

INFLUENCE OF TIN CATIONS ON THE ADSORPTION OF CO₂ ON A SMOOTH PLATINUM ELECTRODE

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Earlier [1, 2] we investigated the influence of tin cations adsorbed on a platinum electrode on electrode processes. It was established that the adsorbed tin ions decrease the adsorption of hydrogen when a cathodic pulse is applied; moreover, the adsorption of tin is accompanied by a partial loss of charge, which increases as the potential is shifted in the cathodic direction. Only at sufficiently anodic potentials is the chemisorbed particle entirely cationic. The principles of the joint adsorption of tin and an organic substance (methanol and formic acid) were studied, and it was shown that as the surface becomes covered with tin, the degree of oxidation of these substances increases, despite a decrease in the coverage of the surface by the organic substance.

In addition to the accelerating influence of tin on the oxidation of methanol and formic acid, known from [3], there are data on the possibility of a cathodic reduction of CO₂ on tin [4]. This reaction is of substantial independent interest from the standpoint of the possibility of fixation of carbon dioxide. In addition, the particle formed in the chemisorption of CO₂ on metals of the platinum group, as it follows from a large number of studies [5-9], is a particle close in composition to the products of the adsorption of such substances as methanol and formic acid, the adsorption of which we studied in the presence of tin.

In this work we investigated the influence of the tin cation on the adsorption, hydrogenation, and oxidation of carbon dioxide adsorbed on a smooth platinum electrode in solutions of 1 N H₂SO₄ by the method of cathodic and anodic potentiodynamic pulses according to the procedure described in [10]. Preliminary treatment of the electrode was performed in such a way as to obtain a reproducibly clean electrode surface in the working solutions containing tin cations and carbon dioxide. The carbon dioxide, delivered from a cylinder, was passed through a system of purification to remove traces of oxygen, carbon monoxide, hydrogen sulfide, and organic compounds. In addition to a column with copper catalyst, the gas passed through solutions of palladium chloride, pyrogallol, and potassium bichromate and was dried in a tube over calcined calcium chloride. Direct measurements of the coverage by chemisorbed carbon dioxide and tin ions in the case of their simultaneous presence in solution were possible because chemisorbed carbon dioxide and chemisorbed tin ions give an oxidation wave to the anodic pulse in different potential regions. For tin this region lies within the range 0.35-0.85 V, and for CO₂ from 0.85 to 1.20 V (Fig. 1). (The values of the potentials are cited relative to a hydrogen electrode in the supporting electrolyte solution.)

Figure 2 presents the dependences of the coverage of the electrode surface by adsorbed carbon dioxide on the volume concentration of tin cations in solution and on the coverage of the surface by tin. In this case the adsorption potentials are different, while the CO₂ concentration equal to its solubility in solution is constant. The time of adsorption is 6 min, which corresponds to the reaching of a static value of the coverage both for CO₂ and for tin cations. From Fig. 2b it can be seen that the coverage of the surface by adsorbed CO₂ particles drops linearly with increasing logarithm of the volume concentration of tin ions, i.e.,

$$\sigma_{\text{CO}_2}' = A - \frac{1}{f} \ln c_{\text{Sn}},$$

where $f \sim 6.9$. At different potentials the slopes of the dependences are the same, but the values of D are different. The larger the cathodic value of the potential, the higher the necessary concentration of tin ions in solution to induce the same decrease in the adsorption of CO₂ on a smooth platinum electrode.

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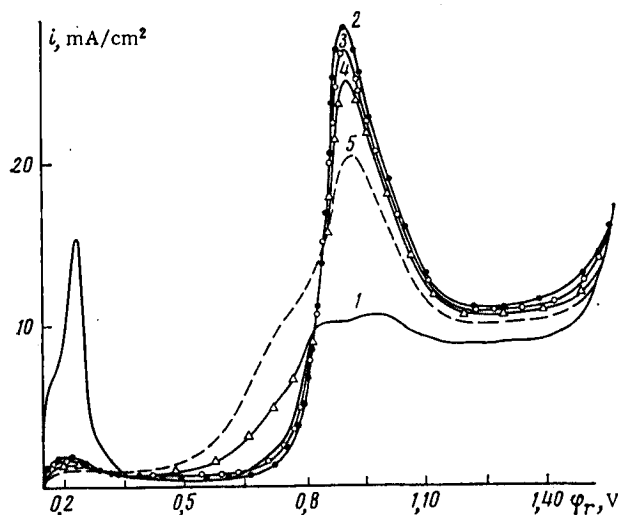


Fig. 1. Anodic pulsed i versus ϕ curves in 1 N H_2SO_4 (1) and in solutions of 1 N H_2SO_4 saturated with CO_2 and containing various SnSO_4 concentrations: 2) 0; 3) 10^{-4} ; 4) $2 \cdot 10^{-4}$; 5) $5 \cdot 10^{-4}$; 6) 10^{-3} . Time of adsorption at $\phi_r = 0.15$ V 6 min. Rate of application of the potential 20 V/sec.

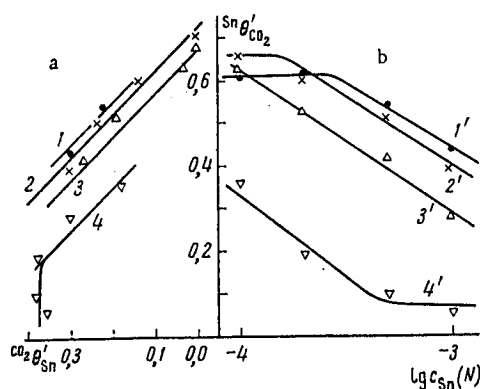


Fig. 2. Dependence of the static coverage of the platinum surface with chemisorbed CO_2 on the coverage of the surface by chemisorbed tin ions (a) and on the volume concentration of SnSO_4 in a solution of 1 N H_2SO_4 saturated with CO_2 (b) at various adsorption potentials (V): 1, 1') 0.05; 2, 2') 0.1; 3, 3') 0.15; 4, 4') 0.2.

From Fig. 2 it can also be seen that the coverage of the surface of a smooth platinum electrode by adsorbed CO_2 decreases linearly as the coverage of the surface by adsorbed tin increases, i.e.,

$$\theta'_{\text{CO}_2} = \theta'_{\text{CO}_2} - \gamma \theta'_{\text{Sn}},$$

where $\gamma \sim 1$ and is the same for all potentials. From the data cited it follows that the influence of the adsorption of tin on the adsorption of CO_2 is mutual (Fig. 2a), i.e., competition is observed between the tin cations and carbon dioxide for the surface of the platinum electrode. The competitive ability of each component is determined by the concentration of tin cations, by the electrode potential, and by the surface concentration of chemisorbed carbon dioxide. This corresponds to the dependence that we observed in the study of the influence of the tin cation on the oxidation of formic acid and methanol [2]. From Fig. 1 it can be seen that when tin is introduced, the summary coverage of the surface by chemisorbed particles, determined according to the decrease in the adsorption of hydrogen, is practically unchanged. An increase in the coverage of the surface by tin occurs at the expense of the coverage of the electrode surface by chemisorbed CO_2 .

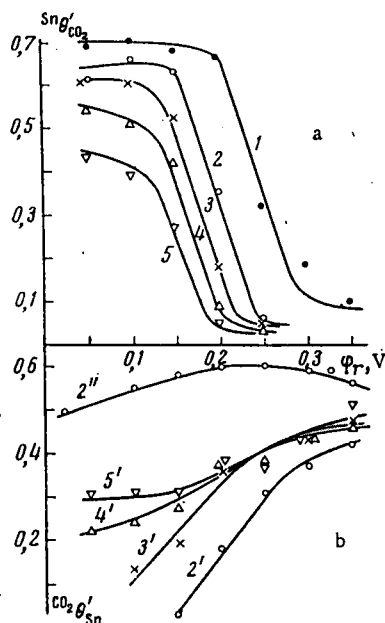


Fig. 3

Fig. 3. Dependence of the coverage of the surface of the platinum electrode by chemisorbed CO_2 (a) and tin (b) on the potential in their joint adsorption from 1 N H_2SO_4 solution saturated with CO_2 and containing various concentrations of SnSO_4 (N): 1) 0; 2, 2', 2'') 10^{-4} ; 3, 3') $2 \cdot 10^{-4}$; 4, 4') $5 \cdot 10^{-4}$; 5, 5') 10^{-3} ; 2'') in the absence of CO_2 .

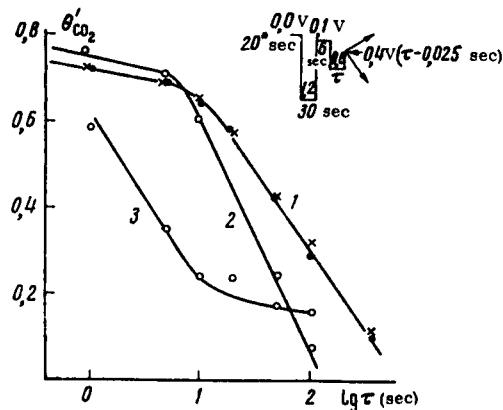


Fig. 4

Fig. 4. Kinetics of the oxidation of adsorbed carbon dioxide in the presence of tin ions (curve 1) and in the presence of 10^{-4} N (2) and $2 \cdot 10^{-4}$ N SnSO_4 (3).

The dependence of the coverage of the platinum surface by chemisorbed carbon dioxide on the potential is presented in Fig. 3. The nature of the dependence in the absence of tin coincides with the data cited in [11-13] (Fig. 3, curve 1). The introduction of tin cations into the solution changes this dependence (Fig. 3a, curves 2-5). The presence of CO_2 in solution, in turn, has an influence on the adsorption of tin, and this influence differs at different potentials. At potentials more cathodic than 0.15 V, close to the hydrogen zero, the decrease in the coverage of the surface with tin is rather substantial; the adsorption of carbon dioxide suppresses the adsorption of tin ions to a greater degree, i.e., the adsorption of carbon dioxide is more competitive on the electrode surface in this potential region. The influence of tin is manifested in the region of more positive potentials, at which maximum coverage with respect to tin is achieved, as in a solution of 1 N $\text{H}_2\text{SO}_4 + 10^{-4}$ N SnSO_4 in the presence of CO_2 (Fig. 3b, curves 2-5).

The kinetics of the removal of chemisorbed CO_2 by its oxidation at 0.6 V in the presence of tin was determined by applying a complex potentiodynamic pulse, indicated in Fig. 4, in which exposure of the electrode at the potential of maximum adsorption of CO_2 , i.e., 0.1 V, is provided for. The measuring pulse used permits a determination of the change in the coverage of the surface by adsorbed carbon dioxide and tin in their simultaneous presence on the surface. Moreover, the measuring cathodic pulse gives the summary coverage of the electrode by adsorbed CO_2 particles and chemisorbed tin ions, while the measuring anodic pulse gives the presence of each component individually. As can be seen from Fig. 4, in oxidation the rate of removal of chemisorbed particles formed in the adsorption of carbon dioxide in the presence of tin increases sharply (by more than an order of magnitude in the presence of $2 \cdot 10^{-4}$ N SnSO_4). (The different slope of curves 2 and 3 can be explained by a difference in the kinetics of the adsorption of tin from these solutions at $\phi_r = 0.6$ V [1].) The acceleration of the reaction is probably due to the fact that adsorbed tin ions serve as centers on which the adsorption of OH_{ads}^- , participating in the slow step of the oxidation, occurs [2].

We investigated the possibility of hydrogenation of chemisorbed carbon dioxide particles in the presence of tin ions. After the usual preliminary treatment and adsorption of CO_2 at $\phi_r = 0.1$ V for 6 min, we determined the coverage of the electrode by chemisorbed CO_2 as a function of the time of exposure of the electrode at the hydrogenation potentials, $\phi_r = -0.02$ and -0.05 V. The independence of $\text{Sn}\theta'_{\text{CO}_2}$ from the time of exposure at the cathodic potential is evidence that the process of cathodic hydrogenation of chemisorbed CO_2 particles does not occur under these conditions. One of the causes may be the low overvoltage of hydrogen on a platinum cathode,

on account of which the possibility of the occurrence of other reactions than the liberation of hydrogen is suppressed.

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DIFFUSION COEFFICIENTS OF URANYL IONS IN MIXED CHLORIDE - FLUORIDE SALT MIXTURES

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Earlier we studied the diffusion of uranyl in molten chlorides of the alkali metals and their mixtures [1]. It is known that partial replacement of chlorine by fluoride anions in a uranyl-containing melt leads to the formation of fluoride complex groups $\text{UO}_2\text{F}_4^{2-}$ that are stronger than the chloride complexes [2]. We were interested in determining how this affects the transport of uranyl ions in solvents of various cationic compositions, all the more in that there is no unanimity in the literature on the influence of fluoride anions on diffusion. For example, in [3-7] a decrease, and in [8] an increase in the rate of diffusion of polyvalent cations in chloride-fluoride melts in comparison with chloride melts are indicated.

For this purpose we measured the diffusion coefficients of uranyl ions by a chronopotentiometric method in salt mixtures NaCl-KCl-NaF , NaCl-CsCl , NaCl-CsCl-NaF , CsCl-CsF in the interval 924-1150°K. The experimental procedure and preparation of the starting materials were described in our previous studies [1, 3]. The experiments were conducted in an inert atmosphere in containers of beryllium oxide. The concentration of the solutions with respect to uranium was 0.2-0.8 mole%. Fluoride ions were introduced into the melt in the form of NaF or CsF "kh.d.a." [analytical grade]. It was assumed in this case that relatively small additions of fluorides (mole ratio $[\text{F}]/[\text{U}]=5$) practically do not change the density and viscosity of the salt solvents [9-13].

The values obtained for the diffusion coefficients of uranyl for all the investigated salt mixtures are presented graphically in a plot of $\lg D$ versus $1/T$ in Fig. 1. The experimental points fit satisfactorily on straight lines that are described by the following empirical equations:

for NaCl-KCl-NaF

$$\lg D = -2.88 - \frac{1820}{T} \pm 0.019;$$

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