

Electrochemical oxidation of iodide in aqueous solution

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Abstract

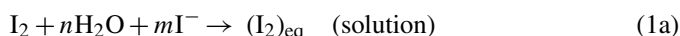
Electrochemical oxidation of iodide on DSA (Ti/RuO₂) anode was investigated in laboratory cell and semi-industrial electrochemical reactor. Anodic polarization curves in the laboratory cell were obtained in solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI in order to determined current densities for electrolysis in the semi-industrial electrochemical reactor. Parameters of the electrolysis were estimated using semi-industrial electrochemical reactor in which concentration of KI and current density were varied. pH and reactor voltage, were measured as a function of time, as well. The electrolysis was carried out until stationary concentration of equivalent iodine was reached. It was concluded that optimal electrolysis conditions based on current efficiency, concentrations of equivalent iodine, and the other parameters, was achieved in solution contained 0.40 mol dm⁻³ KI and with current density of 10 mA cm⁻². Based on the theoretical analysis of the iodine–iodide–water equilibria, it was concluded that at pH 11.6 main electrolysis products were triiodide, hypiodite and IOH₂⁻.

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1. Introduction

Iodine species or equivalent iodine (I₂)_{eq} refers to all species reacting with thiosulphate, such are I₂, I₃⁻, IO⁻, HOI₂⁻ and HOI formed by hydrolysis of iodine generate by electrochemical oxidation of iodide:



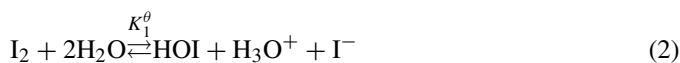
where $n = 0-2$ and $m = 0$ or 1 , see Eqs. (2)–(5).

Equivalent iodine can be used in disinfections, as intermediates in iodate and periodate production, as well as in indirect electroorganic synthesis.

Indirect electroorganic synthesis is based on anodic electrochemical production of a halide active species in situ, which react in solution with organic reactants. Examples of these reactions include the production of gluconic acid or calcium gluconate

by glucose oxidation [1–6] or xylonic acid from xylose [7] with hypobromite or hypobromous acid, or indirect oxidation of cyclohexanole to cyclohexanone with iodine [8], as well as the formation of iodoform and bromoform.

Depending on pH elementary iodine or iodine produced by electrochemical oxidation of iodide hydrolyses in reaction with water, and various products can be obtained. The main products of iodine hydrolysis are I₂, I₃⁻, IO⁻, HOI₂⁻ and HOI [9–12], and the basic reactions and equilibrium constant can be given as follows [9]:



$$K_1^\theta = K_1 = \frac{a(\text{HOI})a(\text{H}_3\text{O}^+)a(\text{I}^-)}{a(\text{I}_2)a^2(\text{H}_2\text{O})} = 5.4 \times 10^{-13} \quad (2a)$$



$$K_2^\theta = K_2 = \frac{a(\text{IO}^-)a(\text{H}_3\text{O}^+)}{a(\text{HOI})a(\text{H}_2\text{O})} = 2.5 \times 10^{-11} \quad (3a)$$

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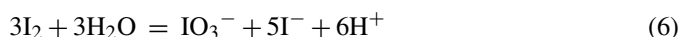


$$K_3^\theta = \frac{a(\text{I}_2\text{OH}^-)a(\text{H}_3\text{O}^+)}{a(\text{I}_2)a^2(\text{H}_2\text{O})} = 1.41 \times 10^{-11} \text{ mol}^{-1} \text{ dm}^3 \quad (4a)$$



$$K_4^\theta = \frac{a(\text{I}_3^-)}{a(\text{I}_2)a(\text{I}^-)} = 729 \text{ mol}^{-1} \text{ dm}^3 \quad (5a)$$

In some extreme conditions, like strong acidic media and at virtual absence of iodide, formation of the iodine cation (H_2OI^+) could be neglected [9]. Formation of iodate by disproportionation of I_2 , HOI , I_2OH^- or IO^- via overall reaction given by:



during the short time and modest temperature could be neglected too, since so called pre-equilibrium conditions which are valid in indirect electroorganic synthesis [8,9].

In this article the influence of iodide concentrations of aqueous solutions and current densities are presented for electrochemical oxidation in laboratory and semi-industrial use in order to estimate the optimal conditions for electrolysis and distribution of iodine species in the electrolyte.

2. Experimental

Polarization measurements in solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI (p.a., Merck) were investigated in tree compartment electrochemical cell. Dimensionally stable anode (DSA) based on Ti/RuO₂ [13], with surface area of 2 cm², was used as anode, saturated calomel electrode was used as reference electrode (while all potentials are referenced to standard hydrogen electrode), and platinum foil was used as counter electrode. Solution mixing was accomplished by nitrogen inlet. All experiments were performed at temperature of 20 °C. A circulating constant temperature bath maintained the temperature of the electrolyte within 0.5 °C. Temperature control was done by thermometer with accuracy of 0.1 °C. Potentiostat/galvanostat PAR 273A was used in all measurements, while ohmic drop used for corrections of the polarization curves between working and reference electrode was determined by electrochemical impedance spectroscopy at high frequency range, using phase sensitive Lock-in Amplifier PAR M5031.

Semi-industrial charge electrochemical reactor with volume of 700 cm³, given in Fig. 1, was used for determination of electrolysis parameters. Electrochemical reactor made of Plexiglas, was consisted of electrolyzer and reaction tank. Electrolyzer dimensions was 55 cm × 13 cm × 1 cm, while dimensions of reaction tank was 8 cm × 22 cm × 8 cm. Reaction tank served for product collection, in order to diminish the time of contact between products and cathode and anode that could lead to side reactions and lower reaction yield. Dimensionally stable titanium anode activated by RuO₂ coating [13] and mild steel cathode with surface area of 50 cm² and with electrode gap of 3 mm, was used. Mixing of the electrolyte was accomplished by

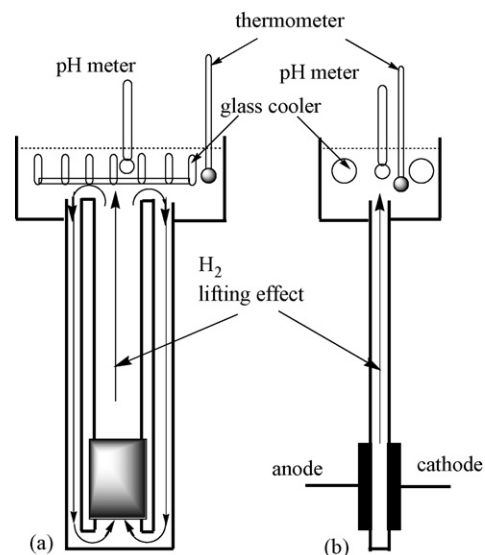


Fig. 1. Schematic representation of the semi-industrial charge electrochemical reactor (a) front and (b) side view.

lifting effect of evolved hydrogen. Electrolyte temperature was maintained using spiral glass cooler in the range of 20 ± 1 °C. Every 10 min of electrolysis, 2 cm³ of electrolyte were taken for titration. Also, voltage of the electrolyzer and pH were measured as a function of time. Electrolysis was performed with constant current density until stationary state of product concentration was reached.

The amount of equivalent iodine in reactor was determined by potentiometric titration, every 10 min of electrolysis, using standardized solution of 0.002 mol dm⁻³ sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$), p.a., Merck. Saturated calomel electrode and platinum sheet was used as reference and indicator electrode, respectively, while magnetic stirrer was used for stirring of the solution during titration.

3. Results and discussion

3.1. Polarization measurements

Polarization measurements in electrochemical cell were performed in order to estimate current densities in different concentrations of iodide that could be further used in electrochemical reactor. Slow potentiodynamic polarization curves ($v = 1 \text{ mV s}^{-1}$) for solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI in non-mixed electrolyte are shown in Fig. 2.

Polarization curves are characterized by two well-defined regions. At low potentials follow exponential Tafel law, see Fig. 4, but at higher potentials, decrease of the current density (without reaching the limiting value) was observed. In the former case, near the electrode dark coloring, probably as a result of evolved elementary iodine was observed. Decrease of the current density at higher potentials could be associated with imbalance in the rate of elementary iodine production (as a low soluble product, Eq. (1)), which increase with electrode potential, and chemical formation of iodine hydrolysis products in solution (as a soluble products, Eqs. (2)–(5)). Second reason could be

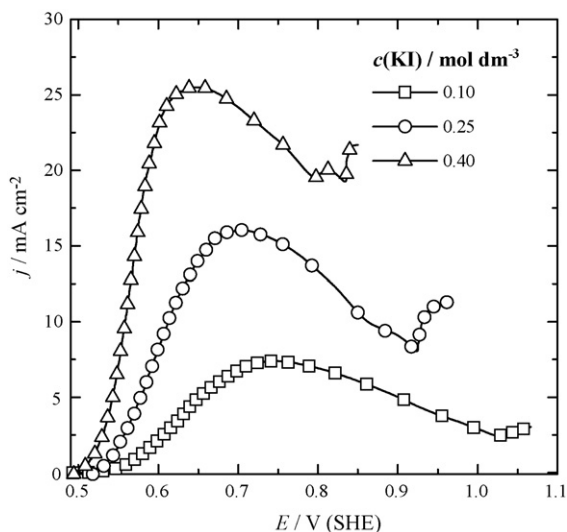
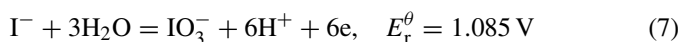


Fig. 2. Anodic polarization curves for iodide oxidation on Ti/RuO₂ anode in non-mixed solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI.

the electrochemical formation of iodate with the overall reaction and standard reversible potential, E_r^θ , given by:



The reversible potential of the reaction given by Eq. (7) is ~ 0.65 V for approximated concentration of iodate of 1×10^{-6} mol dm⁻³ and at pH ~ 7 . Taking into account overvoltage for this reaction of minimum ~ 0.2 V, critical potential at electrochemical formation of iodate can occur is ~ 0.85 V at pH 7.

To distinguish these two processes, Fig. 3 shows comparison of polarization curves obtained at potentiodynamic and steady state conditions in solution contained 0.10 mol dm⁻³ KI where

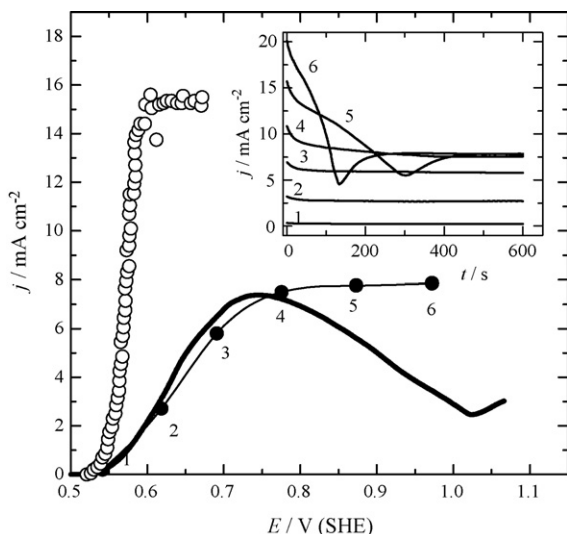


Fig. 3. Potentiodynamic anodic polarization curve for iodide oxidation on Ti/RuO₂ anode in non-mixed (—) and mixed (○) solutions contained 0.10 mol dm⁻³ KI. Numbered points represents steady state polarization curve in non-mixed electrolyte extrapolated from steady state current density from insert of figure. Insert: Chronoamperometric response at potentials of (1) 0.54, (2) 0.62, (3) 0.69, (4) 0.77, (5) 0.87 and (6) 0.97 V.

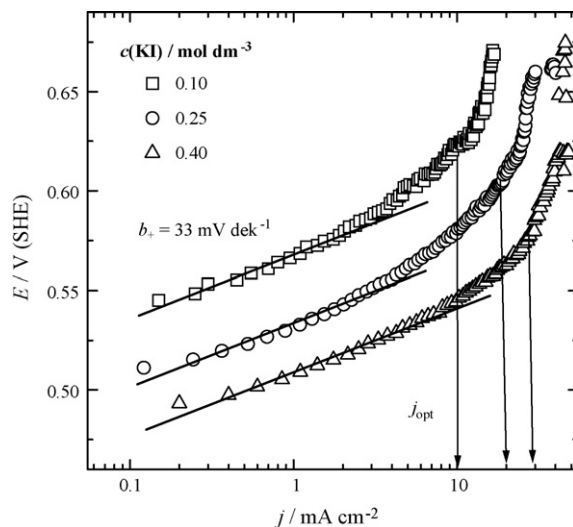


Fig. 4. Anodic polarization curves for iodide oxidation on Ti/RuO₂ anode in mixed solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI.

formation of elementary iodine was most pronounced. Steady state measurements were conducted in freshly prepared electrolyte to avoid influence of products at a constant potential (chronoamperometry), as shown in insert of Fig. 3. Up to potential of ~ 0.77 V steady state current density was reached within 20 s. At the higher potentials, initial decrease and further increase of the current density is observed and steady state conditions were reached after prolonged time. By plotting steady state current density as a function of applied potential corrected for the ohmic drop, the polarization curve (shown with numbered points in Fig. 3), with well-defined limiting current density plateau is obtained. Hence, it is reasonable to conclude that decrease of current density in the potentiodynamic conditions at higher potentials is a consequence of accumulation of low soluble iodine near electrode and slow hydrolysis, rather than electrochemical formation of iodate which theoretically can occur at potential higher than 0.85 V. But, possibility of electrochemical formation of iodate at higher potentials cannot be excluded, so electrolysis should be carried out at anodic potentials smaller than ~ 0.7 V.

Assuming that diffusion controlled chemical formation of soluble ions is slow, it is reasonable to conclude that mixing of the electrolyte will have significant effect, *note*: in electrochemical reactor intensive mixing of the electrolyte occurred as a result of evolved hydrogen at the cathode (lifting effect). Fig. 3 also shows potentiodynamic polarization curve ($v = 1 \text{ mV s}^{-1}$) in solution contained 0.10 mol dm⁻³ KI in mixed electrolyte. As it can be seen in Fig. 3, mixing of the electrolyte has significant effect on increase of the current density with potential, and limiting like current density plateau has been reached. It is important to note that limiting diffusion current density in mixed electrolyte was reached at potential of 0.6 V, where theoretically, electrochemical formation of iodate cannot be expected.

In order to estimate anodic current density for electrolysis, keeping in mind that concentration of iodide decrease during electrolysis, and to avoid possible anodic oxygen evolution or

iodate formation as side reactions, optimal current density value is approximately 30% lower than limiting diffusion current density. Based on polarization curves in mixed solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI (shown in Fig. 4 as Tafel plot) it can be estimated that optimal values of the current densities are 10, 20 and 30 mA cm⁻², respectively. Although, based on these experiments, the nature of species that limit the reaction cannot be distinguished, Tafel slope, b_+ , of 33 mV dec⁻¹ indicates diffusion control of the reaction.

3.2. Iodide oxidation in the semi-industrial electrochemical reactor

In order to determine concentration of equivalent iodine and parameters of electrolysis as a function of time, iodide oxidation was performed in semi-industrial electrochemical reactor. Fig. 5 shows dependence of steady state current density as a function of reactor voltage for solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI. Comparing Figs. 4 and 5 it can be concluded that determined optimum current densities in the laboratory cell are in good agreement with values in the semi-industrial electrochemical reactor.

Fig. 5 also shows that reactor voltage, U , increase with decrease of KI concentration from 0.40 to 0.10 mol dm⁻³. Reactor voltage can be given by the following equation:

$$U = U_0 + I \sum R + \sum |\eta| \quad (8)$$

where U_0 represent differences of reversible potentials of anodic and cathodic reaction, I current, $\sum R$ sum of the ohmic drops in the system, and $\sum |\eta|$ sum of the absolute values of anodic and cathodic overvoltages. Hence, increase of the reactor voltage with decrease of KI concentration is mainly connected with increase of the conductivity of the solution, and overvoltages with decrease of KI concentration in the system.

To determine concentration of equivalent iodine as a function of time at the constant current density, potentiometric titration

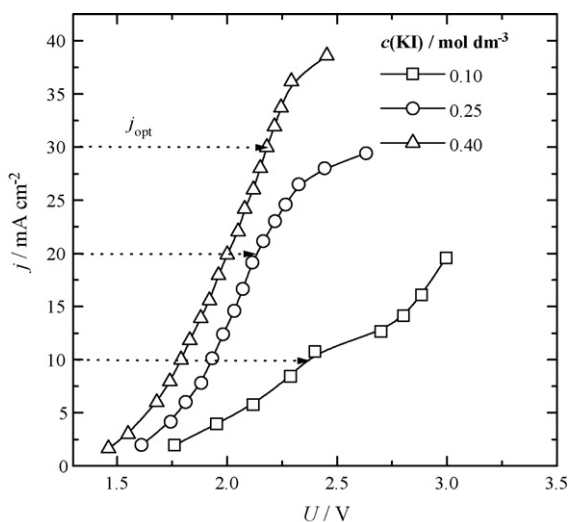


Fig. 5. Dependence of steady state current density as a function of reactor voltage for solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI in the semi-industrial electrochemical reactor.

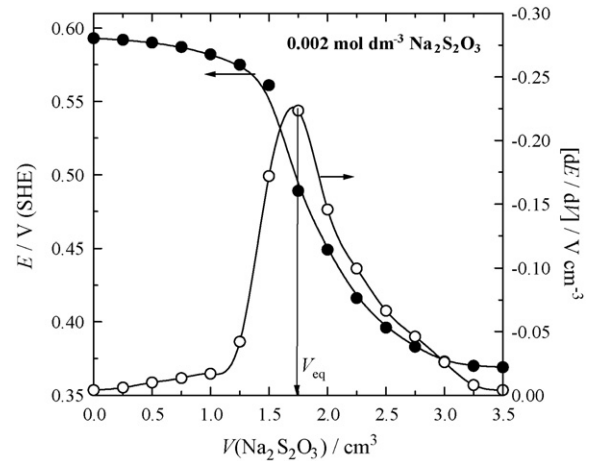
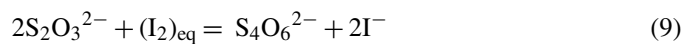


Fig. 6. Dependence of electrode potential on volume of added sodium thiosulphate (●) and its derivate (○).

with standardized solution of thiosulphate presented by the following simplified equation:



was used.

In Fig. 6, characteristic dependence of potential on added volume of thiosulphate in solution contained 0.40 mol dm⁻³ KI after 10 min of electrolysis is given. From the maximum of its derivate, V_{eq} was obtained and used for calculation of concentration of equivalent iodine.

The time dependence of equivalent iodine in solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI at current density of 10 mA cm⁻² is given in Fig. 7. Dash line refers to the theoretical value of equivalent iodine concentration as a function of time which is calculated using Faraday law and assuming that every

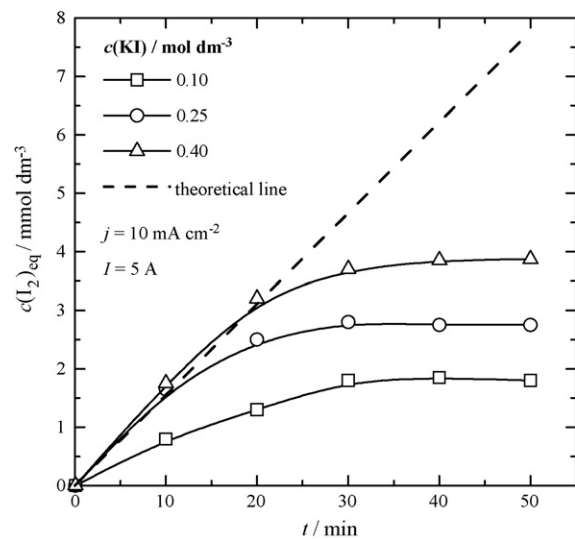


Fig. 7. Dependence of concentration of equivalent iodine as a function of time for electrolysis of solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI at a current density of 10 mA cm⁻² ($I = 5$ A).

Table 1

Characteristic main values of electrolysis parameters in solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI at a current density of 10 mA cm⁻² ($I = 0.5$ A)

$c(\text{KI})$ (mol dm ⁻³)	$c(\text{I}_2)_{\text{eq,ss}}$ (mmol dm ⁻³)	η_{in} (%)	U (V)	pH	w_{sp} (Wh mol ⁻³ dm ³)
0.10	1.81	33	2.71	11.6	621
0.25	2.75	55	2.06	11.6	312
0.40	3.91	73	1.84	11.6	196

active species requires two electrons:

$$n(\text{I}_2)_{\text{eq}} = \frac{It}{2F} \quad (10)$$

Concentration of the equivalent iodine increased over time and after approximately 30 min stationary state was reached. Depending of concentrations of KI, stationary concentration of the equivalent iodine was in the range of 1.85–3.91 mmol dm⁻³, see Table 1. During electrolysis in solution contained 0.10 mol dm⁻³ KI precipitation of elementary iodine at the bottom of the reactor was observed.

Stationary state concentration of equivalent iodine, $c(\text{I}_2)_{\text{eq,ss}}$ could be accomplished with specific balance between rates of electrochemical oxidation of iodide, chemical reactions of iodine hydrolysis (equivalent iodine formation), electrochemical reaction in which formed equivalent iodine is reduced to iodide on the cathode and the chemical reaction in solution of equivalent iodine disproportionation to iodide and iodate, as shown in the simplified scheme in Fig. 8.

Assuming that rate of the first step (oxidation of iodide) is the same for all investigated concentrations, increase of the steady state concentration of equivalent iodine with increase of iodide

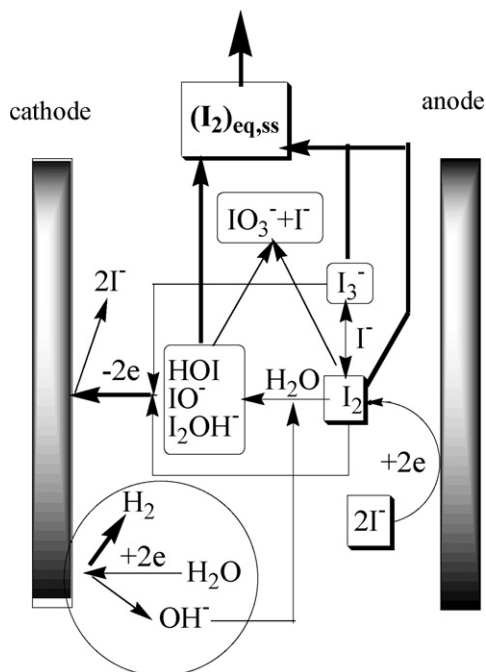


Fig. 8. Schematic representation of equivalent iodine formation in electrode compartment.

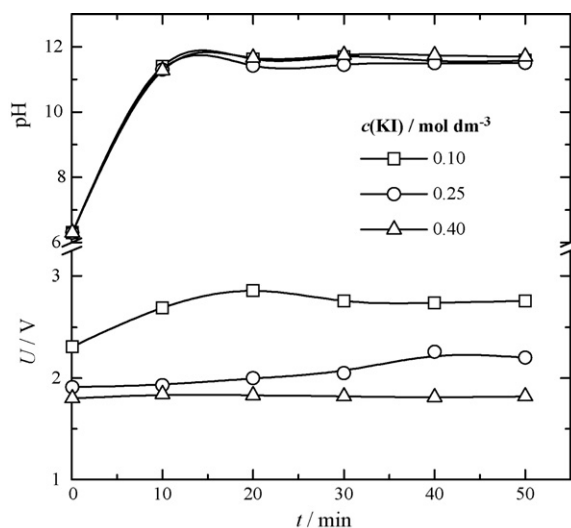


Fig. 9. Time dependences of pH and voltage for the electrolysis of solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI at 10 mA cm⁻² ($I = 5$ A).

concentration at the constant current density could be explained as follows. For low concentration of iodide (0.10 mol dm⁻³), elementary iodine cannot easily form soluble triiodide, and low soluble elementary iodine is formed near anode:



Evolved iodine partially precipitates as an insoluble product and partially undergo to the formation of triiodide and hydrolysis with formation of HOI, I₂OH⁻ and IO⁻, which can be reduced on cathode to iodide. Increasing the concentration of iodide from 0.10 to 0.25 and 0.40 mol dm⁻³ accelerate formation of triiodide that leads to decrease in concentration of HOI, I₂OH⁻ and IO⁻ (see Section 3.3). Hence, increase of steady state concentration of equivalent iodine with increase of iodide concentration can be mainly attributed to the iodine–triiodide equilibria. As it can be seen from Fig. 7 for the times shorter than 15 min calculated theoretical line closely follows experimental points in solutions contained 0.25 and 0.40 mol dm⁻³ KI. Hence, it is reasonable to conclude that chemical formations of iodate do not occur in that period of time.

During electrolysis pH from the initial value of ~6, after 10 min increased to stationary value of ~11.6 in all investigated solutions, as shown in Fig. 9. This can be attributed to the imbalance in consumption of evolved OH⁻ at cathode:



by chemical reaction of iodine hydrolysis near anode, as shown in Fig. 8. Fig. 9 also shows that steady state reactor voltage, increased from 1.8 up to 2.7 V with decreased concentration of KI from 0.40 to 0.10 mol dm⁻³ as explained by Eq. (8).

Calculated current efficiency as a function of time for production of equivalent iodine in solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI is shown in Fig. 10. For the solutions contained 0.25 and 0.40 mol dm⁻³ KI, the initial efficiency was 100% after 10 min of electrolysis. On the contrary, for the solution contained 0.10 mol dm⁻³ KI, the initial efficiency was

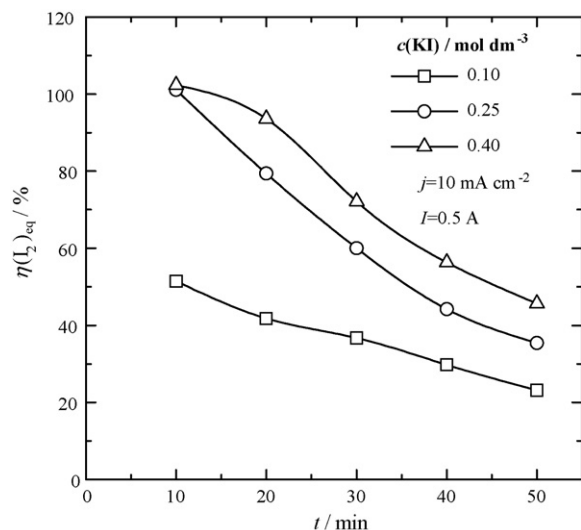


Fig. 10. Dependence of calculated current efficiency as a function of time in solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI at a current density of 10 mA cm⁻² ($I = 5 \text{ A}$).

~55%, which is probably connected with formation of insoluble elementary iodine. Decrease of the current efficiency after prolonged electrolysis was a result of stationary state conditions, mainly reduction of equivalent iodine on the cathode and possible chemical formation of iodate.

The value of the integral current efficiency, defined as the ratio of experimentally determined (ex) and theoretical (T) values of concentration as a function of time is given as:

$$\eta_{in} = \frac{\int_0^t c(I_2)_{eq,ex} dt}{\int_0^t c(I_2)_{eq,T} dt} \cdot 100 \quad (12)$$

Based on above results, characteristic main values of electrolysis parameters in solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI are summarized in Table 1.

From the results summarized in Table 1 it could be concluded that increase of iodide concentration lead to increase of stationary concentration of equivalent iodine, as well as increase of integral current efficiency, decrease of the voltage loss and specific energy consumptions (w_{sp}). According to presented results, optimal value of iodide concentration would be ~0.40 mol dm⁻³.

The influence of the current density, i.e. current, on the concentration of equivalent iodine for electrolysis of 0.40 mol dm⁻³ KI is shown in Fig. 11, and characteristic electrolysis parameters are summarized in Table 2.

Table 2

Values of integral current efficiency and mean voltage for electrolysis of solution contained 0.40 mol dm⁻³ KI at different current densities, i.e. current

$j \text{ (mA cm}^{-2}\text{)}$	$I \text{ (A)}$	$c(I_2)_{eq,ss} \text{ (mmol dm}^{-3}\text{)}$	$\eta_{in} \text{ (%)}$	$U \text{ (V)}$
10	0.5	3.91	73	1.84
20	1.0	3.26	34	2.01
30	1.5	2.23	17	2.18

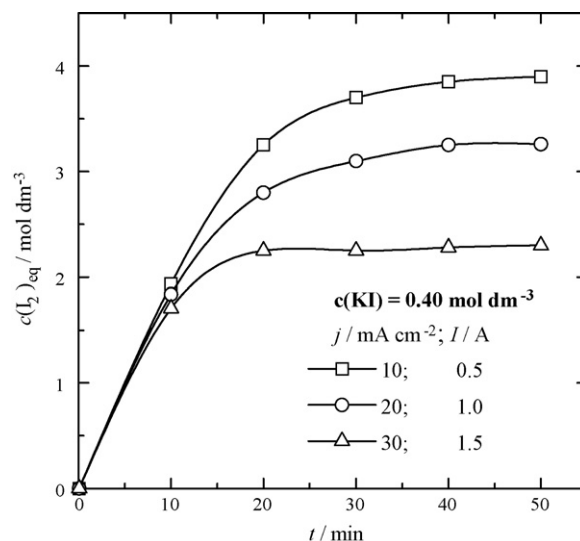


Fig. 11. The influence of current density, i.e. current, on concentration of equivalent iodine for electrolysis of solution contained 0.40 mol dm⁻³ KI.

From Fig. 11 and Table 2 it could be clearly seen that increase of current density lead to decrease of integral current efficiency, decrease in concentration of equivalent iodine and increase of the electrolysis voltage. This is mainly resulted in acceleration of undesirable cathodic reactions of equivalent iodine reduction with increase of the current density and increase of overvoltages. According to Fig. 11 and Table 2, optimal value of current density would be 10 mA cm⁻². Even the integral current efficiency for higher current densities is rather small, for some indirect electroorganic reaction that could be accomplished over short time, higher current densities (e.g. 25–30 mA cm⁻²) can be used due to the initially high current efficiency of equivalent iodine production.

3.3. Distribution of iodine species in aqueous solution in the preequilibrium conditions

The distribution of iodine species (free iodine, triiodide, hypoiodous acid, I_2OH^- and hypoiodite) in a solution contained iodide as a function of pH can be calculated starting from the chemical equilibria, given by Eqs. (2)–(5).

Assuming that concentration corresponds to activity and that water has unit activity, the following procedure was used to determine the distribution of iodine species as a function of pH. The mass-balance equation with respect to free iodine, $c(I_2)_s$, in the solution can be given by:

$$c(I_2)_s = c(I_2)_T - c(I_3^-) - c(HOI) - c(IO^-) - c(I_2OH^-) \quad (13)$$

where $c(I_2)_T$ is the total analytical concentration of iodine in the solution.

Dividing Eq. (13) by $c(I_2)_s$, the following is obtained:

$$1 = \frac{c(I_2)_T}{c(I_2)_s} - \frac{c(I_3^-)}{c(I_2)_s} - \frac{c(HOI)}{c(I_2)_s} - \frac{c(IO^-)}{c(I_2)_s} - \frac{c(I_2OH^-)}{c(I_2)_s} \quad (14)$$

This on rearrangement gives:

$$c(I_2)_s = c(I_2)_T \left[1 + \frac{c(I_3^-)}{c(I_2)_s} + \frac{c(HOI)}{c(I_2)_s} + \frac{c(IO^-)}{c(I_2)_s} + \frac{c(I_2OH^-)}{c(I_2)_s} \right]^{-1} \quad (15)$$

In order to solve Eq. (15), it is necessary to rearrange Eqs. (2a)–(5a) in the following manner:

$$\frac{c(HOI)}{c(I_2)_s} = \frac{K_1}{c(H_3O^+)c(I^-)} \quad (2b)$$

$$c(IO^-) = \frac{K_2 c(HOI)}{c(H_3O^+)} \quad (3b)$$

$$\frac{c(I_2OH^-)}{c(I_2)_s} = \frac{K_3^\theta}{c(H_3O^+)} \quad (4b)$$

$$\frac{c(I_3^-)}{c(I_2)_s} = K_4^\theta c(I^-) \quad (5b)$$

Introducing Eqs. (2b)–(5b) into Eq. (15), the following equation is obtained:

$$\begin{aligned} c(I_2)_s &= c(I_2)_T \left[1 + K_4^\theta c(I^-) + \frac{c(HOI)}{c(I_2)_s} + \frac{K_2 c(HOI)}{c(I_2)_s c(H_3O^+)} + \frac{K_3^\theta}{c(H_3O^+)} \right]^{-1} \\ &= c(I_2)_T \left\{ 1 + K_4^\theta c(I^-) + \frac{c(HOI)}{c(I_2)_s} \left[1 + \frac{K_2}{c(H_3O^+)} \right] + \frac{K_3^\theta}{c(H_3O^+)} \right\}^{-1} \\ &= c(I_2)_T \left\{ 1 + K_4^\theta c(I^-) + \frac{K_1}{c(H_3O^+)c(I^-)} \left[1 + \frac{K_2}{c(H_3O^+)} \right] + \frac{K_3^\theta}{c(H_3O^+)} \right\}^{-1} \end{aligned} \quad (16)$$

From Eq. (16) the pH dependence of the free iodine in the solution can be calculated.

Once the pH dependence of the free iodine concentration is known, it is also possible to calculate, by a similar procedure, the pH dependence of the concentrations of every other species in the solution. Thus, for hypiodous acid, after the introduction of Eqs. (3b), (4b) and (5b) into Eq. (14):

$$1 = \frac{c(I_2)_T}{c(I_2)_s} - K_4^\theta c(I^-) - \frac{c(HOI)}{c(I_2)_s} - \frac{K_2 c(HOI)}{c(I_2)_s c(H_3O^+)} - \frac{K_3^\theta}{c(H_3O^+)} \quad (17)$$

the pH dependence of the hypiodous acid in the solution can be obtained by rearrangement:

$$c(HOI) = c(I_2)_s \left(1 + \frac{K_2}{c(H_3O^+)} \right)^{-1} \left(\frac{c(I_2)_T}{c(I_2)_s} - 1 - K_4^\theta c(I^-) - \frac{K_3^\theta}{c(H_3O^+)} \right) \quad (18)$$

For the determination of the concentration of hypiodite, Eq. (14) must be modified in the following manner:

$$-\frac{c(IO^-)}{c(I_2)_s} = 1 - \frac{c(I_2)_T}{c(I_2)_s} + \frac{c(I_3^-)}{c(I_2)_s} + \frac{c(HOI)}{c(I_2)_s} + \frac{c(I_2OH^-)}{c(I_2)_s} \quad (19)$$

After the introduction of Eqs. (2b), (3b) and (5b) into Eq. (19) and rearranging, the concentration of hypiodite as a function of pH is given by:

$$c(IO^-) = c(I_2)_s \left(\frac{c(I_2)_T}{c(I_2)_s} - 1 - K_4^\theta c(I^-) - \frac{K_1}{c(I^-)c(H_3O^+)} - \frac{K_3^\theta}{c(H_3O^+)} \right) \quad (20)$$

Applying a similar procedure, the concentrations of I_2OH^- and triiodide in the solution as a function of pH can be obtained from a modified form of Eq. (14). Thus, for I_2OH^- rearranged Eq. (14) can be given by:

$$c(I_2OH^-) = c(I_2)_s \left\{ \frac{c(I_2)_T}{c(I_2)_s} - 1 - K_4^\theta c(I^-) - \frac{K_1}{c(H_3O^+)c(I^-)} \left[1 + \frac{K_2}{c(H_3O^+)} \right] \right\} \quad (21)$$

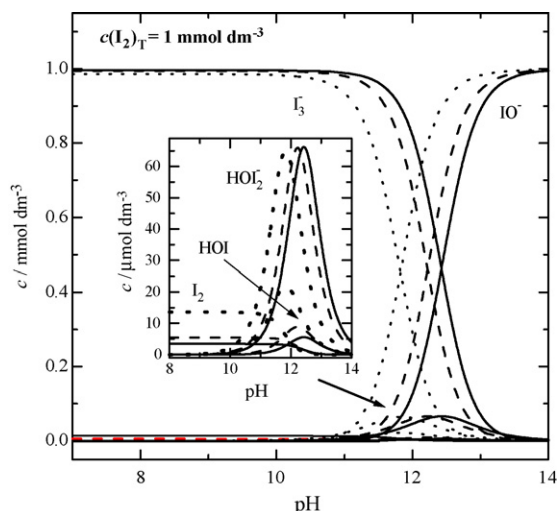


Fig. 12. Calculated distribution of equivalent iodine species in solutions containing (· · ·) 0.10, (---) 0.25 and (—) 0.40 mol dm⁻³ KI as a function of pH.

and for tribromide, by:

$$c(\text{I}_3^-) = c(\text{I}_2)_s \left\{ \frac{c(\text{I}_2)_T}{c(\text{I}_2)_s} - 1 - \frac{K_1}{c(\text{H}_3\text{O}^+)c(\text{I}^-)} \times \left[1 + \frac{K_2}{c(\text{H}_3\text{O}^+)} \right] - \frac{K_3^\theta}{c(\text{H}_3\text{O}^+)} \right\} \quad (22)$$

From Eqs. (16), (18), (20), (21) and (22), it is possible, using a simple mathematical program, to obtain the distribution of iodine species in solution containing iodide as a function of pH.

Based on above given analysis, calculated distribution of equivalent iodine species in solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI as a function of pH are given in Fig. 12. The equivalent iodine concentration of approximately 1.0 mmol dm⁻³ has been assumed for the 5 min electrolysis (which is time in all organic should react) and 100% current efficiency of equivalent iodine production in practically all concentrations of KI.

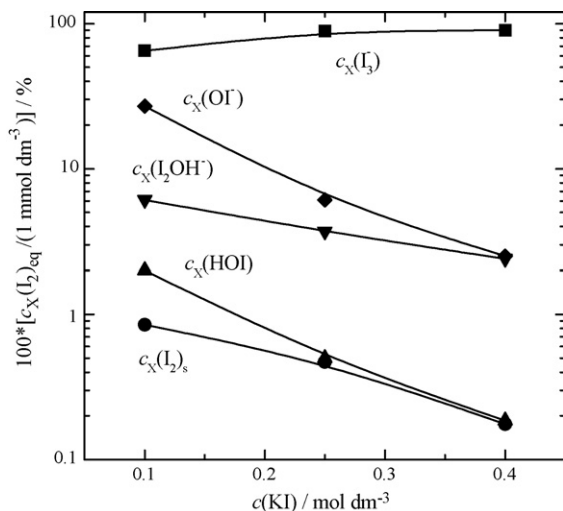


Fig. 13. Concentration of equivalent iodine species at pH 11.6 extrapolated from Fig. 12.

As it can be seen, at pH smaller than 10, main pre equilibrium products are triiodide and small amounts of free iodine. Increase of the pH above 11 lead to decrease in concentration of triiodide and free iodine, and increase of hypoiodous acid, I_2OH^- and hypoiodide.

In Fig. 13 dependence of calculated concentrations of iodine species for different iodide concentrations at pH 11.6 are shown.

Increase of concentration of triiodide, and decrease of free iodine, hypoiodous acid, I_2OH^- and hypoiodide with increase of iodide concentration, as a consequence of chemical equilibria, are in agreement with explanations given in Section 3.2.

4. Conclusion

Based on the experimental investigations in laboratory cell and semi-industrial electrochemical reactor, it has been concluded that optimal current density for electrolysis of solutions contained 0.10, 0.25 and 0.40 mol dm⁻³ KI was 10 mA cm⁻². Concentration of the equivalent iodine (I_2 , I_3^- , IO^- , HOI_2^- and HOI) increased over time and after approximately 30 min stationary state, was reached. Depending of concentrations of KI, stationary concentration of the equivalent iodine was in the range of 1.85–3.91 mmol dm⁻³. Increase of iodide concentration lead to increase of stationary concentration of equivalent iodine, as well as increase of integral current efficiency, decreases of the voltage loss and specific energy consumptions. Based on the theoretical analysis of the iodine–iodide–water equilibria the highest amount of the most active species (I_2OH^- , HOI and OI^-) are obtained in solution contained 0.10 mol dm⁻³ KI at pH 11.6, but due to the smaller voltage loss and better current efficiency, higher concentrations of potassium iodide, 0.4 mol dm⁻³, should be used.

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