SIMULTANEOUS ADSORPTION OF SULFATE AND CHLORIDE IONS ON PLATINIZED PLATINUM IN ACID SOLUTIONS

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UDC 541.135.5-183:546

Radioactive tracers were used to study the simultaneous adsorption of sulfate and chloride ion on platinized platinum from a perchloric acid supporting electrolyte. Data obtained were interpreted quantitatively on the basis of an approach used earlier for mixtures of Na^+ and Cs^+.

A study of the laws of simultaneous ion adsorption is of interest since electrochemical processes are often conducted in mixed electrolytes. In addition, measurements in mixed electrolytes can detect fine distinctions of specific ion absorbabilities [1]. A large amount of data is found in the literature with regard to simultaneous adsorption of ions of a mercury electrode. Quantitative data for simultaneous absorption on platinum has been found only for Na^+ and Cs^+ in acid solutions [2, 3].

In this work, we studied the simultaneous adsorption of SO_4^{2-} and Cl^- from a perchloric acid electrolyte onto a Pt/Pt electrode by a radiochemical method [4]. The perchloric acid served to maintain a constant pH and ionic strength. Perchloric acid was used because ClO_4^- is not reduced in the presence of SO_4^{2-} and Cl^- at room temperature [5].

The studies were conducted on Pt/Pt disks with an apparent surface area of 2.3 cm^2. Preparation of the electrodes was described earlier [6]. The true surface, determined from the hydrogen section of a charging curve in 1 N H_2SO_4, was 0.15 to 0.25 m^2. We used aged electrodes, the surfaces of which showed practically no change with time. The solutions were prepared with double-distilled water and the perchloric was purified by freezing. We used $^{35}SO_4^{2-}$ and $^{38}Cl^-$ as tracers. The radiochemical measurements were calibrated from values on adsorption of sulfate and chloride ions in 10^{-2} H_2SO_4 and 10^{-2} HCl [8]. Potentials (φ_r) were referred to a hydrogen electrode in the same solution. The experiments were conducted at 20±2°C.

Figure 1 shows the relation of SO_4^{2-} adsorption to potential in the presence of various concentrations of perchloric acid (curves 1-3). The physical meaning of $\Gamma_{SO_4^{2-}}$ has been examined in detail in [9]. An increase in the concentration of $HClO_4$ increases adsorption of SO_4^{2-}, in agreement with the results of [10-12]. This effect probably has several explanations. 1) If HSO_4^- is absorbed more readily than SO_4^{2-}, the increased adsorption may be due to a higher concentration of H_2SO_4 in the presence of $HClO_4$. Calculation shows that addition of 0.1 N $HClO_4$ to 10^{-2} N H_2SO_4 increases the concentration of HSO_4^- by a factor of about 2. 2) Addition of $HClO_4$ increases the activity of sulfuric acid anions. 3) A pH decrease in the presence of $HClO_4$ shifts the free zero charge potential in the negative direction along the φ_r scale [13] and should increase anion adsorption at a constant φ_r. 4) With a decrease in pH, oxygen adsorption diminishes at a constant φ_r causing an increase in adsorption of sulfuric acid anions. The relative contribution of the individual factors are difficult to evaluate. It is clear, however, that the adsorbability of ClO_4^- is so much lower than that of sulfuric acid anions that it cannot compete even when the concentration of the latter is several orders of magnitude lower. We subsequently chose 10^{-1} N $HClO_4$ as a supporting electrolyte.

The adsorption of sulfuric acid anions in 10^{-2} N H_2SO_4 + 0.1 N $HClO_4$ in the φ_r range of 0.4 to 0.6 V was found to increase linearly with the logarithm of time, reaching a limit within 1.5 to 2 h.

Figure 1 also shows the relation between $\Gamma_{SO_4^{2-}}$ and φ_r in the presence of Cl^- at various concentrations (curves 4-7). The presence of Cl^- lowers the adsorption of sulfuric acid anions because of the high specific adsorbability of Cl^- compared with sulfate ions [14-16]. Displacement of adsorbed sulfate ions is relatively slow, requiring 1.5-2 h in the presence of 10^{-3} N HCl.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. M. V. Lomonosov Moscow State University. Translated from Élektrokhimiya, Vol. 13, No. 10, pp. 1505-1510, October, 1977. Original article submitted May 19, 1976.

0038-5387/77/1310-1289 $07.50

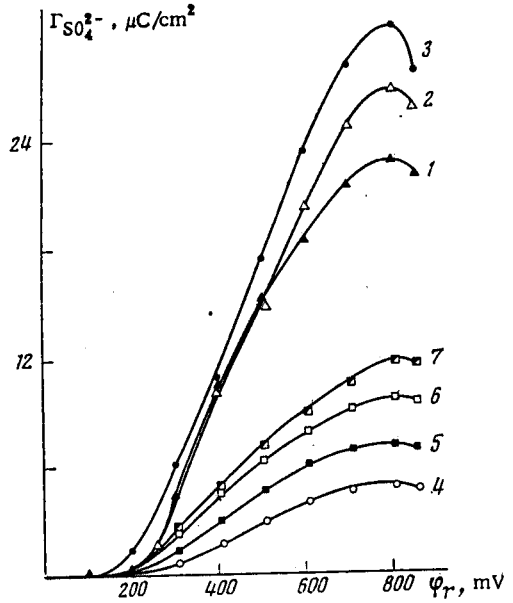

Fig. 1. Relation of adsorption of sulfuric acid anions to the potential of a Pt/Pt electrode in H_2SO_4 with no additions (1) and in the presence of 10^{-1} N $HClO_4$ (2), 1 N $HClO_4$ (3), and 10^{-1} N $HClO_4$ +xHCl (4-7), where $x = 10^{-2}$ (4), 10^{-3} (5), 10^{-4} (6), and $3 \cdot 10^{-5}$ N (7).

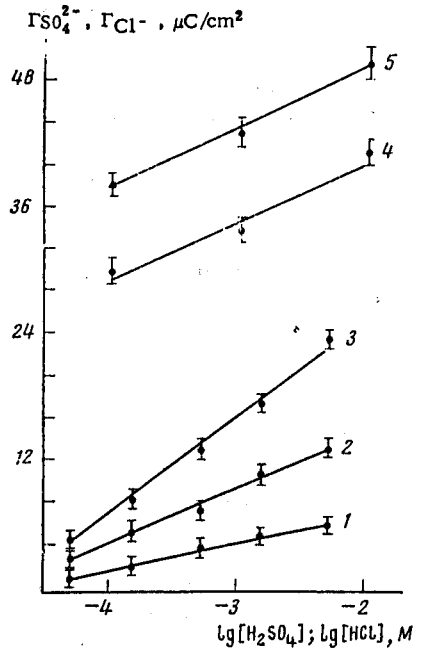

Fig. 2. Relation of sulfate [1-3] and chloride [4-5] ion adsorptions to concentration with a 10^{-1} N $HClO_4$ supporting electrolyte at $\varphi_r = 350$ (1), 500 (2, 4), and 750 mV (3, 5).

Using a supporting electrolyte of 10^{-1} N $HClO_4$, we studied the relation of SO_4^{2-} adsorption to its concentration at φ_r = 350, 500, and 750 mV. Data in Fig. 2 show that adsorption of sulfate ions follows the Temkin logarithmic isotherm at all the potentials studied.* Figure 2 also shows the relation of Cl^- adsorption to concentration. Its adosrption does not depend on the presence of perchloric acid, confirming earlier results [17]. The dependence of Cl^- adsorption to concentration also obeys the Temkin isotherm. Because of the low specific activity of the solution, reliable data on the Cl^- adsorption isotherm could be obtained only by rinsing the electrode and cell free of the solution, after the adsorption equilibrium was reached. We rinsed with 0.1 N $HClO_4$ under potentiostatic conditions. It was found that four to five short rinses did not remove adsorbed Cl^-. Lack of rinsing is indicated by the ion-exchange mechanism on platinum metals presented in [18] rather than an irreversible adsorption.

After we obtained individual adsorption iostherms for SO_4^{2-} and Cl^-, we studied the simultaneous adsorption of these ions using a supporting electrolyte of 10^{-1} N $HClO_4$ at φ_r = 350, 500, and 750 mV. The experimental procedure included flooding the cell sequentially with a solution containing H_2SO_4 and HCl in a fixed ratio, as previously described in [19]. The solutions were tagged with radioactive sulfur. The electrode was held in a solution of given composition for 1.5-2 h, sufficient to reach adsorption equilibrium. Experiments with a constant total H_2SO_4 + HCl concentration showed marked reductions of $\Gamma_{SO_4^{2-}}$ at a Cl^- content of 1%.

Figure 3 shows the relation of SO_4^{2-} adsorption to the logarithm of its concentration at constant Cl^- concentrations of 10^{-4} and $3 \cdot 10^{-4}$ N and φ_r values of 350, 500, and 750 mV. The curves are linear and are also almost parallel when $[Cl^-]$ is raised. We studied the relation of sulfate ion adsorption to Cl^- concentration at a constant H_2SO_4 concentration of 10^{-2} N and φ_r = 350, 500, and 750 mV (Fig. 4). Sulfate ion adsorption drops linearly with an increase of $[Cl^-]$ using the coordinates of $\Gamma_{SO_4^{2-}}$ and log $[Cl^-]$.

Attempts were made to analyze the data obtained quantitatively on the basis of an approach used earlier in a study of Cs^+ and Na^+ adsorption on platinized platinum [2, 3]. According to the relations shown in [2], individual ion adsorption isotherms can be written in the form

$$2.3 \lg \beta_1 c_1 = 2B_{11}\Gamma_1, \tag{1}$$

$$2.3 \lg \beta_2 c_2 = 2B_{22}\Gamma_2, \tag{2}$$

where B_{11} and B_{22} are virial coefficients, β_1 and β_2 are equilibrium adsorption constants, Γ_1 and Γ_2 are the number of adsorbed particles corresponding to 1 and 2, and c_1 and c_2 are their concentrations (in N). Subscript 1 refers to SO_4^{2-} and subscript 2 to Cl^-. Values for B_{11} and B_{22} were determined from slopes of the individual isotherms in coordinates of Γ and log c; values for β_1 and β_2 were found by extrapolating the linear sections of the isotherms to the abscissa. For the relation Γ_1 to log c_1 at c_2 = const, we have [2]

$$2{,}3 \lg \beta_1^{(2)} c_1 = 2B_{11}^{(2)}\Gamma_1, \tag{3}$$

where

$$\lg \beta_1^{(2)} = \lg \beta_1 - (B_{12}/B_{22}) \lg (\beta_2 c_2), \tag{4}$$

$$B_{11}^{(2)} = B_{11} - B_{12}^2/B_{22}, \tag{5}$$

$B_{11}^{(2)}$ is the virial coefficient and $\beta_1^{(2)}$ is the equilibrium adsorption constant in the presence of substance 2. It is evident from Fig. 3 that Eq. (3) is actually the case for adsorption of SO_4^{2-} in the presence of a constant Cl^-. According to Eq. (4), upon increasing the concentration c_2, log $\beta_1^{(2)}$ varies according to

$$\Delta \lg \beta_1^{(2)} = -\frac{B_{12}}{B_{22}} \Delta \lg c_2. \tag{6}$$

By this equation, B_{12} can be determined from $\Delta \log \beta_1^{(2)}$. It is clear from (3) and (4) that straight lines with coordinates of Γ_1, and log c_1 should be parallel to one another at various values of c_2. This conclusion also agrees with experimental data (Fig. 3). Dependence of Γ_1 on log c_2 at c_1 = const can be shown by the equation

$$2.3 \lg \beta_2 c_2 = -2B_{12}\Gamma_1, \tag{7}$$

* Data on the SO_4^{2-} adsorption isotherm given in [10] were obtained for a concentration of $\leq 10^{-4}$ M, precluding any comparison with our results.

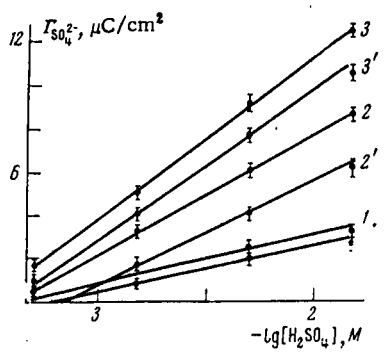

Fig. 3

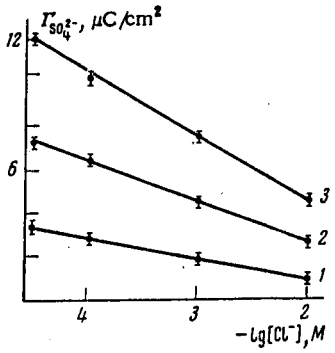

Fig. 4

Fig. 3. Relation of $\Gamma_{SO_4^{2-}}$ to sulfate ion concentrations at Cl^- concentrations to 10^{-4} N (1-3) and $3 \cdot 10^4$ N (1'-3') at φ_r = 350 (1, 1'), 500 (2, 2'), and 750 mV (3, 3').

Fig. 4. Relation of $\Gamma_{SO_4^{2-}}$ to Cl concentration at $[H_2SO_4] = 10^{-2}$ N in background of 10^{-1} N $HClO_4$ at φ_r = 350 (1), 500 (2), and 750 mV (3).

TABLE 1. Parameters Characterizing the Adsorption of Sulfate and Chloride Ions on Pt

φ_r, mV	B_{11}, Å²/ion	B_{22}, Å²/ion	lg β_1	lg β_2	$B_{11}^{(2)}$, Å²/ion	lg $\beta_1^{(2)}$ (exptl) in 10^{-4} N HCl	lg $\beta_1^{(2)}$ (calc) by Eq. (4)	B_{12} by Eq. (8)
350	770	–	4.7	–	870	3.3	–	140
500	360	410	4.8	9.0	350	3.4	3.1	110
750	210	410	4.8	10.8	250	3.5	3.0	

where

$$B_{12}^* = B_{11}B_{22}/B_{12} - B_{12}, \tag{8}$$

$$\lg \beta_2^* = \lg \beta_2 - (B_{22}/B_{12}) \lg(\beta_1 c_1). \tag{9}$$

Analysis of the data showed that the most reliable method for verifying the usefulness of these relations is to calculate B_{12} by Eq. (8) and then to use this value for calculation of $\log \beta_1^{(2)}$ by Eq. (4). Adsorption parameters caclulated according to equations derived from Figs. 2-4 are presented in Table 1.

Thus, not only is a qualitative correspondence observed between the data obtained and the relations given in [2], but satisfactory quantitative agreement is also found between the calculated and experimental values of $\log \beta^{(2)}$.

It must be stated in conclusion that the results obtained in [2] and in the present work also verify the usefulness of Gibbs thermodynamics for describing ionic adsorption on platinum. Indeed, the conclusions in [2] were based on the assumption that $B_{12} = B_{21}$ which is easily shown to result from equality of full differential crossed derivatives of the reversible surface work σ. Thus, the Gibbs adsorption equation for the system we studied, which contained excess ClO_4^- and H^+, can be written as

$$d\sigma = -\Gamma_{SO_4^{2-}} d\mu_{SO_4^{2-}} - \Gamma_{Cl^-} d\mu_{Cl^-}, \tag{10}$$

if the Gibbs water adsorption is $\Gamma_{H_2O} = 0$. It then follows from [20] that

$$\frac{1}{RTB_{21}} = (\partial \Gamma_{SO_4^{2-}}/\partial \mu_{Cl^-})_{r_{Cl^-}} = (\partial \Gamma_{Cl^-}/\partial \mu_{SO_4^{2-}})_{r_{SO_4^{2-}}} = \frac{1}{RTB_{12}}, \tag{11}$$

that is, $B_{12} = B_{21}$.

The authors are grateful to Academician A. N. Frumkin and B. B. Damaskin for reviewing the paper and providing valuable advice and consultation.

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CHARGING OF RUTHENIUM OXIDE – TITANIUM OXIDE ELECTRODES AND THEIR TRUE SURFACE AREA

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UDC 541.138.9:546

The true surface area of mixed ruthenium oxide–titanium (ROTO) films was measured by the BET method as a function of the heat-treatment temperature of the electrodes (370-700°C) and the ratio of the oxides RuO_2 and TiO_2. The obtained data were compared with the amounts of electricity Q (determined from potentiodynamic curves and charging curves) required for electrochemical charging of the films in 1 N sulfuric acid. The true surface of the mixed coatings amounts to several tens of square meters per gram and varies with the heat treatment temperature and the composition of the coating. From the values of the roughness factor and Q the amounts of electricity required for electrochemical charging of unit true surface area were determined, and the degree of surface coverage with oxygen with variation in the composition of the film was estimated.

The purpose of the present work was to study the surface conditions of ruthenium oxide–titanium oxide (ROTO) anodes [1-3].

The electrodes were prepared by thermal decomposition of a mixture of aqueous solutions of ruthenium and titanium chlorides deposited on titanium [1-3]. The electrodes were usually prepared by successive deposition of five layers followed by heating of each layer for 20 min and of the finished electrode (5.5-6.5 g Ru/m^2) for 1 h.

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Translated from Élektrokhimiya, Vol. 13, No. 10, pp. 1511-1515, October, 1977. Original article submitted May 20, 1976.

0038-5387/77/1310-1293 $07.50