ELECTROCAPILLARY PROPERTIES OF A GALLIUM-INDIUM ALLOY

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Extending work on the electrocapillary behavior of binary systems containing gallium [1], the eutectic alloy of gallium with indium was studied (indium content 16.7 atom %, melting point 15.73° [2]). Gallium and indium having a purity of 99.9998 and 99.999%, respectively, were used in the work. The mixture was prepared by dissolving indium in gallium under insignificant heating and under a deoxygenated solution of ~0.1 N KOH, and was kept in a separate reservoir under hydrogen atmosphere. Electrocapillary (EC) curves were measured with the aid of the Gouy capillary electrometer used in [1]. The electrometer was filled with the alloy by a method that excluded contact of oxidized metal with the working part of the capillary. The specific weight of the alloy was determined with the aid of a pycnometer. The measurements were made at 36°, which corresponded to the conditions during measurements made previously [3] on pure gallium. A normal calomel electrode was used as reference electrode. The concentrations of the alloys are given in atom %. Different portions of the EC curves were recorded in solutions of different acidity, as in [3] and [1]: from -0.8 to -1.2 V in salt solutions acidified to 0.1 N; from -1.05 to -1.6 V in salt solutions acidified to 0.001 N, and from -1.5 to -1.8 V in solutions made 0.01 N alkaline with KOH. For acidifying we used the acid having the same anion, except in KI solution which was acidified with hydrochloric acid.

Figure 1 gives EC curves of the gallium-indium alloy in 1 N solutions of KCl, KI, K_2SO_4, and $NaClO_4$, as well as in 1 N KCl solutions to which iso-amyl alcohol, phenyl, and hydroquinone were added. For comparison curves obtained in similar solutions on gallium [3] are given in Fig. 2.*

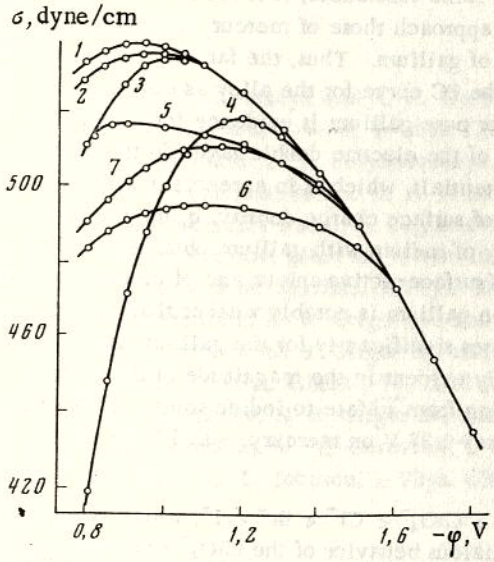

Fig. 1. Electrocapillary curves of the gallium-indium alloy in the solutions: 1) 1 N K_2SO_4; 2) 1 N $NaClO_4$; 3) 1 N KCl; 4) 1 N KI; 5) 1 N KCl + 0.1 M iso-amyl alcohol; 6) 1 N KCl + + 0.5 M phenol; 7) 1 N KCl + 0.5 M hydroquinone.

It is seen from Figs. 1 and 2 that when indium is added to the gallium, the maximum interfacial tension, σ_{max}, is rather strongly depressed and with the alloy studied, it approaches σ_{max} of pure indium.† This effect points to the considerable surface activity of indium as compared to gallium and to a condition of the alloy's surface layer approaching saturation with indium. The potentials of the EC maximum, φ_{max}, of gallium and of the gallium-indium alloy practically coincide for solutions of nonactive electrolytes and electrolytes of low activity, a fact which, evidently, is due to the closeness of the values for the potentials of zero charge (pzc) of gallium and indium. In fact, according to the data of [5] the pzc of In in aqueous chloride solution is -1.03 to -1.08 V (nce).

*The EC curves in solutions containing phenol and hydroquinone were measured only on gallium of 99.996% purity (σ_{max} in 1 N KCl: 603 dyn/cm), and were not reported in [3].

†The value of σ_{max} of indium in aqueous solution can be approximately evaluated by extrapolating the σ_{max} values reported in [4] for amalgams to pure In. According to these data σ_{max} in 1 N Na_2SO_4 at 20° is 525-530 dyn/cm. It must be noted that the σ_{max} values for Ga and In in a LiCl + KCl melt at 450° (which are 650 dyn/cm and 525 dyn/cm, respectively [5, 6]) are very close to the σ_{max} values in aqueous solutions.

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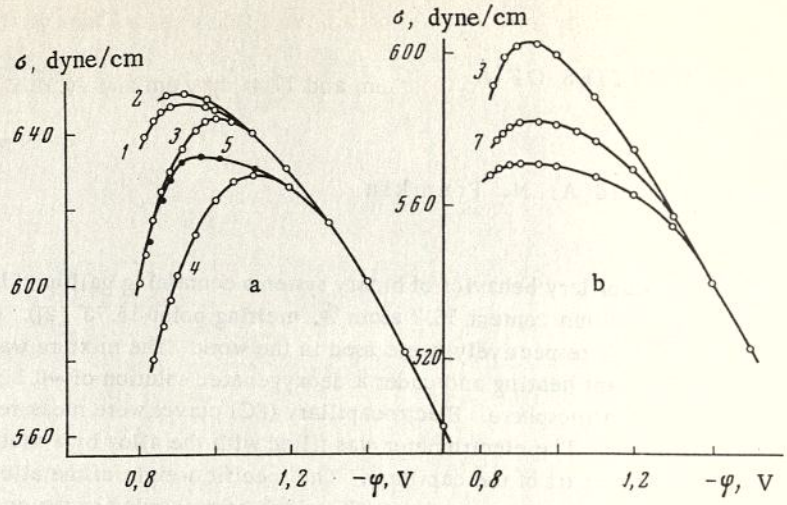

Fig. 2. Electrocapillary curves of gallium in the solutions: 1) 1 N K_2SO_4; 2) 1 N $NaClO_4$; 3) 1 N KCl; 4) 1 N KI; 5) 1 N KCl + 0.1 M iso-amyl alcohol; 6) 1 N KCl + 0.5 M phenol; 7) 1 N KCl + 0.5 M hydroquinone. Purity of gallium: a) 99.9998%; b) 99.996%.

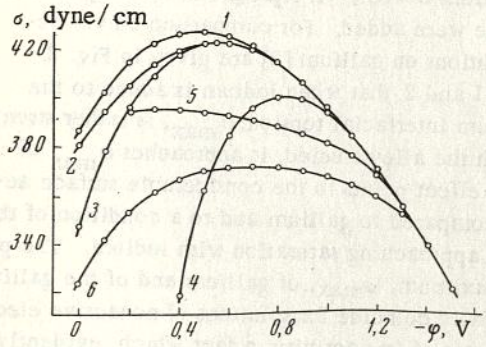

Fig. 3. Electrocapillary curves on mercury in the solutions: 1) 1 N Na_2SO_4; 2) 1 N $NaClO_4$; 3) 1 N KCl; 4) 1 N KI; 5) 1 N KCl + 0.1 M iso-amyl alcohol; 6) 1 N KCl + 0.5 M phenol.

When the EC curves obtained on the Ga-In alloy are compared with curves on gallium and on mercury (Fig. 3) in solutions containing the same substances, it is seen that the EC properties of the alloy approach those of mercury but differ significantly from those of gallium. Thus, the far lower slope of the positive branch of the EC curve for the alloy as compared to that of the curves for pure gallium is evidence for a reduction in the capacity, C, of the electric double layer on the alloy at not too negative potentials, which is in agreement with the data on the dependence of surface charge density, q, on potential, φ, for the 19.2-% alloy of indium with gallium obtained in [7].* The adsorbability of surface-active anions and of neutral organic molecules, which on gallium is notably weaker than it is on mercury [3], increases significantly for the gallium-indium alloy, and this is especially evident in the magnitude of the shift of φ_{max}. Thus in going from sulfate to iodide solutions the shift of φ_{max} ($\Delta\varphi_{max}$) is -0.37 V on mercury, -0.25 V on Ga-In, and -0.18 V on Ga.

The variation of surface activity of the anions in the series $SO_4^{2-} < ClO_4^- < Cl^- < Br^- < I^-$, which is typical for mercury and which in the case of gallium was disturbed by the anomalous behavior of the ClO_4^- ion, is reestablished on the alloy as can be seen by comparing Figs. 1, 2, and 3. In fact, on Ga-In as well as on Hg and on In amalgams [10], the ClO_4^- anion is surface-active, while on Ga it exhibits negative adsorbability in rather concentrated

*Butler and Meehan [7] believe that the direct measurements of capacitance and interfacial tension on gallium as well as its alloys are not sufficiently reliable because a faradaic current due to the dissolution of gallium and the evolution of hydrogen is flowing in the region of the pzc. However, the q-φ curves [7] obtained by analyzing the potentiostatic current-time curves on a rapidly dropping gallium electrode agree well with the results of integrating the experimental C values on gallium from [8]. Moreover, the pzc of both gallium and the gallium-indium alloy in perchlorate solution [7] agree with the corresponding values determined from the minimum in C from [9] and from the maximum of the EC curves in the present work. A certain difference in the concentrations of the alloy between [7] and the present work is of no importance since the position of the pzc does not change when going from gallium to the 16.7% alloy in $NaClO_4$ solutions, and there is no reason to expect a perceptible change when raising the In content in Ga further to 19.2 %.

solutions [3, 11]. It must be noted that according to the data of [10], the specific adsorption of ClO_4^- on concentrated indium amalgam is less than that on mercury. A notable increase in surface activity on the alloy is also observed for neutral organic molecules. Thus, the shifts in σ_{max} and φ_{max} caused by the molecules of iso-amyl alcohol are, respectively, 10 dyn/cm and +0.08 V for gallium and 17.4 dyn/cm and +0.13 V for the gallium-indium alloy.

The similarity in EC properties between the gallium-indium alloy and mercury is also manifest in the EC behavior of aromatic compounds on these interfaces. It is well-known that on a positively charged mercury surface there is π-electron interaction between the metal surface and the aromatic molecules which causes them to become adsorbed although in the case of phenol the adsorption is weakened at large positive surface charge densities by the strong repulsion between the C_6H_5OH molecules [12]. It follows from the shape of the EC curves (Fig. 2) that in the case of gallium, the π-electron interaction is very insignificantly developed, which may be attributed to the presence of a stable layer of chemisorbed water molecules on the surface of gallium. A comparison of Figs. 1 and 3 shows that the behavior of phenol at the Ga-In alloy surface approximates that on mercury. The shift in φ_{max}, which is absent in the case of gallium, is -0.085 V on the alloy. Even more clearly pronounced is the shift of φ_{max} toward negative potentials in the presence of hydroquinone.

The data obtained indicate that there is a difference in the structure of the electric double layer between the Ga-In alloy and Ga, and that is approaches the structure of the double layer on mercury. This hypothesis is in agreement with the results of comparing the excess free energy values, W, of wetting an uncharged metal surface with water for gallium, indium, and mercury. The value of W for indium can be calculated by taking the surface tension of indium as approximately 595-600 ergs/cm^2.* The value of W obtained, which is 135 erg/cm^2, is substantially less than that for gallium (180-190 ergs/cm^2), and only somewhat higher than for mercury (125 ergs/cm^2) [4]. For quantitative conclusions regarding the relative structures of the electric double layer on gallium, the gallium-indium alloy, and mercury experimental measurements of the capacity of the alloy are required which are proposed to be carried out in the future.

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*This value was determined by extrapolating the values of surface tension of indium amalgams in vacuo at 25° reported in [13] to pure indium.