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Abstract

Full Text

PHYSICAL CHEMISTRY

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EFFECT OF CADMIUM IONS ON THE ADSORPTION OF HYDROGEN ON A PALLADIZED PLATINUM ELECTRODE

At the present time there are a number of works in the literature devoted to the study of the specific adsorption of various ions on platinum and palladium by the method of charging curves. Obrucheva (^{1}) studied the effect of adsorption of various cadmium salts ($CdSO_4$, $CdCl_2$, CdJ_2) on hydrogen adsorption on a platinized platinum electrode and found that adsorption of the cadmium ion considerably strengthens the bond of hydrogen with platinum. In a CdJ_2 solution the anodic charging curve has the form characteristic of iodine. The adsorption of halide anions on a palladized platinum electrode was studied (^{2}). It was found that Cl^- ions do not exert a substantial influence on the ionization of hydrogen on palladium, whereas Br^- and J^- disturb the reversibility of the process.

Fig. 1. Charging curves of a Pd electrode in $CdSO_4$ + 1 N H_2SO_4. 1 –in 1 N H_2SO_4 (forward and reverse run); 2 –in 0.01 N $CdSO_4$ + 1 N H_2SO_4; 3 –in 0.1 N $CdSO_4$ + 1 N H_2SO_4; 4 –in 1 N $CdSO_4$ + 1 N H_2SO_4 (forward and reverse run)

In the present work the effect of cadmium ions on hydrogen adsorption on a palladized platinum electrode was studied by the method of recording anodic charging curves. For the measurements the procedure and apparatus described in work (^{3}) were used. The electrode was a platinum plate of area 1 cm^2, onto which a definite amount of palladium was electrodeposited. Measurements

Fig. 2 and Fig. 3: charging curves of a Pd electrode

Figure 2: Fig. 2 and Fig. 3: charging curves of a Pd electrode

were carried out in 1 N H_2SO_4 + $CdSO_4$ (0.01 N; 0.1 N; 1 N); 1 N H_2SO_4 + $CdCl_2$ (0.01 N; 0.1 N; 1 N); 1 N H_2SO_4 + CdJ_2 (10^{-2} N; 10^{-3} N; $5 \cdot 10^{-4}$ N) at 20; 40; 60°. The density of the polarizing current was $2 \cdot 10^{-3}$ A/cm^2; the amount of palladium black on the electrode was 0.0066 g. The solutions used were prepared with bidistillate; sulfuric acid was distilled twice, and salts were recrystallized from bidistillate. The palladized electrode was saturated with hydrogen to the potential of the reversible hydrogen electrode, and then the cadmium salt solution under investigation was introduced and the anodic charging curve was recorded. After the experiments the electrode was cleaned of cadmium ions by washing in sulfuric acid and by anodic polarization until the initial form of the charging curve in 1 N H_2SO_4 was restored. However, in $CdCl_2$ and CdJ_2 it was not possible to wash the electrode, and therefore after each experiment the electrode was again palladi-

it turned out that the charging curves of the electrodes in $1N\ H_2SO_4$ differed little from one another.

In $1N\ H_2SO_4$, when the temperature is raised from 20 to 60°, the region of the $\beta \rightleftarrows \alpha$ phase transition on the charging curve shifts by 25-30 mV in the negative direction, which indicates a weakening of the bond of hydrogen with palladium. These data agree with the results obtained earlier by A. I. Fedorova and A. N. Frumkin (^{4}). The charging curves recorded in solutions

Fig. 2. Charging curves of a Pd electrode in $CdCl_2 + 1N\ H_2SO_4$. 1 –in $1N\ H_2SO_4$ (forward and reverse run); 2 –in $0.01N\ CdCl_2 - 1N\ H_2SO_4$; 3 –in $0.1N\ CdCl_2 + 1N\ H_2SO_4$; 4 –in $1N\ CdCl_2 + 1N\ H_2SO_4$ (forward and reverse run)

Fig. 3. Charging curves of a Pd electrode in $CdJ_2 + 1N\ H_2SO_4$ (forward and reverse run). 1 –in $1N\ H_2SO_4$; 2 –in $5 \cdot 10^{-4}N\ CdJ_2 + 1N\ H_2SO_4$; 3 –in $10^{-3}N\ CdJ_2 + 1N\ H_2SO_4$; 4 –in $10^{-2}N\ CdJ_2 + 1N\ H_2SO_4$

$CdSO_4$ indicate a decrease in the amount of sorbed hydrogen and a strengthening of the bond of hydrogen with palladium; moreover, with increasing concentration of cadmium ions, its adsorption increases (Fig. 1).

Adsorption of cadmium ions on the surface of the Pd electrode makes removal of the adsorbed hydrogen and the transition $H_{\text{abs}} \rightarrow H_{\text{ads}}$ more difficult; therefore the phase transition from the hydrogen-richer β-phase to the α-phase occurs at more anodic potentials. For example, in $0.01N\ CdSO_4$ the region of the $\beta \rightleftarrows \alpha$ transition is located at 85 mV, in $0.1N\ CdSO_4$ at 105 mV, and in $1N\ CdSO_4$ at 125 mV, whereas in $1N\ H_2SO_4$ it is at 75 mV.

The decrease in the amount of sorbed hydrogen is associated with its ionization during the specific adsorption of cadmium ions on the palladium surface according to the scheme:

$$Cd^{2+}_{\text{soln}} \to Cd^{2+}_{\text{ads}}, \qquad H_{\text{ads}} \xrightarrow{-e} H^{+}_{\text{soln}}.$$

The curves recorded in $CdCl_2$ solutions reveal an even more considerable strengthening of the bond of hydrogen with palladium, especially at 20° (Fig. 2). From Fig. 2 it is seen that in $0.01N$ $CdCl_2$ the phase transition occurs at 140 mV,

in $0.1N$ $CdCl_2$ at 215 mV, and in $1N$ $CdCl_2$ at 235 mV. Specific adsorption of Cl' ions decreases the positive charge of the surface, and therefore adsorption of cadmium ions increases sharply.

Table 1

Electrolyte	$1.0N$ H_2SO_4	$0.01N$ $CdSO_4$	$0.1N$ $CdSO_4$	$1N$ $CdSO_4$	$0.01N$ $CdCl_2$	$0.1N$ $CdCl_2$	$1N$ $CdCl_2$
Amount of H, ml	0.75	0.68	0.64	0.62	0.70	0.68	0.68

As is seen from the data in Table 1, the amount of sorbed hydrogen also decreases.

The cathodic charging curves in $CdSO_4$ and $CdCl_2$ proceed as in $1N$ H_2SO_4, i.e., adsorption of cadmium on the surface of the palladized electrode does not prevent reversible saturation of the electrode with hydrogen. At high temperatures, adsorption of cadmium ions is hindered. Thus, in $0.01N$ and $0.1N$ $CdSO_4$ at 40 and 60° there is no change in the shape of the curves compared with $1N$ H_2SO_4, but when the concentration of $CdSO_4$ is increased ($1N$), adsorption of cadmium ions occurs even at 60°. Adsorption of Cd^{2+} from $CdCl_2$ is sharply increased also at high temperatures. At 60° it is observed in $0.1N$ $CdCl_2$, i.e., at a Cd^{2+} concentration 10 times smaller than in the sulfate salt; the influence of chlorine ions is manifested.

The charging curves recorded in a solution of CdJ_2 have an entirely different character (Fig. 3). Even at very low concentrations of CdJ_2 ($5 \cdot 10^{-4}N$) a sharp change in the charging curve is observed. The amount of sorbed hydrogen decreases to 0.22 ml, compared with 0.74 ml in $1N$ H_2SO_4.

With an increase in the concentration of CdJ_2 (10^{-3}; $10^{-2}N$), the phase-transition plateau disappears and the charging curve takes on the form characteristic of iodine. In $10^{-2}N$ CdJ_2 the charging curve has the same form as in $10^{-1}N$ KJ (^{2}), which can be explained by simultaneous adsorption of Cd^{2+} and J^- ions; in this case mutual neutralization of charges occurs on the electrode surface, and the specific adsorption of ions increases.

The cathodic curves (in 10^{-3}; $10^{-2}N$ CdJ_2) are greatly shortened; this indicates that saturation of the electrode with hydrogen is hindered because of adsorption of iodine ions.

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