may be easily explained if one takes into account that in the dropping electrode the current is distributed over the drop surface, which increases from an initial value at the moment of its formation to its maximum value at the moment of the detachment. The current density at a constant current strength also changes accordingly. Hence it follows that the data obtained with the aid of the dropping electrode refer to an average current density, which is considerably

larger than that calculated from the area of the drop at the moment when it detaches itself.

It is possible to calculate the increase in the overvoltage caused by this circumstance. However, before we proceed to this calculation, we should mention some results of an investigation of the mechanism by which the drops form, grow and detach themselves from the capillary at different polarization values. This investigation was carried out by taking micro-moving pictures of the dropping mercury electrode. It proved that while a drop is still small it is almost spherical in shape, and just before it detaches itself, it becomes slightly elongated. After the main large drop detaches itself, a small drop remains hanging on the capillary. In one picture we succeeded in photographing both drops simultaneously.

This investigation made it possible to measure accurately the area of the large drop at the moment when it detaches itself, the area of the remaining small drop, and also the areas of adherence of both of these drops to the capillary (the external diameter of the capillary end served as the scale). Thus the active area of the electrode varies periodically from the area of this small drop, s_1 (minus its adherence area σ_1), up to the maximum area, s_2 (minus the adherence area of the large drop σ_2).

In order to calculate the increase in the overvoltage on the dropping electrode due to the fact just mentioned, let us assume in the first place that the current strength, i', is constant, and that the rate of mercury flow is also constant, *i. e.*,

$$\frac{dm}{dt} \sim \frac{dv}{dt} = \frac{d\left(\frac{4}{3}\pi r^3\right)}{dt}.$$

Consequently, the volume of a drop v at any moment is proportional to the time $t: v = kt$.

Let us denote the time elapsing from any arbitrary initial moment to the moment of the formation of a drop possessing a maximum size by t_2, and the respective time interval which would be necessary for the formation of the small drop remaining after the

main drop detaches itself, by t_1. Then assuming that $s \sim v^{2/3} \sim t^{2/3}$, we get the area of a drop at any time t:

$$s = s_2 t^{2/3} t_2^{-2/3} \quad \text{and} \quad s_1 = s_2 t_1^{2/3} t_2^{-2/3}.$$

Assuming that the overvoltage at $[H^+] = \text{const.}$ is determined by

$$\eta = \frac{2RT}{F} \ln i + \text{const.},$$

where i is the current density, and substituting into this expression the following value of i:

$$i = \frac{i'}{s} = \frac{i' t_2^{2/3}}{s_2 t^{2/3}},$$

we obtain:

$$\eta = \frac{2RT}{F} \ln \frac{i'}{s_2} + \frac{4}{3} \frac{RT}{F} \ln \frac{t_2}{t} + \text{const.}$$

Integrating both sides of the equation we find the mean value of the overvoltage $\bar{\eta}$ between t_1 and t_2:

$$\bar{\eta} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} \eta dt = \frac{2RT}{F} \ln \frac{i'}{s_2} + \frac{1}{t_2 - t_1} \frac{4RT}{3F} \int_{t_1}^{t_2} \ln \frac{t_2}{t} dt + \text{const.}$$

Expressing t_1 and t_2 in terms of the corresponding areas, we get the following relation, as t_1 is small in comparison with t_2:

$$\bar{\eta} = \frac{2RT}{F} \ln \frac{i'}{s_2} + \frac{4}{3} \frac{RT}{F} \left\{ 1 - {}^3/_2 \left(\frac{s_1}{s_2} \right)^{3/2} \ln \frac{s_2}{s_1} \right\} + \text{const.},$$

and, after a corresponding substitution for 20°C

$$\bar{\eta} = 0.116 \lg \frac{i'}{s_2} - 0.116 \left(\frac{s_1}{s_2} \right)^{3/2} \lg \frac{s_2}{s_1} + 0.034 + \text{const.} \qquad (2)$$

An analysis of expression (2) leads to the conclusion that, if the area of the remaining drop s_1 might be neglected, the apparent overvoltage on the dropping electrode should be greater than that

on the stationary one by 34 mV. This conclusion, however, is correct only in the case when Volmer's coefficient α is equal to 0.5. In the opposite case the difference between the values for the overvoltage obtained by these two methods will be equal to $^2/_3 \frac{RT}{\alpha F}$.

A more precise equation, taking into account the area of contact of the drop with the capillary, assumes the following form ($\alpha = 0.5$):

$$\bar{\eta} = 0.116 \lg \frac{i'}{s_2 - \sigma_2} - 0.116 \left(\frac{s_1}{s_2}\right)^{3/2} \lg \frac{s_2}{s_1} + 0.034 + \text{const.} \quad (3)$$

Equation (3) allows of calculating the apparent increase in the overvoltage obtained with the dropping mercury method. For this purpose, besides the current strength i', and the area of the falling drops s_2, the values s_1 and σ_2, which may be obtained from the photomicrographs, must be known.

A substitution of the numerical values found in this manner into equation (2) revealed that if the current density is computed, as is usually done, on the basis of the area of a drop determined by the weight of a definite number of falling drops, then the overvoltage on the dropping electrode should be 35—37 mV higher than that on a stationary electrode. The results of such a calculation agree very well with the experimental data given in Figs. 1 and 2.

In conclusion we feel it our pleasant duty to express our deep gratitude to Prof. A. Frumkin for suggesting the problem and rendering valuable advice while the investigation was being carried out.

Summary

1. With the aid of a dropping mercury electrode η, lg i curves were obtained for 0.1, 1.0 and 6.5 N HCl, and 1.0 and 5.5 N HBr. These curves are compared with the ones obtained with the aid of a stationary electrode.

2. For medium values of the current density, the dropping electrode yields a linear relation between η and lg i. The coefficient

before $\lg i$ is equal to $2.30 \times \frac{2RT}{F}$ just as in the case of the stationary mercury electrode. However, a deviation from the linear relation in the direction of higher values of the overvoltage is observed for high current densities; for small current densities the deviation is in the direction of lower values.

3. In the former case this deviation is due to the decrease in the size of the drops which sets in on account of the decrease in the surface tension with polarization, while in the latter case, it is due to the influence of the non-faradaic current of charging the newly formed electrode surface which becomes pronounced when the polarization current is small.

4. After corrections for the change in the drop area with the polarization and for the non-faradaic current are introduced, the curve assumes a linear course, parallel to the curve obtained with the aid of the stationary method, over practically the entire region measured. It remains 35—40 mV higher than the latter, however. This difference is caused by the fact that the current density on the dropping electrode does not correspond to that calculated from the weight of falling drops, since the area of a drop varies from a minimum value at the moment of its formation to a maximum one at the moment of its detachment.

5. A formula is derived which may be used for the computation of the overvoltage on the dropping electrode, which shows that the overvoltage on a dropping electrode, when calculated according to the usual method of computing the current density, in accordance with experiment, should be higher by 35—37 mV than the overvoltage on a stationary electrode. There exists, therefore, no reason to assume a difference in the mechanism of the electrode processes on a dropping and on a stationary electrode.

6. From the results of the investigation carried out one may draw the conclusion that the dropping electrode, while possessing all the advantages connected with the simplicity of its application and its ability to renew its surface automatically, does not possess, however, any essential qualities which would make it possible to obtain a higher overvoltage as compared with the stationary mercury electrode. On the contrary, its application to the investigation

of polarization is permissible only within a rather limited current density region, and even then one must introduce corrections described in this paper.

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