INFLUENCE OF THE COMPOSITION OF THE SOLUTION ON THE CHEMISORPTION OF CARBON DIOXIDE ON A PLATINIZED PLATINUM ELECTRODE

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The strong influence of the composition of the solution on the structure of an ionic electrical double layer and on the adsorption of hydrogen and oxygen on platinized platinum (see, for example, [1-5]) permitted us to expect a substantial dependence of the processes of interaction of CO_2 with H_{ads} and the electrooxidation of the chemisorbed product on the nature of the background anions and cations. In connection with this, in an investigation of the chemisorption of CO_2 on Pt/Pt, together with measurements in sulfuric acid solutions [6], we conducted a number of experiments in the presence of Cl^-, Br^-, ClO_4^-, $H_2PO_4^-$, HCO_3^-, OH^- anions and the Zn^{2+} cation.

The procedure of the galvanostatic measurements, conditions of purification of CO_2, characteristics of the Pt/Pt electrode, and notations of various quantities are the same as in [6]. The adsorption of CO_2 on Pt/Pt was accomplished by passing carbon dioxide with $\varphi_r = 0$ through until the change in the potential with time became negligible (≤ 0.1 mV/min). In the case of solutions of carbonates (Fig. 4), the conditions of adsorption were analogous, with the exception of the fact that nitrogen was passed through instead of CO_2 (~1.5 h). When the solutions of 1 N H_2SO_4 were replaced by 1 N H_2SO_4 + 0.1 N KCl or 0.01 N KBr (after chemisorption of CO_2), very negligible shifts of φ_r in the negative direction were observed. In experiments when 1 N H_2SO_4 in the working portion of the cell was replaced by solutions with greatly differing pH values, analogous replacement of the solutions was also performed for the reference electrode. In the calculation of the adsorption coefficient K [6], the value of the lag cor-

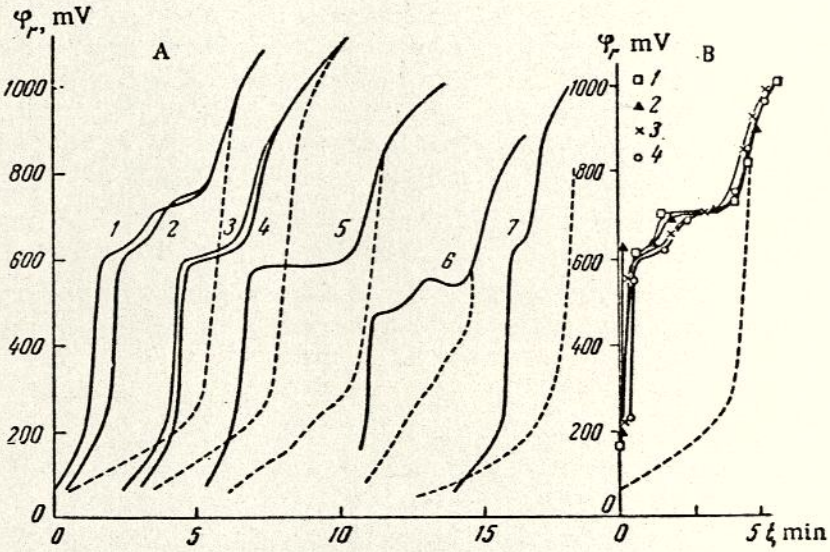


Fig. 1. A) Curves of the electrooxidation of "reduced CO_2" in solutions: 1 N H_2SO_4 + 0.1 N KCl (1, 2), 1 N H_2SO_4 + 0.01 N KBr (3, 4), 1 N H_2SO_4 (5), 1 N KOH (6), 1 N H_2SO_4 + 0.1 N KBr (7). Dotted line) charging curves in the background solution. The chemisorption of CO_2 was performed in solutions: 1 N H_2SO_4 + 0.1 N KCl (1, 5), 1 N H_2SO_4 + 0.01 N KBr (3, 5), 1 N H_2SO_4 (2, 4, 6), 1 N H_2SO_4 + 0.1 N KBr (7). B) Curves of electrooxidation in 1 N H_2SO_4 + 0.1 N KCl of "reduced CO_2" (4) and of CH_3OH (3), HCHO (1), and HCOOH (2), chemisorbed during anodic polarization in 1 N H_2SO_4.

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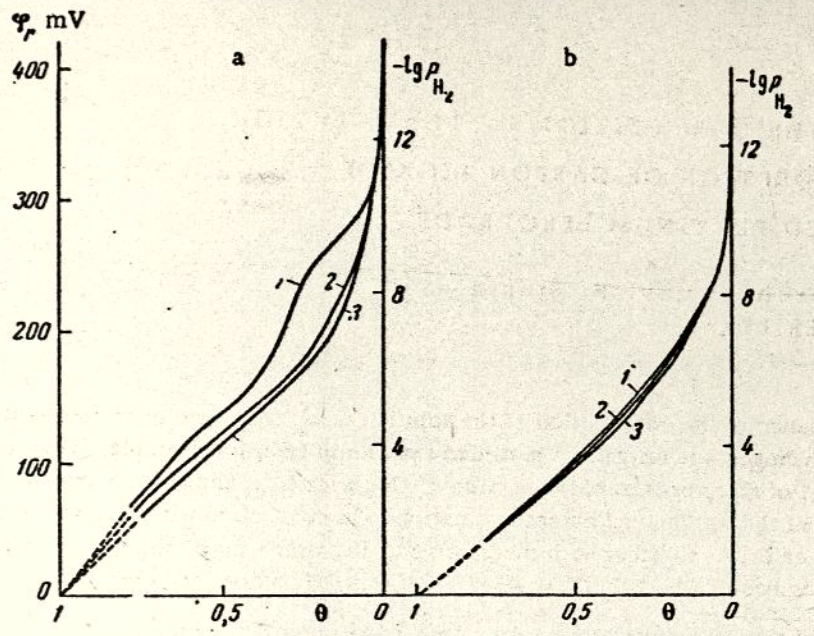


Fig. 2. Isotherms of the adsorption of hydrogen in 1 N H_2SO_4 (1), 1 N H_2SO_4 + 0.1 N KCl (2), and 1 N H_2SO_4 + 0.01 N KBr (3) in the absence (a) and presence (b) of "reduced CO_2" on the surface of Pt/Pt.

responding to the electrooxidation of the chemisorbed product in the given solution was compared with the value of the hydrogen lag in 1 N H_2SO_4. The charging curves were taken with a current density i = 0.36 mA/cm².

As can be seen from Fig. 1a (curves 1 and 2), two lags at φ_r of the "double layer" region correspond to the electrooxidation of chemisorbed CO_2 on Pt/Pt in a solution of 1 N H_2SO_4 + 1 N KCl. The shape of the electrooxidation curve and the potentials of the lags remain practically unchanged even in the case when the chemisorption of CO_2 is performed in 1 N H_2SO_4, while the curve of electrooxidation is taken after the corresponding number of washings (~10) in 1 N H_2SO_4 + 0.1 N KCl (curve 2). In the case of a different order of operation [i.e., chemisorption of CO_2 in 1 N H_2SO_4 + 0.1 N KCl, and electrooxidation of $(CO_2 + H)_{ads}$ in 1 N H_2SO_4], the charging curve obtained (curve 5) is similar to that corresponding to the chemisorption of CO_2 in 1 N H_2SO_4 [6]. Analogous effects are also observed for a solution of 1 N H_2SO_4 + 0.01 N KBr (Fig. 1a, curves 3-5), but in the latter, in contrast to a solution of 1 N H_2SO_4 + 0.1 N KCl, the electrooxidation of "reduced CO_2" is ended at considerably higher potentials (the second lag is indistinctly expressed, since it falls in the region of φ_r of the beginning of liberation of oxygen). The values of the coefficient K for curves 1-5 of Fig. 1 are 0.74-0.81.

Figure 2 presents the adsorption isotherms of hydrogen in solutions of 1 N H_2SO_4, 1 N H_2SO_4 + 0.1 N KCl, 1 N H_2SO_4 + 0.01 N KBr in the absence (a) and presence (b) of reduced CO_2 on the surface. Although the initial isotherms differ appreciably, after the chemisorption of CO_2 the isotherms become practically coinciding.

The data cited, in comparison with the results of [6], show that the amount of the chemisorbed substances under the conditions considered is practically independent of the background anions. Since the shape and potentials of the lag in the electrooxidation of the chemisorbed substance in 1 N H_2SO_4 are practically unchanged with changing composition of the solution in which the adsorption of CO_2 was performed, we may also assume that the composition of the chemisorbed substance was unchanged. Considering the fact that the potential of the point of zero charge (according to the scale of the normal hydrogen electrode) in acid solutions is negligibly displaced with changing pH [3], the potentials at which the chemisorption of CO_2 occurred (0-60 mV), on the basis of the data of [2-5], can be estimated as lying close to the point of zero charge (somewhat more negative in the case of Cl^- and more positive in the case of Br^-). Under these conditions Cl^- and Br^- are adsorbed in small amounts* and evidently relatively weakly, and are readily displaced from the surface by the adsorbed substance. In the region of potentials of the removal of H_{ads}, in the presence of $(CO_2 + H)_{ads}$ on the surface, the influence of halide anions is also inconsequential (Fig. 2b). The adsorption of halide anions begins to have an appreciable effect at the poten-

* According to [7], the adsorption of Br^- at φ_r = 60 mV in a solution of 1 N H_2SO_4 + 0.01 N KBr is ~5 μC/cm² of true surface as against ~ 55 μC/cm² when φ_r = 500 mV.

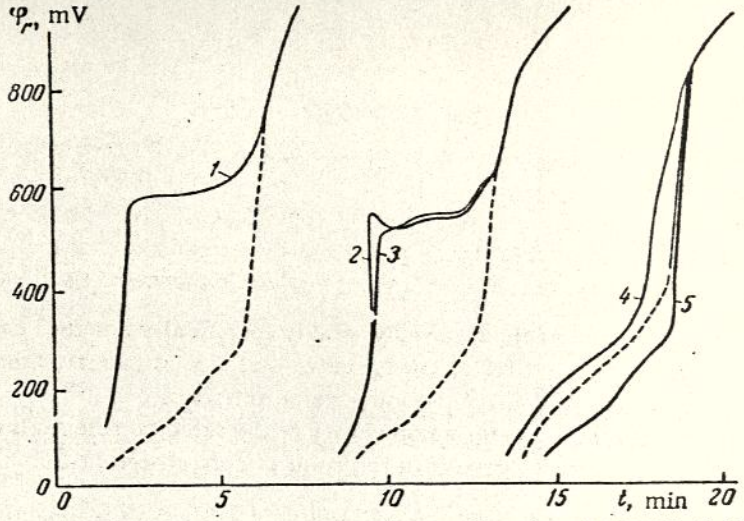


Fig. 3. Curves of the electrooxidation of "reduced CO_2" in 3 M H_3PO_4 (1), 1 N $HClO_4$ (3), 1 N H_2SO_4 + 0.2 N $ZnSO_4$ (4), and of CH_3OH chemisorbed during anodic polarization in 1 N $HClO_4$ (2); dotted line) charging curves in the background solutions; 5) charging curve in 1 N H_2SO_4.

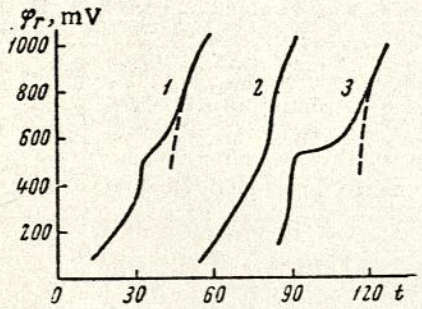


Fig. 4. Charging curves in 0.65 N $KHCO_3$ + 0.3 N K_2CO_3 (1) and 0.53 N K_2CO_3 + 0.1 KOH (2); 3) curve of electroreduction in 0.65 N $KHCO_3$ + 0.3 N K_2CO_3 (pH = 9.5) of "reduced CO_2," chemisorbed in 1 N H_2SO_4.

tials of the double-layer region, and the presence of two lags is apparently associated with the process of deposition of anions on sites freed of the chemisorbed substance. It may be assumed that some rather sharp change in the adsorption of Cl^- and Br^- ions corresponds to the point of inflection on the charging curve of $Pt(CO_2 + H)_{ads}$ at φ_r of the double-layer region. The assumption will require further experimental verification.

The effect under consideration is also characteristic of products chemisorbed in the polarization of a Pt/Pt electrode in solutions of CH_3OH, CH_2O, and HCOOH (Fig. 1b). A great similarity in the electrochemical behavior of these products and of "reduced CO_2" was noted in [6].

The electrooxidation of "reduced CO_2," chemisorbed in 1 N H_2SO_4, also proceeds in two steps in 1 N KOH. The second lag has an anomalous form—it passes through a maximum. Analogous curves have also been observed in the case of electrooxidation in alkalis of methanol, chemisorbed during polarization [8]. It was assumed that the two lags may be due to the oxidation of the dissociated and nondissociated forms of the chemisorbed product. The presence of an analogous effect in acid solutions in the presence of halide anions indicates the possibility of a different cause of the phenomenon, namely, it is more probable to attribute it to the process of adsorption of oxygen on sites freed of the chemisorbed substance.*

According to Fig. 1a (curve 7), in the case of large additions of Br^-, the amount of chemisorbed CO_2 is reduced in comparison with 1 N H_2SO_4; the adsorption coefficient K, determined according to the contraction of the hydrogen lag in the presence of $(CO_2 + H)_{ads}$ in comparison with the background curve (1 N H_2SO_4 + 0.1 N KBr) is ~0.5. Only a small portion of the chemisorbed substance is oxidized at ~630 mV; the remainder is oxidized at the potentials of the liberation of oxygen and dissolution of Pt. Data on the influence of the Br^- concentration on the process of chemisorption of CO_2 permit us to assume an appreciable shift of the point of zero charge in the negative direction with increasing Br^- concentration.

Two points of inflection (at ~530 mV and ~615 mV) are detected on the curve of the electrooxidation of "reduced CO_2" (Fig. 3, curve 3) in 1 N $HClO_4$; the oxidation potentials of $(CO_2 + H)_{ads}$ lie below those in 1 N H_2SO_4 (oxidation begins at ~515 mV, instead of ~585 mV in 1 N H_2SO_4). Points of inflection at the same poten-

* According to Frumkin [9], in the case of alkalis, it is difficult to differentiate between the adsorption of oxygen and the specific adsorption of OH^- anions.

tials are also detected on the curve of electrooxidation in 1 N $HClO_4$ of a substance chemisorbed in the anodic polarization of a Pt/Pt electrode in a solution of CH_3OH (curve 2). It should be assumed that the peculiarities considered are associated with a difference in the adsorption properties of SO_4^{2-} and ClO_4^- anions.*

The charging curve of $Pt(CO_2 + H)_{ads}$ in a solution of 3 M H_3PO_4 (Fig. 3, curve 1) practically does not differ from the analogous curve in 1 N H_2SO_4, i.e., in acid solutions the specific adsorption of $H_2PO_4^-$ anions [10, 11] has no significant influence on the processes of formation and electrooxidation of "reduced CO_2." According to [12], the inhibiting action of anions of phosphoric acid on the process of electroreduction of the products of chemisorption of CH_3OH and C_2H_5OH become significant at neutral pH values (in the presence of HPO_4^{2-} and PO_4^{3-} anions).

An investigation of the influence of the relatively weakly specifically adsorbed cation Zn^{2+} [13] on the process of chemisorption of CO_2 in 1 N H_2SO_4 + 0.2 N $ZnSO_4$ (curve 4 of Fig. 3) indicated that carbon dioxide interacts with H_{ads} to a very small degree ($\theta_{(CO_2H)} < 0.1$). Such a strong influence of Zn^{2+} on the process of chemisorption of CO_2 evidently is associated with their greater adsorbability at the selected potentials of the chemisorption of CO_2, since the latter were considerably more negative than the point of zero charge [3-5].

In order to clarify the question of which of the forms of CO_2($CO_{2(gas)} \rightleftarrows CO_{2(soln)} \rightleftarrows H_2CO_{3(soln)} \rightleftarrows H^+ + HCO_3^- \rightleftarrows 2H^+ + CO_3^{2+}$) interact with H_{ads}, we also performed measurements at neutral and alkaline pH values in solutions of carbonates. The data, presented in Fig. 4, permit us to consider that the CO_3^{2-} anion is not reduced by H_{ads}, while HCO_3^- is reduced, but weakly, which is evidenced by the comparatively small value of the lag at φ_r of the "double layer" region and the large amount of nonbonded hydrogen on the charging curves in solutions of $KHCO_3 + K_2CO_3$ (Fig. 4, curve 1), despite the sufficiently high concentration of the HCO_3^- anion. It is most probable to assume that in acid solutions, chiefly $CO_{2(soln)}$ or $H_2CO_{3(soln)}$ is reduced. Consequently, for Pt/Pt and Hg [14] we can note the presence of a definite analogy in the ability of various forms of CO_2 to be reduced (however, HCO_3^- in the case of Hg is considered to be an entirely nonreduced anion). The results cited contradict the assumption of Schuldiner [15], that the blocking action of CO_2 on H_{ads} may be due chiefly to HCO_3^- and CO_3^{2-} anions. The shape and potentials of the lags corresponding to the electrooxidation of $(CO_2 + H)_{ads}$ in a solution of $KHCO_3 + K_2CO_3$ (curves 1 and 3 of Fig. 4) support the absence of any significant specific adsorption of HCO_3^- and CO_3^{2-} anions.

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Note added in proof. In our previous article on the adsorption of Co_2 Pt [Életrokhimiya, 4, 1004 (1968)], on p. 1006, in Eq. (2'), it should have been $Q_i' = Q_i(1-j)$.

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* Appreciable differences in the structure of the electrical double layer on Pt in H_2SO_4 and $HClO_4$ were recently detected by O. A. Petrii and S. Ya. Vasina (Chair of Electrochemistry of Moscow State University).