JOURNAL OF APPLIED ELECTROCHEMISTRY 3 (1973) 307-314

Individual ionic activities and mass transfer in anodic chlorate formation[*]

MILAN M. JAKŠIĆ

Electrochemistry Department, Institute for Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia

Received 28 February 1973

The individual activity of hypochlorite ion in concentrated neutral salt (NaCl–NaClO$_3$) solutions has been estimated kinetically by measurement of the Faradaic efficiency in a chlorate producing system comprised of a cell and external reactor, with provision for brine re-circulation. By use of this activity in the diffusion relationships developed by Ibl and Landolt [1–3], reasonable agreement has been achieved between the experimental chlorate yield and the yield expected based on the combined hydrolytic and diffusional flux of active chlorine. In this way it has been shown as expected from basic theory that the gradient of chemical potential rather than the concentration difference represents the driving force of diffusion. A formal activity coefficient for active chlorine species is suggested as being a useful term when considering the chlorate cell system.

1. Introduction

Ibl and Landolt [1–3] were the first to point out the unusual and complex nature of the active chlorine[†] concentration profile within the anode diffusion layer of a chlorate cell. Due to the immediate and rapid hydrolysis of chlorine, which mostly occurs in the vicinity of the anode face, two hypochlorous species diffuse both away and towards their generating, and, at the same time, consuming electrode. This creates, in contrast to the Nernst distribution, a certain concentration maximum within the boundary layer.[‡]

Based on this theoretical approach, they described [1–3] the active chlorine profile within the diffusion layer mathematically, and thereafter combined the diffusional and hydrolytic flux of the hypochlorous species $j_{(\mathrm{d+h})}$

$$j_{(d+h)} = -D_2 \left|\frac{\mathrm{d}C_\mathrm{s}}{\mathrm{d}x}\right|_{x=0}$$

$$= -D_2 \frac{C_\mathrm{sc}}{\delta} + \frac{it_1}{2F}\left[\frac{1}{\delta\sqrt{(k_1/D_1)}}[1-\exp(-\delta\sqrt{(k_1/D_1)})]-1\right] \quad (1)$$

where the first term represents a pure diffusional flux at the anode surface and the second gives the additional hydrolytic contribution. A condition of a limiting current for active chlorine oxidation at the anode at a high chloride ion concentration is assumed, i.e. $C_{\mathrm{s}(x=0)} = 0$ (cf. [6]). This means that the active chlorine gradient at the electrode surface defines the Faradaic rate and the stoichiometry of Foerster's reaction (cf. [11]) for anodic chlorate formation. In Equation (1) t_1 denotes the current efficiency; i, the current density; δ, the anode diffusion layer thickness; k_1, the rate constant of chlorine hydrolysis; C_s and C_sc, active chlorine concentrations inside the boundary layer and in

---

[*] Paper presented at 3rd Yugoslav Symposium on Electrochemistry, Dubrovnik, May, 1973.

[†] The usual term 'available chlorine' comprises the sum of the concentrations of hypochlorous acid, hypochlorite ion and dissolved elemental chlorine. However, at the pH value normally encountered in a chlorate cell the latter may be neglected [19], and the more convenient term 'active chlorine' (C_s) will be used throughout for the two hypochlorous species,

$$C_\mathrm{s} = C_{\mathrm{HClO}} + C_{\mathrm{ClO^-}} \quad (1a)$$

[‡] See Appendix.

the bulk, respectively; F, Faraday's constant; D_1 and D_2, diffusion coefficients of elemental chlorine and active chlorine, respectively, while x represents the distance from the electrode surface.

Using dilute chloride solutions and operating in the alkaline pH region at low temperatures, under which conditions all chlorate is formed by electrochemical oxidation of active chlorine species, experimental values of the flux obtained from the chlorate yield agreed well with those calculated from Equation (1) [1–3], i.e. $j_e \approx j_{(d+h)}$.

However, in solutions of the concentration normally used in industry, neither the anodic evolution of oxygen nor the chlorate yield could be reconciled with the flux calculated from either diffusion alone or diffusion plus a hydrolytic contribution [1–5] (cf. [6]). Some additional theories have been advanced in an attempt to resolve these difficulties (cf. [1, 4, 5]).

It is the aim of this paper and another [7] to reconcile the discrepancies between theory and experimental data (derived using concentrated brine solutions) by substitution of activity terms for concentrations in Equation (1). This has been accomplished with some considerable success.

2. Kinetic and Faradaic approach for assessing the individual activities of hypochlorite ions

In order to express Foerster's rate equation for the chemical formation of chlorate [11] as a function of hydronium ion activity and active chlorine content rather than as a function of hypochlorous acid and hypochlorite ion concentrations, the relevant dissociation constant K^* was introduced [8, 9].

$$K^* = \frac{(a_{H_3O^+}) \cdot (C_{ClO^-})}{(C_{HClO})} = K_a \cdot \frac{f_{HClO} \cdot a_{H_2O}}{f_{ClO^-}} \qquad (2)$$

where K^* is dependent on the ionic strength of the brine. The above expression shows the relationship between HClO and ClO^- concentrations as a function of hydronium ion activity in concentrated salt solutions and it allows the calculation of these concentrations from two easily measured quantities (C_s, Equation (1a) and pH) (cf. [9]). The value of K^* (or the right hand side of Equation (2)) thus represents a well-defined and useful constant (at a fixed ionic strength). The equation can be used to calculate the contribution of chemical chlorate formation in determining the Faradaic efficiency [9] of a chlorate cell.

Quite simple combinations of Equations (1a) and (2) with Foerster's kinetic relation for chemical chlorate formation [11] (cf. [8, 9 and 10]) lead to another relevant form of the rate relationship

$$v_1 = -\frac{dC_s}{dt} = 3f_{HClO}^2 \cdot k_r \cdot \frac{K^* \cdot (a_{H_3O^+})^2 C_s^3}{[K^* + (a_{H_3O^+})]^3} \qquad (3)$$

where k_r denotes the reaction rate constant. In addition, by differentiating Equation (3) with respect to hydronium ion activity, one obtains the pH value which provides maximal chemical conversion of active chlorine to chlorate (for the condition $(dv_1/d(a_{H_3O^+}) = 0)$

$$pH_M = pK^* - \log 2 \qquad (4)$$

The thermodynamic value [12,13] of the constant (K_a), predicts an optimal pH region at about pH 7. However, it was experimentally found that at the usual brine composition and temperature for electrolytic chlorate production, the latter shifts by one pH unit to lower values [8, 10]. In other words, it means that at the usual ionic strengths of the brine (5·5 to 6·0 M for both NaCl and $NaClO_3$), the rearranged dissociation constant (K^*) is ten times as large as the thermodynamic (K_a) value ($K^* \approx 10 \times K_a$). The same (average) value was found from steady-state measurements of the Faradaic efficiency for the chlorate cell process [9]†.

---

† It is also possible to express the relationship for current efficiency (Equation (11), ref. [9]) in another suitable form

$$\frac{C_{sc}[2(f_{HClO})_c{}^2 \cdot k_{r,c} \cdot V_c F(a_{H_3O^+})_c{}^2]^{1/3}}{\left\{\left[t_1 - \frac{2}{3}(1 + F\frac{q}{I}\Delta C_s)\right] I\right\}^{1/3}} = (K_c{}^*)^{2/3} + \frac{(a_{H_3O^+})_c}{(K_c{}^*)^{1/3}} \qquad (5)$$

and obtain the rearranged dissociation constant for the cell temperature ($K_c{}^*$) (thereby subscript c) from the slope and intercept of the straight line plot. In Equation (5) q denotes electrolyte flow; I, the cell load; V_c, the cell volume and $(a_{H_3O^+})_c$, bulk hydronium ion activity inside the cell, while all other terms have their usual meanings. The same (average) value also resulted from least square method recalculations of a large number of steady-state measurements of the Faradaic yields in the chlorate producing system (cf. [9]).

Since the activity coefficient of hypochlorous acid for the usual chlorate cell brine is known [14] to be about 2·0, and the activity of water is approximately [15] 0·8, one hence concludes that at this ionic strength of electrolyte, the activity coefficient of hypochlorite ion should be about 0·1†. On the other hand Schwabe [16] pointed out that the individual activity coefficient of hydronium ion is about 10·0 in the same solution (cf. [8]). One thus might also conclude from Equation (2), that the activity coefficient of hypochlorite ion is roughly proportional to the reciprocal of the corresponding value for hydronium ion [16] (i.e. $f_{\mathrm{ClO}^-} \approx 1/f_{\mathrm{H_3O}^+}$). In other words, the average molar activity coefficient of dissociated hypochlorous acid remains approximately equal to unity ($f_{\mathrm{H_3O}^+} \cdot f_{\mathrm{ClO}^-} \approx 1$), although the individual values differ from each other by about two orders of magnitude at the high ionic strength. It is well known that whereas the logarithm of the activity coefficient of cations first decreases, and, after a well-defined minimum, steeply increases as a function of ionic strength, the corresponding value for anions can only continuously decrease [17]. Thus such a low value could be expected. The values for hydrogen and hypochlorite ion activities at the given ionic strength of the solution are mutually related by the hypochlorous acid dissociation equilibrium and should thus be interdependent. Values of hydronium ion activities in concentrated solutions of indifferent neutral salts are now available [16]. Hence the last unknown in the present formula, the activity coefficient of hypochlorite ion, could be assessed from such a kinetic analysis. Although thermodynamicists do not recognize any kinetic method as a reliable tool for the determination of activity coefficients, such an approach could provide values of reasonable accuracy, which might be of practical importance at least in concentrated solutions of indifferent electrolytes. These values might also be useful for kinetic applications.

3. Chemical potential as the driving force of diffusion and activities as the factor governing limiting current

Ibl and Landolt [3, 1] also showed that a definite steady-state concentration of active chlorine (C_{sc}) was established in the bulk liquor of a chlorate system comprising a cell connected in a loop with an external reactor for brine recirculation, and operating under constant conditions (cf. [18]).

Moreover, the same authors [1, 3] were able to show experimentally (Fig. 1) a very interesting and important dependence of the active chlorine concentration (C_{sc}) on the ionic strength of the neutral salt (NaCl). The steady-state concentration of active chlorine exhibits a typical bilogarithmic change to higher values (Fig. 1) at a relatively low ionic strength. However, in concentrated NaCl solutions of practical importance for industrial chlorate production, C_{sc} could not be simply related to the rate of oxygen evolution (cf. [6]), although this should be a direct function of the active chlorine gradient at the electrode due to the Faradaic stoichiometry. Experimental and theoretical fluxes of chlorate, thus also do not coincide with each other.

The dependence of steady-state active chlorine concentration on the ionic strength of the indifferent neutral salt (Fig. 1) is quite similar to the familiar relation between hydronium ion activity and the concentration of the carrying electrolyte but in a reverse direction [16]. This similarity and the typical bilogarithmic plot of the former, as well as the just discovered and discussed interdependence of two individual activity coefficients (i.e. $f_{\mathrm{ClO}^-} \approx 1/f_{\mathrm{H_3O}^+}$), suggests that the change of available chlorine concentration (C_{sc}) is probably due to the dependence of its activity on the indifferent electrolyte content. It is also important to note that such intrinsic concentration, or in other words activity, changes just occur within the usual region of ionic strengths which are characteristic for the most pronounced individual activity coefficient changes [16]. This assumption led to the idea of modifying the diffusion equations by relating the concentration gradient, the resulting flux (Equation (1)), and limiting current relationships, to the activity, instead of to the con-

---

† In some earlier considerations [8] an estimated value of hypochlorite ion activity coefficient of about 1·0 introduced by Imagawa [14] was used and this led to an apparent increase in the thermodynamic dissociation constant (K_a), and to the consequent erroneous conclusions.

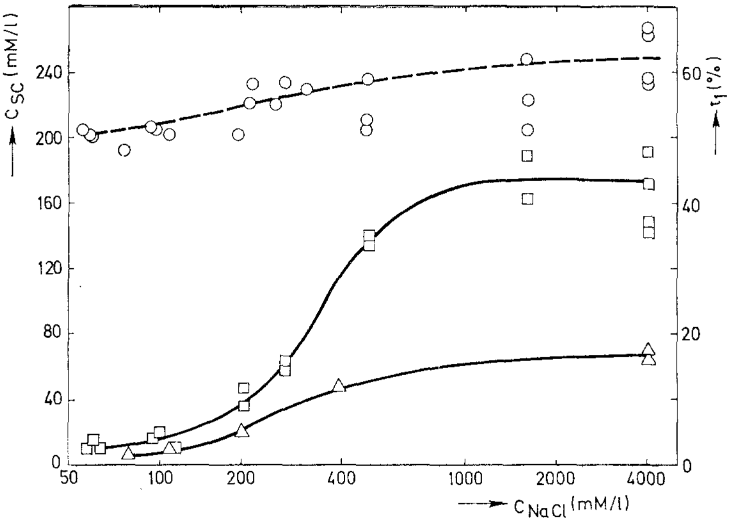

Fig. 1. Steady-state active chlorine concentration and chlorate anodic formation rates at various chloride concentrations in unstirred solutions:
△, □ active chlorine concentrations at $i = 5$ mA cm^{-2}and $i = 20$ mA cm^{-2}, respectively;
○ chlorate yield for both current densities (Ibl and Landolt [1, 3], by kind permission of Professor Ibl).

centration of active chlorine. Following basic definitions, chemical potential represents a driving force, and thus activity should govern diffusion laws and relations better than the corresponding concentrations [26, 22]. The mathematical approach shows that one needs only to introduce the activity coefficient together with the active chlorine concentration in Equation (1). The previously estimated value of hypochlorite ion activity coefficient ($f_{\mathrm{ClO}^-} \approx 0{\cdot}1$), as discussed above, was introduced into the relationship and the corrected diffusional plus hydrolytic flux related to the experimental one for chlorate yield (Table 1). In other words, this diffusion case was considered as the mass transfer of the minor species in a concentrated supporting electrolyte [22].

The agreement with the data of Ibl and Landolt is as good as in dilute chloride solutions [1–3].

It is also important to point out that a similar situation arises with elemental chlorine. Namely, use of its concentration in the Beck–Ibl equation for chlorine flux [1] at the usual current densities and high ionic strengths does not predict complete hydrolysis within the anode boundary layer [1], but use of the activitity does [24] (cf. [7, 10]). Since activities of molecular species are attainable and recognized as thermodynamically significant, the above observation supports the view that diffusion relationships should be related to chemical potential and individual ionic activity gradients (cf. [7]). In other words that such a treatment represents a practical extension and generalization of the simple diffusion laws [24].

4. Formal activity coefficient of active chlorine—its meaning and application

A fundamental question in chlorate electrolysis is whether hypochlorite ions alone, or both active chlorine species simultaneously, are anodically oxidized according to Foerster's reaction theory (cf. [1–6, 21]). Recently it was concluded that oxidation of hypochlorous acid could not take place [1, 4]. The authors based their argument on the grounds of the standard oxidation potentials and on experimental current – potential curves obtained in chloride solutions at various pH values. These reasons were used as a possible explanation for the

Table 1. Combined effect of hydrolytic and diffusional mass-transfer of active chlorine within the anode boundary layer of a chlorate cell on current yields and electrochemical chlorate formation in concentrated NaCl solutions according to Ibl and Landolt [1–3] including corrected values.

No.	NaCl mole l^{-1}	t_c °C	pH$_c$	i mA cm^{-2}	u cm s^{-1}	δ cm × 10^3	E_A mV versus SCE	t_1	C_{sc} m mole l^{-1}	$V_{ClO_3^-}$ mole cm^{-2} s^{-1} × 10^9	j_e mole cm^{-2} s^{-1} × 10^9	j_d mole cm^{-2} s^{-1} × 10^9	j_{h+d} mole cm^{-2} s^{-1} × 10^9	j_e/j_d	j_e/j_{h+d}	$j_e/(j_{h+d})$corr
1	0·47	7·5	3·0	5	13	13·8	1520	0·340	7·8	2·94	8·82	5·7	13·0	1·6	0·7	1·12
2	4·0	1·4	8·9	5	13	13·8	1520	0·578	64	4·98	14·94	46·4	57·8	0·32	0·26	0·93
3	4·0	1·7	5·9	5	13	13·8	1575	0·455	88	3·93	11·79	63·8	73·4	0·18	0·16	0·74
4	4·0	0·3	9·0	5	13	13·8	1580	0·575	56	4·97	14·91	40·6	53 3	0·37	0·28	0·89
5	4·0	1·0	9·0	5	13	13·8	1545	0·670	58	5·78	17·34	42·0	56·3	0·41	0·31	0·94
6	4·0	1·5	9·1	5	13	13·8	1520	0·670	57	5·78	17·34	41·3	55·6	0·42	0·31	0·94
7	4·0	7·0	10·2	5	13	13·8	1600	0·660	44	5·70	17·10	53·0	68·1	0 32	0·25	0·84
8	4·0	7·0	10·0	5	29	8·3	1450	0·534	42	4·62	13·86	50·6	61·7	0·27	0·22	0·86
9	4·0	7·0	10·0	5	29	8·3	1520	0·459	42	3·97	11·91	50·6	60·0	0·23	0·20	0·83
10	4·0	7·0	10·0	5	29	8·3	1450	0·548	40	4·74	14·22	48·2	59·6	0·29	0·24	0·88
11	4·0	7·0	10·0	20	29	8·3	1530	0·570	115	19·6	58·80	139	186	0·42	0·32	0·97
12	2·0	7·0	10·0	10	29	8·3	1530	0·607	59	10·5	31·5	71·1	96·3	0·44	0·33	0·98
13	4·0	7·0	10·0	2·5	29	8·3	1440	0·500	18	2·16	6·48	21·7	26·9	0·30	0·24	0·88
14	4.0	7·0	9·1	10	29	8·3	1550	0·486	~75	8·41	25·23	90·4	110·2	0·28	0·23	0·88
15	4·0	7·0	9·1	10	29	8·3	1620	0·458	~75	7·93	23·79	90·4	109·4	0·26	0·22	0·85
16	4·0	5·4	8·8	5	46	4·3	1410	0·602	34(30)	5·20	15·60	79·0	89·1	0·20	0·18	0·87
17	4·0	7·0	10·2	5	46	4·3	1490	0·468	32	4·05	12·15	74·4	82·3	0·16	0·15	0·79
18	4·0	7·0	10·0	5	46	4·3	1540	0·444	30	3·84	11·52	69·8	77·3	0·17	0·15	0·80
19	4·0	8·5	10·6	10	46	4·3	1490	0·495	55	8·56	25·68	128	145	0·20	0·18	0·86
20	4·0	7·0	10·2	10	46	4·3	1530	0·553	56	9·56	28·68	130	149	0·22	0·19	0·90
21	4·0	7·0	9·1	20	46	4·3	1740	0·410	86	14·2	42·60	200	228	0·21	0·19	0·89
22	4·0	5·0	8·8	5	158	1·1	1480	0·555	16	4·78	14·34	145	149	0·10	0·10	0·78
23	4·0	7·0	9·4	5	158	1·1	1520	0·497	12	4·30	12·90	109	113	0·12	0·12	0·87
24	4·0	7·0	9·3	5	158	1·1	1540	0·479	13	4·14	12·47	118	121	0·10	0·10	0·84
25	4·0	7·0	9·1	5·4	158	1·1	1470	0·662	15·5	6·20	18·60	141	143	0·13	0·13	1·15

NaCl	average value of NaCl concentration in the steady-state.
t_c	average cell temperature (variations with time $\leqslant \pm 0{\cdot}5$°C).
pH$_c$	pH value of the cell ($\pm 0{\cdot}3$ pH).
u	linear flow velocity.
i	anode current density.
E_a	steady-state anode potential.
C_{sc}	steady-state active chlorine concentration in bulk of the cell.
$\nu_{ClO_3^-}$	chlorate formation rate in the steady-state determined from the slope of chlorate concentration versus time curves.
t_1	current yields.
δ	average thickness of Nernst anode diffusion layer, calculated from limiting current measurements for ferricyanide reduction.
j_e	active chlorine flux at the anode determined from experimentally measured chlorate formation rates: $j_e = 3\ \nu_{ClO_3^-}$.
j_d	active chlorine flux at the anode calculated from steady-state total hypochlorite concentration assuming a diffusion controlled electrode process: $j_d = -D_2 C_{sc}/\delta$.
j_{d+h}	combined diffusional and hydrolytic flux of active chlorine at the anode of chlorate cell calculated according to Equation (1).
$(j_{d+h})_{corr.}$	the same flux as above, but corrected for hypochlorite ion activity coefficient.

discrepancy between the theoretical and experimental fluxes of active chlorine at the anode in concentrated chloride solutions [1, 4].

Due to chlorine hydrolysis, that part of the anode diffusion layer in close proximity to the electrode has to be considered as strongly acidic and hence, the active chlorine approaching the anode surface should predominantly exist in the form of hypochlorous acid. On the other hand, the anode potential for chloride oxidation is more positive than those of both active chlorine species and since this reaction represents the basic electrode process in a chlorate cell, one could also expect simultaneous reaction of both active chlorine species (cf. [1, 4]). Finally, even if hypochlorite ions only are oxidized, the reversible rates of the dissociation reaction

$$HClO + H_2O \rightleftharpoons ClO^- + H_3O^+ \qquad (6)$$

are high enough so that the above equilibrium (Equation (6)) is always maintained (as it is for most reactions involving proton exchange). Hence a formal activity coefficient for total available chlorine (f_s) might be introduced [20] into all diffusion relationships and the resulting theoretical diffusion flux may be related to the experimental flux of chlorate (cf. [6, 21]). This concept allows a qualitative explanation of how the previously estimated individual value of hypochlorite ion activity coefficient ($f_{ClO^-} \approx 0{\cdot}1$) may also satisfy the diffusion flux equations within the transition pH region of concentrated sodium chloride solutions by taking into account total bulk activity of both hypochlorous species [7].

A logical relationship to describe the activity coefficient of the active chlorine was derived elsewhere ([7], Equations (12) and (17)). The relationship ([7], Equation (17)) appears pH-dependent since it contains the dissociation constant of hypochlorous acid, as well as its other equilibrium components. In accordance with the nature of the activity coefficient of active chlorine and experimental data that suggests it is pH-independent [7] (cf. [1–3]), it seems appropriate to express the relationship in another way in which f_s is described as a function of the individual values for HClO and ClO^-.

As the reversible rates of reaction (Equation (6)) are extremely fast, active chlorine could be considered statistically as being in a single intermediate state or possibly be imagined as existing momentarily in a hybrid form similar to an active complex in the transition state. Such a conclusion seems probable for the transition pH region at least, where both hypochlorous species exist in comparable amounts. However, as a result of proton interchange between the active chlorine species, their individual activity coefficients change by about one order of magnitude ($f_{HClO} \approx 2{\cdot}0, f_{ClO^-} \approx 0{\cdot}1$).

Each terminal state may be freely transformed into the other and hence two parallel but opposite routes are available leading to active chlorine species interchange, existence and even discharge. Such a situation is analogous to two resistors in parallel connection which have an associated overall resistance. Employing a similar argument, an average formal activity coefficient (f_s) for the active chlorine species may be expressed by Equation (7)

$$f_s = \frac{f_{HClO} \cdot f_{ClO^-}}{f_{HClO} + f_{ClO^-}} \qquad (7)$$

Due to the frequent proton interchange by HClO and ClO^-, which results in a fairly pronounced activity difference, an analogy with resistors in parallel connection seems quite natural to describe their combined activity coefficient, i.e. the coefficient for active chlorine is conceived as an active complex in the transition state, similar to some average resonance hybrid. The resulting value for chlorate cell brine ($f_s = 2 \times 0{\cdot}1/(2+0{\cdot}1) \approx 0{\cdot}1$)) is in good agreement with experimental data [7] (Table 1).

The mutual activity coefficient (f_s) of hypochlorous species according to Equation (7) is expressed in a similar way as 'the effective coefficient of diffusion' [23] which relates the two individual ionic diffusivities of binary electrolytes as the average for the ionic pair (cf. [22]).

The rate constant used for chlorine hydrolysis (k_1) was the thermodynamic value for dilute solution [1–3]. However, k_1 satisfies the flux relationship quite well due to its relatively low value at the low experimental temperature. Further correction for ionic strength would bring better agreement with the theory [7].

When one relates the diffusion flux to individual activities, the diffusion constant, of course, has a different meaning from its usual average value for ionic pairs (the effective coefficient of diffusion [23]). However, its order of magnitude remains practically the same, and hence its estimated value [1–3] ($\sim 10^{-5} \mathrm{cm}^2 \mathrm{s}^{-1}$) seems well suited to the above approximate approach. The physical meaning of individual diffusion constants (self-diffusivities) and the interpretation of Fick's law related to individual ionic activities, with full mathematical interpretations, will be described elsewhere [24].

Acknowledgements

The author has profited by discussions of the questions treated here with Professor N. Ibl, Zurich, Switzerland, Professor K. Schwabe, Dresden, DDR, Professor J. O'M. Bockris, Bedford Park, Australia, Professor G. Milazzo, Rome, Italy and Professor A. R. Despić, Belgrade, Yugoslavia, to all of whom he is deeply grateful.

The author is also greatly indebted to Dr R. Swindells and Dr R. Mayers, ERCO Industries Ltd., Toronto, Canada for their personal interest in this paper and contributions to the direct preparation of the present paper.

Appendix

The relationship for current yields in a chlorate cell process, derived from the active chlorine profile within the anode boundary layer

$$t_1 = \frac{1 - \dfrac{D_2 F}{i\delta} f_{sc} \cdot C_{sc}}{\dfrac{3}{2} - \dfrac{1 - \exp[-\delta\sqrt{(k_1/D_1)}]}{2\delta\sqrt{(k_1/D_1)}}} \tag{A1}$$

was described and discussed elsewhere [7]. It is easily seen that only for $\delta\sqrt{(k_1/D_1)} \ll 1$, when one can approximately expand the exponent and take only the first two terms,

$$\exp[-\delta\sqrt{(k_1/D_1)}] \approx 1 - \delta\sqrt{(k_1/D_1)} \tag{A2}$$

does Equation (A1) describe the linear dependence of the current losses on active chlorine concentration (C_{sc})

$$t_2 = 1 - t_1 = \frac{D_2 F}{i\delta} f_{sc} C_{sc} \tag{A3}$$

or in other words the Nernst concentration distribution. Such a relationship (Equation (A3)) was used by Beck [6] and De Valera [25].

References

[1] D. Landolt, Über den Mechanismus der anodischen Chloratbildung, Ph.D. Thesis, Eidgenössischen Technischen Hochschule Zurich, Prom. Nr. 3673, Juris-Verlag, Zurich, 1965
[2] N. Ibl, *Chem. Ing. Techn.*, **39** (1967) 706.
[3] N. Ibl and D. Landolt, *J. Electrochem. Soc.*, **115** (1968) 713.
[4] D. Landolt and N. Ibl, *Electrochim. Acta*, **15** (1970) 1165.
[5] D. Landolt and N. Ibl, *J. Appl. Electrochem.*, **2** (1972) 201.
[6] T. R. Beck, *J. Electrochem. Soc.*, **116** (1969) 1038.
[7] A. R. Despić, M. M. Jakšić and B. Ž. Nikolić, *J. Appl. Electrochem.*, **2** (1972) 337.
[8] M. M. Jakšić, B. Ž. Nikolić, I. M. Csonka and A. B. Djordjević, *J. Electrochem. Soc.*, **116** (1969) 684.
[9] M. M. Jakšić, A. R. Despić, I. M. Csonka and B. Ž Nikolič, *ibid.*, **116** (1969) 1316; *ibid.*, **117** (1970) 414.
[10] M. M. Jakšić, *ibid.*, submitted for publication.
[11] F. Foerster and E. Müller, *Z. Elektrochem.*, **9** (1903) 171, 195, and F. Foerster, Trans. Am. Electrochem. Soc., **46** (1924) 23.
[12] R. Caramazza, *Gazz. Chim. Ital.*, **87** (1957) 1507.
[13] J. C. Morris, *J. Phys. Chem.*, **70** (1966) 3798.
[14] H. Imagawa, *Bull. Fac. Eng. Yamaguchy Univ.*, Spec. Print., Series 10, No. 1 (1956) p. 147; H. Imagawa, Denki Kagaku (*J. Electrochem. Soc. Japan*) **19** (1951) 271; *ibid.*, **20** (1952) 571; *ibid.*, **25** (1957) 607.
[15] M. Gazith, 'Molal Osmotic Coefficients and Water Activities for Various Electrolytes', p. 9, Israel Atomic Commission, Soreq Nuclear Research Center, 1965.
[16] K. Schwabe, *Electrochim. Acta*, **12** (1967) 67; K. Schwabe, Konzentrierte Elektrolytlösungen, Thermodynamische und Kinetische Eigenschaften, Sitzungsberichte der Sächsischen Akademie der Wissenschaften zu Leipzig, Matematisch-naturwissenschaftliche Klasse, Band 109, Heft 6, Akademie-Verlag, Berlin, DDR, 1972.
[17] A. S. Solvkin, *Electrokhimiya*, **8** (1972) 542; *Zhur. Fiz. Khim.*, **35** (1961) 2123, *ibid.* **36** (1962) 2219 and *ibid.* **37** (1963) 447; and J. O'M. Bockiis, Private Communication.
[18] F. Foerster, 'Electrochemie wässeriger Lösungen', 3 verb. Aufl., p. 672, Fig. 131, J. A. Barth, Leipzig (1923).
[19] D. V. Kokoulina and L. I. Krishtalik, *Elektrokhimiya*, **7** (1971) 346.
[20] M. M. Jakšić, A. R. Despić and B. Ž. Nikolič, *Elektrokhimiya*, **8** (1972) 1573.
[21] N. Ibl. *Chem. Ing. Techn.*, **35** (1963) 353.
[22] J. Newman, 'Transport Processes in Electrolytic Solutions', in Advances in Electrochemistry and

Electrochemical Engineering, Vol. 5, C. W. Tobias, Ed., Interscience, New York, (1967), pp. 87–135.

[23] B. Levich, *Acta Physiocochim. URSS*, **17** (1942) 257.

[24] M. M. Jakšić, to be published.

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

[26] S. Glasstone, K. J. Laidler and H. Eyring, 'Theory of Rate Processes', McGraw-Hill Book, New York (1940) p. 530.