EFFECT OF ANIONS ON THE ADSORPTION OF SODIUM IONS AT NICKEL IN ALKALINE SOLUTIONS

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The adsorption mechanism of the various cations at nickel is very important in connection with their use as modifying additives to the nickel catalysts employed in liquid-phase hydrogenations. It was demonstrated in [1, 2] that even the cations of the alkali metals influence the rate of these processes. Thus, the hydrogenation rate of dimethylethynylcarbinol decreases in the order LiOH, NaOH, KOH. The adsorption of Na^+ ions was studied in [3] on nickel powder in NaOH solutions of different concentrations. These cations were found to exhibit reversible adsorption depending in a complex way on potential.

It was the aim of the present work to investigate how Na^+ ion adsorption at nickel powder depends on the anion of the solution. The radiotracer method involving the isotope Na-22 was used to measure the adsorption as function of time and potential in alkalized NaCl, NaBr, Na_2SO_4, and Na_3PO_4 solutions.

Nickel powder obtained by reducing chemically pure $Ni(OH)_2$ for one hour at 300°C in a current of hydrogen was used as the electrodes. The powder, after having cooled off in the same atmosphere, was flushed into the electrochemical cell with the working solution, which was presaturated with hydrogen. In the cell, it was allowed to settle on a platinum contact fused into the bottom of the cell. All manipulations were done in an atmosphere of hydrogen. The cell design and the technique of varying the potential of the powder electrode were as described in [4]. Via a glass tube having a frit fused to its end, the cell was joined to a radiochemical cell which was inside a device for measuring the radioactivity. The adsorption of Na^+ was determined from the radioactivity change of the solution; small samples of the solution were transferred by gas pressure into the cell for the radiochemical measurements, and afterwards back, at any time during the experiment without interrupting it [5]. Throughout the experiment the solution was stirred with hydrogen or argon without stirring up the powder. The adsorption values were calculated per unit of surface area as determined by the BET method (it was about 15 m^2/g). For each experiment a new, freshly reduced powder sample was used, which after the heating weighed 0.06 g. The solution volume was 10-15 ml. The reversible hydrogen potential in each test solution served as the starting potential. When constant values of solution radioactivity and of current had been attained at a given potential, which was maintained with the aid of a P-5827 potentiostat, the value of φ_r* was varied up to -0.3 V in the cathodic direction, and up to 0.8 to 0.9 V in the anodic direction. The reproducibility of the results of parallel runs was quite satisfactory.

It can be seen from Figs. 1-3 that the adsorption of Na^+ ions at nickel in alkaline solutions of different composition is a function of time and potential. At $\varphi_r = -0.3$ V and $\varphi_r = 0.0$ V, the values of Na^+ adsorption go through a maximum during the initial period of the process; this maximum is only missing in the case of sodium phosphate at $\varphi_r = 0.0$ V. The usual shape of the kinetic adsorption curves, i.e., their increase with time up to some stationary value, was found at high anodic potentials.

The shape of the Γ_{Na^+}-potential dependence is very complex, and is practically the same in all solutions except sodium phosphate (Fig. 4). The Γ_{Na^+} values as referred to the measured surface area are very large, especially for the solutions of sodium sulfate and phosphate. It is not impossible that they are somewhat exaggerated, because the true surface area of the powder may have changed owing to possible peptization during adsorption of the electrolyte.

* φ_r is the potential against a hydrogen electrode in the same solution.

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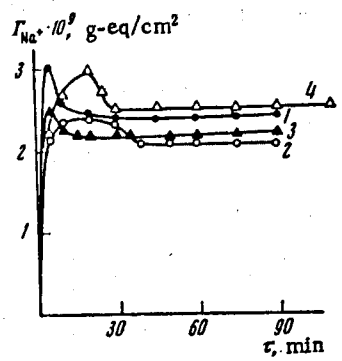


Fig. 1

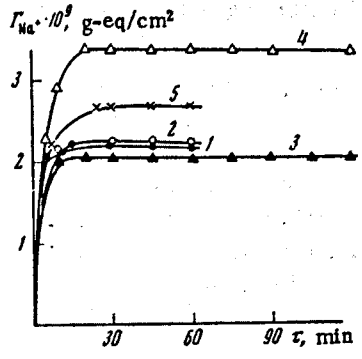


Fig. 2

Fig. 1. The kinetics of Na^+ ion adsorption at $\varphi_r = -0.3$ V from the solutions: 1) $2 \cdot 10^{-2}$ N NaOH; 2) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N NaCl; 3) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N NaBr; 4) $1 \cdot 10^{-2}$ N NaOH + $10 \cdot 10^{-2}$ N Na_2SO_4.

Fig. 2. The kinetics of Na^+ ion adsorption at $\varphi_r = 0.0$ V from the solutions: 1) $2 \cdot 10^{-2}$ N NaOH; 2) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N NaCl; 3) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N NaBr; 4) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N Na_2SO_4; 5) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N Na_3PO_4.

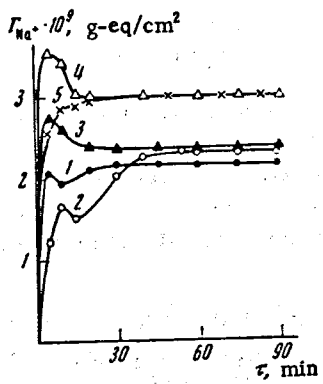


Fig. 3

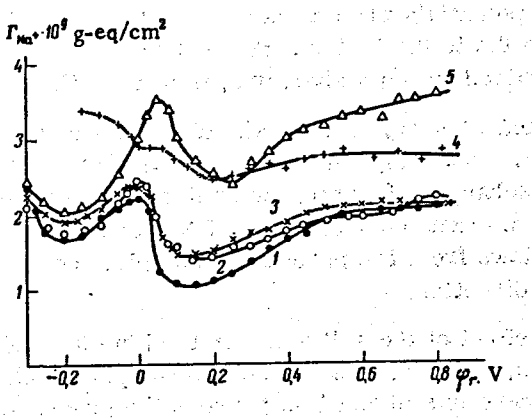


Fig. 4

Fig. 3. The kinetics of Na^+ ion adsorption at $\varphi_r = 0.80$ V from the solutions: 1) $2 \cdot 10^{-2}$ N NaOH; 2) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N NaCl; 3) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N NaBr; 4) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N Na_2SO_4; 5) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N Na_3PO_4.

Fig. 4. The adsorption of Na^+ ions as function of the potential of nickel in the following solutions: 1) $2 \cdot 10^{-2}$ N NaOH; 2) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N NaCl; 3) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N NaBr; 4) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N Na_2SO_4; 5) $1 \cdot 10^{-2}$ N NaOH + $1 \cdot 10^{-2}$ N Na_3PO_4.

The large amounts of Na^+ adsorbed, and the complex potential changes in these amounts, cannot be explained as electrostatic adsorption determined by the charge of the nickel surface.

It was desirable for the interpretation of the data obtained to elucidate the changes in the state of the nickel surface during anodic polarization under the conditions selected. It follows from literature data that hydrogen is evolved in NaOH and KOH solutions at potentials which are more negative than $\varphi_r = -0.2$ V. Oxygen adsorption already begins at $\varphi_r = -0.15$ V. The processes of hydrogen and oxygen adsorption are superimposed upon one another, and are practically inseparable. Nickel dissolves in the φ_r range from

0.0 to 0.15 V. According to existing data, this process begins at potentials which are more negative than $\varphi_r = 0.11$ V, and is accompanied by the formation of the complex anions, $[Ni(OH)_3]^-$ [6-11].

In the present work we have obtained stationary potentiostatic polarization curves for all the solutions investigated. The curve obtained in pure NaOH solution agrees well with an analogous curve obtained in [6] for a porous cermet electrode made from carbonyl nickel, and with a curve obtained in [7] for N-1 nickel. The resemblance of the $i-\varphi$ curves shows that the dissolution and passivation mechanism in NaOH solutions remains the same on nickel samples of different origin. Polarization curves obtained in the present work in the presence of Cl^-, Br^-, HPO_4^{2-}, and SO_4^{2-} ions show that all these anions have a noticeable effect on the dissolution and passivation of nickel. Thus, in the presence of Cl^-, Br^-, and HPO_4^{2-}, nickel hardly passivates, while in the presence of SO_4^{2-} ions the passivation occurs very slowly.

It can be seen from Fig. 4 that Γ_{Na^+} is largest in the potential range of hydrogen adsorption and evolution, and decreases as φ_r is made more anodic. One can assume that at the most cathodic φ_r values, the nickel surface is negatively charged. Assuming that this charge may have an effect, the decrease of Γ_{Na^+} at $\varphi_r = -0.3$ to -0.2 V can be explained in part by decreasing negative charge.

At the potential where oxygen begins to be adsorbed ($\varphi_r = -0.15$ V), an increase in Γ_{Na^+} is observed which continues up to $\varphi_r = 0.0$ to 0.05 V in all solutions except Na_3PO_4, where instead this quantity decreases up to $\varphi_r = 0.2$ V. The increase in Γ_{Na^+}, and its going through a maximum at 0.0 to 0.05 V, is due to a changing state of the nickel surface as it becomes oxidized. In this φ_r range the surface state is least stable, which is reflected in the shape of the kinetic curves of Figs. 1 and 2. At φ_r values between 0.0 and 0.2 V, where nickel dissolves actively in all solutions investigated, Γ_{Na^+} decreases by a factor of almost 2, but with the onset of surface passivation ($\varphi_r > 0.2$ V), it increases again. With the onset of complete (in NaOH) or partial (in the presence of salts) passivity of the nickel ($\varphi_r > 0.3$ V), the adsorption of Na^+ increases until potentials are attained where the nickel forms phase oxides; then it remains practically constant. At $\varphi_r = 0.4$ to 0.8 V, the nickel surface seems to become rapidly stabilized, so that stationary Γ_{Na^+} values are attained within a shorter span of time than at $\varphi_r = -0.3$ to 0.0 V (Figs. 1-3).

Results obtained when trying to wash off with water the Na^+ ions adsorbed at different potentials from solutions of different composition have shown that their bond energy to the nickel surface is small. After two to three exchanges of water, the radioactivity of the powder had been reduced by about 90% of the initial value. It follows that the adsorption of Na^+ at nickel in alkaline solutions is almost reversible. The same conclusion follows from the practically complete coincidence of adsorption curves recorded in the anodic and cathodic direction.

The observed effect of the salt anion on the kinetics and magnitude of Na^+ ion adsorption at nickel, the relative slowness, and the large values of adsorption under conditions of practically complete reversibility indicate that there is a direct link between the processes of cation and anion adsorption in all solutions studied. Evidence for such a link had been obtained previously in [12, 13] for the adsorption of Na^+ and sulfate ions on smooth Ni, and in [14] for the adsorption of Cd^{2+} and the same anions on nickel powder in acidified solutions.

It can be suggested that the anions of the alkaline solutions are specifically adsorbed at nickel, with partial charge transfer, and that they electrostatically attract the Na^+ ions. With such an adsorption mechanism for the cations, their weak bond to the nickel at high degrees of coverage is readily explained, inasmuch as these coverages are brought about by the chemisorbed anions. Apart from the anions of the salts added to the NaOH, adsorption by such a mechanism can also occur with the OH^- ions and with the complex anions obtained upon nickel dissolution. Some stationary state which is characteristic for each potential is set up on the surface as a result of the competitive adsorption of all the anions. Also possible are parallel reactions between nickel and solution components yielding surface compounds of different composition and stability.

On the basis of the results of the present work, the anions of the solutions investigated can be divided into two groups, the first one comprising the anions OH^-, Cl^-, and Br^-, and the second one comprising the oxygen-containing anions of sulfuric and phosphoric acid. The latter have a significantly larger effect on Na^+ adsorption than the three former.

For a further elucidation of the adsorptive properties of nickel towards the various anions and cations, a detailed study of their mutual influence under various conditions is required.

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