STUDY OF THE ADSORPTION OF CATIONS ON PLATINIZED PLATINUM BY THE METHOD OF MEASURING ADSORPTION POTENTIALS

![Fig. 1](image)

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Fig. 1

Figure 1: Fig. 1

Abstract

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STUDY OF THE ADSORPTION OF CATIONS ON PLATINIZED PLATINUM BY THE METHOD OF MEASURING ADSORPTION POTENTIALS

(Presented by Academician A. N. Frumkin, March 4, 1958)

In work (1) the specific adsorption of chlorine, bromine, and iodine anions and of the thallium cation on a platinized platinum electrode was investigated by the method of direct determination of the adsorption shift of the potential. A certain electrolyte, for example $1N$ H_2SO_4, washing an unpolarized electrode lying in the potential interval from 0.3 V to 0.7 V (against the normal hydrogen electrode), was displaced in a nitrogen atmosphere by an electrolyte containing the adsorbing ion, after which the change of potential with time was determined until the potential acquired a new steady value. The shift of potential can serve as an approximate measure of specific adsorption. In addition, the determination of the change in the form of the anodic charging curves, as was described earlier (1) for the case of thallium adsorption, served as a measure of adsorption and of the degree of desorption of cations.

Fig. 1. Effect of adsorption of lead ions on the anodic charging curves of platinized Pt.
1 –in $1N$ $HClO_4$; 2 –in $1N$ $HClO_4 + 0.1N$ $Pb(ClO_4)_2$; 3 –after repeated washing with $HClO_4$ under simultaneous anodic polarization; 4 –after remaining in $HClO_4$ for 20 h.

By these methods, in the present work the specific adsorption was investigated of lead, zinc, and cadmium ions, which shift the electrode potential in the positive direction. Lead was adsorbed from $0.1N$ $Pb(ClO_4)_2$ against a background of $HClO_4$, zinc from $0.1N$ $ZnSO_4$ against a background of $1N$ H_2SO_4, and cadmium–against the same background–from cadmium sulfate, chloride, and iodide. Adsorption equilibrium was practically attained after 20–60 min.

In the case of lead adsorption, the potential shift at an initial potential value of 0.3 V amounted to 0.46 V. The anodic charging curve, recorded in a solution

Fig. 2

Figure 2: Fig. 2

of lead perchlorate after the electrode, whose initial potential was 0.3 V, had remained in it for 24 h, does not show separation into hydrogen and oxygen regions (Fig. 1, 2). After repeated washing of the electrode with perchloric acid under simultaneous anodic polarization up to a potential of 1.6 V, the normal form of the charging curve is almost restored; however, the hydrogen part remains somewhat shortened, and the onset of oxidation is shifted to less positive values of the potential (Fig. 1, 3). With subsequent keeping of such a washed electrode in hydrochloric acid containing no lead ions for 20 h in a nitrogen atmosphere, the hydrogen part of the anodic curve becomes even shorter and the onset of oxidation shifts still more strongly to less anodic values of the potential (Fig. 1, 4). The latter indicates that

when platinum is brought into contact with a solution of $Pb(ClO_4)_2$, lead partially penetrates into the depth of the platinum and gradually emerges back onto the surface after its cleaning. An analogous effect of anions penetrating into the depth of platinum was first observed by N. A. Balashova by the method of radioactive indicators (^{2}), and was confirmed by the present method for the case of iodine and thallium (^{1}). The displacement of the onset of oxidation to more cathodic potential values upon addition of a lead salt to chloroplatinic acid during platinization has already been described earlier (^{3}).

Experiments on adsorption from $0.1\,N$ $CdSO_4$ were carried out at initial potential values of 0.3 V and 0.6 V. In the first case the adsorption shift of the potential was +0.32 V. The anodic charging curve in a solution of $CdSO_4$ (Fig. 2, 2) has an unusual shape, indicating a considerable strengthening of the bond of hydrogen with the metal; this distorted anodic curve, however, in contrast to what is observed in most cases in the presence of significant adsorption effects, is not shortened and practically coincides with the initial curve at 0.9 V. By washing in sulfuric acid with simultaneous anodic polarization to 1.6 V, the initial form of the anodic charging curve can be restored (Fig. 2, 3). In the case of cadmium adsorption, earlier oxidation of platinum is observed, which was also observed upon adsorption of thallium and lead, as well as the emergence, onto the washed platinum surface, of cadmium from deeper layers of the metal. The latter phenomenon, however, is much less pronounced than in the case of Pb. At an initial potential of 0.6 V the adsorption shift of the potential was only 0.085 V, and no penetration of cadmium into the depth of the metal was observed.

Fig. 2. Influence of adsorption of Cd ions from cadmium sulfate on the anodic charging curves of platinized Pt.
1 –in $1N$ H_2SO_4; **2** –in $1N$ $H_2SO_4 + 0.1N$ $CdSO_4$; **3** –after adsorption from $1N$ $H_2SO_4 + 0.1N$ $CdSO_4$ at an initial potential of 0.3 V for 20 h and repeated washing in $1N$ H_2SO_4; **4** –after staying in a solution of H_2SO_4 for 80 h. The

beginning of curves 3 and 4 is shifted along the abscissa axis by 0.2 V.

Table 1

Adsorption shifts of the potential (V) of a platinized Pt electrode upon adsorption of $CdSO_4$, $CdCl_2$, CdI_2, KCl, and KJ. Background 1*N* H_2SO_4

No.	Initial potential, V	0.1*N* $CdSO_4$	0.1*N* $CdCl_2$	0.1*N* CdI_2	0.1*N* KCl	0.1*N* KJ
1	0.3	0.32	0.177	−0.06	−0.06	−0.27
2	0.4		0.146		−0.12	
3	0.5		0.085			
4	0.6	0.085	−0.015	−0.3		
5	0.65		−0.085			−0.46

We also examined the behavior of a Pt electrode in solutions of cadmium chloride and iodide. Since in these salts both the cation and the anion are active, the sign of the adsorption shift of the potential in the presence of the salt depends on the value of the initial potential. Table 1 gives the values of the adsorption shifts of the potential in solutions of cadmium sulfate, chloride, and iodide and, for comparison, adsorption shifts of the potential in solutions of potassium chloride and iodide over a certain range of initial potentials.

As is seen from Table 1, displacement of the initial potential in the anodic direction is accompanied by a decrease in the positive potential shift in the case of $CdSO_4$, by a transition from positive values to negative ones in the case of cadmium chloride and iodide and, for comparison, by adsorption shifts of the potential in solutions of potassium chloride and iodide in a certain interval of initial potentials.

in $CdCl_2$ and an increase in the absolute value of the negative potential shift in CdI_2. Thus, in all cases, more positive values of the initial potential favor adsorption of the anion and hinder adsorption of the cation. The potential shifts observed in solutions of cadmium salts, in all cases, have a more positive or less negative value in comparison with solutions of potassium salts with the same anion, which is caused by the superposition of the adsorption effect of the cation Cd^{2+} on the adsorption effect of the anion. For the solution–air interface, at which specific adsorption of cations is absent, A. N. Frumkin (4) observed a more negative value of the adsorption potential shift in the presence of CdI_2 in comparison with KI solutions of the same concentration; he attributed this to the presence in the CdI_2 solution of complex anions of the CdI_3 type, which have increased adsorbability.

Fig. 3. Effect of adsorption of $CdCl_2$ on anodic charging curves of platinized Pt.
1 –in 1 N H_2SO_4; 2 –in 1 N H_2SO_4 + 0.1 N $CdCl_2$; 3 –in 1 N H_2SO_4 after

Figure 3

Figure 3: Figure 3

Figure 4

Figure 4: Figure 4

adsorption from 1 N H_2SO_4 + 0.1 N $CdCl_2$ at 0.3 V and repeated washing in H_2SO_4; 4 –in 1 N H_2SO_4 after remaining in the solution for 20 h. The origins of curves 3 and 4 are shifted along the abscissa by 0.05 V.

Fig. 4. Effect of adsorption of CdI_2 on anodic charging curves of platinized Pt.
1 –in 1 N H_2SO_4; 2 –in a solution of 1 N H_2SO_4 + 0.1 N CdI_2; 3 –after adsorption of CdI_2 at an initial potential of 0.3 V, washing in H_2SO_4, and a single cathodic polarization; 4 –after further repeated washing in 1 N H_2SO_4 and alternating anodic and cathodic polarization. The origin of curve 4 is shifted along the abscissa by 0.2 V.

The anodic charging curves obtained in the presence of $CdCl_2$ (Fig. 3, 2) indicate the presence of firmly bound hydrogen and a displacement of the onset of oxidation toward more anodic values. The latter, obviously, must be attributed to the influence of the chlorine ion, which masks the displacement of the onset of oxidation toward the cathodic side caused by cadmium adsorption. Repeated washing with sulfuric acid returns the anodic charging curve to its original form (Fig. 3, 3), after which, following the electrode' s stay in sulfuric acid for 20 h, the appearance of cadmium on the electrode surface can again be detected (Fig. 3, 4).

The anodic charging curve in CdI_2 solution (Fig. 4, 2) was brought only to 0.55 V because oxidation begins at more anodic potentials. After adsorption of CdI_2 at a potential of 0.3 V and washing in H_2SO_4, ···

the charging curve (Fig. 4, 3), characteristic of iodine, is obtained. With further washing and alternating anodic and cathodic polarization, the shape of the charging curve approaches the initial one; however, the hydrogen region remains shortened and the onset of oxidation shifted to more positive potentials, as was observed after adsorption of iodine from KI solutions. The delay in the onset of oxidation after adsorption from a CdJ_2 solution is less pronounced than in the case of adsorption from a KJ solution. In this the influence of Cd ions is manifested. The influence of the iodine ion on the shape of the charging curve is more pronounced after adsorption of Cd at an initial potential of 0.6 V; in this case the onset of oxidation is shifted toward more anodic potentials.

The adsorption shifts of the potential in the case of Zn^{2+} were less pronounced than in the case of the other cations investigated in the present work and, against a background of 1 N H_2SO_4 at an initial potential of 0.3 V, amounted to 0.12

V for 0.1 N $ZnSO_4$ and 0.31 V for 1 N $ZnSO_4$.

Adsorption of Li^+, Cs^+, Sr^{2+}, and Ba^{2+} could not be detected either from distortion of the shape of the anodic charging curves or from a potential shift. Earlier (^{1}) an analogous result was obtained in the case of lanthanum and thorium sulfates. The absence of appreciable specific adsorption of these highly charged ions may be associated with their large hydration energy.

The results presented, together with data obtained earlier for thallium on platinum (^{1}) and mercury (^{5}), leave no doubt that cations whose electron shell does not have the configuration of the noble gases can exhibit as strongly pronounced a specific adsorption on metal surfaces as the typical surface-active anion—iodine. Comparison of the data obtained in the present work for cadmium with data relating to the adsorption of Cd on mercury (^{5}) suggests that these phenomena are much more strongly pronounced in the case of adsorption on platinum.

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CITED LITERATURE

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