

Effect of molecular chlorine diffusion on theoretical potential-current density relations for a chlorine evolving electrode

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EFFECT OF MOLECULAR CHLORINE DIFFUSION ON THEORETICAL POTENTIAL-CURRENT DENSITY RELATIONS FOR CHLORINE EVOLVING ELECTRODE

L. J. J. JANSSEN, G. J. VISSER and E. BARENDRECHT

Department of Chemical Technology, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Abstract—The effect of molecular chlorine diffusion upon the theoretical potential-current density relations was calculated for chlorine evolution according to the Volmer-Tafel mechanism as well as the Volmer-Heyrowsky mechanism. It has been found that a minimum Tafel slope of 29.6 mV at 298 K occurs for both mechanisms. This slope occurs for the Volmer-Tafel mechanism when either the Tafel reaction or the chlorine diffusion, away from the electrode surface into the bulk of solution, is the rate-determining step, and for the Volmer-Heyrowsky mechanism when it is the chlorine diffusion that is the rate-determining step.

Moreover, it has been established that only a careful use of both the polarization resistance at the reversible potential and the stoichiometric number from this deduced, is allowed to elucidate the mechanism of electrode reactions with adsorbed atomic intermediates.

NOMENCLATURE

b	slope of potential-log current density relation
b_1	b at $0 \text{ V} < E - E_R < 0.1 \text{ V}$
b_2	b at $-0.1 \text{ V} < E - E_R < 0 \text{ V}$
$[\text{Cl}^-]$	concentration of Cl^- ions in the bulk of solution
$[\text{Cl}_2]$	concentration of molecular chlorine in the bulk of solution
D	diffusion coefficient
E	electrode potential
E_r	reversible electrode potential
E_R	E_r at $[\text{Cl}^-]_R$ and $[\text{Cl}_2]_R$
f	constant factor; $f = F/RT$
F	Faraday constant
h	slope of overpotential-current density relation
h_1	h at $0 \text{ V} < \eta < 0.006 \text{ V}$
h_2	h at $-0.006 \text{ V} < \eta < 0 \text{ V}$
i	current density
i_0	exchange current density
k	rate constant of reaction at E_R
k_a	rate constant of anodic reaction at E_R
k_c	rate constant of cathodic reaction at E_R
k_T	rate constant of Tafel recombination reaction
k_T^*	rate constant of Tafel dissociation reaction
k^*	rate constant of reaction
k_a^*	rate constant of anodic reaction
k_c^*	rate constant of cathodic reaction
m	mass-transfer coefficient; $m = D/\delta$
n	factor; $n = hi_0$
n_1	factor; $n_1 = h_1 i_0$
n_2	factor; $n_2 = h_2 i_0$
R	gas constant
R_0	polarization resistance
T	temperature
z	order of reaction
α	charge-transfer coefficient for anodic reaction
δ	thickness of diffusion layer
η	overpotential; $\eta = E - E_r$
θ	degree of coverage with chlorine atoms
θ_r	θ at E_r
θ_R	θ at E_R

Subscripts

a anodic reaction

c	cathodic reaction
e	at the electrode surface
H	Heyrowsky reaction
r	at bulk concentrations of solution
R	at reference bulk concentrations of solution
T	Tafel reaction
V	Volmer reaction

1. INTRODUCTION

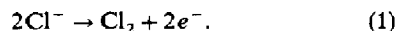
The elucidation of mechanisms of electrode reactions are often based on Tafel slopes. Special attention is paid to the diffusion of reacting species. However, the diffusion of products formed electrochemically, is generally left out of consideration. This negation can lead to an incorrect or dubious mechanism for the electrode reaction concerned, in particular for gas-evolving electrodes with adsorbed atomic intermediates. To explain a 30 mV Tafel slope at 25 °C for the chlorine evolution on graphite anodes[1] and on $\text{RuO}_2/\text{TiO}_2$ anodes[2], Krishtalik *et al.* have proposed a barrierless electrode reaction with a transfer coefficient $\alpha = 1$.

Both the rate-determining chemical desorption (Tafel reaction) and the rate-determining diffusion of the evolved chlorine molecules away from the electrode into the bulk of solution give a Tafel slope of 30 mV at 25 °C[3].

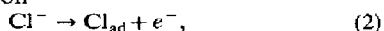
The aim of this study is to determine the effect of molecular chlorine diffusion on theoretical relations between potential and current density for chlorine evolution according to the two likely mechanisms, that is the Volmer-Tafel and the Volmer-Heyrowsky mechanisms.

2. THEORY AND RESULTS

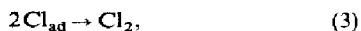
The overall reaction of the chlorine formation by oxidation of chloride ions is



In general, the two mechanisms proposed in literature are the Volmer–Tafel mechanism with two steps: the Volmer reaction

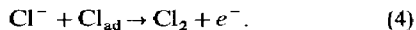


and the Tafel reaction



and the Volmer–Heyrowsky mechanism with two steps:

the Volmer reaction (2) and the Heyrowsky reaction

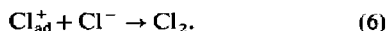


In particular, electrochemists from the U.S.S.R., *eg* Krishtalik[1], propose a mechanism with three reaction steps:

the Volmer reaction followed by the reactions (Krishtalik mechanism):



and



For the three mechanisms mentioned, the theoretical Tafel slope b and the reaction orders z with respect to Cl^- ions and Cl_2 molecules are represented in Table 1[1, 2], assuming a Langmuir-type isotherm for the adsorption of atomic chlorine and a transfer coefficient of 0.5 for the charge transfer reactions. Moreover, it is assumed that the diffusion of both Cl^- and Cl_2 does not affect the E/i relation. The parameters for the Krishtalik mechanism are only partly obtained from[1]; see for the basic equations for the various reactions[3, 4].

2.1 Volmer–Tafel mechanism

The basic equations given in this and following sections are well known[3–5].

The anodic current density for reaction (2) is given by

$$i_V = Fk_{\text{a},V}^*[\text{Cl}^-]_e(1-\theta) \exp[\alpha_V fE] - Fk_{\text{c},V}^* \theta \exp[-(1-\alpha_V) fE]. \quad (7)$$

The rate of reaction (3) is denoted by the current density i_T . The electronation current density

$$i_T = 2Fk_T \theta^2 - 2Fk_T^* [\text{Cl}_2]_e (1-\theta)^2. \quad (8)$$

The total current density $i = i_V = i_T$.

The rate of the diffusion of dissolved molecular

chlorine away from the electrode is also indicated by the electronation current density i . Assuming no bubbles are formed, the transport of chlorine takes place exclusively by diffusion. Using Fick's law of diffusion, we obtain

$$i = -2FD([\text{Cl}_2] - [\text{Cl}_2]_e)/\delta = -2Fm([\text{Cl}_2] - [\text{Cl}_2]_e), \quad (9)$$

where the mass-transfer coefficient $m = D/\delta$.

In the following the effect of chlorine diffusion on the E/i relation is discussed for three cases:

- (1) Both the Volmer and Tafel reaction can affect the E/i relation and $[\text{Cl}_2] \approx 0$.
- (2) The Tafel reaction affects the E/i relation and $[\text{Cl}_2] \approx 0$.
- (3) The Tafel reaction affects the E/i relation and $[\text{Cl}_2] > 0$.

The reversible potential at $[\text{Cl}^-]_R$ and $[\text{Cl}_2]_R$, denoted by E_R , is used as the reference potential. The calculations were performed for only one value of Cl^- concentration. Moreover, no concentration polarization of Cl^- occurs, so that $[\text{Cl}^-] = [\text{Cl}^-]_e = [\text{Cl}^-]_R$.

Evidently, $i = 0$ at E_R and $[\text{Cl}_2]_R$. This means that, in this case, the rate of the recombination Tafel reaction is that of the dissociation Tafel reaction and the rate of the anodic Volmer reaction is that of the cathodic Volmer reaction.

Owing to these equalities, it can be deduced that

$$k_T^* = \frac{k_T \theta_R^2}{[\text{Cl}_2]_R (1-\theta_R)^2} \quad (10)$$

and

$$k_{\text{c},V}^* = k_{\text{a},V}^* [\text{Cl}^-]_R \frac{(1-\theta_R)}{\theta_R} \exp[fE_R]. \quad (11)$$

Introducing $[\text{Cl}_2] = 0$ into (9), from (8)–(10) it follows:

$$i/i_{0,T,R} = \frac{\theta^2}{\theta_R^2 + \{k_T \theta_R^4 (1-\theta)^2\} / \{m[\text{Cl}_2]_R (1-\theta_R)^2\}}, \quad (12)$$

where

$$i_{0,T,R} = 2Fk_T \theta_R^2. \quad (13)$$

After the introduction of $k_{\text{a},V} = k_{\text{a},V}^* \exp[\alpha_V fE_R]$

Table 1. Theoretical parameters for the chlorine evolution at 25°C[1, 2]

Mechanism	Rate-determining step	Tafel slope b (mV)		z_{Cl^-}		z_{Cl_2}	
		$\theta \rightarrow 0$	$\theta \rightarrow 1$	$\theta \rightarrow 0$	$\theta \rightarrow 1$	$\theta \rightarrow 0$	$\theta \rightarrow 1$
Volmer–Tafel	$\text{Cl}^- \rightarrow \text{Cl}_{\text{ad}} + e^-$	118.4	118.4	1	1	0	0
	$2\text{Cl}_{\text{ad}} \rightarrow \text{Cl}_2$	29.6	∞	2	0	0	0
Volmer–Heyrowsky	$\text{Cl}^- \rightarrow \text{Cl}_{\text{ad}} + e^-$	118.4		1		0	
	$\text{Cl}_{\text{ad}} + \text{Cl}^- \rightarrow \text{Cl}_2 + e^-$	39.5	118.4	2	1	0	0
Krishtalik	$\text{Cl}^- \rightarrow \text{Cl}_{\text{ad}} + e^-$	118.4	118.4	1	1	0	0
	$\text{Cl}_{\text{ad}} \rightarrow \text{Cl}_{\text{ad}}^+ + e^-$	39.5	118.4	1	0	0	0
	$\text{Cl}_{\text{ad}}^+ + \text{Cl}^- \rightarrow \text{Cl}_2$	29.6	∞	2	0	0	0

into (7) it can be deduced from (7) and (11):

$$i = Fk_{a,v}[\text{Cl}^-]_R \left\{ (1 - \theta) \exp[\alpha_v f(E - E_R)] - \frac{(1 - \theta_R)\theta}{\theta_R} \exp[-(1 - \alpha_v)f(E - E_R)] \right\}. \quad (14)$$

From (12) and (14) and by inserting $\alpha_v = 0.5$, $f = 38.88 \text{ V}^{-1}$, $[\text{Cl}_2]_R = 5 \times 10^{-5} \text{ mol cm}^{-3}$ and $[\text{Cl}^-]_R = 5 \times 10^{-3} \text{ mol cm}^{-3}$, the relation between $i/i_{0,T,R}$ and $E - E_R$ was calculated for $m = 10^{-2}$ and $10^{20} \text{ cm s}^{-1}$ and for various values of k_T and $k_{a,v}$.

Characteristic results are shown in Fig. 1. From this figure it follows that the chlorine diffusion strongly affects the $(E - E_R)/\log(i/i_{0,T,R})$ curves. To indicate its shape, the slope b_1 at $0 \text{ V} < E - E_R < 0.1 \text{ V}$ and the slope b_2 at $-0.1 \text{ V} < E - E_R < 0 \text{ V}$ are used.

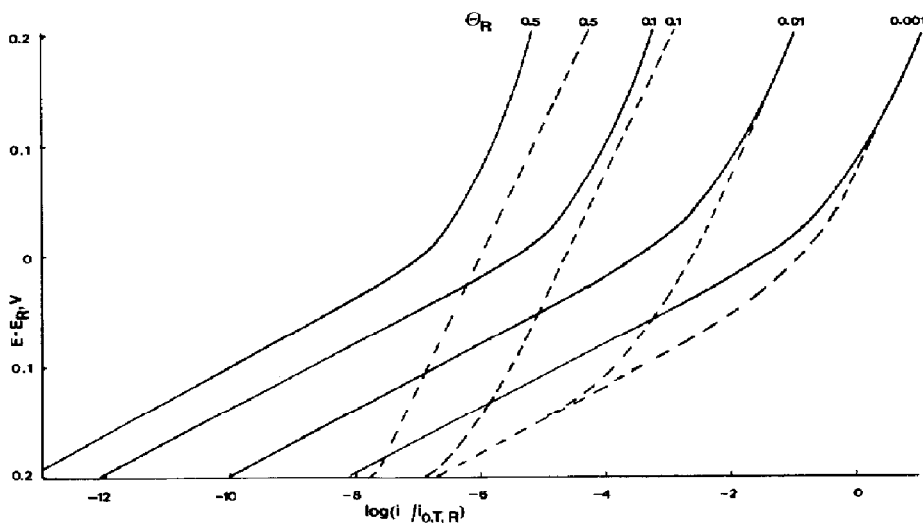


Fig. 1. The potential difference $E - E_R$ is plotted vs $\log(i/i_{0,T,R})$ for chlorine evolution according to the Volmer-Tafel mechanism for a 5 M NaCl solution containing no chlorine and for 298 K, $\alpha_v = 0.5$, $k_{a,v} = 10^3 \text{ cm s}^{-1}$, $k_T = 10 \text{ mol cm}^{-2} \text{ s}^{-1}$, various θ_R as well as for mass-transfer coefficient $m = 10^{-2} \text{ cm s}^{-1}$ (solid lines) and $10^{20} \text{ cm s}^{-1}$ (dotted lines).

The slopes b_1 and b_2 at $m = 10^{-2}$ and $10^{20} \text{ cm s}^{-1}$ at $k_T = 1 \text{ mol cm}^{-2} \text{ s}^{-1}$ are given as a function of $\log k_{a,v}$ in Fig. 2 and those at $k_{a,v} = 10^{-1} \text{ cm s}^{-1}$ as a function of $\log k_T$ in Fig. 3.

Calculations showed that for both curves the maximum of slope is $2RT/F$, viz 118.4 mV at 25°C, and the minimum $RT/2F$, viz 29.6 mV at 25°C. The chlorine diffusion does not affect the maximum and minimum slopes.

The quasi-equilibrium assumption can be used for the Volmer reaction. This gives

$$\theta = \frac{\theta_R}{\theta_R + (1 - \theta_R) \exp[-f(E - E_R)]}. \quad (15)$$

The rate of the Tafel reaction is given by (12). The relation between $E - E_R$ and $\log(i/i_{0,T,R})$ can be obtained from (12) and (15). This relation was calculated for $f = 38.88 \text{ V}^{-1}$, $[\text{Cl}_2]_R = 5 \times 10^{-5} \text{ mol cm}^{-3}$, $m = 10^{-2}$ and $10^{20} \text{ cm s}^{-1}$ and for various k_T and θ_R .

Characteristic results are given in Fig. 4. The chlorine diffusion has no effect on the slopes b_1 and b_2 ; a decrease in diffusion rate causes a parallel shift of $(E - E_R)/\log(i/i_{0,T,R})$ curve to lower current densities. b_1 as well as b_2 at both values of m , are practically equal to 30 mV for $\theta_R = 10^{-2}$ and 10^{-3} , and k_T varies between 10^{-6} and $10^6 \text{ mol cm}^{-2} \text{ s}^{-1}$.

From (8)–(10) it follows:

$$i/i_{0,T} = \frac{\theta^2 - \{\theta_R^2[\text{Cl}_2]_R(1 - \theta)^2\}/\{(1 - \theta_R)^2[\text{Cl}_2]_R\}}{\theta^2 + \{k_T\theta_R^2\theta^2(1 - \theta)^2\}/\{m[\text{Cl}_2]_R(1 - \theta_R)^2\}}, \quad (16)$$

where the exchange current density at E_c is given by

$$i_{0,T} = 2Fk_T\theta^2. \quad (17)$$

To calculate the η/i relation, the dependence of θ on η ($\eta = E - E_c$) has to be calculated. The Volmer

reaction is in quasi-equilibrium. From the rate equation for the Volmer reaction it can be deduced that

$$\theta = \frac{\theta_r}{\theta_r + (1 - \theta_r) \exp[-f(E - E_r)]}. \quad (18)$$

Moreover, it can be shown that

$$\frac{\theta_r}{1 - \theta_r} = \frac{\theta_R}{1 - \theta_R} \left(\frac{[\text{Cl}_2]}{[\text{Cl}_2]_R} \right)^{0.5}. \quad (19)$$

The relation between $i/i_{0,T}$ and η at $|\eta| < 0.010 \text{ V}$ was calculated from (16), (18) and (19) for $f = 38.88 \text{ V}^{-1}$, $[\text{Cl}_2]_R = 5 \times 10^{-5} \text{ mol cm}^{-3}$, $m = 10^{-2}$ and $10^{20} \text{ cm s}^{-1}$ and various $[\text{Cl}_2]$ (5×10^{-5} – $5 \times 10^{-6} \text{ mol cm}^{-3}$), k_T (10^{-6} – $10^6 \text{ mol s}^{-1} \text{ cm}^{-2}$) and θ_R (10^{-4} – 0.5).

It has been found that the slope k_T of the $\eta/(i/i_{0,T})$ curve, ($k_T = d\eta/d(i/i_{0,T})$) depends on chlorine diffusion at $\theta_R > 10^{-3}$ and $k_T > 1 \text{ mol s}^{-1} \text{ cm}^{-2}$. At $m = 10^{-2}$

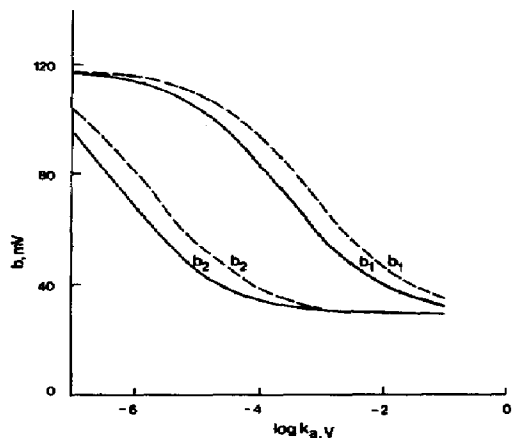


Fig. 2. The slope b_1 and b_2 are plotted vs $\log k_{a,V}$ for chlorine evolution according to the Volmer-Tafel mechanism, for a 5 M NaCl solution containing no chlorine, for 298 K, $\alpha_V = 0.5$, $k_T = 1 \text{ mol cm}^{-2} \text{ s}^{-1}$, $\theta_R = 10^{-3}$ and for mass-transfer coefficient $m = 10^{-2} \text{ cm s}^{-1}$ (solid lines) and $10^{20} \text{ cm s}^{-1}$ (dotted lines).

as well as $10^{20} \text{ cm s}^{-1}$, the factor $k_T i_{0,T}$ increases linearly with $\theta_R < 10^{-2}$ and for the investigated values of k_T . This means that at low degree of coverage the slope of $\log k_T i_{0,T} / \log [\text{Cl}_2]$ is equal to 1, independent of the chlorine diffusion.

2.2 Volmer-Heyrowsky mechanism

The anodic current density for reaction (4) is given by the well-known relation

$$i_H = F k_{a,H}^* [\text{Cl}^-]_c \theta \exp[\alpha_H f E] - F k_{c,H}^* [\text{Cl}_2]_c (1 - \theta) \exp[-(1 - \alpha_H) f E], \quad (20)$$

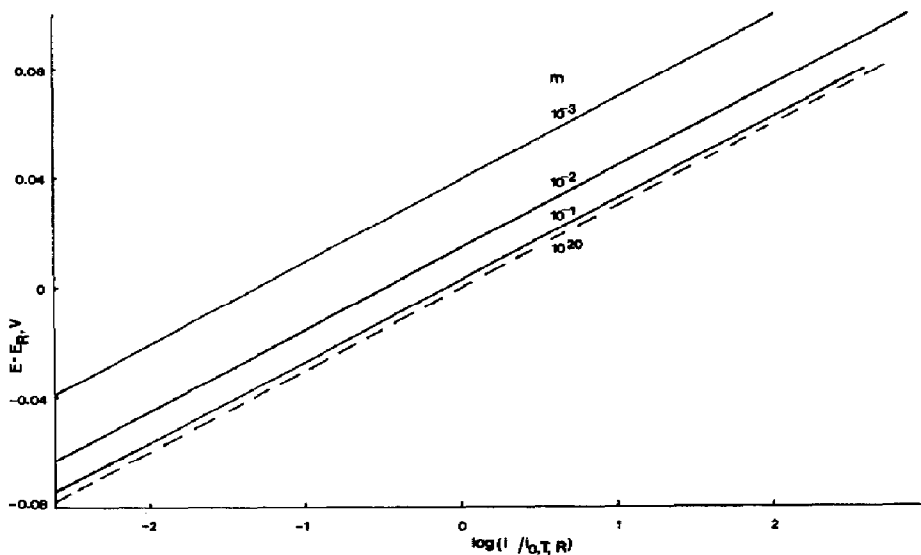


Fig. 4. The potential difference $E - E_R$ is plotted vs $\log(i/i_{0,T,R})$ for chlorine evolution according to the Volmer-Tafel mechanism where the Tafel reaction is rate-determining, for a 5 M NaCl solution containing $5 \times 10^{-2} \text{ M}$ chlorine, for 298 K, $\alpha_V = 0.5$, $k_T = 1 \text{ mol cm}^{-2} \text{ s}^{-1}$, $\theta_R = 10^{-3}$, and for various mass-transfer coefficients (for 10^{-3} , 10^{-2} , 10^{-1} cm s^{-1} , solid lines, and for $10^{20} \text{ cm s}^{-1}$, dotted lines).

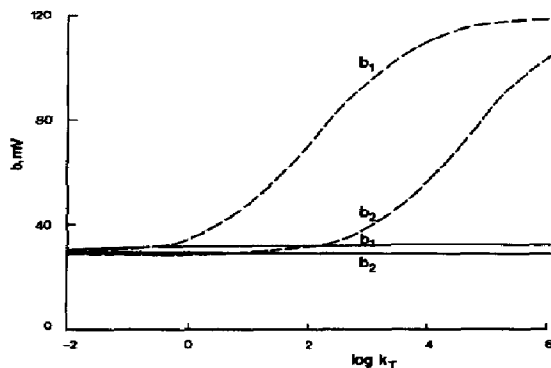


Fig. 3. The slopes b_1 and b_2 are plotted vs $\log k_T$ for chlorine evolution according to the Volmer-Tafel mechanism for a 5 M NaCl solution containing no chlorine, for 298 K, $\alpha_V = 0.5$, $k_{a,V} = 10^{-1} \text{ cm s}^{-1}$, $\theta_R = 10^{-3}$ and for mass-transfer coefficient $m = 10^{-2} \text{ cm s}^{-1}$ (solid lines) and $10^{20} \text{ cm s}^{-1}$ (dotted lines).

and the total current density by

$$i = i_V + i_H \text{ with } i_V = i_H. \quad (21)$$

Analogously to the Volmer-Tafel mechanism, the electronation current density for the diffusion of dissolved chlorine from the electrode surface is

$$i_H = -FD([\text{Cl}_2] - [\text{Cl}_2]_0)/\delta = -Fm([\text{Cl}_2] - [\text{Cl}]_0). \quad (22)$$

The effect of chlorine diffusion on the E/i relation is considered for three cases:

- (1) Both the Volmer and the Heyrowsky reaction can affect the E/i relation and $[\text{Cl}_2] \approx 0$.
- (2) The Heyrowsky reaction affects the E/i relation and $[\text{Cl}_2] \approx 0$.

(3) The Heyrowsky reaction affects the E/i relation and $[Cl_2] > 0$.

As in the case of Volmer-Tafel mechanism, the reference potential E_R is introduced and no concentration polarization of $[Cl^-]$ occurs. Similarly, it is concluded that when $i = 0$ at E_R and $[Cl_2]_R$, the rate of the anodic Volmer reaction equals that of the cathodic Volmer reaction and rate of the anodic Heyrowsky reaction that of the cathodic Heyrowsky reaction.

Owing to these equalities, it can be derived that $k_{c,v}^*$ is given by (11) and

$$k_{c,H}^* = k_{a,H}^* \frac{[Cl^-]_R}{[Cl_2]_R} \frac{\theta_R}{1-\theta_R} \exp[fE_R]. \quad (23)$$

After the introduction of $[Cl_2] = 0$ into (22), from (7), (11), (20) and (22) it follows that

$$i_v = Fk_{a,v}[Cl^-]_R \left\{ (1-\theta) \exp[\alpha_v f(E-E_R)] - \frac{\theta(1-\theta_R)}{\theta_R} \exp[-(1-\alpha_v)f(E-E_R)] \right\} \quad (24)$$

and

$$i_H = \frac{Fk_{a,H}[Cl^-]_R \theta \exp[\alpha_H f(E-E_R)]}{1 + \left\{ \frac{k_{a,H}[Cl^-]_R \theta_R (1-\theta)}{m[Cl_2]_R (1-\theta_R)} \right\} \exp[-(1-\alpha_H)f(E-E_R)]} \quad (25)$$

where

$$k_{a,v} = k_{a,v}^* \exp[\alpha_v fE_R],$$

$$k_{a,H} = k_{a,H}^* \exp[\alpha_H fE_R].$$

Since $i_v = i_H$, from (24) and (25) and by increasing $\alpha_v = \alpha_H = 0.5$, $f = 38.88 \text{ V}^{-1}$, $[Cl_2]_R = 5 \times 10^{-5} \text{ mol cm}^{-3}$, $[Cl^-]_R = 5 \times 10^{-3} \text{ mol cm}^{-3}$, θ was calculated as a function of $E-E_R$ for $m = 10^{-2}$ and $10^{20} \text{ cm s}^{-1}$ and for various $k_{a,H}$ (2×10^{-4} – $2 \times 10^3 \text{ cm s}^{-1}$), $k_{a,v}$ (2×10^{-7} – $2 \times 10^3 \text{ cm s}^{-1}$) and θ_R (10^{-3} – 0.5). From the θ obtained and from (21) and (25) the relation between i/i_0 and $E-E_R$ was calculated where

$$i_{0,VH,R} = \frac{2Fk_{a,H}k_{a,v}\theta_R(1-\theta_R)}{k_{a,H}\theta_R + k_{a,v}(1-\theta_R)}. \quad (26)$$

Characteristic results are shown in Fig. 5. It has been found that the $(E-E_R)/\log(i/i_{0,VH,R})$ curve, and particularly its slope, can be affected by chlorine diffusion. The definitions for b_1 and b_2 are already given in the case of Volmer-Tafel mechanism. Both the slope b_1 and b_2 at $\theta_R = 10^{-3}$ and $m = 10^{-2}$ and $10^{20} \text{ cm s}^{-1}$ at $k_{a,H} = 2 \times 10^1 \text{ cm s}^{-1}$ is given as a function of $\log k_{a,v}$ in Fig. 6 and those at $k_{a,v} = 2 \times 10^1 \text{ cm s}^{-1}$ as a function of $\log k_{a,H}$ in Fig. 7.

Figures 6 and 7 show that the minima of b_1 and b_2 at 25°C are 39.5 mV if chlorine diffusion does not determine the E/i relation and 29.6 mV if the chlorine diffusion co-determines the E/i relation.

Since, in this case, the Volmer reaction is in quasi-equilibrium, it can be deduced from its rate equation that

$$\theta = \frac{\theta_R}{\theta_R + (1-\theta_R) \exp[-f(E-E_R)]}. \quad (27)$$

From (25) and (27) and from $i_{0,H,R} = Fk_{a,H}$

$[Cl^-]_R \theta_R$, the relation between $i/i_{0,H,R}$ and $E-E_R$ was calculated for $\alpha_H = 0.5$, $f = 38.88 \text{ V}^{-1}$, $m = 10^{-2}$ and $10^{20} \text{ cm s}^{-1}$, $[Cl^-]_R = 5 \times 10^{-3} \text{ mol cm}^{-3}$, $[Cl_2]_R = 5 \times 10^{-5} \text{ mol cm}^{-3}$ and various $k_{a,H}$ (10^{-2} – 10^8 cm s^{-1}) and θ_R (10^{-3} – 0.5). The results are shown in Fig. 8.

The slopes b_1 and b_2 and $\theta_R = 10^{-3}$ are given as a function of $\log k_{a,H}$ in Fig. 9. This figure shows that both slopes b_1 and b_2 are 39.5 mV at $k_{a,H} < 10^{-3} \text{ cm s}^{-1}$ and 29.6 mV at $k_{a,H} > 10^2 \text{ cm s}^{-1}$.

To determine the stoichiometric numbers of the species involved, for the electrode reaction, the slopes

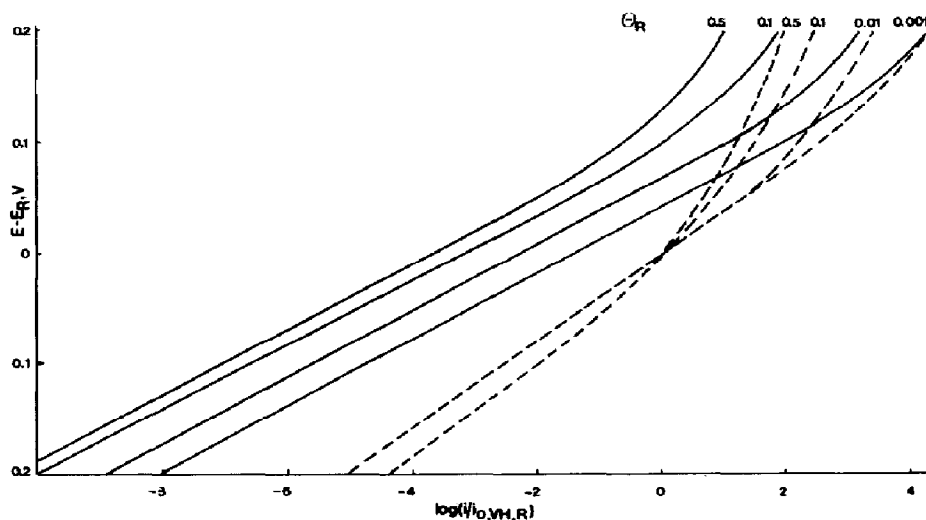


Fig. 5. The potential difference $E-E_R$ is plotted vs $\log(i/i_{0,VH,R})$ for chlorine evolution according to the Volmer-Heyrowsky mechanism for a 5 M NaCl solution containing no chlorine, for 298 K, $\alpha_v = \alpha_H = 0.5$, $k_{a,v} = 10^{-2} \text{ cm s}^{-1}$, $k_{a,H} = 10^{-2} \text{ cm s}^{-1}$, various θ_R , and for mass-transfer coefficient $m = 10^{-2} \text{ cm s}^{-1}$ (solid lines) and $10^{20} \text{ cm s}^{-1}$ (dotted lines).

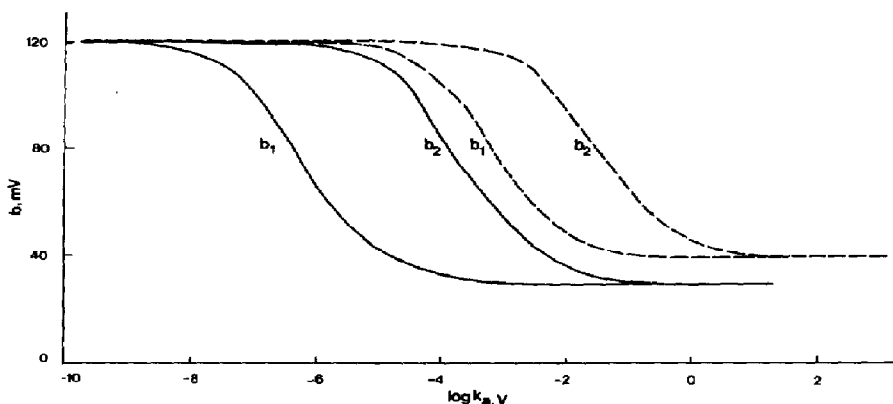


Fig. 6. The slopes b_1 and b_2 are plotted vs $\log k_{a,v}$ for chlorine evolution according to the Volmer-Heyrowsky mechanism for a 5 M NaCl solution containing no chlorine, for 298 K, $\alpha_V = \alpha_H = 0.5$, $k_{a,H} = 20 \text{ cm s}^{-1}$, $\theta_R = 10^{-3}$ and for mass-transfer coefficient $m = 10^{-2} \text{ cm s}^{-1}$ (solid lines) and $10^{20} \text{ cm s}^{-1}$ (dotted lines).

of the η/i curve at very low overpotentials η , for instance $|\eta| < 0.01 \text{ V}$, are used. Also, in this case E_R is chosen as the reference reversible potential and $[\text{Cl}^-]_c = [\text{Cl}^-]_R = [\text{Cl}^-]$.

Moreover, the Volmer reaction is in quasi-equilibrium.

The effect of $[\text{Cl}_2]$ on the slope h_H of the η/i curve at low overpotentials can be calculated as follows.

From Nernst's equation it follows that

$$\frac{[\text{Cl}_2]}{[\text{Cl}_2]_R} = \exp[2f(E_r - E_R)]. \quad (28)$$

$$\frac{i}{i_{0,H}} = \frac{\frac{\theta}{\theta_r} \exp[\alpha f \eta] - \{\theta_R(1-\theta)\}/\{\theta_r(1-\theta_R)\} \left(\frac{[\text{Cl}_2]}{[\text{Cl}_2]_R}\right)^{0.5\alpha_H} \exp[-(1-\alpha_H)f\eta]}{1 + \{k_{a,H}[\text{Cl}^-]_R \theta_R(1-\theta)\}/\{m[\text{Cl}_2]_R(1-\theta_R)\} \left(\frac{[\text{Cl}_2]}{[\text{Cl}_2]_R}\right)^{0.5(1+\alpha_H)} \exp[-(1-\alpha_H)f\eta]} \quad (31)$$

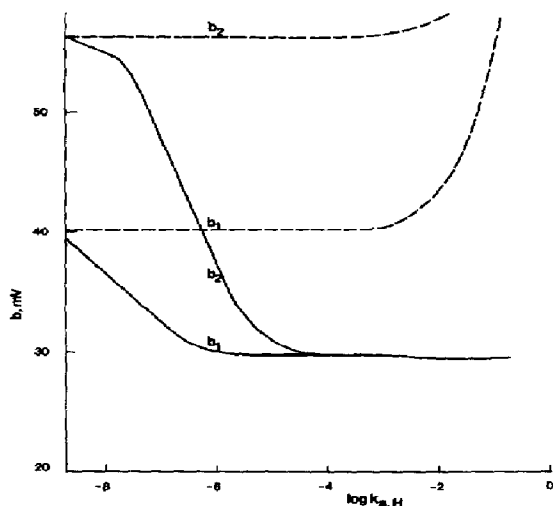


Fig. 7. The slopes b_1 and b_2 are plotted vs $\log k_{a,H}$ for chlorine evolution according to the Volmer-Heyrowsky mechanism for a 5 M NaCl solution containing no chlorine, for 298 K, $\alpha_V = \alpha_H = 0.5$, $k_{a,v} = 2 \times 10^2 \text{ cm s}^{-1}$, $\theta_R = 10^{-3}$ and for mass-transfer coefficient $m = 10^{-2} \text{ cm s}^{-1}$ (solid lines) and $10^{20} \text{ cm s}^{-1}$ (dotted lines).

Moreover, see (19)

$$\frac{\theta_r}{1-\theta_r} = \frac{\theta_R}{1-\theta_R} \left(\frac{[\text{Cl}_2]}{[\text{Cl}_2]_R}\right)^{0.5} \quad (29)$$

and

$$k_{c,H} = k_{a,H} \frac{\theta_R}{1-\theta_R} \frac{[\text{Cl}^-]_R}{[\text{Cl}_2]_R}. \quad (30)$$

Assuming $k_{a,H} = k_{a,H}^* \exp[\alpha_H f E_R]$ and $k_{c,H} = k_{c,H}^* \exp[-(1-\alpha_H) f E_R]$ from (20), (28)–(30) we obtain

where

$$i_{0,H} = F k_{a,H} [\text{Cl}^-]_R \theta_r \left(\frac{[\text{Cl}_2]}{[\text{Cl}_2]_R}\right)^{0.5\alpha_H}. \quad (32)$$

The relation between $i/i_{0,H}$ and η was calculated using (29) and (31). This was performed for $\alpha_H = 0.5$, $f = 38.88 \text{ V}^{-1}$, $[\text{Cl}^-]_R = 5 \times 10^{-3} \text{ mol cm}^{-3}$, $[\text{Cl}_2]_R = 5 \times 10^{-5} \text{ mol cm}^{-3}$, $m = 10^{-2}$ and $10^{20} \text{ cm s}^{-1}$ and for various θ_R (10^{-3} – 0.5), $[\text{Cl}_2]$ (5×10^{-6} – $5 \times 10^{-5} \text{ mol cm}^{-3}$) and $k_{a,H}$ (10^{-7} – 1 cm s^{-1}). Characteristic results are shown in Fig. 10.

It has been found that the slope h_H of $\eta/(i/i_{0,H})$ curve is practically independent of chlorine diffusion at $k_{a,H} < 10^{-5} \text{ cm s}^{-1}$.

In practice, the η/i relation is determined, so that the factor $h_H i_{0,H}$ is of more interest. The factors $h_{1,H} i_{0,H}$ and $h_{2,H} i_{0,H}$ were calculated with $h_{1,H}$ is the slope of $\eta/(i/i_{0,H})$ curve at $0 \text{ V} < \eta < 0.006 \text{ V}$ and $h_{2,H}$ that at $-0.006 \text{ V} < \eta < 0 \text{ V}$.

To determine the reaction order of molecular chlorine, the dependence of the factors $h_{1,H} i_{0,H}$ and $h_{2,H} i_{0,H}$ on $[\text{Cl}_2]$ is of great interest. This dependence was determined by plotting $h_{1,H} i_{0,H}$ and $h_{2,H} i_{0,H}$ vs $[\text{Cl}_2]$ on a logarithmic scale. The slope of $\log h_{1,H} i_{0,H} / \log [\text{Cl}_2]$ is denoted by n_1 and that of $\log h_{2,H} i_{0,H} / \log [\text{Cl}_2]$ by n_2 . Both slopes n_1 and n_2 are

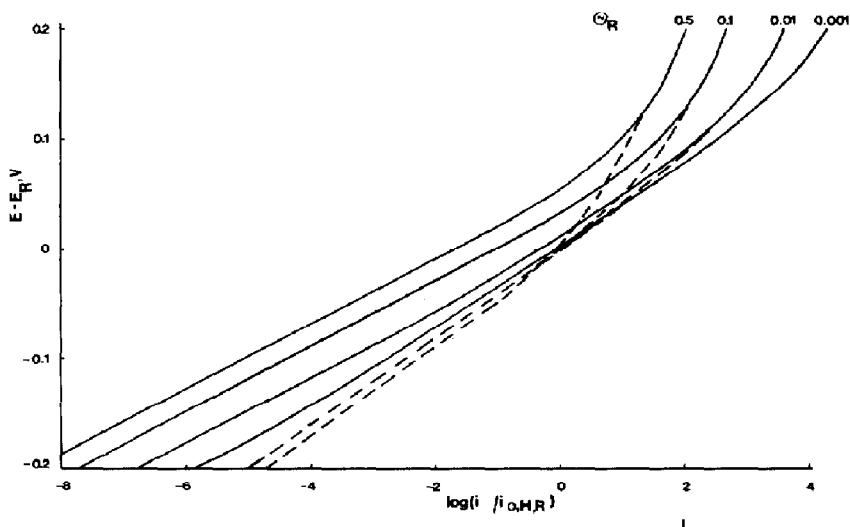


Fig. 8. The potential difference $E - E_R$ is plotted vs $\log(i/i_{0,H,R})$ for the Volmer-Heyrowsky mechanism where the Heyrowsky reaction is rate-determining, for a 5 M NaCl solution containing 5×10^{-3} M chlorine and for 298 K, $\alpha_H = 0.5$, $k_{a,H} = 10^{-2}$ cm s $^{-1}$, various θ_R and for mass-transfer coefficient $m = 10^{-2}$ cm s $^{-1}$ (solid lines) and 10^{20} cm s $^{-1}$ (dotted lines).

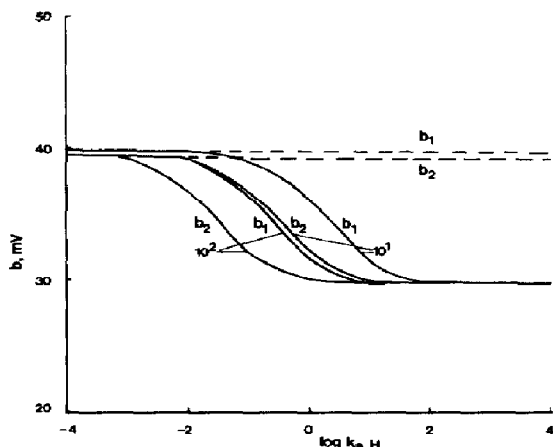


Fig. 9. The slopes b_1 and b_2 are plotted vs $\log k_{a,H}$ for chlorine evolution according to the Volmer-Heyrowsky mechanism where the Heyrowsky reaction is rate-determining, for a 5 M NaCl solution containing 5×10^{-2} M chlorine, and for 298 K, $\alpha_H = 0.5$, $\theta_R = 10^{-3}$ for various mass-transfer coefficients (for 10^{-2} and 10^{-1} cm s $^{-1}$, solid lines, and 10^{20} cm s $^{-1}$, dotted lines).

plotted as a function of $\log k_{a,H}$ at $\theta_R = 10^{-3}$ and $m = 10^{-2}$ and 10^{20} cm s $^{-1}$ in Fig. 11 and as a function of $\log \theta_R$ at $k_{a,H} = 1$ cm s $^{-1}$ and $m = 10^{-2}$ and 10^{20} cm s $^{-1}$ in Fig. 12. These figures show clearly that the diffusion of molecular chlorine can strongly affect the dependence of the slope of the η/i curve on $[\text{Cl}_2]$.

3. DISCUSSION

Relations between potential and logarithm of current density at two mass-transfer coefficients, viz

$m = 10^{-2}$ and 10^{20} cm s $^{-1}$ are shown in Fig. 1 for the Volmer-Tafel mechanism, in Fig. 5 for the Volmer-Heyrowsky mechanism, and in Fig. 8 for the Volmer-Heyrowsky mechanism where the Volmer reaction is in quasi-equilibrium.

The results for $m = 10^{20}$ cm s $^{-1}$ can be considered as the ones without limitation of chlorine diffusion. The potential/log current density curves of Figs 1, 5 and 8 are almost linear, generally over many decades of current densities, after which they bend sharply. The slopes of the linear section of these curves are considered as the Tafel slopes. Only the results at 25° are discussed already.

The Tafel slope depends on many factors, *eg* the rate constants of anodic and cathodic reactions, the mass-transfer coefficient of chlorine, the chlorine concentration, the charge-transfer coefficient and the degree of coverage by chlorine atoms at the reversible reference electrode potential. Since only high Tafel slopes, *viz* 118.4, are found when the Volmer reaction is the rate-determining step, this case is left out of consideration below.

For both the Volmer-Tafel and the Volmer-Heyrowsky mechanism the same minimum Tafel slope has been found, *viz* 29.6 mV. For the Volmer-Tafel mechanism this slope has been found when the rate-determining step is either the Tafel reaction [4, 5] or the chlorine diffusion [3], Figs 1-3). A slope of 29.6 mV has also been found for the Volmer-Heyrowsky mechanism when the chlorine diffusion is the rate-determining step ([3], Figs 5-9). When no limitation of chlorine diffusion occurs, a minimum slope of 39.5 mV has been obtained for the Volmer-Heyrowsky mechanism where the Heyrowsky reaction is the rate-determining step. Consequently, for the Volmer-Heyrowsky mechanism the Tafel slope can be used to decide whether the Heyrowsky reaction or the chlorine diffusion is rate-determining.

For chlorine evolution on anodes based on RuO $_2$ or

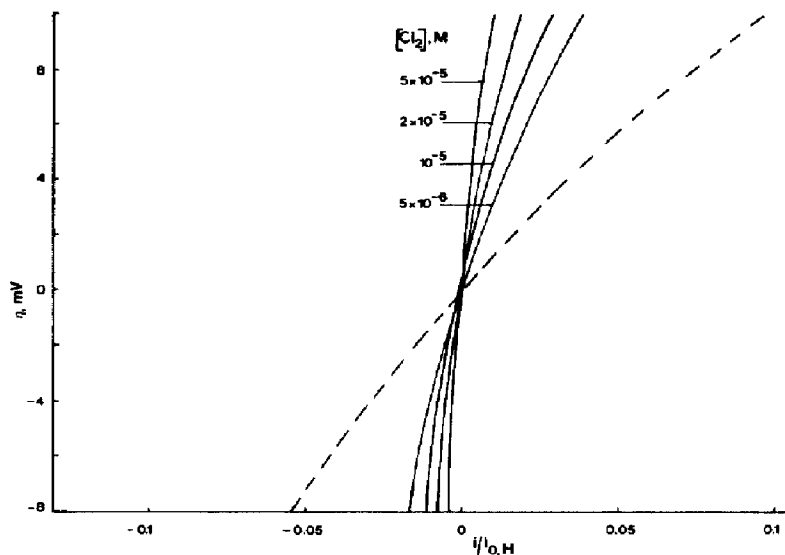


Fig. 10. The overpotential η is plotted vs $i/i_{0,H}$ for chlorine evolution and reduction, both according to the Volmer–Heyrowsky mechanism where the Heyrowsky reaction is rate-determining and for a 5 M NaCl solution with various chlorine concentrations, varying between 5×10^{-2} and 5×10^{-3} M, and for 298 K, $\alpha_H = 0.5$, $k_{a,H} = 10^{-3} \text{ cm s}^{-1}$, $\theta_R = 10^{-3}$ and for mass-transfer coefficient $m = 10^{-2} \text{ cm s}^{-1}$ (solid lines) and $10^{20} \text{ cm s}^{-1}$ (dotted lines).

on, eventually, a mixture of RuO_2 and TiO_2 , experimental Tafel slopes of about 30 and 40 mV have been found[6]. Both slopes can be explained with the Volmer–Heyrowsky mechanism where the Volmer reaction is in quasi-equilibrium. The introduction of a barrierless electrode reaction is not necessary for explanation of the experimental Tafel slopes. Moreover, the formation of a Cl^+ intermediate, proposed by Krishtalik and Rotenberg[1], is very unlikely owing to its probably high heat of formation.

To elucidate the mechanism of chlorine evolution the usefulness of the dependence of the polarization resistance $R_0 = (d\eta/di)_{\eta \rightarrow 0}$ on the chlorine concentration has been determined for two values of mass-

transfer coefficients. For the Volmer–Tafel mechanism, where the Tafel reaction is rate-determining, it has been found that at $\theta_R < 10^{-2}$ the chlorine diffusion does not affect the ratio between R_0 and $[\text{Cl}_2]$. On the other hand, for the Volmer–Heyrowsky mechanism, where the Heyrowsky reaction is rate-determining, the ratio between R_0 and $[\text{Cl}_2]$ depends on the mass-transfer coefficient of chlorine (Fig. 11).

The stoichiometric number of the rate-determining step, ie its repetition number along the whole reaction route, is often used to elucidate the mechanism and is given by

$$v = \frac{nF}{RT} i_{0,e} \left(\frac{d\eta}{di} \right)_{\eta \rightarrow 0}, \quad (33)$$

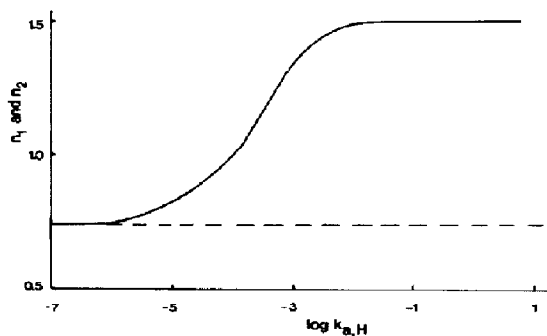


Fig. 11. The slopes n_1 and n_2 are plotted vs $\log k_{a,H}$ for chlorine evolution according to the Volmer–Heyrowsky mechanism where the Heyrowsky reaction is rate-determining, for a 5 M NaCl solution containing 5×10^{-2} M chlorine, for 298 K, $\alpha_H = 0.5$, $\theta_R = 10^{-3}$ and for mass-transfer coefficient $m = 10^{-2} \text{ cm s}^{-1}$ (solid line) and $10^{20} \text{ cm s}^{-1}$ (dotted line).

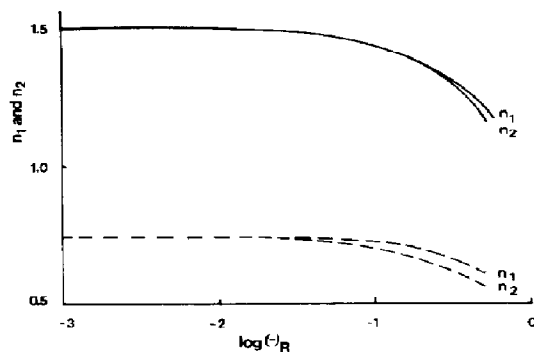


Fig. 12. The slopes n_1 and n_2 are plotted vs $\log \theta_R$ for chlorine evolution according to the Volmer–Heyrowsky mechanism where the Heyrowsky reaction is rate-determining, for a 5 M NaCl solution containing 5×10^{-2} M chlorine, for 298 K, $\alpha_H = 0.5$, $\theta_R = 10^{-3}$ and for mass-transfer coefficient $m = 10^{-2} \text{ cm s}^{-1}$ (solid lines) and $10^{20} \text{ cm s}^{-1}$ (dotted lines).

where $i_{0,e}$ is the exchange current density determined by extrapolation of the Tafel line to the reversible potential. The stoichiometric number is obtained from polarization resistance measurements. Hence, careful use has to be made of both the polarization resistance R_0 and the stoichiometric number to elucidate the mechanism of the gas-evolving electrode reaction with adsorbed atomic intermediates.

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