POTENTIAL DEPENDENCE OF THE ADSORPTION OF SODIUM CATIONS ON PLATINUM AND RHODIUM ELECTRODES IN ACIDIC SOLUTIONS

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The potential dependence of the adsorption of alkali metal cations on platinum and rhodium in acidic solutions was studied in [1-5]. A radioactive-tracer method showed that the adsorption of these cations on positively charged platinum is slight and essentially independent of the electrode potential [1, 2]; an analogous situation is found on rhodium [3]. However, the tracer measurements were carried out in dilute solutions with approximately equal acid and salt concentrations, so hydrogen ions may have participated in the formation of the double layer. It was shown in [5] that in more concentrated solutions containing more Li^+, K^+, and Cs^+ ions than hydrogen ions the adsorption of cations on positively charged surfaces is much more extensive than in the earlier experiments.

For this reason, and because of the availability of the more refined radiochemical method [6], we again turned to a study of the potential dependence of Na^+ adsorption in the presence of various anions. It was taken into account here that a reliable determination of the adsorption depended on minimizing the ratio of the hydrogen ion and Na^+ concentrations in the solutions [7].

The measurements were carried out with Na^{22}, S^{35}, Cl^{36}, and Br^{82} isotopes. The apparent surface area of the electrodes was 2 cm^2, while the actual surface area was 0.2-0.15 m^2. The electrodes were made and prepared for the experiments, and their actual surface area evaluated, as in [8, 9].

The experiments were carried out in the following manner. The electrode was held in the test solution at the given potential by means of a P-5827 potentiostat for 15 min; then it was lowered to the bottom of the cell and the radioactivity measured. Then the potential was abruptly changed by 50 mV, etc. The average rate at which the potential was imposed was thus 0.2 V/h. In iodide solutions the potential was also imposed at a rate of 0.1 V/h, but here no noticeable changes in the extent of Na^+ adsorption were observed. The radioactive background of the solution must be deducted in order to determine the adsorption on the electrode on the basis of the measured radioactivity. This background was found in the following manner. Concentrated sulfuric acid or a saturated solution of stable sodium sulfate was added to the solution in a quantity such that the solution volume did not change significantly but such that the concentration of H^+ or Na^+ cations exceeded the initial concentration by a factor of 50-100. Under these conditions essentially all the adsorbed Na^+ ions were replaced by H^+ ions or stable Na^+ ions [7, 8]. In this case the radioactivity measured as the electrode was lowered to the bottom of the cell was equal to the solution background.

The experiments were carried out at 20±1°C. Here φ_r refers to the potential with respect to the reversible hydrogen electrode in the same solution.

Measurements were carried out on the platinum electrode in solutions having the following compositions: 10^{-3} N $H_2SO_4 + 3 \cdot 10^{-3}$ N Ha_2SO_4, 10^{-3} N $HCl + 3 \cdot 10^{-3}$ N NaCl, 10^{-3} N $HBr + 3 \cdot 10^{-3}$ N NaBr, and 10^{-3} N $H_2SO_4 + 3 \cdot 10^{-3}$ N NaI; the results are shown in Fig. 1. At $\varphi_r = 0$ the Na^+ adsorption is the same in the sulfate, chloride, and bromide solutions, since there is essentially no adsorption of SO_4^{2-}, Cl^-, and Br^- ions at this potential (Fig. 2). In the presence of NaI, the Na^+ adsorption is slightly lower than in solutions of other

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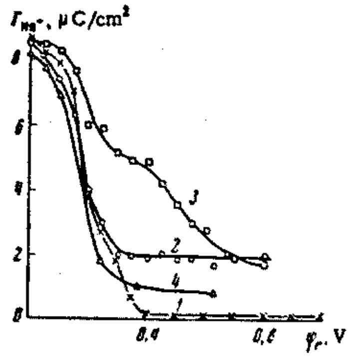

Fig. 1

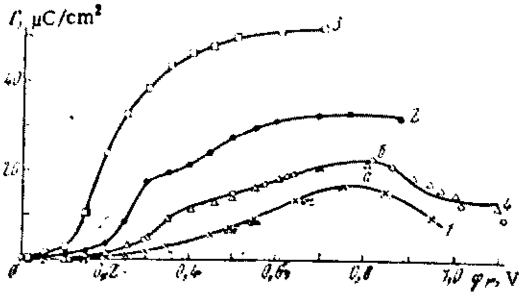

Fig. 2

Fig. 1. Potential dependence of the adsorption of sodium cations on a platinized platinum electrode in the following solutions: 1) 10^{-3} N $H_2SO_4 + 3 \cdot 10^{-3}$ N Na_2SO_4; 2) 10^{-3} N $HCl + 3 \cdot 10^{-3}$ N NaCl; 3) 10^{-3} N $HBr + 3 \cdot 10^{-3}$ N NaBr; 4) 10^{-3} N $H_2SO_4 + 3 \cdot 10^{-3}$ N NaI.

Fig. 2. Potential dependence of the adsorption of SO_4^{2-} (1, 4), Cl^- (2) and Br^- (3) anions on a platinized platinum electrode in the following solutions: 1) 10^{-3} N $H_2SO_4 + 3 \cdot 10^{-3}$ N Na_2SO_4; 2) 10^{-3} N $HCl + 3 \cdot 10^{-3}$ N NaCl; 3) 10^{-3} N HBr + $3 \cdot 10^{-3}$ N NaBr; 4) 10^{-2} N H_2SO_4. a) Tracer-atom measurements; b) adsorption-curve measurements [10]; solid curve) calculated from isoelectrical potential shifts and charging curves [10].

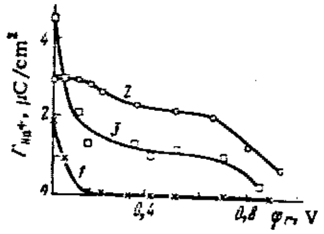

Fig. 3. Potential dependence of the adsorption of sodium cations on a rhodium electrode in the following solutions: 1) 10^{-3} N $H_2SO_4 + 3 \cdot 10^{-3}$ N Na_2SO_4; 2) 10^{-3} N $HCl + 3 \cdot 10^{-3}$ N NaCl; 3) 10^{-3} N $HBr + 3 \cdot 10^{-3}$ N NaBr.

salts, probably because of I^- adsorption at $\varphi_r = 0$ [1b]. When a platinum electrode is held in contact with a NaI solution for 15 h, the increase in the I^- adsorption is accompanied by a decrease in Na^+ adsorption [1b].

Fig. 1 shows that the nature of the Γ_{Na^+}, φ_r, curves depends on the nature of the anion in the salt. For positive surface charges with $\varphi_r < 0.65$ V, the cation adsorption increases in the order $Na_2SO_4 < NaI < NaCl < NaBr$ for solutions of a given concentration. The Na^+ adsorption in the bromide solution, which decreases as Γ_{Na^+} shifts in the anodic direction, becomes nearly equal to $\Phi \sim 0.7$ V.

We also measured the potential dependences of SO_4^{2-} adsorption in 10^{-2} N H_2SO_4. We compared this dependence with that found by the methods of isoelectrical potential shifts and adsorption curves [10]. As Fig. 2 shows, there is a quantitive agreement in the magnitude of the SO_4^{2-} adsorption found by the three independent methods. This is both additional support for the validity of the thermodynamic theory of the platinum electrode and evidence that our experimental data are reliable.*

From the data in Figs. 1 and 2 we can easily determine the zero-free-charge potentials on platinum (the potentials at which the anion and cation adsorption, expressed in electrical units, is the same) [14]: 0.14 V in 10^{-3} N $H_2SO_4 + 3 \cdot 10^{-3}$ N Na_2SO_4, 0.04 V in 10^{-3} N $HCl + 3 \cdot 10^{-3}$ N NaCl, and −0.03 V (n.h.e.) in 10^{-3} N $HBr + 3 \cdot 10^{-3}$ N NaBr. These results are in satisfactory agreement with those in [1, 2, 5, 15]. Figure 3 shows the Γ_{Na^+}, φ_r curves on the rhodium electrode. At $\varphi_r = 0$ the Na^+ adsorption decreases in the order $NaBr > NaCl > Na_2SO_4$. The adsorption of the salt anions decreases in the same order, according to [16]. For $\varphi_r > 0.05$ V, the cation adsorption decreases in the order of $NaCl > NaGr > Na_2SO_4$. The Na^+ adsorption decreases as φ_r is shifted in the anionic direction.

We were thus able to detect a significant adsorption of cations on the positively charged platinum and rhodium surfaces and to ascertain the dependence of this adsorption on the nature of the salt anion.

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*The equilibrium $\Gamma_{SO_4^{2+}}$, φ_r curves obtained in this study and in [1a, 11, 12] differ from the curve obtained in [13], apparently because of a nonuniform potential distribution over the electrode surface in [13].

The adsorption of Na^+ on positively charged surfaces presumably results from superequivalent adsorption of solution anions. In this case it follows from these results that superequivalent adsorption of anions on platinum increases in the order $SO_4^{2-} < I^- < Cl^- < Br^-$, while that on rhodium increases in the order $SO_4^{2-} < Br^- < Cl^-$; the adsorptivity of the anions on platinum-group metals increases in the order $SO_4^{2-} < Cl^- < Br^- < I^-$ [1, 2, 10, 16]. A qualitative explanation can be found for the discrepancy between the adsorptivity and superequivalent-adsorption orders by assuming that the state of the adsorbed anions becomes more nearly atomic as the adsorptivity increases or, in the terminology of Lorenz [17], that there is an increase in the transfer of anionic charge to the surface. The superequivalent adsorption of the anions should increase as the adsorptivity increases, while, as a result of charge transfer, the effective charge of the superequivalently adsorbed ions and thus the number of cations attracted by them should decrease. The approximate constancy or the decrease in Na^+ adsorption with increasing φ_r is probably due to an increase in the degree of anionic charge transfer as the potential shifts in the anodic direction. A comparison of the platinum and rhodium data shows that transfer of anionic charge to the metal surface is greater for rhodium. This has been attributed to the more negative zero-charge potential of rhodium [3, 9].

A comparison of these results with those in the literature for a mercury electrode [18] shows a significant difference in the behavior of adsorbed anions on mercury and on platinum-group metals, although the magnitudes of the superequivalent adsorption of anions on platinum in several cases is even slightly greater than on mercury.

According to the thermodynamic theory [19, 20], the Esin-Markov coefficient is governed by the magnitude and sign of the derivative $(\partial\Gamma_{C^+}/\partial\Gamma_{A^-}]\mu_{CA^{\pm}}$:

$$(\partial\varphi/\partial\mu^{\pm}_{CA})_{\varepsilon} = -\frac{1 + (\partial\Gamma_{C^+}/\partial\Gamma_{A^-})_{\mu^{\pm}_{CA}}}{1 - (\partial\Gamma_{C^+}/\partial\Gamma_{A^-})_{\mu^{\pm}_{CA}}},$$

where Γ_{A^-} and Γ_{C^+} are the anionic and cationic adsorption, $\mu_{CA^{\pm}}$ is the average chemical potential of the salt ions, ε is the double-layer charge, and φ is the potential with respect to a constant reference electrode (Γ and μ are expressed in electrical units). It follows from these results that we have $(\partial\Gamma_{C^+}/\partial\Gamma_{A^-})\mu_C \leq 0$ at potentials in the double-layer region. We thus have $(\partial\varphi/\partial\mu_{\pm CA})_{\varepsilon} \geqslant -1)$ on platinum and rhodium, as has actually been found to be the case in direct determinations of the Esin-Markov coefficient [10, 16, 21].

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