

## AUTOCATALYTIC REDUCTION OF IODATE AT THE PLATINUM ELECTRODE IN 0.5 M H<sub>2</sub>SO<sub>4</sub> SOLUTIONS

Gabriela Elena BADEA\*

Department of Thermal Energy, University of Oradea, Universităţii 1, 410087 Oradea, Roumania

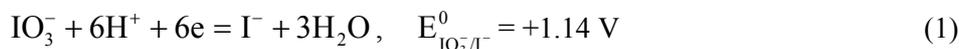
*Received February 3, 2006*

Electrochemical reduction of iodate (IO<sub>3</sub><sup>-</sup>) at platinum electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> deaerated solutions was studied by the potentiostatic method as function of the bulk concentration. The shape of the cathodic polarization curves and the kinetic parameters strongly depend on the iodate concentration. At concentration ≥ 0.01 M IO<sub>3</sub><sup>-</sup>, the reduction reaction is characterized by Tafel slopes of 30-40 mV/decade and an exponential increase of the limiting current density with iodate concentration, corresponding to an autocatalytic mechanism. The reaction is catalysed by intermediate reaction products: I<sub>2</sub> and I<sub>3</sub><sup>-</sup> whose formation is promoted by high iodate concentrations.

### INTRODUCTION

The redox system IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> is a complex<sup>1,2</sup> one. In the reduction process six electrons are transferred, which presumes several electrochemical steps

associated with chemical reactions. In acidic solutions the electrochemical reduction of IO<sub>3</sub><sup>-</sup> may follow one of the reactions:<sup>3</sup>



According to reaction (1), the iodate reduction takes place up to I<sup>-</sup>, while the final product of reaction (2) is the solid iodine. The standard

potentials are enough close to develop in parallel. The solid iodine is soluble in mineral acids and the following equilibrium can appear:<sup>4</sup>



The iodate ion is a strong oxidant and it can oxidize I<sup>-</sup> to I<sub>2</sub> or I<sub>3</sub><sup>-</sup>, according to the following

chemical reactions:<sup>1,5</sup>



Also, I<sub>2</sub> ↓, I<sub>2</sub>, I<sub>3</sub><sup>-</sup> and I<sup>+</sup> could be electrochemical reduced reactions:<sup>1,3,6</sup>

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\* E-mail: gbadea@uoradea.ro



The regions of relative stability for different species in the I-H<sub>2</sub>O system are shown in the potential-pH diagrams<sup>7,8</sup>, presented (Fig. 1a and b)

for two total dissolved iodide concentrations: [I] = 10<sup>-3</sup> M and 10<sup>-1</sup> M.

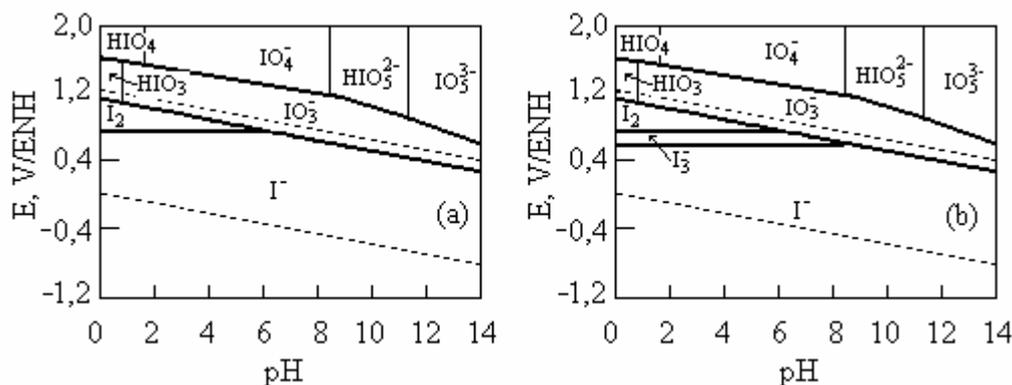


Fig. 1 – Potential–pH diagrams for the I-H<sub>2</sub>O system: (a) [I]=10<sup>-3</sup> M, (b) [I]=10<sup>-1</sup> M.<sup>8</sup>

I(V) exists as HIO<sub>3</sub> below pH=1 and as IO<sub>3</sub><sup>-</sup> above this value. The reduction products of IO<sub>3</sub><sup>-</sup>, *i.e.*, I<sub>2</sub> and I<sup>-</sup>, appear (just below the upper water stability line) in Fig. 1a. In Fig. 1b, corresponding to a higher iodide concentration, a narrow region of I<sub>3</sub><sup>-</sup> sandwiched between I<sup>-</sup> and I<sub>2</sub> domains is also observed. The comparison of Fig. 1a and 1b reveals that the increase of [I] facilitates I<sub>3</sub><sup>-</sup> formation.

In some previous works,<sup>5,9,10</sup> the addition of iodine over a certain concentration to iodate solution was presented to have a catalytic effect on the electrochemical reduction of IO<sub>3</sub><sup>-</sup>. The intermediate product, iodine (reaction 2), can act as a catalytic agent. The question is at what IO<sub>3</sub><sup>-</sup> concentration the autocatalytic effect appears; this is the aim of the paper. With this purpose, potentiostatic polarisation curves were recorded for different IO<sub>3</sub><sup>-</sup> concentrations (1×10<sup>-4</sup>, 1×10<sup>-3</sup>, 1×10<sup>-2</sup>, 0.1 and 0.2 M) in 0.5 M H<sub>2</sub>SO<sub>4</sub> in order to study the influence on the electrochemical parameters and to establish a probable reaction mechanism.

## EXPERIMENTAL

The measurements were performed in a conventional three-compartment electrochemical cell separated by fritted glass disk with a PS 2 potentiostat, using the stepwise technique of 20 and 40 mV/ 1 minute. The working electrode, having the geometrical area of 0.06 cm<sup>2</sup>, was made of polycrystalline platinum. Before the measurements, the electrode was treated as follows: boiled in 50% nitric acid solution and washed with doubly distilled water. A platinum sheet with an area of 1 cm<sup>2</sup> was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode.

The solutions were prepared from chemically pure reagents and doubly distilled water. The iodate ion was added as potassium salt. Before the measurement the solutions were deaerated with purified nitrogen for 45 minutes. All measurements were carried out at room temperature (23±1°C).

## RESULTS AND DISCUSSION

The cathodic polarisation curves of the iodate reduction on the polycrystalline platinum electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> deaerated solutions are shown in Fig. 2. The associated electrochemical parameters are presented in Table 1.

Table 1

Electrochemical parameters for the iodate reduction on the Pt electrode in 1N H <sub>2</sub> SO <sub>4</sub>						
IO <sub>3</sub> <sup>-</sup> conc. M	*b <sub>1</sub>	(αn) <sub>1</sub>	i <sub>p</sub> mA/cm <sup>2</sup>	i <sub>L</sub> mA/cm <sup>2</sup>	**b <sub>2</sub>	(αn) <sub>2</sub>
0.0001	222	0.26	0.018	0.0166	310	0.19
0.001	161	0.37	0.188	0.3166	307	0.19
0.01	35	1.68	3.500	3.7500	287	0.20
0.1	40	1.47	17.167	22.500	275	0.21
0.2	40	1.47	12.167	100.000	316	0.19

\*Tafel slope of the first charge transfer step, mV/decade;

\*\*Tafel slope for the hydrogen evolution, mV/decade.

Three charge transfer steps could be observed on the cathodic curves, two associated with the iodate reduction and the last with the hydrogen evolution reaction.

For the first charge transfer step (in the approximate potential domain: +0.7 ÷ +0.3 V/SCE), the shape of the curves is strongly dependent on the iodate bulk concentration. All curves show a limiting current in a large potential domain. The current increase at potentials more negative than -0.2V is due to the hydrogen evolution reaction.

In the case of curves 1 and 2 from Fig. 1, corresponding to the iodate concentrations of 1×10<sup>-4</sup> M and 1×10<sup>-3</sup> M, respectively, the current densities increase slowly with the potential shift in the cathodic sense and after the appearance of a small maximum and a minimum, the reaction rate is

limited. The curve 3 from Fig. 2, corresponding to the concentration of 1×10<sup>-2</sup> M KIO<sub>3</sub>, shows a rapid increase of the reaction rate followed by a limiting current.

The curves 4 and 5 from Fig 2, corresponding to the 0.1 and 0.2 M KIO<sub>3</sub>, respectively, are clearly different *versus* curves 1-3. After a rapid increase of the current density, the well-marked maximum and a minimum, dependent of IO<sub>3</sub><sup>-</sup> bulk concentration, are visible. Both peaks (maximum and minimum current density) decrease when the concentration increases from 0.1 to 0.2 M. In these solutions the limiting current densities indicate a significant increase of the iodate reduction rate, much more than proportional to the bulk concentration.

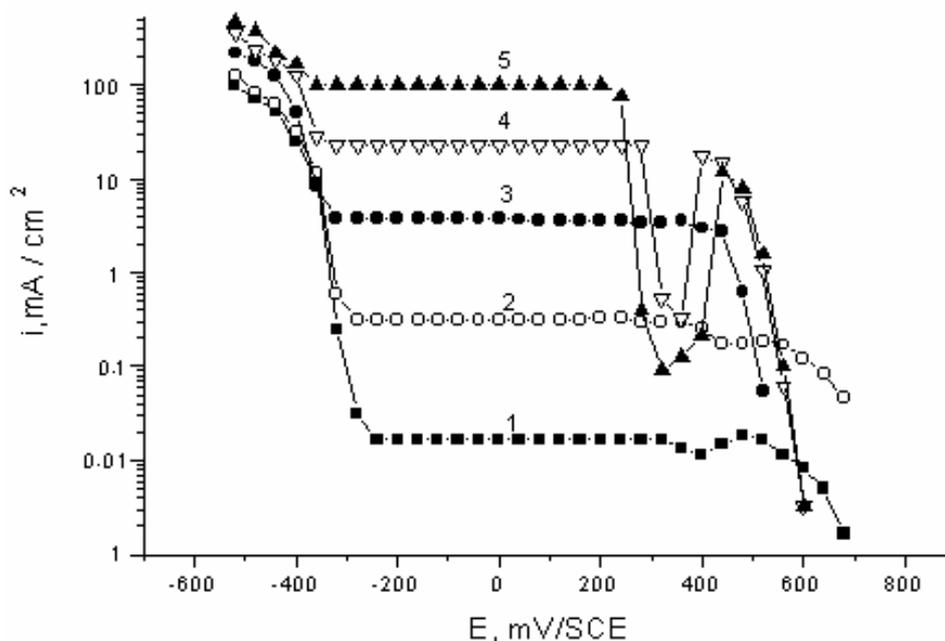


Fig. 2 – Cathodic polarisation curves (40 mV/1 min) of the iodate reduction on Pt electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> deaerated solutions for various IO<sub>3</sub><sup>-</sup> concentrations (M): 1–1×10<sup>-4</sup>; 2 –1×10<sup>-3</sup>; 3 –1×10<sup>-2</sup>; 4 –0.1; 5 – 0.2.

Fig. 3 shows the Tafel behavior of the iodate reduction, in the first charge transfer step. In the solutions containing  $1 \times 10^{-4}$  and  $1 \times 10^{-3}$   $\text{MIO}_3^-$ , the Tafel slopes obtained (Table 1) correspond to a slow reaction. The low value of the  $(\alpha n)_1$  parameter may be associated with some adsorption processes.

At higher concentrations of  $\text{IO}_3^-$  (0.01, 0.1 and 0.2 M), the obtained Tafel slopes of 35-40 mV/decade indicate a catalytic mechanism<sup>11</sup> and the values of  $(\alpha n)_1$  parameter (1.47-1.68) correspond to a surface reaction.<sup>12</sup>

The peak current density has a polynomial variation with the iodate concentration, passing through a maximum (Fig. 4). This behaviour leads to the supposition that an intermediate reaction

product, which appears in a large quantity at higher  $\text{IO}_3^-$  concentration, remains probably on the electrode surface and acts as the inhibitor. This fact could explain the accentuated decrease of the current density after the peak, when the  $\text{IO}_3^-$  concentration increases. After the minimum, the second charge transfer step develops at a high rate, being controlled by the concentration polarisation. At low  $\text{IO}_3^-$  concentrations ( $1 \times 10^{-4}$ - $1 \times 10^{-2}$  M) the dependence of the current density on concentration is linear (Fig. 5a), while at higher concentrations ( $1 \times 10^{-2} \div 0.2 \text{ MIO}_3^-$ ) the dependence is exponential (Fig. 5b), which is an argument for an autocatalytic process.

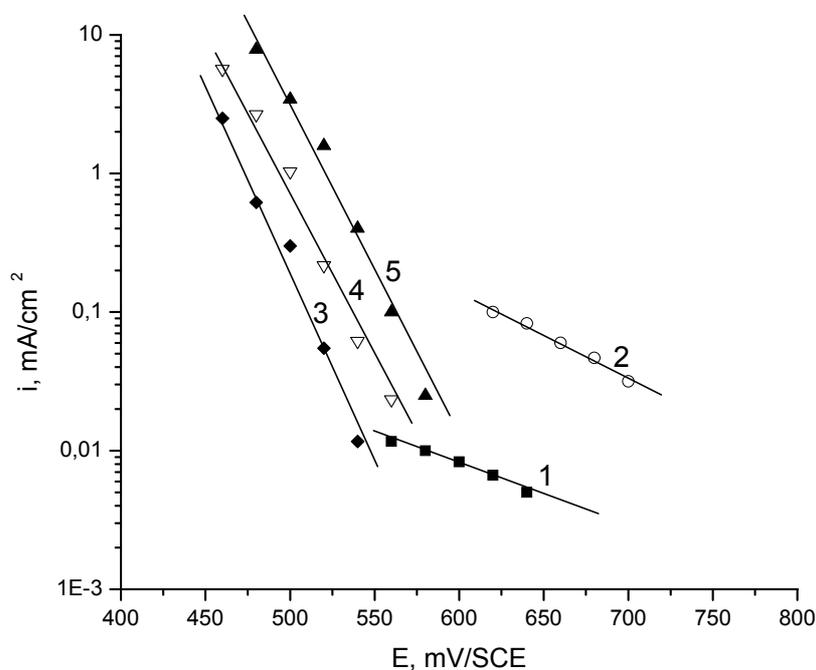


Fig. 3 – Tafel lines for iodate reduction in the first charge transfer step at different  $\text{IO}_3^-$  concentrations (M):  
1- $1 \times 10^{-4}$ ; 2- $1 \times 10^{-3}$ ; 3- $1 \times 10^{-2}$ ; 4-0.1; 5-0.2.

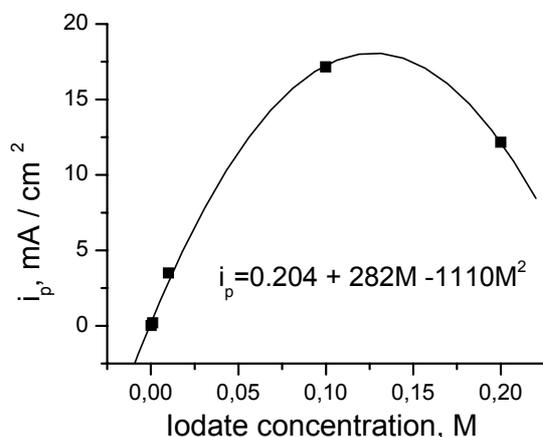


Fig. 4 – Plot of the peak current density vs. iodate concentration.

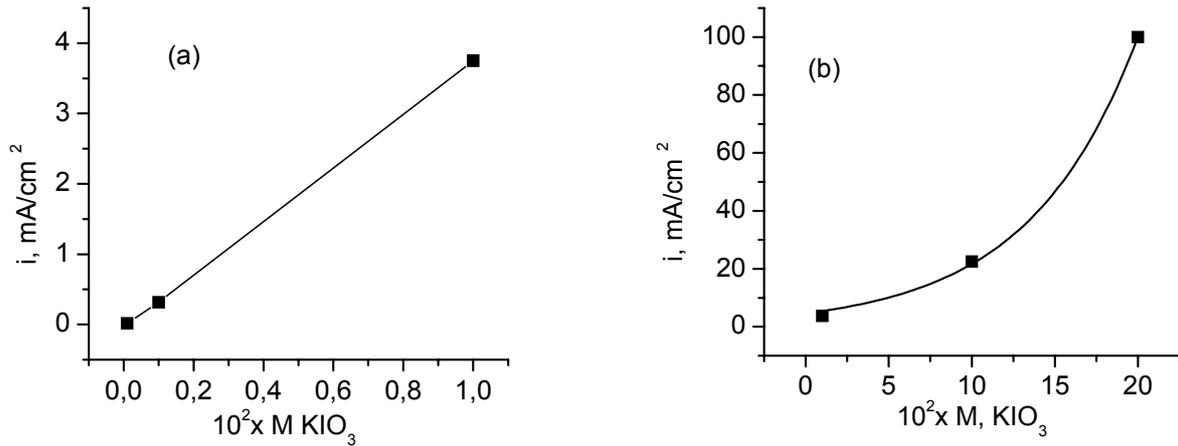


Fig. 5 – Plots of the limiting current density vs. iodate concentration: (a)  $\leq 0,01$  M; (b)  $\geq 0,01$  M.

The reaction order vs.  $\text{IO}_3^-$  ion,  $p_{\text{IO}_3^-}$ , calculated according to relation: <sup>1</sup>

$$\left( \frac{\partial \log i_k}{\partial \log c_{\text{IO}_3^-}} \right)_{E_c} = p_{\text{IO}_3^-} \quad (11)$$

The reaction orders *versus*  $\text{IO}_3^-$  for all the three charge transfer steps are shown in Figs. 6-8. For the first and the second charge transfer steps the reaction order is approximately 1, while for the

third charge transfer it is practically equal to zero, corresponding to the hydrogen evolution reaction, the only one in this potential range.

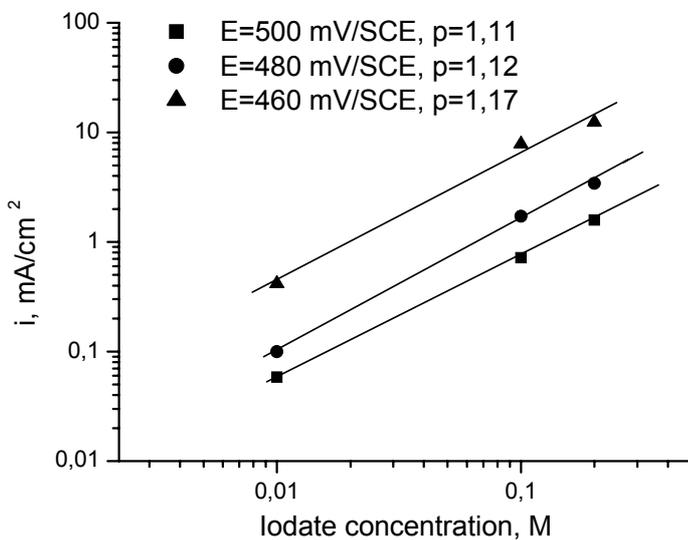


Fig. 6 – Plot of the cathodic current density vs.  $\text{IO}_3^-$  concentration at different potentials in the first charge transfer step.

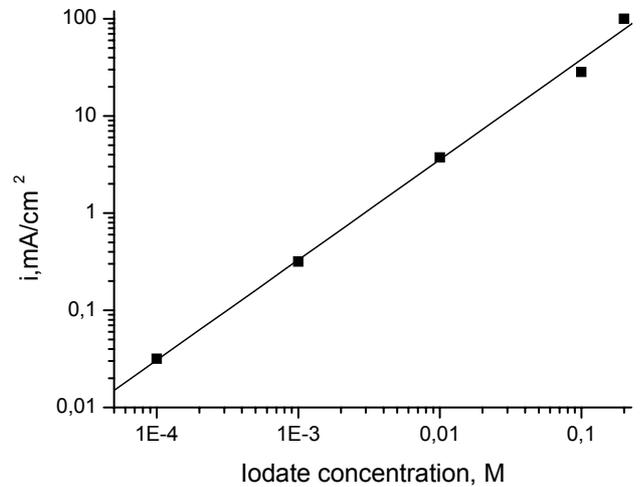


Fig. 7 – Plot of the limiting current density vs.  $\text{IO}_3^-$  concentration.

Finally, the hydrogen evolution reaction is characterized by a Tafel slope with the average value of 399 mV/decade and a  $(\alpha n)_2$  parameter of 0.2 (Fig. 9 and Table 1). The low value of the  $(\alpha n)_2$

parameter indicates the presence of adsorbed iodine species ( $\text{I}^-$  or/and  $\text{I}_2 \downarrow$ ) on the surface of the electrode.

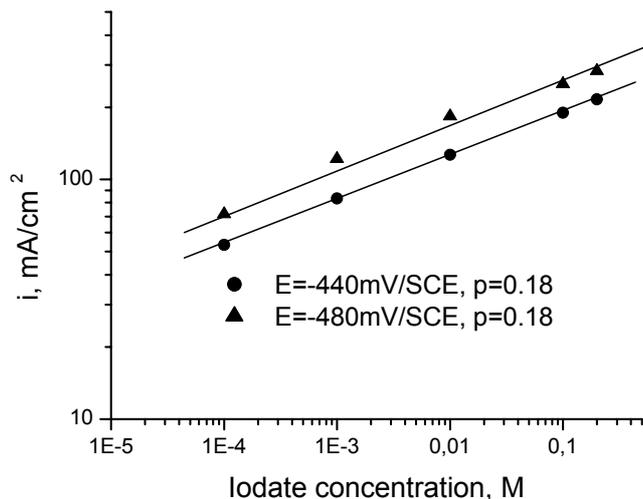


Fig. 8 – Plot of the current density vs.  $\text{IO}_3^-$  concentration at different potentials in the potential region of hydrogen evolution.

### DISCUSSION

The direct reduction of  $\text{IO}_3^-$  on Pt electrode in acid solutions, according to reaction (1) is a slow process.<sup>5,9</sup> According to Desideri,<sup>9</sup> the  $\text{I}^-$  ion diffuses from the Pt surface in solution, where it reacts rapidly with  $\text{IO}_3^-$  forming  $\text{I}_2(\text{aq})$  according to the chemical reaction (5). The  $\text{I}_2(\text{aq})$  is transported to the electrode surface and reduced to  $\text{I}^-$  (reaction 8), setting up a catalytic loop. Beran and Bruckenstein<sup>10</sup> reported also a catalytic effect of  $\text{I}_2$  on the reduction of iodate. They concluded that addition of  $\text{I}_2$  increases the surface coverage with  $\text{I}_{\text{ads}}$  and thus the generation of  $\text{I}^-$  in the diffusion layer promotes a faster reaction (5).

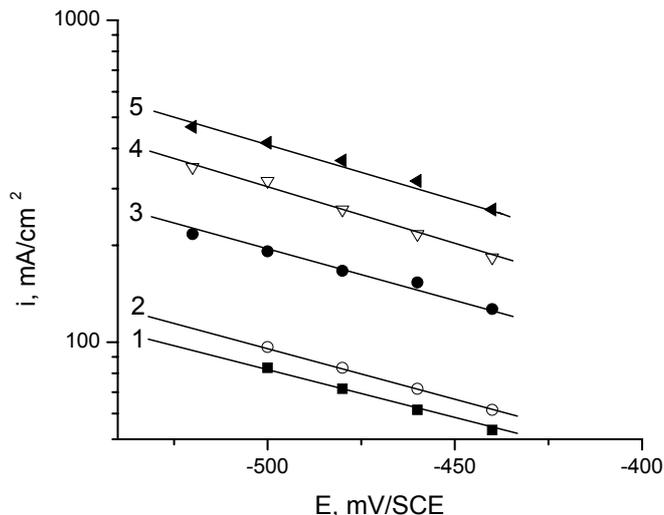


Fig. 9 – Tafel lines in the domain of hydrogen evolution for different iodate concentrations (M): 1 –  $1 \times 10^{-4}$ ; 2 –  $1 \times 10^{-3}$ ; 3 –  $1 \times 10^{-2}$ ; 4 – 0.1; 5 – 0.2.

Badoz-Lambling,<sup>5</sup> studying the iodate reduction in 1N  $\text{HClO}_4$ , found that an addition of  $\text{I}_2$  in concentration higher than  $10^{-4}$  N catalyses this reaction. He considered that the  $\text{I}_3^-/\text{I}^-$  system catalyses iodate reduction, *via* the chemical reaction (6). The electrochemical reaction is reaction (9).

The experimental results reported in this work show that the increase of  $\text{IO}_3^-$  concentration in the base electrolyte (0.5 M  $\text{H}_2\text{SO}_4$ ), has an autocatalytic effect on iodate reduction at Pt electrode, significantly intensifying the reaction rate. At high iodate concentrations, in the first charge transfer step, parallel and competitive electrochemical and chemical reactions could take place, as follows:

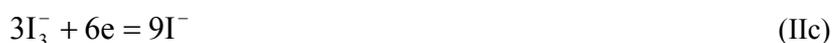
Simplifying with 4 the total reaction of the first charge transfer step (I), it becomes identical to reaction (Ia), according to the reaction order *vs.*  $\text{IO}_3^-$  whose value is about 1 (Fig. 6).

The reaction (Ib), whose product is the solid iodine ( $\text{I}_2 \downarrow$ ), is promoted by higher bulk concentration of  $\text{IO}_3^-$ . The solid iodine, being soluble in mineral acids, passes into solution (Ic) and it reduces to  $\text{I}^-$  (eq. Ie).  $\text{I}^-$  oxidizes to  $\text{I}_2$ , according to reaction (Id), setting up a catalytic loop. The Tafel slope of 35-40 mV/decade (Table 1), obtained in solutions with iodate concentration  $\geq 0.01$  M, sustains the catalytic mechanism.<sup>11</sup> At iodate concentration  $\geq 0.1$  M, a part of the produced solid iodine (eq. Ib) remains on the surface of the electrode and forms a film, which inhibits the reaction. The formation of the solid iodine on the surface of the electrode, in acid solutions at high  $\text{IO}_3^-$  concentration, was reported also by Anik,<sup>8</sup> who studied the iodate reduction on copper.

The intermediate product of the reaction (Ib) may, on the one side, increase the rate of the total reaction (I) *via* reactions (Ic)-(Ie) and, on the other side, it leads to the increase of a solid iodine film on the surface the electrode. At a certain thickness, the solid iodine layer acts as an inhibiting barrier for the reaction, determining the decrease of the reaction rate. This fact is sustained by smaller values of both peak and minimum current density at 0.2 M comparatively with 0.1 M  $\text{IO}_3^-$  (Fig. 4 and Table 1).

At low  $\text{IO}_3^-$  concentration ( $\leq 1 \times 10^{-3}$  M), the high values of the Tafel slopes indicate a slow non-catalytic reaction, accompanied by the adsorption processes (Fig. 4 and Table 1). In this case, the predominant reaction could be (Ia) whose product  $\text{I}^-$  is adsorbed on the surface of the electrode.

The increase of the current density after the minimum is due to a new charge transfer step (II). The reactions could be:



In the second charge transfer step, the current starts to increase at the potential of 0.280 V/SCE (0.530 V/ENH), value closed to the standard potential of the solid iodine reduction (0.536 V, according to eq. 7). Thus, the solid iodine film is reduced to  $\text{I}^-$  (IIa), promoting the chemical reaction (IIb) whose product, the complex ion  $\text{I}_3^-$ , is finally reduced to  $\text{I}^-$  (IIc).

The formation of the complex ion  $\text{I}_3^-$ , is according to the pH-potential diagram (Fig. 1b), in solution with high concentration of total iodine. The  $\text{I}_3^-/\text{I}^-$  system acts as a catalyst in this second charge transfer step, as shown previously by Baldoz-Lambleng.<sup>5</sup> The catalytic role of this system is sustained by the exponential dependence of the limiting current density on iodate concentration (Fig. 5b). The reaction order *vs.*

$\text{IO}_3^-$ , equal to 1 (Fig. 7), is according to the total reaction of the second charge transfer step (II). This step is controlled by the concentration polarization. The iodate reduction rate could be limited either by the chemical reaction rate (IIb), or by the diffusion rate of  $\text{IO}_3^-$  to the electrode surface, depending on the iodate bulk concentration. At small iodate concentrations, the reaction rate is limited by the diffusion rate of the reactant to the electrode surface, fact sustained by the linear dependence of the limiting current density on  $\text{IO}_3^-$  concentration (Fig. 5a). The exponential dependence of the limiting current density on iodate concentration, in the range 0.01–0.2 M, shows a catalytic process, controlled by the chemical reaction (IIb).

At the concentration of 0.2 M  $\text{IO}_3^-$ , the solid iodine layer formed on the surface of the electrode,

is not completely reduced in the second charge transfer step. At high cathodic polarization and high rate of hydrogen evolution, the detachment of the film from the surface of the electrode was observed and the characteristic iodine color appearance. This fact confirms the formation of the solid iodide film on the surface of the electrode, at high iodate concentration.

### CONCLUSIONS

The kinetics of the iodate reduction on platinum electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> deaerated solution depends on its bulk concentration.

At concentrations  $\geq 0.01$  M IO<sub>3</sub><sup>-</sup>, the electrochemical reduction of iodate is an autocatalytic process. The Tafel slopes have values of 35-40 mV/decade and the limiting current density increases exponentially with the IO<sub>3</sub><sup>-</sup> concentration.

The solid iodine and the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> system, formed as intermediate products at high iodate concentrations, act as catalysts of the reduction process.

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