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

Up to the present time, quantitative data on the structure of the double electric layer and on its influence on ion adsorption have been obtained mainly on the mercury electrode. On solid electrodes, carrying out analogous studies presents substantial difficulties. It was of interest to verify whether the quantitative regularities obtained on mercury are preserved on other liquid metals. A suitable object for solving this problem is gallium, whose melting point is 29.75°. However, until now the literature has contained almost no data on the study of the structure of the double electric layer on gallium of high purity. Differential-capacitance curves on a dropping gallium electrode were recorded in work (1) in a limited number of solutions. According to 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 Ga used is not specified. The capacitance values on solid and liquid gallium given in work (2) are referred to the entire surface of the electrode under investigation and therefore cannot be used for quantitative comparison with the theory of the double layer.

In the present work, curves of the differential capacitance C were measured on a dropping gallium electrode in solutions of Na_2SO_4, $NaClO_4$, LiCl, NaCl, KCl, CsCl, KJ, KCNS. In order to prevent the formation of an oxide film on gallium, on the one hand, and to shift as far as possible the region in which hydrogen evolution begins toward negative potentials, on the other, as also in work (3), different portions of the capacitance curve were recorded in solutions with different pH. In the potential interval from −1.9 to −1.2 V vs. the n.c.e., measurements were carried out in neutral salt solutions; from −1.3 to −1.1 V—in solutions acidified to 0.01 N; and from −1.15 V and more positive—in solutions acidified to 0.1 N. Acidification was carried out with an acid having the same anion, except in the KJ and KCNS solutions, in which acidification was carried out with HCl. The total concentration of electrolyte was 1 N. To construct the complete differential-capacitance curve from its sections, values of C were used which, within the pH values of the solutions employed, did not depend on the magnitude of the pH. The maximum shift toward positive

Fig. 1

Figure 1: Fig. 1

potentials was limited by the onset of oxide-film formation, accompanied by a sharp drop in capacitance. The formation of an adsorption layer of oxygen, preceding the phase oxide, should have been accompanied by an increase in capacitance; however, we did not observe this effect.

The purity of the gallium corresponded to 99.9998%.* The solutions were prepared with twice-distilled water. The reagents used were carefully purified: acids by distillation, salts by recrystallization and ignition. Measurements were carried out at 30°. The dropping electrode in its construction did not differed from that used in work (4). To prevent Ga from adhering to the glass and to avoid clogging the capillary with gallium oxide formed when the metal comes into contact with atmospheric O_2, the cell into which the gallium was poured and the capillary were first wetted with a weak solution of pure alkali (pH $\sim$ 10), which dissolves gallium oxide. The cell of the dropping electrode and the capillary were filled with gallium anew before each experiment. The flow rate of gallium was $\sim$ 15 mg/sec. The differential capacitance was measured on an ordinary four-arm AC bridge at fixed frequencies from 318 Hz to 80 kHz. Since the hydrogen overvoltage on gallium is $\sim$ 0.3 V lower than on mercury, measurements in a certain potential interval ($-1.5 \div -1.9$ V vs. NCE) were carried out while the reaction current of hydrogen evolution was passing. Under these conditions gallium was no longer an ideally polarizable electrode, and the measured impedance was a quantity that can be represented by the equivalent circuit shown in Fig. 1.

Fig. 1. Equivalent substitution circuit; differential-capacitance curves at negative potentials on a gallium electrode in 1 N solutions: 1 –LiCl, 2 –NaCl, 3 –KCl, 4 –CsCl

The solution resistance R_p was found by measuring the resistance in the usual series substitution circuit at different frequencies and extrapolating the obtained values to infinitely high frequency. A special electronic setup (5) made it possible to determine the bridge balance time with an accuracy of up to 0.1%. A platinum cylinder served as the auxiliary electrode.

The results of the measurements are given in Figs. 1 and 2. All potentials are given vs. the NCE. It is seen from Fig. 1 that at negative potentials corresponding to the region of cation adsorption, the differential capacitance increases on going from Li^+ to Cs^+. In solutions containing different anions but the same

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* Gallium purified by the method of the Institute of Rare Metals. We take this opportunity to express our gratitude to Corresponding Member of the USSR Academy of Sciences N. P. Sazhin for assistance in obtaining it.

Fig. 2

Figure 2: Fig. 2

cation (Fig. 2), the differential-capacitance curves at negative potentials practically merge. A small discrepancy between the values of C in KCl, KBr, KI, and KCNS solutions, on the one hand, and Na_2SO_4 and $NaClO_4$, on the other, is associated with the different nature of the cations Na^+ and K^+. At potentials corresponding to the onset of anion adsorption, the capacitance begins to increase rapidly, and the following sequence is observed:

$$ClO_4^- < SO_4^{2-} < Cl^- < Br^- < J^- < CNS^-.$$

Fig. 2. Differential-capacitance curves on gallium in 1 N solutions: 1 –$NaClO_4$, 2 –Na_2SO_4, 3 –KCl, 4 –KBr, 5 –KJ, 6 –KCNS.
Fig. 2a: dashed line –Graham' s data for 0.1 N KCl; solid curve –our data

The measured capacitance did not depend on frequency in the frequency interval from 318 Hz to 30 kHz and expressed, conse-

correspondingly, the capacitance of the electrical double layer. The absence of capacitance dispersion indicates the irreversibility of the gallium dissolution process, which already occurs in the region of more positive potentials.

At still more positive potentials, a certain delay is observed on the capacitance curve in KJ solution, resembling a "hump" on the curves of the differential capacitance of mercury near the potential of zero charge. In mercury, however, the latter under the conditions of our experiments is observed in the presence of other anions studied by us, and not J^-. The capacitance curves in solutions containing Cl^- and Br^- are very close. In Na_2SO_4 and $NaClO_4$ solutions, at potentials more negative than -1.00 V, the capacitance curves coincide. At more positive potentials the increase of C with potential in $NaClO_4$ solution proceeds more slowly than in Na_2SO_4. The decrease in capacitance in $NaClO_4$ solution shown in Fig. 2 is apparently associated with the formation of a film of phase oxide on the electrode surface (3). An analogous decrease in capacitance was observed in all the solutions we studied. Near the potentials corresponding to the decrease, the measured capacitance begins to depend on frequency, which is probably connected with the appearance of a pseudocapacitance of the gallium dissolution process at these potentials.

In Fig. 2a the C, φ curves for Ga in 0.1 N KCl, obtained in the present work (solid line) and in work (1) (dashed line), are compared. As can be seen, at negative potentials there is satisfactory agreement of the values of C; however, at more positive potentials the capacitance measured by us proved much higher. It is not possible at present to establish the cause of the discrepancy.

Fig. 3. Dependences of charge density ε on potential on gallium in 1 N solutions: 1–$NaClO_4$, 2–Na_2SO_4, 3–KCl, 4–KBr, 5–KJ, points on curve 5–

Fig. 3. Dependences of charge density ε on potential on gallium in 1 N solutions: 1—$NaClO_4$, 2—Na_2SO_4, 3—KCl, 4—KBr, 5—KJ, points on curve 5—KCNS. Dashed line—ε, φ curve on mercury in 1 N Na_2SO_4

Figure 3: Fig. 3. Dependences of charge density ε on potential on gallium in 1 N solutions: 1—$NaClO_4$, 2—Na_2SO_4, 3—KCl, 4—KBr, 5—KJ, points on curve 5 —KCNS. Dashed line—ε, φ curve on mercury in 1 N Na_2SO_4

KCNS. Dashed line—ε, φ curve on mercury in 1 N Na_2SO_4.

By integrating the differential-capacitance curves we obtained curves of the dependence of the charge density ε on gallium on the potential in solutions of different composition. The integration constant was determined from the charging current flowing to the dropping gallium electrode in 1 N KCl solution, carefully freed from O_2, at a potential of -1.45 V, at which gallium behaves practically as an ideally polarizable electrode. As can be seen from Fig. 1, at this potential the capacitance of the gallium electrode does not depend on the nature of the anion in solution. The results of the calculation are shown in Fig. 3. In the same figure the dashed line gives the ε, φ curve for a mercury electrode in 1 N Na_2SO_4 solution.

When comparing the data obtained in the present work with the results of analogous measurements on mercury, it should be noted that the capacitance on gallium, on going 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 solutions studied the increase in capacitance on Ga is much more pronounced than in the case of Hg. Thus, at the point of zero charge in 1 N Na_2SO_4 the differential capacitance is, respectively, $C_{Ga} = 135$ μF/cm^2 and $C_{Hg} = 29.5$ μF/cm^2. On the other hand, adsorption of anions on Ga, as follows from the positions of the points of zero charge (Fig. 3)

and especially from the values of the interfacial tension (^{9}), is expressed more weakly than on mercury. Thus, the increase in capacitance on Ga when φ is shifted to less negative values cannot be explained by adsorption of anions, although the latter does play some role, especially in the case of J^- and CNS$^-$ ions. As follows from the independence of the values of C used from pH, the increase in capacitance likewise cannot be associated with the appearance on the surface of adsorbed O atoms or OH groups (the initial stage of oxidation). In any case, this effect was eliminated by the method we used for constructing the C, φ curve. It could also be supposed that the increase in capacitance is caused by an increase in the number of gallium ions present in the interfacial layer, since the charge of the gallium entering into their composition, according to the thermodynamic theory of electrocapillarity (^{10}), also affects the effective capacitance of the electrode, like the charge of the metal surface.

To test this supposition, the differential capacitance was measured in a 1 N solution of KAl(SO$_4$)$_2$ with respect to SO$_4^{2-}$. The aluminum ions present in high concentration should have replaced gallium ions in the interfacial layer. The dependence of capacitance on potential observed in 1 N Na_2SO_4, however, is fully retained in this solution. The increase in capacitance should apparently be associated with adsorption of water on gallium. A stronger bond between water and gallium as compared with mercury was indicated in ([11]). It may be supposed that, as the Ga potential is shifted, water dipoles are oriented toward gallium with their negative end, which should lead to an increase in the differential capacitance. This question will be considered in more detail in the next communication.

From the ε, φ curve it is seen that on Ga, in all the solutions we investigated, near the point of zero charge ε increases with electrode potential considerably more rapidly than on Hg. As the distance from the point of zero charge increases, the increase slows and becomes the same as that which occurs on Hg. It follows from this that identical states of the electrical double layer on gallium and mercury will be attained on Ga at a more positive potential relative to the point of zero charge than on Hg.

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REFERENCES CITED

1. D. C. Grahame, Proc. IV Conf. on Electrochemistry, Moscow, 1959, p. 27; *Anal. Chem.*, **30**, 1736 (1958).
2. D. I. Leikis, E. S. Sevastyanov, DAN, **144**, 1320 (1962).
3. A. N. Frumkin, A. V. Gorodetskaya, *Zs. Phys. Chem.*, **136**, 215 (1928).
4. K. Sabo, I. A. Bagochkaya, ZhFKh, **37**, 2581 (1963).
5. G. A. Tedoradze, L. L. Knots, G. G. Dubovik, *Advanced Scientific and Technical Experience. Instruments for Chemical and Physicochemical Research*, Moscow, 1963, p. 31.
6. D. C. Grahame, *J. Electrochem. Soc.*, **98**, 343 (1951).
7. A. N. Frumkin, B. B. Damaskin, N. V. Nikolaeva-Fedorovich, DAN, **115**, 751 (1957).
8. B. B. Damaskin, N. V. Nikolaeva-Fedorovich, A. N. Frumkin, DAN, **121**, 129 (1958).

9. A. N. Frumkin, N. S. Polyanovskaya, N. B. Grigor' ev, DAN, **157**, No. 5 (1964).

10. A. Frumkin, *Zs. Phys. Chem.*, **103**, 43 (1923).

11. A. Frumkin, *Electrochim. Acta*, **9**, 465 (1964).

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