EFFECT OF THE STRUCTURE ON THE ELECTRICAL DOUBLE LAYER AND THE SOLUTION pH ON THE HYDROGEN OVERVOLTAGE OF GALLIUM

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Data on the effect of the structure of the electrical double layer on the kinetics of the electrochemical liberation of hydrogen form one of the main criteria for determining the reaction mechanism.

Up to now the effect of the structure of the electrical double layer on the hydrogen overvoltage has been studied quantitatively mainly on mercury. The difficulties encountered in analogous investigations on solid metals are connected with the heterogeneity of the electrode surface and poor reproducibility of its state. It seemed interesting to determine whether the rules of the effect of the structure of the electrical double layer on the hydrogen overvoltage observed for mercury also apply to metals with lower values of η. A suitable subject for solving this problem is a gallium electrode on which the hydrogen overvoltage is ~0.3 V less than on mercury. The melting point of gallium (29.78°) is close to room temperature so that measurements may be made both on liquid and solid gallium in aqueous solutions of various concentrations.

In the present work we investigated the change in η on liquid gallium with 0.01 N HCl + xKCl solutions at constant pH in relation to the total electrolyte concentration C and also the effect of the solution pH on η at constant C. In this case, solutions with the composition xKCl + yHCl were used and the total electrolyte concentration in them was 1 g-equiv./liter. Analogous measurements were carried out by V. S. Bagotskii et al. [1] on mercury.

We also studied the effect of the I^- anion and tetrabutylammonium cation, $(C_4H_9)_4N^+$, separately and together on the hydrogen overvoltage on gallium. It is known that the iodine anion may have different effects on η. Adsorption of I^- on mercury [2] leads to a fall in η, on iron [3] and silver [4], to a rise in it. Depending on the experimental conditions, I^- may either raise or lower η on lead [5]. The fall in η under the effect of I^- is explained by a displacement of the ψ_1-potential toward negative values in its presence. A rise in η in the presence of I^- is usually related to its chemisorption and a decrease in the energy of the $Me-H_{ads}$ bond. However, the reason for the different effects of I^- on η has not been fully elucidated. It was considered that a comparison of data on the effect of I^- on the hydrogen overvoltage on solid (η_s) and liquid (η_l) gallium may explain the effect of the aggregate state of the electrode on the mechanism of the effect of I^- on η.

Most of the measurements were carried out with a static gallium electrode, though some were carried out with a dropping electrode. The procedure for measuring the hydrogen overvoltage on a static gallium electrode was described previously [6]. It was shown in [6] that in 1 N H_2SO_4, $\eta_s < \eta_l$. However, when small amounts of O_2 entered the solution, η_s increased and became considerably greater than η_l in time. Therefore, in order to introduce the additives containing I^- and $(C_4H_9)_4N^+$ into the solution, the appropriate salts were first placed in an auxiliary cell connected through a tap to the main cell containing the gallium electrode. After the auxiliary cell had been filled with hydrogen, a 1 N H_2SO_4 solution saturated with H_2 was pumped into it through a tap from the main cell, the salts dissolved, and the solution transferred to the main cell by hydrogen pressure. During this time, the cathode polarization of the electrode continued. Measurements were carried out at 32° on a static liquid gallium electrode and at 28° on a solid one. The form of the gallium dropping electrode was the same as the mercury dropping electrodes normally used. Measurements were carried out with the dropping electrode at 32°.

Figure 1 gives the relation of η on liquid gallium to the logarithm of the total electrolyte concentration in the solution C with a constant solution pH. The curves of η against log i in solutions with different pH values and the same total electrolyte concentration in the solution are given in Fig. 2. Figure 1 shows that η increases linearly with

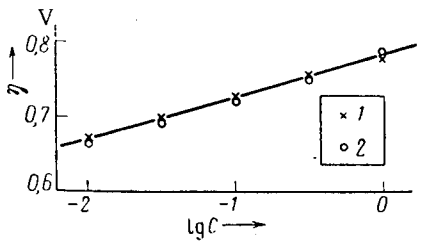

Fig. 1. Relation of η to log C in 0.01 N HCl + xKCl solutions on a static liquid (1) and dropping (2) gallium electrodes at $i = 3.2 \cdot 10^{-4}$ a/cm^2.

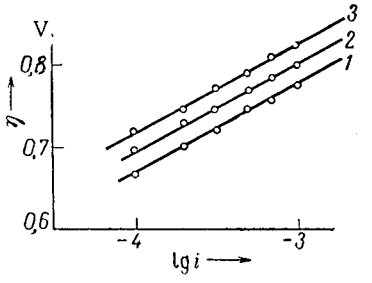

Fig. 2. Curves of η against log i (a/cm^2) in xHCl + yKCl solutions with a constant electrolyte concentration in the solution of 1 g-equiv./liter and different [H$^+$] ion concentrations: 1) 0.1, 2) 0.03 and 3) 0.01 N.

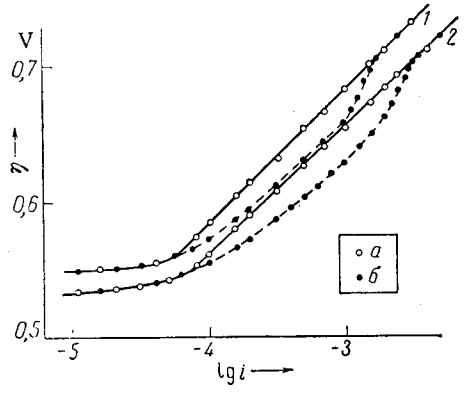

Fig. 3. η on liquid (1) and solid (2) gallium in a) 1 N H_2SO_4, b) 1 N H_2SO_4 + 0.1 N KI.

log C and an increase in the total electrolyte concentration in the solution by a factor of 10 led to a 50-55 mV increase in η. The hydrogen overvoltage on gallium increased by 48-50 mV with an increase in the HCl concentration of the solution from 0.01 to 0.1 N (Fig. 2). The values obtained for the slope of the curve of η against log C at pH = const and the change in η per pH unit when C = const were close to 50 mV, a value which was predicted by the theory of slow discharge [7] using an approximate expression for the ψ_1-potential in solutions with constant pH and variable C and neglecting the ψ_1-potential in solutions with constant C and variable pH at 32° and $\alpha = 0.54$. The value of α was calculated from the slope of the polarization curve. The data obtained support the hypothesis that the discharge of the hydrogen ion is the slow stage on gallium. This conclusion is confirmed by the absence of a pseudocapacity with respect to adsorbed hydrogen on gallium. Christov et al. [8] studied the relation of the hydrogen overvoltage to the pH of HCl solutions of different concentrations without the addition of a foreign electrolyte. In accordance with the conclusions drawn from the theory of slow discharge, in their experiments the overvoltage on gallium did not change with a change in the pH from 0.4 to 2.2. The 60 mV fall in η on liquid gallium observed by Sh. Z. Khamudkhanova and A. M. Murtazaev [9] with a change from 0.1 N to 1 N H_2SO_4 without the addition of a foreign electrolyte contradicts the data in [8] and requires further checking.

Figure 3 gives the data on the effect of a 0.1 N concentration of I^- on η on solid and liquid gallium in 1 N H_2SO_4. Figure 4 shows the effect of the tetrabutylammonium cation, $(C_4H_9)_4N^+$ at a concentration of 0.01 N and in combination with I^- on η on liquid gallium in 1 N H_2SO_4 solution. For a comparison, Fig. 4 also gives the values of η in 1 N H_2SO_4 + 1 N KI. The $(C_4H_9)_4N^+$ cation was introduced into the solution in the form of the salt $(C_4H_9)_4NBr$. A special experiment showed that the Br^- anion at a concentration of 0.01 N had no effect on η on gallium in 1 N H_2SO_4.

Figure 3 shows that the I^- anion lowers η on both solid and liquid gallium in the same region of potentials and by the same amount, namely, 25-30 mV. A comparison of the data showed that the effect of 1 N I^- on η on gallium is much weaker than on mercury. Adsorption of I^- on mercury started at a potential that was ~0.5 V more negative than the zero charge point while on gallium this difference was 0.10-0.15 V [10]. The fall in η on mercury reached ~300 mV while on gallium it was only 40 mV. The slight fall in η on gallium under the effect of I^- cannot be explained as the result of the superposition of the two effects of I^- on η, namely, its fall due to adsorption in the electrical double layer and displacement of the ψ_1-potential toward negative values, on the one hand, and, on the other, its rise due to the decrease in the energy of the $Me-H_{ads}$ bond with chemisorption of I^-. Actually, one might expect a decrease in the fall in η with time when there is chemisorption of I^- as a result of the strengthening of the iodine–metal bond, as occurs, for example, in the case of iron [11]. However, as has been stated above, in the presence of I^- there is no change in η on gallium with time. Thus, the data obtained indicate that I^- is adsorbed relatively weakly on gallium and its effect on η is the result of the displacement of the ψ_1-potential toward

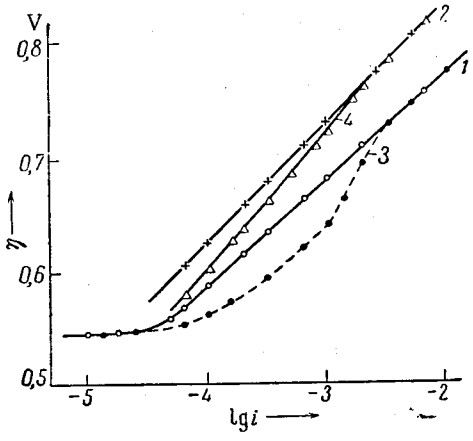

Fig. 4. η on liquid gallium in solutions of 1) 1N H_2SO_4; 2) 1N H_2SO_4 + 0.01 N $(C_4H_9)_4NBr$; 3) 1N H_2SO_4 + 1N H_2SO_4 + 1N KI; 4) 1N H_2SO_4 + 1N KI + 0.01 N $(C_4H_9)_4NBr$.

negative values. The effect of I^- on η on gallium is the same regardless of its aggregate state and this indicates that the structure of the electrical double layer is the same on solid and liquid gallium. D. I. Leikis and É. S. Sevast'yanov [12] came to an analogous conclusion on the basis of capacity measurements.

The $(C_4H_9)_4N^+$ cation increased η on gallium (Figs. 4, 2) in accordance with the displacement of the ψ_1-potential toward positive values in its presence. With the addition of 1 N H_2SO_4 + 001 N · $(C_4H_9)_4NBr$1 N KI to the solution, η on gallium fell, but remained, however, higher than the values of η in solutions of 1 N H_2SO_4 and 1 N H_2SO_4 + 1 N KI (Fig. 4, 4). Over a certain range of potentials, corresponding to a positive surface charge, under the joint effect of the tetrabutylammonium cation and iodine anion η on mercury [13] was found to be lower in a 1 N HCl solution than in a solution of 1 N HCl + 1 N KI. The authors explained this effect by the increase in adsorption of I^- produced by the $(C_4H_9)_4N^+$ cation. Thus, the data on the joint effect of the $(C_4H_9)_4N^+$ cation and I^- anion on η also indicate weaker adsorption of I^- on gallium.

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