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Author(s)	BAGOTSKAYA, I. A.; POTAPOVA, E. N.
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ON HYDROGEN OVERVOLTAGE AT LIQUID Ga AND AT THE EUTECTIC In-Ga ALLOY IN ACID AND ALKALINE SOLUTIONS

By

I. A. BAGOTSKAYA*) and E. N. POTAPOVA*)

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Abstract

Data are presented on the dependence of the potential of hydrogen evolution at a given rate on pH in the pH range 0.3~13.7 and on the overall electrolyte concentration c in acidified and alkalinized solutions of inorganic cations at liquid gallium and at the eutectic In-Ga alloy. The results obtained show that the alkali metals cations (Li^+ , Na^+ , K^+) in the potential range studied do not participate markedly in the hydrogen evolution process and do not affect its rate. At $i=1 \times 10^{-3}$ a/cm² and $pH < 9$ hydroxonium ions are mainly discharged both at Ga and the In-Ga alloy, while at $pH > 9$ water molecules. Accordingly the overvoltage η is higher in alkaline solution than in an acid one of the same concentration. The values of the coefficients $(\partial\varphi/\partial pH)_{i,c}$ and $(\partial\varphi/\partial \log c)_{i,pH}$ correspond quantitatively to these predicted by the slow discharge theory both at $pH < 9$ and at $pH > 9$. The results obtained are at variance with those of KITA and KURISU¹⁸⁾.

Introduction

The majority of studies on hydrogen evolution have been carried out in acid solutions on account of the difficulties associated with formation of amalgams and incorporation of alkali metals cations into cathodes¹⁾ in the hydrogen overvoltage region at high pH values. But of importance to the theory are data obtained in a wide pH range as well as their dependence on the metal nature. Electrodes from liquid gallium and its eutectic alloy with indium (16.4 at. % In) have proved to be convenient for use in investigations of the hydrogen overvoltage in a wide pH range. In the In-Ga system In is the surface-active component²⁾ and therefore the overvoltage η at the In-Ga alloy approaches the value at In. The alkali metals cations discharge at Ga and In-Ga alloy during cathodic polarization in alkaline solutions at the potentials not more negative than -2.05 V^{**)} at Ga and

*) Institute of Electrochemistry of the Academy of Sciences of the U.S.S.R., Moscow.

***) All potentials given in this paper are referred to the NCE.

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-2.25 V at In-Ga ($i \leq 10^{-2}$ a/cm²) occurs in any case at a rate much lower than the hydrogen evolution rate and does not affect the value of η . The hydrogen evolution at the In-Ga alloy containing 19.2 at. % In in 0.1 M HClO₄ solution was studied by BUTLER and MEEHAN³.

In this paper are given the data on the effect on η of pH in the range 0.3~13.7 at constant overall electrolyte concentration in acidified and alkalinized solutions of salts and in buffer solutions as well as on that of the overall electrolyte concentration at $pH = \text{const.}$ in acidified and alkalinized solutions.

Experimental

The measurements were performed at 32°C at dropping electrodes from gallium GL-000 (Soviet Union) 99.9998% pure and gallium+indium IN-00 (Soviet Union) 99.999% pure. The reactants used were carefully purified notwithstanding the fact that the constantly renewed surface of the dropping electrode made it less sensitive to the impurities present in solution as compared to a stationary electrode. The acids were 2~3 times redistilled, the salts repeatedly recrystallized and when possible calcinated, the alkaline solutions were prepared by decomposition of respective amalgams in twice-distilled water. The solutions in which the measurements were performed were additionally purified by prolonged pre-electrolysis on a large mercury cathode with periodically renewed surface.

Some measurements were performed at stationary Ga and In-Ga electrodes. The technique of these measurements was the same as in reference (4). On account of the high self-dissolution rate of Ga and the In-Ga alloy, it was possible to measure the hydrogen overvoltage only at current densities exceeding 10^{-4} a/cm². In this paper, just as in reference (4), drops 10~15 mm in diameter placed in a small glass bowl with a sealed in glass platinum contact were used as electrodes. In calculations of the current density, the spherical area of a hemisphere, whose diameter was found from the drop weight, was taken to be the electrode surface.

Results and discussion

Fig. 1 shows the plots of the potential versus the density of the cathodic polarization current in 0.5 M LiCl, LiOH, NaOH, KCl, RbCl, CsCl solutions at Ga⁵) and in 0.5 M LiCl, NaCl, KCl, CsCl solutions at the In-Ga alloy. It is clear from the figure that both at Ga and the In-Ga alloy the φ , $\log i$ curves in solutions containing Li⁺, Na⁺ and K⁺ coincide and in the solu-

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tion of Cs^+ are shifted in the direction of less negative potentials by 40~45 mV and in the Rb^+ solution at Ga by 25~30 mV. The slope of the polarization curves is 0.110~0.120, does not depend on the cation nature and corresponds to an irreversible one-electron transfer process.

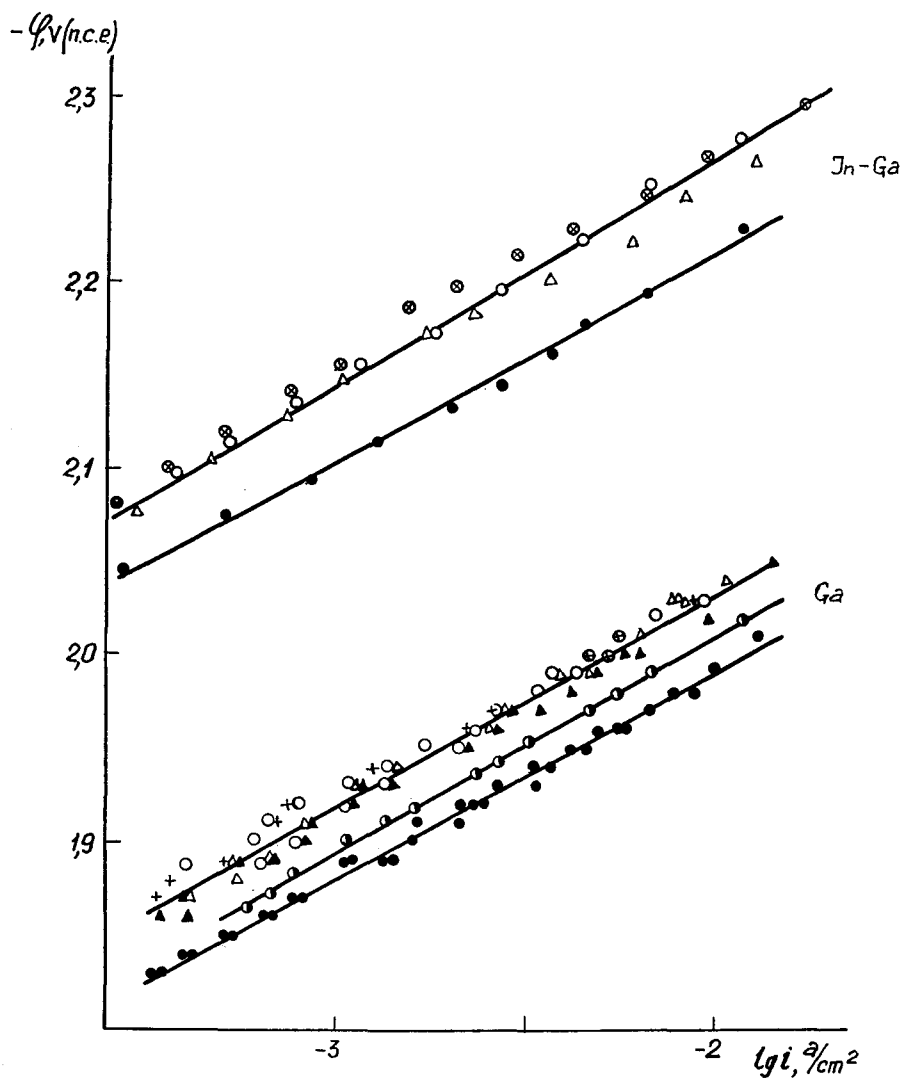


Fig. 1. Plots of φ vs $\log i$ at Ga and the In-Ga alloy measured at dropping electrodes in 0.5 M solutions of \blacktriangle LiOH, \triangle LiCl, + NaOH, \otimes NaCl, \circ KCl, \bullet RbCl, \bullet CsCl. Potentials referred to NCE.

The insignificant dependence of the polarization curves on the nature of the cation in solution indicates that at least the main portion of the current flowing to the electrodes in the potential range investigated is not associated with the discharge of the alkali metals cations. Even if the alkali metals cations are discharged at a low rate, they by no means affect the hydrogen evolution potential. In fact, the potentials corresponding to the formation of alkali metals amalgams depend essentially on the nature of the discharging cation. Thus, the half-wave potential of the deposition of potassium on mercury is equal to 2.17 V, whereas that of lithium -2.34 V⁶⁾.

In order to find out whether alkali metals accumulate on the electrode surface during cathodic polarization¹⁾, the curves of the potential drop with time after current interruption were measured at a stationary liquid gallium electrode in 4 M LiCl solution^{5,*)}. The capacity calculated from the curves was equal to $14\sim 18$ $\mu F/cm^2$, did not depend on the time of cathodic polarization of the electrode and was close to the capacity of the electric double layer at negative potentials⁸⁾. It was shown recently in the investigation of the incorporation of lithium into solid gallium from nonaqueous propylene carbonate solutions of LiClO₄ that during cathodic polarization gallium forms the compound LiGa, whose equilibrium potential is by 0.9 V more positive than that of lithium in the same solution⁹⁾. Hence it follows that in water the equilibrium potential of LiGa lies at -2.4 V and is at least by 0.3 V more negative than the potential which we reached in our measurements.

It can be concluded from these data that the polarization curves shown in Fig. 1 characterize the electrochemical hydrogen evolution at Ga and the In-Ga alloy. The less negative values of the potentials of hydrogen evolution from a solution containing Cs⁺ cations seem to be due to a certain specific adsorption of the Cs⁺ ions¹⁰⁾, which shifts the ψ' -potential in the direction of less negative values and thus increases the potential difference between the electrode and the layer in which the discharging water molecules are located. The coincidence of the φ , $\log i$ curves measured at Ga in 0.5 M LiOH and 0.5 M LiCl solutions shows that in the solutions investigated the hydrogen evolution rate does not depend on pH and consequently, water molecules are the proton donors¹¹⁾.

It was of interest to determine quantitatively the pH of the transition at a given current density from the predominant hydroxonium ions discharge to the predominant water molecules discharge.

Fig. 2 gives the dependence of the Ga and In-Ga electrode potentials

*) LiCl was chosen as electrolyte because some data are available in literature according to which lithium incorporates into liquid gallium⁷⁾ from aqueous Li⁺ solutions.

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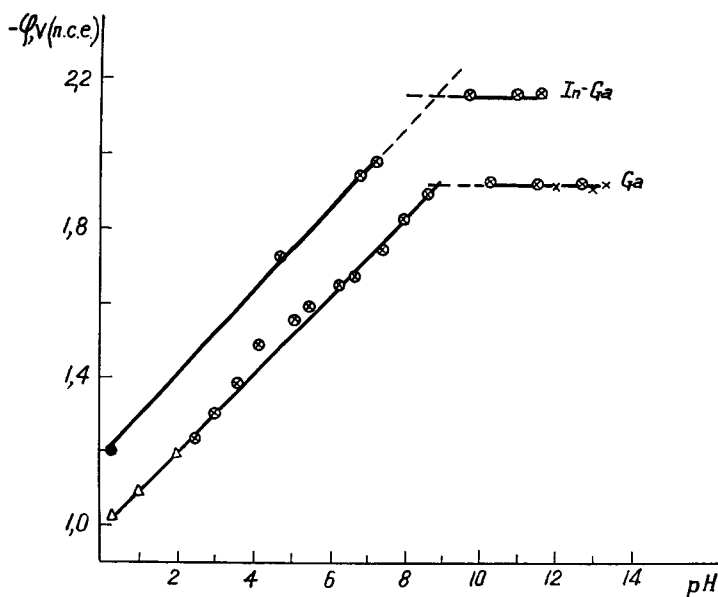


Fig. 2. Dependence of the potential of Ga and In-Ga electrodes on pH at $i=1 \times 10^{-3} \text{ a/cm}^2$ in the solutions: \triangle $x \text{ M HCl} + y \text{ M KCl}$, \times $x \text{ M NaOH} + y \text{ M KCl}$, $x+y=0.5 \text{ M}$; \bullet 0.5 M HClO_4 , \otimes $0.1 \text{ M KH}_2\text{PO}_4 + 0.2 \text{ M KCl} + \text{HCl}$ or NaOH .

in acidified and alkalinized salts solutions and in buffer solutions on pH at $i = \text{const}$, calculated from the polarization curves measured in the same solutions. The hydrogen overvoltage values obtained by us at Ga in 0.5 M HCl and at the eutectic In-Ga alloy in 0.5 M HClO_4 agree with those measured by BUTLER and MEEHAN³⁾ at Ga and the In-Ga alloy (19.2 at. % In) in 0.1 M HClO_4 . According to our data, at $i = 1 \times 10^{-3} \text{ a/cm}^2$, η is 0.72 V at Ga and 0.90 V at In-Ga, whereas according to reference (3), η is equal to 0.72 V and 0.89 V , respectively. It is clear from Fig. 2 that the dependence of φ on pH is represented by two straight lines with different slopes intersecting at $pH \sim 9$. At $pH < 9$ $(\partial\varphi/\partial pH)_{i,c} \sim -(0.108 \sim 0.105) \text{ V}$ and at $pH > 9$ $(\partial\varphi/\partial pH)_{i,c} = 0$. Hence, in accordance with the slow discharge theory¹¹⁾, it follows that at $pH < 9$ it is the hydroxonium ions which are mainly discharged and at $pH > 9$ the water molecules. The values of φ as a function of pH in buffer and acidified KCl solutions fall satisfactorily on one straight line. This indicates that at Ga and the In-Ga alloy, just as at mercury¹²⁾ and potassium amalgam¹³⁾ at 0.3 M buffer concentration and $pH < 9$, the H_2PO_4^- ions do not participate markedly as proton donors in the hydrogen evolution process.

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TABLE.

Solution composition	Ga	In-Ga
0.5 M HClO ₄ (H ₂ SO ₄ , HCl)	$a=1.015\sim 1.025$ $b=0.095\sim 0.100$	$a=1.240$ $b=0.115$
0.5 M NaOH	$a=1.200$ $b=0.115$	$a=1.420$ $b=0.120$
x M HCl + y M KCl $c=x+y=0.5$ M	$(\partial\varphi/\partial pH)_{i,c} = -0.105$ (exp) $(\partial\varphi/\partial pH)_{i,c} = -0.109^*$ (calc)	— —
x M NaOH + y M KCl $c=x+y=0.5$ M	$(\partial\varphi/\partial pH)_{i,c} = 0$ (exp) $(\partial\varphi/\partial pH)_{i,c} = 0$ (calc)	— —
0.1 M KH ₂ PO ₄ + 0.2 M KCl + HCl or NaOH	$pH < 9$ $(\partial\varphi/\partial pH)_{i,c} = -0.105$ (exp) $pH > 9$ $(\partial\varphi/\partial pH)_{i,c} = 0$ (exp)	$pH < 9$ $(\partial\varphi/\partial pH)_{i,c} = -0.110$ (exp) $pH > 9$ $(\partial\varphi/\partial pH)_{i,c} = 0$ (exp)
0.03 M HCl + y M KCl; $y = 0.03$ M; 0.1 M; 0.3 M; 1.0 M.	$(\partial\varphi/\partial \log c)_{i,pH} = -(0.038\sim 0.040)$ (exp) $(\partial\varphi/\partial \log c)_{i,pH} = -0.049^*$ (calc)	— —
y M KCl; $y = 0.01$ M; 0.1 M; 0.3 M.	$(\partial\varphi/\partial \log c)_{i,c} = 0.046\sim 0.051$ (exp) $(\partial\varphi/\partial \log c)_{i,c} = 0.060$ (calc.)	— —

* assuming $\alpha = 0.55$

The values of the constants a and b in the Tafel equation for Ga and In-Ga alloy in pure alkali and acid solutions, as well as those of the coefficients $(\partial\varphi/\partial pH)_{i,c}$ and $(\partial\varphi/\partial \log c)_{i,pH}$ (c the electrolyte concentration in solution) in acid and alkaline solutions determined experimentally and calculated from the slow discharge theory with account taken of the influence of the electric double layer on the hydrogen evolution rate are compared in the Table. The values of α were calculated from the slope of the polarization curves in the corresponding solution.

It is clear from the Table that at the electrodes investigated the value of a in an alkaline solution is much higher than in an acid solution of the same concentration. This means that the transition from the hydroxonium ions discharge to the water molecules discharge should occur at $pH > 7$, which agrees with the data in Fig. 2. The experimentally observed dependence of the hydrogen evolution potentials at $i = \text{const.}$ on pH and the

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overall electrolyte concentration in solution are in fair agreement with the slow discharge theory*).

The results of the measurements carried out earlier by one of the authors at gallium of lesser purity (99.996%)¹⁵⁾ agree qualitatively with those obtained by us now, although the absolute values of η at gallium 99.996% pure were higher, particularly in alkaline solutions (at $i=1 \times 10^{-3}$ a/cm², $\Delta\eta = -\Delta\phi \sim 170$ mV). In accordance with this fact, the transition from the hydroxonium ions discharge to the water molecules discharge at less pure gallium occurred at higher pH values ($pH \sim 10$). The effect of impurities in gallium on the interfacial tension was discussed in reference (16). According to reference (16), the difference in the interfacial tension values of gallium 99.9998% pure and 99.996% pure at the potential of zero charge is 40 dyne/cm and increases as the potential is shifted in the negative direction, reaching ~ 60 dyne/cm at the negative end of the electrocapillary curve, which testifies to greater adsorption of impurities when Ga is negatively charged. This result is in qualitative agreement with the larger discrepancy in the hydrogen overvoltage values at Ga samples of different purity in alkaline solutions, as compared with acid ones.

The comparison of the interfacial tension and hydrogen overvoltage values of different Ga samples of high purity carried out in reference (17) showed that for Ga 99.9998% pure and better the impurities present in it no longer have an appreciable effect on its electrochemical properties.

The relation between the hydrogen overvoltage values at liquid Ga and the In-Ga alloy in acid and alkaline solutions observed by us is at variance with the conclusions of the paper of KITA and KURISU¹⁸⁾, in which a study was made of the dependence of η in alkaline solutions on the position of the element in the Periodic System. According to reference (18), at sp metals, including Ga and In, the hydrogen overvoltage in alkaline solutions is lower than in acid ones. In order to exclude a possible discharge of the alkali metals cations, the authors of reference (18) performed measurements in 1 M (CH₃)₄NOH. The hydrogen evolution potential at Ga at $i=1 \times 10^{-3}$ a/cm² in 1 M (CH₃)₄NOH calculated from the η value in 1 M (CH₃)₄NOH of reference (18), is equal to -1.7 V and is by 0.22 V more positive than the value observed by us for the case of hydrogen evolution from 0.5 M LiCl, LiOH, NaOH and KCl solutions (Fig. 1). According to reference (18), in the case of In at $i=1 \times 10^{-2}$ a/cm², $\phi = -2.06$ V, which is by 0.20 V more positive than the value obtained for the In-Ga alloy in 0.5 M LiCl, NaCl and KCl

* The independence of η of the concentration in pure acid solutions, predicted by the slow discharge theory, was first demonstrated for Ga in reference (14).

(Fig. 1)*). In reference (18) the purity of Ga and In was not indicated. The comparison of the overvoltage values measured by BUTLER *et al.* at the In-Ga alloy (19.2 at. % In)³⁾ and In¹⁹⁾ in a pure acid solution shows that at $i=1 \times 10^{-3}$ a/cm² the hydrogen overvoltage at In is greater than at the In-Ga alloy by approximately 0.03 V. Moreover, as was shown for the case of Hg in reference (20) and Ga (99.996% pure) in reference (15), the hydrogen evolution potentials from solutions of tetraalkylammonium bases and salts are shifted in the negative direction, as compared to the solutions containing alkali metals cations. The slopes of the polarization curves in reference (18) were for Ga 0.175 and for In-Ga 0.190.

The discrepancies between the data in reference (18) and our cannot be explained by the use of different electrodes (a stationary electrode in reference (18) and a dropping one in this work). Control experiments with stationary Ga and In-Ga electrodes in 0.5 M NaCl showed satisfactory agreement with the results of measurements with dropping electrodes. The slopes of the polarization curves were at Ga 0.115~0.120 and at In-Ga 0.125~0.130. Somewhat lower values of η for stationary electrodes than for dropping electrodes (by ~50 mV at Ga and by ~30 mV at the In-Ga alloy) seem to be due to the fact that the true surface of the stationary electrodes was greater than the calculated one, since the shape of the electrodes was that of ellipsoids of rotation and not of a sphere as was assumed in calculations. Besides, owing to good wetting of the surface in alkaline solutions, the solution crept under the drop base. However, it should be pointed out that whereas at the In-Ga alloy the values of η were stable, at Ga the slope of the polarization curves increased with time and η decreased, particularly at low current densities. Reproducible results could be obtained only at a fresh drop.

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* It is not possible to compare the hydrogen evolution potentials at In and In-Ga at $i=1 \times 10^{-3}$ a/cm² because at $i=2 \times 10^{-3}$ a/cm² the φ , $\log i$ curve of In in reference (18) showed a sharp drop of η down to the values corresponding to the steady state potential.

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