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A NOTE ON THE PAPER OF A. MITUYA
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PLATINUM ANODES IN ACID SOLUTIONS".

By

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MITUYA¹⁾ measured the hydrogen overvoltage in 0.1 N HCl on mercury at very low current densities from 0.7×10^{-11} to 1.36×10^{-7} a/cm². On the basis of the results obtained, he made a number of conclusions, confirming in his opinion the theory of hydrogen overvoltage on mercury advanced by HORIUTI. In view of the significance of this problem, it is quite natural to pay particular attention to the experimental method employed by MITUYA, which underlie his theoretical conclusions. One cannot help noticing then that the values of the overvoltage found by him, which lie in that part of the η , $\lg i$ curve for which parallel data of other authors are available, are too low. Thus at $i = 1.36 \times 10^{-7}$ the value η found by MITUYA, is equal to 379 mv. But LEVINA and SARINSKY²⁾ found for the same value of i in the same electrolyte $\eta = 603$ mv. The discrepancy between these two values becomes still somewhat greater, if one takes into consideration the fact that the measurements of LEVINA and SARINSKY were made at 22°C and the measurements of MITUYA at 12°. These measurements were twice repeated at our laboratory by JOFA³⁾, who found $\eta = 616$ mv for the same current density at 20°C and by BAGOZKY⁴⁾, whose values are practically identical with those of JOFA. Such agreement between the results of three independent investigations leaves no doubt as to their correctness; consequently, the value found by MITUYA is lower than those found by other authors by 0.2 v. It seemed to me that the occurrence of this lower value could be accounted for by the fact that in the apparatus used by MITUYA a platinum electrode with a large surface was placed too close to the mercury cathode, and therefore platinum traces could find their way to the surface of mercury. According to MITUYA, however, a lowering of the overpotential with time should have been observed then, which was not the case. In view of these considerations, I suggested that perhaps, when platinum comes into contact

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with solution, some of it passes into the latter at the expense of the destruction of the oxide film, present on the surface of platinum, but that no further deposition of platinum occurs later. These considerations stimulated MITUYA⁵⁾ to write his paper published in the Journal of Physical Chemistry (Журнал Физической химии). In my opinion, this investigation is of great interest, in view of the originality of the method employed, but it cannot disprove the ideas brought forward by me, because we do not know the relative degree of sensitivity of the detection of platinum traces by the method used by MITUYA and of that, which is made on the basis of the lowering of the overvoltage on mercury at small current densities. Judging from practical experience of measuring hydrogen overvoltage on mercury, it is not permissible to place a large platinum electrode close to the surface of mercury without the risk of obtaining too low values of the overvoltage. In any case, no other explanation for the discrepancy between the values of MITUYA and those obtained in our investigations have been suggested as yet.

In conclusion, I should like to stress the fact that in making theoretical interpretations of the results of measurements at very small current densities, and consequently, at very small overvoltages it is necessary, as it follows from a large number of investigations, to allow for the anion adsorption, which was not done in the papers of the Japanese authors.

Literature

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