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Chlorate electrosynthesis current efficiency equations based on dimensionless groups

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Various mathematical models for the electrosynthesis of chlorate are analysed taking into account that the current efficiency is mainly affected by the distribution of the two competing reactions forming chlorate, i.e. the anodic oxidation and the autoxidation of hypochlorite. It is shown that the current efficiency is determined by four dimensionless groups one of which is commonly negligible. Results are compared with a known current efficiency equation. Two new current efficiency equations, representing the limiting operating conditions of chlorate systems, are proposed for industrial application.

List of Symbols

a	activity (−)
A	electrode surface area (m^2)
c	concentration of hypochlorite ($mol\,m^{-3}$)
C, C'	numerical constants, Equations 19 and 45
F	Faraday constant ($F = 96\,487\,A\,s\,mol^{-1}$)
H	electrode height (m)
I	total current (A)
I_1, I_2	partial currents of chloride oxidation (A)
I_a	partial current of hypochlorite oxidation (A)
I_v	loss currents (A)
K^*	equilibrium constant of Reaction 6 (−)
K_a	anodic oxidation number (−)
k_d	mass transfer coefficient ($m\,s^{-1}$)
k_r	reaction rate constant of chemical hypochlorite oxidation ($m^6\,mol^{-2}\,s^{-1}$)
K_{rC}	autoxidation number of cell (−)
K_{rR}	autoxidation number of chemical reactor (−)
$N^\blacksquare$	flux of total hypochlorite ($mol\,s^{-1}$)
Re	Reynolds number (−)
S	cross-sectional area of fluid flow (m^2)
Sc	Schmidt number (−)
Sh	Sherwood number (−)
St	Stanton number, Equation 32 (−)
t	time (s)
V	volume (m^3)
$V_L^\blacksquare$	liquid flow rate ($m^3\,s^{-1}$)
x	coordinate in flow direction (m)
ε	current efficiency (−)

Subscripts

a	anodic oxidation of hypochlorite
C	cell
i	entrance cell
o	exit cell
r	autoxidation of hypochlorite
R	chemical reactor

1. Introduction

Hypochlorite, understood as total hypochlorite, $ClO^- + HClO$, generated by the anodic oxidation of chloride

$$2Cl^- - 2e^- \longrightarrow Cl_2 \tag{1}$$

may be transformed to chlorate preferably by autoxidation (or chemical oxidation). The mechanism proposed by Foerster [1] has been confirmed recently [2] and is now generally accepted:

$$2HClO + ClO^- \longrightarrow ClO_3^- + 2H^+ + 2Cl^- \tag{2}$$

The unwanted competing reaction is the anodic oxidation of hypochlorite:

$$3ClO^- + 1.5H_2O - 3e^- \longrightarrow ClO_3^- + 3H^+ + 2Cl^- + 0.75\,O_2 \tag{3}$$

The latter reaction requires 50% more current than the other. These two competing paths of generating chlorate have the major affect on the current efficiency and exceed the effect of other efficiency losses due to inevitable side reactions. All chlorate systems are designed and operated to reduce Reaction 3 in favour of Reaction 2.

The oxidation of hypochlorite, Equation 1, depends on the temperature and the concentration of hypochlorite and on the available reaction volume. It is known that the current efficiency of the autoxidation reaction is affected by further operational parameters, mainly an appropriate choice of the pH [3]. This effect was thoroughly studied [4–6] and is taken into account in all modern chlorate plants. In contrast, the anodic oxidation, Equation 2, is mass transfer controlled, at least in concentrated chloride solutions [3, 7, 8], and depends on the hypochlorite concentration.

The interaction of parameters in suppressing the anodic oxidation is not as well understood as is desirable in view of the economical importance of the process, although numerous investigations of the

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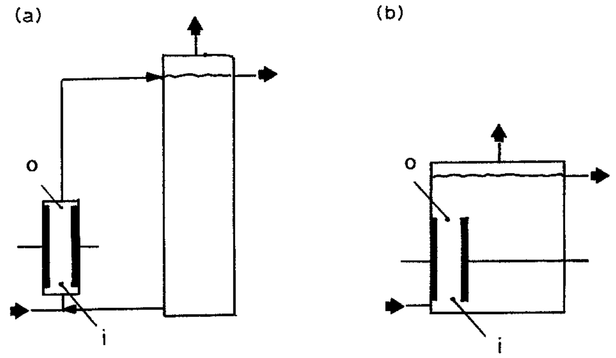

Fig. 1. (a) Electrochemical reactor with external chemical reactor; (b) electrochemical reactor with integrated chemical reaction volume. (i) inlet electrolyser, (o) outlet.

problem have been carried out. They include the important contributions by Ibl and Landolt to clarify the mechanisms of anodic hypochlorite oxidation [9–11] and the papers by Jaksić and co-workers to consider the interaction of all relevant parameters in chlorate electrosynthesis [12–14]. (For further details see [3].) Attempts to describe the current efficiency in a chlorate system were made by Beck [15, 16], who idealized the system as being composed of two perfectly stirred tank reactors and showed quantitatively the mutual interaction of the chemical reaction in both reactors and the mass transfer effect on anodic hypochlorite oxidation in the cell. Beck presented the results in dimensionless form [15], and demonstrated some agreement of the model with empirical data [16].

In industrial plants, flow occurs through the interelectrode gap of the cells in a definite direction (mainly by buoyancy of the gas–electrolyte dispersion unless a circulating pump is used). The electrochemical reactor, at least in modern plants, acts as a tubulat reactor with varying axial concentration [17]. The condition in the chemical reactor is somewhat different. In several modern plants this reactor is a separate vessel, in others it is integrated into the cell case [3, 18, 19], Fig. 1. In either case the flow lies between the limiting conditions of plug-flow and perfect mixing.

The variations of current efficiency are studied in the following three models:

(A) The electrochemical reactor and the chemical reactor, including the piping system, act as idealized tubular reactors.

(B) The electrochemical reactor acts as an idealized tubular reactor, whereas the autoxidation takes place in a perfectly mixed reactor.

(C) Both reactors act as idealized stirred tank reactors with perfect mixing.

2. Current efficiency

For an estimate of the current efficiency the total anodic current in the electrochemical reactor may be divided into four components:

$$I = I_1 + I_2 + I_a + I_v \tag{4}$$

The sum $(I_1 + I_2)$ denotes the current required for indirect generation (via chloride oxidation) of the hypochlorite fluxes $(N_1^\blacksquare + N_2^\blacksquare)$. From Equation 1 together with the reactions leading to the formation of hypochlorite [3]

$$Cl_2 + H_2O \longrightarrow HClO + H^+ + Cl^- \tag{5}$$

$$HClO \longrightarrow H^+ + ClO^- \tag{6}$$

there follows

$$I_1 + I_2 = 2F(N_1^\blacksquare + N_2^\blacksquare) \tag{7}$$

But only the hypochlorite flux $N_1^\blacksquare$ is subsequently chemically transformed to chlorate, requiring no further current, whereas $N_2^\blacksquare$ denotes the flux transformed to chlorate by anodic oxidation requiring the additional current

$$I_a = 1FN_2^\blacksquare \tag{8}$$

I_v denotes the fraction of the anodic current which is not productive for chlorate. Chlorine is directly, or after reaction, lost by any of the loss reactions (the cathodic reduction of hypochlorite and of chlorate, the catalytic decomposition of hypochlorite and its loss with the effluent stream, the anodic oxidation of chlorate to form perchlorate, and the desorption of chlorine or chlorine dioxide) in addition to water decomposition [3, 18]. All these losses are fairly independent of the distribution of chlorate formation among the Reactions 2 and 3 in modern plants. In the present context they will not be distinguished separately but handled as a whole, particularly since they are associated with not more than 3 to 4% total efficiency loss.

The sum $(I_1 + I_2)$ represents the minimum current required to generate chlorate, and $(I_a + I_v)$ are the loss currents. The current efficiency of the process is thus defined by

$$\epsilon \equiv \frac{I_1 + I_2}{I} \tag{9}$$

or when inserting Equation 4 into Equation 9

$$\epsilon = 1 - \frac{I_a + I_v}{I} \tag{10}$$

Inserting Equations 4, 7, and 8 into Equation 9 yields a current efficiency equation

$$\epsilon = \frac{2}{3}\left(1 - \frac{I_v}{I} + \frac{N_1^\blacksquare}{I/F}\right) \tag{11}$$

Inserting Equation 8 into Equation 10 results in a second equation:

$$\epsilon = 1 - \frac{I_v}{I} - \frac{N_2^\blacksquare}{I/F} \tag{12}$$

3. Models

Three different models will be used to describe the fluxes $N_1^\blacksquare$ and $N_2^\blacksquare$ in Equations 11 and 12 and to combine both equations into one.

3.1. *Model A: Both reactors are tubular reactors*

It is assumed that the flow in the chemical reactor is idealized plug-flow with concentration gradients in the main flow direction but uniform concentration distribution in each cross-section. This assumption is a good representation in plants, according to the scheme of Fig. 1a, where the chemical reactor also comprises the circulation pipes.

For the electrochemical reactor a deviation from the conventional plug-flow model is inevitable, because radial concentration gradients exist, which induce mass transfer of hypochlorite from the bulk to the anode surface. The varying concentration in the main flow direction is the average concentration in the cross-section.

From the investigations of Ibl and Landolt [9, 10] it is known that the flux $N_2^{\blacksquare}$ consumed by anodic oxidation is solely controlled by mass transfer of hypochlorite from the liquid bulk to the electrode surface and proceeds approximately under limiting current conditions, at least under industrial operation conditions. It is generally true that

$$N_2^{\blacksquare} = \int_0^A k_d c \, dA \tag{13}$$

A locally invariable mass transfer coefficient k_d and a linear axial concentration profile over the total height H of the interelectrode space between entrance cell, $x = 0$ with $c = c_i$, and exit, $x = H$ with $c = c_0$, are assumed.

$$c = c_i + (c_0 - c_i)\frac{x}{H} \tag{14}$$

Both assumptions involve noticeable deviations from reality in that k_d generally depends on the distance from the leading edge of the flow channel and on the flow velocity, which is itself strongly dependent on the fraction of gas, i.e. mainly of hydrogen formed at the cathode and oxygen formed by anodic oxidation of hypochlorite, Equation 3. Furthermore, in every electrochemical reactor with gas evolution, the gas fraction strongly affects the current distribution, which itself affects the axial distribution of the gas fraction [20, 21]. The axial concentration profile in the flow direction is the result of the interaction of various complex effects. For the sake of simplicity of the model, a linear profile, Equation 14, and the assumption of invariable mass transfer coefficient, $dk_d/dA = 0$, are assumed. Integration of Equation 13 yields the hypochlorite flux consumed through anodic oxidation.

$$N_2^{\blacksquare} = k_d A \frac{(c_i + c_0)}{2} \tag{15}$$

From Equation 12 the current efficiency results in

$$\epsilon = 1 - \frac{I_v}{I} - \frac{k_d A}{I/F}\frac{(c_i + c_0)}{2} \tag{16}$$

The total flux of hypochlorite transformed chemically, $N_1^{\blacksquare}$, is composed of a fraction $N_{1R}^{\blacksquare}$ consumed in the chemical reactor (including the pipes), i.e. the space between the positions o and i in Fig. 1, and the flux $N_{1C}^{\blacksquare}$ consumed inside the cell.

$$N_1^{\blacksquare} = N_{1R}^{\blacksquare} + N_{1C}^{\blacksquare} \tag{17}$$

The kinetics of autoxidation of hypochlorite can be described by [3]

$$\frac{dc}{dt} = -C'k_r c^3 \tag{18}$$

with

$$C' \equiv 3\frac{K^*/a_H^+}{(1 + K^*/a_H^+)^3} \tag{19}$$

Equation 19 exhibits a maximum $C' = 0.45$ [16]. If the pH of the solution is maintained within narrow limits, as is the case in modern plants, C' may be considered approximately constant.

The amount of hypochlorite oxidized chemically outside the cell can be expressed by use of the flow rate of electrolyte in the circulation system, $V_L^{\blacksquare}$:

$$N_{1R}^{\blacksquare} = V_L^{\blacksquare}(c_0 - c_i) \tag{20}$$

The total volume V_R available for autoxidation *outside* the electrolyser comprises the volume of the chemical reactor and the volume of the pipes. From Equation 18, there follows, after integration over the retention time $V_R/V_L^{\blacksquare}$ between electrolyser exit and entrance,

$$\frac{1}{c_i^2} - \frac{1}{c_0^2} = 2C'k_r\frac{V_R}{V_L^{\blacksquare}} \tag{21}$$

Inserting Equation 21 into Equation 20 introduces the kinetic parameters into the expression for the flux of hypochlorite oxidized outside the electrolyser

$$N_{1R}^{\blacksquare} = C'k_r V_R c_i^3 \frac{2}{(1 + c_i/c_0)c_i/c_0} \tag{22}$$

The amount of hypochlorite consumed by autoxidation *inside* the cell is also obtained from Equation 18. With the linear concentration distribution from Equation 14 one obtains, by integration over the volume V_C of the interelectrode space,

$$N_{1C}^{\blacksquare} = \int_0^{V_C}\frac{dc}{dt}\,dV \tag{23}$$

$$N_{1C}^{\blacksquare} = C'k_r V_C c_0^3 \frac{(1 + c_i/c_0)[1 + (c_i/c_0)^2]}{4} \tag{24}$$

To simplify the mathematical treatment Equation 24 is approximated by

$$N_{1C}^{\blacksquare} = C'k_r V_C c_0^3 \frac{(1 + c_i/c_0)^3}{4} \tag{25}$$

The ratio of Equations 25 and 24

$$\frac{(1 + c_i/c_0)^3}{(1 + c_i/c_0)[1 + (c_i/c_0)^2]} = 1 + \frac{2}{c_0/c_i + c_i/c_0} \tag{26}$$

remains within the limits 1 and 2, because $0 < c_i/c_0 < 1$. Equation 25 thus gives values of the flux $N_{1C}^{\blacksquare}$ which are larger than the more accurate Equation 24. Nonetheless it will be shown below that the flux $N_{1C}^{\blacksquare}$ of hypochorite consumed through autoxidation inside the electrolyser, even calculated by use of Equation 25, is negligibly small compared with the flux $N_{1R}^{\blacksquare}$

consumed outside the electrolyser. This finding justifies the simplification made by the transition from Equation 24 to 25.

Combination of Equations 17, 20, and 25 with Equation 11 connects the current efficiency with the total flux $N_1^{\blacksquare}$ consumed through autoxidation:

$$\begin{aligned} N_1^{\blacksquare} &= [1.5\,\epsilon - (1 - I_v/I)]I/F \\ &= V_L^{\blacksquare}(c_i - c_0) + C' k_r V_C \frac{(c_i + c_0)^3}{4} \end{aligned} \qquad (27)$$

Equations 17, 22, and 27 form a system defining the current efficiency. Combining these equations and eliminating the concentrations yields the current efficiency equation

$$\begin{aligned} \frac{K_{rR}}{K_a^3} &= \frac{1.5\,\epsilon - (1 - I_v/I)}{[(1 - I_v/I) - \epsilon]^3} \\ &\times \left\{\left[1 - \left[\left[\frac{1.5\,\epsilon - (1 - I_v/I)}{(1 - I_v/I) - \epsilon}\right.\right.\right.\right. \\ &\left.\left.\left.\left. - 2\frac{K_{rR}}{K_a^3}\frac{K_{rC}}{K_{rR}}[(1 - I_v/I) - \epsilon]^2\right]\frac{K_a}{2}\right]^2\right]^2 + \frac{K_{rC}}{K_{rR}}\right\}^{-1} \end{aligned} \qquad (28)$$

where the following dimensionless groups are used.

$$K_{rR} = C' \frac{k_r V_R (I/F)^2}{V_L^{\blacksquare 3}} \qquad (29)$$

$$K_{rC} = C' \frac{k_r V_C (I/F)^2}{V_L^{\blacksquare 3}} \qquad (30)$$

$$K_a = \frac{k_d A}{V_L^{\blacksquare}} \qquad (31)$$

K_{rR} and K_{rC} represent the autoxidation in the chemical reactor including the pipes, and in the cell, respectively, and will be called the autoxidation numbers, K_a is an anodic oxidation number. It equals the so-called circulation rate number defined by Beck [15]. Introducing the Stanton number for mass transfer

$$St \equiv \frac{Sh}{Re\,Sc} = \frac{k_d}{V_L^{\blacksquare}/S} \qquad (32)$$

K_a may also be interpreted as a modified Stanton number

$$K_a = St\frac{A}{S} \qquad (33)$$

The ratio K_{rC}/K_{rR} in Equation 28 equals the ratio of the volume of the interelectrode space of the cell and the volume of the chemical reactor including the pipes.

$$\frac{K_{rC}}{K_{rR}} = \frac{V_C}{V_R} \qquad (34)$$

Values of K_{rC}/K_{rR} of industrial systems are commonly smaller than 0.01. A numerical analysis of Equations 28 shows that such small values are of no significant effect on the current efficiency and justify neglect of K_{rC}. Autoxidation in the electrolyser is, therefore, negligible. Equation 28 takes the simpler form

$$\frac{1.5\,\epsilon - (1 - I_v/I)}{[(1 - I_v/I) - \epsilon]^3} = \frac{K_{rR}}{K_a^3} \times \left\{1 - \left[\frac{1.5\,\epsilon - (1 - I_v/I)}{(1 - I_v/I) - \epsilon}\frac{K_a}{2}\right]^2\right\}^2 \qquad (35)$$

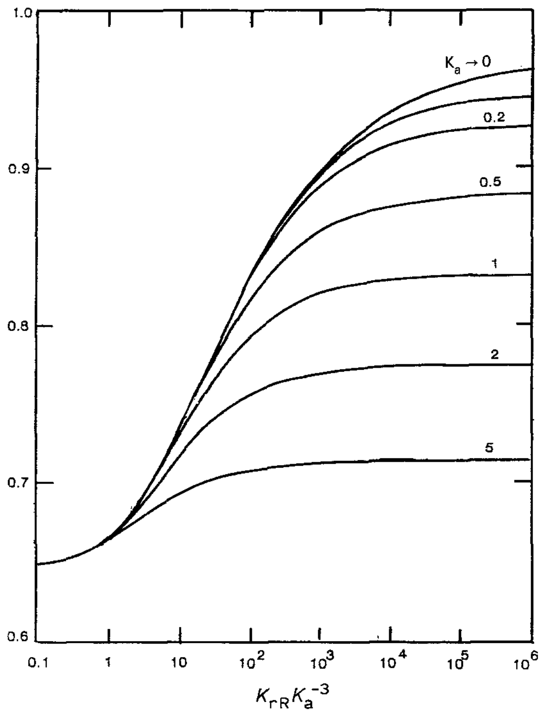

Fig. 2. Model A: Current efficiency as a function of the dimensionless group $K_{rR}K_a^{-3}$ and the anodic oxidation number K_a, Equation 35 setting $I_v/I = 3\%$, $K_{rC} = 0$.

Equation 35 is a reasonable approximation of the much more complex Equation 28. It is seen that the current efficiency depends approximately on three dimensionless groups: $\epsilon = \epsilon(K_a, K_{rR}/K_a^3, I_v/I)$. Equation 35 is shown in Figs 2 and 3 (setting $I_v/I = 0.03$).

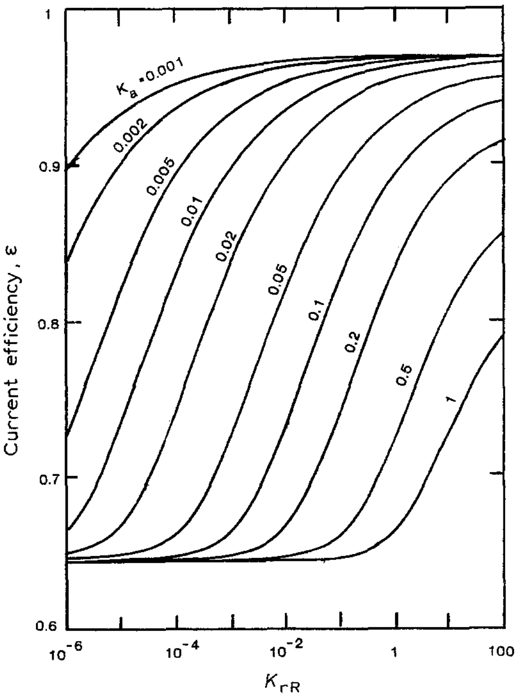

Fig. 3. Model A: Current efficiency as a function of the autoxidation number K_{rR} and the anodic oxidation number K_a, Equation 35 setting $I_v/I = 3\%$, $K_{rC} = 0$.

3.2. *Model B: Plug flow electrolyser; stirred tank chemical reactor*

The assumptions of idealized flow behaviour in the tubular electrochemical reactor from model A are maintained. Autoxidation inside the electrolyser is again assumed to be negligble, $N_{1C}^{\blacksquare}/N_{1R}^{\blacksquare} \rightarrow 0$. The autoxidation outside the electrolyser is now assumed to take place in a region of idealized, perfect mixing without concentration gradients. The assumptions of the model are representative of plants according to the scheme of Fig. 1b.

Since the hypochlorite concentration in the chemical reactor is constant and equals the entrance concentration of the electrolyser, $c = c_i$, one obtains from Equation 17, 18, and 20

$$N_1^{\blacksquare} \approx N_{1R}^{\blacksquare} = V_L^{\blacksquare}(c_0 - c_i) = C_1 k_r V_R c_i^3 \qquad (36)$$

and after insertion into Equation 11

$$1.5\,\epsilon - \left(1 - \frac{I_v}{I}\right) = C_1 \frac{k_r V_R c_i^3}{I/F} \qquad (37)$$

Combination of Equations 16, 20, and 37 with elimination of the concentrations results in a current efficiency equation

$$\epsilon = \frac{(1 - I_v/I)(1 + 2K_a^{-1}) - 2\{[1.5\epsilon - (1 - I_v/I)]K_{rR}^{-1}\}^{1/3}}{1.5 + 2K_a^{-1}} \qquad (38)$$

3.3. *Model C: Both reactors as stirred tank reactors*

In the third and most simple of the models to be discussed, the liquid in the electrolyser, as well as in the chemical reactor (including the pipes if present), is perfectly mixed. The hypochlorite concentration is locally constant, and of value c_0, in the electrolyser; autoxidation in the chemical reactor runs at a constant concentration c_i. These assumptions have already been made by Beck [15]. Autoxidation in the electrolyser is again neglected.

Equation 37, representing the autoxidation at constant concentration c_i, remains unchanged. Equation 15 for the anodic oxidation in the cell at $c = c_0$ takes the form

$$N_2^{\blacksquare} = k_d A c_0 \qquad (39)$$

Combining Equations 20, 37, and 39 together with Equations 11 and 12 and eliminating the concentrations yields the current efficiency

$$\epsilon = \frac{(1 - I_v/I)(1 + K_a^{-1}) - \{[1.5\epsilon - (1 - I_v/I)]K_{rR}^{-1}\}^{1/3}}{1.5 + K_a^{-1}} \qquad (40)$$

Setting $I_v = 0$, i.e. neglecting the numerous loss reactions mentioned above, Equation 40 coincides with the efficiency equation presented by Beck [15] for negligible autoxidation in the electrochemical reactor.

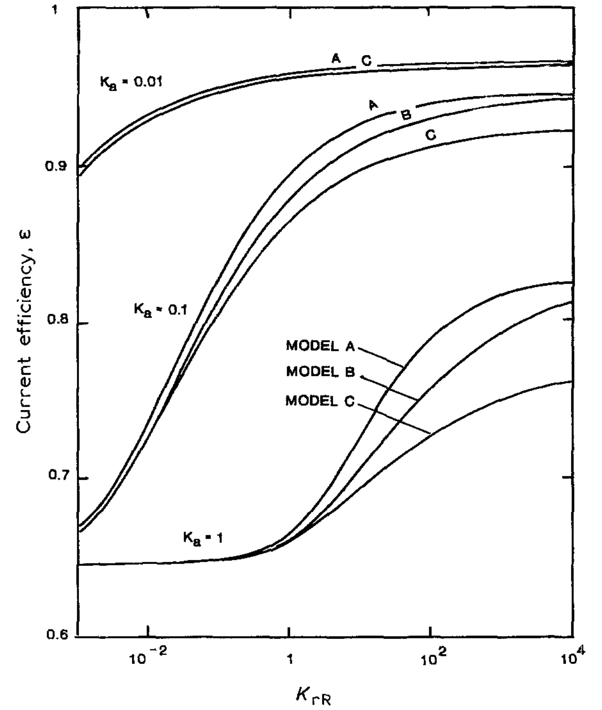

Fig. 4. Comparison of the models A, B, and C. (A) Equation 35; (B) Equation 38; (C) Equation 40, setting $I_v/I = 3\%$.

4. Discussion

4.1. *Practicabilty of the models*

The assumption of the electrolyser as a tubular reactor (with negligible mixing in the main flow direction but distinct axial concentration gradients) as used in the models A and B is a reasonable approximation for the narrow interelectrode gaps of modern electrolysers. The model A is fairly representative of chlorate systems with separate external chemical reactor as shown in Fig. 1(a); model B represents systems with integrated chemical reactors, Fig. 1(b). Both models describe limiting operation conditions. Modern industrial chlorate plants are, therefore, expected to operate under conditions within a range the bounds of which are given by the models A and B. Equations 35 and 38 are recommended for practical application.

Model C, with the assumption of perfect mixing in both reactors provides an inadequate description of the real conditions.

It is interesting to compare the numerical differences of the current efficiency equations of the three models, Equations 35, 38, and 40. As seen from Fig. 4 the differences are negligible for all values of K_a much smaller than unity, $K_a \ll 1$. Increasing values of K_a produce distinct differences among the models, particularly with large values of the autoxidation number K_{rR}. The results of model A exhibit the largest efficiency and those of model C the smallest. Since realistic values of the autoxidation number are of order $0.1 > K_a > 1$ the choice of the appropriate model, A or B, for a particular system may be of importance.

4.2. *Empirical parameters*

It is common industrial practice to characterize chlorate electrosynthesis systems by a number of empirical parameters, i.e. the so-called current concentration, defined as current per unit volume of reactor, I/V_R, the ratio of current and liquid flow rate, $I/V_L^{\blacksquare}$, and, of course, the current density I/A. It can easily be shown that the autoxidation number K_{rR} contains the first two of these ratios:

$$K_{rR} = C' \frac{k_r}{F^2} \left(\frac{I}{V_L^{\blacksquare}}\right)^3 \left(\frac{I}{V_R}\right)^{-1} \tag{41}$$

The latter two ratios can be found in the anodic oxidation number:

$$K_a = k_d \left(\frac{I}{A}\right)^{-1} \frac{I}{V_V^{\blacksquare}} \tag{42}$$

Finally, the ratio K_{rR}/K_a^3 in Equation 35 contains the current density together with the current concentration:

$$\frac{K_{rR}}{K_a^3} = C' \frac{k_r}{F^2 k_d^3} \left(\frac{I}{V_R}\right)^{-1} \left(\frac{I}{A}\right)^3 \tag{43}$$

Therefore, the present dimensionless groups do not upset the validity of the conventional operational parameters, but combine them with each other and further quantities without increasing the total number of variables, although the complete system of parameters is taken into consideration. In fact, the total number of independent variables is reduced to 3 including that representative of the loss currents.

4.3. *Effect of the liquid flow rate*

From Equation 35 it might appear preferable to use a combined dimensionless group K_{rR}/K_a^3 instead of K_a and K_{rR} because K_{rR}/K_a^3 is explicitly free of the liquid flow rate $V_L^{\blacksquare}$:

$$\frac{K_{rR}}{K_a^3} = C' \frac{k_r V_R (I/F)^2}{(k_d A)^3} \tag{44}$$

However, the mass transfer coefficient k_d is itself dependent on the flow rate. The effect of the flow rate on K_a and K_{rR}/K_a^3 is seen from a typical mass transfer equation for forced flow

$$Sh = C\, Re^m Sc^n \tag{45}$$

Hence, the effect of liquid flow on the mass transfer coefficient is

$$k_d \sim (V_L^{\blacksquare}/S)^m \tag{46}$$

and from Equations 29 and 31

$$K_a \sim (V_L^{\blacksquare}/S)^{m-1} \tag{47}$$

and

$$K_{rR}/K_a^3 \sim (V_L^{\blacksquare}/S)^{-3m} \tag{48}$$

In turbulent flow (with velocities $V_L^{\blacksquare}/S \geqslant 0.01\ \mathrm{m\,s^{-1}}$) the exponent m is approximately 0.8 corresponding to

$$K_a \sim V_L^{\blacksquare -0.2} \tag{49}$$

and

$$K_{rR}/K_a^3 \sim V_L^{\blacksquare -2.4} \tag{50}$$

It is seen that K_a is much less affected by the liquid flow rate $V_{L\,L}^{\blacksquare}*$ than K_{rR}/K_a^3. Equation 35 and Fig. 2 show that, at small values of the flow rate (corresponding to large values of K_{rR}/K_a^3), the current efficiency is only weakly affected by K_{rR}/K_a^3. But any increase in the liquid flow rate lowers K_a, and thus increases the current efficiency. At large values of the flow rate (and small values of K_{rR}/K_a^3) the action on the current efficiency is reversed. The anodic oxidation number K_a loses its effect, but increasing liquid flow rate lowers K_{rR}/K_a^3 and, hence, the current efficiency, Fig. 2. The current efficiency, therefore, exhibits a maximum as the flow rate is varied. This finding has already been stated by Jaksić [12] and Ibl [3].

4.4. *Effect of the current density*

It is known [3, 12, 18, 22] that increasing current density raises the current efficiency. The finding is supported by Equations 35, 38 and 40. Since the anodic oxidation number K_a remains unaffected by the current density, Equation 42, but the dimensionless group $K_{rR} K_a^{-3}$ increases strongly as the current density increases, Equation 43, an increase of the current density, with all other parameters kept constant, improves the current efficiency, as clearly seen from Fig. 2.

5. Conclusions

Equation 28 represents a complete system of four dimensionless groups K_{rR}, K_{rC}, K_a, and I_v/I for description of the current efficiency of chlorate electrosynthesis systems, where K_{rC} can be set equal to zero without noticeable loss of accuracy in industrial systems, Equation 35. The current efficiency is thus shown to depend essentially on three dimensionless groups containing all empirical parameters used in industry to characterize chlorate systems. The dimensionless groups combine these parameters and reduce the number of independent variables.

Two models, both considering the electrochemical reactor as an idealized tubular reactor, where the autoxidation of hypochlorite is assumed to occur either in a tubular reactor (model A) or in a reactor with perfect mixing (model B), yield expressions for the current efficiency, Equations 35 and 38, which are likely to represent the limiting conditions for the current efficiency of industrial plants. The assumptions used for the third model are less realistic.

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