ADSORPTION OF IONS ON PALLADIUM

III. ADSORPTION OF SODIUM AND CESIUM CATIONS FROM ALKALINE SOLUTIONS

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Burshtein et al. [1] investigated adsorption of Na^+ and Cs^+ cations on palladium powders from the change in the electrical conductivity of NaOH and CsOH solutions. They observed a decrease in the adsorption of these cations with an increase in potential toward the positive side from the reversible hydrogen potential, with preferential adsorbability of Cs^+ throughout the range of potentials. In [2] these authors showed that Cs^+ has a greater effect than Na^+ on the amount of hydrogen adsorbed on the surface of palladium powder. To elucidate the mechanism of ionic adsorption and to determine the structure of the double electric layer on palladium, it was of interest to make a further investigation of adsorption of singly charged cations on palladium.

Using the method of radioactive indicators, we have investigated the adsorption kinetics of Na^+ and Cs^+ cations and the kinetics of their exchange with these ions in NaOH and CsOH solutions at different electrolytic palladium potentials; we have also determined how the adsorption values depend on the potential.

Adsorption was determined from the radioactivity of the electrode without withdrawing it from the solution during the experiment [3]; Na-22 and Cs-134 isotopes were used for this purpose. The procedure used for the adsorption and exchange experiments is described in [4, 5]. The conditions for obtaining electrolytic palladium deposits and for their preliminary treatment were the same as in [4]. Before the experiments the solutions of cp NaOH and CsOH were subjected to electrochemical purification on a large platinized platinum electrode for several days.

The curves of Na^+ and Cs^+ adsorption vs time have the same character. In both cases a constant adsorption value is reached in 5-7 min and no change is observed for many hours (12-15 h); this indicates rapid establishment of adsorption equilibrium. It will be seen from the kinetic curves (Fig. 1a) that for Na^+ at a reversible hydrogen potential, adsorption reaches $5.8 \cdot 10^{-11}$ g-eq/cm^2 of true surface, which is double that for adsorption from an acidified Na_2SO_4 solution of the same concentration [4]. Adsorption of Cs^+ under analogous conditions is $8.6 \cdot 10^{-11}$ g-eq/cm^2, i.e., 1.4 times greater than adsorption of Na^+. This ratio agrees closely with that for adsorption of these cations from 0.01 N NaOH and CsOH solutions on platinized platinum [6].

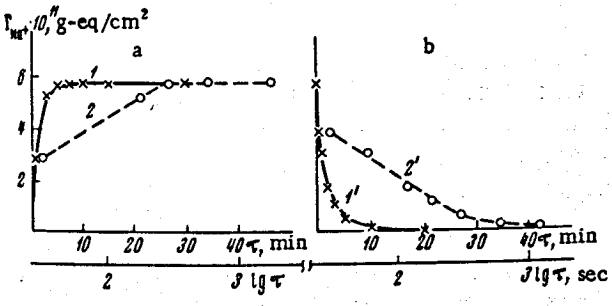


Fig. 1. Kinetics of adsorption (a) and exchange (b) of Na^+ cations, adsorbed from $1 \cdot 10^{-3}$ N NaOH at a reversible hydrogen potential: 1-1') adsorption and exchange in $\Gamma - \tau$ coordinates; 2-2') adsorption and exchange Γ – log τ coordinates.

Exchange between adsorbed Na^+ cations and Na^+ ions in the solution takes place at the reversible hydrogen potential at virtually the same rate as their adsorption. More than 90% of the adsorbed amount is exchanged in the 7 min required to attain a steady adsorption value (Fig. 1b). Exchange is completed in 15-20 min. The kinetic curve of exchange of Cs^+ with Cs^+ ions of the solution for a period of 2 min or more coincides with the curve for Na^+. It is not improbable that in the very early stage of the process differences

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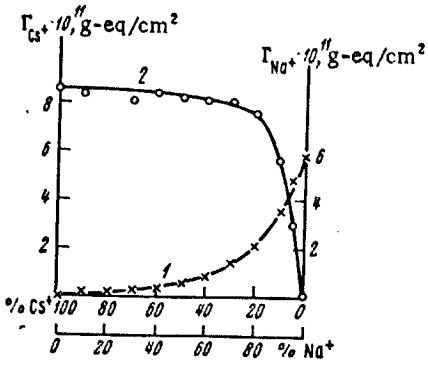


Fig. 2

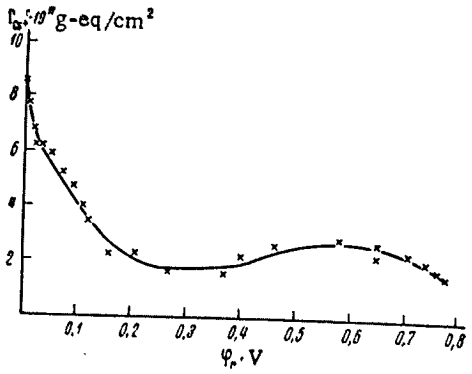


Fig. 3

Fig. 2. Simultaneous adsorption of Na^+ and Cs^+ from a mixture of NaOH and CsOH solution with an overall concentration of $1 \cdot 10^{-3}$ N at the reversible hydrogen potential.

Fig. 3. Adsorption of Cs^+ vs palladium potential in $1 \cdot 10^{-3}$ N CsOH. The potentials are given with respect to the reversible hydrogen potential in the same solution.

are manifested between the adsorption and exchange kinetics of these two cations, but they cannot be accurately recorded by the procedure used.

If Γ is plotted vs log τ, the kinetic curves of adsorption and exchange have linear sectors (curves 2, 2', Fig. 1) and are therefore described by the equations: $\theta = a + (1/\alpha f) \ln \tau$ and $\theta = b - (1/\beta f) \ln \tau$, characteristic for a uniformly nonhomogeneous surface and also for the case of repulsive reaction of adsorbed particles [7]. Calculation of the constants in these equations is, however, impossible because saturation of the palladium surface by Cs^+ and Na^+ cations has not yet been reached in this concentration range ($1 \cdot 10^{-3}$–$1 \cdot 10^{-2}$ N).

Despite the absence of kinetic differences between adsorption of Cs^+ and Na^+ and their exchange with the same ions in CsOH and NaOH solutions, the adsorption values at the reversible hydrogen potential indicate preferential adsorbability of the cesium ion. This is also seen from the mutual competition of Cs^+ and Na^+ cations during simultaneous adsorption from a mixture of NaOH and CsOH at this potential (Fig. 2). Curves 1 and 2 were constructed from the equilibrial values of ion adsorption for each solution composition, the overall concentration of which was $1 \cdot 10^{-3}$ N in all cases. Curve 1 was obtained by adding a radioactive solution of CsOH to a stable NaOH solution, curve 2 by adding stable CsOH to radioactive NaOH. The same adsorption value of both cations is obtained when the Cs^+ content of the mixture is 6.5%. For the case of adsorption of these cations under analogous conditions on platinized platinum, Kasarinov et al. [6] have shown that the same adsorption value is observed at a Cs^+ content of 4%.

Preferential adsorbability of Cs^+ in comparison with Na^+ may also be inferred from data on mutual exchange of these cations. At the reversible hydrogen potential, exchange of Na^+ for Cs^+ is completed in ~10 min, whereas exchange of Cs^+ for Na^+ is much slower. In this case, ~70% of the initial amount of adsorbed Cs^+ for Na^+ takes more than 30 min. The amount of rapidly exchanged Cs^+ cations is approximately equal to the total amount of adsorbed Na^+.

To determine more closely the potential dependence of adsorption of Cs^+ cations and of the strength of their bond with the palladium surface, we plotted the adsorption curve in Fig. 3. It will be seen that adsorption of Cs^+ is maximal at the reversible hydrogen potential and falls as its is displaced toward the positive side. A marked decrease of Cs^+ adsorption is observed in the potential range 0.0–0.05 V, i.e., in the region of β-phases. The small maximum in the range φ_r = 0.4–0.8 V may be attributed to the appearance of adsorbed oxygen [2], which changes the adsorption properties of the palladium surface. However, the rate of exchange of Cs^+ cations, adsorbed in this region of φ_r, does not differ from that at the reversible hydrogen potential.

Our data on the adsorption values and their dependence on the solution concentration do not completely agree with the data of Burshtein et al. [1]. With a change in the CsOH concentration from $1 \cdot 10^{-3}$ to $5 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ N, adsorption of Cs^+ at the reversible hydrogen potential is respectively $8.6 \cdot 10^{-11}$, $9.5 \cdot 10^{-11}$,

and $11.0 \cdot 10^{-11}$ g-eq/cm^2 and varies by a logarithmic law. In [1] this dependence was much stronger. With a change in the CsOH concentration from $1 \cdot 10^{-2}$ to $1 \cdot 10^{-1}$ N, adsorption of Cs^+ increased at this potential from $3 \cdot 10^{-10}$ to $11 \cdot 10^{-10}$ g-eq/cm^2, i.e., it increased by a factor of 3.6. These discrepancies cannot be attributed to errors in the determination of the true electrode surface, because they were calculated from hydrogen adsorption by Burshtein's method [8]. It may be postulated that one of the causes of these discrepancies is the different adsorption activities of palladium obtained by different methods. In [4] we observed differences between palladium deposits obtained under different electrolysis conditions and kept for different periods after preparation. A second cause might be the possibility of changes of the electrical conductivity of solutions in [1] not only due to adsorption of cations, but also to auxiliary processes, for example, solution of palladium in alkaline solutions.

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