

## Mechanism and kinetics of the electrosorption of sulphate anions on the (111) face of silver

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The processes of adsorption of sulphate anions onto the (111) face of silver have been investigated by analysis of the cyclic voltammetry and potentiostatic pulse results. It was shown, by fitting the experimentally recorded  $\theta - E$  dependences, that the adsorption of anions follows Frumkin adsorption isotherm. The adsorbed structure was found to be less dense than expected for the dense packed anion monolayer and the process was characterized by high value of the interaction parameter and the Gibbs energy of adsorption ( $f = 16.5$  and  $\Delta G_{\text{ads}, \theta \rightarrow 0}^{\circ} = -64 \text{ kJ mol}^{-1}$ ). From the slope of the  $E_{\text{p,a}} - \log(c_0)$  dependence it was concluded that complete charge transfer between the adsorbed anions and the silver substrate occurs. This is supported by the  $E_{\text{p,a}} - \log v$  linear dependence in the region of high sweep rates ( $v > 10 \text{ V s}^{-1}$ ) with rational value of line slope ( $\approx 60 \text{ mV dec}^{-1}$ ) which is possible only if the complete charge transfer reaction occurs. The electrosorption process of sulphate anions was found to be complex electrochemical reaction, taking place through three steps. It was proposed that the rate-determining step is the second step, *i.e.*, the electrochemical formation of  $(\text{SO}_4)_{\text{ads}}$  species.

*Key words:* (111) face of silver, sulphate anions, complete charge transfer, Frumkin adsorption isotherm, mechanism and kinetics of electrosorption.

The adsorption of sulphate anions onto silver substrates has been the subject of very few investigations.<sup>1-4</sup>

Vitanov and Popov<sup>1-3</sup> investigated the process of sulphate anion adsorption onto the (111) and (100) faces of silver by differential capacity measurements in order to obtain data about the influence of the growth steps on the value of the zero charge potential, which, accordingly to their results, was found to be about  $-0.7 \text{ V}$  (SCE) on the (111) face of silver. Although the zero charge potential in solutions of perchlorate and fluoride anions was found to be independent of the growth steps,<sup>5</sup> in the case of a  $0.005 \text{ M}$  sulphate solution it was shown that the zero charge potential moves towards more negative values with increasing number of growth steps. This was explained by adsorption of sulphate anions on the growth steps and not on the

flat terraces of the (100) or (111) orientation.<sup>1,2</sup> It should be mentioned here that these results were obtained on "electrolytically grown" silver single crystals, developed by the Bulgarian school, which show different characteristics during the investigation of the electrochemical processes taking place on such surfaces than on the commercially available silver single crystals.

Using a slightly different approach to obtain  $C - E$  curves, Jović *et al.*<sup>4</sup> found a minimum, appearing between two maxima (Fig. 6 of Ref. 6) at about the same potential on the  $C - E$  curves for the (111) face of silver. As this minimum was present on the  $C - E$  curves recorded in solutions of low and high concentration of sulphate anions, this point most probably cannot be considered as a zero charge potential, since a very similar value was obtained for the adsorption of fluoride anions.<sup>6-9</sup>

In the same paper, Jović *et al.*<sup>4</sup> also showed that the process of sulphate anions adsorption could not fit any other equivalent circuit except for the case in which the presence of a charge transfer resistance connected in series with the adsorption capacitance is assumed, indicating that charge transfer between the adsorbed anions and the silver substrate occurs.

Recently, two different approaches of the process to chloride anion adsorption on the (111) face of silver have been performed.<sup>10,11</sup>

In the first paper,<sup>10</sup> the broad peak on the  $C_{ad} - E$  curves was analyzed under the assumption that the adsorption of chloride anions obeys Langmuir adsorption isotherm. In such a case, following the equations derived in Refs. 4 and 10, one should obtain linear dependences between the  $\log(C_{ad})$  and  $\log(1/R_{ct})$  as functions of the  $\log[\theta(1-\theta)]$  (Eqs. (4) and (5) of Ref. 10). Relatively well defined  $\log(C_{ad}) - \log[\theta(1-\theta)]$  and  $\log(1/R_{ct}) - \log[\theta(1-\theta)]$  linear dependences, with slopes slightly different to those predicted by the model, were used for the analysis in order to obtain data about the charge transfer coefficient ( $l$ ) and the rate constant of adsorption ( $k_s$ ). It was shown that the value of  $l$  is equal to 1, indicating complete charge transfer between the adsorbed chloride anions and the silver substrate. The value of the constant for the adsorption rate of about  $8.5 \times 10^{-6} \text{ cm s}^{-1}$  obtained in the solution of a low concentration of chloride ions of  $0.005 \text{ mol dm}^{-3}$  and corresponding standard value  $k_s^\circ$  of about  $8.5 \times 10^{-3} \text{ cm s}^{-1}$  demonstrated that the process of chloride anion electrosorption is very fast.

In the second paper,<sup>11</sup> an attempt was made to use cyclic voltammetry and potentiostatic pulse results for the analysis of the kinetics and the mechanism of chloride anion electrosorption onto the (111) face of silver. The sweep rate dependence of the peak potentials ( $E_p - \log v$ ) in the range from  $0.1 \text{ V s}^{-1}$  to  $100 \text{ V s}^{-1}$  was used to obtain data about the apparent transfer coefficient  $\alpha_a$ . The reaction mechanism of chloride anion electrosorption was evaluated from the values of  $\alpha_a$ . It was shown that the first (broad) peak on the cyclic voltammograms corresponds to the formation of randomly distributed layers of adsorbed Cl (as it was assumed by Zei)<sup>12</sup>

and AgCl, taking place through three steps, with the rate-determining one being the chemical reaction of the formation of the adsorbed AgCl layer. The second (sharp) peak was ascribed to a phase transformation process (in accordance with the results of other authors)<sup>12,13</sup> including all three previously mentioned steps and a fourth, the rate-determining one, the crystallization to a 2D layer of the (111) oriented AgCl. Also, it was shown, by a more detailed analysis of the  $\theta - E$  dependences, that the adsorption follows a Frumkin adsorption isotherm, with the interaction parameter  $f$  being positive ( $f = 12$ ) for the broad peak and negative ( $f = -1.4$ ) for the sharp peak.

In this paper an attempt was made to apply the same procedure as in the case of chloride anions adsorption<sup>11</sup> (cyclic voltammetry and potentiostatic pulse investigations) to the process of sulphate anions adsorption on the (111) face of silver, in order to obtain data about the kinetics and the mechanism of the electrosorption process.

## EXPERIMENTAL

All experiments were carried out in a specially designed electrochemical cell at  $25 \pm 1$  °C in an atmosphere of purified nitrogen.

The procedure of single crystal surface preparation was the same as that given in great detail in previous papers.<sup>4,10,11</sup> The counter electrode was a large platinum sheet placed parallel to the working electrode surface. A saturated calomel electrode (SCE) was used as the reference electrode.

All solutions were made of Aristar grade chemicals and four times distilled Milli-Q water.

The linear sweep voltammetry (LSV) was performed using a potentiostat and waveform generator (PAR M-273). The voltammograms obtained at sweep rates lower than  $0.5 \text{ V s}^{-1}$  were recorded on an X-Y recorder (Philips PM8033). The voltammograms obtained at high sweep rates ( $0.5 - 150 \text{ V s}^{-1}$ ), as well as potentiostatic  $j - t$  transients were recorded on a digital oscilloscope (Nicolet Explorer II) and transferred to a X-Y recorder (Houston Instruments 2000R). Pulse durations were 50 ms for all pulse measurements.

The impedance measurements were performed with a PAR impedance measurement system made of a lock-in amplifier (PAR M-5301), a potentiostat (PAR M-273) and an IBM computer (PS2 M30), using the software for impedance measurements (PAR M-378). Ohmic drops obtained from these data were used for the  $IR_{\Omega}$  corrections of the peak potentials,  $E_{p,a}$ .

The fitting procedure was performed using the computer programme.

## RESULTS

The voltammogram recorded at the sweep rate of  $0.1 \text{ V s}^{-1}$  in a 0.2 M solution of sulphate anions is shown in Fig. 1a. As can be seen this voltammogram is characterized with two anodic peaks, the main one being at about  $-0.46 \text{ V}$ , with the same feature in the cathodic branch, with the main cathodic peak being at about  $-0.52 \text{ V}$ . It can also be seen that the anodic current density starts to rise at about  $-0.8 \text{ V}$ , indicating the beginning of the adsorption of sulphate anions. As is seen from Fig. 1b, with increasing anodic potential limit, there is no indication of a "crystallization loop", as is the case with chloride anion solutions.

One should mention here that there is a systematic small difference in the position of peak potentials for the anodic and cathodic peaks of about 60 mV

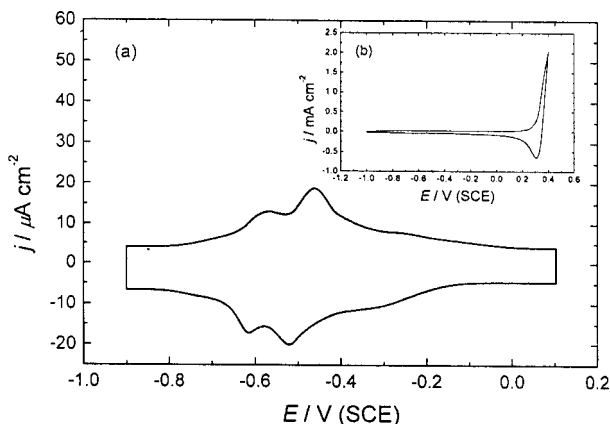


Fig. 1. a) Cyclic voltammogram of the adsorption and desorption of sulphate anions on the (111) face of silver recorded in a solution of 0.2 M  $\text{Na}_2\text{SO}_4$  at a sweep rate of  $0.1 \text{ V s}^{-1}$  to the anodic limit of 0.2 V (SCE) and b) to a more positive value of the anodic limit of 0.4 V. (Note the difference in the current density scales).

independently on the sweep rates, if they were smaller than the critical value of about  $v_c \approx 4 \text{ V s}^{-1}$  (cf. Fig. 8). The theory of the reversible monolayer electrosorption for the simple processes predicts that the anodic and cathodic peaks should be symmetric, but also that the peak potential should be independent on the sweep rate. There are number of examples in the literature when the on-going sweeps show the independence of the peak potential on the sweep rates and are treated as reversible adsorption peaks, while the reverse sweeps show larger or smaller peak potential differences. The larger differences were explained by the irreversibility of the reduction of the additionally formed product,<sup>14</sup> while for the smaller peak-potential differences authors often this problem ignore.<sup>15,17</sup>

We do not have a good explanation for this small asymmetry of adsorption/desorption peaks observed here, but we would like to point out that we observed similar asymmetry for the electrosorption of  $\text{Br}^-$ ,<sup>18</sup> and acetate<sup>19</sup> ions on Ag and also  $\text{Cl}^-$  on Ag.<sup>10,11</sup> Since symmetry of the peaks is not a *conditio sine qua non* for treating the anodic peaks as reversible or irreversible ones, we shall use the peak potential –  $\log v$  dependence as a valid criterion for the reversibility of the process. Much more work is needed to find out why in the number of cases small peak-potential differences appear in the real systems, as mentioned previously.

A potentiostatic pulse technique was applied to obtain the value of the charge needed for the adsorption of the structure corresponding to the anodic peaks. A potential of  $-0.9 \text{ V}$  was used as the starting potential, since at this potential the cyclic voltammogram shows the characteristics of a typical double layer charging voltammogram. The pulses were applied in steps of  $0.1 \text{ V}$  towards more positive potentials, up to the value of  $0.1 \text{ V}$  (SCE). Time scale plotted in Fig. 2 is 4 ms and it is taken only for the sake of diagram clarity, while the real pulse duration was 50

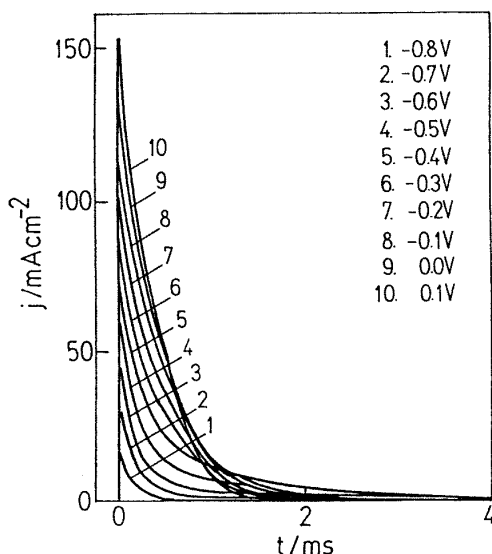


Fig. 2. Potentiostatic  $j-t$  transients of the adsorption of sulphate anions on the (111) face of silver electrode recorded in a solution of 0.2 M  $\text{Na}_2\text{SO}_4$ . Starting potential  $E_s = -1.0$  V. The potentials of the pulses are marked in the figure. Note that pulse duration was 50 ms, while for the clarity of the diagram only first 4 ms are presented.

ms, what gave sufficiently large time window for the establishment of the equilibrium, as for the similar type of measurements.<sup>20,21</sup>

The  $j-t$  transients recorded for all the applied pulses of potential are shown in Fig. 2. As can be seen at more positive potentials the anodic current densities are higher and, accordingly, the charge under the  $j-t$  transients increases. In the potential region from  $-0.2$  V to 0.1 V, the  $j-t$  transients overlap and the increase of the anodic charge become less pronounced.

The measured charge ( $\sigma_m$ ), obtained by integration of the area under the  $j-t$  transients of Fig. 2, is shown in Fig. 3. Assuming that the double layer capacity in this solution amounts  $20 \mu\text{F cm}^{-2}$ , the charge needed for a double layer charging ( $\sigma_{dl}$ ) can be calculated for each applied potential and subtracted from the measured one. In such a way one obtains the charge needed for the adsorption of the sulphate anions only ( $\sigma_m - \sigma_{dl}$ ), which is also presented as a function of potential in Fig. 3. The maximum charge ( $\sigma_{max}$ ) was found to be  $47 \mu\text{C cm}^{-2}$ .

For further analysis of the of sulphate anions adsorption process it was necessary to determine (concerning our previous results)<sup>4</sup> the number of electrons exchanged in the adsorption reaction. This number can be determined according to Gileadi<sup>22</sup> using equation

$$E_{p,a} = E_{ads}^0 - 2.3 \frac{RT}{nF} \log(c_0) + \left( \frac{RT}{nF} \times \frac{f}{2} \right) \quad (1)$$

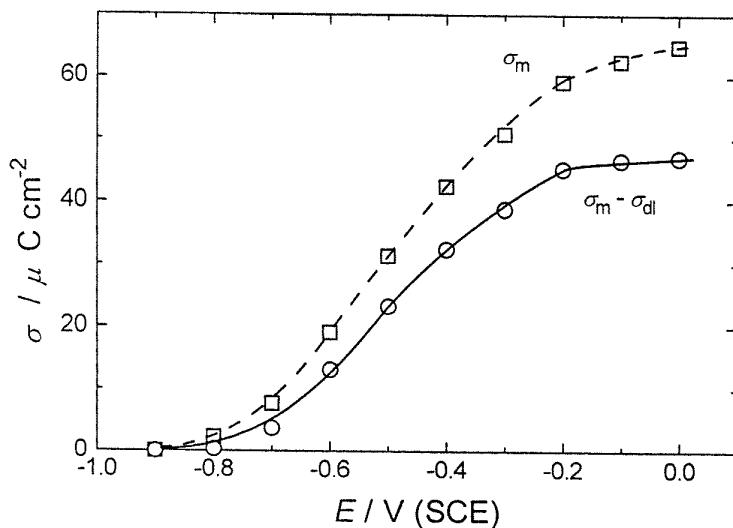


Fig. 3. Dependence of the measured ( $\sigma_m$ ) charge and the charge corrected for the double layer changing ( $\sigma_m - \sigma_{dl}$ ) on the potential, obtained by integration of the surface under the  $j - t$  transients presented in Fig. 2.

where  $E_{p,a}$  represents the potential of the anodic peak,  $E_{ads}^0$  the standard potential of electroadsorption and  $c_0$  the concentration of adsorbing anions in the bulk of the solution and  $f$  the Frumkin interaction parameter ( $f = r/RT$ ), as defined in Eq. (2). Hence, by plotting  $E_{p,a}$  (recorded at the sweep rate of  $100 \text{ mV s}^{-1}$ , which is sufficiently low rate to have voltammograms in the reversible reaction region, *i.e.*, lower than the critical sweep rate)<sup>22</sup> as a function of  $\log(c_0)$ , it is possible to determine the total number of electrons exchanged in the electroadsorption process from the slope of the  $E_{p,a} - \log(c_0)$  dependence.

The result of such an analysis, obtained using the results presented in this paper as well as the results of previous investigations,<sup>4</sup> is shown in Fig. 4. As can be seen, a well defined linear dependence with a slope of  $-29.8 \text{ mV dec}^{-1}$  is obtained, indicating that two electrons are exchanged in the electroadsorption reaction.

Knowing the value of  $n$  and the dimensions of the sulphate anion,<sup>23</sup> it can be calculated that a full coverage of the (111) face of silver can be achieved when the value of the charge amounts  $223 \mu\text{C cm}^{-2}$ . Hence, the maximum value of  $47 \mu\text{C cm}^{-2}$  indicates that the adsorbed structure is less dense than a monolayer of sulphate species.

Taking into account the previous statement and using  $\sigma_{max} = 47 \mu\text{C cm}^{-2}$ , the  $\sigma - E$  dependence (corrected for a double layer charge, Fig. 3) has been transformed into a  $\theta - E$  dependence, shown in Fig. 5 by the points (open circuits). The shape of the  $\theta - E$  dependence indicates that a Langmuir adsorption isotherm cannot be applied and that a Frumkin adsorption isotherm should be used for describing the adsorption process.

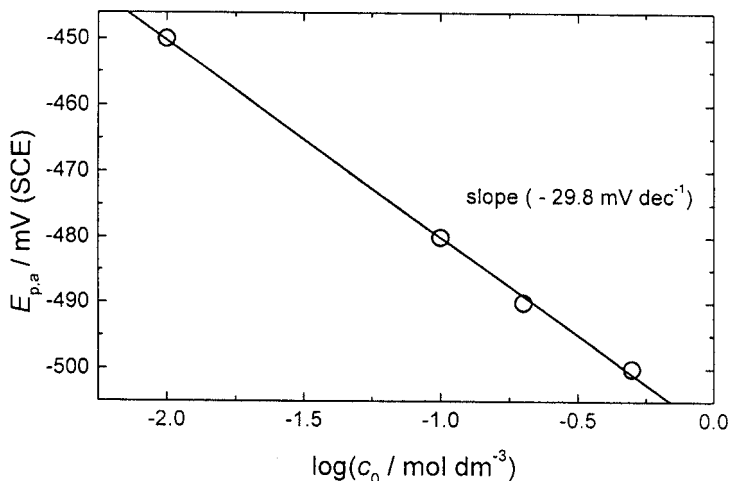


Fig. 4. Dependence of the anodic peak potential ( $E_{p,a}$ ) on the logarithm of the sulphate anion concentration ( $\log(c_0)$ ), recorded at a sweep rate of  $0.1 \text{ V s}^{-1}$ .

For this purpose Frumkin isotherm for electrosorption in a form

$$\left( \frac{\theta}{1-\theta} \right) \exp(f\theta) = K_{\text{ads},\theta \rightarrow 0}^{\circ} c_0 \exp\left(\frac{FE}{RT}\right) \quad (2)$$

was used.

Standard state in this case has to be  $\theta_1 = 0.5$  but taking as the reference state extrapolated situation when  $\theta \rightarrow 0$  and  $E = 0.0 \text{ V(SHE)}$  for  $c_0^{\circ} = 1 \text{ mol dm}^{-3}$ . In a well argued paper of Conway *et al.*<sup>24</sup> showed that for the adsorption isotherms of the Frumkin type when the interaction parameter is larger than zero ( $f > 0$ ) the often used thermodynamically well defined standard state  $\theta^{\circ} = 0.5$  is valid only for  $f = 0$ , *i.e.*, Langmuir isotherm. If  $f > 0$  it loses its sense since  $\theta^{\circ}$  should be different for different  $f$  values. This is so because the left-hand side of Eq. (2) can be equal to unity (condition for the standard state) only for different combinations of  $f$  and  $\theta^{\circ}$ . For example (see Ref. 25) for  $f = 10$   $\theta^{\circ}$  should be about 0.16. The  $f$  value is not only a characteristics of the adsorbent-adsorbate combination but also it might depend on the possible co-adsorption of other species present in the electrolyte (*e.g.*, other anions, organic species, *etc.*). If so, one could expect that standard state  $\theta^{\circ}$  for the studied adsorbing species is a function of all the other species present in the solution, including their concentrations. This would be absurd. Therefore, using as a reference state  $\theta \rightarrow 0$  is more rational, relating the Gibbs energy of adsorption only to the species studied without the interference of all other components present in the electrolyte. Extrapolation to  $\theta \rightarrow 0$  means that all lateral interactions become negligible (*i.e.*,  $f \rightarrow 0$ ). It comes out that for small  $\theta$  one can treat system as a

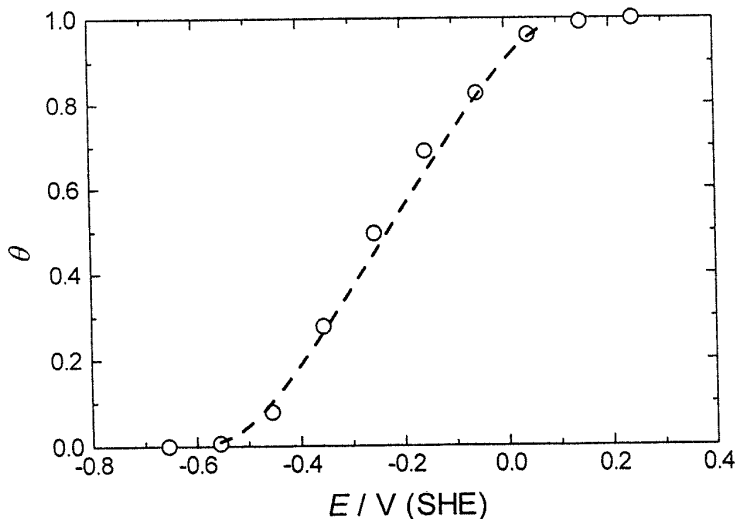


Fig. 5. Adsorption isotherm for sulphate anions obtained by analysis of the results presented in Fig. 3. The fitted curve is presented by the dashed line, while open circles represent experimentally recorded results.

hypothetical Langmuir case and evaluate only the adsorbate-adsorbent interactions, *i.e.*,  $\Delta G^{\circ}_{\text{ads},\theta \rightarrow 0}$ . This is similar to the situation with the electrolytic solutions, when the standard chemical potentials of the dissolved species are taken as a hypothetical state of unit concentration and infinite dilution (*i.e.*, when the practical activity coefficient  $\gamma \rightarrow 1$  for  $c \rightarrow 0$ ). Only for this condition the Gibbs energy of the system depends on the ion-solvent interaction with no interference of Coulombic interactions with the neighbouring ions. The problem of the standard state for the Frumkin isotherm is also discussed by Jastrzebska *et al.*<sup>26</sup>

Adsorption constant  $K^{\circ}_{\text{ads},\theta \rightarrow 0}$  which in principle is independent of potential in order to be numerically calculated from the measured data, due to the impossibility of measuring absolute potentials, has to be calculated for  $E = 0$ , *i.e.*, at the zero potential *versus* the reference electrode. Hence, in practice the numerical value of the adsorption constant  $K^{\circ}_{\text{ads},\theta \rightarrow 0}$  depends on the reference potential scale used. So does the Gibbs energy of adsorption, which is calculated using  $K^{\circ}_{\text{ads},\theta \rightarrow 0}$  by the equation

$$\Delta G^{\circ}_{\text{ads},\theta \rightarrow 0} = -RT \ln K^{\circ}_{\text{ads},\theta \rightarrow 0} \quad (3)$$

and also depends on the reference potential scale used. SHE is for this purpose the most adequate since SHE scale is the basis of the Gibbs energies of formation tables which take that for  $\text{H}^+$   $\Delta_{\text{f}}G^{\circ} = 0$ .

By fitting the  $\theta - E$  dependence with the Eq. (2), the interaction parameter  $f$  ( $f = r/RT$ ) and the Gibbs energy of adsorption for  $\theta \rightarrow 0$  ( $\Delta G^{\circ}_{\text{ads},\theta \rightarrow 0}$ ) were determined, being  $\Delta G^{\circ}_{\text{ads},\theta \rightarrow 0} = -64 \text{ kJ mol}^{-1}$  and  $f = 16.5$ . The fitted curve is presented in Fig. 5 by the dashed line.



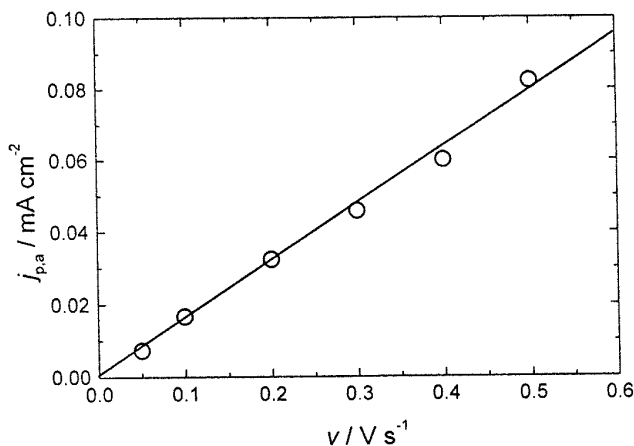


Fig. 6. Dependence of the anodic peak current density ( $j_{p,a}$ ) on the sweep rate ( $v$ ), recorded in a solution of 0.2 M  $\text{Na}_2\text{SO}_4$ .

In the region of lower sweep rates (up to  $5 \text{ V s}^{-1}$ ), where the peak potential does not change with the sweep rate (reversible region), the interaction parameter  $f$  can also be determined from the slope of the dependence of the anodic peak current density ( $j_{p,a}$ ) on the sweep rate ( $v$ ),<sup>22</sup> using the equation

$$j_{p,a} = \left( \frac{\sigma_{\max} nF}{4RT} \right) \left[ \frac{1}{1 + \left( \frac{f}{4} \right)} \right] v \quad (4)$$

where  $\sigma_{\max}$  represents the charge needed for the adsorbed structure (*i.e.*,  $47 \mu\text{C cm}^{-2}$ ), assuming a two electrons exchange, while the values of  $j_{p,a}$  are corrected for the current density of the double layer charging.

The result of such an analysis is shown in Fig. 6. A well defined linear dependence is obtained, while the value of  $f$  was found to be  $f = 15$ , which is somewhat lower than the value obtained by fitting the adsorption isotherm.

Hence, the adsorption of sulphate anions onto a silver substrate follows a Frumkin adsorption isotherm with a high value of  $f$ , indicating rather strong repulsion between the adsorbed species.

At higher values of  $v$  ( $v > 10 \text{ V s}^{-1}$ ) the shape of the voltammograms slightly changes, with the first anodic peak becoming a shoulder while the main one becomes sharper. Also, the anodic peak potential becomes more positive with increasing value of  $v$ , while the cathodic one moves towards more negative values, as is shown in Fig. 7. Such a change can be caused by the pseudo-ohmic polarization effect and/or by the irreversibility of the electrochemical reaction.

The dependence shown in Fig. 8 is obtained by plotting the value of the anodic peak potential ( $E_{p,a}$ ), corrected for the  $IR_{\Omega}$  drop ( $R_{\Omega}$  is determined from impedance measurements – see Experimental), as a function of  $\log v$ . As can be seen the value

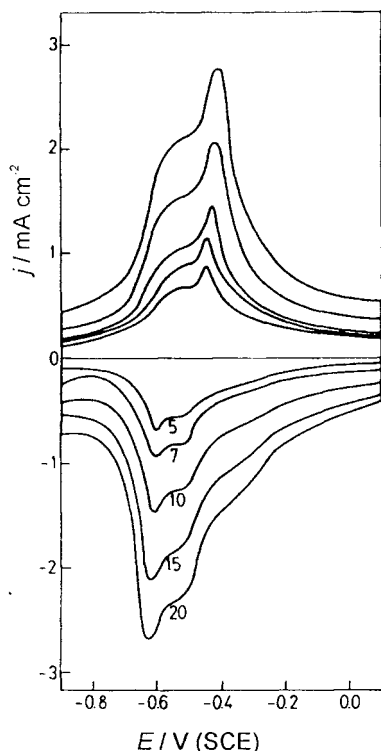


Fig. 7. Cyclic voltammograms of the adsorption and desorption of sulphate anions on the (111) face of silver recorded in the solution of 0.2 M  $\text{Na}_2\text{SO}_4$  at high sweep rates (marked in the figure in  $\text{V s}^{-1}$ ).

of  $E_{p,a}$  does not change with  $\log v$  up to about  $5 \text{ V s}^{-1}$ , while a linear dependence, with a slope of  $58 \text{ mV dec}^{-1}$ , is obtained at higher values of  $\log v$ .

According to the literature<sup>22,27,28</sup> such a dependence indicates irreversibility of the process at these rates, while the slope depends on the value of the symmetry factor  $\beta$ , or, for more complex reactions, on the value of the apparent transfer coefficient  $\alpha_a$ . This value can be used as one of the diagnostic criteria for the evaluation of the reaction mechanism (see Discussion).

#### DISCUSSION

The slope of the  $E_{p,a} - \log(c_0)$  dependence, presented in Fig. 4, of  $-29.8 \text{ mV dec}^{-1}$ , indicates two electrons exchange in the overall reaction of sulphate anions electrosorption, which means the complete charge transfer between the adsorbed anions and the silver substrate.

The maximum charge ( $\sigma_{\text{max}}$ ) needed for the adsorption of sulphate anions of  $47 \mu\text{C cm}^{-2}$  indicates a very rare structure of the adsorbate, since the charge for adsorption (with complete charge transfer) of a close packed monolayer of sulphate (taking into account the tetrahedral structure and the dimensions of sulphate an-

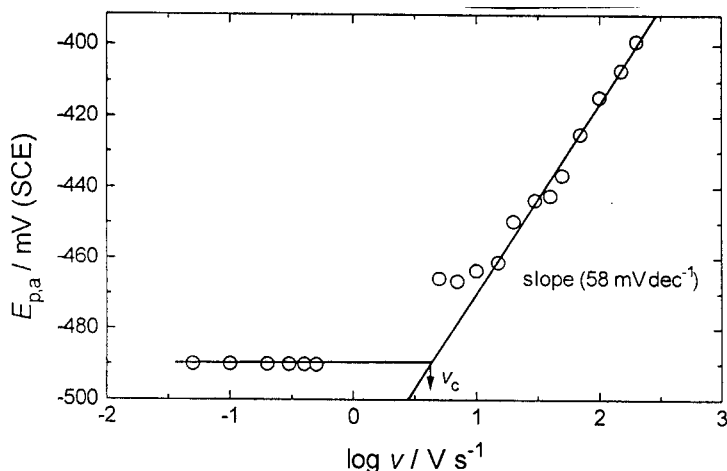


Fig. 8. Dependence of the anodic peak potential ( $E_{p,a}$ ) as a function of the logarithm of the sweep rate ( $\log v$ ), obtained by analysis of the voltammograms presented in Fig. 7.

ions)<sup>23</sup> amounts to  $223 \mu\text{C cm}^{-2}$ . The values of the interaction parameter  $f = 16.5$  and the Gibbs energy of adsorption (for  $\theta \rightarrow 0$ ),  $\Delta G_{\text{ads}, \theta \rightarrow 0}^{\circ} = -64 \text{ kJ mol}^{-1}$ , obtained by the fitting procedure, confirm the existence of an adsorbed structure with high repulsive forces between the adsorbed species. Hence, the process of sulphate anion adsorption also follows a Frumkin adsorption isotherm.

In accordance with our previous results obtained for the adsorption of chloride anions on the (111) face of silver,<sup>11</sup> a possible reaction mechanism will be analyzed.

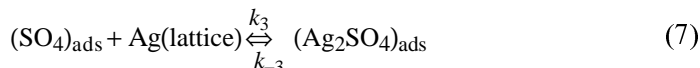
It can be seen from Figs. 1–3 that the examined range of potentials lies between the potential of zero charge for Ag(111) in sulphate containing solution and the reversible potential of the formation of  $\text{Ag}_2\text{SO}_4$  (0.40 V (SCE)).<sup>29</sup> In such a case it is reasonable to expect contact (*i.e.*, specific) adsorption of sulphate anions, a two electrons charge transfer reaction and also, most probably, the formation of an adsorbed  $\text{Ag}_2\text{SO}_4$  layer.

This can also be confirmed by the shape of the voltammograms recorded at more positive potentials (Fig. 1b). Such a behaviour indicates that, most probably, the adsorbed structure does not undergo a phase transformation process, since the solubility of  $\text{Ag}_2\text{SO}_4$ , being 0.57 g/100 ml is about four orders of magnitude higher than that of  $\text{AgCl}$  ( $8.9 \times 10^{-5}$  g/100 ml).

As in the cases of chloride<sup>11</sup> and acetate<sup>19</sup> adsorption, the value of the apparent transfer coefficient can be determined from the slope of the  $E_{p,a} - \log v$  dependence. As it is shown in Fig. 8, this slope amounts to  $58 \text{ mV dec}^{-1}$ , indicating a value of  $\alpha_a = 1$ .

In such a case the following reaction mechanism can be postulated





Assuming that reaction (6) is a rate-determining step and taking into account that the adsorption follows a Frumkin adsorption isotherm, the anodic current density will be

$$j_a = zFk_2\theta_1 \exp\left[\frac{\Delta G_{\theta \rightarrow 0}^{\neq} - (1-\gamma)r\theta_1 - (1-\beta)FE}{RT}\right] \quad (8)$$

where  $\theta_1$  is the coverage of the electrode surface with the  $(\text{SO}_4^-)_{\text{ads}}$  species,  $\beta$  is the symmetry factor and  $\gamma$  its equivalent for the chemical energy change effect.

If reaction (6) is in pseudo-equilibrium the coverage  $\theta_1$ , if  $0.2 < \theta_1 < 0.8$ , may be taken to be a linear function of potential<sup>28</sup> in a way given by the following equation

$$r\theta_1 = FE + C_1 \quad (9)$$

Replacing (9) in (8) one obtains

$$j_a = k_2 \exp\left[\frac{(2-\gamma-\beta)FE}{RT}\right] \quad (10)$$

Assuming<sup>27</sup> that  $\gamma = \beta = 0.5$ , it follows that  $\alpha_a = 2 - \gamma - \beta = 1$ , which corresponds to a slope of  $60 \text{ mV dec}^{-1}$ .

Hence, the process of electroadsorption of sulphate anions on the (111) face of silver is controlled, most probably, by the electrochemical reaction of the formation of  $(\text{SO}_4)_{\text{ads}}$  species (*i.e.*, reaction (6) is the rate-determining step), while in the overall reaction complete charge transfer between the adsorbed sulphate anions and the silver substrate occurs.

Cyclic voltammogram in the positive potential domain shows the continuous increase of the anodic current (*cf.* Fig. 1b) opposite to the case of chloride solution, where the crystallization loop was observed.<sup>10,11</sup> This can be explained by much higher solubilities of  $\text{Ag}_2\text{SO}_4$  as compared to the sparingly soluble  $\text{AgCl}$ . On the other hand the lack of crystallization peaks probably is the consequence of the impossibility of monolayer formation of 2D crystal lattice. Namely,  $\text{Ag}_2\text{SO}_4$  forms the orthorhombic crystals with 16 Ag ions and 8  $\text{SO}_4$  groups in an elementary cell so that the prerequisite for the formation of 2D crystal that each particle can form the adsorption bond to the surface cannot be fulfilled.

## CONCLUSIONS

It can be concluded from the presented results that the process of sulphate anions adsorption follows Frumkin adsorption isotherm, that the adsorbed structure

is less dense than a monolayer and is characterized by high Gibbs energy of adsorption and high repulsive forces between the adsorbed particles.

A complete charge transfer between the sulphate anions and the silver substrate takes place.

At sweep rates higher than several volts per second, the electrosorption process becomes activation controlled with the transfer coefficient  $\alpha_a \approx 1$ . A reasonable assumption which satisfy the observed kinetic criteria is that the electrosorption process occurs through three steps. The rate-determining step is most probably the electrochemical reaction of the formation of  $(\text{SO}_4)_{\text{ads}}$  species.

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### ИЗВОД

#### МЕХАНИЗАМ И КИНЕТИКА ЕЛЕКТРОСОРПЦИЈЕ СУЛФАТНИХ АНЈОНА НА (111) ПЉОСНИ СРЕБРА

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Проучаван је процес адсорпције сулфатних анјона на (111) пљосни монокристала сребра методама цикличне волтаметрије и потенциостатских пулсева. На основу експериментално одређених  $\theta$ - $E$  зависности показано је да се на адсорпцију може применити Фрумкинова адсорпциона изотерма. Нађено је да је густина адсорбованог слоја мања него када би слој био максимално могуће густо пакован као и да адсорпцију карактеришу високе вредности Фрумкиновог параметра интеракције ( $f=16,5$ ) и Гибсове енергије адсорпције ( $\Delta G_{\text{ads},\theta \rightarrow 0}^{\circ} = -64 \text{ kJ mol}^{-1}$ ). На основу нагиба зависности  $E_{\text{p,a}} - \log(c_0)$  закључено је да се при електросорпцији одиграва и потпуна измена набоја анјона са супстратом. Овај закључак подржава добијена линеарна зависност  $E_{\text{p,a}} - \log v$  у области великих брзина промене потенцијала ( $v > 10 \text{ V s}^{-1}$ ) са рационалном вредношћу нагиба ( $\approx 60 \text{ mV dek}^{-1}$ ), а која се може добити само при одигравању потпуне размене набоја. Утврђено је да је електросорпција сулфатних анјона сложена електрохемијска реакција која се одиграва у три ступња. Ступањ који одређује брзину укупне реакције је други ступањ, електрохемијско стварање интермеђијера  $(\text{SO}_4)_{\text{ads}}$ .

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