

A STUDY OF THE EFFECT OF pH AND ELECTROLYTE CONCENTRATION ON THE HYDROGEN OVERVOLTAGE AT THE DROPPING GALLIUM ELECTRODE

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It has been shown in an earlier communication [1] that the hydrogen overvoltage, η , on gallium in $\chi\text{HCl} + y\text{KCl}$ solutions increases linearly with the pH when the total electrolyte concentration, c , is held constant at 1 geq/liter. η increases linearly with $\log c$ in 0.01 N $\text{HCl} + y\text{KCl}$ solutions of fixed pH. The experimentally determined values for the coefficients, namely $\left(\frac{\partial \eta}{\partial \text{pH}}\right)_{c,i} = 48-50 \text{ mv}$ and $\left(\frac{\partial \eta}{\partial \log c}\right)_{\text{pH},i} = 50-55 \text{ mv}$, are close to those predicted by the theory of delayed discharge.

The effect of pH on the hydrogen overvoltage on gallium has been studied over the pH interval from 1.8 to 14 in the present work. Measurements were carried out in $\chi\text{K}_3\text{PO}_4 + y\text{Na}_2\text{SO}_4 + z\text{H}_2\text{SO}_4$ or $z\text{NaOH}$ phosphate buffers and in $\chi\text{NaOH} + y\text{Na}_2\text{SO}_4$ solutions holding the total electrolyte concentration, c , at 1 geq/liter. Measurements were also made in pure NaOH solutions of various concentrations, and in 0.01 N $\text{NaOH} + \chi\text{Na}_2\text{SO}_4$ solutions in which the total electrolyte concentration was varied at a constant pH of 12. The measurements were made on a dropping gallium electrode at 32° , following the technique described in [2]. The gallium used in this work had a purity of 99.996%. The K_3PO_4 was CP grade and was calcined before being put into solution; the Na_2SO_4 was subjected to a double recrystallization and then calcined; the H_2SO_4 was doubly distilled; and, the NaOH solutions were prepared by decomposing an amalgam with doubly distilled water and then carrying out cathodic polarization to remove traces of mercury. The pH was determined from the potential of a reversible hydrogen electrode immersed in the test solution.

$\chi\text{K}_3\text{PO}_4 + y\text{Na}_2\text{SO}_4 + z\text{H}_2\text{SO}_4$ (or $z\text{NaOH}$) $x + y + z = 1 \text{ geq}$	$\text{pH} < 10; \left[\left(\frac{\partial \eta}{\partial \text{pH}}\right)_{c,i}\right]_{\text{exp}} \approx 49 \text{ mv}$ $\left[\left(\frac{\partial \eta}{\partial \text{pH}}\right)_{c,i}\right]_{\text{calc}} = 2,3 \frac{1-\alpha}{\alpha} \frac{RT}{F} = 52 \text{ mv}$ $\text{pH} > 10; \left[\left(\frac{\partial \eta}{\partial \text{pH}}\right)_{c,i}\right]_{\text{exp}} \approx -58 \text{ mv}$ $\left[\left(\frac{\partial \eta}{\partial \text{pH}}\right)_{c,i}\right]_{\text{calc}} = -2,3 \frac{RT}{F} = -59 \text{ mv}$
$x\text{NaOH} + y\text{Na}_2\text{SO}_4; x + y = 1 \text{ geq/liter}$	$\left[\left(\frac{\partial \eta}{\partial \text{pH}}\right)_{c,i}\right]_{\text{exp}} \approx -58 \text{ mv}$ $\left[\left(\frac{\partial \eta}{\partial \text{pH}}\right)_{c,i}\right]_{\text{calc}} = -2,3 \frac{RT}{F} = -59 \text{ mv}$
$x\text{NaOH}; x = 0,01 \text{ N}; 0,03 \text{ N}; 0,1 \text{ N},$ $0,33 \text{ N and } 1 \text{ N}$	$\left[\left(\frac{\partial \eta}{\partial \text{pH}}\right)_i\right]_{\text{exp}} \approx -113 \text{ mv}$ $\left[\left(\frac{\partial \eta}{\partial \text{pH}}\right)_i\right]_{\text{calc}} = -2,3 \frac{2RT}{F} = -118 \text{ mv}$
$0,01 \text{ N NaOH} + x\text{Na}_2\text{SO}_4;$ $0,01 \text{ N} + x = 0,01 \text{ N}; 1,1 \text{ N and } 1 \text{ N}$	$\left[\left(\frac{\partial \eta}{\partial \log c}\right)_{\text{pH},i}\right]_{\text{exp}} \approx -49 \text{ mv}$ $\left[\left(\frac{\partial \eta}{\partial \log c}\right)_{\text{pH},i}\right]_{\text{calc}} = -2,3 \frac{RT}{F} = -59 \text{ mv}$

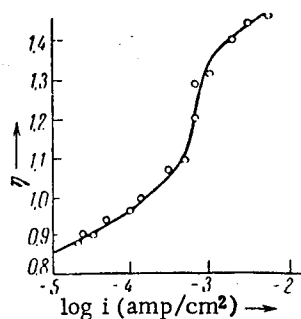


Fig. 1. Polarization curve for the dropping gallium electrode in a 0.1 N $\text{K}_3\text{PO}_4 + y\text{Na}_2\text{SO}_4 + z\text{H}_2\text{SO}_4$; pH = 6.4; $c = 0.1 \text{ N} + y + z = 1 \text{ geq/liter}$.

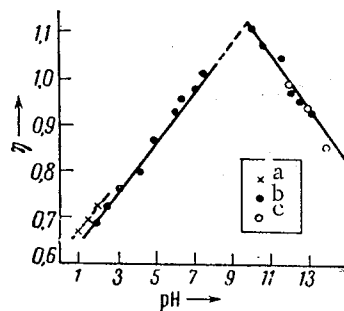


Fig. 2. The relation between η and pH at a total electrolyte concentration of 1 geq/liter and $i = 1 \cdot 10^{-4} \text{ amp/cm}^2$, for the solutions: a) $x\text{HCl} + y\text{KCl}$; b) $x\text{K}_3\text{PO}_4 + y\text{Na}_2\text{SO}_4 + z\text{H}_2\text{SO}_4$ (or $z\text{NaOH}$); c) $x\text{NaOH} + y\text{Na}_2\text{SO}_4$.

Straight line polarization (η vs $\log i$) curves with 0.120-0.130 v slope were obtained for buffer solutions with pH ranging from 1.8 to 4 and 9 to 14, for the $x\text{NaOH} + y\text{Na}_2\text{SO}_4$ solutions, and for the pure alkaline solutions. The fact that polarization curves of normal slope were obtained for the alkaline solutions is an indication that the alkali metals do reversibly separate out on gallium in the region of the hydrogen overvoltage. This conclusion is confirmed further by the fact that identical η vs $\log i$ curves were obtained for alkaline and neutral solutions containing Na^+ and K^+ ions at fixed total electrolyte concentration. It was also substantiated by capacitance measurements on the gallium drop electrode in alkaline solutions, which were made with an alternating current bridge working at a frequency of 318 cps*, and by calculations based on curves showing the time alteration of potential following application of an anodic impulse to a gallium electrode drop which had been previously polarized at a potential in the region of hydrogen overvoltage. The capacitance proved to be of the order of magnitude of $20\text{-}25 \mu\text{f/cm}^2$, corresponding to the capacitance of the double electric layer in both cases. This matter will be considered in detail in a separate communication.

Distorted polarization curves were obtained for buffer solutions with pH falling in the interval from 4 to 9 (Fig. 1). Here the slope rapidly increased to 0.2 v, or more, on reaching a certain definite current density, and then fell off once more to the normal value of 0.120-0.130 v.

Figure 2 shows the variation of η at $i = 1 \cdot 10^{-4} \text{ amp/cm}^2$ with pH in various buffers†, and in acid and alkaline‡ solutions containing a foreign electrolyte at a total electrolyte concentration of 1 geq/liter. It is seen that the η vs pH curve consists of two straight lines of different slopes. η increases linearly with the pH when $\text{pH} < 10$ and

$\left(\frac{\partial \eta}{\partial \text{pH}}\right)_{c, i} \approx -48\text{-}50 \text{ mv}$ while η diminishes with the $\text{pH} > 10$ and $\left(\frac{\partial \eta}{\partial \text{pH}}\right)_{c, i} \approx -58 \text{ mv}^{**}$. The fact that the hydrogen overvoltage on gallium increases with the pH up to $\text{pH} \sim 10$ is in agreement with the results obtained in similar measurements on mercury [3, 4]. The buffer solution measurements of [4] were used to extend the η vs pH relation for mercury in acidic solutions [3] to $\text{pH} \sim 10$. Measurements on mercury are difficult to carry out at high pH, the mechanism of amalgam decomposition being chemical rather than electrochemical [4].

*The alternating current bridge measurements of the capacitance of the gallium drop electrode were carried out in this laboratory by N. B. Grigor'ev.

†For buffer solutions showing an anomalous polarization curve, the value of η at $i = 1 \cdot 10^{-4} \text{ amp/cm}^2$ corresponds to the initial section of a normal polarization curve.

‡Data on the relation between η and pH in acidic $x\text{HCl} + y\text{KCl}$ solutions with $c = x + y = 1 \text{ geq/liter}$ has been taken from [1].

**The value of η at pH 14 was obtained in a 1 N NaOH solution and lies somewhat lower than would be anticipated from an extension of the η vs pH curve to $\text{pH} > 10$. This situation probably arises from the fact that the activity of Na^+ is somewhat higher in 1 N NaOH than in $x\text{NaOH} + y\text{Na}_2\text{SO}_4$ (with $y \neq 0$) and $x\text{K}_3\text{PO}_4 + y\text{Na}_2\text{SO}_4 + z\text{NaOH}$ solutions of the same analytic concentration.

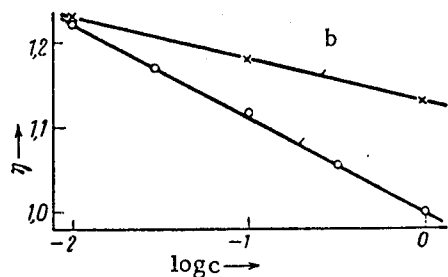


Fig. 3. The relation between η and $\log c$ at $i = 1 \cdot 10^{-3}$ amp/cm² in the following solutions: a) xNaOH; b) 0.01 N NaOH + xNa₂SO₄ at pH 12.

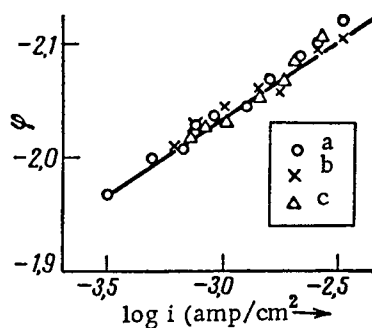


Fig. 4. ϕ vs $\log i$ curve for 0.33 N solutions: a) Na₂SO₄; b) KI; c) NaOH. ϕ values are relative to the normal hydrogen electrode.

The fact the hydrogen overvoltage on gallium is essentially the same in buffer solutions and in solutions containing an inert electrolyte (Fig. 2) is indication that the H_2PO_4^- ions do not function as active proton donors for hydrogen evolution at $\text{pH} < 10$. This is probably due to the fact that the surface layer concentration of these ions is low at negative ψ_1 -potentials, the evolution of hydrogen proceeding through H_3O^+ ion discharge. Direct discharge of H_2PO_4^- ions has been reported to occur on mercury in strong buffer solutions [4]. The greatest difference between the observed η values for buffer and acid solution was of the order of 15-20 mv; this probably reflects the fact that inert cation activity is lower for buffer solutions containing K_3PO_4 , Na_2SO_4 , and H_2SO_4 than for $x\text{HCl} + y\text{KCl}$ solutions of the same analytic concentration. The data obtained here on the η vs pH relation at $c = \text{const}$ are not consistent with the results of [5] where the hydrogen overvoltage on gallium was reported to be independent of the pH in acidic and basic solutions containing 0.5 N Na₂SO₄. The origin of this discrepancy is not clear. Figure 3 shows the relation between η at $i = 1 \cdot 10^{-3}$ amp/cm² and pH in pure alkaline solutions, and the relation between η and $\log c$ at pH 12.*

A comparison is made in Table 1 of the experimentally determined values of the coefficients $(\partial \eta / \partial \text{pH})_{c, i}$ (measured at $\text{pH} < 10$ and at $\text{pH} > 10$ in buffers and alkaline solutions free of foreign electrolytes), $(\partial \eta / \partial \text{pH})_{\text{pH}, i}$ (measured in 0.01 N NaOH + xNa₂SO₄ solutions with $\text{pH} = \text{const}$) with corresponding values calculated from the theory of delayed discharge by setting $\alpha = 0.54^\dagger$ and $\psi_1 = \text{const} + RT/F \ln c$, and assuming electrode discharge to involve hydrogen ions at $\text{pH} < 10$ and water molecules at $\text{pH} > 10$.

The fact that good agreement was obtained between the theoretically calculated and experimentally determined values of the coefficients $(\frac{\partial \eta}{\partial \text{pH}})_{c, i}$, $(\frac{\partial \eta}{\partial \text{pH}})_i$ and $(\frac{\partial \eta}{\partial \log c})_{\text{pH}, i}$ is indication that the theory of delayed discharge is applicable to the separation of hydrogen on gallium, water molecules participating in the elementary electrochemical step at pH's in excess of 10. This last statement is confirmed by the observation that the ϕ vs $\log i$ curves for neutral salt solutions are identical with the analogous curves for alkaline solutions of the same concentration (Fig. 4).

The existence of a limiting kinetic current is indicated by the passage of the polarization curve from an initial segment of normal slope to a second segment in buffer solutions with pH falling in the interval from 4 to 9; this passage, in turn, results from the fact that hydronium are furnished by the $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$ reaction which proceeds at a finite rate. The analytical concentration of hydronium ions at $\text{pH} > 5$ is so low that the ion supply cannot be maintained by diffusion from the interior of the solution, the limiting ionic current calculated from the Ilkovic Eq. being less than 10^{-4} amp/cm² at $\text{pH} \sim 6$. The third segment of the polarization curve corresponds to water molecule discharge.

A kinetic current determined by the rate of H_2PO_4^- dissociation was recently reported in [6] where study had been made of the catalytic separation of hydrogen on mercury in the presence of H_2PO_4^- ions which functioned as proton donors. We will return in another communication to the nature of the limiting current on gallium in buffer solutions.

*Values of $\log c$ have been plotted on the axis of abscissas in Fig. 3. Alteration of $\log c$ by one unit is equivalent to a one unit alteration of the pH of a pure alkaline solution.

† The value of α was determined from the slopes of the 32° polarization curve.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
