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The effect of kinetic and hydrodynamic factors on current efficiency in the chlorate cell process*

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An equation has been derived which relates the current efficiency of chlorate production to the operational parameters of the process and the constants connected with the events in the diffusion layer of the anode. The latter have been estimated using available literature data and the equation has been tested for the temperature dependence of current efficiency by comparison with experimental results. A fair degree of agreement has been achieved.

1. Introduction

Current efficiency in the electrochemical production of chlorates exhibits a rather complex dependence on the numerous operational variables of the process, such as the rate of circulation of the electrolyte, q, cell load, I, the total electrode surface area, A, pH of the electrolyte, the ratio of the volumes of the cell, V_c, and of the holding vessel in which chemical conversion of active chlorine into chlorate takes place, V_h, and their respective temperatures, t_c and t_h. The theory developed so far has been able to relate some of these parameters to current efficiency [1]. However, these relations contained the concentrations of available chlorine† in the cell, C_{sc}, and in the holding volume, C_{sh}, as additional variables which had to be assessed experimentally for each particular run. It is obvious, however, that these variables themselves are dependent on the operational variables and a theory is needed which would give the dependence of current efficiency and the two concentrations on operational parameters only.

In effect, the relation resulting from the existing theory (cf. Equation (4) below) reflects merely the stoichiometry of two possible processes taking part in the system: that of direct electro-oxidation of chloride to chlorate, and that in which electro-oxidation of chloride to hypochlorite is followed by chemical conversion of the latter into chlorate. As such, it could be usefully employed for confirming the validity of the Foerster [2] stoichiometric equations over a large range of variables [1]. However, it takes no account of the basic causes of variation in the current efficiency which are related to the electrode process kinetics. Hence, it could not explain such effects as the dependence of current efficiency on the velocity of motion of the electrolyte past the anode [3] (cf. [4]), buffering action of chromate [5], etc.

It was the purpose of this work to develop a theory encompassing all these effects and to investigate some experimental results in view of its predictions.

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† 'Available chlorine' comprises the sum of concentrations of hypochlorous acid, hypochlorate ion and dissolved elemental chlorine. However, at the pH of electrolytic chlorate production the latter can be neglected; the term active chlorine will therefore be used for hypochlorous species only.

2. Derivation of current efficiency in the chlorate cell process

2.1. *Treatment of the complex diffusion conditions*

Ibl and Landolt [6] have shown that the diffusion layer in the chlorate cell process is of a very complex nature. The hydrolysis of chlorine, generated at the anode, into hypochlorous species (acid and its anion) takes place within the diffusion layer. Hence, those species diffuse in two directions—towards the electrode and towards the bulk of solution. Ibl and Landolt were able to show that the concentration profile of these species can exhibit a maximum even inside the diffusion layer [6].

They have derived an equation for the concentration gradient of active chlorine at the electrode surface. Their equation, however, was strictly applicable to dilute solutions only. In the concentrated electrolyte of the chlorate cell it is the activity gradient which is the driving force of diffusion and the activities of chlorine and water govern the rate of hydrolysis.

A complication arises when one attempts to take this into account. This is because the active chlorine is not a single species and the activity coefficients of hypochlorite ion and hypochlorous acid can differ considerably (see below). In an attempt to make the Ibl–Landolt equation applicable to concentrated solutions, a formal activity coefficient of available chlorine, f_{sc}, was introduced and the implications are discussed further below. With such a concept the corrected Ibl–Landolt equation could be written as

$$\left(\frac{\partial a_{sc}}{\partial x}\right)_{x=0} = \frac{it_1}{2FD_2} + \frac{1}{\delta}\left\{f_{sc}C_{sc} - \frac{it_1[1-\exp(-\delta\sqrt{k_1/D_1})]}{2FD_2\sqrt{k_1/D_1}}\right\} \qquad (1)$$

i is the current density, t_1 is the current efficiency of chloride oxidation to chlorine, k_1 is the rate constant of hydrolysis of chlorine at the high ionic strength of the electrolyte, D_1 and D_2 are diffusion coefficients of elemental chlorine and the hypochlorous species, respectively, while δ is the Nernst diffusion layer thickness. The latter is related to the velocity of flow of electrolyte past the anode.

In one of his earlier papers Ibl [7] assumed that all the available chlorine that reaches the electrode is oxidized into chlorate. Hence, he found no need to make distinction between fluxes of hypochlorous acid and of hypochlorite ions. As will be seen later, this assumption does not seem to be fully justified and a possible way around it is suggested below. However, this way is only an approximate one. A more complete model is currently being developed and will be reported on later. If, as a first approximation, Ibl's assumption were adopted one could equate

$$\frac{it_2}{F} = D_2\left(\frac{\partial a_{sc}}{\partial x}\right)_{x=0} \qquad (2)$$

where t_2 is the fraction of the current used for that oxidation. Since $t_1+t_2=1$, combining Equations (1) and (2) it is possible to derive an equation for the current efficiency of chloride oxidation, t_1, as

$$t_1 = \frac{1-\dfrac{D_2F}{i\delta}\cdot f_{sc}C_{sc}}{\dfrac{3}{2}-\dfrac{1-\exp(-\delta\sqrt{k_1/D_1})}{2\delta\sqrt{k_1/D_1}}} \qquad (3)$$

If, for the chlorate formation, one considered as 100% efficient, the process in which the electrochemical oxidation went only to the hypochlorous species and chlorate was obtained by further chemical conversion (the Foerster equation [2]), one can show that the current efficiency of chlorate formation is the same as that of chloride oxidation.

The current efficiency t_1 is seen to be a complex function of the properties of the system (k_1, D_1, D_2, f_{sc}), of the operational parameters i, δ and of the bulk concentration of the active chlorine C_{sc}. t_1 is also temperature-dependent since, k_1, D_1, D_2, f_{sc} and C_{sc} are all temperature-dependent entities.

At a steady state operation of the chlorate cell the available chlorine concentration C_{sc} is itself a complex variable [1]. Hence, implicit in Equation (3) are also all other operational parameters, mentioned at the outset of this work.

2.2. *Current efficiency as a function of operational parameters only*

To eliminate the variable C_{sc}, one can use the material balance equation for the cell (cf. [1])

$$\frac{3}{2}\frac{I}{F}\left(t_1 - \frac{2}{3}\right) = (C_{sc} - C_{sh})q \qquad (4)$$

where C_{sh} is the available chlorine concentration in the holding volume.

In Equation (4) one has neglected the contribution of the chemical conversion of available chlorine into chlorate in the cell and the effect of that on current efficiency (cf. [1]). This is the more justified the smaller is the cell compared to the holding volume ($V_c \ll V_h$) and the larger is the temperature difference between the two parts of the system.

For the holding volume one can write [1] the balance as

$$q(C_{sc} - C_{sh}) = 3k_{r,h}\, V_h \cdot \frac{K_h^* \cdot (a_{\mathrm{H_3O^+}})_h^2 \cdot C_{sh}^3}{[K_h^* + (a_{\mathrm{H_3O^+}})_h]^3} \qquad (5)$$

where

$$k_{r,h} = f_h^2 \cdot k_{r,h}^0 \qquad (6)$$

and $k_{r,h}^0$ is the rate constant of chemical conversion of available chlorine into chlorate in the holding volume at infinite dilution, V_h is the holding volume and K_h^* is a modified dissociation constant of hypochlorous acid (cf. [8]).

In Equation (6) f_h is the activity coefficient of hypochlorous acid and f_h^2—Brönsted kinetic coefficient. Combining Equations (3), (4) and (5) one can eliminate both C_{sc} and C_{sh} to obtain

$$a^3 t_1^3 + 3a^2 b t_1^2 + (3ab^2 - c)t_1 + b^3 + \frac{2}{3}c = 0 \qquad (7)$$

where

$$a = -\frac{\frac{3}{2} - [1 - \exp(-\delta\sqrt{k_1/D_1})]/2\delta\sqrt{k_1 D_1}}{D_2 \cdot F \cdot f_{sc} \cdot A/I\delta} - \frac{3}{2}\frac{I}{Fq} \qquad (8)$$

$$b = \frac{I}{Fq} + \frac{I}{D_2 F A f_{sc}} \qquad (9)$$

$$c = \frac{I \cdot [K_h^* + (a_{\mathrm{H_3O^+}})_h]^3}{2 \cdot k_{r,h} \cdot F \cdot V_h \cdot K_h^* \cdot (a_{\mathrm{H_3O^+}})_h^2} \qquad (10)$$

and A is the electrode surface area.

Explicit solution of Equation (7) for t_1 is not possible. It can be seen, however, that t_1 in this equation depends on the operational parameters of the process only and in a well-defined way. The dependence of t_1 on temperature is contained primarily in the temperature dependence of k_1, $k_{r,h}$ and k_h^*.

In this work it is this latter dependence that has been investigated experimentally. The results of these experiments as well as the interpretation based on the use of Equation (7) are shown below.

3. Experimental and results

The apparatus for investigating the dependence of t_1 on the holding volume temperature consisted of an electrolytic cell 0·6 l in volume and a holding vessel of 2·2 l connected in a loop, so as to allow constant circulation of electrolyte at a given flow rate ($q = 8{\cdot}2 \times 10^{-4}$ l sec^{-1}). pH in the cell was maintained constant (6·0 ± 0·1) by means of a pH-stat. The electrolyte was stirred both in the cell and in the holding vessel so that they operated as back-mix-flow reactors.

Stirring in the cell was helped by the cathodic evolution of hydrogen and an appropriate positioning of both the platinum gauze anode and the wire cathode.

In the described setup and at the given hydrodynamic conditions, the diffusion layer thickness was determined experimentally to be $8{\cdot}2 \times 10^{-4}$ cm, by measuring the steady-state limiting diffusion current of the oxidation of ferrocyanides from an appropriate electrolyte (cf. [6]).

The cell load was maintained at 4·5 A. With the electrolyte surface area $A = 67{\cdot}5$ cm^2, that implied a current density of 66·7 mA cm^{-2}.

The cell temperature was maintained at 25°C, while that of the holding vessel was varied between 15 and 80°C.

The details of the apparatus and of the determination of t_1 have been described elsewhere [1].

The results of the investigation are presented in Fig. 1.

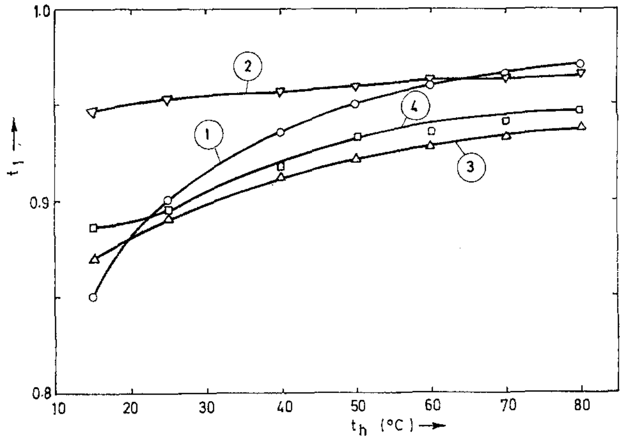

Fig. 1. Current efficiency of chlorate production as a function of holding volume temperature at constant temperature (25°C) and pH (6·0) in the cell. Curve 1—experimental data; curve 2—calculated values using Equation (7) and f_{sc} according to Equation (19); curve 3—calculated values according to Equation (7) using $f_{sc} = 0{\cdot}1$; curve 3—calculated values according to Equation (3) using experimental values of C_{sc}.

4. Discussion

To verify the applicability of Equation (7) for determining the current efficiency of chlorate production at any one temperature, one needs the values of the parameters of the system k_1, D_1, D_2, f_{sc}, $k_{r,h}$ and K_h^*, contained in the constants defined by (8), (9), and (10) in addition to the known operational parameters. Of these, the temperature dependence is needed only for the last two which define the constant c, since they pertain to the holding volume whose temperature has been changed in the described experiments.

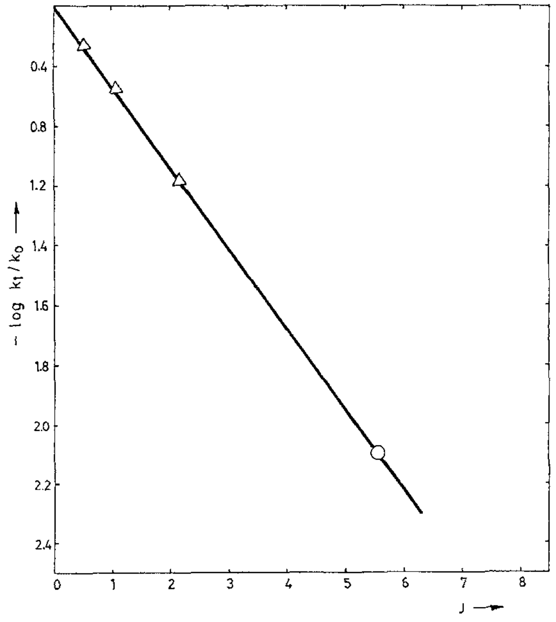

Fig.2. The rate constant of chlorine hydrolysis at 25°C in Na_2SO_4 solution as a function of ionic strength (according to Spalding [9]).

4.1. *The rate constant of chlorine hydrolysis at high ionic strength*

Spalding [9] has found the value of the rate constant of chlorine hydrolysis at infinite dilution to be 21 sec^{-1}. This is in fair agreement with the data of Brain *et al.* [10, 11]. Moreover, he has investigated the effect of ionic strength on the rate constant using sulphate solution. His data are plotted in Fig. 2 (triangles).

It is reasonable to assume that the ionic strength effect would be similar in chloride solutions. Hence, at an ionic strength of 5–6, as is that of the brine for chlorate production, k_1 can be expected to be about 0·17 sec^{-1} (Fig. 2).

4.2. *Diffusion coefficients of elemental chlorine and hypochlorous species*

Chao [12] used chronopotentiometry to determine diffusion coefficients of Cl_2, HOCl and OCl^- in aqueous media as functions of temperature and ionic strength. He has shown that the product of the viscosity (η) of the solution and diffusion coefficients of the species remains virtually constant with ionic strength. Hence, using his values of the ηD products at 25°C for ionic strength equal to 1 and the values of viscosity of brine at the ionic strength 5–6 one can calculate D_1 and D_2 as $6{\cdot}7\times10^{-6}$ $cm^2\ sec^{-1}$ and $1{\cdot}2\times10^{-5}$ $cm^2\ sec^{-1}$, respectively.

One should note that there are indications that diffusion coefficients do not change appreciably with ionic strength, *provided* activity gradients of the diffusing species are employed in the Fick's equations for computing the fluxes. After the activity coefficient of available chlorine had been estimated at the ionic strength of the brine, this point was also proven by analysing some results of Ibl (see below).

4.3. *Activity coefficient of available chlorine*

This problem appears to be of fundamental importance for quantitative interpretations of relationships in chlorate electrolysis.

If indeed both species are oxidized at the electrode independently at their diffusion limiting currents, or, even if OCl^- ions only are oxidized but the forward and reverse rates of the dissociation reaction

$$HClO + H_2O \rightleftharpoons ClO^- + H_3O^+ \tag{11}$$

are so high that at any point and time the equilibrium (11) is maintained, the formal activity coefficient of available chlorine should be related to the activity coefficients of hypochlorous species by the equality

$$f_{sc}C_{sc} = f_{sc}(C_{ClO^-} + C_{HClO}) = f_{ClO^-}C_{ClO^-} + f_{HClO}C_{HClO} \tag{12}$$

Activity coefficients f_{ClO^-} and f_{HClO} can be assessed from the existing experimental material.

Thus, f_{HClO} at the ionic strength of the brine should be of the order of 2 [13].

On the other hand, f_{ClO^-} can be estimated if the data of Landolt and Ibl [6] on the oxidation of available chlorine at high pH values are analysed. The experimentally obtained fluxes, over a wide range of conditions of current density, diffusion layer thickness, and temperature and at a pH in the cell at which all the available chlorine must be in the form of ClO^-, can be interpreted quantitatively by Equation (1), only if the activity coefficient is taken to be of the order of 0·1 [14].

One can find the concentrations C_{HClO} and C_{ClO^-} in the cell from the following equations

$$C_{HClO} + C_{ClO^-} = C_{sc} \tag{13}$$

$$\frac{C_{ClO^-}}{C_{HClO}} = K_{ac}\frac{f_{HClO}\cdot a_{H_2O}}{f_{ClO^-}\cdot a_{H_3O^+}} = \alpha \tag{14}$$

where K_{ac} is the thermodynamic equilibrium constant for reaction (11) at the cell temperature. Hence

$$C_{HClO} = \frac{C_{sc}}{1+\alpha} \tag{15}$$

and

$$C_{ClO^-} = \frac{\alpha\cdot C_{sc}}{1+\alpha} \tag{16}$$

Inserting (15) and (16) in (12) and rearranging, one obtains

$$f_{sc} = f_{ClO^-}\cdot f_{HClO}\cdot \frac{a_{H_3O^+} + K_{ac}\cdot a_{H_2O}}{f_{ClO^-}\cdot a_{H_3O^+} + f_{HClO}\cdot K_{ac}\cdot a_{H_2O}} \tag{17}$$

With the above values for f_{ClO^-} and f_{HClO} and taking $K_{ac} = 2{\cdot}9\times10^{-8}$ at 25°C[15], one obtains the function of f_{sc} vs. pH which is shown in Fig.

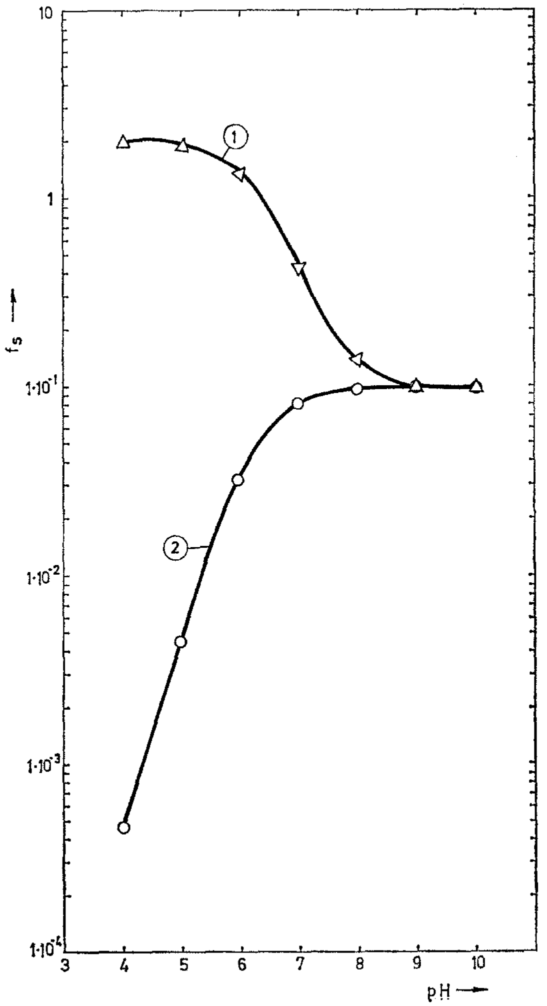

Fig. 3. The formal activity coefficient of active chlorine according to the two models of events at the anode. Curve 1— Equation (17); curve 2—Equation (19).

3 (curve 1). From this it is seen that at pH = 6, $f_{sc} \approx f_{ClO^-}$. On the other hand, one should not overlook the possibility that only OCl^- ions are oxidized (as maintained by Ibl [6] in his more recent work, and as indeed seems reasonable on the basis of the standard oxidation potentials), and the reaction (11) is slow so that in a limiting case no equilibration takes place in the reaction layer at rates necessary to allow discharge of OCl^-. In such a case it is only the flux of OCl^- ions that reduces the current efficiency t_1. Hence, all the derived equations are valid but one should use an appropriate value of f_{sc} which arises from the following consideration: $f_{sc}C_{sc}$ in Equation (1) should be replaced by $f_{ClO^-} \cdot C_{ClO^-}$. Using Equation (16) for C_{ClO^-} one obtains

$$f_{ClO^-} \cdot C_{ClO^-} = \frac{f_{ClO^-} f_{HClO} K_{ac} \cdot a_{H_2O}}{a_{H_3O^+} f_{ClO^-} + K_{ac} f_{HClO} \cdot a_{H_2O}} \cdot C_{sc} \qquad (18)$$

Hence, in Equations (8) and (9) one should use

$$f_{sc} = \frac{f_{ClO^-} f_{HClO} \cdot K_{ac} \cdot a_{H_2O}}{a_{H_3O^+} f_{ClO^-} + K_{ac} f_{HClO} \cdot a_{H_2O}} \qquad (19)$$

instead of that given by equation (17).

Inserting the values of f_{ClO^-}, f_{HClO}, a_{H_2O} and K_{ac} used above, one obtains an f_{sc} function shown also in Fig. 3 (curve 2).

4.4. *Rate constant for chemical conversion and its temperature dependence*

Using the experimental data of Foerster, De Valera [5] worked out the temperature dependence of the rate constant for chemical conversion of available chlorine to chlorate in dilute solutions ($k^0_{r\,h}$). Our experimental values in high ionic strengths (5–6) also confirmed the Foerster constant for the same reaction [1]. These data were used in our calculations. Imagawa [16] has shown, both by theoretical consideration and by experiment, that the Brönsted kinetic coefficient for the conversion of available chlorine into chlorate at higher ionic strengths of neutral salt solutions could be effectively replaced by the square of the activity coefficient of hypochlorous acid (f^2) (cf. (5)). Imagawa [13, 16] also determined the dependence of f on ionic strength and temperature, the latter dependence is slight and may be ignored.

4.5. *Dissociation constant of hypochlorous acid and its temperature dependence*

Caramazza [17] showed the temperature dependence of the thermodynamic dissociation constant of hypochlorous acid to follow the equation

$$pK_a = \frac{800}{T} + 4{\cdot}892 \qquad (20)$$

In some earlier considerations [8] it was shown that the relevant equilibrium constant for calculating the actual concentrations of the hypochlorous species at the ionic strength of the brine for the holding volume is

$$K_h^* = \frac{a_{\mathrm{H_3O^+}} \cdot C_{\mathrm{ClO^-}}}{C_{\mathrm{HClO}}} = K_a \cdot \frac{f_{\mathrm{HClO}} \cdot a_{\mathrm{H_2O}}}{f_{\mathrm{ClO^-}}} \approx 10 \cdot K_a \quad (21)$$

Hence, combining (20) and (21), the necessary data were obtained for calculating the values of the constant c (equation (10)) at different temperatures. The activity used for water was approximated as 0·8 [5. 18].

4.6. *Test of equation* (7)

The dependence of the current efficiency on the holding volume temperature is reflected in the temperature dependence of C_{sc} in Equation (3) and in the constant c of Equation (7) (cf. Equation (10)).

Equations (3) and (7) have been tested using the above derived values of the system parameters and the operational parameters used in experiment.

For the two models of the events at the anode and the corresponding f_{sc} values shown in Fig. 3, two pairs of curves have been calculated with the help of a digital computer.

The value of f_{sc} of 1·4, which is in accordance with the model of equal reactivity of ClO^- and HClO at the anode, renders unacceptable negative solutions for t_1. The result of the use of the f_{sc} value of $3{\cdot}2 \times 10^{-2}$ is contrasted with experiment in Fig. 1 (curves 2 and 1). It is seen that an accordance is achieved at higher temperatures only. Obviously, the assumption that the dissociation of HClO in the reaction layer is negligible does not hold at lower temperatures of the holding volume. An intermediate f_{sc} value of 0·1 gives the most reasonable fit (curve 3 of Fig. 1). Thus, further development of the theory to encompass dissociation of HClO is indicated. Some progress along this line is being made and will be reported at a later date.

Acknowledgement

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References

[1] M. M. Jakšić, A. R. Despić. I. M. Csonka and B. Ž. Nikolić, *J. Electrochem. Soc.* **116** (1969) 1316; *ibid.*, **117** (1970) 414.

[2] F. Foerster and E. Müller, *Z. Elektrochem.*, **9** (1903) 171, 195; and F. Foerster, *Trans. Am. Electrochem. Soc.*, **46** (1924) 23.

[3] A. R. Despić, M. M. Jakšić, B. Ž. Nikolić and M. D. Spasojević, to be published.

[4] Krebs & Co. A.G. Zurich, Brit. Pat. 948, 287 (Nov. 13, 1961).

[5] V. de Valera, *Trans. Faraday Soc.*, **49** (1953) 1338.

[6] D. Landolt, 'Über den Mechanismus der anodishen Chloratbildung', Ph.D. thesis, Eidgenössischen Technischen Hochschule, Zurich, Prom, Nr. 3673 Juris-Verlag, Zurich, 1965; N. Ibl and D. Landolt, *J. Electrochem. Soc.*, **115** (1968) 713; N. Ibl, *Chem. Ing. Techn.*, **39** (1967) 706.

[7] N. Ibl, *Chem. Ing. Techn.*, **35**, (1963) 353.

[8] M. M. Jakšić, B. Ž. Nikolić, I. M. Csonka and A. B. Djordjević, *J. Electrochem. Soc.*, **116** (1969) 684.

[9] C. W. Spalding, 'The Absorption of Chlorine into Aqueous Media in Light of the Penetration Theory', Ph.D. thesis, Lawrence College, Appleton, Wisconsin, 1961; and C. W. Spalding, *A. I. Ch. E. Journal*, **8** (1962) 685.

[10] P. L. T. Brian, J. E. Vivian and A. G. Habib, *A. I. Ch. E. Journal*, **8** (1962) 205.

[11] P. L. T. Brian, J. E. Vivian and C. Piazza, *Chem. Eng. Sci.*, **21** (1966) 551.

[12] M. S. Chao, *J. Electrochem. Soc.*, **115** (1968) 1172.

[13] H. Imagawa, *Bull. Fac. Eng. Yamaguchy Univ.*, Spec. Print., Series 10, No. **1** (1956) p. 147.

[14] M. M. Jakšić, 'Theoretical Basis and Practical Application of Modified Technological Procedure for the Electrolytic Chlorate Production', Doctor's Dissertation, Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, 1970.

[15] J. C. Morris, *J. Phys. Chem.*, **70** (1966) 3798.

[16] H. Imagawa, *Denki Kagaku* (*J. Electrochem. Soc. Japan*) **18** (1950) 382; **19** (1951) 271; **20** (1952) 571; **21** (1953) 520; and **25** (1957) 607.

[17] R. Caramazza, *Gazz. Chim. Ital.*, **87** (1957) 1507.

[18] M. Gazith, 'Molal Osmotic Coefficients and Water Activities for various Electrolytes', p. 9, Israel Atomic Energy Commission, Soreq Nuclear Research Center, 1965.

[19] A. R. Despić and M. M. Jaškić, to be published.