KINETICS AND MECHANISM OF THE BROMATE ELECTROCHEMICAL REDUCTION AT PLATINUM ELECTRODE

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The electrochemical reduction of the bromate ions in 1N H_2SO_4 solution at the platinum cathode has been studied by the method of the potentiostatic polarisation curves. The development of the reaction implicates two steps of the charge transfer, controlled by the mass transfer at large current densities. The electrochemical kinetics parameters − Tafel slopes, charge transfer coefficient, peak and limiting current densities, peak potential and reaction orders− determined as function of the bromate ion concentration and a reaction mechanism are proposed.

INTRODUCTION

Many inorganic anions, such as nitrate, perchlorate, bromate and others are pollutants for the drinking water.[1] Recently interest in bromate ion reduction arose because of its carcinogenic properties.[2, 3] The bromate concentration in the drinking water is regulated under Stage 1 Disinfectants/disinfecting by-products Rule[4] at 10 µg/L. The presence of bromate in the drinking water bromate is commonly produced from bromide during the ozonation of the drinking water or during water treatment with advanced oxidation processes.[5-7]

The removing of the bromate anions from water makes, generally, by reduction to bromide, an innocuous product.

The literature data refer to the chemical bromate reduction by means of different metallic ions,[8-10] such as: Ce(III), Mn(II), Np(V), in the presence of humic acid and/ or Fe^{3+}, Fe^{2+} ions, respectively zero-valent iron.[11, 12] Other papers report the bromate reduction by denitrifying bacteria.[13, 14] However, the results of the study presented in the work[13] indicate that biological bromate removal in the water treatment processes may not be very promising. There are few studies on the electrochemical bromate reduction and these refer to the electrocatalytic reduction at the modified glassy carbon electrode with molybdophosphate anion[15] or with the sodium molybdate.[16]

In this paper we investigate the bromate ion reduction at the platinum electrode in 1N H_2SO_4 solution and a reaction mechanism is proposed.

EXPERIMENTAL

The measurements were performed in the conventional three-compartment electrochemical cell separated by a fretted glass disk. The working electrodes, having the geometrical area of 0.06 cm^2, were made of polycrystalline platinum. Before to the measurements, the electrode was treated as follows: boiling in 50% nitric acid solution, washing with doubly distilled water. A platinum sheet with an area of 1 cm^2 was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode.

As polarisation instrument a PS 2 potentiostat was employed, using the stepwise technique of 20-mV/ 1 minute.

The solutions were prepared from chemically pure reagents and doubly distilled water. The bromate ion was added as potassium salt. All measurements were made at room temperature ($23\pm1^{o}C$).

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RESULTS AND DISCUSSION

Fig. 1 shows the cathodic potentiostatic polarization curves of the bromate ion reduction at the platinum electrode in 1N H_2SO_4 solution.
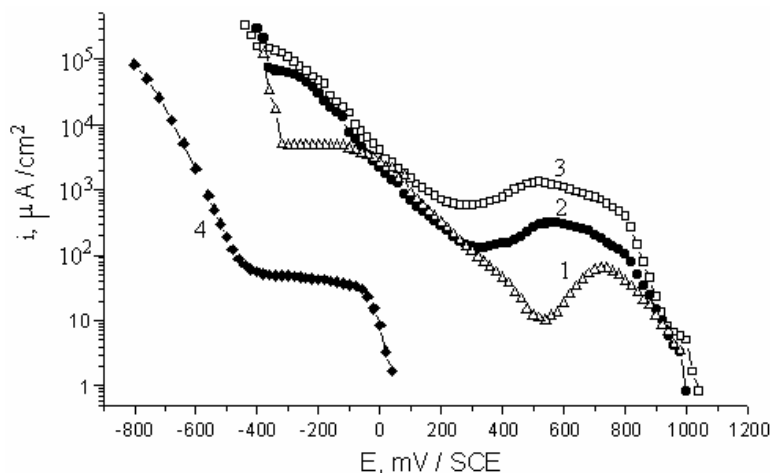

Fig. 1 – Cathodic potentiostatic (20mV/min) polarization curves at the platinum electrode in de-aerated 1N H_2SO_4 solutions for different bromate anion concentrations (M): 1−0.01; 2−0.1; 3−0.2; 4−0.0 (aerated solution).

Curve 4 in Fig. 1 corresponds to the fond solution. The processes that take place, in this case, are the reduction of the dissolved oxygen and of the hydrogen ions. These reactions take place in the negative potential domain, therefore they are not superposed over the bromate ion reduction, reason for which the solution deaeration is not essential. It can be concluded that the electrochemical reactions of the fond solution do not interfere with the bromate and intermediates reduction in the conditions of this study.

On curve 4 the oxygen diffusion limiting current density is observed, whose value is 41.6 $\mu A/cm^2$. At a potential more negative than −400 mV/SCE, the current increase is due to the evolution of hydrogen. The Tafel slopes of these two electrode processes are shown in Fig. 2. They are 105 and 124 mV/decade for the reaction of oxygen reduction, respectively, for the hydrogen ions reduction, values in a good accord with the literature data.[17] This agreement confirms the correctness of the results concerning the bromate ion reduction obtained.
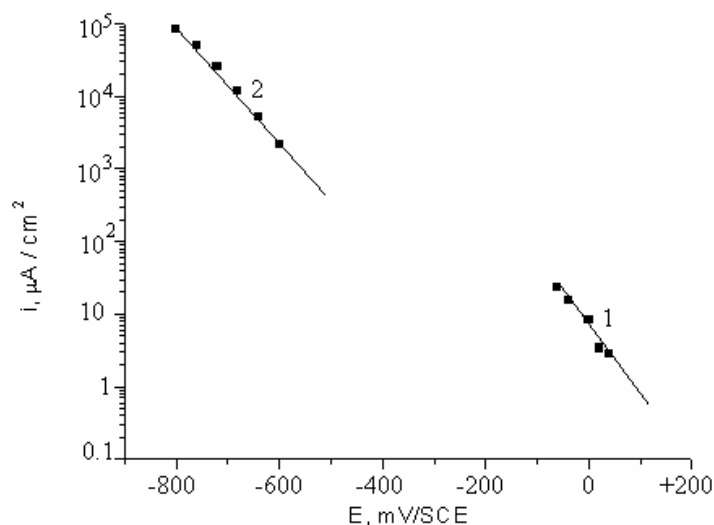

Fig. 2 – Tafel slopes for oxygen reduction (1) and hydrogen evolution (2) at the Pt electrode in 1N H_2SO_4 solution.

In accordance with Fig. 1, the electrochemical reduction of the bromate ion in the acid solution implicates two steps of charge transfer, controlled by mass transfer at large current densities. The two steps develop between +1000 mV and 550-300 mV/SCE, respectively, between 550-300 and −400 mV/SCE, in function of the bromate concentration.

The first charge step of the bromate electrochemical reduction

Fig. 3 shows the Tafel behaviour of the bromate reduction reaction in the first charge transfer step. The electrochemical parameters for this reaction step are shown in Table 1.

Table 1

Electrochemical parameters of the first charge transfer step for bromate ion reduction
at the Pt electrode in 1N H_2SO_4 solution

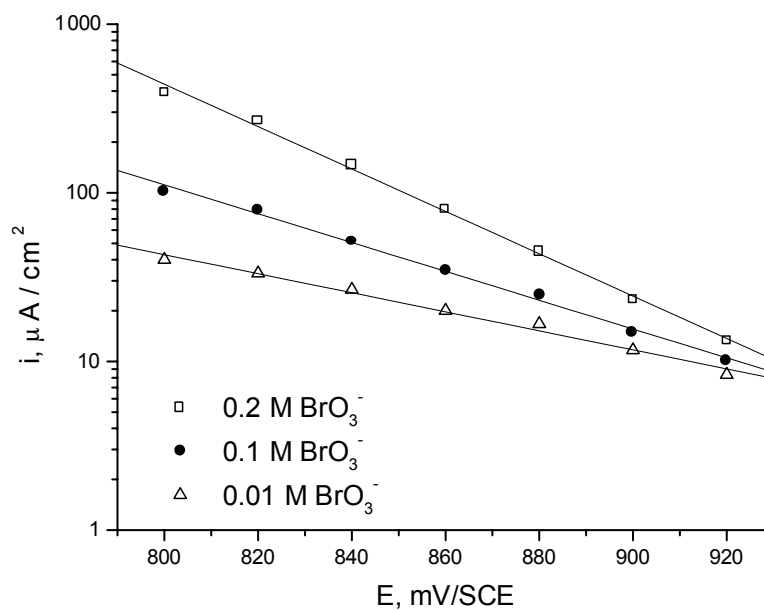| BrO_3^- Conc.	0.01M	0.1M	0.2M
b_1 mV/decade	177	117	80
$(\alpha n)_1$	0.33	0.50	0.73
E_P, mV/SCE	720	580	520
i_p, $\mu A/cm^2$	62.5	316.6	1333

Fig. 3 – Tafel behaviour of the first charge transfer step for bromate ion reduction
at the Pt electrode in 1N H_2SO_4 solution.

The Tafel slopes decrease with the bromate concentration increase, that is the first step of the reaction does not implicate BrO_3^- adsorption on the electrode surface. This behaviour is sustained also by the $(\alpha n)_1$ parameter whose mean value is 0.52.

In Fig. 4 are shown the relationships between the measured values of log i_c and log $c_{BrO_3^-}$ at different potentials situated in the Tafel domain of the first charge transfer step. The reaction order *vs*. the BrO_3^- ion, $p^I_{BrO_3^-}$, is calculated according to the relation:[18]

$$\left(\frac{\partial \log i_c}{\partial \log c_{BrO_3^-}} \right)_{E_c} = p^I_{BrO_3^-}$$

The reaction order, $p^I_{BrO_3^-}$ <1 (the mean value is 0.746), indicates the formation of free radicals in this first step of the bromate ion reduction.

The shift to the negative potential values of the peak potential, E_P, with the increase of the bromate ion concentration, sustains an irreversible charge transfer process.

The first step of bromate reduction is characterized by a peak current, whose value increases with the BrO_3^- ion concentration. A linear relation it found between the current density logarithm and the bromate ion concentration (Fig. 5), that is the peak current increases exponentially with the bulk bromate ion concentration.
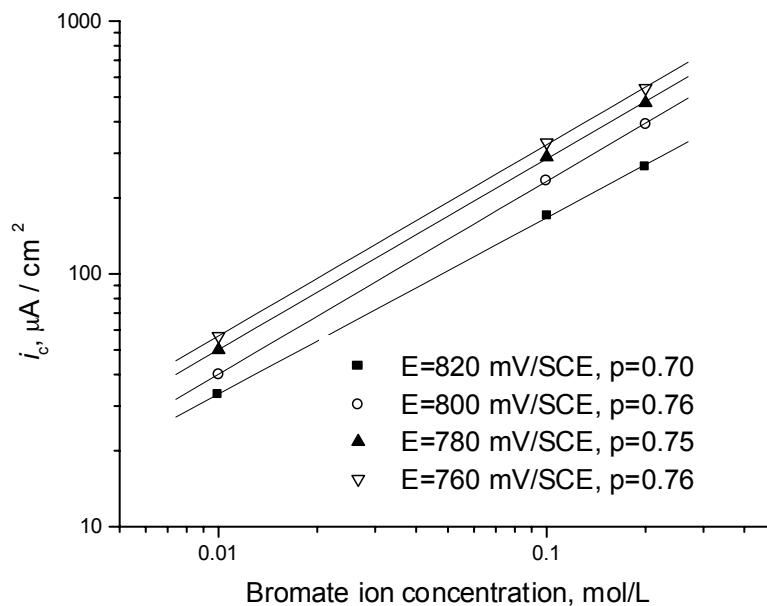

Fig. 4 – Plots of the cathodic current density *vs* bromate ion concentration at different potentials, E, located in the first charge transfer step (p = $p^I_{BrO_3^-}$ – reaction order).
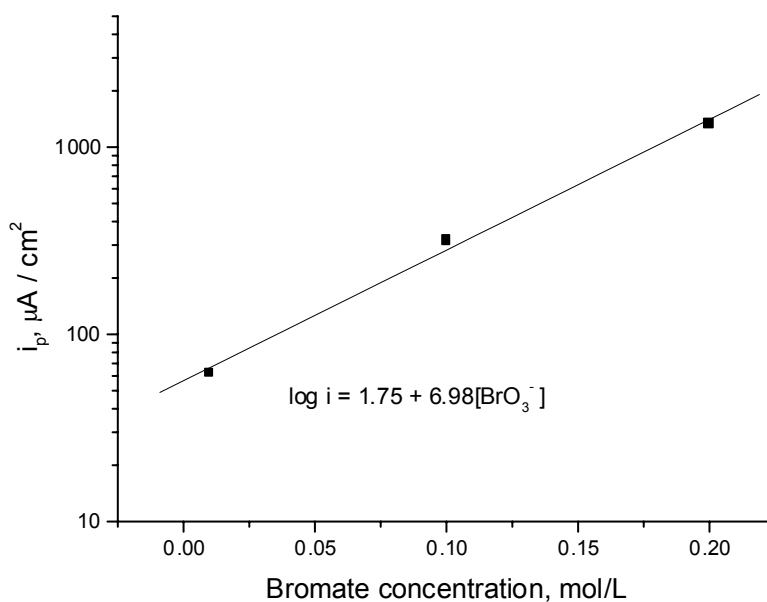

Fig. 5 – The peak current density dependence of the bromate ion concentration for the first step of the BrO_3^- ion reduction at the Pt electrode in 1N H_2SO_4.

The second charge transfer step of the bromate electrochemical reduction

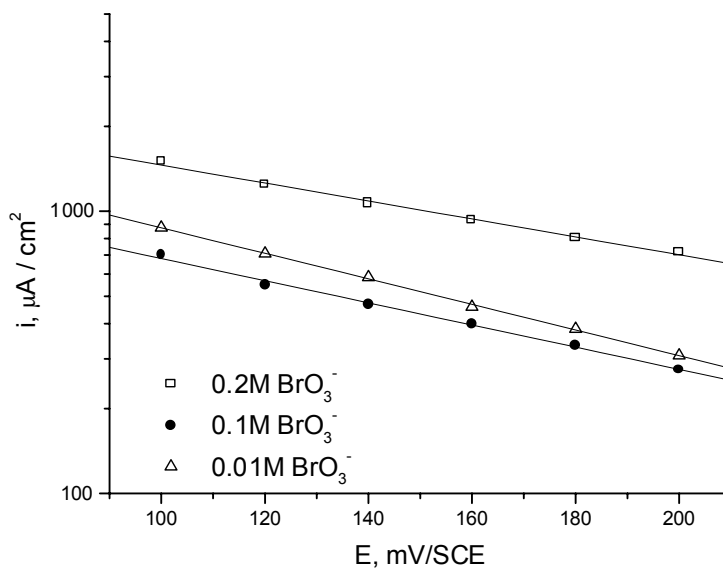The characteristics of the second charge transfer step are shown in Figs. 6-8 and in Table 2.

Fig. 6 – Tafel slopes for the second charge transfer step of the bromate ion reduction
at the Pt electrode in 1N H_2SO_4 solution.

Table 2

Electrochemical parameters of the second charge transfer step for bromate ion reduction
at the Pt electrode in 1N H_2SO_4 solution

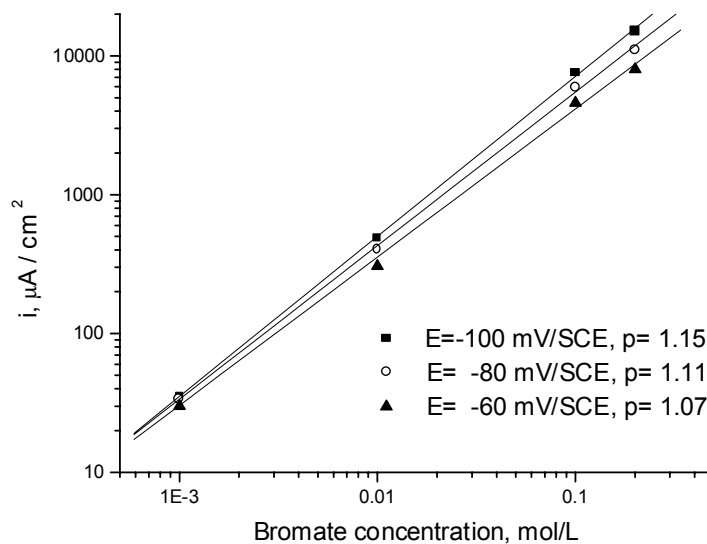| BrO_3^- Conc.	0.01M	0.1M	0.2M
b_2 mV/decade	221	254	314
$(\alpha n)_2$	0.27	0.23	0.19
i_L, $\mu A/cm^2$	4750	67500	146667

Fig. 7 – Plots of the cathodic current density *vs* bromate ion concentration at different potentials
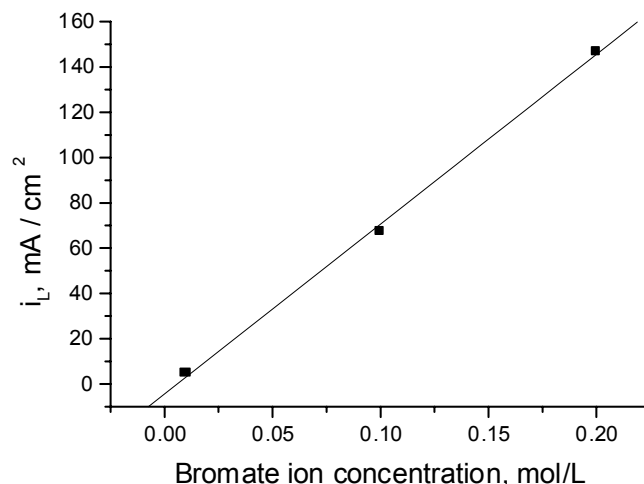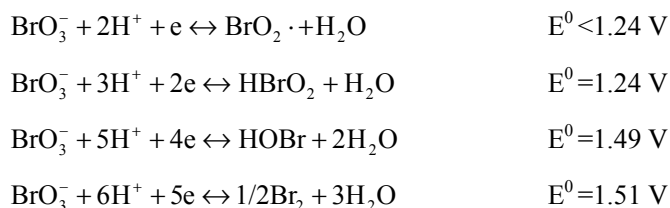in the second charge transfer step (p = $p^2_{BrO_3^-}$ – reaction order).

Fig. 8 – The limiting current density dependence of the BrO_3^- concentration in the second charge step
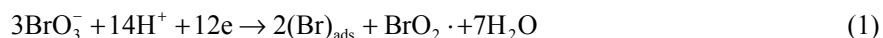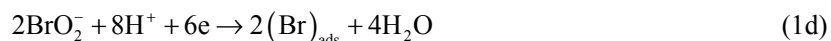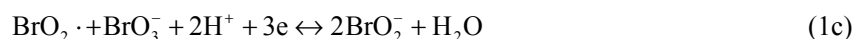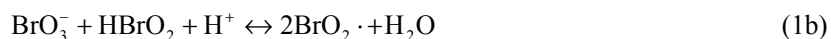of the bromate ion reduction at the Pt electrode in 1N H_2SO_4 solution.

The Tafel slope values for the second charge transfer step increase with the bromate ion concentration. This behaviour together with the low mean value of $(\alpha n)_2$, of only 0.23, indicate that this step implicates a surface reaction. This means, that the reaction product of the first charge transfer step results as an adsorbed species on the electrode surface. According to Fig. 7, the reaction order vs the BrO_3^- ion, $p_{BrO_3^-}^2$, is practically equal to the unit. The limiting current density, i_L, is directly proportional to the initial bromate ion concentration in solution, as can be seen in Fig. 8.

The reaction mechanism

The possible complications of this system are illustrated by the following potentials for different stages of the bromate reduction based on values given in Latimer,[19] on the free energy of formation of the bromite ion by Lee and Lister,[20] and on the observation of Buxton and Daiton[21] that $BrO_2 \cdot$ is unstable with respect to disproportionation:

$$BrO_3^- + 2H^+ + e \leftrightarrow BrO_2 \cdot + H_2O \qquad\qquad E^0 < 1.24\ V$$

$$BrO_3^- + 3H^+ + 2e \leftrightarrow HBrO_2 + H_2O \qquad\qquad E^0 = 1.24\ V$$

$$BrO_3^- + 5H^+ + 4e \leftrightarrow HOBr + 2H_2O \qquad\qquad E^0 = 1.49\ V$$

$$BrO_3^- + 6H^+ + 5e \leftrightarrow 1/2Br_2 + 3H_2O \qquad\qquad E^0 = 1.51\ V$$

According to the experimental results, the bromate reduction starts at a potential of about 1.00 V/SCE, that is 1.24 V/NHE, the reaction order for the first charge transfer step is lower than the unit, indicating the free radical formation and the peak current increases exponentially with the bromate ion concentration, indicating an autocatalytic reaction. These results can be satisfied by the following mechanism:

$$BrO_3^- + 3H^+ + 2e \leftrightarrow HBrO_2 + H_2O \qquad\qquad (1a)$$

$$BrO_3^- + HBrO_2 + H^+ \leftrightarrow 2BrO_2 \cdot + H_2O \qquad\qquad (1b)$$

$$BrO_2 \cdot + BrO_3^- + 2H^+ + 3e \leftrightarrow 2BrO_2^- + H_2O \qquad\qquad (1c)$$

$$2BrO_2^- + 8H^+ + 6e \rightarrow 2(Br)_{ads} + 4H_2O \qquad\qquad (1d)$$

$$3BrO_3^- + 14H^+ + 12e \rightarrow 2(Br)_{ads} + BrO_2 \cdot + 7H_2O \qquad\qquad (1)$$

The first stage of the bromate reduction is the formation of bromite acid, in accordance with reaction (1a). This reacts with the bromate ion and forms the radical intermediate $BrO_2 \cdot$ (reaction 1b). The radical is unstable and interacts with the bromate ion, forming the bromite ion (reaction 1c). This last is reduced in the rate-determining step to bromine (reaction 1d).

The reaction product of the first charge transfer step of the bromate ion reduction is adsorbed bromine.

The exponential relation between the peak current density and the bromate ion concentration, as shown in Fig. 5, confirms the catalytic role of the radical intermediate $BrO_2 \cdot$. Thompson and co-authors[10] with reference to the redox system bromate/Ce(III) made evident the formation of this radical and its catalytic role in the reaction of bromate reduction .

The final product of the electrochemical bromate reduction is the bromide ion, and the reaction that takes place in the second charge transfer is given by the equation:

$$\left(Br\right)_{ads} + e \rightarrow Br^- \tag{2}$$

Therefore, the bromate ion, a carcinogenic compound, can be directly reduced, in sulfuric acid solutions on the platinum electrode, to the bromide ion, an innocuous product for the human health.

CONCLUSION

The electrochemical bromate ion reduction at the platinum cathode in 1N H_2SO_4 solution takes place in two charge transfer steps; the first step is accompanied by a peak current while the second step presents a limiting current.

The Tafel slopes of the two charge transfer steps are differently influenced by the bromate ion concentration, and their values indicate that the second charge transfer step takes place in the adsorbed phase.

In the first charge transfer step the radical intermediate $BrO_2 \cdot$, is formed which has a catalytic effect on the bromate ion reduction.

The reaction product of the first step is adsorbed bromine, which is reduced in the second charge transfer step to bromide, an innocuous product for the human health.

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