SPECIFIC ADSORPTION OF CESIUM IONS ON A PLATINUM ELECTRODE

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In other investigations [1-5] the specific adsorbability of the cations of alkali metals has been shown to increase in the series $Li^+ < Na^+ < Cs^+$, the Li^+ ion being adsorbed only slightly more strongly than H^+ ion. It was of interest therefore to determine the values of the specific adsorption of Cs^+ ions on platinum.

With this aim we have utilized in the present work the method of determining specific adsorption of ions from solutions of constant ionic strength, proposed by Hurwitz [6] and by Dutkiewicz and Parsons [7].

We consider this method as applied to a platinum–hydrogen electrode. We assume that the platinum electrode is immersed in a solution of composition $y\,N\,H_2SO_4 + ax\,N\,Li_2SO_4 + a(1-x)\,N\,Cs_2SO_4$, in which the concentration of acid, which is considerably less than the total concentration of lithium and cesium sulfates, is equal to a, but all the concentrations are quite low. In the system considered, it is obvious that with change in x the values of the chemical potentials of the ions H^+ and SO_4^{2-} will remain practically constant, and the Gibbs adsorption equation can be represented as:

$$d\sigma = -Q d\varphi_r - \Gamma_{Li^+} d\mu_{Li^+} - \Gamma_{Cs^+} d\mu_{Cs^+}, \tag{1}$$

where σ is the free surface energy, Q is the surface charge [8], φ_r is the electrode potential referred to a reversible hydrogen electrode in the same solution. Γ_{Li^+} and Γ_{Cs^+} are the Gibbs adsorptions, and μ_{Li^+} and μ_{Cs^+} are the chemical potentials of the lithium and cesium ions, respectively. The values of Γ and μ are expressed in electrical units; the position of the interface was selected in agreement with the condition $\Gamma_{H_2O} = 0$. Then it is possible to write:

$$\Gamma_{Li^+} = \Gamma'_{Li^+} + \Gamma''_{Li^+}, \tag{2}$$

$$\Gamma_{Cs^+} = \Gamma'_{Cs^+} + \Gamma''_{Cs^+}, \tag{3}$$

where the symbol Γ' denotes adsorption of an ion in the solid part and Γ'' denotes adsorption of the ion in the diffuse part of the double layer. We assume that $\Gamma'_{Li^+} = 0$, and for Γ''_{Li^+} and Γ''_{Cs^+} the following relationship is fulfilled [6, 7]:

$$\frac{\Gamma''_{Li^+}}{\Gamma''_{Cs^+}} = \frac{x}{1-x}. \tag{4}$$

Since $d\mu_{Li^+} = (RT/F) d \ln x = (RT/F)(dx/x)$ and $d\mu_{Cs^+} = (RT/F) d \ln(1-x) = -(RT/F)(dx/1-x)$, then equation (1) can be rewritten as

$$d\sigma = -Q d\varphi_r - \Gamma'_{Cs^+} d\mu_{Cs^+} \tag{5}$$

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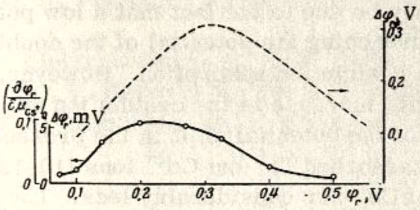

Fig. 1

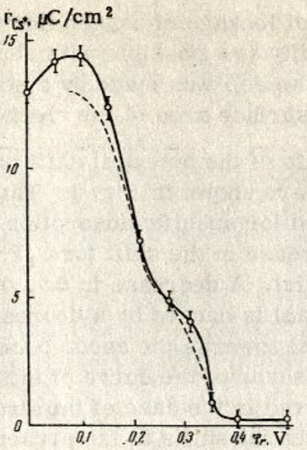

Fig. 2

Fig. 1. Plot of the potential shift at a platinized platinum electrode on replacing a solution of 10^{-3} N H_2SO_4 + $9 \cdot 10^{-3}$ N Li_2SO_4 + 10^{-3} N Cs_2SO_4 by a solution of 10^{-3} N H_2SO_4 + 10^{-3} N Li_2SO_4 + $9 \cdot 10^{-3}$ Cs_2SO_4. Dashed line: dependence of the potential shift on the initial potential on replacing a solution of 1 N H_2SO_4 by a solution of 1 N H_2SO_4 + 0.1 N $CdSO_4$ according to [10].

Fig. 2. Dependence of the adsorption of cesium ions on the potential in a solution of 10^{-3} N H_2SO_4 + $5 \cdot 10^{-3}$ N Li_2SO_4 + $5 \cdot 10^{-3}$ N Cs_2SO_4. Dashed line: calculated from equation (6). Vertical lines show the accuracy of the experimental determination of Γ_{Gs^+}.

From equation (5) follows the relationship:

$$\left(\frac{\partial\varphi_r}{\partial\mu_{Cs^+}}\right)_Q = -\left(\frac{\partial\Gamma'_{Cs^+}}{\partial Q}\right)_{\mu_{Cs^+}} = -\left(\frac{\partial\Gamma'_{Cs^+}}{\partial\varphi_r}\right)_{\mu_{Cs^+}} : \left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu_{Cs^+}}. \tag{6}$$

For the general case of replacement of a surface-inactive ion by a surface-active ion i with preservation of constant total concentration it is possible to write:

$$\left(\frac{\partial\varphi_r}{\partial\mu_i}\right)_Q = -\left(\frac{\partial\Gamma_i'}{\partial\varphi_r}\right)_{\mu_i} : \left(\frac{\partial Q}{\partial\varphi_r}\right)_{\mu_i}, \tag{7}$$

where μ_i is the chemical potential of the surface-active ion.

Equation (7) is identical with the equation introduced in reference [7] if the concept regarding the charge formulated in [8] is accepted. An analogous relationship was obtained in [2] (Eq. (26) of the work cited) for the case where the adsorbability of the ion i is so great that it displaces all other ions from the double layer. Under these conditions in place of Γ'_i in the equation Γ_i is introduced, i.e., the total adsorption of the specific adsorbed ions.

Equation (7) is applicable for determining the specific adsorption of ions in the solutions HA + KA or HA + HA* at constant ionic strength, where K is the specific adsorbed cation and A* the specific adsorbed anion.

Experiments were carried out at a Pt/Pt electrode at 20 ± 1°C. The conditions for the electrode preparation and the estimation of its true surface area were the same as those in an earlier [9]. Determination of $(d\varphi_r/d\mu_{Cs^+})_Q$ was carried out by replacing a solution of 10^{-3} N H_2SO_4 + $9 \cdot 10^{-3}$ N Li_2SO_4 + 10^{-3} N Cs_2SO_4 by a solution of 10^{-3} N H_2SO_4 + 10^{-3} N Li_2SO_4 + $9 \cdot 10^{-3}$ N Cs_2SO_4 under isoelectric conditions [9]. Because of the comparatively small value of the specific adsorbability of cesium ions the shift in potential is not very large. Thus the maximum shift is about 6 mV. Therefore carrying out the experiments required careful stabilization of the potential in the initial solution, careful purification of the solutions from aerial oxygen, and prevention of leakage of oxygen into the system. Since the solution was dilute with respect to H^+ and a change in acidity was possible with change in potential, then frequent replacement of the solution in the working part of the cell was made by a solution of the specified composition, which was monitored by titration. The true surface area of the electrode used for measurements was 8.1 m^2.

The measurements of the potential shift on replacing Li^+ ions by Cs^+ ions at different potentials of the platinum electrode are shown in Fig. 1. The Cs^+ ion gives rise to a potential shift towards the anode, which might be expected for specific adsorption of the cation. The value of the shift depends on the electrode potential. A decrease in the shift for $\varphi_r \to 0$ may be due to the fact that a low potentials Γ'_{Cs^+} hardly changes with the potential. A decrease in $\Delta\varphi_r$ on approaching the potential of the double-layer region (right-hand branch of maximum) is caused by a decrease in cesium ion adsorption. However, even at $\varphi_r \sim 500$ mV a small shift in potential towards the anode occurs with increase in the cesium ion concentration in the solution. In general, the shape of the curve of the plot of the potential shift in the presence of cesium ions is analogous to that observed in the case of the strongly adsorbed Tl^+ and Cd^{2+} ions [10-12], though the absolute values of the potential shifts in the presence of Cs^+ are considerably less. The small value of the shifts caused by Cs^+ ions and also the disadvantageous ratio of the concentrations of these ions and hydrogen ions are the reasons that these shifts were not recorded previously in [12].

The derivative $(\partial Q/\partial \varphi_r)_{\mu_{Cs^+}}$, required for equation (6) calculation, was obtained by graphical differentiation of the equilibrium charging curve [14], measured in a solution of 10^{-3} N H_2SO_4 + $5 \cdot 10^{-3}$ N Cs_2SO_4 + $5 \cdot 10^{-3}$ N Li_4SO_4. From the values of $(\partial \varphi_r/\partial \mu_{Cs^+})_Q$ and $(\partial Q/\partial \varphi_r)_{\mu_{Cs^+}}$ and using equation (6) the dependence of the specific adsorption of Cs^+ ions on potential was calculated. For this, in order to determine the absolute values of Γ'_{Cs^+}, it is necessary to know the integration constants. The latter were determined in the following way. In a solution of the composition indicated above the dependence of the adsorption of Cs^+ ions on the potential was determined by the described method [15]. This dependence is shown in Fig. 2. At $\varphi_r > 400$ mV the adsorption of Cs^+, within the limits of accuracy of measurements measured by means of a radioactive indicator method, practically equals zero, though according to measurements of the isoelectric shifts of potential, as noted above, there remains at these potentials a certain dependence on the adsorption potential of Cs^+. It seems a plausible assumption that the small adsorption of Cs^+ at $\varphi_r > 400$ mV is equal to the specific adsorption of these ions at the considered potentials.

The results of the calculation of Γ'_{Cs^+} and the determination of Γ_{Cs^+} by the tagged atoms method are compared in Fig. 2. From the figure it is evident that with $\varphi_r > 0.06$ V the $\Gamma'_{Cs^+}, \varphi_r$ curve is close to the Γ_{Cs^+}, φ_r curve* not only in shape but also in the adsorption values of the cesium ions. The maximum difference is 1 ± 1.5 $\mu C/cm^2$. The experimental results indicate that a considerable part of the cesium ions (more that 90%) is found in the solid part of the double layer. The conclusion is confirmed by the fact that the adsorption of cesium from a solution of 10^{-3} N H_2SO_4 + $5 \cdot 10^{-3}$ N Li_2SO_4 + $5 \cdot 10^{-3}$ N Cs_2SO_4 at $\varphi_r = 0$ is 12.5 $\mu C/cm^2$, and from a solution of 10^{-3} N H_2SO_4 + 10^{-2} N Cs_2SO_4 is approximately 13 $\mu C/cm^2$. From these results it follows that the quantity of cesium ions in the diffuse part of the double layer is no more than 0.5 $\mu C/cm^2$. In solutions of 10^{-3} N H_2SO_4 + $5 \cdot 10^{-3}$ N Na_2SO_4 + $5 \cdot 10^{-3}$ N Cs_2SO_4 the adsorption of Cs^+ is 10.5 $\mu C/cm^2$ [16], i.e., in this case about 80% of the adsorbed cesium ions are in the solid layer.

By comparing the results of the determination of the specific adsorption of Cs^+ given in reference [17] with those of the present study it can be concluded that the specific adsorption of Cs^+ cations on platinum is considerably greater than on mercury.

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*The nature of the maximum on the Γ_{Cs^+}, φ_r curve has already been discussed [14].

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