ELECTRIC-DOUBLE-LAYER STRUCTURE AT THE PLATINIZED–PLATINUM ELECTRODE IN THE PRESENCE OF CHEMISORBED METHANOL

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Organic substances have a strong effect upon the adsorption of ions at the platinum electrode [1-3]; however, the influence of even the simplest organic compounds on the potential of zero charge (PZC) has until recently remained an open question. We have studied the effect of methyl alcohol on the structure of the ionic electric double layer (EDL) at the platinized platinum electrode.

The experiments were carried out in the presence of methanol adsorbed in advance. In this case the surface is covered with tightly chemisorbed species of the composition HCO [4-8]. It was established in special experiments that additional introduction of CH_3OH into the system is not reflected in the amounts of ions adsorbed.

The potential dependence of ionic adsorption was studied in acidified solutions containing weakly surface-active ions (Na^+, Cs^+, SO_4^{2-}) as well as strongly surface-active ions (Zn^{2+}, Tl^+, Cl^-).*

Ionic adsorption was measured with the aid of the isotopes Na-22, Cs-134, Zn-65, Tl-204, S-35, and Cl-36 following the technique presented in [9]. The methods of solution and electrode preparation were the same as in [7, 8]. The sodium chloride and sodium sulfate solutions were brought into contact with the electrode at the hydrogen potential. In view of the hysteresis found on the potential dependence of Zn^{2+} [10] and Tl^+ [11] ion adsorption, solutions containing these cations were brought into contact with the electrode at $\varphi_r = 0.3$ V (Zn^{2+}) and $\varphi_r = 0.2$ V $(Tl)^+$.† The electrode potential was maintained with a potentiostat in order to prevent its shifting to the anodic side, as well as to prevent partial electro-oxidation of the chemisorbed product. Then the electrode potential was brought to the reversible hydrogen value using hydrogen, and kept there for 2 h, whereupon the radioactivity of the adsorbed ions was measured. The electrode potential was then further shifted toward the anodic side, and ionic adsorption was measured every 50 mV after keeping the electrode for 15 to 30 min at this potential. This time sufficed for establishing stationary adsorption values. After measuring the potential dependence of ionic adsorption the electrode was cleaned and activated by alternating anodic and cathodic polarization in three portions of 10^{-3} N H_2SO_4. The CH_3OH was adsorbed under anodic polarization during 30 min from 0.1 N H_2SO_4 + 0.5 M CH_3OH solution using a current of 1 mA/cm^2. Maximum coverage of the electrode surface by chemisorbed methanol was then reached, corresponding to an occupation of about 80% of the platinum surface atoms [4]. The potential dependence of ionic adsorption was again measured as described after washing the electrode and the cell with 0.1 N H_2SO_4, twice-distilled water, and 10^{-3} N H_2SO_4, all saturated with argon. The data of the present work concerning the adsorption of ions on a surface of platinized platinum free from chemisorbed methanol are in complete agreement with the results of earlier work [12-14].

The exchange of Na^+, Cs^+, Zn^{2+}, and Tl^+ ions adsorbed both in the presence of chemisorbed methanol and on a surface free from it was studied at $\varphi_r = 0$. When stationary adsorption had been attained, the labeled electrolyte solution was replaced by nonlabeled, and the change in radioactivity of adsorbed cations was measured as a function of time.

* The effect of methanol on the adsorption of Br^- ions will be considered in another communication.

† φ_r is the potential against the reversible hydrogen electrode in the same solution.

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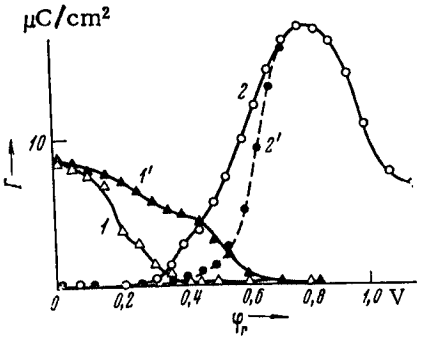

Fig. 1

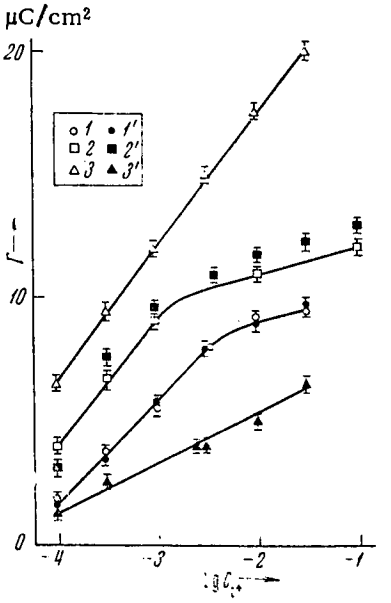

Fig. 2

Fig. 1. Ionic adsorption as function of electrode potential; 10^{-3} N H_2SO_4 + $3 \cdot 10^{-3}$ N Na_2SO_4. Na^+ (1) and SO_4^{2-} (2) on a surface free from methanol; Na^+ (1') and SO_4^{2-} (2') in the presence of chemisorbed methanol.

Fig. 2. Adsorption of cations as a function of their concentration in solution at $\varphi_r = 0$. 1) Na^+ (pH 3); 2) Cs^+ (pH 3); and 3) Zn^{2+} (pH 0) in the absence of chemisorbed methanol; 1'), 2'), and 3') the same in the presence of chemisorbed methanol.

The results of the experiments are shown in Figs. 1-3. The potential dependence of ionic adsorption at $\varphi_r >$ 0.5 V is plotted as a dashed line because in this region of φ_r, electrooxidation of the chemisorbed product occurs, and the coverage by HCO particles decreases. In Fig. 1 it can be seen that in 10^{-3} N H_2SO_4 + $3 \cdot 10^{-3}$ N Na_2SO_4 solution, the potential where equal amounts of cations and anions are adsorbed is shifted by about 200 mV to the positive side when chemisorbed methanol is present. Similar data have been obtained in 10^{-3} N HCl + $3 \cdot 10^{-3}$ N NaCl. Within the framework of a certain electric-double-layer model, this potential can conditionally be considered as the potential of zero free charge (PZC) [15]. Hence the HCO species, like chemisorbed oxygen, produces a positive potential drop at the platinum–electrolyte interface. It must be remembered, however, that the PZC shift cannot be equated to the adsorption potential drop caused by the methanol (in the sence in which this is done when organic substances are adsorbed on mercury) because while the PZC shifts by about 200 mV to the positive side, there occurs also a change in the potential drops which are produced by hydrogen or oxygen.

It follows from the plots shown that the EDL capacity calculated from the relation $C = \Delta\varepsilon/\Delta\varphi = \Delta(\Gamma_{A^-} - \Gamma_{C^+})/\Delta\varphi$ (where Γ_{C^+} is the adsorption of the cation, Γ_{A^-} that of the anion, ε is the charge density on the ionic side of the EDL at a given electrode potential φ_r) decreases in the presence of chemisorbed methanol. On these premises one can explain the experimental data obtained in the same way as in the case of the mercury electrode [1].

In fact, Γ_{A^-} is found to be considerably lower near the potential of zero charge in the presence of chemisorbed methanol $(PZC)_{org}$ than it is at the same potential in its absence (Fig. 1). As the potential shifts to the positive side, the ionic adsorption values are seen to converge, which is due to the electrooxidation of HCO particles; as the potential shifts from PZC_{org} towards the cathodic side one could expect the $\Gamma_{C^+} - \varphi_r$ plots to approach one another, and later to cross. It is seen from Fig. 1 that this approach takes place and that at $\varphi_r = 0$, Γ_{Na^+} in the absence and presence of chemisorbed methanol is the same.

The equality of the amounts of adsorbed sodium ions just at $\varphi_r = 0$ must be considered to be accidental. This coincidence means that the change in the potential drop produced by a changing EDL capacity is compensated by the adsorption potential drop produced by the chemisorbed methanol. It would have been natural also to expect a change in the bond strength between the adsorbed ions and the platinum surface in the presence of chemisorbed methanol. However, from the exchange measurements on the cations Na^+ and Cs^+, one cannot ascertain any difference in the

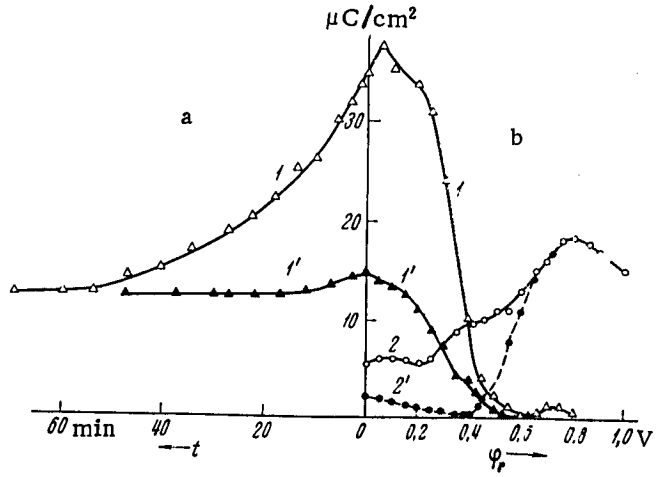

Fig. 3. a) The amount of adsorbed Zn^{2+} ions remaining on the surface, as a function of the exchange time at $\varphi_r = 0$ in 10^{-2} N $H_2SO_4 + 3 \cdot 10^{-3}$ N $ZnSO_4$, 1) in the absence and 1') in the presence of chemisorbed methanol; b) the potential dependence of the adsorption of Zn^{2+} (1, 1') and SO_4^{2-} (2, 2') ions in the same solution, 1) and 2) on a surface free from methanol, and 1') and 2') in the presence of chemisorbed methanol.

exchange kinetics by the technique employed (in both cases the exchange occurs practically within 5 min, and its rate is evidently diffusion-controlled).

Within experimental error, chemisorbed methanol does not affect the adsorption isotherms of Na^+ and Cs^+ at $\varphi_r = 0$ (Fig. 2, curves 1, 1', 2, 2'). This shows that the compensation noted above remains in effect when the electrolyte concentration changes.

Because Cs^+ ions are specifically adsorbed on platinum [16], while chemisorbed methanol has no effect on the adsorption of Na^+ or Cs^+ at $\varphi_r = 0$ over a wide concentration range, it could be expected that even in the presence of chemisorbed organic material, the adsorption of Cs^+ ions will remain specific. This conclusion could be confirmed when it was found that the addition of 5% Cs_2SO_4 to 10^{-3} N $H_2SO_4 + 10^{-3}$ N Na_2SO_4 solution depresses the adsorption of Na^+ ions by a factor of almost 2, both in the presence and absence of chemisorbed methyl alcohol [17].

The effect of chemisorbed methanol on the adsorption of surface-active cations was studied with Zn^{2+} and Tl^+. It is seen from Fig. 3 that over the entire potential range investigated, the adsorption of Zn^{2+} ions is lowered. The conditional potential of zero charge in $ZnSO_4$ solution is shifted to the positive side; however, it is not possible to define this shift accurately because electrooxidation of methanol begins at potentials more cathodic than PZC_{org}. For the same reason it is not possible either to observe an increase in $\Gamma_{Zn^{2+}}$ in the presence of chemisorbed mechanol. A lowering of $\Gamma_{Zn^{2+}}$ under the influence of chemisorbed methanol takes place at $\varphi_r = 0$ over a $ZnSO_4$ concentration range of 10^{-4} to 10^{-1} N (base electrolyte 10^{-2} N H_2SO_4) (Fig. 2, curves 3 and 3'). From the exchange experiments one can conclude that in the presence of chemisorbed methanol, the lowering of $\Gamma_{Zn^{2+}}$ occurs at the expense of weakly bound Zn^{2+} ions (Fig. 3). Chemisorbed methanol has a similar effect on the adsorption of Tl^+ ions.

Thus, while with weakly surface-active cations (Na^+ and Cs^+), only an increase in the value of Γ_{C^+} takes place on platinum in acidic solutions when chemisorbed methanol is present, with strongly surface-active cations (Zn^{2+} and Tl^+) one observes a decrease in Γ_{C^+}. The effect due to the PZC shift is overcompensated by the competition between the adsorbing species.

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