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Abstract

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Measurement of Differential Capacitance on Solid and Liquid Electrodes

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As is known, significant differences have been found in the electrochemical properties of a number of solid metals and mercury. Some of these differences—for example, the action of anions on the electrochemical properties of iron and mercury—are readily explained by the properties of the metals being compared, independently of the state of aggregation of the electrodes. In this case the question of the state of aggregation of the electrodes does not arise, because certain other solid metals have proved similar to mercury (1). However, the curves of capacitance as a function of potential, obtained in experiments on solid metals (2-4) in solutions of moderate concentration, in the region of the potential of zero charge and at somewhat more negative potentials, differ from those for mercury. These differences in solid electrodes are usually attributed to surface heterogeneity. Indeed, smoothing the surface of solid lead electrodes (3, 5) diminishes this difference between solid metals and mercury; but even on the most highly smoothed electrodes it is not possible completely to eliminate the indicated difference. Therefore, naturally, the question arises of the limits of applicability to solid electrodes of the theory of the double layer developed and confirmed for mercury.

To resolve this question, we considered it necessary first of all to carry out capacitance measurements on a solid and a liquid electrode made of one and the same metal. Capacitance measurements on solid and liquid surfaces had previously been performed on mercury (6, 7), and no significant differences in capacitance were observed. However, because of the low freezing point of mercury (−38.7°), these measurements naturally could not be carried out in aqueous solutions of moderate concentration at room temperature, i.e., precisely under those conditions where the differences mentioned were observed.

We chose metallic gallium as the electrode to be studied; its melting point is +29.75°. Gallium was also of interest as an object of measurement because a change in the hydrogen overvoltage upon freezing had been observed on it (8, 9), and from this it could be assumed that there would be a difference in the structure of the double layer on gallium in different states of aggregation. No less important in choosing the object of investigation was the fact that the liquid gallium electrode has been studied fairly thoroughly both by electrocapillary and by capacitance methods (⌒11, ⌒12). According to these data, the capacitance curves of liquid gallium and mercury are very similar to one another, which made it possible, as a first approximation, to exclude from consideration individual differences in the structure of the double layer of these metals in the same state of aggregation.

The procedure for working with solid and liquid gallium took into account a number of its special features, such as its ability to supercool (it freezes at −30°), the expansion of gallium upon solidification, and its ready oxidation in air and in the aqueous solutions used by us.

To solve the problems posed, capacitance was measured at various potentials on liquid and solid gallium in a 1 N solution of Na_2SO_4 + 0.01 N HCl at a frequency of 10 kHz*. The capacitance curves obtained are shown in Fig. 1**. As is seen from Fig. 1, the capacitance curves for the solid electrode practically coincide with the curves for the liquid one. It should be noted that our data obtained for a liquid gallium electrode agree well with the data for a dropping electrode ([12]).

For a more complete comparison of the surface properties of liquid and solid gallium, their adsorption properties were studied in solutions containing hexyl alcohol***. Using the theory of the influence of an electric field on the adsorption of organic molecules, developed in the works of A. N. Frumkin ([13]), it is possible, on the basis of measurements of the dependence of capacitance on potential, to establish whether the gallium surface changes upon freezing. Without dwelling on the theoretical side of the question, which has been analyzed in sufficient detail in the work of A. V. Gorodetskaya and M. A. Proskurnin ([6]), we shall point out that if, upon adsorption of the same surface-active organic substance on a solid and on a liquid electrode, the capacitance-potential curves coincide, then the true surfaces of the electrodes must also be equal. In addition, measurements in the presence of a surface-active organic substance gave us the possibility, at least qualitatively, to consider the question of the energetic heterogeneity of the solid surface of the electrode. Indeed, if various types of crystal faces are present on the metal surface, each of which has its own zero point and its own potential of sharp change in adsorption capacity, one might expect the existence of several desorption peaks of correspondingly smaller height, or of one broad and low peak. Therefore, by comparing the shape of the desorption peaks of liquid and solid gallium, it is possible to decide whether appreciable physical heterogeneity of the surface arises upon solidification of gallium. As is seen from Fig. 2, the shape and position of the peaks on the curves for solid and liquid gallium in a 1 N solution of Na_2SO_4 saturated with *n*-hexyl alcohol coincide completely. This indicates that the surface of gallium upon freezing practically does not change in magnitude, and that the solid and liquid surfaces are energetically equivalent from the point of view of interest to us.

Fig. 1. Dependence of the capacitance of liquid and solid gallium on the electrode potential in 1 N Na_2SO_4 + 0.01 N HCl (frequency $f = 10$ kHz). The solid curve refers to liquid gallium, the dashed curve to solid gallium ($t = 26°$).

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Fig. 2

Figure 2: Fig. 2

It was desirable to carry out additional measurements on a metal that may undergo noticeable changes of surface upon solidification. Proceeding from these considerations, Wood' s alloy was chosen as the electrode to be studied. Capacitance measurements on solid and liquid Wood' s alloy had previously been carried out by Karpachev et al. (^{14}). The authors observed an increase in the surface of the alloy upon solidification, although no noticeable differences in the dependence of capacitance on potential were found. Since in that work no

* At frequencies of 10 kHz and higher, no appreciable capacitance dispersion was observed.

** Along the abscissa axis in all graphs are plotted values of potentials referred to the saturated calomel electrode. The plotted values of differential capacitance are not referred to 1 cm^2 of surface, as is usually done, but to the entire surface of the electrode under investigation. The point is that at present there are no sufficiently reliable methods suitable in this case for determining the true surface of solid electrodes. However, since the main purpose of the work was to investigate the change of capacitance with potential, we considered it possible to make such a comparison of changes in capacitance referred to the whole surface of the electrode.

*** Hexyl alcohol was chosen because it gives sufficiently well-pronounced desorption peaks.

adsorption properties of the alloy were studied and, moreover, the accuracy of the capacitance measurements was not high; we considered it advisable to carry out measurements on Wood' s alloy similar to those performed on gallium.

Fig. 2. Dependence of the capacitance on the potential of a liquid and solid gallium electrode in a 1 N solution of Na_2SO_4 saturated with n-hexyl alcohol (frequency $f = 2$ kHz). [Symbols as in Fig. 1.]

The results of the measurements are presented in Figs. 3 and 4. The curves for the solid surface, as can be seen from the figures, are located somewhat higher (by approximately 10–15%) than the curves for the liquid alloy, which indicates an increase in the surface area of the alloy upon solidification*. However, the

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

shape of the curves obtained on the solid and liquid surfaces of the alloy differs little. Thus, on the basis of the data obtained, it may be concluded that neither in adsorption properties nor in the structure of the double layer do the liquid and solid (both smooth and matte) surfaces of the electrodes studied differ noticeably from one another. The previously observed difference between mercury and solid electrodes should be explained on the basis of the individual properties of the metals under investigation. Thus, for example, in light of recent ideas about changes in the electrochemical properties of metals upon formation of their compounds with alkali metals ([15]), one may attempt to explain the indicated phenomenon by the different ability of metals to form such compounds, as well as by the different properties of the latter. From this point of view, the smoothed and unsmoothed surfaces of lead may also differ in their ability to form such compounds.

Fig. 3. Dependence of the capacitance of a liquid and solid electrode made of Wood' s alloy in 1 N Na_2SO_4 (frequency $f = 10$ kHz). The solid curve refers to liquid ($t = 85°$), the dashed curve to solid ($t = 61°$) Wood' s alloy.

Fig. 4. Dependence of the capacitance on the potential of a liquid and solid electrode made of Wood' s alloy in a 1 N solution of Na_2SO_4 saturated with *n*-hexyl alcohol (frequency $f = 2$ kHz). The solid curve refers to liquid ($t = 76°$), the dashed curve to solid ($t = 73°$) Wood' s alloy.

* It should be noted that, unlike gallium, the surface of Wood' s alloy loses its luster upon solidification and becomes matte.

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