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# Voltammetric study of the underpotential deposition of Bi on polycrystalline Pt electrode in acidic Bi<sup>3+</sup> sulphate solutions

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The underpotential deposition (UPD) of bismuth on a smooth polycrystalline platinum electrode was studied in Bi<sup>3+</sup> solution in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 20 °C by means of cyclic voltammetry. The bismuth UPD and stripping processes were examined depending on a bismuth bulk concentration, potential (*E*) sweep window, scan rate and application of successive *E* sweeps. It was demonstrated that the stabilized potentiodynamic *i/E* profiles were similar to those recorded earlier for Bi<sup>3+</sup> perchlorate solutions. At the same time, certain differences related mainly to the features of the reduction of surface platinum oxide in solutions of different types in the presence of Bi<sup>3+</sup> were also considered. An analysis of the charge density flow observed for the stabilized voltammetric curves was made using the Clavilier et al. supposition as to the nature of charge transfer at underpotentials.

**Key words:** bismuth, underpotential deposition, platinum electrode, sulphate solutions

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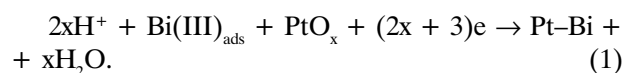
## INTRODUCTION

Underpotential deposition (UPD) of metal (M) ions on a foreign metal substrate (S) has been studied extensively over the recent decades. Monolayer- or submonolayer- modified electrodes obtained by UPD are of great importance since they can give wide changes in the electronic and electrocatalytic properties of a metal surface. UPD can also aid in the understanding of primary steps in a metal crystallite growth. Investigations of UPD phenomena up to 1978 are summarized by Kolb [1], and more recent studies are those by Budevski, Staikov and Lorenz [2].

Bismuth adlayers deposited underpotentially on Pt have received much attention [3–33], mainly in view of their prospects for an electrocatalysis [7, 19–33]. The studies on the Bi UPD have been made in two basic directions. The first direction has covered investigations of Bi redox processes taking place on an initially bare Pt electrode in a solution containing Bi(III) species in the circumstances when the external current (*i*) or potential (*E*) is applied [3–11, 16–18]. The second direction has been associated with the electrochemical behaviour of Bi(III) species irreversibly adsorbed on Pt at open-circuit potential (OCP) [12–14, 17, 18] and also with an investigation of localization of Bi adatoms on the

surface of Pt electrode of different orientation [3, 5, 8–10, 12–15, 18].

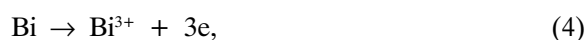
In their electrochemical investigations of the Bi redox process at underpotentials (*E*<sub>UPD</sub>) on Pt, Cadle and Bruckenstein [5] showed that the beginning of Bi(III) reduction corresponds rather exactly with the surface platinum oxide reduction, and they supposed that the initial reduction of adsorbed Bi(III) species might occur simultaneously with the platinum oxide reduction in one concerted step:



A two-step mechanism of the formation of adsorbed Bi layer at less positive *E*<sub>UPD</sub> was proposed by Szabo and Nagy [8]. The first step was a bulk deposition of Bi with simultaneous ionization of adsorbed hydrogen:



and the second one was the formation of Bi adlayer with simultaneous ionization of an equivalent of bulk Bi (it was also proposed that bulk Bi can be transformed into adsorbed Bi only in the presence of Bi<sup>3+</sup> in solution):



Later, taking into account the known fact that a Pt electrode surface as a consequence of its exposition to a Bi(III) solution gets covered spontaneously with adsorbed Bi(III) species [3, 5], Clavilier et al. [12] suggested that the formation of the Bi adlayer could be a result of the PtOH formation at  $E$  lower than the beginning of the Bi UPD. Such a mechanism combining  $-\text{OH}$  formation with Bi(III) species adsorption at a lower oxidation degree was proposed to lead to a simultaneous accumulation of both oxygenated bismuth and bismuth(0) species at a Pt(hkl) surface. These species at a Pt(111) surface could be of the following types: (i)  $(\text{BiO})_{\text{ads}}$  or  $[\text{Bi}(\text{OH})_2]_{\text{ads}}$  as a stable adsorbate formed spontaneously; (ii)  $(\text{BiOH})_{\text{ads}}$  which is a less oxidized intermediate formed during the adsorbate redox process; (iii)  $\text{Bi}_{\text{ads}}$ , as a species blocking the hydrogen adsorption sites, formed in the region of lower  $E$  values. Therefore, a two-electron mechanism was suggested to be related to the following reversible valency change on a Pt(111) surface [12]:



Interestingly, Clavilier et al. [12] also suggested that the redox process of the adsorbed Bi species

can be a good evidence for a detection of the (111) domains on Pt surface.

Recently, in full agreement with the study [12], Kolb et al. [18] also found that bismuth was not desorbed oxidatively on the subsequent anodic scan and t remained on a Pt(111) surface even during cycling in a Bi(III)-free perchloric acid solution. At the same time, from electrochemical and UHV measurements, in contrast to the study [12], it was inferred that the adsorbed Bi remained in its zero-valent state over the entire  $E$  range (+0.7 to +0.4 V (SHE)). The charge flow during the  $E$  perturbation was assumed to be attributed to a  $\text{OH}^-$  adsorption on the Bi-covered Pt(111) surface rather than to a change in a valence state of the adsorbed Bi species.

So, the mechanism of the Bi UPD onto a Pt electrode is explained differently so far.

Reviewing the studies of the second direction, it should be noted that much effort has been expanded on the investigation of the arrangement of Bi adatoms on the Pt electrode surface depending on coverage and a Pt single-crystal orientation [3, 5, 8–10, 12–15, 17, 18]. In particular, it has been established that a number of Pt surface sites occupied by a Bi adatom ( $S$ ) is very sensitive to the Bi adatom localization on Pt surface, which in its turn is governed mainly by Pt orientation (Table). In most cases, investigations of the further electrochemical behaviour of Bi(III) species adsorbed irreversibly at

Table 1. Experimental values of the number of platinum surface sites occupied by a bismuth adatom (from the H UPD measurements)

Electrode	Electrolyte		Conditions of Bi adsorption	$S$	Refs.
	H UPD measurement	Formation of Bi adlayer			
pc Pt	$\text{Bi}^{3+}$ in HCl and $\text{HClO}_4$	$\text{Bi}^{3+}$ in HCl and $\text{HClO}_4$	Electrochemical (LSV)	2	[3]
pc Pt	$\text{Bi}^{3+}$ in $\text{HClO}_4$	$\text{Bi}^{3+}$ in $\text{HClO}_4$	– “–	at $\theta_{\text{Bi}} < 0.3$ 2; at $\theta_{\text{Bi}} > 0.3$ > 2	[5]
Pt-Pt	– “–	– “–	– “–	2	[8]
pc Pt	$\text{Bi}^{3+}$ in $\text{H}_2\text{SO}_4$	$\text{Bi}^{3+}$ in $\text{H}_2\text{SO}_4$	Electrochemical (LSV, potential step)	3	[9]
pc Pt	$\text{Bi}^{3+}$ in $\text{HClO}_4$	$\text{Bi}^{3+}$ in $\text{HClO}_4$	Electrochemical (LSV)	3	[10]
Pt(100)	$\text{H}_2\text{SO}_4$	– “–	Immersion (without applying external potential)	2	[11–13]
Pt(111)	– “–	$\text{Bi}(\text{NO}_3)_3(\text{aq})$	– “–	3	[14]
Pt(111)	– “–	$\text{Bi}^{3+}$ in $\text{H}_2\text{SO}_4$	– “–	3	[15]
Pt(111)	– “–	$\text{Bi}^{3+}$ in $\text{HClO}_4$	– “–	3	[11]

OCP have been carried out to characterize the Bi-modified Pt electrode [19–33].

Studies on the Bi UPD on Pt have been conducted mainly in Bi(III) solutions in HCl and HClO<sub>4</sub>. An exception is the studies carried out by Furuya and Motoo [9], who determined the parameter *S* in sulphate solution, and by Adžić and Marković [11], who examined an adsorption of Bi(III) species on oxidized Pt in 1·10<sup>-3</sup> M Bi<sup>3+</sup> solution in 0.05 M H<sub>2</sub>SO<sub>4</sub>.

The present paper deals with the Bi UPD in the Bi<sup>3+</sup> solution in 0.5 M H<sub>2</sub>SO<sub>4</sub> onto a smooth polycrystalline (pc) Pt electrode followed by cyclic voltammetry.

## EXPERIMENTAL

0.01–0.9 mM Bi<sup>3+</sup> solution in 0.5 M H<sub>2</sub>SO<sub>4</sub> was used in our experiments. Bi<sup>3+</sup> ion exhibits a tendency toward hydrolysis, but it is believed that in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution this ion does not hydrolyze, as noted in [34]. The working solution (WS) was obtained by addition of an appropriate volume of a stock solution of 1 mM Bi<sup>3+</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> to a supporting electrolyte of 0.5 M H<sub>2</sub>SO<sub>4</sub>. The stock solution was prepared by dissolution of Bi(OH)<sub>3</sub> in a hot 5 M H<sub>2</sub>SO<sub>4</sub> solution during 2 h followed by cooling to ambient temperature and proper dilution. The highest purity H<sub>2</sub>SO<sub>4</sub>, analytical pure Bi(OH)<sub>3</sub> (both from Russia) and triply distilled water were used for preparation of the WS. Prior to each experiment the WS was deaerated with argon.

All experiments were performed at 20 ± 0.1 °C in a JASE-2 three-electrode thermostated electrochemical cell (made in Belarus). The working electrode (WE) was a vertical disc made from a mat pc Pt foil (99.99% purity) and sealed into a soft glass tube. The geometric area of the WE was 1 cm<sup>2</sup>. The real electrode surface area was determined electrochemically from the hydrogen adsorption voltammetric profile (see below, Fig. 1, curve 1) at 50 mV s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, taking the theoretical hydrogen adsorption charge of 210 μC cm<sup>-2</sup>, as noted in [35, 36]. The roughness factor (*f*) was found to be equal to 3.3 ± 0.1. The counter electrode was a Pt sheet of ca. 6 cm<sup>2</sup> in area. The reference electrode was a Ag/AgCl/KCl(sat.) electrode placed in an expanded part of a Luggin capillary. All potentials in the text are referred to the SHE scale. Unless otherwise noted, all currents and charges are reported on the basis of the geometric area.

To ensure cleanliness of the surface of the WE and to achieve a good reproducibility of electrochemical data, the electrode was subjected to a pretre-

atment as follows: (i) a slight mechanical polishing with diamond paste down to 0.1 μm; (ii) an immersion in chromic acid for 4 h at ambient temperature followed by an immersion in 0.5 M H<sub>2</sub>SO<sub>4</sub> for 24 h and thorough rinsing in doubly distilled water; (iii) an electrochemical activation by a repetitive triangular cycling between  $E_{s,c} = +0.05$  and  $E_{s,a} = +1.30$  V in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 50 mV s<sup>-1</sup> for 15 h (the volume of solution was changed several times); (iv) prior each experiment, an immersion in chromic acid for 10 min followed by an immersion in the 0.5 M H<sub>2</sub>SO<sub>4</sub> solution for 0.5 h and an electrochemical activation through a repetitive *E* cycling in the 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 50 mV s<sup>-1</sup> from the initial potential  $E_i \approx +0.80$  V between  $E_{s,c} = +0.05$  and  $E_{s,a} = +1.30$  V with the first negative-going scan (the potential scan was stopped during the cathodic half-cycle at +0.4 V); (v) without rinsing, a transfer of electrode, the surface of which was protected by a drop of electrolyte, to the other JASE-2 electrochemical cell with the WS; (vi) after contacting the WE with solution and waiting for 5 min at OCP the electrode was polarized first anodically up to  $E_{s,a} = +1.30$  V, and then a reverse scan was applied.

The quality of pretreatment of the WE was checked by a comparison of a cyclic voltammogram (CV) obtained at 50 mV s<sup>-1</sup> in the supporting electrolyte of 0.5 M H<sub>2</sub>SO<sub>4</sub> (Fig. 1, curve 1) with CV presented in [35, 36] and claimed to be typical of a clean pc Pt electrode. In addition, the  $Q_{H,a}/Q_{H,c}$  ratio was found to be about unity, the  $i_{pa,2}/i_{pa,1}$  and  $i_{pc,2}/i_{pc,1}$  ratios to 0.9 and 0.7, respectively, indicating that the WE was properly prepared ( $Q_{H,c}$  and  $Q_{H,a}$  are the H adsorption and ionization charges,  $i_{pa,1}$ ,  $i_{pa,2}$ ,  $i_{pc,1}$  and  $i_{pc,2}$  the anodic and cathodic current peaks, respectively).

The cyclic voltammetry (CV) was performed using a PI 50-1 potentiostat, a PR-8 programmer and an LKD-003 X–Y recorder (all made in Belarus). The CV curves were recorded after a steady-state shape of curves was obtained in the quiescent WS. In separate experiments, the effect of repetitive cycling was also monitored. Unless otherwise stated, the WE was allowed to stand at OCP for 3 min, and afterwards the *E* cycling started from OCP ≈ +0.80 ± 0.02 V in the negative direction. Between runs the cell and accessory components were cleaned with warm concentrated H<sub>2</sub>SO<sub>4</sub>, rinsed repetitively with doubly distilled water and left in it overnight.

In the present work, the Nernstian potential for a Bi/Bi<sup>3+</sup> couple was not calculated. The commencement of visible bulk Bi deposition was evaluated here from a voltammetric curve *i/E* recorded with a

Bi electrode and also from a comparison with the data presented in [37].

**RESULTS**

Figure 1 shows the effect of  $\text{Bi}^{3+}$   $c$  on a stabilized CV at  $50 \text{ mV s}^{-1}$ . As can be seen, the pairs of current peaks  $c1/a1$  and  $c2/a2$  attributed to the hydrogen UPD/ionization processes [5] become continuously suppressed with increasing the  $c$  of  $\text{Bi}^{3+}$ . Similar results have already been reported for perchlorate and chloride solutions [3–5, 7–9, 12–17]. It can be easily shown that the displacement of the adsorbed H by Bi adatoms represented arbitrarily as the  $Q_{\text{H,c}}$  plotted vs.  $c$  of  $\text{Bi}^{3+}$  will be linear, as might be expected from the data reported by Cadle and Bruckenstein [5]. The height of cathodic current peak  $c3$  ( $i_{\text{pc}3}$ ) is sensitive to the presence of  $\text{Bi}^{3+}$ , also in agreement with the observations in the solutions of another composition [5, 7]. However, unlike perchlorate solutions where an increase in  $i_{\text{pc}3}$  alone in the presence of  $\text{Bi}^{3+}$  has been reported [5, 7], the relationship between  $i_{\text{pc}3}$  and the bulk  $c$  of  $\text{Bi}^{3+}$  is non-linear for the present system. The slope  $\delta \log i_{\text{pc}3} / \delta \log c$  was found to be equal to  $ca. 0.15$  over the whole range of  $c$  of  $\text{Bi}^{3+}$ . The position of this peak was found to be independent of the  $c$  of  $\text{Bi}^{3+}$ . This feature differs from that reported earlier [5], where the negative shift of the peak potential has been revealed after addition of  $\text{Bi}^{3+}$ .

With increasing the  $c$  of  $\text{Bi}^{3+}$  the height of cathodic current peak denoted as  $c4$  increases linearly with a slope of  $\delta \log i_{\text{pc}4} / \delta \log c = 1.1 \pm 0.05$  and its

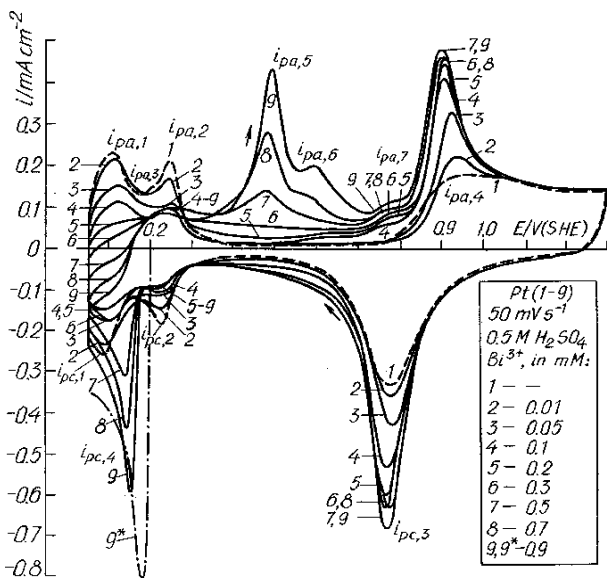


Fig. 1. Stabilized cyclic voltammograms for pc Pt (I–9) and a Bi (9\*) electrodes at  $50 \text{ mV s}^{-1}$  in  $0.5 \text{ M H}_2\text{SO}_4$  solution without or with  $\text{Bi}^{3+}$ . Potential scan range  $+1.30 \dots +0.05 \text{ V}$

position shifts positively by  $\delta E_{\text{pc}4} / \delta \log c \approx 0.070 \text{ V dec}^{-1}$  (Fig. 1), indicating that this peak is most likely attributable to the bulk Bi deposition.

On the reverse scan, the  $i/E$  profile recorded at  $50 \text{ mV s}^{-1}$  between  $E_{\text{s,c}} = +0.050 \text{ V}$  and  $E_{\text{s,a}} = +1.30 \text{ V}$ , consists of at least four anodic current peaks: the well-defined peak a4 with the peak potential shifting slightly negatively from  $+0.93$  to  $+0.89 \text{ V}$  with increasing  $c$  of  $\text{Bi}^{3+}$  from  $0.01$  to  $0.9 \text{ mM}$ , another well-defined peak a5 at  $ca. +0.48 \text{ V}$ , peaks a6 and a7 appearing as shoulders at  $ca. +0.58 \text{ V}$  and  $ca. +0.74 \text{ V}$  (Fig. 1). A comparison of CVs recorded in the presence of  $\text{Bi}^{3+}$  with the CV in the supporting electrolyte indicates that the emergence of the anodic current peak a4 (more strictly, its increase), a5, a6 and a7 should be related with the oxidation of Bi-containing species adsorbed at the pc Pt electrode at  $E_{\text{UPD}}$ .

In general, the  $i/E$  profiles recorded here (Fig. 1) are rather similar to those presented earlier for a Pt electrode in perchlorate solutions [4, 5]. Again, the features of anodic stripping of Bi-covered Pt electrode in the region of current peak a4 appear to be also in agreement with previous results [4, 5, 7, 12, 16].

When  $E$  was cycled between the same limits but at a lower scan rate, *e.g.* at  $2 \text{ mV s}^{-1}$ , the stabilized quasi-stationary  $i/E$  curves somewhat changed (Fig. 2). Firstly, a new cathodic peak in a form of hump becomes revealed in the  $E$  region of  $ca. +0.65$  to  $+0.75 \text{ V}$ . The height of this peak increases gradually with  $c$  of  $\text{Bi}^{3+}$ . Secondly, the reverse scan gave rise to a sharp anodic current peak at  $ca. +0.20 \text{ V}$ , which was not observed at  $50 \text{ mV s}^{-1}$ . Referring to the study of oxidation of a multilayer Bi(0)

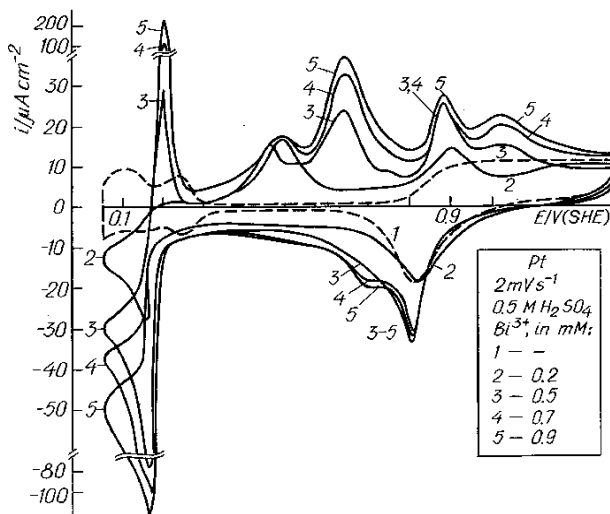


Fig. 2. Stabilized cyclic voltammograms for pc Pt electrode at  $2 \text{ mV s}^{-1}$  in  $0.5 \text{ M H}_2\text{SO}_4$  solution without or with  $\text{Bi}^{3+}$ . Potential scan range  $+1.30 \dots +0.05 \text{ V}$

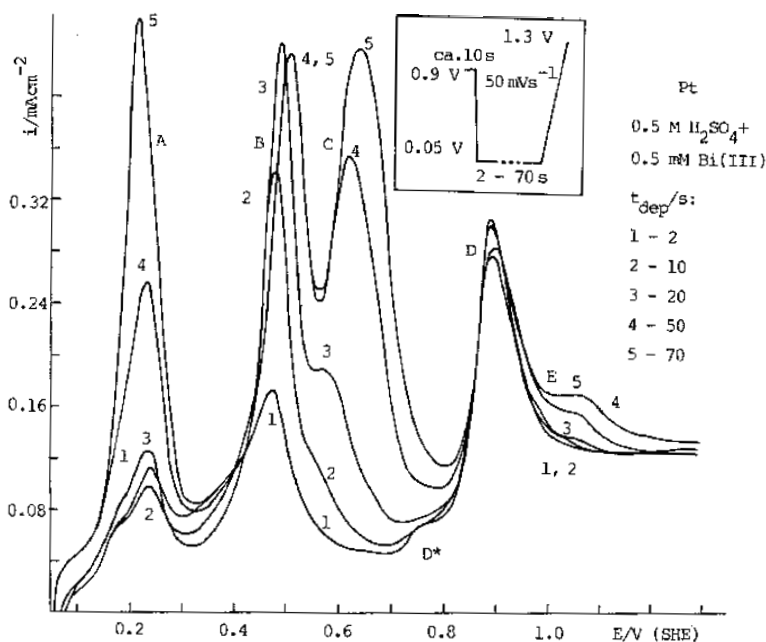


Fig. 3. Anodic voltammograms recorded at  $50 \text{ mV s}^{-1}$  after potentiostatic deposition of bismuth(0) multilayer on a pc Pt electrode at  $+0.050 \text{ V}$  for various time ( $t_{\text{dep}}$ ) in  $0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ mM Bi}^{3+}$  solution. The inset shows the variation of the electrode potential with time

film in a perchlorate solution [5], it seems that this peak, in the case of sulphate solution, is also caused by the oxidation of the bulk Bi deposit. This suggestion can be confirmed by the anodic  $i/E$  curves recorded for the Pt electrode kept at  $+0.05 \text{ V}$  for various time ( $t_{\text{dep}}$ ) before subsequent scanning anodically to strip a Bi(0) multilayer (Fig. 3). The general shape of the stripping curves obtained here is rather close to that reported previously for perchlorate solution [5]. The Bi(0) multilayer is oxidized in at least five distinct  $E$  regions, viz. the formation of anodic peaks denoted as A, B, C, D and E is observed (Fig. 3). The height of peak A continues to increase with  $t_{\text{dep}}$ , i.e. with a charge consumed to deposit a Bi layer, in the same manner as for perchlorate solution [5]. However, while the peak A was found to be the only peak increasing continuously with  $t_{\text{dep}}$  in the latter solution [5], in our case, a distinct  $t_{\text{dep}}$ -dependence of peak height was established for the peaks C and E as well. The peak B was found to depend on  $t_{\text{dep}}$  only in the range of short  $t_{\text{dep}}$ . The peak D was almost independent of this variable and had previously been identified as being associated with the oxidation of both Pt and Bi(0) adlayer deposited underpotentially [5].

From Figs. 1 and 3 it follows that there is a relatively good correlation between the following pairs of the anodic peak potentials:  $E_{\text{pa5}}$  and  $E_{\text{B}}$ ,  $E_{\text{pa6}}$  and  $E_{\text{C}}$ ,  $E_{\text{pa4}}$  and  $E_{\text{D}}$ ,  $E_{\text{pa7}}$  and  $E_{\text{D}^*}$  (at deposition times not exceeding 10 s). It is interesting to note that the peak E (Fig. 3) seems to have no corres-

ponding peak on the stabilized CV (cf. Fig. 1, curve 7). A certain dissimilarity in the peak heights at the same magnitude of  $v$ , specifically for the peaks a4 and D, may be caused by the different conditions of experiment governing the deposition of Bi(0) multilayer and Bi(0) monolayer. On the other hand, there is a certain correlation between the peak E (Fig. 3) and the anodic current peak at ca.  $+1.00 \text{ V}$  on the stabilized CV recorded at  $2 \text{ mV s}^{-1}$  (Fig. 2, curve 3). However, in the light of experimental data obtained here and available in the literature, a reasonable explanation of some differences in the  $i/E$  profiles discussed above still presents difficulties.

From the repetitive CVs it follows that the general shape of  $i/E$  curves is not affected strongly by the number of successive scans (Fig. 4). In particular, Fig. 4a shows that, in the case of low  $c$  of  $\text{Bi}^{3+}$ , e.g. at  $0.01 \text{ mM}$ , with increasing  $n$ , the complementary peaks

in the "hydrogen" region and the peaks c3 and a4 become more distinct. On the other hand, the charge obtained by integrating the voltammetric waves

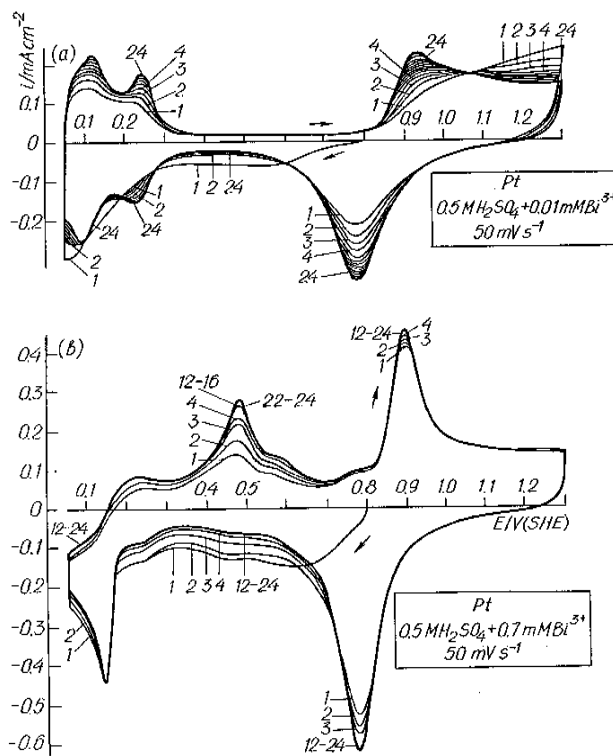


Fig. 4. Repetitive cyclic voltammograms for pc Pt electrode in  $0.5 \text{ M H}_2\text{SO}_4$  solution containing  $0.01$  (a) or  $0.7$  (b)  $\text{mM Bi}^{3+}$  at  $50 \text{ mV s}^{-1}$ . Number at curve denotes the number of scan

in the “hydrogen” region was found to be almost independent of  $n$ , viz. after the 24th scan the quantity  $Q_{H,c}$  became smaller only by 5%. This implies that only an insignificant change in a Bi coverage occurs during such a potentiodynamic “ageing”. In the case of 0.7 mM  $\text{Bi}^{3+}$  solution, the effect of successive scans is more prominent in the  $E$  ranges wherein the anodic current peaks a5 and a6 exhibit themselves and also between the peaks c3 and c4, as shown in Fig. 4b. Note that the latter peak was found to be quite insensitive to increasing  $n$ .

Figure 5 illustrates the  $\nu$ -dependences of the height and position of peaks c3 and a4 for the Pt WE in 0.5 M  $\text{H}_2\text{SO}_4$  solution without or with 0.2 mM  $\text{Bi}^{3+}$ . As can be seen, the linear relationships between  $\log i_p$  and  $\log \nu$  with a slope of 0.93 (Fig. 5a), and between  $E_p$  and  $\log \nu$  with slopes 0.023–

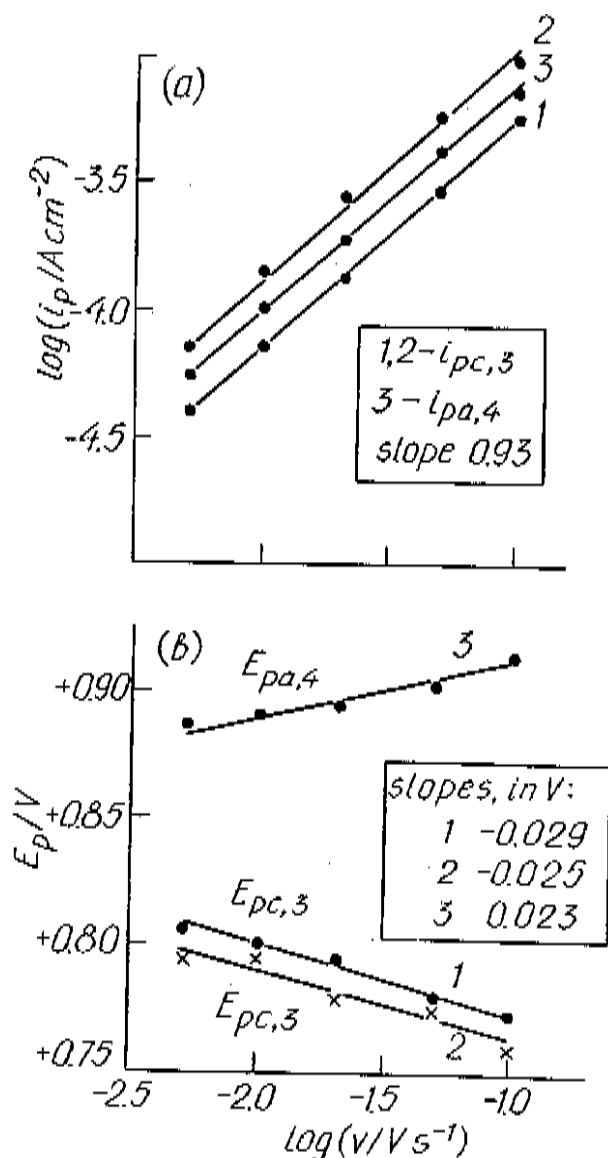


Fig. 5. Plots of  $\log i_p$  vs.  $\log \nu$  (a) and of  $E_p$  vs.  $\log \nu$  (b) for pc Pt electrode in 0.5 M  $\text{H}_2\text{SO}_4$  solution without (1) or with 0.2 mM  $\text{Bi}^{3+}$  (2, 3). Peaks: c3 – 1, 2, a4 – 3.

0.029 V decade $^{-1}$  (Fig. 5b) are preserved in either case. The quantity of  $\delta \log i_p / \delta \log \nu$  for both current peaks was found to be quite close to unity, as predicted by theory for surface reduction [38, 39], and also to be almost independent of  $\text{Bi}^{3+}$ . The quantity of  $\delta E_{pc3} / \delta \log \nu$  was shown to be only slightly dependent on the presence of these metal ions.

## DISCUSSION

It is well known that UPD processes involve three different kinds of interaction emerging between respective elements taking place in these processes. The first interaction emerges between the surface of a substrate (S) and a UPD atom, the second one between a UPD atom and an anion in a supporting electrolyte, and the third one between an anion and the surface of S. Therefore, it seems reasonable to consider the inferred effect of adsorbed anion on the Bi UPD. The adsorption of sulphate (in a general sense,  $\text{SO}_4^{2-}$  or  $\text{HSO}_4^-$ ) species on Pt in metal ion-free acidic solution has been investigated intensively in recent years [40–65]. Our attempts to summarize the findings of these experiments are presented in Appendix (see below). As this very brief review shows,  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  are adsorbed specifically onto Pt surface and this adsorption is governed both by the  $E$  window and by the structural characteristics of the Pt surface. It should be also noted that, as far as we know, rather little attention has been paid to the formation of Bi and (bi)sulphate coadsorbate structures onto a Pt surface. Thus, the presence of Bi adatoms in advance adsorbed irreversibly on the Pt(111) electrode surface (e.g. due to immersion in the absence of external voltage in Bi(III) solution) was found to lead, at  $E$  scan, to a diminution of the total charge involved in the electrosorption of hydrogen and sulphate species [12, 15, 17]. To our knowledge, no similar study has been undertaken for a pc Pt electrode. Moreover, it is worth noting that no specific adsorption of  $\text{SO}_4^{2-}$  anion has been established on a bulk Bi [66]. Therefore, in the light of these results, one might reasonably expect that, under conditions of our experiment, any complication in the Bi UPD due to a coadsorption of Bi and (bi)sulphate species onto Pt would be insignificant, especially at higher values of  $\theta_{\text{Bi}}$ .

Although the  $i/E$  profiles recorded here are principally similar to those for perchlorate solutions, there are also some differences in the voltammetry of the Bi UPD onto a pc Pt electrode in solutions of both types.

(i) Firstly, it was shown that the peak potential  $E_{pc3}$  shifted with pH by 70 mV per pH unit for a Bi-covered Pt(hkl) electrode in  $\text{H}_2\text{SO}_4$  solution [12]

and by 74 mV per pH unit for a Bi-covered Pt(111) electrode in HClO<sub>4</sub> solution [18]. These values are not very far from 60 mV per pH unit for a one-electron controlling process. Because of this Kolb et al. [18] suggested that the specific adsorption of OH<sup>-</sup> may play a dominant role in the electrochemical behaviour of Bi-covered Pt electrode and also related the charge flow during an *E* cycling between +0.70 and +0.40 V (SHE) to OH<sup>-</sup> adsorption/desorption rather than to a Bi/Bi<sup>2+</sup> surface redox couple.

The character of the  $i_{pc,3}$  vs. bulk *c* of Bi<sup>3+</sup> plot mentioned above, which shows a certain “saturation” with bismuth, is most likely associated with only partial removal of bismuth deposited at underpotentials during the preceding stage of oxidation and hence with the Pt surface being never entirely free of Bi when a repetitive cycling is applied, as suggested earlier in [5, 12] and recently in [18]. The “Tafel approximation” for the peak c3 (Fig. 5b) yielded a slope of 0.029 V decade<sup>-1</sup> in a pure 0.5 M H<sub>2</sub>SO<sub>4</sub> solution being in good agreement with the data in [66]. As already noted, this parameter remained actually unchanged in the presence of Bi<sup>3+</sup> (curve 2). The analogous *v*-dependence of  $E_{pa,4}$  yields 0.023 V decade<sup>-1</sup> in the presence of 0.2 mM Bi<sup>3+</sup> (Fig. 5b, curve 3). This quantity is rather close to a value of 0.021 V dec<sup>-1</sup> [66] for pure 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

As this consideration suggests, a certain parallelism of the Pt surface oxide reduction and the Bi adlayer formation due to a reduction of Bi(III) species adsorbed onto Pt at *E* more positive than  $E_{pc,3}$  is adopted as a reasonable mechanism of the Bi UPD at *E* > ca. +0.70 V.

(ii) The second difference is also connected with the current peak c3. As was reported earlier [5], after addition of Bi<sup>3+</sup> to a perchlorate solution,  $E_{pc,3}$  shifted in the negative direction. In contrast, it will be recalled that the  $E_{pc,3}$  and also the slope of  $E_{pc,3}$  vs. log *v* plot were shown here to be actually insensitive to the presence of Bi<sup>3+</sup> in the sulphate solution.

(iii) Finally, the ability of resolution of the new cathodic peak extending from +0.75 to nearly +0.65 V with the height increasing gradually with *c* of Bi<sup>3+</sup> at a lower scan rate (Fig. 2) may be named as the third difference. As mentioned above, this current peak was difficult to be resolved at a higher *v* in sulphate solution and was not detected in the event of perchlorate solution.

For the most part, the data obtained here and discussed in the comments (i)–(iii) are in line with the supposition of Kolb et al. [18]. The nature of species taking place in the charge flow at more negative *E* remains to be elucidated.

As is usual in UPD studies, an estimation of the electroadsorption valency ( $\gamma_{Bi}$ ) for Bi adlayer stripping

in the sulphate solution was carried out using the equation [68]:

$$\Delta E_p = K + (RT/F)(1/\gamma_{Bi} - 1/z) \ln a_{Bi^{3+}} \quad (7)$$

where  $\Delta E_p$  is the underpotential shift, *z* is the valency of complete oxidation of Bi (*z* = 3).  $\Delta E_p$  was evaluated from the  $E_{pa,4}$  (Fig. 1) and the peak potential for peak A (Fig. 3). The results presented in Fig. 6 show that  $\gamma_{Bi} = 1.03$ . This indicates that the Bi oxidation in sulphate solution within the zone of *E* of current peak a4 (Fig. 1) proceeds through the reaction (6), as already suggested by Clavilier et al. for Pt(111) in perchlorate solution [12].

When calculating the amounts of charge (*Q*) involved in the cathodic and anodic processes, it was obtained that the charge density, like the current density (Figs. 1, 2), depended strongly on the value of  $E_{UPD}$  and on the bulk *c* of Bi<sup>3+</sup> (Figs. 7, 8). In order to gain an additional knowledge of the interaction between Pt surface and Bi<sup>3+</sup>, the experimental data on *Q* were preliminarily considered for two *E* cycling intervals of different width.

In the case of extended *E* range used for CV, e.g. +1.15 to +0.3 V (this *E* interval is essentially of the same width as that analyzed in [18]), the charge density flow was evaluated from the stabilized CVs at 50 mV s<sup>-1</sup> and corrected for the blank experiment in 0.5 M H<sub>2</sub>SO<sub>4</sub>. It was obtained that the cathodic accumulated charge ( $Q_{c,accum}$ ) amounted to ca. 0.48 or 0.89 μC at 0.1 or 0.5 mM Bi<sup>3+</sup>, respectively. With regard to *f* ≈ 3.3, the cathodic charge density flow became equal to ca. 0.15 mC cm<sup>-2</sup> or to 0.27 mC cm<sup>-2</sup>, respectively. The corresponding values for the anodic-going scan were obtained to be ca. 0.16 or 0.39 mC cm<sup>-2</sup>, respectively. Hence, an almost balanced charge density flow for the cathodic and anodic scans was observed at the lower bulk *c* of Bi<sup>3+</sup>. However, this balance became unsettled at the higher *c* of Bi<sup>3+</sup>, when  $Q_{a,accum}$  was about 44%

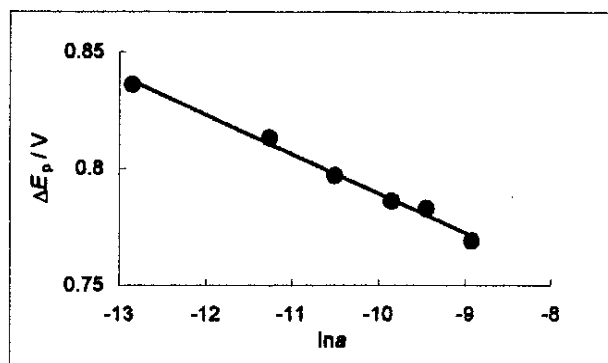


Fig. 6. Dependence of an underpotential shift  $\Delta E_p = E_{pa,4} - E_{p,A}$ , where the peak potential  $E_{pa,4}$  was taken from Fig. 1 and  $E_{p,A}$  from Fig. 3, on the logarithm of the activity of Bi<sup>3+</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution

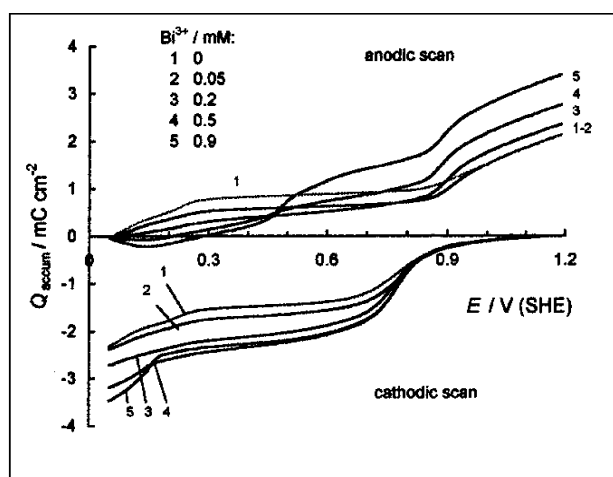


Fig. 7. Variation of the accumulated charge amount  $Q_{\text{accum}}$  consumed during the  $E$  scan at  $50 \text{ mV s}^{-1}$  (from the stabilized CVs) with the potential of the pc Pt electrode and the concentration of  $\text{Bi}^{3+}$  in  $0.5 \text{ M H}_2\text{SO}_4$  solution

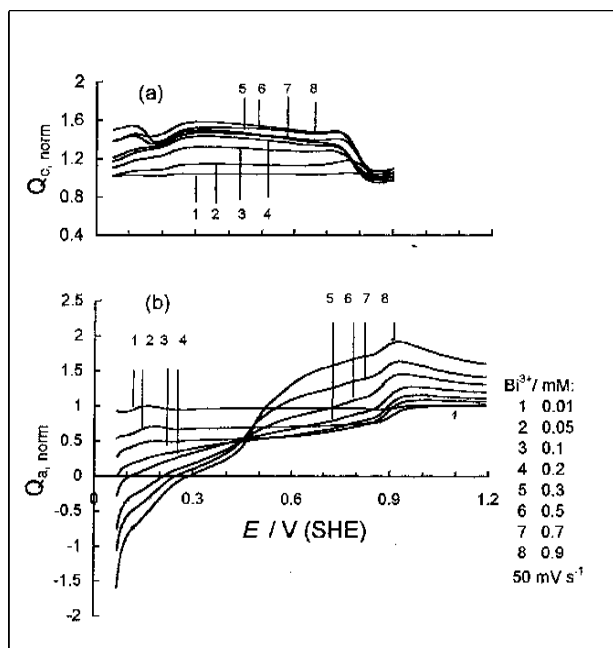


Fig. 8. Variation of the normalized charge amount taken as  $Q_{\text{norm}} = Q_{\text{accum}}^{\text{Bi}} / Q_{\text{accum}}^0$ , where  $Q_{\text{accum}}^{\text{Bi}}$  and  $Q_{\text{accum}}^0$  are accumulated charge amounts during the cathodic (a) or anodic (b)  $E$  scans in  $0.5 \text{ M H}_2\text{SO}_4$  solution with or without  $\text{Bi}^{3+}$ , respectively (from Fig. 7), with the potential of the pc Pt electrode and the concentration of  $\text{Bi}^{3+}$

above  $Q_{\text{c,accum}}$ . At present we have no ready explanation for this phenomenon. Apparently, to draw any reasonable conclusion on this matter, the balance of charges should be studied more systematically.

One more feature to note is the fact that the increase in the charge under the peak c3 due to the presence of  $\text{Bi}^{3+}$  was kept nearly constant with increasing  $c$  of  $\text{Bi}^{3+}$ . It came out to  $70 \pm 5\%$  of the

total  $Q_{\text{c,accum}}$  attributable to the Bi UPD over this  $E$  interval ( $+1.15$  to  $+0.3 \text{ V}$ ), *i.e.* comprised most of the latter quantity. These findings are additionally illustrated by the  $Q_{\text{norm}}$  vs.  $E$  plots (Fig. 8), where  $Q_{\text{norm}} = Q_{\text{accum}}^{\text{Bi}} / Q_{\text{accum}}^0$ , the superscripts 0 and Bi denote the  $Q_{\text{accum}}$  (related to  $1 \text{ cm}^2$  geometrical area of the WE surface) in the absence and in the presence of  $\text{Bi}^{3+}$  in  $0.5 \text{ M H}_2\text{SO}_4$  solution.

In the case of a more narrow  $E$  interval, *e.g.* when the  $E$  cycling was performed between  $+0.80$  and  $+0.30 \text{ V}$ , the cathodic charges were *ca.*  $0.143$  or  $0.277 \text{ mC}$  at  $0.05$  or  $0.5 \text{ mM Bi}^{3+}$ , respectively. The corresponding cathodic charge density flow was obtained to be equal to  $0.043$  or  $0.083 \text{ mC cm}^{-2}$ . The same magnitudes of charge density flows were also calculated for the positive  $E$  scan, *i.e.* the cathodic and anodic charges were balanced, suggesting a high reversibility of the process under the conditions of steady-state run of  $i/E$  profile.

At this point, different assumptions can be made. First, assuming this charge flow to be solely due to the Bi adlayer formation/ionization when three Pt surface sites can be blocked by each Bi adatom, it follows that the charge density of *ca.*  $0.14 \text{ mC cm}^{-2}$  might be expected for the reversible two-electron Bi adlayer formation onto the bare Pt surface, as proposed in [12]. Then, a comparison with the results obtained here shows that, under conditions of our experiment, the experimental charge density comprises *ca.*  $31$  or *ca.*  $60\%$  of the expected value. Similarly, for the possible three-electron process one will obtain *ca.*  $20$  and  $40\%$ . Taking into account that at  $\nu = 50 \text{ mV s}^{-1}$  in either case the formation of Bi adlayer is likely to occur under non-equilibrium conditions, such a difference seems to be quite possible.

Second, the assumption that the observed charge can be associated with the dominant contribution of specific adsorption of anions seems to be less plausible (see, *e. g.*, Appendix and also considerations above).

## CONCLUSIONS

The main features of electrochemical behaviour of a smooth polycrystalline Pt electrode in acidic  $\text{Bi}^{3+}$  sulphate solution at  $E$  positive of reversible  $E$  for the couple  $\text{Bi}/\text{Bi}^{3+}$  was shown to be rather similar to those in perchlorate solutions. On the other hand, there are some dissimilarities associated mainly with the  $E$  range corresponding to the reduction of surface Pt oxide. The presence of a certain amount of adsorbed Bi species not freed by successive cycling within limits of  $+0.30$  and  $+1.20 \text{ V (SHE)}$  was confirmed. Therefore, under conditions of repetitive



scans, the Bi UPD proceeds onto the substrate surface partially covered with metal to be deposited. The charge density flow associated with the Bi species reduction/oxidation diminishes as the concentration of Bi<sup>3+</sup> increases when the steady-state voltammograms are taken for examination.

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## Appendix

### The main features of adsorption of (bi)sulphate at Pt electrode:

(i) experimental data obtained by means of various electrochemical and non-electrochemical techniques have given an unquestionable evidence for a strong specific (contact) adsorption of sulphate species on a platinum electrode;

(ii) this adsorption was found to be strongly sensitive to a topography and crystallographic orientation of the platinum electrode surface;

(iii) a specific adsorption of sulphate species occurs simultaneously with an adsorption of water molecules (*i.e.* in the double-layer  $E$  range on Pt the adsorption of sulphate species competes with the adsorption of water molecules);

(iv) in the event that sulphate species serve as a source for adsorbed anions and as a base electrolyte, bulk effects involving rather a considerable pH change and ion transport take place in a cavity of a thin layer [43, 45];

(v) the amount of adsorbed sulphate species does not likely depend on a bulk  $c$  of  $H_2SO_4$  in the range of higher  $c$  of acid, but depends on this variable when lower  $c$  of  $H_2SO_4$  are used for experiments (*e.g.* when HF or  $HClO_4$  solutions were employed as supporting electrolytes);

(vi) until very recently, the composition of specifically adsorbed species has been discussed, in particular, an

adsorbed sulphate species has been described as: a)  $HSO_4^-$  for Pt(111) [40, 42, 48–52, 58, 59, 63], Pt(100) [46, 52, 59, 64], Pt(110) [52, 59] and pc Pt electrodes [42, 43] (in some instances there are also indications that the adsorbed sulphate species is predominantly  $HSO_4^-$  [42, 43]); b)  $SO_4^{2-}$  for Pt(100), Pt(110) and Pt(111) electrodes [53] or predominantly  $SO_4^{2-}$  for Pt(111) electrode [62]; c) both  $HSO_4^-$  and  $SO_4^{2-}$  for Pt(111) electrode [54, 57] and pc Pt electrode [45, 55, 65] (a ratio  $SO_4^{2-}/HSO_4^-$  decreases as the potential becomes more positive, as reported in [44, 57, 65]); d) the adsorbed sulphate species is not adequately described as either  $SO_4^{2-}$  or  $HSO_4^-$  and, in particular as pointed out in the study [56], the recorded IR-spectra are more consistent with the adsorbed  $H_3O^+-SO_4^{2-}$  ion pair;

(vii) the lower and upper limits of  $E$  range, within which specific adsorption of sulphate species has been identified, were shown to correspond approximately to commencement of hydrogen UPD and formation of surface platinum oxide, respectively [42, 43, 45, 48, 50, 51, 53, 55, 56, 58, 60–63];

(viii) considering a coverage of sulphate species on platinum, it has been established that the upper limit of this parameter for  $HSO_4^-$  on pc Pt is equal to 0.15 at 0.8 V [55], to 0.22 [62] or 0.16 [64] on Pt(111) electrode and to 0.4 for the sum  $HSO_4^- + SO_4^{2-}$  on Pt(111) electrode [54];

(ix) it was proposed that: a)  $SO_4^{2-}$  ions are predominantly adsorbed through two oxygen atoms presenting a  $C_{2v}$  symmetry at pc Pt [44], Pt(100) and Pt(110) electrodes [53], while the same anion exhibits a three-fold coordination at Pt(111) electrode; b) the major  $HSO_4^-$  orientation corresponds to a three-fold symmetric arrangement  $C_{3v}$  at pc Pt electrode, each of the unprotonated O interacting with a platinum atom [42, 45, literature cited in Refs. 56] while in the case of Pt(111) electrode  $HSO_4^-$  takes a pseudo  $C_{3v}$  structure and bonds through single or three O atoms [48];

(x) a specific (contact) adsorption of  $SO_4^{2-}/HSO_4^-$  at pc Pt electrode is much weaker than at Pt(111) electrode surface [64];

(xi) the electrosorption valency of  $HSO_4^-$ , was shown to equal unity, indicating a strong interaction with the surface of Pt(111) and high charge transfer [47].

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### VOLTAMPEROMETRINIAI BI PRIŠVOLTĄŽINIO NUSODINIMO ANT POLIKRISTALINĖS Pt ELEKTRODO RŪGŠČIUOSE SULFATINIUOSE $Bi^{3+}$ TIRPALUOSE TYRIMAI

#### S a n t r a u k a

Ciklinės voltamperometrijos būdu tirtas bismuto priešvoltage nusodinimas ant glotnaus polikristalinės Pt elektrodo 0,5 M  $H_2SO_4$  tirpaluose esant 20 °C temperatūrai. Tirta bismuto priešvoltage nusodinimo ir nutirpinimo priklausomybė nuo bismuto tūrinės koncentracijos, potencialo skleidimo intervalo, potencialo skleidimo greičio ir nuo nuosekliai pasikartojančių  $E$  skleidimų. Nustatyta, kad stabilizuoti potenciodinaminiai  $i/E$  profiliai panašūs į anksčiau gautus profilius  $Bi^{3+}$  perchloratiniuose tirpaluose. Be to, nustatyti kai kurie skirtumai, susiję su paviršinių plati-

nos oksidų redukcija įvairiuose Bi<sup>3+</sup> tirpaluose. Naudojantis Clavilier et al. pažiūromis apie krūvio pernešimo priešvoltažio zonoje kilmę, išanalizuoti krūvio tankiai, apskaičiuoti iš stabilizuotų voltamperinių kreivių.

**А. Степонавичюс, Л. Гудавичюте**

**ВОЛЬТАМПЕРОМЕТРИЧЕСКИЕ  
ИССЛЕДОВАНИЯ ОСАЖДЕНИЯ ВІ В ЗОНЕ  
НЕДОНАПРЯЖЕНИЯ НА ЭЛЕКТРОДЕ  
ПОЛИКРИСТАЛЛИЧЕСКОЙ Pt В КИСЛЫХ  
СУЛЬФАТНЫХ РАСТВОРАХ ВІ<sup>3+</sup>**

**Р е з ю м е**

Методом циклической вольтамперометрии исследовано осаждение Ві в зоне недоныпряжения на гладком

электрoде поликристаллической Pt в растворах 0,5 М Н<sub>2</sub>SO<sub>4</sub> при температуре 20 °С. Исследовано осаждение и растворение Ві в зоне недоныпряжения в зависимости от объемной концентрации Ві, интервала развертки потенциала, скорости развертки потенциала, а также от применения повторяющейся циклической развертки *E*. Установлено, что стабилизированные потенциодинамические *i/E* профили сходны с полученными ранее профилями Ві<sup>3+</sup> в перхлоратных растворах. Кроме того, установлено некоторое несходство, обусловленное редукцией поверхностных платиновых оксидов в разных растворах Ві<sup>3+</sup>. На основе Clavilier et al. представлений о природе переноса заряда в зоне недоныпряжения сделан анализ плотности зарядов, вычисленной из стабилизированных вольтамперометрических кривых.