STUDY OF THE SPECIFIC ADSORPTION OF IONS AND POSITION OF THE ELECTROCAPILLARY ZERO BY MEANS OF TRACERS

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Most investigations on the structure of the electrical double layer under various conditions, published at the present time in the work by Gouy, A. N. Frumkin, Grahame, and other investigators were carried out on liquid mercury by means of electrocapillary curves and capacity. There are still very few sufficiently direct and reliable data for solid metals, though the structure of the surface layer on solid electrodes used in practice is of considerable importance in the kinetics of electrode processes. The first work establishing the relation between the adsorption of ions and the formation of the double layer on solid metals was that of A. N. Frumkin and A. D. Obrucheva with a platinum electrode [1]. In later work of Kolthoff and Kameda [2], A. N. Frumkin, A. I. Shlygin, and V. I. Medvedovskii [3], and many others, these ideas were developed and refined by means of various electrochemical methods.

In the last few years in the Institute of Physical Chemistry, Academy of Sciences USSR, there have been developments in the study of the adsorption of ions on solid metals for elucidating the characteristics of the structure of the double layer by means of tracers. In these cases the method of tracers is applied as a direct adsorption method, making it possible to determine the qualitative and quantitative compositions of the surface layer under various conditions on actual electrodes.

This method has been used previously for studying processes occurring on metal surfaces in the work of Hevesy [4], Erbacher [5], Haissinsky [6], and others but without sufficient allowance for the electrochemical characteristics of the metal.

We developed variants of the procedure for measuring the amount of ions adsorbed on an electrode surface in relation to potential, time, temperature, and the composition of the solution labeled with one or several radioactive isotopes of the elements present in the ions studied. The total adsorption was measured from the change in radioactivity of the solution or the electrode itself. The experiments were carried out in normal glass electrochemical cells, fitted with a device for transferring the solution with the gas at the required moment of the experiment into a separate cell in which the activity was measured.

In the present work we present some results from the study of the adsorption of SO_4^{2-}, HPO_4^{2-}, I^-, Br^-, Cs^+, Sr^{2+}, La^{3+}, and Y^{3+} on a platinized platinum electrode.

The electrochemical behavior of a platinum electrode has been studied quite thoroughly in many works, and therefore it may be compared with adsorption behavior which has been studied inadequately. These works include numerous investigations of A. N. Frumkin and his co-workers, beginning with the earlier works of A. D. Obrucheva, A. I. Shlygin, B. V. Érshler, et al. [1, 3, 7], and also some investigations of foreign scientists [8]. From these works it is known that the electrocapillary zero of platinum, determined by various methods, lies within the potential range of 0.11 to 0.27 v relative to a normal hydrogen electrode. It has been shown that at more negative potentials the surface is charged negatively and adsorbs cations and at more positive potentials it adsorbs anions. At a potential of 0.4-0.5 v, when oxygen appears on platinum, its adsorption properties change, and the weakly oxidized surface first acquires a negative charge, and at higher anodic potentials (to a potential of 1.2 v, it is again positive.

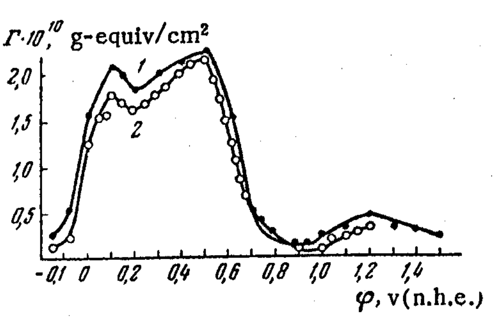

Fig. 1. Potential dependence of the adsorption of SO_4^{2-}. (Solution 0.01 N H_2SO_4.)
1) From measurements with tracers;
2) from measurements of electrical conductivity.

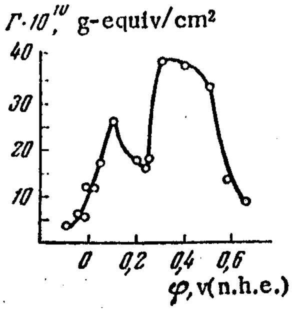

Fig. 2. Potential dependence of the adsorption of I^- (1 N H_2SO_4+0.01 N KI).

The adsorption properties of platinum with a further increase in potential have not been investigated. In the recent work of V. I. Veselovskii [9] on the mechanism of oxygen liberation on platinum which was carried out with labeled oxygen, it was shown that at different anode potentials the form of the bond of oxygen with the surface differed substantially. All the data obtained previously agree satisfactorily with the relatively simple scheme for the structure of the double layer.

Our experiments with tracers on a polarized platinum electrode made it possible to study the finer details of the adsorption of ions and showed that the relation of the adsorption of anions and cations on platinum to its potential is much more complex than was considered previously.

In general, adsorption depends on potential and, consequently, on the charge of the surface in approximate accordance with the ideas on the structure of the double layer; namely, the adsorption of anions increases with an increase in the positive and decreases with an increase in the negative charge of unoxidized platinum, while adsorption of cations decreases with a decrease in the negative charge. However, together with this there is adsorption of anions and cations on similarly charged surface in the region of the electrocapillary zero.

An examination of the curves of the relation between the adsorption of anions and the potential of unoxidized platinum, allowing for the fact that adsorption of oxygen begins at potentials above 0.4 v, shows that they are similar for all the anions studied. Figs. 1 and 2 show the most characteristic adsorption curves for SO_4^{2-} anions, which are considered surface-inactive, and I^- anions, which are typical surface-active anions. According to the simple scheme of the structure of the double layer, in the absence of specific adsorption, anions should be adsorbed at potentials which are more positive than the electrocapillary zero. As the experimental curves show, the adsorption of SO_4^{2-} changes in relation to potential analogously to the adsorption of surface-active anions I^-. For all the anions studied, with a negative charge on the surface of pure platinum, there was comparatively low adsorption, which increased rapidly with an increase in the negative charge. Close to the potential of 0.1-0.2 v there was a slight minimum, the nature of which is yet unknown. The results obtained, which show that not only surface-active anions I^- and Br^- but also surface-inactive anions SO_4^{2-} and HPO_4^{2-} are specifically adsorbed on platinum, and are in agreement with the data of Grahame [10], who showed that all anions with the exception of the ion F^- are adsorbed on mercury, and also with the hypotheses of Ya. M. Kolotyrkin [11] on the adsorption of H_2SO_4 on lead, thallium, and cadmium, which changes the kinetics of hydrogen liberation.

With the appearance of and an increase in, the positive charge, there is an increase in the adsorption of all anions up to the beginning of platinum oxidation. The amount of adsorption of all the anions studied differed ed strongly at all charges of the surface and the ions may be arranged in the following series with respect to increasing adsorbability $HPO_4^{2-} < SO_4^{2-} < Br^- < I^-$. The strength of the bond of the anions with the platinum surface also changes in the same series.

The amount of adsorption with the surface positively charged is greater for all the anions than is required for the formation of an ionic double layer. The values obtained correspond approximately to monolayer and for iodine to polylayer covering, if the size of the surface determined for the charging curves is used for the calculation. However, a considerably larger part of the platinum surface is apparently used in the adsorption process and the results of electrochemical measurements of the true surface are low.

An increase in adsorption with time over a period of several hours and a fall in it with an increase in temperature are also characteristics of the adsorption of all the anions studied on platinum. We associate these phenomena with the penetration of ions into the depth of the platinum, which is measured directly with time from the increase in the activity of the electrodes, which have first been washed free from active solution. At the same time there is an increase in the irreversibility of adsorption with time, which may be explained by strengthening of the bond of the specifically adsorbed anions with the surface of the metal.

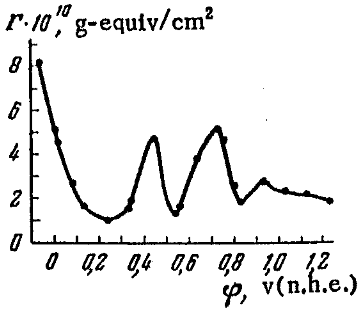

Fig. 3. Potential dependence of the adsorption of Cs^+. (Solution 0.01 N Cs_2SO_4; pH 2.5.)

Thus, with some approximation it is possible to separate adsorption on the external surface of the platinum, which occurs quite rapidly, from processes occurring slowly on it and from the penetration of anions into the platinum. This process, which is clearly expressed on platinum, does not occur on all metals. We have observed it on iron and steels but it is not detected on gold.

As is shown by the curves of the potential dependence of anion adsorption presented in Figs. 1 and 2, with comparatively rapid oxidation of the platinum, beginning at potentials of 0.4-0.5 v, there is sharp desorption of anions due to the formation of a dipole bond of oxygen with the platinum, as a result of which the surface is charged negatively. A further increase in potential evidently leads to the appearance of positive charges on the surface, which is caused by a slight increase in the adsorption of anions (Fig. 1). At high anode potentials there is a whole series of such adsorption maxima and minima, indicating the instability of the adsorption properties of platinum. The amount of adsorption of anions on positively charged oxidized platinum is less than on unoxidized platinum. For example, for a potential of 2.1 v, the adsorption of SO_4^{2-} anions is 1% of the adsorption of these anions at a potential of 0.3 v.

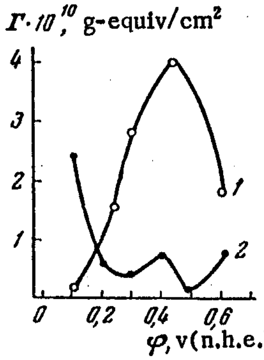

Fig. 4. Curves of the coadsorption of Cs^+ and SO_4^{2-}. (Solution $5 \cdot 10^{-3}$ N Cs_2SO_4; pH 2.7.) 1–SO_4^{2-}; 2–Cs^+.

The results we obtained on the adsorption of cations are closely connected with the specific adsorption of anions on platinum. Figure 3 gives a characteristic curve of the potential dependence of the adsorption of cations for Cs^+. The curves have an analogous form for Sr^{2+}, Y^{3+}, and La^{3+}. According to the simple scheme of the structure of the double layer, the adsorption of cations should occur only with the surface negatively charged and be absent with positive and zero charges. As Fig. 3 shows, a more complex picture was observed experimentally. The greatest adsorption of cations was observed with a negative charge on unoxidized platinum and with a decrease in this charge there was a fall in adsorption. Close to the electrocapillary zero point, the adsorption of cations was minimal, and with the appearance of an increase in the positive charge it again increased to the beginning of platinum oxidation. We explain the adsorption of cations on positively charged platinum by the presence at these potentials of overequivalent adsorption of anions, holding cations in the outer envelope of the double layer, as on mercury.

Thus, it is possible to determine the overequivalent adsorption of anions experimentally from the amount of adsorption of cations on a positively charged surface. According to our data, it is 3.10^{-11} g-equiv/cm^2 for SO_4^{2-}. With the appearance of adsorbed oxygen, overcharging the surface, there is desorption of cations bound by anions adsorbed in more than equivalent amount on the positive surface, but then there is again adsorption of cations on the negatively charged surface, the charge of which is caused by dipoles of oxygen with platinum. Further increase in potential leads to new overcharging of the surface and desorption of cations and adsorption of anions. The desorption of cations is greatest at potentials close to the potential of oxygen liberation, at which all the cations studied that are adsorbed on negatively charged unoxidized platinum, are desorbed almost completely after 1 - 2 min.

A study of the coadsorption of cations and anions makes it possible to determine the capillary zero at which the amount of adsorbed anions and cations are equal. This may be done most accurately for different potentials by simultaneous measurements of the adsorption of the cations and anions present in solution, as the amount of adsorption and the position of the electrocapillary zero depends to a considerable extent on the state of the surface, which is difficult to reproduce in different experiments. The use of tracers makes possible a rapid determination of the amounts of simultaneously adsorbed anions and cations by the use of appropriate radioactive tracers which differ considerably in the energy or the character of the radiation.

Figure 4 gives curves of the coadsorption of CS^+ and SO_4^{2-} on platinized platinum. As these curves show, with the greatest adsorption of cations there is the least adsorption of anions. The amounts of adsorption of the two types of ions became equal at a potential of 0.18 v, which agrees well with results obtained previously for the electrocapillary zero of platinum by other methods.

The amount of adsorption at the electrocapillary zero gives the amount of specific adsorption of anions on an uncharged surface of unoxidized platinum and corresponds to the maximum of the electrocapillary curve. For the case of SO_4^{2-}, this value is practically zero on mercury while, according to our data, on platinum it is 8.10^{-11} g-equiv/cm^2.

We subsequently hope to study the adsorption of ions on various metals to refine our ideas on the structure of the surface layer at a metal-solution boundary.

LITERATURE CITED

[1] A. N. Frumkin and A. D. Obrucheva, Z. anorg. Chem. 158, 84 (1926).

[2] J. Kolthoff, and Kameda, J. Am. Chem. Soc. 51, 2888 (1929).

[3] A. I. Shlygin and A. N. Frumkin, Acta Physicochim. USSR 3, 791 (1935); A. I. Shlygin, A. N. Frumkin, and V. I. Medvedovskii, Acta Physicochim. USSR 4, 911 (1936).

[4] G. Hevesy, and W. Billitz, Z. phys. Chem. 3, 271 (1929).

[5] O. Erbacher. Z. phys. Chem. 182, 243, 253, 256 (1938).

[6] M. Haissinsky, J. chim. phys. 29, 453 (1932); 30, 27 (1933); 31, 43 (1934); 32, 116 (1935); 33, 97 (1936).

[7] A. N. Frumkin, Sow. Phys. 4, 246 (1933); B. V. Ershler and M. A. Proskurnin, Zhur. Fiz. Khim. 8, 689 (1936); B. V. Ershler, Acta Physicochim. USSR 7, 327 (1937); B. V. Ershler, G. A. Deborin, and A. N. Frumkin, Acta Physicochim. USSR 8, 565 (1938); V. I. Nesterova and A. N. Frumkin, Zhur. Fiz. Khim. 26, 1178 (1952); A. D. Obrucheva, Zhur. Fiz. Khim. 26, 1148 (1952).

[8] E. Wicke and B. Weblus, Z. Elektrochem. 56, 169 (1952); F. Todt and W. Meyer, Z. Elektrochem. 57, 29 (1953); M. Bonnemay, Compt. rend. 237, 1235 (1953); A. K. Wiebe and C. A. Winkler, Canad. J. Chem. 31, 665 (1953).

[9] K. I. Rozental' and V. I. Veselovskii, Zhur. Fiz. Khim. 27, 1163 (1953).

[10] D. Graham, J. Am. Chem. Soc. 76, 4819 (1954).

[11] Ya. M. Kolotyrkin and N. Ya. Bunĕ, Zhur. Fiz. Khim. 21, 581 (1947); Ya. M. Kolotyrkin and L. A. Medvedeva, Zhur. Fiz. Khim. 25, 1355 (1951).