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**Abstract**

**Full Text**

## PHYSICAL CHEMISTRY

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### SOME PROPERTIES OF MERCURY SULFIDE FILMS ON THE SURFACE OF A MERCURY ELECTRODE

*(Presented by Academician A. N. Frumkin, December 13, 1963)*

Mercury ions passing into solution during anodic polarization of a mercury electrode, depending on the nature and concentration of the electrolyte anion, form either readily soluble compounds (for example, with the anions  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ) or sparingly soluble compounds (with  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{J}^-$ ,  $\text{HS}^-$ ,  $\text{S}^{2-}$ ,  $\text{OH}^-$ ). The formation of such sparingly soluble compounds occurs directly on the surface or near the surface of the electrode, which therefore becomes covered with a film. The rate of ionization of mercury in the presence of a film on its surface decreases. In the opinion of Kolthoff and Miller <sup>(1)</sup>, based on experiments with a dropping mercury electrode (under polarographic conditions), the role of the film, in particular  $\text{Hg}_2\text{Br}_2$ , is reduced to the inclusion of an ohmic potential drop in it; overcoming this drop upon further increase of the voltage at the electrodes causes a new rise in the current to the level of the limiting diffusion current for the anion entering into the composition of the film. As a result, the polarographic wave splits.

Still higher ohmic polarization was observed <sup>(2)</sup> during polarization of a stationary mercury electrode (hanging drop) in contact mainly with concentrated solutions of a number of salts. Apart from a current decrease practically to zero and a new rise of the current at a higher voltage, no data were given in this work on the current-voltage curves that would be connected with the features of film formation on mercury.

Characteristic details of voltammetric curves associated with the formation of a film and its influence on the kinetics of anodic dissolution of mercury were revealed in the study of dilute sodium sulfide solutions. Figure 1 reproduces a current-voltage curve for a cell, one of whose electrodes was a hanging-drop mercury electrode, in a millimolar solution of sodium sulfide. As can be seen, this curve contains several well-reproducible rises and falls of current.

The appearance on the electrode surface of a film of a sparingly soluble and poorly electrically conducting compound is equivalent to the inclusion in the electrical circuit of an additional large ohmic resistance <sup>(1)</sup>. The potential of the mercury-film boundary, which determines the kinetics of mercury ionization

Fig. 1

Figure 1: Fig. 1

under these conditions, shifts toward more negative values, and the ionization of mercury is slowed. A new rise of the current occurs as the moment of compensation of the ohmic potential drop in the film is approached by the continuously increasing voltage on the cell.

If a voltage is applied to the cell in the region of anodic dissolution of mercury and, without changing it, the change in anodic current with time is recorded, the curves shown in Fig. 2 are obtained. On these curves the initially high value of the current rapidly decreases, and on the current-decay curve there are several more or less clearly separated regions.

The experimental data set forth indicate layer-by-layer deposition of mercury sulfide on the surface of the mercury electrode. The first two minima on the voltammetric curve (Fig. 1) evidently correspond to the completion of formation of the first and second monomolecular layers of mercury sulfide. Individual regions of the curves in Fig. 2 also correspond to the formation of separate layers of mercury sulfide, which change the diffusion conditions and the reaction rate especially sharply at the moment when formation of the next layer is completed.

This assumption is confirmed by the fact that the quantities of electricity that can be determined from the  $i, \varphi$  curves (Fig. 1) and the  $i, t$  curves (Fig. 2) in individual characteristic sections correspond to coverage of the electrode by separate monomolecular layers of mercury sulfide. In these calculations it was assumed that one HgS molecule occupies  $14 \text{ \AA}^2$  of area on the electrode surface<sup>(3,4)</sup>. Figure 1 shows the values of the areas under the first two peaks in relative units. It is evident that these values are close to one another and to the value obtained by calculation (28 of the same units). Similar values are shown in Fig. 2, for which the calculated values are 55 (curve *a*) and 27 (curve *b*) arbitrary units.

**Fig. 1.** Polarograms of  $10^{-3}$  M  $\text{Na}_2\text{S}$  with a hanging mercury drop electrode (drop weight 3.2 mg). Rate of change of voltage: 0.8 V/min. Points on the abscissa axis mark the potentials at which the  $i, t$  curves were measured (see Fig. 2)

In evaluating the results of calculations from the  $i, \varphi$  curves, it is necessary to bear in mind that the moment at which formation of a monomolecular HgS layer is completed cannot be determined precisely from these data, since the position of the minimum only approximately indicates it. The minimum is determined mainly by the ratio between the rate of change of the potential of the mercury-film boundary as the cell voltage increases and the ohmic voltage drop in the film, which changes especially strongly at the moment when the construction of the individual monomolecular HgS layers is completed. The position of the minimum is also affected by changes in diffusion with time. Taking this into

Fig. 2

Figure 2: Fig. 2

account, the agreement between the calculated and experimental values of the quantities of electricity should be considered satisfactory.

From the  $i, t$  curves one can estimate the number of monomolecular layers of mercury sulfide which, at the measurement potential of a given  $i, t$  curve, completely stops the anodic dissolution of mercury, i.e., shifts the potential of the mercury-film boundary to the boundary of the region of anodic dissolution of mercury. For this purpose, the quantity of electricity corresponding to the entire  $i, t$  curve must be divided by the quantity of electricity corresponding to the deposition of one HgS layer. It turned out that the number of HgS layers is a linear function of the cell voltage; moreover, one monomolecular layer of mercury sulfide produces an ohmic voltage drop of, on average, 20 mV. The direct proportionality of the number of HgS layers to the voltage evidently reflects the fact that the individual HgS layers have the same resistance. The magnitude of this resistance can be estimated approximately from Fig. 1. The voltage difference between points 1 and 2 is close to the ohmic voltage drop in two HgS layers, although it is not exactly equal to it, since during the time elapsed in going from point 1 to point 2 the thickness of the diffusion layer changed. In reality, the voltage difference corresponding to the ohmic voltage drop in two monomolecular HgS layers is somewhat smaller than the voltage difference at points 1 and 2. If the influence of this factor is disregarded, the resistance of one HgS layer will be approximately 50,000  $\Omega$ .

Thus, ionization of mercury even in the presence on it of a sulfide layer

of mercury proceeds at appreciable rates, provided that the potential of the mercury-film boundary is sufficient for this process to occur in the absence of the film. The latter, in accordance with the ideas of Kolthoff and Miller <sup>(1)</sup>, plays mainly the role of an ohmic resistance.

Phenomena analogous to those analyzed here were also observed <sup>(5)</sup> in the study of HCl solutions, in which mercury is covered with a film of calomel.

**Fig. 2.** Dependence of the anodic current on time in a  $10^{-3}$  M solution of  $\text{Na}_2\text{S}$  (the same potassium nitrate as in Fig. 1) at voltages  $\varphi = -0.72$  V (a) and  $\varphi = -0.62$  V (b).

A thorough theoretical treatment of the data allowed the authors to draw important conclusions about the mechanism and kinetics of growth of calomel layers on mercury.

In conclusion, we note that the ohmic resistance of films covering mercury must be taken into account when considering electrocapillary curves.

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*Note: Figure translations are in progress. See original paper for figures.*

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