DETERMINATION OF THE CONTACT POTENTIAL DIFFERENCE BETWEEN GALLIUM AND MERCURY ON THE BASIS OF SPACE-CHARGE-LIMITED CURRENTS IN PHTHALOCYANINES

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In previous papers [1, 2] the contact potential difference (cpd) between metals was determined on the basis of the space-charge-limited currents in phthalocyanines (Pc). The contact potentials obtained were in good agreement with the zero-charge potentials of mercury, thallium amalgam, and indium amalgam as determined by the electrochemical method. In the present communication, data for the cpd between gallium and mercury obtained by measuring injection currents in copper Pc are reported.

A large number of papers has recently been devoted to studies of the electrochemical properties of gallium. By electrocapillary [3] and capacity measurements [4] the difference in the zero-charge potentials between mercury and gallium was determined and found to be 0.45 V. It was noted in [4] that this figure considerably exceeds the potential difference of these metals (0.17 V) at equal charges in the negative potential region. Under these conditions the water molecules have the same orientation on the surfaces of both metals, according to [4]; therefore, the value of 0.17 V must be close to the cpd between gallium and mercury in vacuum. In this context it is of particular interest to determine the cpd between these metals by another method.

Injection currents were measured in the following systems: Ni-CuPc-Hg and Ni-CuPc-Ga. The technique for recording the volt-ampere characteristics and for preparing the Pc films was described in a previous communication [1]. The experiments were carried out in the following manner. At first the volt-ampere characteristics were measured for the system Ni-CuPc-Hg. The characteristics for the system Ni-CuPc-Ga were then measured on the same CuPc film and with the same nickel contact, by replacing the mercury with gallium. In this method those errors are eliminated which are due to the irreproducibility of the surface properties of nickel and to the presence of an additional potential drop caused by the surface states of CuPc. The desired cpd was found as the difference in the values of the cpd between gallium and nickel and between mercury and nickel. In order to avoid contamination of gallium with mercury the substrate with the film was pulled out into the air after studying the first system, and the cell was washed free from Hg traces. Then the substrate was again placed into the cell, which was pumped out to a residual pressure of $5 \cdot 10^{-6}$ mm Hg. For the work, gallium of a high degree of purity (99.9998%) was employed, which was cleaned from oxides by consecutive filtration through three capillaries of 0.25, 0.22, and 0.1 mm diameters. The purified gallium was filled up into ampoules with breakable bottoms, which were opened under vaccum just prior to the experiment.

In Table 1 the results of five experiments on the cpd between gallium and mercury are given. These data were obtained by extrapolating the $i^{1/2}$-V relation to i = 0, as in earlier papers [1, 2].

It is seen from the table that the mean value of $\Delta\varphi$ is considerably less than the difference in zero-charge potentials between mercury and gallium. It is close to the potential difference between mercury and gallium at the same value of charge in the negative potential region (0.17 V). The result obtained by us differs from the value of the contact potential difference (0.30 V) between gallium and mercury measured in vacuum (10^{-6} mm Hg) by Osipova, Shurmovskaya, and Burshtein [5]. The reasons for the discrepancy are not clear as yet. In this way the hypothesis put forward in [3] is confirmed, according to which the specific adsorption of water is stronger on Ga than

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TABLE 1. The Contact Potential Difference ($\Delta\varphi$, in V) between Gallium and Mercury

No. of expt.	1	2	3	4	5	Mean value
$\Delta\varphi$, V	0,22	0,12	0,12	0,17	0,15	0,16±0,06

TABLE 2. Electron Work Function, in eV

Metal	Mercury	Thallium amalgam (saturated)	Indium amalgam (saturated)	Gallium
Work function	4,50	4,04	3,96	4,34

on mercury, and an additional potential drop of 0.29 V enters the difference in zero-charge potentials between these metals. On the basis of the present comparison it can also be suggested that the copper Pc molecules cause identical adsorption potential drops at the surfaces of Ga and Hg. From this one can conclude that the inner cpd between the metals in Pc as determined by us is close to that in vacuum. This makes it possible to evaluate the electron work function in vacuum for gallium and, on the basis of previous studies [1, 2], for the amalgams of thallium and indium. The electron work functions for the metals mentioned are given in Table 2. The work function for mercury was taken as 4.5 eV [6].

From the experimental results obtained in the present work and also on the basis of our previous studies [1, 2], it can be concluded that the space-charge-limited currents can in a number of cases successfully be employed for determining the contact potentials of metals.

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