STRUCTURE OF THE ELECTRIC DOUBLE LAYER ON EUTECTIC In – Ga ALLOY IN AQUEOUS AND ACETONITRILE SOLUTIONS

III. STRUCTURE OF THE ELECTRIC DOUBLE LAYER IN ACETONITRILE SOLUTIONS

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UDC 541.13

It has been shown [1, 2] that in aqueous solutions of electrolytes the structure of the electric double layer on a eutectic alloy of In–Ga (16.5 at. % In) differs from that on Hg. In this report we give the results of measurements of the differential capacitance at a dropping electrode on In–Ga eutectic alloy and on Hg in acetonitrile solutions. The literature data on the structure of the electric double layer on Hg in acetonitrile are scanty [3-6], and they cannot be used for comparison with In–Ga owing to possible differences in the potential jumps at the boundaries of the liquid connection between the aqueous solution of the reference electrode and the acetonitrile in [3-6] and in the present authors' work.

The method of measuring the differential capacitance at the dropping electrode was the same as in [7]. The ac frequency was in the range 310-5000 Hz. In some cases, as well as recording differential capacitance curves, we measured the polarization curves. The reference electrode was an aqueous saturated calomel electrode. The measurements were made at 32° C.* The acetonitrile, of "pure" grade, was distilled at atmospheric pressure four times over P_2O_5 to remove water, and twice without the P_2O_5. The purified acetonitrile had electrical conductivity $1.5 \cdot 10^{-7}\ \Omega^{-1} \cdot cm^{-1}$, close to the literature value [8]. We made control measurements of the differential capacitance on an In–Ga electrode in acetonitrile purified without P_2O_5 by the method in [9] and distilled in a rectification column. The results agreed with those obtained in solutions of acetonitrile purified by our present method. The $LiClO_4$ and KI were purified by recrystallization from aqueous solutions and dried under vacuum.

Figure 1 shows the potential dependences of the differential capacitance on the In–Ga alloy and Hg in acetonitrile in $LiClO_4$ solutions of various concentrations (0.1, 0.01, and 0.001 N). We also show the (C, φ) curve of In–Ga alloy in acetonitrile in 0.1 N KI. From this figure we see that in acetonitrile, as in water, at negative potentials in 0.1 N solutions of $LiClO_4$ and KI the capacitance of the electric double layer of In–Ga alloy varies little with the electrode potential; however, the absolute values of the capacitance in acetonitrile on In–Ga are less than in water. Thus the minimum value of the capacitance in 0.1 N $LiClO_4$ in acetonitrile is 10 $\mu F/cm^2$, whereas in water it is 16.9 $\mu F/cm^2$. When the electrode potential is shifted towards more negative values, we observe a sharp rise in capacitance. In a solution containing I^- anions, as in water, the capacitance rises at more negative potentials than in a solution containing ClO_4^- anions.

Comparison of the capacitance values on In–Ga and Hg electrodes in $LiClO_4$ solutions of various concentrations (Fig. 1) reveals that in acetonitrile, as in water, in dilute solutions the (C, φ) curves have a minimum due to the diffuseness of the electric double layer; the depth of the minimum increases as the solution is diluted. The potential of the minimum, both for In–Ga alloy and for Hg, is independent of the $LiClO_4$ concentration. Hence it follows that the ClO_4^- anion is not specifically adsorbed from acetonitrile onto In–Ga or Hg, and the potentials of the minima correspond to the zero-charge potentials $\varphi_{\varepsilon=0}$ of the test electrodes.

*The choice of experimental temperature was dictated by the fact that we intend to investigate the structure of the electric double layer in acetonitrile and on liquid gallium. The melting point of gallium is 29.8° C, and therefore the main data for liquid gallium in aqueous solutions are obtained at 32° C.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 9, No. 11, pp. 1676-1680, November, 1973. Original article submitted March 21, 1973.

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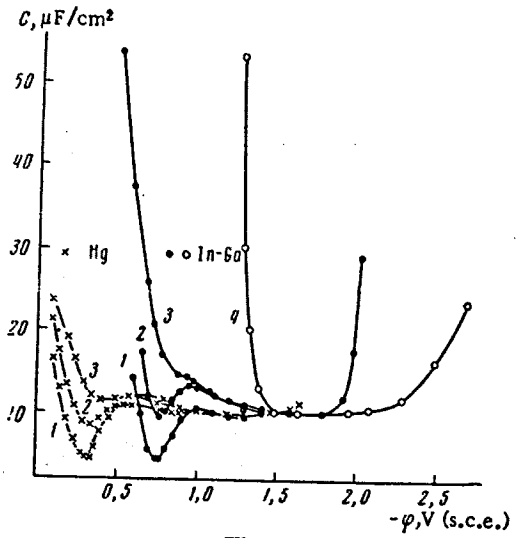


Fig. 1

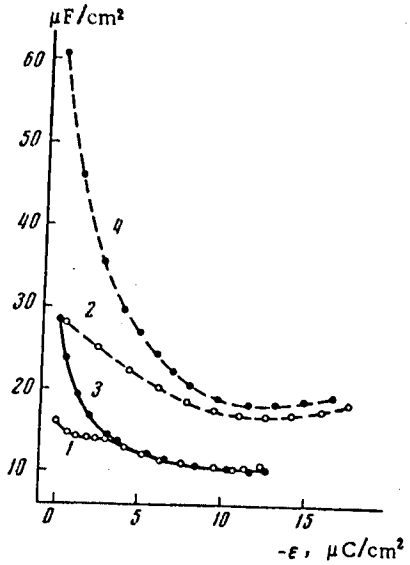


Fig. 2

Fig. 1. Differential capacitance curves in acetonitrile on Hg and In–Ga alloy in $LiClO_4$ solutions of the following concentrations: 1) 0.001; 2) 0.01; 3) 0.1 N; 4) 0.1 N KI.

Fig. 2. Capacitance of compact layer C_g vs electrode charge ε in solutions of inactive electrolytes in acetonitrile (1, 3) and water (2, 4), for Hg (1, 2) and In–Ga (3, 4). Solutions: 1, 3, 4) 0.1 N $LiClO_4$; 2) 0.1 N NaF.

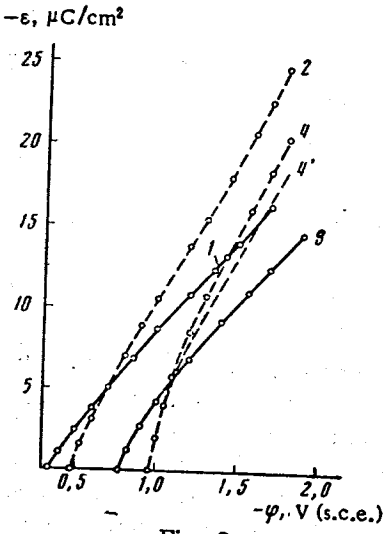


Fig. 3

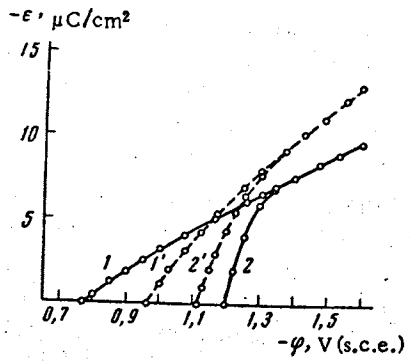


Fig. 4.

Fig. 3. Charge ε vs electrode potential φ in solutions of inactive electrolyte in acetonitrile (1, 3) and water (2, 4, 4') on Hg (1, 2) and In–Ga (3, 4, 4'). Curve 4' was plotted from curve 4 by multiplying the value of ε by $0.9 = C_g^{Hg} / C_g^{In-Ga}$.

Fig. 4. Charge ε vs potential φ on In–Ga alloy in acetonitrile (1, 2) and water (1', 2'), in the following solutions: 1, 1') 0.1 N $LiClO_4$; 2, 2') 0.1 KI.

We tested the applicability of the Gouy-Chapman theory to In−Ga and Hg electrodes in acetonitrile solutions. The calculation was performed by the method of Grahame [10]. For the dielectric constant in the diffuse layer we took the value 38.8 corresponding to the bulk value. The capacitance of the compact part of the double layer C_g was calculated from the data for 0.1 N $LiClO_4$. Both on mercury and the alloy in 0.01 and 0.001 N solutions of $LiClO_4$, at potential near the zero-charge point, the theoretical capacitances agreed with the experimental values.

The dependences of the double-layer capacitance C_g on the charge ε on In−Ga or Hg in aqueous and acetonitrile solutions of inactive electrolytes are plotted in Fig. 2. From this figure we see that in acetonitrile, at charges corresponding to adsorption of cations, in solutions of the same cation, the values of C_g on In−Ga and Hg are similar, whereas in water $C_g^{Hg}/C_g^{In-Ga} \sim 0.9$ [1].* As the negative charge decreases, both in acetonitrile and in water, C_g on In−Ga begins to rise more sharply than on Hg.

With the aim of elucidating the influence of the nature of the solvent on the value of $\Delta\varphi_\varepsilon = \varphi_\varepsilon^{Hg} - \varphi_\varepsilon^{In-Ga}$ at ε = const, we compared the (ε, φ) curves in aqueous and acetonitrile solutions (Fig. 3). In acetonitrile, the values of ε were calculated by integrating the (C_g, φ) curves, beginning from $\varphi_{\varepsilon=0}$. In aqueous solutions, similar curves were obtained by integrating the (C, φ) curves in 1 N Na_2SO_4.† Curve 4' in Fig. 3 was obtained by multiplying the values of ε calculated for In−Ga in water by the factor $0.9 = C_g^{Hg}/C_g^{In-Ga}$; in this way we tried to make a correction to the difference in the capacitance values on In−Ga and Hg in water at high negative charges.

From Fig. 3 (curves 1-3 and 4') we see that $\Delta\varphi_{\varepsilon=0}$ depends on the nature of the solvent; in acetonitrile, $\Delta\varphi_{\varepsilon=0} = 0.4$ V, in water, 0.48 V. At equal, sufficiently negative, charges $\Delta\varphi_\varepsilon = 0.33$-$0.3$ V, and it ceases to depend on the nature of the solvent and the charge on the electrode. A similar law in aqueous solution was found for the first time for Ga and Hg [7]. In the case of Ga and Hg, $\Delta\varphi_{\varepsilon=0} = 0.48$ V, whereas at negative charges $\Delta\varphi_\varepsilon = 0.17$ V, and it does not depend on ε; its absolute value is close to the contact potential difference between Ga and Hg [11]. We can suppose that $\Delta\varphi_\varepsilon$ between In−Ga and Hg, at equal sufficiently negative charges, also corresponds to the contact potential difference. Unfortunately there are no literature data on the work function of an electron for the eutectic alloy In−Ga.

The difference between the values of C_g on In−Ga and Hg at small negative charges shows that in acetonitrile, as in water, the adsorption of the solvent is observed to depend on the nature of the electrode metal at potentials close to the zero-charge point. At potentials remote from $\varphi_{\varepsilon=0}$, the structure of the electric double layer is the same on In−Ga as on Hg in acetonitrile. For In−Ga and Hg, the values of $(\Delta\varphi_{\varepsilon=0} - \Delta\varphi_{\varepsilon=q})$, $q \ll 0$, corresponding to the difference of adsorption potentials of the solvent, are 0.14 V in water and 0.09 V in acetonitrile.

Figure 4 compares the (ε, φ) curves on In−Ga in 0.1 N $LiClO_4$ and KI solutions in water and acetonitrile. The values of ε were found by integrating the (C, φ) curves in the corresponding solutions. As the constant of integration we took the value of ε at the potential of coalescence of the (C, φ) curves in 0.1 N $LiClO_4$ and 0.1 N KI. The difference between the capacities due to the nature of the cation was not taken into account. From the figure it follows that the adsorption potential drop of I^- on In−Ga in water is less than that in acetonitrile. This is evidently due both to the higher adsorbability of the I^- anion from acetonitrile solution and to the lower values of the compact-layer capacitance in acetonitrile than in water.

As we see from Fig. 1, at very negative potentials, both in $LiClO_4$ and KI solution the measured capacitance on In−Ga alloy in acetonitrile increases, and in contrast with the region of less negative potentials it depends on the ac frequency. A cathode current begins to flow to the electrode, and it rapidly increases as the potential becomes more negative. In $LiClO_4$ solution the rise in capacitance and the flow of current are observed at less negative potentials than in KI solution, the difference being about 0.5-0.6 V. These data indicate discharge of the alkali-metal cations on In−Ga alloy. In aqueous solutions it is not possible to reach potentials corresponding to discharge of alkali-metal cations on an In−Ga electrode or Ga electrode, owing to the emission of hydrogen by discharge of water molecules. On mercury in aqueous solutions, the half-wave potential of Li^+ is about 190 mV more negative than that of K^+ [12]. The separation of Li^+ on In−Ga alloy from acetonitrile solution at potentials more negative than for K^+ ($\Delta\varphi \sim 0.5$-0.6 V) cannot be explained by a possible difference between the concentrations of Li^+ and K^+ in the solutions caused by the formation of associates, because the resistances of 0.1 N solutions of $LiClO_4$ and KI in acetonitrile are of the same order. The difference between the reduction potentials of Li^+ and K^+ also

*This will be dealt with in a separate report.

†In 1 N solutions, the measured capacitance is close to C_g, and can thus characterize the specific interaction of the solvent with the electrode material.

cannot be explained by the difference between the potential jumps at the boundary of the liquid connection between the aqueous solution of the reference electrode and the 0.1 N solutions of $LiClO_4$ and KI in acetonitrile. The observed phenomenon must apparently be attributed to the high value of the free energy of formation of an intermetallic compound containing Li^+ [13].

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