STUDY OF THE STRUCTURE OF THE ELECTRIC DOUBLE LAYER ON GALLIUM BY THE METHOD OF MEASURING THE DIFFERENTIAL CAPACITANCE

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Up to the present time, the quantitative data on the structure of the electric double layer and its influence on the adsorption of ions were obtained chiefly on the mercury electrode. Conducting analogous investigations on solid electrodes presents substantial difficulties. It was of interest to verify whether the quantitative principles obtained on mercury are also preserved on other liquid metals. A suitable subject for the solution of this problem is gallium, the melting point of which is 29.75°. However, up to the present time there were practically no data in the literature on the investigation of the structure of the electric double layer on high-purity gallium. The differential capacitance curves on a dropping gallium electrode were taken in [1] in a limited number of solutions. According to the data of these measurements, the differential capacitance curves on Ga are very similar to the capacitance curves on Hg, although the absolute value of the capacitance C on gallium is somewhat higher. The purity of the gallium used was not stipulated. The values of the capacitance on solid and liquid gallium, cited in [2], are related to the entire surface of the investigated electrode and hence cannot be used for a quantitative comparison with the theory of the double layer.

In this work we measured the curves of the differential capacitance C on a dropping gallium electrode in solutions of Na_2SO_4, $NaClO_4$, LiCl, NaCl, KCl, CsCl, KI, KCNS. In order to prevent the formation of an oxide film on gallium, on the one hand, and for maximum displacement of the region of the beginning of liberation of hydrogen toward negative potentials, on the other, just as in [3], various portions of the capacitance curve were taken in solutions with different pH. Within the range of potentials from -1.9 to -1.2 V, with respect to the saturated calomel electrode, the measurements were conducted in neutral solution of salts; from -1.3 to -1.1 V they were conducted in solutions acidified to 0.01 N, and for potentials from -1.15 V and more positive, they were conducted in solutions acidified to 0.1 N. The acidification was accomplished with acid with the same anion, except for the solutions of KI and KCNS, in which the solutions were acidified with HCl. The summary concentration of the electrolyte was 1 N. To construct the complete curve of the differential capacitance according to its portions, we used the values of C, which were independent of the pH within the limits of the pH values of the solutions used. The maximum displacement toward positive potentials was limited by the beginning of formation of an oxide film, accompanied by a sharp drop in the capacitance. The formation of an adsorption layer of oxygen, preceding the phase oxide, should have been accompanied by an increase in the capacitance; however, we did not detect this effect.

The purity of the gallium corresponded to 99.9998%.* The solutions were prepared on the basis of double-distilled water. The reagents used were thoroughly purified: the acids by distillation, the salts by recrystallization and calcining. The measurements were conducted at 30°. The dropping electrode did not differ in its design from that used in [4]. To avoid the adhesion of Ga to the glass and clogging of the capillary with gallium oxide, formed upon contact of the metal with the atmospheric oxygen, the cell into which the gallium was poured and the capillary were preliminarily wet with a weak solution of pure alkali (pH ~ 10), which dissolves gallium oxide. The cell of the dropping electrode and the capillary were refilled with gallium before each experiment. The rate of outflux of the gallium corresponded to ~15 mg/sec. The differential capacitance was measured on the usual four-arm

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*Gallium, purified according to the method of the Rare Metals Institute. Let us take this opportunity to express our gratitude to Corresponding Member of the Academy of Sciences, USSR, N. P. Sazhin for his aid in its production.

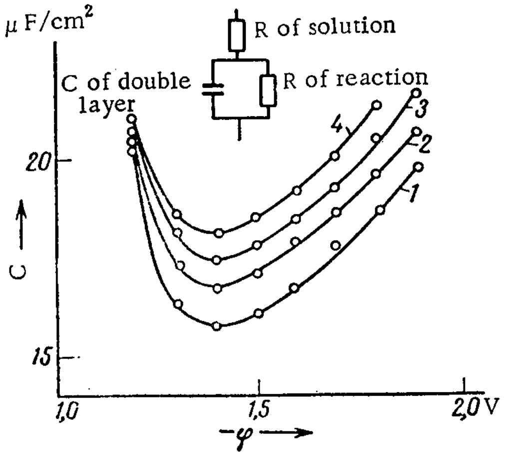

Fig. 1. Equivalent replacement circuit; curves of the differential capacitance at negative potentials on a gallium electrode in 1 N solutions of: 1) LiCl; 2) NaCl; 3) KCl; 4) CsCl.

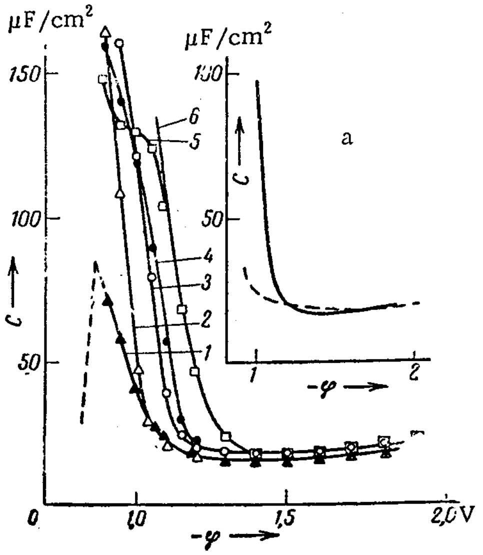

Fig. 2. Curves of the differential capacitance on gallium in 1 N solutions: 1) $NaClO_4$; 2) Na_2SO_4; 3) KCl; 4) KBr; 5) KI; 6) KCNS., a) Dotted line—data of Grahame for 0.1 N KCl; solid curve—our data.

alternating-current bridge at fixed frequencies from 318 cps to 80 kc/sec. As a result of the fact that the hydrogen overvoltage on gallium is ~0.3 lower than on mercury, the measurements within a certain range of potentials (−1.5 to −1.9 V with respect to saturated calomel electrode) were conducted during passage of the current of the reaction of hydrogen evolution. Under these conditions, gallium was no longer an ideally polarized electrode, and the measured impedance was a quantity that can be represented by the equivalent circuit depicted in Fig. 1. The resistance of the solution R_{soln} was found by measuring the resistance on the usual series replacement circuit at various frequencies and extrapolating the values obtained to an infinitely great frequency. A special electronic setup [5] made it possible to determine the balance time of the bridge with an accuracy of 0.1%. A platinum cylinder served as an auxiliary electrode.

The results of the measurements are cited in Figs. 1 and 2. All the potentials are given with respect to the saturated calomel electrode. It is evident from Fig. 1 that at negative potentials, corresponding to the region of adsorption of cations, the differential capacitance increases as we pass from Li^+ to Cs^+. In solutions containing different anions but the same cation (Fig. 2), the curves of the differential capacitance at negative potentials practically merge. The small discrepancy between the values of C in solutions of KCl, KBr, KI and KCNS, on the one hand, and Na_2SO_4 and $NaClO_4$, on the other, is related to the different nature of the cations Na^+ and K^+. At potentials corresponding to the beginning of adsorption of the anions, the capacitance begins to rise rapidly, the following sequence being observed: $ClO_4^- < SO_4^{2-} < Cl^- < Br^- < I^- < CNS^-$. The measured capacitance did not depend on the frequency within the interval of frequencies from 318 cps to 30 kc/sec, and consequently, expressed the capacitance of the electric double layer. The absence of dispersion of the capacitance indicates irreversibility of the process of solution of gallium, which already occurs in the region of more positive potentials.

At still more positive potentials, a certain lag is observed on the capacitance curve in a solution of KI, resembling the "hump" on the differential capacitance curves of mercury close to the potential of zero charge. However, on mercury the latter is observed in the presence of the other anions that we investigated, and not I^- under the conditions of our experiments. The capacitance curves in solutions containing Cl^- and Br^- are very close. In solutions of Na_2SO_4 and $NaClO_4$, at potentials more negative than −1.00 V, the capacitance curves coincide. At more positive potentials, the increase in C with the potential in a solution of $NaClO_4$ occurs more slowly than in Na_2SO_4. The capacitance drop in a solution of $NaClO_4$, cited in Fig. 2, is apparently related to the formation of a phase oxide film on the surface of the electrode [3]. An analogous capacitance drop was observed in all the solutions that we investigated. Close to the potentials corresponding to the drop, the measured capacitance begins to depend on the frequency, which is probably related to the appearance of a pseudocapacitance of the process of solution of gallium at these potentials.

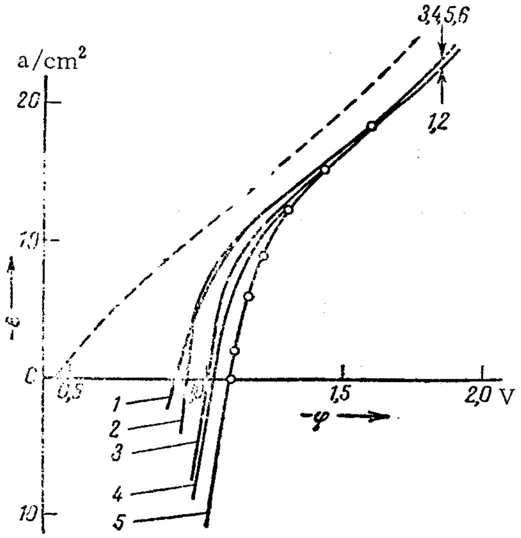

Fig. 3. Dependence of the charge density ε on the potential on gallium in 1 N solutions: 1) $NaClO_2$; 2) Na_2SO_4; 3) KCl; 4) KBr; 5) KI, points on curve; 5) KCNS. Dotted line – ε, φ curve on mercury in 1 N Na_2SO_4.

Figure 2a, compares the curves of C, φ on Ga in 0.1 N KCl, obtained in this work (solid line) and in [1] (dotted line). As can be seen, at negative potentials satisfactory coincidence of the values of C is observed; however, at more positive potentials, the capacitance that we measured proved far higher. At the present time, it does not seem possible to elucidate the cause of the discrepancy.

By integrating the curves of the differential capacitance, we obtained curves of the dependence of the charge density ε on gallium on the potential in solutions of various compositions. The integration constant was determined from the charging current, flowing on a dropping gallium electrode in a solution of 1 N KCl, thoroughly freed of O_2 at a potential of -1.45 V, at which gallium practically behaves like an ideal polarized electrode. As can be seen from Fig. 1, at this potential the capacitance of a gallium electrode does not depend on the nature of the anion in solution. The results of the calculation are depicted in Fig. 3. In this same figure, the ε, φ curve for a mercury electrode in a solution of 1 N Na_2SO_4 is depicted by a dotted line.

In a comparison of the data obtained in this work with the results of analogous measurements on mercury, it should be mentioned that the capacitance on gallium as we pass from Li^+ to Cs^+ increases in the same sequence as on mercury: $C_{Li^+} < C_{Na^+} < C_{K^+} < C_{Cs^+}$ [7, 8]. At potentials more positive than -1.2 V, in all the investigated solutions the increase in the capacitance on Ga is considerably more pronounced than in the case of Hg. Thus, at the point of zero charge of 1 N Na_2SO_4, the differential capacitance is $C_{Ga} = 135\ \mu F/cm^2$ and $C_{Hg} = 29.5\ \mu F/cm^2$, respectively. On the other hand, the adsorption of anions on Ga, as it follows from the position of the points of zero charge (Fig. 3), and especially from the values of the boundary tension [9], is more weakly pronounced than on mercury. Thus, the increase in the capacitance on Ga as φ is displaced toward more negative values cannot be explained by the adsorption of anions, although the latter does play a certain role, especially in the case of the ions I^- and CNS^-. As it follows from the independence of the values of C used from the pH, the increase in the capacitance likewise cannot be related to the appearance of adsorbed O atoms or OH groups on the surface (initial stage of oxidation). In any case, this effect was eliminated in the method that we used for constructing the C, φ curve. It might also be assumed that the increase in the capacitance is due to an increase in the number of gallium ions present in the boundary layer, since the charge of the gallium that they contain, according to the thermodynamic theory of electrocapillarity [10], also influences the effective capacitance of the electrode, like the charge of the surface of the metal. To verify this hypothesis, we measured the differential capacitance in a solution $KAl(SO_4)_2$, 1 N with respect to SO_4^{2-}. Aluminum ions, present in high concentration, should have replaced the gallium ions in the boundary layer. The potential dependence of the capacitance observed in 1 N Na_2SO_4, however, is entirely preserved in this solution. The increase in the capacitance should apparently be related to the adsorption of water on gallium. A stronger bond between water and gallium in comparison with mercury was indicated in [11]. It might be assumed that as the potential of Ga is shifted, the dipoles of water are oriented with their negative ends toward gallium, which should lead to an increase in the differential capacitance. This question will be discussed in greater detail in our next communication.

It is evident from the ε, φ curve that in all the solutions that we investigated, close to the point of zero charge, ε on Ga increases with the electrode potential substantially more rapidly than on Hg. As the distance from the point of zero charge increases, the increase slows down and becomes the same as that on Hg. From this it follows that the same state of the electric double layer on gallium and mercury will be reached on Ga at a more positive potential, with respect to the point of zero charge, than on Hg.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.