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Abstract

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ELECTROCAPILLARY CURVES OF LIQUID GALLIUM

The data available in the literature on the electrocapillary behavior of gallium are extremely few ([1,2]). In the cited works the measurements were carried out with simplified capillary electrometers, since the amount of gallium used was too small for the application of more accurate methods. The purity of the gallium was 99.7%. The aim of the present work was to study electrocapillary (e.c.) phenomena and the adsorption of surface-active substances on gallium of the highest possible purity, and also to determine the influence of the degree of purity of the metal on its e.c. properties. Unless otherwise stated, the measurements were carried out with gallium of 99.9998% purity, purified by the method of the Institute of Rare Metals*.

Measurements of the e.c. curves were made with a Gouy capillary electrometer, described in ([3]), of reduced dimensions, with a barometric tube 2 mm in diameter and a conical capillary having, at its cut, a diameter of about 60 μ. The design of the instrument made it possible to carry out measurements with 40 g of metal. The electrometer was filled with liquid gallium by a method excluding the entry of oxidized metal into the working part of the capillary. The capillary depression of gallium was determined in a separate U-shaped vessel, having two limbs of the same diameters as the two tubes of the electrometer. The entire apparatus was placed in an air thermostat; the measurements were carried out at 36°. The electrometer constant K, by means of which the measured effective heights of the gallium column were converted into values of the interfacial tension σ, was determined from 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 with mercury, determined in the usual 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 respectively to 6.09 and 13.51. Before the beginning of the work the electrometer was checked each time by recording a curve in $1N$ KCl + HCl, in which the most complete and well-reproducible data were obtained.

Figure 1 gives a series of e.c. curves (potentials relative to the n.c.e.). To avoid interference with the measurements due to the formation of oxide films,

Figure 1

Figure 1: Figure 1

observed at potentials more negative than that of the alkaline solution ([1]), and due to hydrogen evolution under cathodic polarizations, the curves with each anion were recorded successively in three or four solutions of different acidity: from −0.80 V to −0.95 V–in $1N$ acid (only curves 1 and 2, Fig. 1); from −0.86 V to −1.1 V–in a salt solution in the presence of $0.1N$ acid; from −1.0 V to −1.6 V–in a salt solution in the presence of $0.001N$ acid; from −1.5 V to −1.8 V–in a salt solution in the presence of $0.01N$ alkali. The values of σ obtained in the overlapping potential intervals agreed well, which indicates the absence of any effect of adsorption of hydroxyl and hydrogen, respectively, at the anodic and cathodic ends of each section of the curve, which should have led to a dependence of σ on the pH of the solution. However, it was not possible to join the sections of the curve recorded in $1N$ H_2SO_4 and $1N$ $Na_2SO_4 + 0.1N$ H_2SO_4 (curve 1); between the curves of these two solutions at −0.95 V a difference of 4 dyn/cm was observed; the intermediate section on the curve is therefore indicated by a dashed line.

* We express our gratitude to Corresponding Member of the Academy of Sciences of the USSR N. P. Sazhin for assistance in obtaining samples of this gallium.

Measurements at potentials more positive than, for example, −0.95 V in a solution of $1N$ KCl $+0.1\,N$ HCl were carried out with anodic polarization of the meniscus in the capillary (the normal potential of the gallium electrode is −0.81 V), which, however, apparently did not lead to any difficulties.

We compared the experimental electrocapillary curves with σ, φ-curves calculated by the method of double integration from data on the dependence of the differential capacitance C on potential, obtained on a gallium dropping electrode with the same degree of metal purity ([4]). The integration constants for KCl + HCl were chosen so as to ensure coincidence of the observed and calculated curves at the electrocapillary maximum; for the other solutions, on the basis of the assumption that the descending branches of the electrocapillary curves for different anions coincide at sufficiently negative φ. As is seen from Fig. 1, in all cases the results obtained by the two different methods agree well, which confirms the reliability of the electrocapillary measurements. By contrast, the capacitance values given in ([5]) are in sharp contradiction with the electrocapillary measurements.

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 KJ + 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 for isoamyl alcohol and the corresponding background curve KCl + HCl (2′) are shown in a separate graph, since they were obtained with a Ga sample of somewhat lower purity.
a –experimental data, *b* –data calculated from capacitance measurements.

Table 1 gives the potentials of zero charge of gallium φ_0 in various solutions, determined from electrocapillary curves (I) and from the dependence of charge density on potential ([4]) (II), as well as the values of the maximum surface 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 recalculated on the basis of measurements with the anions SO_4^{2-} and Cl^-, which were performed with both samples. Comparison of electrocapillary curves obtained on gallium with curves in solutions containing the same anions, measured on mercury (Fig. 2), shows that the surface activity of the anions SO_4^{2-} (or HSO_4^-), Cl^-, Br^-, J^- changes in the same order as on mercury, but is less strongly expressed. This is especially reflected in the magnitude of the shift of φ_0. Thus, in going from sulfate solutions to iodide solutions, the decrease in σ_{max} and the shift of φ_0 are, respectively, 20 dyn/cm and −0.18 V in the case of gallium, 26.5 dyn/cm and −0.37 V in the case of mercury. Other characteristic differences in the behavior of anions at the gallium interface

Table 1

Electrolyte	$NaClO_4 + HClO_4$	$Na_2SO_4 + H_2SO_4$	KCl + HCl	KBr + HCl	KJ + 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

compared with the interface with mercury are the similarity of the adsorbabilities of the ions Cl^- and Br^-, the absence of surface activity for the ion ClO_4^-, and the more clearly expressed surface activity of the ion SO_4^{2-} (or HSO_4^-).

A considerable decrease in the activity of a substance adsorbed on gallium is observed in the case of isoamyl alcohol (Figs. 1 and 2). At the same time, however, the shape of the electrocapillary curve characteristic of aliphatic alcohols on mercury is also preserved on gallium.

As follows from direct measurements (4) and from the shape of the electrocapillary curves, the capacitance of the electrical double layer on gallium at not too negative potentials is very large. The sharp asymmetry of the electrocapillary curves, which on mercury is observed only in the case of the most surface-active anions, such as, for example, J^-, is a general phenomenon in the case of gallium. It has already been pointed out that these high values of C cannot likewise be explained by adsorption of hydroxyl or by oxidation of the surface. We assume that the features of the electrocapillary behavior of gallium are determined by chemisorption of water molecules.

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 −1N KCl + 0.1 N HCl, 4 −1 N KBr + 0.1 N HCl, 5 −1 N KJ + 0.1 N HCl, 6 −1 N KCl + 0.1 N HCl + 0.1 M isoamyl alcohol

Figure 2: 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 −1N KCl + 0.1 N HCl, 4 −1 N KBr + 0.1 N HCl, 5 −1 N KJ + 0.1 N HCl, 6 −1 N KCl + 0.1 N HCl + 0.1 M isoamyl alcohol

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Frumkin pointed out that the gain in free energy upon wetting an uncharged gallium surface with water (180-190 erg/cm^2) is considerably greater than upon wetting mercury (125 erg/cm^2) (6). Unfortunately, an exact calculation of the first quantity is made difficult by the fact that measurements of the tension at the gallium–water interface at the electrocapillary maximum and gallium–vacuum were carried out with preparations of different degrees of purity (see below)*.

As the potential is shifted toward less negative values, the water dipoles turn with their negative, i.e., oxygen, ends toward the gallium surface. The stronger bond of gallium with water explains the decrease in the adsorbability of the ion ClO_4^- and of aliphatic alcohols in going from Hg to Ga. The adsorbability of the ion ClO_4^- and of aliphatic compounds is determined primarily by their expulsion from the bulk of the solution as a result of interaction between water molecules (5, 8); the presence at the interface of a layer of strongly bound water should hinder the adsorption process.

The orientation of the water dipoles with their negative ends toward the metal should adversely affect the adsorbability of anions as a result of electrostatic interaction. It is possible that this interaction explains the fact that at the anodic end of the electrocapillary curve the capacitance of gallium in iodide solutions is no greater, and 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 between the values of φ_0 for mercury and gallium in the absence of anion adsorption (0.42 V) considerably exceeds the difference between the potential values corresponding to equal values of the charge e

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* The data of work (7), in which the measurements were carried out in H_2 and CO_2 on one side and in 0.1-0.2 N HCl on the other (without applying polarization), indicate a value of $\sim$ 170 erg/cm^2.

Fig. 3. Electrocapillary curves in solutions of 1 N HCl and 1 N KCl + HCl on Ga of purities 99.99999% (1), 99.9998% (2), 99.996% (3)

Figure 3: Fig. 3. Electrocapillary curves in solutions of 1 N HCl and 1 N KCl + HCl on Ga of purities 99.99999% (1), 99.9998% (2), 99.996% (3)

at negative surface charges (0.17 V) ([4]), although another explanation can also be given for the latter phenomenon.

A number of the above-listed features of anion adsorption on gallium, however, still require further consideration. It should finally be noted that the idea of reorientation of adsorbed water dipoles when the potential changes has recently already been invoked 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 perhaps lead to some reconsideration of conclusions concerning mercury.

Fig. 3. Electrocapillary curves in solutions of 1 N HCl and 1 N KCl + HCl on Ga of purity 99.99999% (1), 99.9998% (2), 99.996% (3)

We have found a strong influence of the degree of purity of gallium on the electrocapillary curve. In Fig. 3 it is seen that in the case of gallium of purity 99.996% the maximum of the surface tension lies in KCl at −0.92 V, which agrees with the data given in earlier works. The value of $\sigma_{\max}$ is reduced, in comparison with curve 2, by 41 dyn/cm. Curve 1 in Fig. 3 was obtained with gallium of purity 99.99999% (Eagle Picher, USA), a sample of which we had received by the time the present work was completed thanks to the kindness of Prof. J. O' M. Bockris. In this case σ is still somewhat higher (by 4-6 units) than on curve 2; the value of φ_0 is the same. Comparison of the values of σ obtained at different pH indicates a somewhat easier passivation of gallium of the very highest purity at the positive end of the curve.

The dependence of the electrocapillary properties of gallium on its purity indicates the possibility of controlling the purity of gallium from electrocapillary data.

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Note: Figure translations are in progress. See original paper for figures.