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PHYSICAL CHEMISTRY

V. B. LAZAREV, Yu. I. MALOV

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

V. B. LAZAREV, Yu. I. MALOV

PHOTOELECTRIC PHENOMENA

IN DILUTE AMALGAMS OF ALKALI METALS

(Presented by Academician I. I. Chernyaev, March 19, 1965)

In work ([1]) we showed that, in the case of dilute potassium amalgams, the concentration dependences of the electron work function and of the surface tension are graphically expressed by curves of analogous character; moreover, noticeable changes in the work function were observed already at a concentration of 10^{-6} atomic fraction of potassium. It was also shown that study of the photoemission current from the surface of potassium amalgams made it possible to draw certain conclusions about potassium adsorption not only in the liquid phase, but also in the solid phase.

Fig. 1. Concentration dependences of the photocurrents from the surface of cesium (1), potassium (2), and sodium (3) amalgams at an incident-light wavelength of 3136 Å

At the present time, using the previously described method ([1]), we have measured the values of the photoemission currents from the surface of mercury-sodium solutions containing from 0 to 0.7 at.% sodium, and mercury-cesium solutions containing from 0 to 0.001 at.% cesium. These measurements were carried out in the temperature range from $+25^\circ$ to -80°.

As is seen from Fig. 1, which gives the dependences of the photoemission-current values on the concentration of the alkali metal in cesium, potassium, and sodium amalgams at one and the same wavelength of the incident light (3136 Å), the magnitude of the external photoelectric effect from the surface of cesium amalgams considerably exceeds the photoeffect from the surface of potassium amalgams, which in turn is greater than the photoeffect from the surface of sodium amalgams.

Having determined the values of the electron work function φ from the surface

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Fig. 2

Figure 2: Fig. 2

of sodium and cesium amalgams, we compared them with the data ([8]) on the surface tension σ of these same amalgams and found, as is seen from Fig. 2, that an analogy in the form of the curves graphically expressing the concentration dependences of the quantities σ and φ also holds in the case of sodium and cesium amalgams ([1]). If one compares the values of the derivatives $(-\partial\varphi/\partial C)_{C\to 0} = \chi$, where C is the concentration, for amalgams of alkali metals, it turns out that

$$\chi_{\mathrm{Cs}} > \chi_{\mathrm{K}} > \chi_{\mathrm{Na}}.$$

In cesium amalgams a noticeable change in the work function (0.8 V) was observed already at a cesium concentration of 10^{-8} atomic fraction in the melt.

As far as we know, there are no indications in the literature of the possibility of such considerable changes in the work function from the surface of a metallic cathode when its composition is changed by only 10^{-8} atomic fraction ([3]). The experimentally observed influence of small impurities of alkali metals on

the work function, as well as in the case of surface tension, can be explained by the considerable surface activity of alkali metals on mercury, so that even at a very low content of alkali metal in the bulk of the amalgam its concentration in the surface layer may turn out to be very high (4-6).

Fig. 2. Electron work function (a) and surface tension (b) of cesium (1) and sodium (2) amalgams as functions of the concentration of the alkali metal

It is known from the literature (2, 8) that the maximum value of the adsorption of cesium $\Gamma^{\mathrm{e}}_{\mathrm{Cs}}$ in mercury-cesium solutions is greater than the corresponding value in mercury-potassium solutions $\Gamma^{\mathrm{e}}_{\mathrm{K}}$, and still greater than in mercury-sodium solutions $\Gamma^{\mathrm{e}}_{\mathrm{Na}}$:

$$\Gamma^{\mathrm{e}}_{\mathrm{Cs}} > \Gamma^{\mathrm{e}}_{\mathrm{K}} > \Gamma^{\mathrm{e}}_{\mathrm{Na}},$$

whereas the values of the concentrations of the surface-active additives at which these extreme adsorption values (C^{e}) were reached satisfied the inequality:

$$C^{\mathrm{e}}_{\mathrm{Cs}} < C^{\mathrm{e}}_{\mathrm{K}} < C^{\mathrm{e}}_{\mathrm{Na}}.$$

The data presented in Fig. 1 are in good agreement with these conclusions of works (2, 8), since in the case of cesium amalgams the photoemission currents exceeding the photocurrents from the surface of the corresponding potassium and sodium amalgams are reached already at significantly lower concentrations of the alkali metal (see Fig. 1).

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Fig. 3

Figure 3: Fig. 3

Figure 4: Concentration dependences of photocurrents from the surface of cesium (a) and sodium (b) amalgams in the molten (1) and solid states (2).

Figure 4: Figure 4: Concentration dependences of photocurrents from the surface of cesium (a) and sodium (b) amalgams in the molten (1) and solid states (2).

In works (2, 8) there was also a conclusion about the existence of sharp maxima on the adsorption isotherms of potassium and cesium.

Fig. 3. Temperature dependences of the photoemission current from the surface of cesium amalgam (1) (cesium concentration–0.00039 at.%) and from the surface of sodium amalgam (2) (sodium concentration 0.6 at.%) at an incident-light wavelength of 3136 Å

If one adheres completely to the views developed by Gibbs (7), who held that adsorption can be represented as the product of the thickness of the surface layer by the difference between the bulk concentrations of the substance in the boundary layer and in the phases adjacent to it, then, in order to explain the existence of such sharp maxima, it is necessary to assume that either the thickness of the surface layer decreases as the concentration of alkali metal in the bulk increases, which is unlikely, or that the concentration of alkali metal in the surface layer at some point begins to decrease with increasing content of alkali metal in the bulk; however, this supposition is not consistent with the steady increase we observed in the photocurrent values with increasing concentration of, respectively, cesium, potassium, or sodium in the melt, as is evident from Fig. 1.

In studying the dependence of the photocurrents on temperature in the case of sodium, potassium, and cesium amalgams, a noticeable increase in the photoemission current was found as the temperature was lowered, as well as a shift of the "red boundary" of the photoeffect toward longer wavelengths. Figure 3 shows, as an example, the dependence of the photoemission current on temperature in the case of sodium and cesium amalgams. This form of the temperature dependence can be explained by an increase in the adsorption of the alkali metal when the temperature is lowered.

Fig. 4. Concentration dependences of photocurrents from the surface of cesium (a) and sodium (b) amalgams in the molten (1) and solid states (2).

Comparison of the form of the curves expressing the dependence of the photoemission current on the surface of sodium and cesium amalgams in both the liquid and solid states, shown in Fig. 4, can apparently be regarded as confirmation of the fact that in amalgams alkali metals, adsorbing at the melt-gas

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boundary, retain this property also at the solid-gas boundary and, consequently, are surface-active at this phase boundary as well.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

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