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Study of the Influence of pH and Electrolyte Concentration on the Hydrogen Overvoltage at a Dropping Gallium Electrode

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In a previous communication (^{1}) we showed that in solutions of composition $x\mathrm{HCl} + y\mathrm{KCl}$, with a constant total electrolyte concentration $c = 1$ g-equiv/l, the hydrogen overvoltage on gallium η increases linearly with increasing pH. In solutions of 0.01 N HCl+yKCl, at $\mathrm{pH} = \mathrm{const}$, η increases linearly with $\lg c$. The experimentally found coefficients $\left(\frac{\partial\eta}{\partial \mathrm{pH}}\right)_{c,i} = 48\text{–}50$ mV and $\left(\frac{\partial\eta}{\partial \lg c}\right)_{\mathrm{pH},i} = 50\text{–}55$ mV are close to the values predicted by the theory of slow discharge.

In the present work we studied the influence on η on gallium of pH over the range of its variation from 1.8 to 14. The measurements were carried out in phosphate-buffer solutions of composition $x\mathrm{K_3PO_4} + y\mathrm{Na_2SO_4} + z\mathrm{H_2SO_4}$ (or zNaOH) and in solutions $x\mathrm{NaOH} + y\mathrm{Na_2SO_4}$, with a total electrolyte concentration $c = 1$ g-equiv/l. In addition, we carried out measurements of η in pure NaOH solutions of various concentrations and in solutions with constant pH 12, 0.01 N NaOH + $x\mathrm{Na_2SO_4}$, and variable total electrolyte concentration. The measurements were made on a dropping gallium electrode at 32°. The procedure is described in (^{2}). The purity of the gallium used in this work was 99.996%. Chemically pure grade $\mathrm{K_3PO_4}$ was calcined before preparation of the solutions; $\mathrm{Na_2SO_4}$ was twice recrystallized and calcined; $\mathrm{H_2SO_4}$ was twice distilled; NaOH solutions were prepared by decomposition of the corresponding amalgam in bidistilled water, followed by removal of traces of mercury by cathodic polarization. The pH of the solution was determined from the value of the potential of a reversible hydrogen electrode in the solution under study.

The polarization curves $\eta, \lg i$ in buffer solutions with pH from 1.8 to 4 and from 9 to 14, and also in $x\mathrm{NaOH} + y\mathrm{Na_2SO_4}$ solutions and pure alkali, are straight lines with a slope of 0.120–0.130 V. The normal slope of the polarization curves in alkaline solutions indicates the absence of reversible deposition of an alkali metal on gallium in the region of hydrogen overvoltage. This conclusion is confirmed by the coincidence of the $\varphi, \lg i$ curves taken in alkaline and neutral solutions containing the cations $\mathrm{Na^+}$ and $\mathrm{K^+}$ at a constant total electrolyte concentration. The absence of alkali-metal deposition is also indicated by the capacitance values measured by an alternating-current bridge at a dropping gallium electrode in an alkali solution at 318 Hz,* as well as those calculated

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

from the curves of potential change with time upon application of an anodic pulse to a gallium drop previously polarized at a potential corresponding to the region of hydrogen overvoltage. In both cases the capacitance was of the order of 20–25 μF/cm^2 and corresponded to the capacitance of the electrical double layer. A detailed consideration of this question will be given in a separate communication.

In buffer solutions with pH from 4 to 9, the polarization curves have a distorted shape (Fig. 1). Beginning at a certain current density, the slope coefficient rapidly increases, reaching 0.2 V and still higher values, and then again approaches the normal value, corresponding to 0.120–0.130 V.

In Fig. 2, the values of η at $i = 1{\cdot}10^{-4}$ A/cm^2 are compared at various pH values, obtained in buffer solutions* and in solutions of alkali and acid**, containing a foreign electrolyte under the condition that the total electrolyte concentration in the solution remains constant and equal to 1 g-eq/L. As can be seen, the η,

Fig. 1. Polarization curve on a dropping gallium electrode in a buffer solution $0.1\,N\ K_3PO_4 + yNa_2SO_4 + zH_2SO_4$;
pH 6.4;
$c = 0.1\,N + y + z = 1$ g-eq/L

Fig. 2. Dependence of η on pH in solutions with constant total electrolyte concentration 1 g-eq/L at
$i = 1 \cdot 10^{-4}$ A/cm^2
in solutions:
a–$xHCl + yKCl$;
b–$xK_3PO_4 + yNa_2SO_4 + zH_2SO_4$ (or $zNaOH$);
v–$xNaOH + yNa_2SO_4$

pH curve consists of two straight lines with different slope coefficients. At pH < 10, η increases linearly with pH,

$$\left(\frac{\partial\eta}{\partial \text{pH}}\right)_{c,i} \approx 48\text{–}50 \text{ mV},$$

and at pH > 10 it decreases with its increase,

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* Capacitance measurements on the dropping gallium electrode by the alternating-current bridge were carried out in our laboratory by N. B. Grigor' ev.

$$\left(\frac{\partial\eta}{\partial \mathrm{pH}}\right)_{c,i} \approx -58\ \mathrm{mV}^{***}.$$

The increase of η with pH up to pH $\sim$ 10 observed on gallium is in good agreement with the data of analogous measurements on mercury (^{3,4}). By measurements in buffer solutions on mercury (^{4}), the curve of the dependence of η on pH obtained in acidic solutions (^{3}) was extended to pH ~ 10. Measurements of η on mercury at high pH values are associated with difficulties caused by the transition of the electrochemical mechanism of amalgam decomposition to the chemical one (^{4}).

The practical coincidence of the values of η obtained on gallium in buffer solutions and in acid solutions containing an indifferent electrolyte (Fig. 2) indicates that at pH < 10 the $H_2PO_4^-$ ions do not noticeably participate in the hydrogen-evolution process as proton donors, which is probably explained by their low concentration in the surface layer at negative values of the Ψ_1-potential, and hydrogen evolution proceeds through the discharge of H_3O^+. Direct discharge of $H_2PO_4^-$ in strong

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* The values of η at $i = 1 \cdot 10^{-4}$ A/cm^2 in buffer solutions with an anomalous polarization-curve shape correspond to the first section of the polarization curve with normal slope.

** The dependence of η on pH in acidic solutions $xHCl + yKCl$ at $c = x + y = 1$ g-eq/L is taken from work (^{1}).

*** The value of η at pH 14, obtained in a $1\,N\ NaOH$ solution, lies somewhat lower than follows from continuation of the straight line η—pH at pH > 10. This is probably due to the fact that the activity of Na^+ in $1\,N\ NaOH$ is somewhat higher than the activity of the cations in solutions $xNaOH + yNa_2SO_4$ at $y \neq 0$ and $xK_3PO_4 + yNa_2SO_4 + zNaOH$ at the same analytical concentration of them.

in buffer solutions on mercury was observed in work (4). The greatest discrepancy between the values of η obtained in buffer solutions and in acid solutions, of the order of 15-20 mV, is possibly connected with the smaller value of the activity of indifferent cations in the buffer solution, which contains, in addition to $\mathrm{K_3PO_4}$, $\mathrm{Na_2SO_4}$ and $\mathrm{H_2SO_4}$, as compared with a solution $x\mathrm{HCl} + y\mathrm{KCl}$ at one and the same analytical concentration of them. The data obtained in the present work on the dependence of η on pH at $c = \mathrm{const}$ are not in agreement with the results of the measurements of work (5), in which η on gallium in acidified and alkalized solutions of $0.5\,N\ \mathrm{Na_2SO_4}$ did not change with the pH of the solution.

Fig. 3. Dependence of η on $\lg c$ at $i = 1 \cdot 10^{-3}$ A/cm^2 in solutions:
xNaOH and b—$0.01\,N$ NaOH $+ x\mathrm{Na_2SO_4}$ at pH 12

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

Fig. 4. Curves of φ, $\lg i$ in solutions of $0.33\,N$ concentration. a—Na_2SO_4; b—KJ; v—NaOH. The values of φ are measured relative to the normal hydrogen electrode.

The reason for the disagreement is not clear to us. The dependence of η at $i = 1 \cdot 10^{-3}$ A/cm^2 on pH in solutions of pure alkali and on $\lg c$ at pH 12 is presented in Fig. 3*.

Table 1

Solutions	Coefficients
$xK_3PO_4 + yNa_2SO_4 + zH_2SO_4$ (or zNaOH)$x + y + z = 1$ g-equiv/l	pH < 10; $\left[\left(\frac{\partial\eta}{\partial \mathrm{pH}}\right)_{c,i}\right]_{\mathrm{exp}} \approx$ 49 mV; $\left[\left(\frac{\partial\eta}{\partial \mathrm{pH}}\right)_{c,i}\right]_{\mathrm{calc}} = 2.3\,\frac{1-\alpha}{\alpha}\,\frac{RT}{F} = 52$ mVpH $>$ 10; $\left[\left(\frac{\partial\eta}{\partial \mathrm{pH}}\right)_{c,i}\right]_{\mathrm{exp}} \approx$ −58 mV; $\left[\left(\frac{\partial\eta}{\partial \mathrm{pH}}\right)_{c,i}\right]_{\mathrm{calc}} = -2.3\,\frac{RT}{F} = -59$ mV
$x\mathrm{NaOH} + yNa_2SO_4$; $x + y =$ 1 g-equiv/l	$\left[\left(\frac{\partial\eta}{\partial \mathrm{pH}}\right)_{c,i}\right]_{\mathrm{exp}} \approx$ −58 mV; $\left[\left(\frac{\partial\eta}{\partial \mathrm{pH}}\right)_{c,i}\right]_{\mathrm{calc}} = -2.3\,\frac{RT}{F} = -59$ mV
xNaOH; $x =$ $0.01\,N$; $0.03\,N$; $0.1\,N$,$0.33\,N$ and $1\,N$	$\left[\left(\frac{\partial\eta}{\partial \mathrm{pH}}\right)_{i}\right]_{\mathrm{exp}} \approx$ −113 mV; $\left[\left(\frac{\partial\eta}{\partial \mathrm{pH}}\right)_{i}\right]_{\mathrm{calc}} = -2.3\,\frac{2RT}{F} = -118$ mV

Solutions	Coefficients
$0.01\,N$ NaOH$+x$Na$_2$SO$_4$;$0.01\,N+x=0.01\,N$; $1.1\,N$ and $1\,N$	$\left[\left(\frac{\partial\eta}{\partial\lg c}\right)_{\mathrm{pH},i}\right]_{\mathrm{exp}}\approx -49$ mV; $\left[\left(\frac{\partial\eta}{\partial\lg c}\right)_{\mathrm{pH},i}\right]_{\mathrm{calc}}=-2.3\frac{RT}{F}=-59$ mV

Table 1 compares the experimentally observed values of the coefficients $\left(\frac{\partial\eta}{\partial\mathrm{pH}}\right)_{c,i}$ at pH <10 and pH >10, determined in buffer solutions and in alkali solutions in the presence of an indifferent electrolyte, $\left(\frac{\partial\eta}{\partial\mathrm{pH}}\right)_{c,i}$—in solutions of pure alkali, and $\left(\frac{\partial\eta}{\partial\lg c}\right)_{\mathrm{pH},i}$—in solutions of $0.01\,N$ NaOH $+x$Na$_2$SO$_4$ at pH $=$ const, with those calculated from the theory of slow discharge for $\alpha=0.54$*, assuming $\Psi_1=\mathrm{const}+RT/F\ln c$, and that at pH <10 hydrogen ions are discharged at the electrode, while at pH >10 water molecules are discharged.

The agreement of the theoretical values of the coefficients $\left(\frac{\partial\eta}{\partial\mathrm{pH}}\right)_{c,i}$, $\left(\frac{\partial\eta}{\partial\mathrm{pH}}\right)_{i}$, and $\left(\frac{\partial\eta}{\partial\lg c}\right)_{\mathrm{pH},i}$ with those observed experimentally speaks in favor of the applicability of the theory of slow discharge to the process of hydrogen evolution on gallium, and in favor of the assumption according to which, in the elementary electrochemical act at pH >10, water molecules participate. The latter is further confirmed by the coincidence of the curves $\varphi,\lg i$ recorded in solutions of neutral salts and in an alkali solution of the same concentration (Fig. 4).

In buffer solutions with pH from 4 to 9, the transition of the polarization curve from the first section with a normal slope to the second indicates the presence of a limiting kinetic current which is possibly associated with the finite rate of the dissociation reaction

$$\mathrm{H_2PO_4^-}+\mathrm{H_2O}\rightleftarrows\mathrm{H_3O^+}+\mathrm{HPO_4^{--}},$$

which supplies hydroxonium ions. At pH >5, the supply of hydroxonium ions cannot be provided by their diffusion from the bulk of the solution, since their

* In Fig. 3 the values of $\lg c$ are plotted on the abscissa axis. In solutions of pure alkali, a change in $\lg c$ by one unit is equivalent to a change in pH by one unit.

analytical concentration is too small and the limiting diffusion current of them, calculated by the Il' kovich formula at pH $\simeq$ 6, cannot exceed 10^{-4} a/cm^2. The third section of the polarization curve corresponds to discharge of water molecules.

A kinetic current determined by the rate of dissociation of $H_2PO_4^-$ was recently found in work (6), devoted to the study of catalytic hydrogen evolution on mercury in the presence of $H_2PO_4^-$, acting as a proton donor. We shall return to consideration of the question of the nature of the limiting current in buffer solutions on gallium in another communication.

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* The value of α was calculated by us from the slope of the polarization curves at 32°.