MEASUREMENT OF THE DIFFERENTIAL CAPACITY AT SOLID AND LIQUID ELECTRODES

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It is well known that considerable differences are observed between the electrochemical properties of a number of solid metals and those of mercury. Part of these differences, as for example the difference in the effect of anions on the electrochemical properties of iron and of mercury, are easily explained in the terms of the metals under comparison, independently of the state of aggregation of the electrodes. The question of the state of aggregation of the electrodes does not arise in this case for the reason that some other solid metals have turned out to be similar to mercury [1]. However, the curves of capacity as a function of potential, found from experiments on solid metals [2-4] in solutions of moderate concentration, in the region of the zero charge potential and at somewhat more negative potentials differ from those taken on mercury. These differences observed with solid electrodes are usually assumed to come from surface inhomogeneity. Actually, smoothing the surface of solid lead electrodes [3-5] reduces the difference between this solid metal and mercury, but it is not possible to remove the difference completely even on the most highly polished electrodes. Therefore the question naturally arises as to the limits of applicability of the double layer theory, developed and confirmed on mercury, when it is used for solid electrodes.

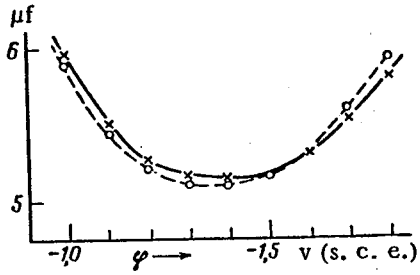

Fig. 1. Capacity of liquid and solid gallium electrode as a function of potential in 1N Na_2SO_4 + 0.01 + N HCl (frequency f = 10 kc). The solid curve is for liquid gallium, and the dotted curve is for solid gallium (t = 26°).

In order to settle this question, we have felt it necessary first of all to make capacity measurements on a solid and liquid electrode consisting of the same metals. Capacity measurements on solid and liquid surfaces have been made previously on mercury [6-7], no great differences in capacity having been observed. However, because of the low freezing point of mercury (-38.7°), the measurements could naturally not be made in water solutions of moderate concentration at room temperature, i.e., under precisely those conditions where the differences were observed.

We have chosen as our test electrode metallic gallium, which melts at +29.75°. Making measurements on gallium was also of interest because of the fact that a change in hydrogen over-voltage has been observed on it during freezing [8-9], and, with this in mind, it was to 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 material for study was the fact that the liquid gallium electrode has been rather completely studied by both electrocapillary and capacity methods [11-12]. This data shows that the capacity curves of liquid gallium and mercury are very similar to one another, which has made it possible to a first approximation to eliminate from consideration any individual difference in the structure of the double layer of these metals in the same state of aggregation.

The technique of working with solid and liquid gallium took account of a number of its special properties, such as its tendency toward supercooling (it freezes at +30°), the expansion of gallium on solidification and the fact that it is easily oxidized in air and in the aqueous solutions that we used.

In order to solve the problems presented, a capacity measurement was made on liquid and solid gallium at vari-

ous potentials in a solutions of 1N Na_2SO_4 + 0.01N HCl at a frequency of 10 kc*. The resulting capacity curves are given in Fig. 1**. As may be seen from Fig. 1, the capacity curves for the solid electrode are practically the same as the curves for the liquid electrode. It should be noted that our data taken for the liquid gallium electrode are in good agreement with the data for the dropping electrode [12].

In order to make a more thorough comparison between the surface properties of liquid and solid gallium, a study was made of their adsorptive properties in solutions containing hexyl alcohol***. Using the theory of the effect of an electric field on the adsorption of organic molecules, developed in the work of A. N. Frumkin [13], we could find from the measurements of capacity as a function of potential whether or not the gallium surface changes on freezing. Without stopping to consider the theoretical side of the question, which has been worked out in sufficient detail in the paper by A. V. Gorodetska and M. A. Proskurnin [6], we shall point out that if the capacity–potential curves are the same when the same surface-active organic substance is adsorbed on a solid and on a liquid electrode, the true surfaces of the electrodes must be equal. In addition, making measurements in the presence of a surface-active organic substance has provided us with the possibility, if only qualitatively, of considering the question of energy inhomogeneity in the solid electrode surface. Actually, if different types of crystal faces are present on the metal surface, and each of them has its own zero point and its own potential where the adsorptivity changes sharply it was to be expected that there would be several desorption peaks of correspondingly less height or one broad and one low peak. Therefore, comparing the form of the desorption peaks for liquid and solid gallium, we can decide whether or not any appreciable physical inhomogeneity occurs in the gallium surface when it solidifies. As may be seen from Fig. 2, the form and position of the peaks on the curves for solid and liquid gallium in 1 N Na_2SO_4 solution saturated with n-hexyl alcohol are, on the whole, the same. This indicates that the amount of gallium surface is practically unchanged by freezing and further that the solid and liquid surfaces are energetically equivalent from the point of view of our interest.

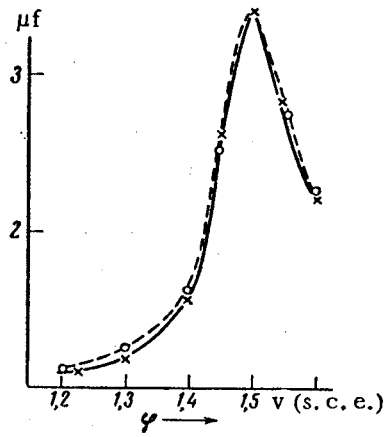

Fig. 2. Capacity as a function of the potential of a liquid and solid gallium electrode in 1 N Na_2SO_4 solution saturated with n-hexyl alcohol (frequency f = 2 kc). Nomenclature as in Fig. 1.

It was desirable to make some additional measurements on a metal which can show appreciable surface changes on solidification. With this idea in mind we decided to make some tests on a Wood's metal electrode. Some capacity measurements had previously been made on solid and liquid Wood's metal by Karpachev et. al. [14]. These authors observed an increase in surface of the alloy on solidification, although no appreciable differences were observed in the variation of capacity with potential. Since the adsorptive properties of the alloy were not investigated in this work and the accuracy of the capacity measurements was not great, we felt that it was a good idea to make some measurements on Wood's metal similar to those made on gallium.

The results of the measurements are given in Figs. 3 and 4. The curves for the solid surface, as may be seen from the figures, are located somewhat (about 10-15%) above the curves for the liquid alloy, which shows that there is an increase in surface of the alloy on solidification****. But there is very little difference in the form of the curves whether they are taken on a solid or a liquid alloy surface.

*At frequencies of 10 kc and above no considerable amount of dispersion of the capacity was observed.

**The abscissas in all the graphs are potentials referred to a saturated calomel electrode. The ordinates are the differential capacities referred not to 1 cm^2 of surface as is usually done, but to the whole surface of the test electrode. The thing is that at the present time there are no sufficiently reliable methods that can be used in the present case to find the true surface of the solid electrodes. However since the main purpose of the work was to investigate the change in capacity with potential, we felt that it was possible to make such a comparison of the changes in capacity by referring it to the whole electrode surface.

***Hexyl alcohol was chosen in view of the fact that it gives quite well defined desorption peaks.

****It should be noted that, unlike gallium, when the Wood's metal hardens the surface loses its lustre and becomes dull.

Thus, we may conclude from the data obtained that the liquid and solid surfaces of the electrodes studied do not differ appreciably from one another either in their adsorptive properties or in the structure of the double layer whether they are bright or dull. The differences observed previously between mercury and solid electrodes must be explained in terms of the individual properties of the metals studied. Thus for example in the light of the most recent ideas on the change in the electrochemical properties of metals when they form compounds with alkaline metals [15], we can make an attempt to explain the present phenomenon as a difference in ability of the metals to form

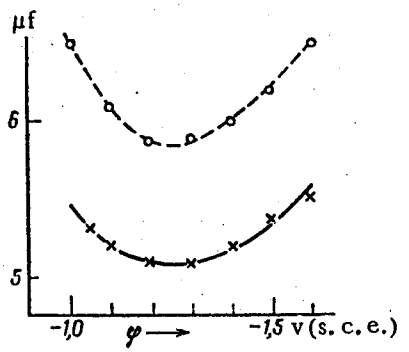

Fig. 3. Capacity of a liquid and a solid Wood's metal electrode in 1 N Na_2SO_4 (frequency f = 10 kc). The solid curve is for liquid (t = 85°) and the dotted curve is for solid (t = 61°) Wood's metal.

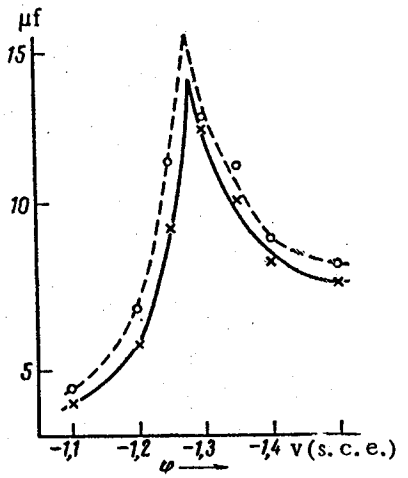

Fig. 4. Capacity as a function of potential of a liquid and a solid Wood's metal electrode in 1 N Na_2SO_4 solution saturated with n-hexyl alcohol (frequency f = 2 kc). The solid curve is for liquid (t = 76°) and the dotted curve is for solid (t = 73°) Wood's metal.

such compounds as well as in terms of differences in the properties of the compounds themselves. From this point of view, the polished and unpolished lead surfaces may also differ in their ability to form compounds of this sort.

We consider it a pleasant duty to express our gratitude to Academician A. N. Frumkin and Prof. B. N. Kabanov for their valuable advice which has made the present work possible.

LITERATURE CITED

1. Z. A. Iofa, É. I. Lyakhovetskaya, and K. Sharifov, DAN, 84, 543 (1952). Tza Chuang-sin and Z. A. Iofa, DAN, 131, 137 (1960).
2. T. I. Borisova, B. V. Érshler, and A. N. Frumkin, ZhFKh, 22, 925 (1948).
3. T. I. Borisova and B. V. Érshler, ZhFKh, 24, 337 (1950).
4. É. O. Ayazyan, DAN, 100, 473 (1955).
5. D. I. Leikis and B. N. Kabanov, New Methods of Physico-Chemical Investigation, Collection No. 2, [in Russian] p. 5 (Moscow, 1957).
6. A. V. Gorodetskaya and M. A. Proskurnin, ZhFKh, 12, 411 (1938).
7. V. L. Kheifits and B. S. Krasikov, DAN, 94, 517 (1954).
8. F. Bowden and E. O'Connor, Proc. Roy. Soc., Ser. A, 128, 326 (1930).
9. S. Christov and S. Rajceva, Naturwiss 48, 127 (1961).
10. A. Frumkin and A. Gorodezkaja, Zs. Phys. Chem., 136, 215 (1928).
11. Murtazajew and A. Gorodezkaja, Acta Physicochimia URSS, 4, 75 (1936).
12. D. C. Grahame, Transactions of the IV Conference on Electrochemistry [in Russian] Moscow , p. 27 (1959).
13 A. N. Frumkin, Collection of Papers from the L. Ya. Karpov Chemical Institute [in Russian] No. 5, 3 (1926).
14. S. Karpachev, I. Ladygin, and V. Zykov, ZhFKh, 17. 75 (1943).
15. B. N. Kabanov, D. I. Leikis et. al. DAN, 144, No. 5 (1962).