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Abstract

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Determination of the Potential of Zero Charge of Silver

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For the potential of zero charge of silver there are a number of values in the literature that differ substantially from one another. From adsorption measurements for silver a value $\varphi_{\text{n.z}}{}^*$ equal to +0.05 V was obtained (1). From capacitance measurements values of +0.05 V (2), −0.15 V (3) were obtained. From observations of the smoothing of silver it follows that $\varphi_{\text{n.z}} \approx -0.3$ V (4). By recording electrocapillary curves in melts (with recalculation, using the value of $\varphi_{\text{n.z}}$ for lead), a potential of zero charge of −0.6 V was obtained for silver (5). In spite of the recalculation, the last method is probably one of the most reliable methods for determining $\varphi_{\text{n.z}}$, since the measurements are carried out on a liquid metal, the surface of which is, naturally, more homogeneous than the surface of a solid metal. The data obtained by this method for almost all the metals investigated agree well with data obtained by other methods in aqueous solutions at room temperature. Silver was an exception. In order to clarify the indicated contradictions, we considered it expedient to measure $\varphi_{\text{n.z}}$ of silver in aqueous solutions by recording curves of the dependence of the double-layer capacitance on the potential in solutions of different composition. This method has been successfully used to determine the potential of zero charge of Pb (6,7), Cd (6), Tl (6), PbO_2 (8). The method of measurements in alternating current did not differ from that described previously (7,8). The measurements were carried out on a silver wire sealed into molybdenum glass. Before the measurements the electrode was cleaned with wet fine glass powder and degreased by boiling in alkali for 1 min, after which it was thoroughly washed with bidistillate and subjected to cathodic polarization at a potential of −0.5 V. The data obtained are shown in Fig. 1. As is seen from Fig. 1, on curves 1 and 2, recorded in dilute Na_2SO_4 solutions, at $\varphi = -0.7$ V a well-pronounced minimum is observed, becoming deeper with dilution. For comparison, curve 3 is given, recorded in a 1 N solution. In accordance with the theory of the double layer, in the potential interval from −0.6 to −0.8 V there is no capacitance minimum on it of the kind observed in dilute solutions. On the basis of the data presented, we concluded that for silver $\varphi_{\text{n.z}} = -0.7 \pm 0.05$ V.

To confirm the correctness of this conclusion, we considered it necessary to compare the data obtained in dilute K_2SO_4 solutions with data obtained in

Fig. 1-3

Figure 1: Fig. 1-3

dilute KCl and KBr solutions, i.e., in solutions containing anions of different surface activity. It could be expected that $\varphi_{\mathrm{n.z}}$ would shift in the negative direction upon successive replacement of SO_4^{2-} by Cl^- and Br^-. Figure 2 gives curves recorded in 0.01 N solutions of K_2SO_4 (curve 1), KCl (curve 2), and KBr (curve 3). As is seen from Fig. 2, the expected phenomenon is indeed observed. It should be noted that the accuracy of our determination of $\varphi_{\mathrm{n.z}}$ can was called into question by ascribing to the SO_4^{2-} ion a high surface activity with respect to silver and assuming that, in reality, $\varphi_{\mathrm{n.z.}}$ of silver has a more positive value than follows from Fig. 1. However, the absence of a shift of the potential of the minimum in the positive direction upon dilution of the solution (curves 1 and 2 in Fig. 1) contradicts such an assumption.

In addition to the measurements indicated above, in order to provide further confirmation of the correctness of our determination of $\varphi_{\mathrm{n.z.}}$, we carried out measurements of the differential capacitance of the double layer on silver in the presence of hexyl alcohol. As is known, hexyl alcohol is adsorbed near the potential of zero charge and is desorbed when a sufficiently large

Fig. 1. Dependence of the capacitance of a silver electrode on potential: 1 –in 0.002 N Na_2SO_4; 2 –in 0.01 N Na_2SO_4; 3 –in 1 N Na_2SO_4

Fig. 2. Dependence of the capacitance of a silver electrode on potential: 1 –in 0.01 N K_2SO_4; 2 –in 0.01 N KCl; 3 –in 0.01 N KBr

Fig. 3. Dependence of the capacitance of a silver (1) and mercury (2) electrode on potential in a 1 N Na_2SO_4 solution saturated with hexyl alcohol

magnitude of both negative and positive surface charge is reached, as a result of which desorption peaks are observed, located to the right and to the left of $\varphi_{\mathrm{n.z.}}$ [9]. Although it is not possible in this way to determine $\varphi_{\mathrm{n.z.}}$ exactly, since the orientation of the adsorbed dipolar molecule may differ somewhat on different metals, nevertheless, in view of the large discrepancy of the earlier results among themselves and with the value obtained by us, we considered it useful to carry out these additional measurements, which, by an independent method, may indicate the region containing $\varphi_{\mathrm{n.z.}}$.

Figure 3 shows the curves obtained on silver (curve 1) and on mercury (curve 2) in 1 N Na_2SO_4 solutions saturated with hexyl alcohol at a frequency of 2 kHz.* The desorption peaks on silver are expressed somewhat less distinctly than on mercury (which is probably associated with the nonuniformity of the solid metal),

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* All potential values are given relative to the normal hydrogen electrode.

* The measurements on mercury were carried out at the Department of Electrochemistry of Moscow State University by Satya Narayan, to whom we express our gratitude.

however, is sufficiently clear (see Fig. 3). The value of $\varphi_{\text{n.z}}$ for silver found by us (−0.7 V) lies within the interval of potentials between the desorption peaks. It should be noted that the desorption peaks on silver lie at potentials approximately 0.3 V more negative than on mercury; from this it may also be concluded that $\varphi_{\text{n.z}}$ for silver is more negative than $\varphi_{\text{n.z}}$ for mercury, equal to −0.2 V.

On the basis of the foregoing, we consider that the potential of zero charge of silver is equal to -0.7 ± 0.05 V. The value of $\varphi_{\text{n.z}}$ obtained by us agrees with the results of measuring $\varphi_{\text{n.z}}$ by the method of electrocapillary curves in melts (5) with the same accuracy as for other metals.

In studying the dependence of the capacitance of the double layer on silver on the potential, we found that strong cathodic polarization in solutions of Na_2SO_4 and K_2SO_4 is not without effect on the properties of the silver surface. Thus, in particular, polarization of silver in the potential region from −1.3 to −1.4 V leads to irreversible changes in the properties of the silver surface. Therefore, in carrying out the measurements, the cathodic polarization of silver was not brought to such negative values.

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