Capacity of the Solid Mercury Electrode

By *A. Gorodetzkaja* and *M. Proskurnin*

In our laboratory a method was developed which allows of measuring the capacity of a clean mercury surface, and for the first time capacity values were obtained corresponding to those calculated from the electrocapillary curve [1].

It was of interest to compare the capacities of the solid and liquid electrodes of the same metal, which would make it possible to ascertain whether the thickness of the double layer varies with a change in the state of aggregation of the metal.

Experimental

The procedure used by the authors was described in previous papers [1].

The vessel in which the measurements were carried out was made of Jena glass, and in the lower part had no soldered parts, which enabled it to be rapidly cooled when placed in a Dewar vessel with cooled alcohol. The experiment was carried out in an atmosphere of hydrogen which also served for stirring the solution during its cooling. The measurements with solid mercury were made at —40°C; those with liquid mercury, at —38°C [2]. Upon cooling, the mercury gradually solidified, the surface of the solid mercury remaining bright.

[1] M. Proskurnin a. A. Frumkin, Trans. Farad. Soc., **31**, 110 (1935). T. Borissowa a. M. Proskurnin, Acta Physicochimica URSS, **4**, 819 (1936).

[2] The temperature coefficient of capacity is not great, and hence there was no necessity of strictly regulating the temperature.

A K_2CO_3 solution[3] was chosen as a suitable electrolyte. The dry salt was preliminarily ignited at 850° in a platinum dish. The suitableness of the solution was determined empirically by testing it for non-freezing at — 45°C. Its concentration was ca. 50%. It is known that a 39,6% K_2CO_3 solution freezes at —36,5°[4] (eutectic point), so that at the temperature of the authors' experiments the solution was undoubtedly supersaturated. Hence, particular atten-

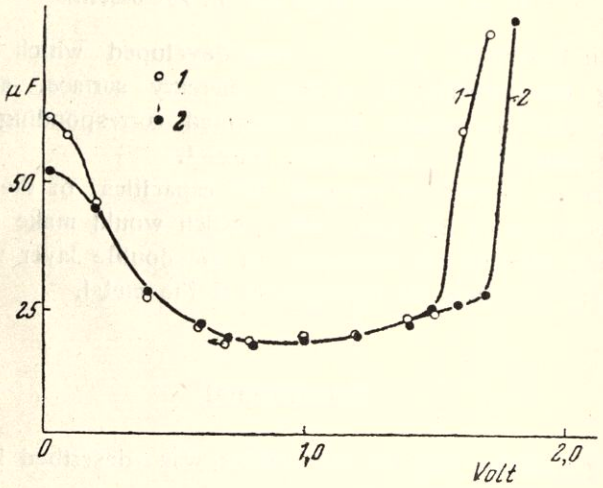

Fig. 1. 50% K_2CO_3 solution. *1* — liquid mercury; *2* — solid mercury.

tion had to be paid to its purity. The reference electrode was a mercury electrode in the same solution saturated with $HgO \cdot HgCO_3$.

It was established that the potential of this electrode is ca. 0,1 V more cathodic than that of the normal calomel electrode. The capacity curves shown in the figures are referred to this electrode. As will be seen from Fig. 1, the capacity curve for the solid electrode in a K_2CO_3 solution coincides with the curve for the liquid electrode with the exception of the cathodic end. The minimum

[3] As is known from electrocapillary measurements, K_2CO_3 does not contain ions specifically adsorbed at the interface mercury solution.

[4] Landolt, Phys. Tab., 1, 658 (1923).

capacity is 18 μ F/cm.², in accordance with the value obtained by calculating the capacity from the electrocapillary curve (17—18 μ F/cm.²). A rise in the cathodic part of the curve connected with the formation of the amalgam begins at 1,5 V for liquid mercury, while for solid mercury it begins only at 1,7 V. The formation of amalgam undoubtedly takes place much more slowly with solid mercury, which is confirmed by the measurements of the residual current. The residual current with solid mercury was four times smaller than on liquid mercury.

When confining oneself to a measurement of the electrode capacity in a K_2CO_3 solution and having no information on the way in which the surface area of mercury varies with freezing, it is impossible to determine the value of the capacity of solid mercury per square centimeter of the true surface area.

On the basis of a theory developed by A. Frumkin concerning the influence of the electric field on the adsorption of organic molecules [5], this uncertainly may be eliminated by measuring the capacity in a solution containing a capillary-active organic substance.

According to this theory, the expression determining W, the work gained during adsorption of a mol of the organic substance at a given potential φ, has the following form (assuming $\varphi = 0$ at the electrocapillary maximum):

$$W = W_0 - \frac{1}{2} C \varphi^2 + \frac{1}{2} C' \varphi (\varphi - 2\varphi_N), \qquad (1)$$

where W_0 is the value of W at the maximum of the electrocapillary curve, C and C' are the capacities of the double layer (per square centimeter of surface) in the absence and in the presence of the capillary-active substance, respectively; φ_N is the change of potential corresponding to the maximum of the electrocapillary curve, due to the presence of the capillary-active substance.

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[5] A. Frumkin, Z. Physik, **35**, 792 (1926).

When the same organic substance is adsorbed on solid and liquid mercury, W_0 and φ_N must have closely approaching values, and the change of the potential φ, at which the work of adsorption is

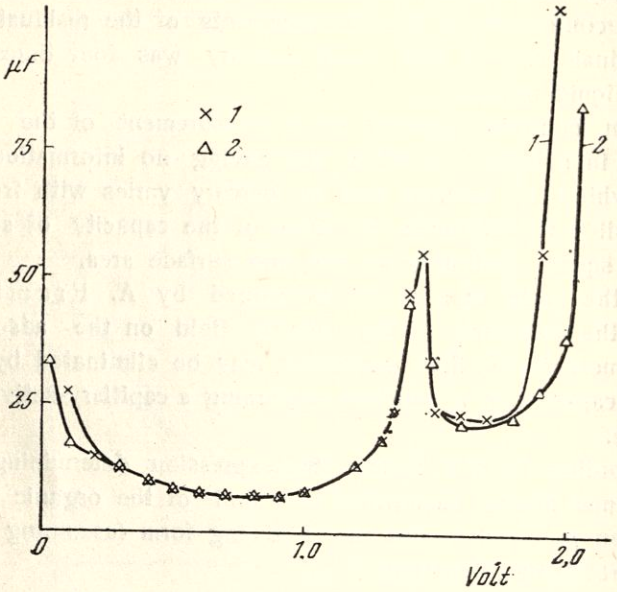

Fig. 2. 50% K_2CO_3 solution saturated with ethyl alcohol. *1* — liquid mercury; *2* — solid mercury.

equal to zero, *i. e.*, at which

$$W_0 = \frac{1}{2} C\varphi^2 - \frac{1}{2} C' \varphi(\varphi - 2\varphi_N),$$

is determined only by the change in the values of C and C'.

Hence, if C and C' have the same value on solid and liquid mercury, the adsorption of the organic substance must cease at the same potential.

Thus, having determined the potential φ corresponding to the boundary of the adsorption region of some organic substance on

liquid and solid mercury, as well as the apparent values of C and C', it is possible to determine whether the capacity of mercury per cm.^{2} of the true surface area changes upon its freezing.

As a capillary-active substance we chose ethyl alcohol, the solubility of which in a 51,2% K_2CO_3 solution at a temperature of —38° is equal to 0,2%[6]. The alcohol was purified as shown in the preceding paper. In the same paper it has been shown that, at a potential corresponding to the boundary of the adsorption region of an organic substance, the capacity curve gives a sharp rise (peak).

The location of the peaks on the curves for solid and liquid mercury in a solution of ethyl alcohol (Fig. 2) fully coincides, and the capacity value (C') in the middle portion of the curves is the same.

Considering the constancy of the apparent value of C, it may be concluded that both the capacity per cm.^{2} of the true surface area and the surface area of the mercury itself remain practically unchanged upon freezing. The determination of the position of the peak may be in error by 0,05 V; this leads to an error in the estimation of the true value of C according to eq. (1) amounting to ca. 10 per cent.

We can therefore assume that the surface area of the mercury remains constant upon freezing within the same limits of error.

Conclusions

It was shown by measurements of the capacity of solid and liquid mercury in an electrolyte solution and in the presence of a capillary-active substance that both the capacity per square centimeter of true surface area and the surface area of the mercury remain practically unchanged upon freezing.

This investigation was undertaken on the suggestion of prof. A. Frumkin. We take this opportunity of expressing our sincere

[6] Seidell, Solubilities of inorganic and organic compounds, 1, 510 (1919).

gratitude to him for his valuable advice during this and previous work.

The Karpow Institute for Physical Chemistry,
Moscow.

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