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Abstract

Full Text

Physical Chemistry

K. Sabo and I. A. Bagotskaya

Investigation of the Influence of the Structure of the Electrical Double Layer and the pH of the Solution on the Hydrogen Overvoltage on Gallium

(Presented by Academician A. N. Frumkin, January 30, 1963)

Data on the influence of the structure of the electrical double layer on the kinetics of the electrochemical evolution of hydrogen serve as one of the principal criteria for establishing the reaction mechanism.

Up to the present time, the quantitative influence of the structure of the electrical double layer on the hydrogen overvoltage has been studied primarily on mercury. Carrying out analogous investigations on solid metals presents difficulties connected with the inhomogeneity of the electrode surface and the poor reproducibility of its state. It was of interest to trace whether, on metals with lower values of η, the regularities observed on mercury with respect to the influence of the structure of the electrical double layer on the hydrogen overvoltage are preserved. A gallium electrode is a suitable object for solving the stated problem, since the hydrogen overvoltage on it is about 0.3 V lower than on mercury. The melting point of gallium, 29.78°, lies close to room temperature, which makes it possible to carry out measurements both on liquid and on solid gallium in aqueous solutions of different concentrations.

Fig. 1. Dependence of η on $\lg C$ in solutions of $0.01\,N$ HCl + xKCl on quiescent liquid (1) and dropping (2) gallium electrodes at
$i = 3.2 \cdot 10^{-4}$ A/cm^2

In the present work we investigated the change in η on liquid gallium in solutions of constant pH of composition $0.01\,N$ HCl + xKCl as a function of the total electrolyte concentration C, as well as the influence of the pH of the solution on η while maintaining C in the solution constant. In this case the measurements were carried out in solutions of composition xKCl + yHCl, in which the total

Fig. 2

Figure 2: Fig. 2

electrolyte concentration was 1 g-equiv/l. Analogous measurements on mercury were carried out by V. S. Bagotskii and co-workers ([1]).

We also studied the influence on the hydrogen overvoltage on gallium of the anion J^- and the tetrabutylammonium cation $(\mathrm{C_4H_9})_4\mathrm{N}^+$, separately and in combination with one another. As is known, the iodide anion can exert different effects on η. Adsorption of J^- on mercury ([2]) leads to a decrease in η, while on iron ([3]) and silver ([4]) it leads to an increase. On lead ([5]), depending on the experimental conditions, J^- can either lower or raise η. The decrease in η under the influence of J^- is explained by a shift of the ψ_1-potential in its presence in the negative direction. The increase in η in the presence of J^- is usually attributed to its chemisorption and to a decrease in the bond energy Me—$\mathrm{H_{ads}}$. However, the reason for the different influence of J^- on η has not yet been fully clarified. It was supposed that comparison of data on the action of J^- on the hydrogen overvoltage on solid η_s and liquid η_l gallium might make it possible to elucidate the influence of the aggregate state of the electrode on the mechanism of action of J^- on η.

Measurements were carried out mainly on a stationary gallium electrode; however, a certain number of measurements were also performed on a dropping electrode. The method for measuring the hydrogen overvoltage on a stationary gallium electrode has been described earlier (ˆ6). In (ˆ6) it was shown that in a 1 N solution of H_2SO_4, $\eta_t < \eta_\mathrm{liq}$. However, when small amounts of O_2 enter the solution, η_t increases and with time becomes substantially higher than η_liq. Therefore, in order to introduce into the solution additives containing J^- and $(C_4H_9)_4N^+$, the corresponding salts were first placed in an auxiliary cell connected by a stopcock to the main cell, in which the gallium electrode was located. After the auxiliary cell had been filled with hydrogen, a saturated-H_2 1 N solution of H_2SO_4 was pumped into it through the stopcock from the main cell; the salts dissolved, and the solution was then transferred back into the main cell under hydrogen pressure. The cathodic polarization of the electrode was not interrupted in the process. Measurements on the stationary liquid gallium electrode were carried out at 32°, and on the solid electrode at 28°. The design of the dropping gallium electrode did not differ from that of the commonly used dropping mercury electrodes. Measurements on the dropping electrode were carried out at 32°.

Fig. 2. Curves of $\eta, \lg i$ (a/cm^2) in solutions $xHCl + yKCl$ with a constant total electrolyte concentration in the solution, equal to 1 g-eq/l, and with different contents of $[H^+]$ ions: 1—0.1, 2—0.03, and 3—0.01 N.

Figure 1 shows the dependence of η on liquid gallium on the logarithm of the total electrolyte concentration in the solution, C, under conditions of constant

Figure 3 and Figure 4

Figure 3: Figure 3 and Figure 4

pH of the solution. Curves of $\eta, \lg i$ in solutions with different pH and one and the same total electrolyte concentration in the solution are shown in Fig. 2. From Fig. 1 it is seen that η increases linearly with $\lg C$; moreover, a tenfold increase in the total electrolyte concentration in the solution leads to an increase in η by 50–55 mV. When the HCl concentration in the solution is increased from 0.01 to 0.1 N, the hydrogen overvoltage on gallium increases by 48–50 mV (Fig. 2). The obtained values of the slope coefficient of the $\eta, \lg C$ curve at $pH = \text{const}$, and of the change in η per unit pH of the solution at $C = \text{const}$, are close to 50 mV—the value predicted by the theory of slow discharge (ˆ7) when using an approximate expression for the ψ_1-potential in solutions with constant pH and variable C, and without taking into account the change in 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 assumption according to which, on gallium, the slow stage is the discharge of the hydrogen ion. This conclusion is confirmed by the absence of pseudocapacitance due to adsorbed hydrogen on gallium. The dependence of the hydrogen overvoltage on pH in HCl solutions of different concentration without addition of a supporting electrolyte was studied by Khristov and co-workers (ˆ8). In agreement with the conclusions from the theory of slow discharge, the overvoltage on gallium in their experiments did not change when the pH was varied from 0.4 to 2.2. The decrease in η on liquid gallium by 60 mV observed by Sh. Z. Khamudkhanova and A. M. Murtazaev (ˆ9) on going from 0.1 N H_2SO_4 to 1 N without addition of supporting electrolyte contradicts the data of (ˆ8) and requires additional verification.

Figure 3 presents data on the influence of J^- at a concentration of 0.1 N on η on solid and liquid gallium in 1 N H_2SO_4. The influence of the tetrabutylammonium cation $(C_4H_9)_4N^+$ at a concentration of 0.01 N, and of the same cation in combination with J^-, on η on liquid gallium in a 1 N H_2SO_4 solution is presented in Fig. 4. For comparison, Fig. 4 also gives values of η in 1 N $H_2SO_4 + 1N\ KJ$. The cation $(C_4H_9)_4N^+$ was introduced into the solution in the form of the salt $(C_4H_9)_4NBr$. In a special experi-

it was shown that the effect of the anion Br^- at a concentration of 0.01 N on η on gallium in 1 N H_2SO_4 is not observed.

From Fig. 3 it is seen that the anion J^- lowers η both on solid and on liquid gallium in the same potential region and by the same amount, 25–30 mV. From comparison with data on the effect of J^- at a concentration of 1 N on η, gallium is affected much more weakly than mercury. On mercury the adsorption of J^- begins

Fig. 3. η on liquid (*1*) and solid gallium (*2*) in:

a–1 *N* H_2SO_4,
b–1 *N* $H_2SO_4 + 0.1\,N$ KJ

Fig. 4. η on liquid gallium in solutions:
1–1 *N* H_2SO_4;
2–1 *N* $H_2SO_4 + 0.01\,N$ $(C_4H_9)_4NBr$;
3–1 *N* $H_2SO_4 + 1\,N$ KJ;
4–1 *N* $H_2SO_4 + 1\,N$ KJ $+0.01\,N$ $(C_4H_9)_4NBr$

at a potential about −0.5 V more negative than the point of zero charge, whereas on gallium this distance is 0.10-0.15 V (10). The decrease of η on mercury itself reaches ∼ 300 mV, while on gallium it is only 40 mV. The small decrease of η on gallium under the influence of J^- cannot be explained as the result of the superposition of the dual action of J^- on η: its lowering owing to adsorption in the electrical double layer and a shift of the ψ_1-potential in the negative direction, on the one hand, and, on the other, its increase owing to a decrease in the bond energy Me—H_{ads} during chemisorption of J^-. Indeed, one might have expected that in the presence of chemisorption of J^- the decrease of η with time would diminish owing to strengthening of the iodine bond with the metal, as occurs, for example, in the case of iron (11). However, as already stated above, η on gallium in the presence of J^- does not change with time. Thus, from the data obtained it follows that J^- is adsorbed relatively weakly on gallium and that the effect of its action on η is due to a shift of the ψ_1-potential in the negative direction. The action of J^- on η on gallium is the same irrespective of its aggregate state, which indicates an identical structure of the electrical double layer on solid and liquid gallium. D. I. Leikis and E. S. Sevastyanov (12) arrived at an analogous conclusion on the basis of capacitance measurements.

The cation $(C_4H_9)_4N^+$ increases η on gallium (Fig. 4, 2) in accordance with the shift of the ψ_1-potential in its presence in the positive direction. When 1 *N* KJ is added to a solution of 1 *N* $H_2SO_4 + 0.01\,N$ $(C_4H_9)_4NBr$, η on gallium decreases, but remains higher than the value of η in solutions of 1 *N* H_2SO_4 and 1 *N* $H_2SO_4 + 1\,N$ KJ (Fig. 4, 4). On mercury (13), under the combined action of the tetrabutylammonium cation and the iodine anion in a 1 *N* HCl solution in a certain potential region corresponding to a positive surface charge, η proves to be lower than the value observed in a solution of 1 *N* HCl +1 *N* KJ. This effect was explained by the authors as an enhancement of the adsorption of J^- by the cation $(C_4H_9)_4N^+$. Thus, the data on the combined action of the cation $(C_4H_9)_4N^+$ and the anion J^- on η also indicate a weaker adsorption of J^- on gallium.

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