ELECTROCAPILLARY CURVES AND OVERVOLTAGE OF HYDROGEN ON HIGH-PURITY GALLIUM

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The overvoltage of hydrogen on a dropping gallium electrode was measured on four samples of high-purity gallium in pure solutions of 1N H_2SO_4 and 1N $HClO_4$ and in solutions of 1N H_2SO_4 containing halide anions Cl^-, Br^-, and I^-, as well as the cation $(C_4H_9)_4N^+$, separately and in conjunction with the Br^- and I^- anion. The electrocapillary curves were taken at the same time in a solution of 1N KCl. A certain number of measurements were performed in solutions of 1N KCl containing the $(C_4H_9)_4N^+$ cation in various concentrations.

The bulk of the measurements of the hydrogen overvoltage on liquid gallium were conducted on an electrode at rest and were aimed at determining the influence of the aggregated state of gallium on the hydrogen overvoltage on it. The purity of the gallium used in the studies [1] was not specified; in [2] it corresponded to 99.99%, [3]—99.996%, [4]—99.999%, and [5]—99.9998%. The absolute values of the hydrogen overvoltage obtained in the studies mentioned differ appreciably. This is apparently due to the insufficient degree of purity of gallium, on the one hand, and the difficulty of performing precise measurements on a stationary electrode, on the other. The overvoltage on a dropping gallium electrode was first measured in [6]; however, the purity of the gallium used was low, corresponding to 99.996%.

In this work the overvoltage of hydrogen was measured on a dropping gallium electrode on four samples of gallium, namely: on 99.9998% pure gallium, purified according to the method of the State Rare Metals Institute, Moscow (Ga^I), on 99.9999% gallium, which we received from Professor P. Epelboin, Paris (Ga^{II}),* brand T/77 gallium, with a purity of 99.9999%, from Hungary (Ga^{III}), and "electronic grade" gallium form Eagle Peicher Company, United States (Ga^{IV}). The electrocapillary curves were taken simultaneously on Ga^I, Ga^{II}, and Ga^{III} in 1N KCl. The electrocapillary curves on Ga^I and Ga^{IV} were taken earlier in [7]. The hydrogen overvoltage η was measured in 1N H_2SO_4; a certain number of measurements on Ga^I were performed in 1N $HClO_4$. The value of η in a solution of $HClO_4$ was of interest in connection with the fact that ClO_4^- ions disturb the structure of the layer of dipoles of water molecules chemisorbed on gallium at potentials close to the point of zero charge [8, 9].

In addition to the measurements of the hydrogen overvoltage in pure solutions of acids, we studied the influence of halide anions Cl^-, Br^-, and I^-, as well as the cation $(C_4H_9)_4N^+$, separately and in conjunction with the Br^- and I^- anions, on η. The electrocapillary curves on Ga^I in solutions of anions of various concentrations were studied in [9], and were taken in the presence of $(C_4H_9)_4N^+$ in this work.

The procedure of measurements on a dropping gallium electrode in no way differed from that described in [6], and that on the Gui capillary electrometer was similar to that in [7]. In all the experiments the polarization curve of η versus log i was taken preliminarily in a pure background solution, and then the additive was introduced in an atmosphere of hydrogen, as described in [3]. The electrocapillary curves were taken relative to the saturated calomel electrode, the hydrogen overvoltage relative to the hydrogen electrode in the investigated solution. The reagents used were thoroughly purified: acids by two redistillations under vacuum, halide salts by two recrystallizations and calcination, KI in a stream of hydrogen. The measurements were performed at 32°C.

The electrocapillary curves in a solution of 1N KCl are cited in Fig. 1. As can be seen from the figure, the values of the surface tension σ on Ga^I, Ga^{II}, and Ga^{III} practically coincide: σ_{max} = 646-647 dyn/cm, φ_{max} = −1.02 V. The dispersion of the values of σ at the same potential does not exceed 1 dyn/cm. Such a coincidence should be recognized as all the more satisfactory in that the reproducibility of the electrocapillary curves on the same sample of gallium varies within the same limits. On Ga^{IV} [7], the surface tension as a function of the electrode

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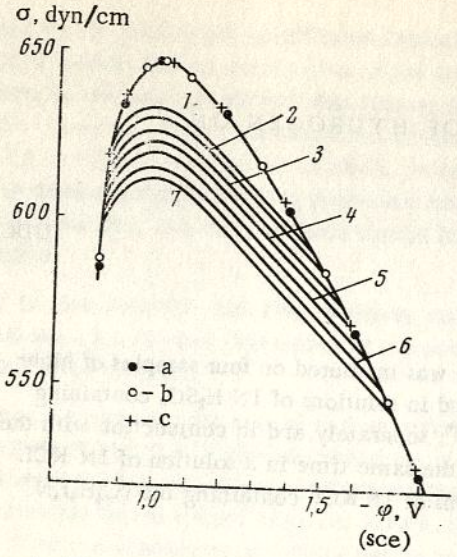


Fig. 1. Electrocapillary curves in 1N KCl on Ga^{I} (a), Ga^{II} (b), Ga^{III} (c), and in 1N KCl + $x(C_4H_9)_4NBr$ on Ga^{I}; x = 1) 10^{-4}; 2) $2 \cdot 10^{-4}$; 3) $5 \cdot 10^{-4}$; 4) 10^{-3}; 5) $2 \cdot 10^{-3}$; 6) $5 \cdot 10^{-3}$; 7) 10^{-2}N.

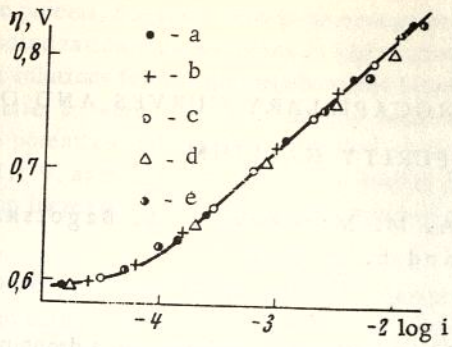


Fig. 2. Overvoltage of hydrogen in 1N H_2SO_4 on Ga^{I} (a), Ga^{II} (b), Ga^{III} (c), Ga^{IV} (d), and in 1N $HClO_4$ on Ga^{I} (e).

potential was 2-4 dyn/cm higher than on the samples that we investigated; however, it cannot be established with sufficient reliability whether this difference is real, since the measurements were performed on a different apparatus, which lowers the accuracy of the comparison.

The results of polarization measurements on Ga^{I} Ga^{II}, Ga^{III}, and Ga^{IV} in 1N H_2SO_4 and Ga^{I} in 1N $HClO_4$ are cited in Fig. 2. The values of the hydrogen overvoltage on different samples of high-purity gallium are close and do not depend on the nature of the acid. The constants a and b in the Tafel equation, corresponding to the polarization curve cited, correspond to a = 1.015–1.025; b = 0.095–0.100. The absolute values of the hydrogen overvoltage on the samples of gallium that we investigated differ appreciably when the values of the hydrogen overvoltage measured in a dropping electrode of 99.996% pure gallium: a = 1.040; b = 0.110 [6] and on Ga^{I} in the case of a stationary electrode a = 1.070, b = 0.125 [5].

Recently a communication appeared [10] in which the influence of additions of Hg and In to Ga on the hydrogen overvoltage was studied. The value of the hydrogen overvoltage cited in [10] for $i = 10^{-3}$ A/cm^2 on pure gallium is 0.720 and is in good agreement with the data of our measurements at the same current density $\eta = 0.722$. As can be seen from Fig. 3, when halide salts are added to the solution of acid, the hydrogen overvoltage on gallium increases somewhat. In the case of Cl^- and Br^-, this effect of ~10 mV is practically independent of the nature of the anion and lies within the limits of the possible increase in η with increasing total concentration of the electrolyte as a result of the introduction of the salt into the acid solution. The anion I^- increases the overvoltage by 20 mV. From the large value of $\Delta\eta$ in the presence of the I^- ion in comparison with $\Delta\eta$ observed when Cl^- and Br^- are added to a solution of 1N H_2SO_4 in the same concentration, it follows unambiguously that the I^- anion is specially adsorbed on gallium. The identical values of the increase in the overvoltage in the presence of KCl and KBr indicate the closeness of the adsorption properties of Cl^- and Br^- on gallium. This conclusion agrees with the data of capacitance [8] and electrocapillary measurements [9].* At low current densities $\Delta\eta$ is somewhat larger in the presence of halide anions. This phenomenon may be due, on the one hand, to the influence of anions on the anodic process, and consequently on the stationary potential, and on the other hand, to an increase in the adsorption of the anion as the electrode potential is shifted in the positive direction.

The aggregate of data obtained permit us to conclude that halide anions increase the overvoltage of hydrogen on high-purity gallium. The decrease in the hydrogen overvoltage by halide anions previously observed in the work of one of the authors [6] is apparently explained by the presence of some sort of impurities in the gallium used, the purity of which corresponded to 99.996%.

According to the concepts advanced in [11], an increase in the hydrogen overvoltage by halide anions is observed in those cases when the strength of the bond of the specifically adsorbed anion to the metal is great and the bond has a pronounced covalent character. The energy of the bond of hydrogen to the metal drops in this case, and the overvoltage increases. However, such a mechanism of an increase in the overvoltage of hydrogen is not applicable

*We have shown by measurements in more concentrated solutions of halide anions, 4N KCl and 4N KBr, that the adsorbability of Br^- on gallium, just as on other metals, is somewhat higher than that of Cl^-, although the difference is not large.

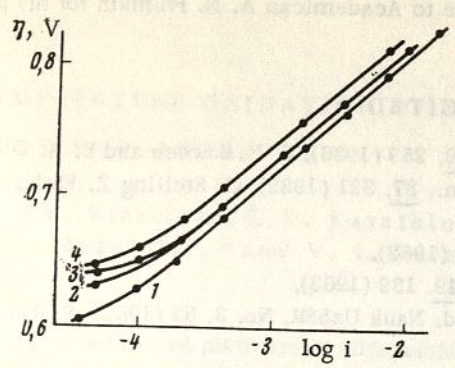


Fig. 3. Hydrogen overvoltage on Ga^{IV} in solutions: 1) 1N H_2SO_4; 2) 1N H_2SO_4 + 1N KCl; 3) 1N H_2SO_4 + 1N KBr; 4) 1N H_2SO_4 – 1N KI.

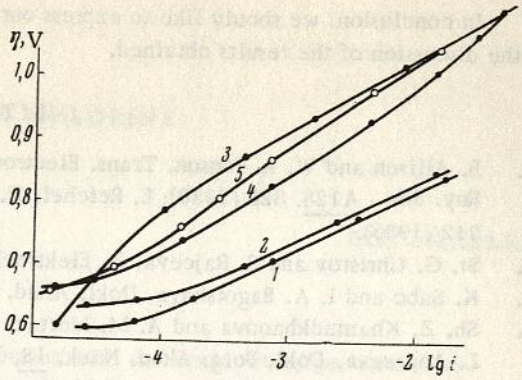


Fig. 4. Hydrogen overvoltage on Ga^{I} in solutions: 1) 1N H_2SO_4; 2) 1N H_2SO_4 + 1N KI; 3) 1N H_2SO_4 + $5 \cdot 10^{-4}$N $(C_4H_9)_4NBr$; 4) 1N H_2SO_4 + $5 \cdot 10^{-4}$N $(C_4H_9)_4NBr$ + 1N KI; 5) 1N H_2SO_4 + $5 \cdot 10^{-4}$N $(C_4H_9)_4NBr$ + 1N KBr.

to a gallium electrode, since halide anions, according to electrocapillary measurements [9], are adsorbed more weakly on gallium than on mercury. On a mercury electrode the halide anions lower the overvoltage of hydrogen according to a shift in the ψ' potential in the negative direction in their presence.

In a consideration of the phenomena of adsorption on gallium, the presence of a chemisorbed layer of water on its surface must be taken into consideration. Apparently the influence of halide anions on the overvoltage of hydrogen on gallium is due to changes in the structure of this layer upon the adsorption of Cl^-, Br^-, and I^-. However, in this case the coincidence of the polarization curves in solutions of sulfuric and perchloric acids remains incomprehensible. The electrocapillary curves in solutions of $(C_4H_9)_4N^+$ of various concentrations are cited in Fig. 1.* Data on the influence of $(C_4H_9)_4N^+$ separately and in conjunction with Br^- and I^- on the overvoltage of hydrogen on gallium are depicted in Fig. 4. From the electrocapillary curves we calculated the adsorption of $(C_4H_9)_4N^+$, which proved equal to $1.83 \cdot 10^{-10}$ mole/cm^2, did not depend on the concentration, and can thus be considered limiting. The limiting adsorption of $(C_4H_9)_4N^+$ on mercury is $2.17 \cdot 10^{-10}$ mole/cm^2 [12] and somewhat exceeds the limiting adsorption on gallium. We were unable to take the electrocapillary curves in more dilute solutions of $(C_4H_9)_4N^+$ on account of the extremely slow establishment of equilibrium at the interface.

φ_{max} on gallium in the presence of $(C_4H_9)_4N^+$, just as on mercury, is shifted in the positive direction; however, the absolute value of $\Delta\varphi_{max}$ on gallium is very low, ~50 mV. On mercury $\Delta\varphi_{max}$ is 250 mV. This is due to the very large values of the capacitance on gallium close to the zero charge potential [8], as a result of which the same value of the adsorption of $(C_4H_9)_4N^+$ on mercury and gallium produces substantially smaller changes in φ_{max} in the case of gallium. The hydrogen overvoltage on gallium in the presence of $(C_4H_9)_4N^+$ increases in accord with the shift of the ψ' potential in the positive direction. The absolute value of the increase in the overvoltage depends on the electrode potential; first it increases as the electrode potential is shifted from the point of zero charge (-0.975 V relative to the saturated calomel electrode) in the direction of negative values, then it becomes practically constant, ~200 mV, and close to the analogous value on mercury [13].

However, the ratios between $\Delta\eta$ and the shift of the zero charge potential $\Delta\varphi_{max}$ on gallium and mercury differ substantially. On gallium the ratio of the value of $\Delta\eta$ to $\Delta\varphi_{max}$, due to the adsorption of $(C_4H_9)_4N^+$, corresponds to four, whereas on mercury, depending on the concentration of tetramethylammonium, it is 0.7-0.8. This is explained by the very large difference in the values of the electrical double-layer capacitance on gallium at the zero charge potentials and negative values corresponding to the region of the hydrogen overvoltage [8], as a result of which the same value of the adsorption of $(C_4H_9)_4N^+$ at potentials far removed from the point of zero charge leads to substantially larger changes in the ψ' potential than it follows from the electrocapillary measurements.

As can be seen from Fig. 4, the overvoltage of hydrogen in solutions containing $(C_4H_9)_4N^+$ in conjunction with Br^- and I^- is lower than in solutions of $(C_4H_9)_4N^+$ without these additives; moreover, the effect increases from Br^- to I^-.

*The cation $(C_4H_9)_4N^+$ was introduced into solution in the form of the salt $(C_4H_9)_4NBr$. In this case we assumed that the adsorption of Br^- from solutions of such low concentrations could be neglected.

In conclusion, we should like to express our deep gratitude to Academican A. N. Frumkin for his participation in the discussion of the results obtained.

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