ELECTROCAPILLARY CURVES OF LIQUID GALLIUM

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The data available in the literature on the electrocapillary behavior of gallium are extremely scanty [1, 2]. In the cited works, measurements were conducted with simplified capillary electrometers, since the amount of gallium used was too small for the use of more accurate methods. The purity of the gallium was 99.7%. The purpose of this work was to study the electrocapillary phenomena and adsorption of surface-active substances on as pure gallium as possible, as well as to reveal the influence of the degree of purity of the metal on its electrocapillary properties. The measurements, unless indicated otherwise, were conducted with gallium 99.9998% pure, purified according to the method of the Rare Metals Institute.*

The measurements of the electrocapillary curves were conducted with the Gui capillary electrometer, described in [3], of reduced dimensions, with a barometric tube 2 mm in diameter and a conical capillary, possessing a diameter of about 16 μ at the ground joint. The construction of the instrument permitted the performance of measurements with 40 g of the metal. The electrometer was filled with liquid gallium according to a method excluding penetration of oxidized metal into the working portion of the capillary. The capillary depression of gallium was determined in an individual U-shaped vessel, possessing two bends of the same diameters as the two tubes on the electrometer. The entire setup was situated in an air thermostat; the measurements were conducted at 36°.

The constant of the electrometer K, by which the measured effective heights of the gallium column were converted to values of the boundary tension σ, was determined according to the formula

$$K_{\mathrm{Ga}} = K_{\mathrm{Hg}} \frac{d_{\mathrm{Ga}}}{d_{\mathrm{Hg}}},$$

where K_{Hg} is the constant of the electrometer, calibrated according to mercury, determined in the well-known way from measurements of the effective heights of the mercury column in a solution of Na_2SO_4; d_{Ga} and d_{Hg} are the densities of Ga and Hg at 36°, equal to 6.09 and 13.51, respectively. Before the beginning of operations, the electrometer was checked each time by taking the curve in a 1 N solution of KCl + HCl, in which the most complete and well-reproducible data were obtained.

Figure 1 presents a series of electrocapillary curves (potentials with respect to saturated calomel electrode). To avoid interference with conducting the measurements, as a result of the formation of oxide films, observed at more negative potentials, the more alkaline the solution [1], and the evolution of hydrogen during cathode polarizations, the curves were taken from each anode successively in three or four solutions of different acidity: from -0.80V to -0.95 V in 1 N acid (only curves 1 and 2, Fig. 1); from -0.86 V to -1.1 V in a solution of salt in the presence of 0.1 N acid; from -1.0 V to -1.6 V in a solution of salt in the presence of 0.001 N acid; from -1.5 V to -1.8 V in a solution of salt in the presence of 0.01 N alkali. The values of σ, obtained in the overlapping potential intervals, coincided well, which indicates the absence of any influence of the adsorption of hydroxyl and hydrogen on the anode and cathode ends of each portion of the curve, respectively, which should have led to a dependence of σ on the solution pH. However, it was not possible to make the parts of the curve taken in 1 N H_2SO_4 and 1 N Na_2SO_4 + 0.1 N H_2SO_4 (curve 1) coincide; a difference of 4 dyn/cm was observed between the curves of these two solutions at -0.95 V; the intermediate portion on the curve was therefore denoted by a dotted line. The measurements at

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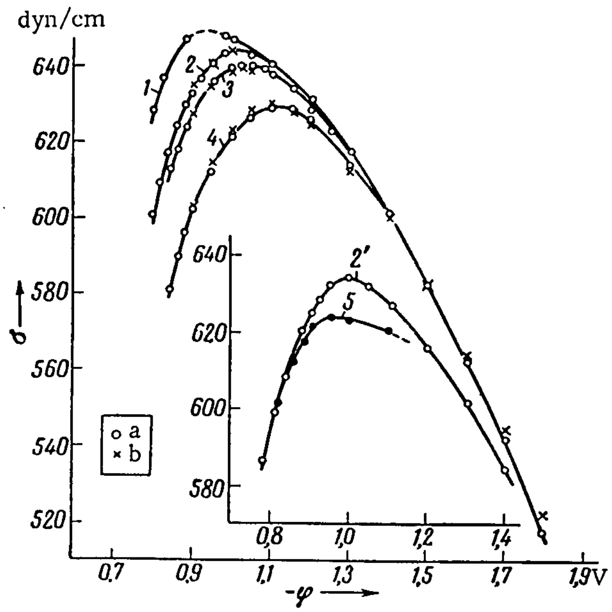

Fig. 1. Electrocapillary curves of Ga (99.9998%) in solutions: 1) 1 N H_2SO_4 and 1 N $K_2SO_4 + H_2SO_4$; 2) 1 N HCl and 1 N KCl + HCl; 3) 1 N KBr + HCl; 4) 1 N KI + HCl; 5) 1 N HCl + 0.1 M isoamyl alcohol and 1 N KCl + 0.1 N HCl + 0.1 M isoamyl alcohol. The curve of isoamyl alcohol and the curve of the background KCl + HCl corresponding to it (2') were separated in an individual graph, since they were obtained with a sample of Ga of somewhat lower purity. a) Experimental data; b) data calculated from capacitance measurements.

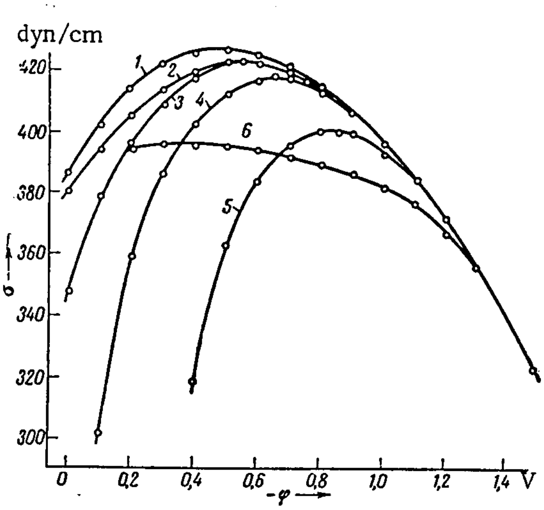

Fig. 2. Electrocapillary curves of Hg in solutions: 1) 1 N Na_2SO_4 + 0.1 N H_2SO_4; 2) 1 N $NaClO_4$ + 0.1 N $HClO_4$; 3) 1 N KCl + 0.1 N HCl; 4) 1 N KBr + 0.1 N HCl; 5) 1 N KI + 0.1 N HCl; 6) 1 N KCl + 0.1 N HCl + 0.1 M isoamyl alcohol.

potentials more positive, for example, than −0.95 V in a solution of 1 N KCl + 0.1 N HCl, were performed during anode polarization of the meniscus in the capillary (the normal potential of a gallium electrode lies at −0.81 V), which, however, apparently did not lead to any difficulties.

We compared the experimental electrocapillary curves with the σ, φ curves calculated by the method of double integration from the data of the dependence of the differential capacitance C on the potential, obtained on a dropping gallium electrode at the same degree of purity of the metal [4]. The integration constants for KCl + HCl were selected so as to guarantee coincidence of the observed and calculated curves at the electrocapillary maximum; for the remaining solutions, they were selected on the basis of an assumption of coincidence of the descending branches of the electrocapillary curves of various anions at sufficiently negative φ. As can be seen from Fig. 1, in all cases the results obtained by the two different methods coincide well, which is a confirmation of the reliability of the electrocapillary measurements. On the other hand, the values of the capacitance cited in [5] are in sharp contradiction to the electrocapillary measurements.

Table 1 presents the potentials of the zero charge of gallium φ_0 in various solutions, determined from the electrocapillary curves (I) and from the potential dependence of the charge density [4] (II), as well as the values of the maximum boundary tension σ_{max}. The values of φ_0 (I) and σ_{max} for $NaClO_4 + HClO_4$ were determined only for gallium of a somewhat lower degree of purity and were calculated on the basis of measurements with the anions SO_4^{2-} and Cl^-, which were performed with both samples. In a comparison of the electrocapillary curves obtained on gallium with the curves in solutions containing the same anions, taken on mercury (Fig. 2), it can be seen that the surface activity of the anions SO_4^{2-} (or HSO_4^-), Cl^-, Br^-, I^- vary in the same sequence as on mercury, but more weakly pronounced. This has an especially great effect on the value of the displacement of φ_0. Thus, as we pass from sulfate solutions to iodide solutions, the decrease in σ_{max} and the shift of φ_0 comprise 20 dyn/cm and −0.18 V, respectively, in the case of gallium, 26.5 dyn/cm and −0.27 V in the case of mercury. Other characteristic differences in the behavior of anions on the boundary with gallium, in comparison with the boundary with mercury, are closeness of the adsorbabilities of the Cl^- and Br^- ions, the absence of surface activity in the ClO_4^- ion, and the more pronounced surface activity in the SO_4^{2-} (or $H_2SO_4^-$) ion.

A substantial reduction of the activity of the adsorbed substance on gallium is observed in the case of isoamyl alcohol (Figs. 1 and 2). In this case, however, the shape of the electrocapillary curve characteristic of aliphatic alcohols on mercury is also preserved on gallium.

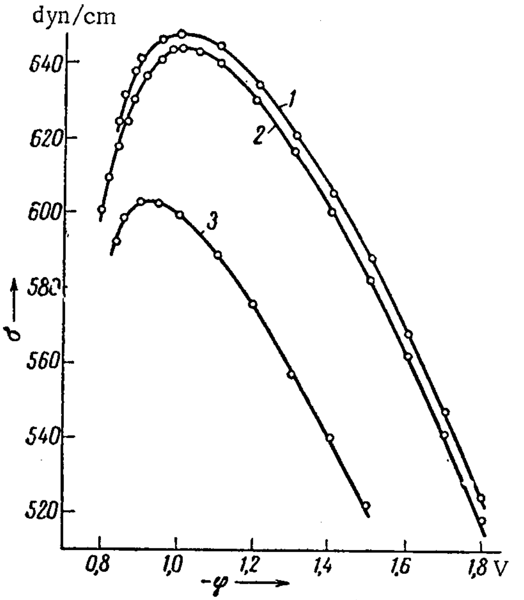

Fig. 3. Electrocapillary curves in solutions of 1 N HCl and 1 N KCl + HCl on Ga with purity 99.99999% (1), 9.9998% (2), 99.996% (3).

Electrolyte	$NaClO_4$ + $HClO_4$	Na_2SO_4 + H_2SO_4	KCl + HCl	KBr + HCl	KI + HCl
φ_0 (I)	−0,90	−0,93	−1,01	−1,04	−1,11
φ_0 (II)	−0,89	−0,925	−1,00	−1,03	−1,10
σ_{max}	653,9	648,9	644,0	640,3	628,9

As it follows from the direct measurements of [4], and the slope of the electrocapillary curves, the capacitance of the electric double layer on gallium at not too negative potentials is very great. The sharp asymmetry of the electrocapillary curves, which is observed on mercury only in the case of the most surface-active anions, such as, for example, I^-, is a general phenomenon in the case of gallium. It has already been indicated that these high values of C likewise cannot be explained by the adsorption of hydroxyl or by oxidation of the surface. We assume that the characteristics of the electrocapillary behavior of gallium are determined by the chemosorption of water molecules.

Frumkin has indicated that the gain in free energy when an uncharged surface of gallium is wet with water (180-190 erg/cm^2) is substantially greater than in the wetting of mercury (125 erg/cm^2) [6]. Unfortunately, an exact calculation of the first value is hindered by the fact that the measurements of the tension on the gallium-water boundary at the electrocapillary maximum and on the gallium-vacuum boundary were performed with preparations of different degrees of purity (see below).*

With the shift in the potential toward more negative values, the dipoles of water are turned with their negative, i.e., oxygen,ends toward the surface of the gallium. The stronger bond of gallium to water explains the decrease in the adsorbability of the ClO_4^- ion and aliphatic alcohols as we pass from Hg to Ga. The adsorbability of the ClO_4^- ion and aliphatic compounds is determined primarily by their repulsion from the volume of the solution as a result of the interaction between the water molecules [5, 8]; the presence of a layer of firmly bound water at the boundary of separation should prevent the adsorption process.

The orientation of the water dipoles with their negative ends toward the metal should have an unfavorable influence on the adsorbability of the anions as a result of electrostatic interaction. This interaction may explain the fact that on the anode end of the electrocapillary curve, the capacitance of gallium in solutions of iodide is no greater, but even somewhat smaller,than in solutions of other anions [4]. The change in the orientation of water with polarization is also confirmed by the fact that the difference in the values of φ_0 for mercury and gallium in the absence of adsorption of anions (0.42 V) substantially exceeds the difference between the values of the potential corresponding to different values of the charge ε at negative charges of the surface (0.17 V) [4], although another explanation can also be given for the latter phenomenon.

The series of peculiarities of the adsorption of anions on gallium, enumerated above, however, still requires additional consideration. Finally, it should be mentioned that the idea of reorientation of the adsorbed dipoles of water upon a change in the potential has recently been enlisted to explain the electrocapillary behavior of water on mercury [9-11]. These phenomena are apparently more pronounced in the case of gallium; the results obtained with gallium may also lead to a reconsideration of the conclusions pertaining to mercury.

We detected a strong influence of the degree of purity of the gallium on the electrocapillary curves. It can be seen in Fig. 3 that in the case of gallium 99.996% pure, the maximum of the boundary tension lies at − 0.92 V

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*The data of [7], in which measurements were conducted with H_2 and CO_2, on the one hand, and in 0.1-0.2 N HCl, on the other, indicates a value of ~170 erg/cm^2.

in KCl, which coincides with the data cited in the old studies. The value of σ_{max} is lowered in comparison with curve 2 by 41 dyn/cm. Curve 1 of Fig. 3 was obtained with gallium 99.99999% pure (Eagle Paicher Company, United States), a sample of which we obtained as we were completing this work, thanks to the kindness of Professor J. O'M. Bockris. In this case σ is even somewhat higher (by 4-6 units) than on curve 2; the value of φ_0 is the same. A comparison of the values of σ obtained at various pH indicates the somewhat easier passivation of gallium of the highest purity at the positive end of the curve.

The dependence of the electrocapillary properties of gallium on its purity indicates the possibility of a check on the purity of gallium according to electrocapillary data.

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