STRUCTURE OF THE ELECTRICAL DOUBLE LAYER ON PLATINUM IN THE PRESENCE OF SURFACE-ACTIVE CATIONS AND ANIONS

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The method of radioactive indicators is used to study the structure of the electrical double layer on platinum in acid solutions of cadmium sulfate, bromide and iodide. It is shown that, in these solutions with 0.1 N H_2SO_4 as base electrolyte, the zero charge points are at 0.65, 0.45, and 0.01 V, respectively (n.h.e.). At constant potential, adsorption of Cd^{2+} increases from sulfate to cadmium iodide solutions. It follows that adsorbed cadmium ions are linked to the platinum by a covalent bond. The authors discuss the mechanism by which a potential difference is formed at the interface between the platinum and the solutions of surface-active ions.

Various authors [1-3] have discussed the specific adsorption of cations on mercury in solutions of cadmium and thallium salts: they used the method of electrocapillary curves. For a platinum electrode this has been confirmed [4-6] by the methods of adsorption potentials and charging curves. In a previous paper [7] we have discussed the structure of the electrical double layer on platinum in a cadmium sulfate solution.

The aim of the present article is to study the structure of the electrical double layer on platinized platinum when surface-active cadmium cations and halide anions are simultaneously present in the solution. For this purpose we measured how the adsorption of the cations and anions depends on the duration of adsorption, the solution concentration, and the potential of the platinum electrode in acid solutions of cadmium sulfate, chloride, bromine and iodide.

The amount of adsorption was measured by means of radioactive indicators—the isotopes Cd^{115M}, Br^{82}, S^{35}, and I^{131}. As in our previous experiments [8] the adsorption was determined by measuring the radioactivity of the electrode when removed from the solution after immersion for a given time at a given potential. Features of the individual measurements will be described below, together with the results. The experimental temperature was $20 \pm 3°C$. In all the figures, the adsorption values are given per unit true electrode surface; this latter was calculated from the length of the hydrogen part of the charging curve in 0.1 N H_2SO_4—it was two to four thousand times the apparent surface. The potentials are given relative to a normal hydrogen electrode.

EXPERIMENTAL RESULTS

A number of authors have shown that, in the adsorption of halide anions on platinum, equilibrium is reached only slowly. For surface-active Cd^{2+} cations, the present authors have studied the time dependence of the adsorption of various cadmium salts at reversible hydrogen potential in acid solutions. The results of these experiments are plotted in Fig. 1. The experimental procedure was as follows: the electrode potential in 0.1 N H_2SO_4 was brought to the reversible hydrogen value. This solution was then replaced by acidified cadmium salt solution in which the electrode was immersed for a measured time at reversible hydrogen potential and was then removed into the air so as to measure its radioactivity with an end-window counter. The electrode was then put back in the same solution, its potential was brought to the reversible hydrogen value by creating a hydrogen atmosphere, and all the operations were repeated in the same order. Each kinetic curve was measured with the same electrode, not freed from adsorbed cadmium after each measurement.

As will be seen from Fig. 1, the time required to reach constant cadmium adsorption increases from sulfate to iodide. By comparing the final adsorption values, we see that the amount of Cd^{2+} cations adsorbed increases in the same order. However, this is only the case for a certain ratio between the cadmium ion concentration and the halide anion concentration, as can be seen from Fig. 2, which shows the final values of the Cd^{2+} adsorption for each case.

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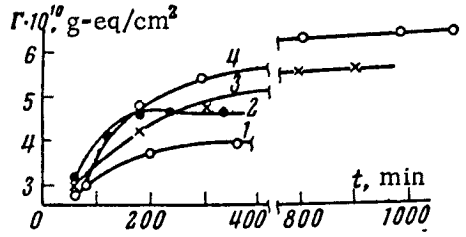


Fig. 1

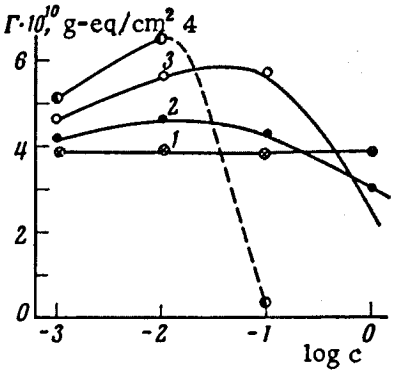


Fig. 2

Fig. 1. Kinetics of adsorption of Cd^{2+} cations at reversible hydrogen potential from 10^{-2} solutions of 1) $CdSO_4$, 2) $CdCl_2$, 3) $CdBr_2$, 4) CdI_2 (base electrolyte, 10^{-1} N H_2SO_4).

Fig. 2. Adsorption of Cd^{2+} versus logarithm of concentration of (1) SO_4^{2-}, (2) Cl^-, (3) Br^-, (4) I^- anions, at reversible hydrogen potential, from solution of 10^{-2} N $CdSO_4 + 10^{-1}$ N H_2SO_4, with added sodium salts.

The procedure for the experiments whose results are plotted in Fig. 2 was the same as above. Increase of halide anion concentration was carried out by adding sodium salts to the same solution of cadmium salt. (It was specially demostrated that the presence of sodium ions had no effect on the adsorption of cadmium cations at any of the halide ion concentrations studied.)

Figures 3-5 plot the results of experiments to study the relations between the adsorption of surface-active cations and anions at various potentials. In all cases the initial potentials were reversible hydrogen potentials. After it had attained equilibrium adsorption at this potential, the electrode was polarized by a decreasing anode current to the required potential, at which it was kept for six hours. The adsorption obtained at each potential was close to the equilibrium value. We then measured the radioactivity of the electrode, which was then replaced in the same solution and all the operations repeated.

It should be noted that in our previous work [9] the Cd^{2+} adsorptions at all potentials for cadmium sulfate solution are not the equilibrium values in the conditions of these experiments, and therefore differ from those in Fig. 3.

The halide salt solutions were acidified with sulfuric acid up to concentration 0.1 N. Since the adsorbabilities of Br^- and I^- are greater than that of SO_4^{2-}, we can neglect the adsorption of the latter. With platinum, previously oxidized in air, at 0.8 V we did not observe adsorption of Cd^{2+} ions from acid cadmium sulfate, bromide or iodide solutions, even with adsorption times of 36 hours. In these experiments, we observed a pink coloration of the solution in the case of bromide. It did not disappear even after a long time (a month). This phenomenon complicates the study of the structure of the electrical double layer in such solutions with anodic platinum potentials.

DISCUSSION OF RESULTS

In solutions not containing surface-active ions (e.g., in acidulated Cs_2SO_4 or Na_2SO_4), the zero charge potential of platinum is 0.17-0.18 V [9-12]. Surface-active anions shift the zero-charge point of platinum towards the negative. In acid NaI solution it is close to −0.5 V [12]. In the presence of surface-active cations the zero-charge point of platinum shifts to more positive potentials [7, 9].

An examination of the adsorption of cations and anions from cadmium sulfate solution at various potentials (Fig. 3) will reveal that the potential at which the adsorption values of cations and anions are equal, which can be regarded as the zero-charge potential of platinum, is equal to 0.65 V.* At potentials to the negative of 0.65 V, cations are adsorbed to a greater extent than anions. This indicates that the surface is negatively charged. The increase in cation adsorption occuring when the potential becomes more positive indicates that the negative charge is growing larger. The occurrence of marked adsorption of anions at these potentials shows that part of the Cd^{2+}

*The zero-charge potential in the same solution was given in [9] as approximately 0.9 V; this was due to inaccuracy in the measurements of SO_4^{2-} adsorption, which was a very small quantity. More accurate measurements of these values made it possible to get more reliable values for the position of the zero-charge potential.

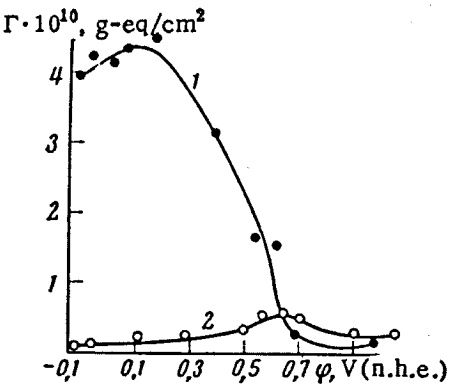


Fig. 3

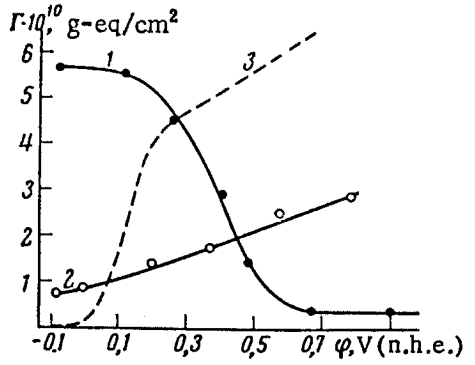


Fig. 4

Fig. 3. Potential dependence of Cd^{2+} adsorption (1) and SO_4^{2-} adsorption (2) from 10^{-2} N $CdSO_4$ + 10^{-2} N H_2SO_4.

Fig. 4. Potential dependence of adsorption of Cd^{2+} (1) and Br^- (2) from 10^{-2} NaBr (3) with base electrolyte of 10^{-1} N H_2SO_4.

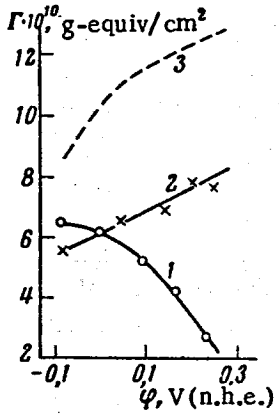


Fig. 5. Potential dependence of adsorption of Cd^{2+} (1) and I^- (2) from 10^{-2} N CdI_2 and I^- from 10^{-2} N NaI (3) with base electrolyte 10^{-1} N H_2SO_4.

ions are adsorbed specifically, and the SO_4^{2-} anions are attracted to them by their charges. If the number of cations thus adsorbed were to increase with increase of negative charge, the number of adsorbed anions should also increase. However, in the experiments we observe a decrease in the adsorption of SO_4^{2-} ions when the adsorption of Cd^{2+} ions increases. Consequently when the potential moves towards the negative from the zero charge point in cadmium sulfate solution, super-equivalent adsorption of the surface-active cations decreases while the total number of adsorbed cations rises.

The strength of the bond between the platinum and the Cd^{2+} ions adsorbed at negative charges (potentials –0.08 V, 0.15 V, 0.30 V) is very great, because in these conditions the ions are exchanged with Cd^{2+} ions from the solution only very slowly. After three hours only about 20% of the total adsorbed quantity has been exchanged. This fact indicates that many of the adsorbed cadmium cations are in a state intermediate between the ionic and atomic, and are joined to the platinum by a covalent bond. We can suppose that dipoles $^-Pt-Cd^+$ are formed and are oriented with the positive end towards the solution.

The potential drop caused by these dipoles has a negative sign, while that caused by specifically adsorbed cadmium cations and sulfate anions has a positive sign. If the total drop is large enough, the latter may predominate over the potential drop in the dense part of the double layer.

When the potential moves towards the positive from the zero-charge point, we should expect the adsorption of cations to decrease and that of anions to increase. From Fig. 3 we see that in fact the adsorption of cations actually decreases, but that of anions also falls. This is explained by the fact that oxygen is adsorbed at these potentials.

The most involved double layer structure on platinum is found when there is simultaneous adsorption of surface-active cations and anions. From our results on the kinetics of Cd^{2+} adsorption at reversible hydrogen potential it will be seen (Fig. 1) that, in the presence of the surface-active anions Cl^-, Br^- and I^- at equal concentrations, the adsorption of Cd^{2+} ions on the electrode increases with increase of the surface activity of the anion. Simultaneously there is an increase in the time required to attain constant cation adsorption. The smallest adsorptions and times are observed in the presence of weakly surface-active SO_4^{2-} ions. Hence we can infer that the adsorption of Cd^{2+} ions is associated with the specific adsorptions of the anions.

This is also confirmed by the fact that adsorption of halide anions increases simultaneously with the increase in the adsorption of Cd^{2+}, occuring with the passage of time. For example, in the case of CdI_2 solution the adsorptions after 1 hr and 17 hr are $3.5 \cdot 10^{-10}$ and $6.5 \cdot 10^{-10}$ respectively for Cd^{2+}, and $4.0 \cdot 10^{-10}$ and $5.5 \cdot 10^{-10}$ for I^- (in g-eq/cm^2). The observed association between the adsorptions of the two surface-active ions during the forma-

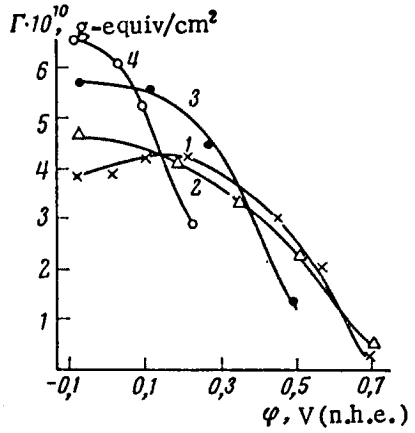


Fig. 6. Potential dependence of adsorption of Cd^{2+} from 10^{-2} N solutions of $CdSO_4$ (1), $CdCl_2$, (2) $CdBr_2$, (3) and CdI_2 (4) with base electrolyte 10^{-1}N H_2SO_4.

tion of a double layer can be more closely studied with the aid of data on the adsorption of cations and anions versus platinum potential in solutions of cadmium halides. As will be seen from Fig. 1, at reversible hydrogen potential the adsorption of Cd^{2+} ions increases as we go from sulfate to chloride, bromide and iodide. The same conclusion follows from Figs. 2 and 6.

The same law is followed in the case of the adsorption of halide ions (Figs. 4, 5). Since the total potential drop at the platinum-solution interface remains constant, an increase in anion adsorption must lead to an increase in cation adsorption. This is particularly clear from Fig. 2, which shows that for constant total potential drop (reversible hydrogen potential) and constant concentration of cadmium cations (10^{-2} N) an increase in the concentration of halide anions leads to an increase inthe adsorption of Cd^{2+} ions.

At all potentials the adsorption of anions in the presence of Cd^{2+} ions is less than in solutions of sodium halides (curves 2 and 3, Figs. 4 and 5). It is only between −0.1 and 0.06 V in cadmium bromine solution that the adsorption of anions in the presence of cadmium ions is greater than in their absence. Here we see a phenomenon similar to that described for the case of mercury with adsorption of I^- anions in the presence of Al^{3+} [13], Cs^+ and La^{3+} [14]: it was explained as due to attraction of cations to the electrical double layer by super-equivalent adsorbed cations with negative charge on the platinum. This conclusion cannot be verified from the experimental results of the present work for the case of iodine anions because the zero charge point of platinum in NaI solution is more negative than the reversible hydrogen potential. This effect should be very small for sulfate anions owing to their small surface activity, and apparently for this reason the measured adsorptions of these anions from $CdSO_4$ solution at potentials more negative than the zero charge point in Na_2SO_4 (0.18 V) are very low. In the case of cadmium bromide solution (Fig. 4) the amounts of adsorbed cation and anions are equal at 0.45 V, while in cadmium iodide this occurs at 0.01 V (Fig. 5).

The structure of the electrical double layer on platinum in the simultaneous presence of surface-active cations and anions can be represented as follows. As in cadmium sulfate solution, Cd^{2+} ions form with the platinum a dipole $^-Pt-Cd^+$. Halide anions, in turn, as in NaI, NaBr and NaCl solutions, form with the platinum dipoles $^+Pt-I^-$ (Br^-, Cl^-), with their negative ends turned towards the solution, and causing a positive potential drop [12]. We can also postulate that ion pairs CdI^+ ($CdBr^+$, $CdCl^+$) are formed on the platinum surface. Bearing in mind the signs of the charges of these pairs, we should expect their adsorption to increase with shift of potential towards the negative from the zero-charge point. However, as shown by the experiments (curves 1,2 in Figs. 4, 5), the number of adsorbed halide anions actually decreases. It follows that such pairs on the platinum are formed either not at all or only in very small numbers.

Specifically adsorbed cations and anions, of which the charge is neutralized in the diffusion part of the double layer, also take part in creating the total potential drop. From the present results it follows that the number of I^- anions in the diffusion part of the double layer for negative surface charge, and the number of Cd^{2+} ions for positive surface charge, are very small. This conclusion follows from the results of experiments on the influence of the SO_4^{2-} ion concentration on the adsorption of I^-, which showed that the adsorption of the latter remains constant when the concentration of sulfate ions is varied by more than an order of magnitude. The same conclusion is confirmed by the low quantities of iodine anions exchanges with I^- ions from the solution.

Finally, complex ions of the anion type, specifically adsorbed on the platinum, may also take part in creating the total potential drop. With negative surface charge their number is small, as seen from the data in Fig. 2, which show that cadmium adsorption decreases in conditions leading to the formation of complex ions (large excess of halide ions). This is especially clearly shown in the presence of iodine anions, which are known to possess a marked tendency to form complexes with cadmium.

At potentials more positive than the zero charge point, in solutions of cadmium halides the adsorption of anions continuously increases, that of cations falls, not to zero, but rather to a certain value depending on the nature of the anion. In the case of iodine this value is small. The nature of this residual adsorption of Cd^{2+} ions is not yet fully understood. From the available data we can guess that it is associated with incomplete reversibility of adsorption of Cd^{2+} in the presence of halide ions. For sulfate ions the process is reversible, as was shown by special experiments.

We can confirm that this phenomenon is not associated with adsorption of oxygen, because, as shown above, the adsorption of Cd^{2+} ions from solutions of halides in an atmosphere of air onto previously oxidized platinum at 0.8 V is close to zero.

In conclusion we may note that the phenomenon observed in the specific adsorption of Cd^{2+} ions show that, after the act of adsorption, the latter find themselves on the platinum surface in a state intermediate between the ionic and atomic state at potentials much more positive than their discharge potential. This is important for an understanding of the mechanism of electrodeposition of metals: we must remember that the primary act of these processes is the act of adsorption of the ion being discharged. The effect of halide anions on the adsorption of cadmium ions indicates the possibility of explaining the relation between the structure and properties of electrolyte metal coatings and the nature of the electrolyte.

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