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JOINT ADSORPTION OF CADMIUM AND SULFATE IONS AT PLATINIZED PLATINUM

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The joint adsorption of cadmium and sulfate ions has been studied in [1-4]. According to [1, 2], Cd^{2+} adsorption leads to a significant decrease in sulfate ion adsorption. Horanyi and coworkers [3, 4], to the contrary, found an increase in the adsorption of SO_4^{2-} ions in the presence of cadmium ions over the potential range from the reversible hydrogen potential to 0.4 V. At more positive potentials, the adsorption of sulfate ions decreased with increasing Cd^{2+} concentration in the solution. The existence of two forms of sulfate ion in the solution, free and bound to Cd^{2+} ions, has been suggested in order to explain this effect. The first form is adsorbed at higher potentials, the second form at low potentials.

The joint adsorption of cadmium and sulfate ions at the platinized platinum electrode has been studied in the present work by the radiotracer technique using isotopes ^{115}Cd and ^{35}S with the procedure of [5]. The labeled solutions were prepared and purified similarly to [6]. The platinized electrodes were prepared and their true surface areas estimated as in [7]. Electrodes with an apparent surface area of about 2 cm^2 and true surface areas of 0.3 to 0.4 m^2 were used. The experiments were performed at 22 ± 2°C.

The adsorption of cadmium ions ($\Gamma_{Cd^{2+}}$) is presented as a function of φ_r in Fig. 1 (φ_r is the potential referred to the reversible hydrogen electrode in the same solution). The procedure used to measure the Γ vs φ_r curves was similar to [8]. The electrode was brought in contact with the solution at $\varphi_r = 0.8$ V. Then the electrode potential was shifted in the cathodic direction; at any given φ_r the electrode was held for a time

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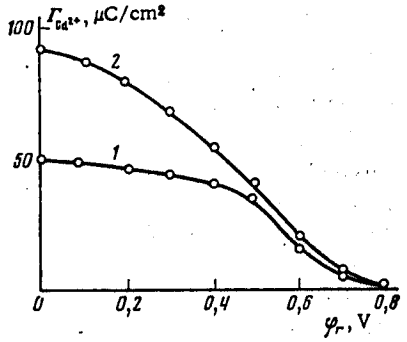

Fig. 1

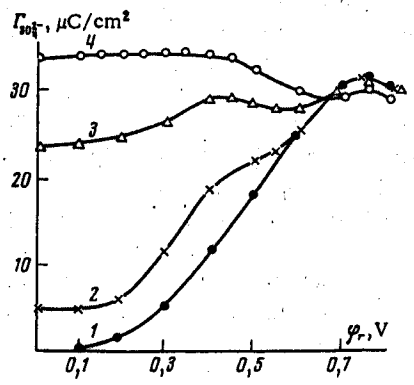

Fig. 2

Fig. 1. Adsorption of cadmium ions as a function of potential at the Pt/Pt electrode in $5 \cdot 10^{-3}$ N $Cd(ClO_4)_2$ solutions in 1 N $HClO_4$ (1) and 1 N H_2SO_4 (2).

Fig. 2. The adsorption of sulfate ions as a function of potential on the Pt/Pt electrode in $5 \cdot 10^{-3}$ N H_2SO_4 + 1 N $HClO_4$ solution without cadmium (1) and with $Cd(ClO_4)_2$ in concentrations of 10^{-3} (2), 10^{-2} (3), and 10^{-1} N (4).

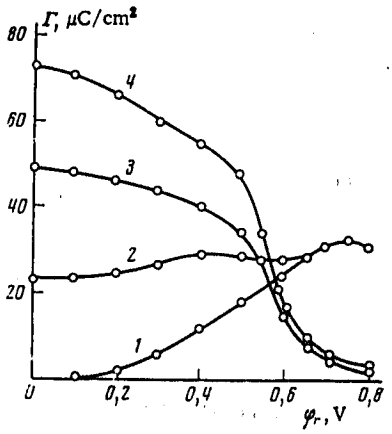

Fig. 3

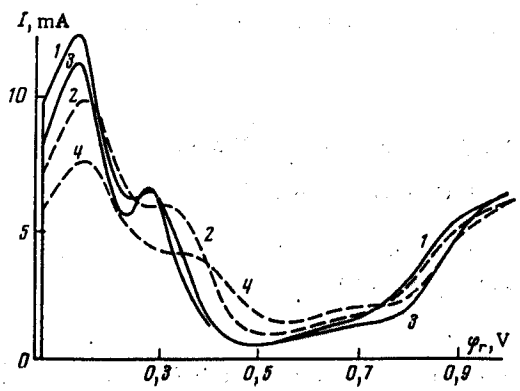

Fig. 4

Fig. 3. The adsorption of sulfate ions (1, 2) and of cadmium ions (3, 4) as functions of potential on the Pt/Pt electrode in different solutions: 1) $5 \cdot 10^{-3}$ N H_2SO_4 + 1 N $HClO_4$; 2) and 4) same as in 1), with 10^{-2} N $Cd(ClO_4)_2$; 3) 10^{-2} N $Cd(ClO_4)_2$ + 1 N $HClO_4$.

Fig. 4. Potentiodynamic curves of the Pt/Pt electrode in the following solutions: 1) 1 N $HClO_4$; 2) 1 N $HClO_4$ + 0.1 N $Cd(ClO_4)_2$; 3) 1 N $HClO_4$ + 0.1 N H_2SO_4; and 4) 1 N $HClO_4$ + 0.1 N $CdSO_4$.

sufficient for a practically time-invariant Γ value to be established. After reaching $\varphi_r = 0$ V the electrode potential was changed in the anodic direction. Practically complete coincidence of the anodic and cathodic Γ vs φ_r curves was observed. The $\Gamma_{Cd^{2+}}$ values obtained in sulfuric acid solution are close to those reported in [8]. One can see by comparing curves 1 and 2 of Fig. 1 that there is a considerable increase in the adsorption of cadmium ions when the perchlorate ions in the solution are replaced by sulfate ions; this effect increases as the potential is made more cathodic.*

*Reduction of ClO_4^- [9] appears not to have an important effect on the results obtained, since it practically ceases in the presence of SO_4^{2-} ions, while the Cl^- ions produced do not pass into the solution at $\varphi_r > 0$ V.

The adsorption of sulfate ions ($\Gamma_{SO_4^{2-}}$) is reported in Fig. 2 as function of φ_r in solutions containing different concentrations of cadmium ions. An increase in $\Gamma_{SO_4^{2-}}$ with increasing cadmium perchlorate concentration in the solution is found, in harmony with the data of Horanyi [3, 4], over the potential range from 0.0 to 0.6 V. At more anodic potentials, the $\Gamma_{SO_4^{2-}}$ values are close to those found in a solution not containing cadmium ions; we did not observe any decrease in $\Gamma_{SO_4^{2-}}$ with increasing $Cd(ClO_4)_2$ concentration in this potential range, in contrast to [3, 4]. This discrepancy appears to be due to the fact that in our experiments, solutions with higher H_2SO_4 concentrations than in [3, 4] have been used. Thus, one can conclude from the data of Figs. 1 and 2 that the adsorbabilities of SO_4^{2-} and Cd^{2+} are mutually enhanced when these ions are jointly present in the solution.

The dependences of $\Gamma_{CD^{2+}}$ and $\Gamma_{SO_4^{2-}}$ on φ_r in solutions of different compositions are compared in Fig. 3. One can see that the increase in SO_4^{2-} adsorption which occurs in the presence of Cd^{2+} ions practically coincides with the increase in Cd^{2+} adsorption observed in the presence of SO_4^{2-} ions. The results obtained concerning the joint adsorption of Cd^{2+} and SO_4^{2-} point to superequivalent Cd^{2+} ion adsorption on the Pt/Pt electrode surface.

Charging curves and potentiodynamic curves in 1 N $HClO_4$ solutions containing $Cd(ClO_4)_2$ and $CdSO_4$ were measured in order to examine the influence of Cd^{2+} ions on hydrogen adsorption. In contrast to the data obtained in [3, 4], we could observe an effect of cadmium ions on the charging curves, both in the presence of $CdSO_4$ and in the presence of $Cd(ClO_4)_2$, but in the first case the effects were more pronounced. The influence of Cd^{2+} on hydrogen adsorption can be seen more clearly from the potentiodynamic curves (Fig. 4). The effects observed can be explained in a manner similar to [8].

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