# THE ADSORPTION OF ALKALI METAL CATIONS ON LIQUID GALLIUM

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An investigation of the effect of alkali metal [1] and alkaline-earth metal [2] cation type on the kinetics of electrochemical hydrogen evolution on liquid gallium has shown that the potentials of hydrogen evolution, $\varphi_{H_2}$, coincide in solutions containing $Li^+$, $Na^+$, and $K^+$. In a $Cs^+$ solution of the same concentration $\varphi_{H_2}$ is shifted to less negative values by 40-50 mV, in $Sr^{+2}$ and $Ba^{+2}$ solutions by 75 mV, and in $Ca^{+2}$ solution by 110 mV. It was noted in [2] that, for additions of lithium and also potassium chloride to solutions of the alkaline-earth metal cations, $\varphi_{H_2}$ is displaced in the negative direction. The magnitude of the displacement depends on the nature of the alkali metal cation and increases in the series $Li^+$ to $K^+$. The results obtained attested to the partial displacement of alkaline-earth metal cations from the electrical double layer by the $Li^+$ and $K^+$ ions, and also to the different strength of $Li^+$ and $K^+$ adsorption on the gallium electrode.

The present paper deals with a systematic investigation of the effect of the nature of the alkali metal cations $Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$ on their adsorption strength on liquid gallium. To this end $\varphi - \log i$ curves were recorded at a dropping gallium electrode (purity of the gallium – 99.9998%, brand GL-000) at 32°C in solutions of 0.5 N $CaCl_2$ + 1.5 N MeCl where Me = $Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$, and also in 1.5 N solutions of KCl, RbCl, and CsCl. Solution purification techniques were the same as in [2].

The quantity $\Delta\varphi_{H_2} = \left(\varphi_{H_2}^{1.5N\ MeCl+0.5N\ CaCl_2} - \varphi_{H_2}^{1.5N\ MeCl}\right)_i$ characterizes the ability of alkali metal cations to be displaced from the surface layer by $Ca^{++}$ ion and can serve as a measure of the strength of adsorption of $Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$ on liquid gallium (it should be noted that the mechanism of $Ca^{++}$ action in the kinetics of hydrogen evolution on gallium from alkaline solutions still remains unexplained). Choice of the relationships between the $CaCl_2$ and MeCl concentrations in the solutions studied was chosen in order to achieve maximum sensitivity in the quantity $\Delta\varphi_{H_2}$.

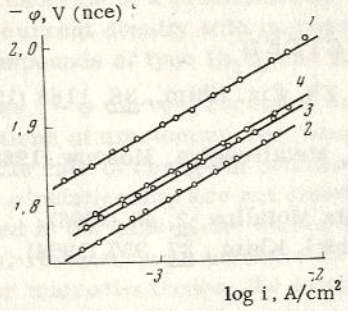



Fig. 1

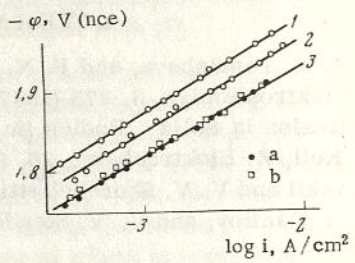



Fig. 2

Fig. 1. Polarization curves in: 1) 1.5 N KCl; 2) 1.5 N LiCl + 0.5 N $CaCl_2$; 3) 1.5 N NaCl + 0.5 N $CaCl_2$; 4) 1.5 N KCl + 0.5 N $CaCl_2$.

Fig. 2. Polarization curves in: 1) 1.5 N RbCl; 2) 1.5 N CsCl; 3a) 1.5 N RbCl + 0.5 N $CaCl_2$; 3b) 1.5 N CsCl + 0.5 N $CaCl_2$.

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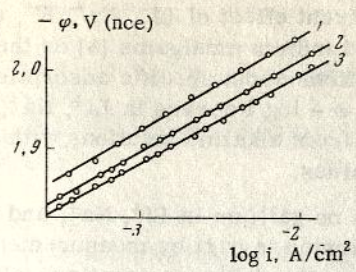



Fig. 3

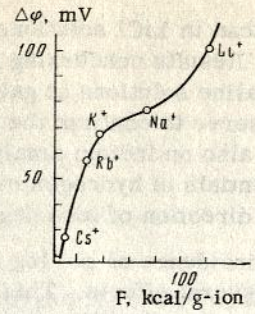



Fig. 4

Fig. 3. Polarization curves in 0.5 N solutions: 1) KCl, LiCl, NaCl; 2) RbCl; 3) CsCl. The results for 0.5 N LiCl, NaCl, KCl, and CsCl solutions were taken from [1].

Fig. 4. Dependence of $\Delta\varphi_{H_2}$ on the hydration energy F of alkali metal cations.

TABLE 1

| Change in solution composition | $(\Delta\varphi_{H_2})i$ mV |
|---|---|
| 1,5 *N* LiCl → 1,5 *N* LiCl + 0,5 *N* $CaCl_2$ | 100 |
| 1,5 *N* NaCl → 1,5 *N* NaCl + 0,5 *N* $CaCl_2$ | 76 |
| 1,5 *N* KCl → 1,5 *N* KCl + 0,5 *N* $CaCl_2$ | 67 |
| 1,5 *N* RbCl → 1,5 *N* RbCl + 0,5 *N* $CaCl_2$ | 57 |
| 1,5 *N* CsCl → 1,5 *N* CsCl + 0,5 *N* $CaCl_2$ | 27 |

$\varphi$ – log i curves in solutions of 1.5 N KCl and 1.5 N KCl (LiCl and NaCl) + 0.5 N $CaCl_2$ are presented in Fig. 1. The polarization curves in LiCl, NaCl, and KCl solutions coincide as was shown in [1]. Results of measurements in 1.5 N solutions of RbCl and CsCl and also 1.5 N RbCl (CsCl) + 1.5 N $CaCl_2$ are presented in Fig. 2.

Polarization curves for hydrogen evolution from alkaline solutions of rubidium salts have not been studied previously. From Fig. 2 it can be seen that the hydrogen evolution potential for 1.5 N RbCl is shifted in the negative direction by 20-25 mV with respect to the hydrogen evolution potential for a CsCl solution of the same concentration. The polarization curve at liquid gallium in 0.5 N RbCl in Fig. 3 coincides with the $\varphi$ – log i curves measured earlier [1] in 0.5 N LiCl, NaCl, KCl, and CsCl solutions. The $\varphi$ – log i curve in 0.5 N RbCl occupies an intermediate position between $\varphi$ – log i curves in 0.5 N solutions of LiCl, NaCl, and KCl, on one side, and CsCl on the other;

$$\left|\varphi_{H_2}^{LiCl,\ NaCl,\ KCl}\right| > \left|\varphi_{H_2}^{RbCl}\right| > \left|\varphi_{H_2}^{CsCl}\right|,\quad \varphi_{H_2}^{RbCl} - \varphi_{H_2}^{LiCl,\ NaCl,\ KCl} \sim 27\ \text{mV},$$

$$\varphi_{H_2}^{CsCl} - \varphi_{H_2}^{RbCl} \sim 15\ \text{mV}.$$

It is seen from Figs. 1 and 2 that addition of 0.5 N $CaCl_2$ to 1.5 N MeCl solutions results in a lowering of the $\varphi$ – log i curves towards less negative values. The slope of the polarization curves is not changed in this case. The absolute values of $[\Delta\varphi_{H_2}]_i$ depend on the nature of the alkali metal cation and increase in the following order: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ (see Table 1).*

The latter attests to a decrease in adsorption strength on gallium of the cations studied in the same order: $Li^+ < Na^+ < Rb^+ < Cs^+$. The observable effect is not directly dependent on the ionic hydration energy in the series $Li^+$ to $Cs^+$. Indeed, as is seen from Fig. 4 where the changes in $\Delta\varphi_{H_2}$ are plotted vs the hydration energy of the corresponding cations for infinite dilution [3], the change in $\Delta\varphi_{H_2}$ on going from $Na^+$ to $Li^+$ and from $Rb^+$ to $Cs^+$ is significantly larger than in the sequence $Na^+$, $K^+$, and $Rb^+$. Apparently, in order to account for the observable effects it is necessary to call on the idea of specific adsorption of alkali metal cations on gallium.

In [4] during measurement of electrocapillary curves in LiCl and KCl solutions it was noted that the lowering of the gallium surface tension for one and the same ionic activity in the solution is noticeably

* The possible amount of displacement in $\varphi_{H_2}$ towards less negative values, because of the increase in the bulk electrolyte concentration on addition of 0.5 N $CaCl_2$ to 1.5 N alkali metal chloride solutions, is within 6 mV according to calculation.

larger in KCl solutions than in LiCl solutions. The latter attested to the large adsorbability of $K^+$ with respect to $Li^+$ on gallium. Results concerning the different effect of $Li^+$, $Na^+$, $K^+$, and $Cs^+$ on hydrogen evolution overvoltage in alkaline solutions at gallium and indium amalgams [6] on the one hand, and on antimony [7] on the other also serve to confirm the assumptions about specific adsorption of alkali metal cations. Whereas on gallium and also on indium amalgam [6] $\varphi - \log i$ curves in $Li^+$, $Na^+$, and $K^+$ solutions coincide, on antimony [7], the potentials of hydrogen evolution from alkaline solutions with change from $Li^+$ to $Cs^+$ continuously shift in the direction of less negative values.

Apparently, the coincidence of $\varphi - \log i$ curves on gallium in $Li^+$, $Na^+$, and $K^+$ solutions is a result of the superposition of several effects. This is confirmed in part by measurements of differential capacity. As was shown [8], the capacity of gallium and mercury [9] electrodes continuously increase in the series $Li^+ > Na^+ > K^+ > Cs^+$ for a negatively charged surface.

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