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SPECIFIC ADSORPTION OF THE CHLORIDE ION ON A POLYCRYSTALLINE SILVER ELECTRODE

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A strong adsorption of chloride ions has been observed when studying the electrical double layer on polycrystalline and monocrystalline silver electrodes in chloride solutions [1, 2]. To establish the laws governing the adsorption it was of particular interest to investigate quantitatively the adsorption of chloride ions, for instance, by means of the mixed electrolyte method [3, 4]. With this aim in mind, the relationship between the differential capacity C and the potential of a polycrystalline silver electrode was established in this article in solutions of x M KCl + (0.2−x) M KF, with x varying from 10^{-3} to 10^{-1}.

In distinction from the end-face electrode used in earlier work [1], the electrode used in the present study was made of a silver wire (length ~1.5 cm, diameter ~1.5 mm), with both ends pressed into a Teflon holder, so that the measurements were made only on the lateral surface of the wire. The electrode surface was pretreated using the procedure described in [5, 6]. It was found that a smoother surface was obtained by polishing with anodic currents of 0.03-0.1 A/cm^2 without mixing of the solution.

When changing the differential capacity of solid electrolytes, the results depend strongly on the pretreatment of the surface which determines the region of the ideal polarization of the electrode, the degree of reduction, and the roughness [7]. In the case of polycrystalline silver there is also the possibility of influence of the pretreatment on the surface heterogeneity of the electrode [1, 8]. All indicated properties of the electrode can be assessed from the measurement of the differential capacity in solutions of a specifically inactive electrolyte, for instance in KF solutions.

Figure 1 shows the C, E curves for a polished silver electrode in KF solutions. The measurements were made at a frequency of 210 Hz since at this frequency the active component is independent of the electrode potential in the potential region more positive than −1.3 V. It should be pointed out that, in the region of the minimum, the capacity component increases by 6% when changing from 210 to 30 Hz. This can be related to the surface roughness as well as to the electrode process. All curves presented were obtained at cathodic polarization currents, whereby the currents did not exceed a few μA per cm^2 of the apparent electrode surface in the potential region from −0.7 to 1.3 V [6, 8].

It can be seen from Fig. 1 that in the case of such a silver electrode a minimum at −0.97 V is observed on the C, E curves in dilute KF solutions. This value is in full agreement with the zero charge potential (z. c. p.) of polished polycrystalline silver [1, 8]. At the z. c. p. a linear relationship exists between the reciprocal capacities given in Fig. 1 and the theoretical capacities of the diffusion layer [9], the cotangent of the slope angle of which is equal to 1.5. If we assume that the deviation of the cotangent from unity is due to surface roughness [7], the roughness coefficient of the electrode must be equal to 1.5.

TABLE 1. Zero Charge Potential Shift for Mercury [14], Silver, and Gold [15] as Function of KCl Concentration

KCl concentration, M	Z.c.p. shift, mV			KCl concentration, M	Z.c.p. shift, mV		
	mercury	silver	gold		mercury	silver	gold
0,001	0	10	–	0,05	15	50	210
0,01	5	25	180	0,1	25	60	270

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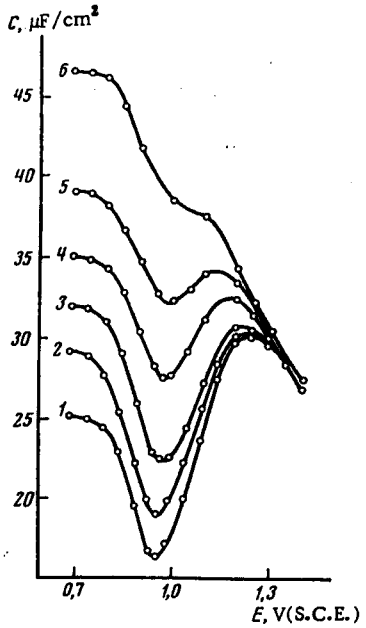

Fig. 1

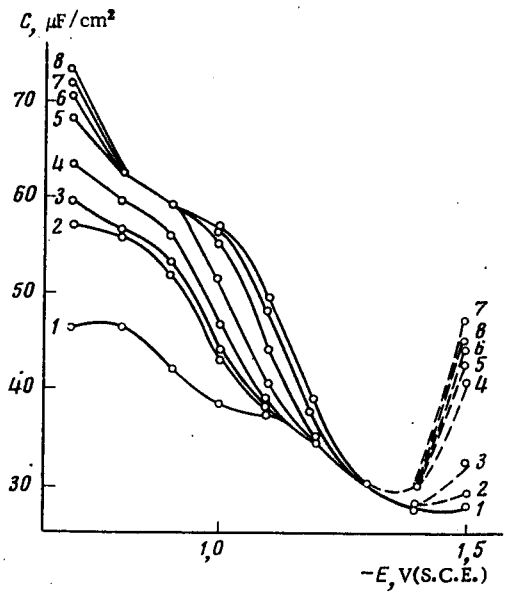

Fig. 2

Fig. 1. C,E curves in KF solutions, M: 1) 5×10^{-3}, 2) 10^{-2}, 3) 2×10^{-2}, 4) 5×10^{-2}, 5) 10^{-1}, 6) 2×10^{-1}.

Fig. 2. C,E curves in solutions of x M KCl + (0.2 − x) M KF when x is: 1) 0, 2) 10^{-3}, 3) 2×10^{-3}, 4) 4×10^{-3}, 5) 10^{-2}, 6) 2.5×10^{-2}, 7) 5×10^{-2}, 8) 10^{-1}. Explanations are given in the text.

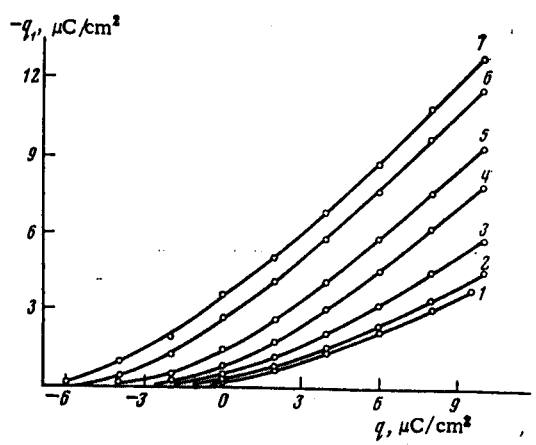

Fig. 3

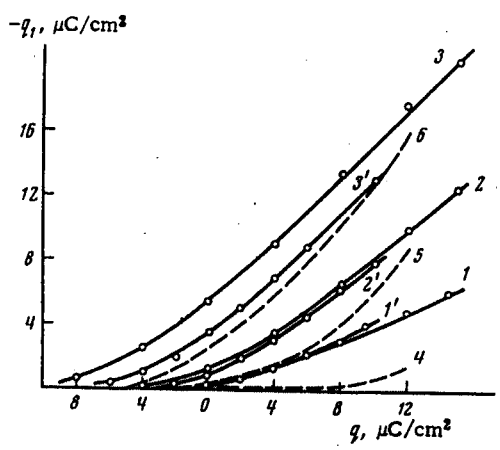

Fig. 4

Fig. 3. Curves representing the charge density of specific adsorbed ions q_1 as function of the total charge density of the electrode q in solutions of x M KCl + (0.2 − x) M KF when x is: 1) 10^{-3}, 2) 2×10^{-3}, 3) 4×10^{-3}, 4) 10^{-2}, 5) 2.5×10^{-2}, 6) 5×10^{-2}, 7) 10^{-1}.

Fig. 4. Curves representing the charge density of specific adsorbed ions q_1 as function of the total charge density q of the electrode on silver in solutions of x M KCl + (0.2 − x) M KF (curves 1-3 and 1'-3') and on mercury in solutions of x M KCl + (1 − x) M KF (curves 4-6). Curves 1-3 were calculated without account of the roughness coefficient. The values of x are: 1, 1', 4) 10^{-3}; 2, 2', 5) 10^{-2}; 3, 3', 6) 10^{-1}.

The C,E curves for the system x M KCl + (0.2 − x)M KF shown in Fig. 2 have a shape which is characteristic for differential capacity curves in mixed electrolyte solutions. In the region of potentials more negative than 1.3 V an increase in the capacity component of impedance is observed on the C,E curves (shown on Fig. 2 by broken lines) which increases with increasing KCl concentration. An increase in the active component of impedance is observed in this potential region and a sharp increase of the polarization current with increasing KCl concentration. All this proves that in this potential region the capacity component to be measured reflects not only the capacity of the double layer but also the electrode process. Assuming that this process is controlled by the discharge stage we have calculated the capacity of the double layer starting from a parallel replacement scheme for the electrode/electrolyte boundary [10]. It was here assumed that the electrolyte resistance is equal to the resistance measured in the region of potentials more positive than −1.3 V. The calculated capacities agree with the capacities measured in a pure KF solution (maximum difference 7%, see curve 1, Fig. 2). This allows the conclusion to be drawn that a practically complete desorption of chloride ions takes place at potentials more negative than −1.3 V.

To determine the charge of specifically adsorbed ions q_1 from the differential capacity curves shown in Fig. 2, the electrode charge densities q as function of potential were determined by the reverse integration method [11]. The experimental values of the differential capacity were divided by the roughness coefficient of the electrode, equal to 1.5, and the value of the potential minimum on the C,E curves in diluted KF solutions was taken as the integration constant. The values of q_1 were calculated using the method given in [12]. It became apparent during the calculations that the logarithms of the changes in surface pressure were proportional to the concentration of the active component. In accordance with [13] this simplified the calculation of the charge of specifically adsorbed ions.

Figure 3 shows the final results of the calculations. It can be seen that a significant adsorption of chloride ions on the silver takes place at all concentrations investigated and that at $x > 2.5 \times 10^{-2}$ M and $q > 0$ this adsorption leads to overcharging of the electrode surface.

To assess the effect of the assumed value of the roughness coefficient of the electrode on the q_1, q curves, the q_1-versus-q relationships were plotted on Fig. 4 with and without account of the roughness coefficient. It can be seen that at the same surface charges the charge caused by specific adsorbed chloride ions on silver is higher than on mercury (broken lines) and that this difference decreased with increasing chloride ion concentration and surface charge.

The specific adsorption of the ion on different metals can be compared by comparing the z.c.p. shifts at the same ion concentration in the solution. The data in Table 1 show that the z.c.p. shift is higher for silver than for mercury, but significantly smaller than for gold. Thus, the adsorption of chloride ions on silver is higher than on mercury and other metals similar to mercury [16, 17], but significantly smaller than on gold [18, 19].

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POTENTIOMETRIC INVESTIGATION OF THE ASSOCIATION OF POTASSIUM IONS WITH HEXACHLORIDE COMPLEXES OF IRIDIUM AND THE RATE OF ACTIVATION OF THE ION PAIRS FORMED

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In a study of the kinetics and mechanism of the reactions in which ions participate in electrolyte solutions, considerable attention is paid to the elucidation of the role of the processes of formation of ion pairs and other associates [1]. In the investigation of the reactions of ion pairs, which may differ not only in composition but also in structure, it is important to use various methods [2].

In [3] it was shown that the stability constants of the ion pairs $M^{z+} \cdot IrBr_6^{3-}$, determined according to the dependence of the reaction rate of activation of the complexes $IrBr_6^{3-}$, on the one hand, and the equilibrium potential of the system $IrBr_6^{2-}-IrBr_6^{3-}$, on the other hand, on $[M^{z+}]$ agree in the case of $M^{z+}=Ba^{2+}$ and differ ~2-fold in the case of the associates $Cd^{2+} \cdot IrBr_6^{3-}$. In this work we investigated the composition and stability of the ion pairs formed in the association of $IrCl_6^{3-}$ complexes with K^+ ions at an ionic strength $\mu = 0.1$. Earlier [4] the association of K^+ ions with complexes $IrCl_6^{3-}$ was investigated in a solution of 3 M (LiCl + KCl).

The rate constant of the activation of $IrCl_6^{3-}$ complexes was determined by a potentiometric method, based on a study of the time dependence of the potential of the redox system $IrCl_6^{2-}-IrCl_6^{3-}$ immediately after electrogeneration of $IrCl_6^{3-}$ complexes [5, 6]. The initial solution usually contained $2 \cdot 10^{-4}$ M K_2IrCl_6. Iridium electrodes were used as the indicator electrodes. The reference electrode was a calomel half-cell in a saturated solution of NaCl, the temperature of which was the same as the temperature of the investigated solution (with an accuracy within ± 0.1°C).

The experimental procedure and treatment of the results were described in [3, 5, 6].

Table 1 presents average (of 4-5 measurements) values of the rate constant of the activation of hexachloride complexes of iridium(III), which were calculated from the initial linear portions of the φ versus t curves. The standard deviation of the determination of $K_{1,\,obs}$ does not exceed 2%. Evidently the observable rate constant systematically decreases with increasing $[K^+]$, which is evidence in support of the formation of less reactive associates from the $IrCl_6^{3-}$ complexes and K^+ ions.

In dilute solutions of acids, the complexes $IrCl_6^{3-}$ evidently do not form appreciable amounts of associates with hydrogen ions, which is confirmed by practically the same values of the rate constant of aquation in 10^{-2} and 10^{-1} M HCl [6]. Therefore it can be assumed that in 0.1 M ($HClO_4$ + KCl), hexachloride complexes of iridium(III) are present in the form of free $IrCl_6^{3-}$ complexes and ion pairs of the $K^+ \cdot IrCl_6^{3-}$ type. If the $IrCl_6^{3-}$ complexes form ion pairs of the general form $K^+ \cdot IrCl_6^{3-}$, according to [2] the following relationship should be fulfilled:

$$(k_1 - k_{1,\,obs}) \cdot [K^+]^{-1} = -k_1' K_{K^+ \cdot IrCl_6^{3-}} + k_{1,\,obs} \cdot K_{K^+ \cdot IrCl_6^{3-}}, \quad (1)$$

where $k_{1,\,obs}$ is the experimentally determinable rate constant of the aquation reaction; k_1 and k_1' are the rate constants of the aquation of the complexes $IrCl_6^{3-}$ and the ion pairs $K^+ \cdot IrCl_6^{3-}$, respectively; $K_{K^+ \cdot IrCl_6^{3-}}$

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