ELECTROCAPILLARY PROPERTIES OF THE GALLIUM-MERCURY SYSTEM

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There are now a number of studies devoted to the electrocapillary behavior of liquid gallium [1-4]. A study of the electrocapillary properties of binary systems, containing gallium, as a result of which information can be obtained on the surface composition of liquid electrodes of this kind, is also of considerable interest. Information on the structure of the surface layer of gallium and indium amalgams is contained in [5, 6]. On the other hand, an electrocapillary study of gallium containing impurities of other metals is of interest in connection with the detection in [3] of a phenomenon of substantial dependence of the electrocapillary properties of gallium upon the degree of its purity.

We selected the gallium–mercury system as the object of investigation. According to the literature data [7], the solubility of mercury in gallium at 35°C is 6.1% by weight (2.27 atomic %). In the work we used metallic gallium 99.9998% pure and triple-distilled mercury. The mercury was dissolved in gallium under a deoxygenated solution of 0.1 N KOH; the mixture obtained was left in an atmsophere of hydrogen overnight for homogenization.

The electrocapillary (EC) curves were measured with a Gouy capillary electrometer of reduced dimensions, designed earlier [3] to take EC curves on pure gallium. The inner cross-sectional diameter of the conical capillary was about 60 μ. The electrometer was filled with gallium according to a method eliminating penetration of the oxidized metal into the working portion of the capillary. The measurements were conducted at 36°C. The electrometer constant K, with the aid of which the measurable effective heights of the column of gallium were converted to values of interfacial tensions σ, was determined analogously to that described in [3]. The density of gallium with additions of mercury d was calculated on the assumption of additivity. For gallium the value of the density at 36°C, equal to 6.090, was taken from [8-10]. The density of mercury at 36°C, according to the table data, is 13.51. The value of d obtained for Ga + 2.09 atomic % Hg is in good agreement with the values cited in [11], determined for this system with the aid of a pycnometer (6.289 and 6.283, respectively). In order to continue the measurements as far as possible in the anodic and cathodic directions, which is hindered by the formation of an oxide film on gallium and the evolution of hydrogen, respectively, just as in [3], different portions of each EC curve were taken in solutions of different acidities: from −1.8 to −1.5 V in 1N KCl, alkalinized with a solution of KOH to 0.01 N; from −1.6 to −1.05 V in 1N KCl, acidified with hydrochloric acid to 0.001 N; and from −1.2 to −0.84 V in KCl, acidified to 0.1 N. The measurements in the region of more positive potentials could not be continued through a further increase in the acidity on account of a substantial evolution of gas bubbles in the capillary.

The figure presents the EC curves of gallium with additions of mercury in concentrations from 0.001 to 2.18 atomic % in acidified and alkalinized solutions of 1N KCl (the potentials are given with respect to the normal calomel electrode). As can be seen from the figure, a 0.001% inpurity of mercury does not influence the interfacial tension of gallium. When the mercury concentration in the gallium is further increased, a decrease in σ is observed, while beginning with an addition of 0.18%, a shift in the electrocapillary maximum in the direction of more positive values is also observed. The decrease in the maximum interfacial tension $\sigma_{\max}$ on gallium containing 2.18% Hg, in comparison with $\sigma_{\max}$ of pure gallium, reaches 170 dyn/cm. The shift of the zero charge potential φ_0 of the system Ga + 1.06% Hg from φ_0 of pure Ga is 0.2 V. The latter quantity is approximate, since measurements in the anodic region could not be continued to potentials more positive than φ_0.

Our data on the zero charge potentials of the system Ga + Hg do not agree with the data of Butler[11], who obtained a value $\varphi_0 = -0.87$ V by measuring the current flowing on a drop in a solution of 0.1 N $HClO_4$ for the system Ga + 1.64% Hg (I). As can be seen from the figure, in a solution of 1N KCl on Ga + 1.43% Hg (II), φ_0 lies at a more positive potential, while on the basis of the greater adsorbability of Cl^- in comparison with ClO_4^- on gallium and considering the shift of φ_0 in the positive direction with increasing Hg concentration in Ga, φ_0 of system I should have been more positive than φ_0 of system II. The decrease in the EC curve with increasing mercury content in the gallium is an indication of positive adsorption of Hg on the surface of the alloy within the investigated potential region. The EC curves of gallium and gallium with additions of mercury are broken off in the anodic region too

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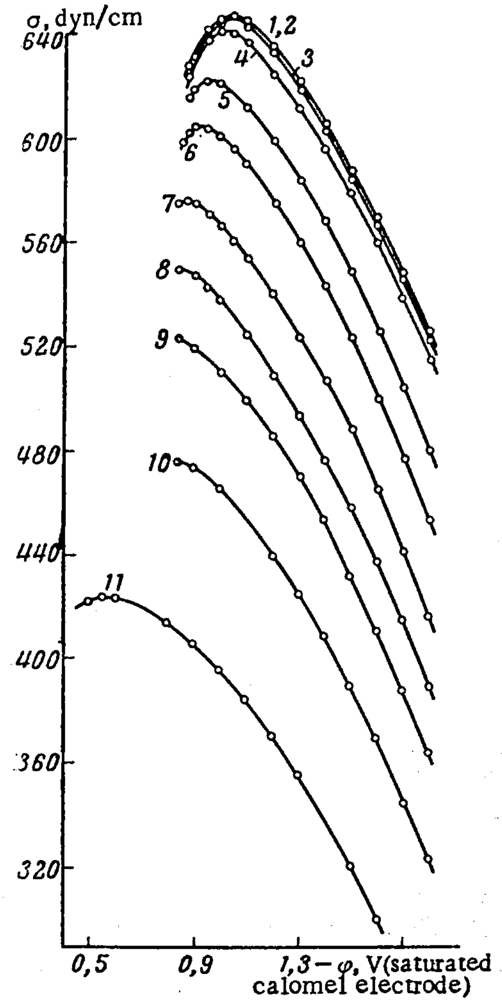

Fig. 1. Electrocapillary curves of gallium with additions of mercury (atomic %): 1) 0; 2) 0.001; 3) 0.004; 4) 0.03; 5) 0.18; 6) 0.36; 7) 0.70; 8) 1.06; 9) 1.43; 10) 2.18; 11) 100.0.

early to be able to speak of the point of their intersection. Such intersection of the EC curves has been observed on alloys of Cd−Sn [12] and Te−Bi [13] and indicated a transition of the positive adsorption of Sn and Bi, respectively, in the surface layer of the alloy to negative adsorption when the potential was shifted in the direction of more positive values. It may be that in the case of Ca + Hg the point of intersection lies in the region of potentials more positive than those at which electrocapillary measurements can be conducted in this system.

From the data of the dependence of the interfacial tension upon the mercury concentration in gallium at constant potential, we can calculate the value of the positive adsorption of Hg on the surface of the alloy, using the Gibbs equation of the adsorption isotherm $\Gamma_{\mathrm{Hg}} = -\frac{1}{RT}(\partial\sigma / \partial \ln a_{\mathrm{Hg}})_{\varphi}$, where Γ_{Hg} is the surface excess of Hg with respect to gallium; a_{Hg} is the activity of mercury in gallium. The literature known to us contains no information on the values of a_{Hg}. The results of determinations of the activity of mercury in gallium and a calculation of the value of Γ_{Hg} in the system Ga + Hg will be published in our following communication.

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