STRUCTURE OF THE ELECTRIC DOUBLE LAYER AND THE ZERO-CHARGE POTENTIAL AT THE (111) FACE OF A BISMUTH SINGLE CRYSTAL

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UDC 541.13:546.87

Most of the data on the structure of the electrical double layer and the adsorption of organic compounds applies either to liquid metals or to metals with a polycrystalline surface. However, it is well known that, compared with a liquid electrode, the special characteristics of the solid electrode include the presence of various types of inhomogeneities, the distribution of dislocations, and the various orientations of the crystal faces in relation to the electrode surface. A particularly important part in the determination of the zero-charge potential is played by the difference in the work functions of the electron for various faces (amounting to 0.3-0.4 V) and also the difference in the dipole potential jumps of the solvent. To determine the characteristics of the double layer of a metal it is, of course, necessary to make measurements on the individual faces of a single crystal. Detailed researches into the structure of the electrical double layer at the faces of monocrystalline electrodes including silver [1-3], gold [4], zinc [5], and copper [6, 7] have appeared in the literature comparatively recently.

In the present work the structure of the electrical double layer at the (111) face of a single crystal of bismuth was investigated by measurement of the differential capacitance. The choice of subject for investigation was based on the following facts: 1) there are reliable quantitative data on the structure of the electrical double layer and on the adsorption of organic compounds at a polycrystalline bismuth electrode; 2) in work by Piontelli [7] a close relation was obtained between the hydrogen overpotential and the crystallographic index of the face; 3) bismuth readily cleaves along the (111) face not only at liquid nitrogen temperature but also at room temperature, and the cleavage plane has a small number of dislocations.

A single crystal of "special purity" bismuth (State Scientific-Research Institute of Rare Metals), obtained by zone melting, was used. Rectangular parallelepipeds (5 × 5 × 10 mm) were cut from a piece of the single crystal strictly perpendicular to the (111) face, and they were then machined to cylinders 2-3 mm in diameter on a lathe. The working electrode was the end of the cylinder. The main difficulty in the work with this electrode is to obtain reliable insulation for the side surface. In the method which was first tried the side surface was coated with polystyrene (dissolved in toluene). However, the results from measurements with this method of insulation were not reproducible, and the differential capacitance at the minimum of the C, φ curve in 0.01 N potassium fluoride solution had a value of $\sim 30\ \mu F/cm^2$, which is probably due to entry of the solution on account of poor adhesion between the polystyrene and the bismuth, unlike zinc, where this effect was not observed [8]. In the second method the electrode was pushed into a heated Teflon holder (with a 0.2-0.3-mm clearance). In this case the reproducibility of the results was also unsatisfactory, and the capacitance was too high. As shown by the measurements, the best method was a combination of these two methods, i.e., the side surface of the electrode was coated with polystyrene and the electrode was pushed into a Teflon holder. In this way it was possible practically to eliminate access of the solution to the side surface.

Measurements were made either on the cleavage plane or after additional electrochemical polishing of the cleaved surface in a solution of saturated potassium iodide containing 1% hydrochloric acid at a

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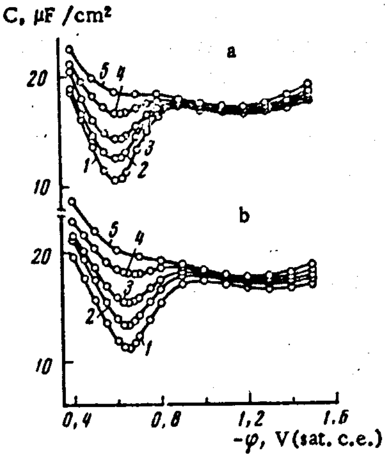

Fig. 1

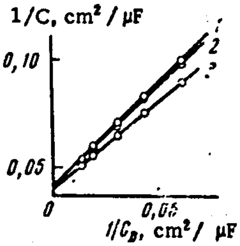

Fig. 2

Fig. 1. Differential capacitance curves for polycrystalline bismuth electrode (a) and the (111) face of the bismuth single crystal (b) in potassium fluoride solutions: 1) 0.005; 2) 0.001; 3) 0.02; 4) 0.05; 5) 0.1 M.

Fig. 2. Dependence of $1/C$ on $1/C_D$ (potassium fluoride solutions) at $\varphi_{\varepsilon=0}$ for bismuth with various electrode surface structures: 1) fused polycrystalline; 2) electrochemically polished polycrystalline; 3) electrochemically polished (111) face of single crystal.

current density of 0.7 A/cm^2. A certain number of measurements were made on an electrochemically polished polycrystalline electrode with the same configuration. The electrode was prepared in the same way as in the case of the single crystal. The polycrystalline electrode was obtained by drawing molten bismuth into a glass tube.

Twice recrystallized and calcined salts were used. The twice-distilled water was additionally purified with activated charcoal. The differential capacitance measurements were made on an R-568 alternating-current bridge at frequencies between 110 and 2000 Hz. With the optimum solution of the electrode-mounting problem it was possible to reduce the variance to 2-3%. The auxiliary electrode was a platinum hemisphere, and the reference electrode was a saturated calomel electrode.

The differential capacitance curves for the electrochemically polished single crystal of bismuth (111 face) in potassium fluoride solutions with various concentrations at 210 Hz are given in Fig. 1. Here analogous curves for the polycrystalline electrode are given for comparison. From the figure it is seen that in both cases the C, φ curves have identical form. It is necessary to note the quantitative agreement in the values for the capacitance at the electrochemically polished and fused [9] polycrystalline electrodes; this demonstrates the possibility of making accurate measurements on the electrochemically polished electrode, which is simpler to use.

The main difference between the series of curves in Figs. 1a and 1b is the different position of the potential corresponding to the minimum $\varphi_{\min}$ and, accordingly, the zero-charge potential $\varphi_{\varepsilon=0}$ on the C, φ curves in fairly dilute solutions, which reaches 30 mV. The potentials of the minimum on the cleavage plane and the polished single crystal coincide, but the values for the capacitance at the cleavage plane are somewhat higher and depend more on the concentration at the potentials of the cathodic minimum.

The potentials of the minima in potassium fluoride and potassium sulfate solutions for the various bismuth electrodes, referred to a saturated calomel electrode, are given below:

	(111) face	Fused polycrystalline	Polished polycrystalline
KF	−0.65	−0.65	−0.62
K_2SO_4	−0.68	−0.68	−0.65

TABLE 1

Electrolyte	Concentration, N			
	10^{-2}	10^{-3}	10^{-4}	10^{-5}
KCl	0,010 (0,015)	0	—	—
KBr	0,085 (0,100)	0,010 (0,020)	0	—
KI	—	0,150 (0,200)	0,060 (0,075)	0,015 (0,025)

It should be noted that the difference $\Delta\varphi_{min}$ in potassium fluoride and potassium sulfate solutions is identical for the single crystal and the polycrystalline electrode, whereas the φ_{min} value in potassium sulfate solutions is 30 mV more negative in both cases on account of the unsymmetrical nature of the electrolyte. The arrest, characteristic of the polycrystalline electrode, near $\varphi_{\varepsilon=0}$ on the C, φ curves in 0.1 N potassium fluoride solution does not appear in the single crystal.

The 1/C, $1/C_D$ relations for the single crystal and the fused and electrochemically polished polycrystalline electrodes are given in Fig. 2. For the fused and electrochemically polished electrodes the slope is close to unity (roughness factor 1.05), whereas the slope for the single crystal is 1.25. This value cannot be due to the roughness of the electrode, since the electropolishing conditions used for the single crystal and the polycrystalline electrode were identical, and the capacitance values at the potentials of the cathodic minimum are similar. An analogous effect was observed in [10] for a gallium electrode and was explained by the effect of specific adsorption of water dipoles on the distribution of the ions in the diffuse layer. It can be supposed that specific adsorption of the solvent dipoles can affect the structure of the diffuse layer in the case of the bismuth single crystal, but it is at present difficult to give a detailed explanation of the present behavior, since data on the structure of the electrical double layer and the adsorption of organic compounds on polycrystalline bismuth indicate that the adsorption characteristics of the ordinate mercury are similar. It is interesting to note that all the straight lines in Fig. 2 intersect with the ordinates axis at one point, i.e., the capacitance of the compact layer has the same value on the single crystal and the polycrystalline electrode.

The displacements of φ_{min} due to adsorption of halide ions on the bismuth single crystal were determined. The values of $\Delta\varphi_{min} = \varphi_{\varepsilon}^{KF} - \varphi_{min}^{KX}$ (V), where X = Cl^-, Br^-, and I^-, are given in Table 1. The values for the fused electrode are given in parentheses [11].

The data in the table show that the adsorbability of the halide ions decreases on passing from the polycrystalline electrode to the single crystal. Additional experimental investigations are required for a more definite conclusion. The next report will be devoted to quantitative investigation of the adsorption of I^- ions on a single crystal of bismuth.

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