DESORPTION AND EXCHANGE OF ADSORBED IONS FOR IONS FROM THE SOLUTION AT PLATINUM AND RHODIUM ELECTRODES

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The adsorption kinetics of ions on platinum metals and the exchange of adsorbed ions for like ions from the solution have been studied in a number of papers (for a review see [1-3]). The results obtained have been interpreted with the concept that strong chemisorption bonds are formed between the metal and the adsorbed ions and that the surface of the electrodes studied is inhomogeneous. Appreciably fewer are the data on the desorption behavior of the adsorbed ions and on the displacement of these ions by ions of a different kind that are introduced into the solution. An examination of such phenomena will, in our opinion, allow a more detailed picture to be presented of the ion-exchange processes on the platinum metals. Extensive experimental data on the mutual displacement of adsorbed anions were gathered by Schwabe and co-workers [4, 5]. The analysis of these results presents a number of difficulties, unfortunately, because this work was done on oxidized platinum, and the degree of oxidation was not controlled.

The present paper reports the results of an examination concerning the displacement of adsorbed Na^+, Cs^+, and Zn^{2+} ions by cations from the solution at platinized and rhodium-plated platinum electrodes. The measurements were done by a radiotracer method following the technique of [6], and using the isotopes Na-22, Cs-134, and Zn-65. The conditions of manufacturing the electrodes and of preparing them for the experiments were the same as in [7-9]. During the measurements the potential was kept constant with the aid of a P-5827 potentiostat. The potentials φ_r refer to a reversible hydrogen electrode in the same solution. The experiments were done at 20±2°C.

The experimental sequence was as follows. The electrode was maintained at a preset potential in contact with a solution containing the radioactive ions until a standard adsorption value had been attained. Then the solution was drained, cell and electrode were rinsed a few times with twice distilled water that had been freed from the oxygen of the air, the radioactivity of the electrode was recorded, and an argon-purged solution containing only stable ions was introduced into the system. The kinetics of displacement of the adsorbed ions by ions from the solution was studied by following the change in radioactivity of the electrode. Portions of solution in the working compartment of the cell were replaced by fresh ones to the extent that radioactive ions became desorbed.

It was found that at φ_r from 0.0 to 1.0 V on the Pt/Pt electrode, the rate of adsorption of Na^+ and Cs^+ ions is high in 10^{-3} N H_2SO_4 + 10^{-2} N Cs_2SO_4 (or Na_2SO_4) and 10^{-2} N NaOH or CsOH solutions, and cannot be examined quantitatively with the radiochemical technique used. In these cases equilibrium adsorption values are attained within 2 to 3 min after contacting the electrode with the solution being investigated. A similar conclusion holds also for the exchange of adsorbed Na^+ and Cs^+ ions with like ions at constant potential. Figure 1 shows as examples the results for the exchange of adsorbed Na^+ ions for like ions at $\varphi_r = 0$ in 10^{-3} N H_2SO_4 + 10^{-2} N Na_2SO_4 (curve 1) and in 10^{-2} N NaOH (curve 2). A practically complete exchange takes place within 2-3 min. The same high exchange rate was also found in the case of Cs^+ ions. In alkaline solutions we could not find any difference in the exchange rate of adsorbed Na^+ or Cs^+ ions for like ions when going from $\varphi_r = 0$ to $\varphi_r = 0.5$ and $\varphi_r = 1.1$ V, in agreement with the data of [10]. Relatively slow

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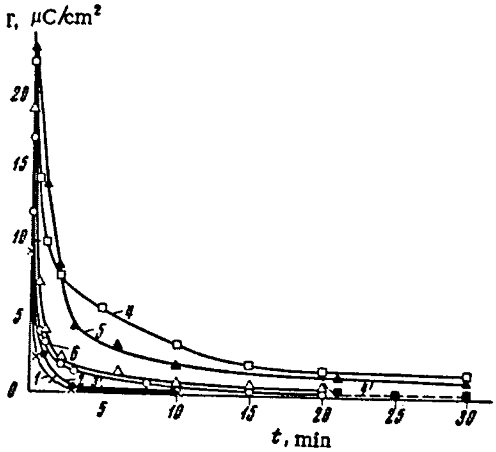

Fig. 1

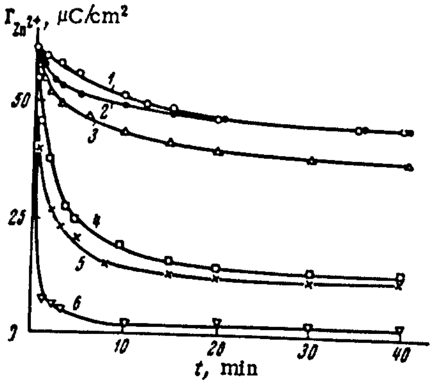

Fig. 2

Fig. 1. The amount of adsorbed labeled ions as a function of time on a platinized platinum electrode at $\varphi_r = 0$ (1-4) and on an anodically oxidized electrode (5, 6): 1) Exchange of Na^+ for Na^+ from 10^{-3} N H_2SO_4 + 10^{-2} N Na_2SO_4; 2 and 5) exchange of Na^+ for Na^+ from 10^{-2} N NaOH; 3) displacement of Cs^+ ions by Na^+ ions from 10^{-3} N H_2SO_4 + 10^{-2} N Na_2SO_4; 4) displacement of Cs^+ by Na^+ ions from 10^{-2} NaOH; 4') exchange of the remaining Cs^+ ions for Cs^+ ions from 10^{-2} N CsOH; 6) exchange of Cs^+ ions for Cs^+ from 10^{-2} N CsOH.

Fig. 2. The amount of adsorbed zinc ions as function of time on a rhodium-plated platinum electrode at $\varphi_r = 0$ in the solutions: 1) 10^{-2} N H_2SO_4; 2) 10^{-2} N Na_2SO_4 + 10^{-2} N H_2SO_4; 3) 10^{-2} N $MgSO_4$ + 10^{-2} N H_2SO_4; 4) 10^{-2} N H_2SO_4 + 10^{-2} N $ZnSO_4$; 5) 10^{-2} N H_2SO_4 + 10^{-2} N $CdSO_4$; and 6) 10^{-2} N H_2SO_4 + 10^{-2} N Tl_2SO_4. The adsorption of the zinc ions had taken place in advance from 10^{-2} N H_2SO_4 + 10^{-2} N $ZnSO_4$ at $\varphi_r = 0$.

exchange in alkaline solutions has only been observed on electrodes that were preoxidized by anodic polarization at potentials corresponding to oxygen evolution; this was done in 0.01 N H_2SO_4 (the current density during polarization was 5-20 mA/cm² of apparent surface area, the time was 10-20 min; see curves 5 and 6). On such electrodes the adsorption of Na^+ is found to be higher than that of Cs^+.

It was noted previously [8] that desorption of Na^+ and Cs^+ ions occurs slowly when the electrode is washed with twice-distilled hydrogen-saturated water. Thus washing can be used to determine the adsorption of ions at $\varphi_r = 0$ in relatively concentrated solutions (up to 0.5 N).

It was a further interesting peculiarity that one can observe a relatively slow displacement of the preferentially adsorbing ions by the ions having lower surface activity. Thus, data are shown in Fig. 1 which pertain to the displacement of adsorbed Cs^+ ions by Na^+ ions at $\varphi_r = 0$ in acidic and alkaline solutions. The displacement is slower than the exchange for like ions under the same conditions, especially in alkaline solution, where the difference in adsorbability between Cs^+ and Na^+ is higher [11]. In this case part of the Cs^+ ions is not displaced by Na^+ even after 30 min. However, if after 20 min of exchange the NaOH solution is replaced by CsOH, practically complete displacement of the initially adsorbed Cs^+ ions by Cs^+ ions from the solution takes place (Fig. 1, curve 4').

On strongly oxidized platinum one observes preferential adsorption of Na^+ ions. Therefore, under these conditions a relatively slow displacement of the adsorbed Na^+ ions by Cs^+ ions takes place. The phenomena described appear more clearly yet when the desorption and exchange of zinc ions is studied on platinum and rhodium electrodes. In this case many hours' of washing the electrodes with twice-distilled water will not produce any noticeable desorption of the adsorbed zinc ions. Figure 2 shows results for the displacement of zinc ions adsorbed from solution by H^+, Na^+, Mg^{2+}, Cd^{2+}, and Tl^+ ions and also by Zn^{2+} ions. These measurements were carried out at $\varphi_r = 0$ on a rhodium electrode. The data reported show that the exchange of the adsorbed Zn^{2+} ions for like ions from the solution is about 75% within the first 20 min of exchange. However, desorption of zinc ions in 10^{-2} N H_2SO_4 is only about 20-25% during a period of more than 5 h. Thus, the displacement of Zn^{2+} ions by the relatively weakly adsorbing H^+ ions [8, 12, 13] occurs slowly, in contrast to the exchange for like ions. For like adsorption values of Zn^{2+} ions, the initial rate of displacement is an order of magnitude lower than the rate of exchange. The slowness of displacement cannot be explained by a bond strengthening of the zinc ions with time, because special experiments have shown that after 5 h of contact with rhodium, Zn^{2+} ions exchange at approximately the same rate with zinc ions from the solutions as do those that have been in contact with the electrode for only 15-20 min. The rate of displacement of the Zn^{2+} ions by Na^+ ions at first is somewhat higher than the rate of displacement by hydrogen ions, but it, too, is less than the rate of exchange with Zn^{2+} ions.

The slowness of displacement is not due to the fact that H^+ and Na^+ are univalent while Zn^{2+} ions are divalent. In fact, the displacement of the Zn^{2+} ions by Mg^{2+} ions is again an appreciably slower process than is exchange with Zn^{2+} ions. But with Tl^+ ions, which have the highest adsorbability on rhodium among the cations studied, fast and practically complete displacement of the adsorbed Zn^{2+} ions occurs. The initial rate of displacement of Zn^{2+} ions by Tl^+ ions is about five times larger than the rate of exchange of adsorbed Zn^{2+} ions with like ions from the solution.

In examining the displacement of Zn^{2+} ions by Cd^{2+} ions it was found that the rate of displacement increases directly proportionally to the concentration of Cd^{2+} ions in the solution.

Thus, according to the data obtained, the rate of displacement of adsorbed ions is determined by the bond energy of the cations with the electrode surface, and increases with it. A similar result was obtained when examining the displacement of zinc ions by foreign cations at $\varphi_r = 0.1$ V, and also when examining this effect on a platinum electrode.

From the results reported it can be concluded that the desorption of ions from platinum metals does not occur via an electrochemical mechanism (in the usual meaning of this term), where the desorption of the ion being displaced and the adsorption of the displacing ion would be statistically independent processes, and the rate of desorption would only depend on electrode potential. On the platinum metals this process must be considered as a chemical replacement reaction of adsorbed cations with cations from the solution. The desorbing cation, which is present in solution, turns out to be involved in the transition state of the process. As a result the rate of displacement is determined by the ratio of adsorption energies of the cations on the corresponding adsorption site. In this respect one observes an analogy between the behavior of the platinum metals and that of ordinary ion exchangers.

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