DETERMINATION OF THE INNER CONTACT POTENTIAL DIFFERENCE BETWEEN MERCURY AND ALKALI METAL AMALGAMS ON THE BASIS OF SPACE-CHARGE LIMITED CURRENTS IN PHTHALOCYANINE FILMS

S. D. Levina, L. A. Korob, and G. E. Kalenchuk

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In our laboratory [1, 2] a method has been developed for determining the inner contact potential difference $\Delta\varphi$ between metals on the basis of currents limited by the space charge in phthalocyanine (Pc) films. The $\Delta\varphi$ values between mercury and the amalgams of thallium and indium obtained by this method agreed with the data from electrocapillary measurements for the potentials of zero charge of the same metals in aqueous solutions [3].

It was of interest to apply this method to the alkali metal amalgams, too, as handling these amalgams in aqueous solutions entails great experimental difficulties, due to their high oxidizability and rapid decomposition in electrolyte solutions. Results obtained with potassium amalgams of various concentrations are described in the present communication. The methods used for applying the Pc films and for recording the volt-ampere characteristics have been described before [1, 2, 4]. All operations in the preparation of the amalgams were carried out in vacuo (10^{-6} mm Hg). Potassium of 99.95% purity* was used; it was twice distilled under vacuum as an additional measure. A magnetic hammer was used to open in the same system

*Obtained from the Institute of Inorganic Chemistry of the Karelian Branch of the Academy of Sciences.

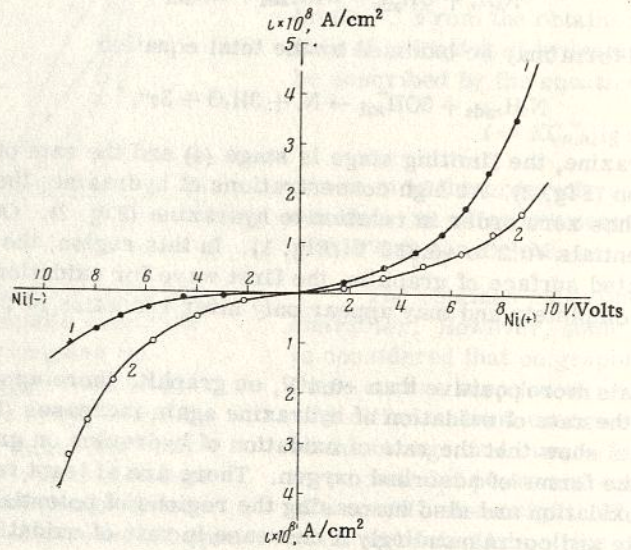


Fig. 1. Volt-ampere characteristics: 1) Ni–CuPc–K amalgam ($9 \cdot 10^{-1}$ at.%); 2) Ni–CuPc–Hg.

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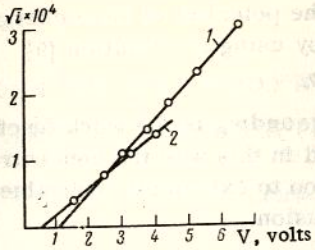


Fig. 2. Dependence of $i^{1/2}$ (A/cm^2) on V (volts): 1) Ni–CuPc–K amalgam ($9 \cdot 10^{-1}$ at.%; 2) Ni–CuPc–Hg.

TABLE 1

Potassium conc. in the amalgam, %	Inner contact potential difference, V			Work function* of K amalgam, eV
	Ni – Hg	K amalgam–Ni	K amalgam–Hg	
9×10^{-1}	0,40	1,05	1,45	3,05
$2,5 \times 10^{-1}$	0,60	0,70	1,30	3,20
$1,19 \times 10^{-1}$	0,45	0,80	1,25	3,25
$4,9 \times 10^{-2}$	0,30	0,90	1,20	3,30
$3,5 \times 10^{-2}$	0,80	0,90	1,25	3,35
$4,4 \times 10^{-3}$	0,60	0,40	1,00	3,50
$5,3 \times 10^{-4}$	0,70	0,030	0,73	3,77

*Work function of mercury : 4.5 eV.

a vial containing mercury that had been purified and twice vacuum-distilled in advance. It was allowed to collect in a flask into which the required quantity of potassium was distilled. The flask and vials with breakable bottom fused to it were fused off from the system. After careful mixing the amalgam was filled up into the vials which were then fused off. In order to determine the alkali metal concentration a vial with amalgam was broken in weak sulfuric acid. After dissolution of the amalgam the acid was titrated, and the mercury weighed. At very low concentrations the alkali metal was determined by flame spectrophotometry.

Amalgams with a potassium content ranging from $9 \cdot 10^{-1}$ to $5.3 \cdot 10^{-4}$ at.% were studied. Currents limited by the space charge in the systems Ni–CuPc–Hg and Ni–CuPc–K amalgam were studied in order to determine the contact potential difference between potassium amalgam and mercury. The potential differences were measured between Ni and mercury as well as between Ni and potassium amalgam. From these values the contact potential difference between mercury and potassium amalgam was found. The inner contact potential difference $\Delta\varphi$ between metals separated by a thin layer of dielectric is determined, according to Wright's equation [5], by extrapolating to i = 0 the quadratic portion of the volt-ampere curve in a plot of $i^{1/2}$ against V. The volt-ampere characteristics for systems with mercury and with the amalgam were measured at the same Pc film [1, 2].

Figure 1 shows the volt-ampere curves for the systems Ni–CuPc–Hg and Ni–CuPc–K amalgam ($9 \cdot 10^{-1}$ at.%); the thickness of the Pc film was $7.5 \cdot 10^{-4}$ cm. The shape of the curves is similar to that for the systems with mercury and with Tl amalgam of [1]. The two characteristics are nonlinear, and at V > 2 V the current in the nonblocking direction varies as the square of potential. Rectification is observed with both systems. When Hg is replaced by the amalgam, rectification increases, in harmony with the electronic work functions for the amalgam and for mercury. With Ni(+) the potassium amalgam injects electrons owing to its lower work function as compared to mercury. With Ni(–) the nonblocking direction corresponds to hole injection from mercury [1]. The shape of the volt-ampere curves for potassium amalgams of other concentrations is similar to that shown in Fig. 1.

Figure 2 shows $i^{1/2}$–V curves constructed from the data of the volt-ampere characteristics (Fig. 1). Contact potential differences were determined with an accuracy of about 0.05 V.

Values for the work function (φ) of amalgams with different potassium contents are given in Table 1. The work functions of the amalgams decrease with increasing potassium concentration. The $\varphi - \log c_{\text{potassium}}$ curve has two linear portions, the steeper slope being observed at small potassium concentrations (see Fig. 3). Lazarev and Malov [6, 7] have determined the work functions of potassium amalgams by a photoelectric method at 10^{-8} mm Hg. On the $\varphi - \log c_{\text{potassium}}$ curves following from their data, three linear sections are observed; the work functions are lower than our results by about 0.2 eV, and by a little more in the range of intermediate concentrations. So far it is not clear how to explain this discrepancy. Under a vacuum of 10^{-6} mm Hg, adsorbed films of residual gases may exist on the samples studied. However, we have shown previously [2] that the layer of adsorbed gas molecules is broken up and the pure metal surface is laid open when the Pc film is placed upon the liquid metal. On the other hand, a decrease rather than an increase in work function is observed, according to [6, 8], when going from a vacuum of 10^{-8} mm Hg to one of 10^{-6} mm Hg. The use of different methods for determining the amalgam concentrations (volumetric dosing from a microburet in [6, 7], analysis of each sample in our experiments) may also affect the data, especially at low concentrations.

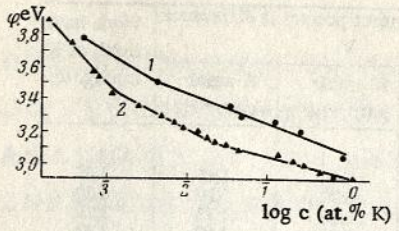


Fig. 3. The electron work function φ of potassium amalgams as a function of the log of potassium concentration: 1) as obtained on the basis of space-charge limited currents; 2) from the photoelectric measurements of Lazarev and Malov.

Our values for the work functions of amalgams with different potassium content allow us to compute the potential of zero charge for these systems in electrolyte solutions, by using the relation [9]

$$\varphi_{\varepsilon=0} = w_e - 4.72,$$

where $\varphi_{\varepsilon=0}$ is the potential of zero charge and w_e is the work function. However, at the values of $\varphi_{\varepsilon=0}$ obtained in this way the concentration of alkali metal in the amalgam would drop to extremely low values, so that it is impossible to verify our conclusion.

Work continues at present with potassium amalgam as well as with the amalgams of other alkali metals.

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