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

S. I. Zhdanov and B. A. Kiselev

Institute of Electrochemistry, Academy of Sciences, USSR
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Depending on the nature and concentration of the electrolyte anion, mercury ions passing into solution during anode polarization of a mercury electrode form either readily soluble (e.g., with NO_3^-, ClO_4^- anions) or poorly soluble (with Cl^-, Br^-, HS^-, I^-, S^{2-}, OH^-) compounds. These poorly soluble compounds form immediately on or near the electrode surface, which is therefore covered with a film. The rate of mercury ionization under a film of this kind is reduced. According to Kolthoff and Miller [1] (based on experiments with a dropping mercury electrode under polarographic conditions) the role of the film, particularly on Hg_2Br_2, is to introduce an concurrent fall in resistance and potential; when this is overcome with further increase in the voltage on the electrodes, it causes a fresh surge in current to the level of the limiting diffusion current with respect to the anion forming part of the film. The polarographic wave is thus split.

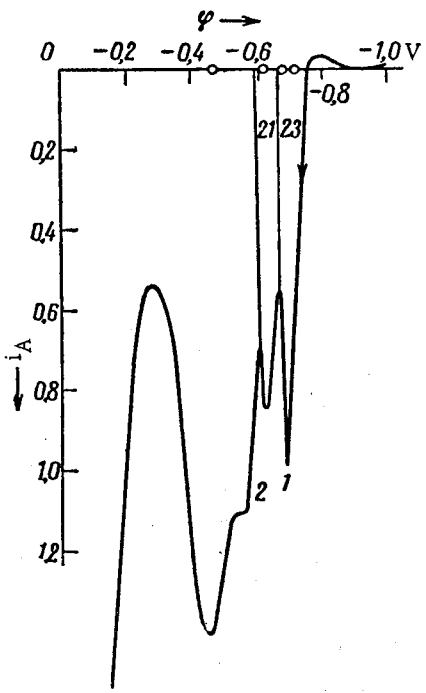

Fig. 1. Polarograms of 10^{-3} M Na_2S with a hanging drop mercury electrode (drop weight 3.2 mg). Rate of voltage variation 0.8 V/min. Points on abscissa denote potentials at which i, t curves were measured (see Fig. 2).

Even higher ohmic polarization was observed [2] when polarizing a stationary mercury electrode (hanging drop) in contact mainly with concentrated solutions of a series of salts. Apart from a fall in current almost to zero and fresh current surge at higher voltage on the current-voltage curves, [2] gives no data which might be associated with the special features of film formation on mercury.

The typical features of the volt-ampere curves due to film formation and its effect on the anode dissolution kinetics of mercury were determined by examining dilute solutions of sodium sulfide. Figure 1 gives the current-voltage curve in a cell, one of whose electrodes was a dropping mercury electrode, in a millimolar solution of sodium sulfide; the curve displays a number of well-reproducible rises and falls in current.

The appearance on the electrode surface of a film of a difficultly-soluble and poorly conducting compound is tantamount to switching an additional strong resistance [1] into an electric circuit. The mercury-film boundary potential, which governs the kinetics of mercury ionization under these conditions, is displaced to the negative side and mercury ionization is retarded. A fresh rise in current sets in as it approaches the point where the concurrent fall in resistance and potential in the film is compensated by a continually increasing voltage in the cell.

If voltage is applied to the cell in the region of anodic dissolution of mercury, and if without changing it we record the change in anode current strength with time, we obtain the curves shown in Fig. 2. On these curves the initial high current value decreases rapidly, while the current decrement curve has more or less clearly defined sectors.

These experimental data indicate the laminar deposition of mercury sulfide on the mercury electrode surface. The two first minima on the

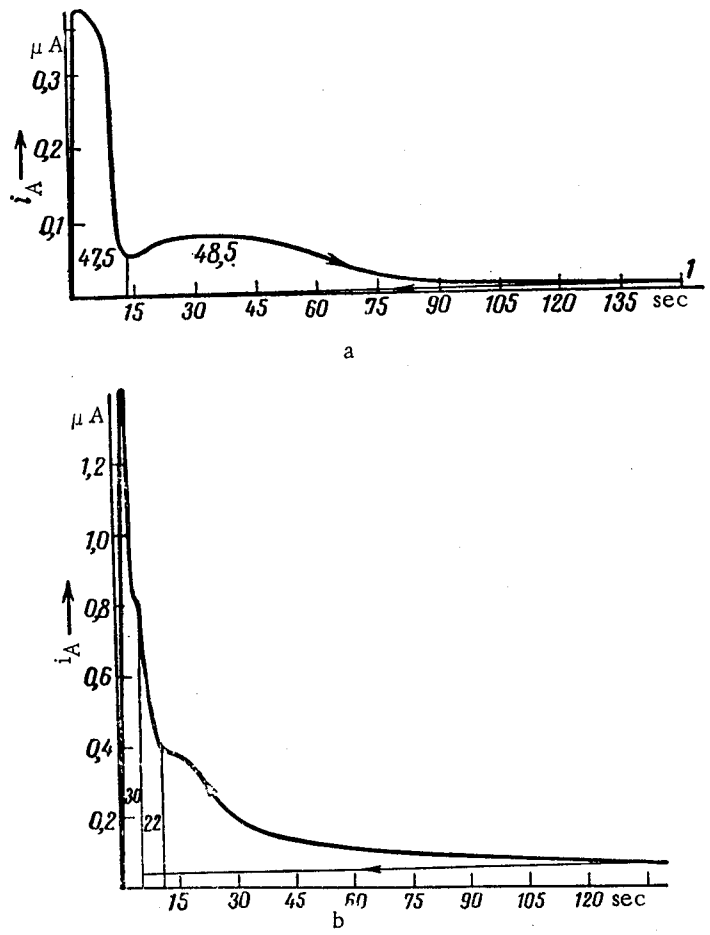

Fig. 2. Anode current strength versus time of a 10^{-3} M solution of Na_2S (same hanging drop as in Fig. 1), at voltage $\varphi = -0.72$ V (a) and $\varphi = -0.62$ V (b).

volt-ampere curve (Fig. 1) apparently correspond to the completion of the first and second monomolecular layers of mercury sulfide. Individual sectors of the curves in Fig. 2 also correspond to formation of individual layers of mercury sulfide which alter the diffusion conditions and reaction rate very markedly when the next layer is completely formed.

This conclusion is confirmed insofar as the amounts of electricity determined from the curves $\underline{i}$, φ (Fig. 1) and $\underline{i}$, $\underline{t}$ (Fig. 2) on separate specific typical sectors correspond to the coating of the electrode with individual monomolecular layers of mercury sulfide. In these calculations it was assumed that one HgS molecule occupies 14 A^2 area on the electrode surface [3, 4]. Figure 1 shows areas under the first two peaks (in relative units). It is clear that these values are close to each other and to the calculated value (28 of these units). Similar results are shown in Fig. 2 where the calculated values are 55 (curve a) and 27 (curve b) arbitrary units.

When judging the results of calculation by the $\underline{i}$, φ curves it should be remembered that from these data one cannot determine accurately the moment of completion of the layer of monomolecular HgS, because the position of the minimum gives only an approximate indication of this. The minimum is determined basically by the ratio of the rates of change of the mercury-film boundary potential with increasing voltage in the cell and the ohmic reduction in voltage in the film; this changes particularly markedly at the time of complete formation of the individual monomolecular layers of HgS. The position of the minimum is also affected by changes in diffusion with time. Taking all this into account, the agreement between the calculated and experimental values for the amounts of electricity must be considered satisfactory.

The i, t curves can serve for determining the number of monomolecular layers of mercury sulfide which, at the measurement potential of the given i, t curve, completely arrest anode dissolution of mercury, i.e., dis-lace the mercury-film boundary potential to the boundary of anode dissolution of mercury. This requires that the amount of electricity corresponding to the whole i, t curve be divided by the amount of electricity equalling one deposited layer of HgS. It was found that the number of HgS layers is a linear function of the cell voltage, one monomolecular layer of HgS causing an average ohmic drop in voltage of 20 mV. The fact that the number of HgS layers is directly proportional to the voltage evidently indicates that the individual HgS layers have the same resistance. The value of the latter can be roughly judged from Fig. 1. The difference in voltage between points 1 and 2 approximates to the ohmic voltage drop in the two HgS layers, but is not its exact equal, because during the time taken to pass from point 1 to point 2, there was a change in the thickness of the diffusion layer. In fact the voltage difference corresponding to the ohmic voltage drop in two monomolecular HgS layers is slightly less than the voltage difference between points 1 and 2. Without this factor, the resistance of of one HgS layer will be ~ 50,000 ohms.

Ionization of mercury, even in the presence of an HgS layer, therefore occurs at considerable speeds, provided the mercury-film boundary potential is sufficient to allow this process to take place where no film is present. According to Kolthoff and Miller [1], the role of this film is chiefly that of an ohmic resistance.

Analogous phenomena were noted [5] in an investigation of HCl solutions in which mercury is coated with a calomel film. Thorough analysis of the data by the authors of [5] led to important conclusions on the mechanism and kinetics of calomel layer growth on mercury.

In conclusion, we should note that the ohmic resistance of films on mercury should be taken into account when examining electrocapillary curves.

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