

Analysis of the Volmer–Krishtalic mechanism for the chlorine electrode reaction

José L. Fernández, María R. Gennero de Chialvo, Abel C. Chialvo*

Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, 3000 Santa Fe, Argentina

Received 8 June 2000; received in revised form 19 June 2000; accepted 19 June 2000

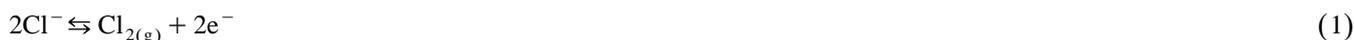
Abstract

The dependencies of the current density and surface coverage of the adsorbed intermediates on overpotential were established without kinetic approximations for the chlorine electrode reaction under the Volmer–Krishtalic mechanism. Tafelian regions were obtained which slope values cannot be derived from the use of the rate determining step criteria, such as $2.3026(2RT/3F)$ and $2.3026(RT/F)$, as well as two or three Tafel regions with different slopes in the same anodic or cathodic curve. The existence of limiting kinetic current densities was also demonstrated. Finally, the results obtained were analysed and discussed, comparing them with those obtained by the usual methods. © 2000 Elsevier Science S.A. All rights reserved.

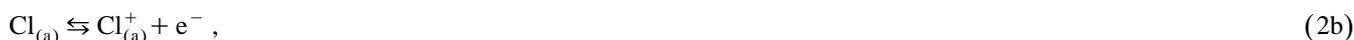
Keywords: Chlorine evolution; Volmer–Krishtalic mechanism; Tafel slopes

1. Introduction

The chlorine electrode reaction (CIER):



has been discussed in many papers through the Volmer–Krishtalic mechanism [1–4]:



Considering alternatively each step ($i = 1, 2, 3$) as the rate determining and the others at quasi-equilibrium, the Tafel slopes (b_i) corresponding to each case were determined [5,6]. Thus, the values $b_1 = 2.3026RT/2F$, $b_2 = 2.3026RT/(1 + \alpha)F$ and $b_3 = 2.3026RT/\alpha F$ were obtained, α being the symmetry factor. Nevertheless, it should be taken into account that the CIER can display limiting kinetic current densities [4–7]. The approximated resolution of the Volmer–Krishtalic mechanism can describe this situation only if a barrierless anodic process is verified [6]. Furthermore, the consideration that two of the elementary steps are in the quasi-equilibrium state is a very restrictive condition and it is rather difficult to be accomplished.

It is likely that the descriptive capability of the kinetic mechanism is reduced by the approximations used in its resolution. Therefore, the present work evaluates the dependencies of the current density (j) and the surface coverage on overpotential (η) without kinetic approximations for the Volmer–Krishtalic mechanism.

* Corresponding author. Tel.: +54-342-457-1164, Ext. 2519; fax: +54-342-457-1162.
E-mail address: achialvo@fiqus.unl.edu.ar (A.C. Chialvo).

2. Theoretical considerations

2.1. Basic equations

In the mechanism given by Eqs. (2a)–(2c) there are three elementary steps and two intermediate species, $Cl_{(a)}$ and $Cl_{(a)}^+$. Consequently, the whole reaction (1) can be verified only through one route. Its occurrence in steady state implies the fulfillment of the following equalities:

$$V = v_1 = v_2 = v_3, \tag{3}$$

where V is the overall reaction rate and v_i ($i = 1, 2, 3$) the corresponding reaction rate of the step i . The expressions of the reaction rate of the elementary steps, for a Langmuir type adsorption of the adsorbed species and in absence of mass transfer limitations, are [8]:

$$v_1 = v_1^e \left[\frac{(1 - \theta_I - \theta_{II})}{(1 - \theta_I^e - \theta_{II}^e)} e^{\alpha_1 f \eta} - \frac{\theta_I}{\theta_I^e} e^{-(1 - \alpha_1) f \eta} \right], \tag{4}$$

$$v_2 = v_2^e \left[\frac{\theta_I}{\theta_I^e} e^{\alpha_2 f \eta} - \frac{\theta_{II}}{\theta_{II}^e} e^{-(1 - \alpha_2) f \eta} \right], \tag{5}$$

$$v_3 = v_3^e \left[\frac{\theta_{II}}{\theta_{II}^e} - \frac{(1 - \theta_I - \theta_{II})}{(1 - \theta_I^e - \theta_{II}^e)} \right], \tag{6}$$

θ_I and θ_{II} being the surface coverage of $Cl_{(a)}$ and $Cl_{(a)}^+$, respectively. The superscript e indicates equilibrium condition, α_1 and α_2 are the symmetry factors of steps 1 and 2, respectively and $f = F/RT$ (38.92039 V⁻¹ at 298.16 K). Besides, η values are considered positive for the anodic direction.

2.2. Dependence of the surface coverage

Substituting the expressions of the reaction rate of the corresponding steps (4–6) on the equalities of Eq. (3), considering $\alpha_1 = \alpha_2 = \alpha$, the following expressions for θ_I and θ_{II} can be obtained:

$$\theta_I = \frac{\theta_I^e [m_3 + m_2 e^{-(1 - \alpha) f \eta} + m_2 m_3 e^{-f \eta}]}{(1 - \theta_I^e - \theta_{II}^e) [m_2 m_3 + m_2 e^{-(2 - \alpha) f \eta} + m_3 e^{-f \eta}] + \theta_I^e [m_3 + m_2 e^{-(1 - \alpha) f \eta} + m_2 m_3 e^{-f \eta}] + \theta_{II}^e [m_2 m_3 + m_2 e^{\alpha f \eta} + m_3 e^{-f \eta}]}, \tag{7}$$

$$\theta_{II} = \frac{\theta_{II}^e}{[\theta_{II}^e - (1 - \theta_I^e - \theta_{II}^e) m_2 e^{-f \eta}]} \left\{ 1 - \left[1 + \frac{(1 - \theta_I^e - \theta_{II}^e)}{\theta_I^e} (m_2 + e^{-f \eta}) \right] \theta_I \right\}, \tag{8}$$

Table 1

Values of the Tafel slope ($b/2.3026$) and the corresponding ranges of θ_i^e ($i = I, II$) and m_i ($i = 1, 2$) values for the Volmer–Krishtalic mechanism

Anodic reaction	Cathodic reaction	Eq. surface coverage	$m_2; m_3$ or m_2/m_3
∞	∞	$\theta_I^e \leq 0.9; 0.1 \leq \theta_{II}^e \leq 0.9$	$1 \leq m_2/m_3$
	2RT/F; ∞	$\theta_I^e < 10^{-2}; (1 - \theta_{II}^e) \leq 10^{-2}$	$0.1 \leq m_2/m_3 \leq 1$
	RT/F; ∞	$0 < (1 - \theta_I^e - \theta_{II}^e) \leq 2 \cdot 10^{-6}$	$10^3 \leq m_2/m_3$
	RT/2F; ∞	$\theta_I^e < 10^{-3}; (1 - \theta_{II}^e) \leq 10^{-3}$	$10^3 \leq m_2/m_3$
	RT/F; 2RT/F(*)	$(\theta_I^e + \theta_{II}^e) = 1; 10^{-3} < \theta_{II}^e$	$10^{-4} < m_2; m_3 \leq 10^{-2}$
	RT/2F; 2RT/F; ∞	$\theta_I^e < 10^{-4}; (1 - \theta_{II}^e) \leq 10^{-4}$	$10^2 \leq m_2/m_3 \leq 10^3$
2RT/F; ∞	∞	$\theta_I^e \leq 0.9; \theta_{II}^e \leq 10^{-4}$	$m_2 \leq 0.1; 0.1 \leq m_2/m_3 \leq 1$
	2RT/F; ∞	$10^{-4} \leq (1 - \theta_{II}^e)$	$m_2 \leq 1; m_2/m_3 \leq 10^{-2}$
	RT/F; ∞	$(1 - \theta_I^e) \leq 10^{-2}; \theta_{II}^e < 10^{-2}$	$m_3 \leq 10^{-2}; 0.1 \leq m_2/m_3 \leq 1$
	2RT/3F; ∞	$\theta_I^e \leq 10^{-4}; \theta_{II}^e < 0.9$	$10^2 \leq m_3; 1 \leq m_2/m_3$
	2RT/3F; 2RT/F; ∞	$(1 - \theta_I^e) \leq 10^{-2}; \theta_{II}^e < 10^{-2}$	$1 \leq m_3; m_2/m_3 \leq 10^{-3}$
RT/F; ∞	∞	$\theta_I^e \leq 0.9; \theta_{II}^e \leq 10^{-4}$	$m_2 \leq 10^3; 10^2 \leq m_2/m_3 \leq 10^5$
	RT/F; ∞	$(1 - \theta_I^e) \leq 10^{-2}; \theta_{II}^e < 10^{-2}$	$m_2 \leq 10^3; 10^2 \leq m_2/m_3 \leq 10^5$
	RT/F; 2RT/F(*)	$(\theta_I^e + \theta_{II}^e) = 1; \theta_{II}^e \leq 10^{-3}$	$10^{-4} < m_2; m_3 \leq 10^{-2}$
RT/F; 2RT/F; ∞	∞	$\theta_I^e \leq 0.9; \theta_{II}^e < 10^{-4}$	$10^{-3} < m_3 \leq 0.1; 10 < m_2/m_3 < 10^3$
	RT/F; ∞	$(1 - \theta_I^e) < 0.1; \theta_{II}^e < 10^{-4}$	$10^{-3} < m_3 \leq 0.1; 10 < m_2/m_3 < 10^3$
2RT/3F; ∞	2RT/F; ∞	$\theta_I^e \leq 10^{-5}; 0.1 \leq \theta_{II}^e$	$m_3 \leq 10; 10^{-8} \leq m_2/m_3 \leq 10^{-4}$
2RT/3F; 2RT/F; ∞	2RT/F; ∞	$10^{-4} \leq \theta_I^e < 0.1; \theta_{II}^e \leq 0.1$	$m_2/m_3 \leq 10^{-7}$
RT/2F; ∞	∞	$\theta_I^e \leq 10^{-3}; 10^{-5} \leq \theta_{II}^e \leq 10^{-3}$	$1 \leq m_2; m_3 \leq 10^{-3}$
RT/2F; 2RT/3F; ∞	∞	$\theta_I^e \leq 10^{-6}; \theta_{II}^e \cong 10^{-10}$	$10^{-6} \leq m_2 \leq 10^{-5}; 10^{-7} \leq m_3 \leq 10^{-6}$
RT/2F; 2RT/F; ∞	∞	$\theta_I^e \leq 10^{-3}; \theta_{II}^e < 10^{-6}$	$10^{-2} \leq m_2; m_3 \leq 10^{-3}$

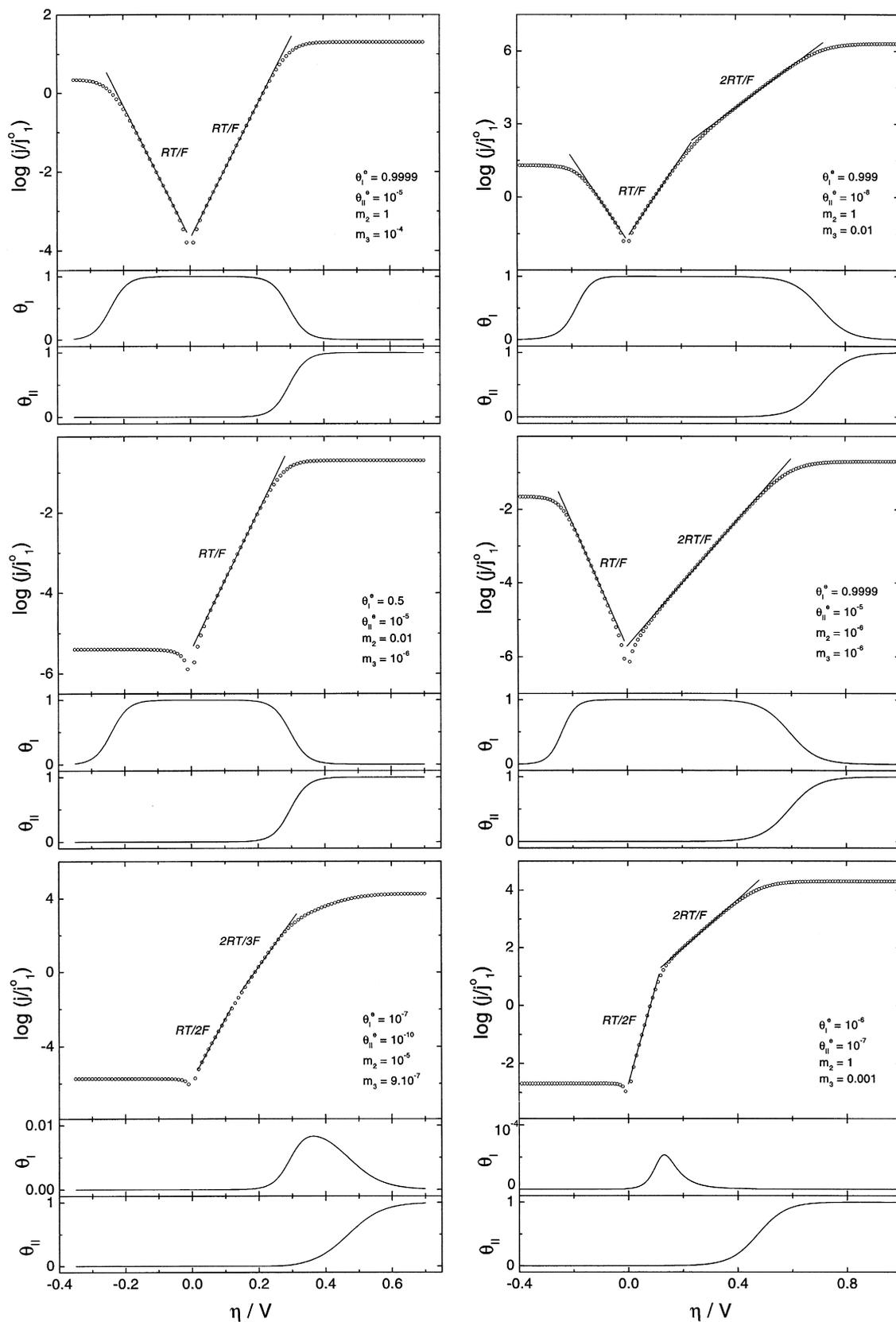


Fig. 1. Dependence of $\log j/j_1^0$ and θ_i ($i = I, II$) on η for some particular values of the elementary kinetic parameters, which are indicated in the figure.

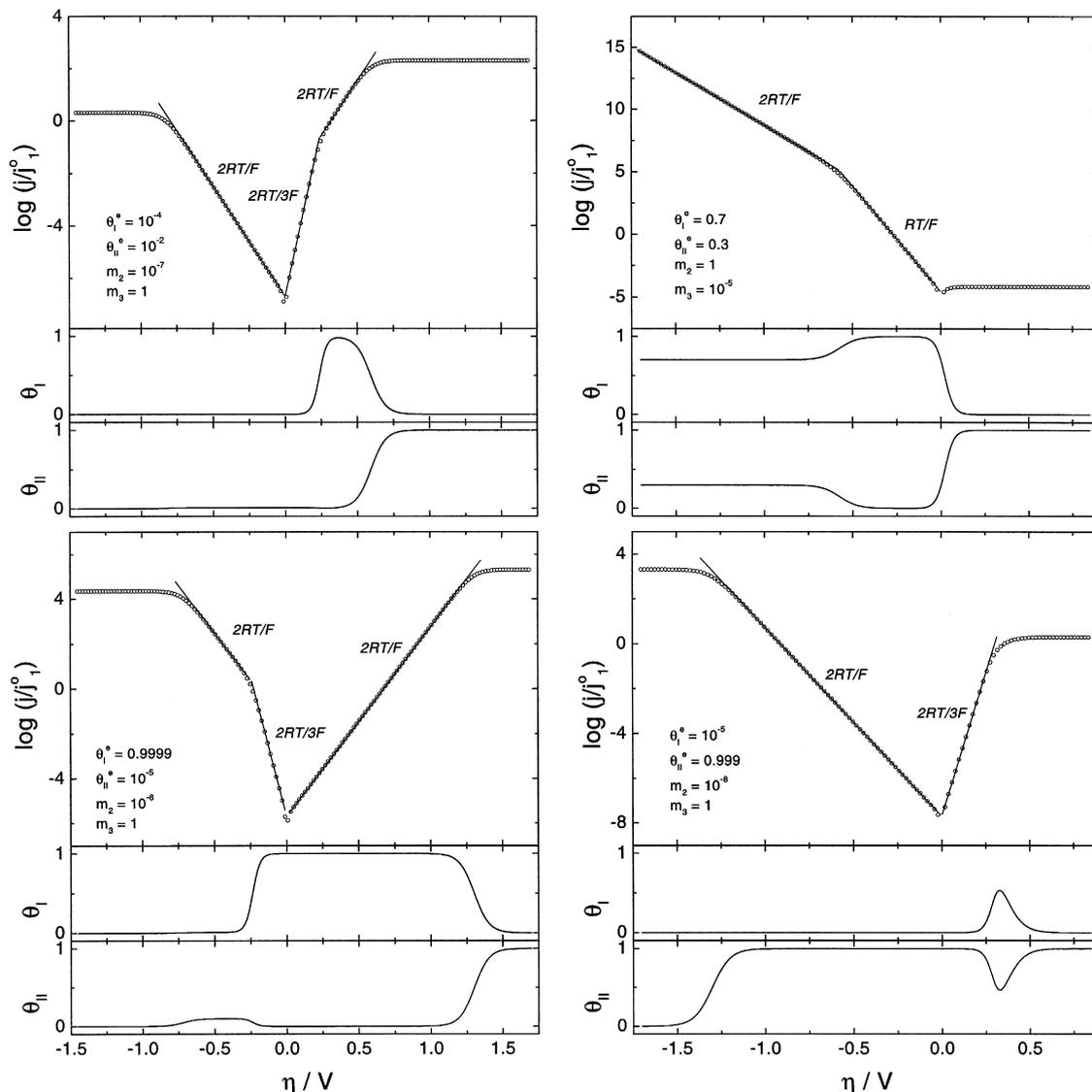


Fig. 2. Dependence of $\log j/j_1^0$ and θ_i ($i = I, II$) on η for some particular values of the elementary kinetic parameters, which are indicated in the figure.

where $m_2 = v_2^e/v_1^e$ and $m_3 = v_3^e/v_1^e$. Eqs. (7) and (8) verify that $\theta_i(\eta = 0) = \theta_i^e$ ($i = I, II$) and the following limiting behaviour for $\theta_1^e \neq (1 - \theta_{II}^e)$:

$$\lim_{\eta \rightarrow \infty} \theta_I = \theta_{I(+)}^* = 0, \quad \lim_{\eta \rightarrow \infty} \theta_{II} = \theta_{II(+)}^* = 1, \tag{9}$$

$$\lim_{\eta \rightarrow -\infty} \theta_I = \theta_{I(-)}^* = 0, \quad \lim_{\eta \rightarrow -\infty} \theta_{II} = \theta_{II(-)}^* = 0. \tag{10}$$

When $\theta_1^e = (1 - \theta_{II}^e)$, it can be demonstrated from Eq. (8) that $\theta_I(\eta) = [1 - \theta_{II}(\eta)]$ and the following limits are satisfied:

$$\lim_{\eta \rightarrow \infty} \theta_I = \theta_{I(+)}^* = 0, \quad \lim_{\eta \rightarrow \infty} \theta_{II} = \theta_{II(+)}^* = 1, \tag{11}$$

$$\lim_{\eta \rightarrow -\infty} \theta_I = \theta_{I(-)}^* = \frac{\theta_1^e m_2}{\theta_1^e (m_2 - 1) + 1}, \quad \lim_{\eta \rightarrow -\infty} \theta_{II} = \theta_{II(-)}^* = \frac{\theta_{II}^e}{\theta_1^e (m_2 - 1) + 1}. \tag{12}$$

2.3. Dependence of the current density

The rate of reaction (1) is related to the current density by $j = 2FV$. From any of the equalities of Eq. (3), the dependence of the current density on overpotential can be obtained:

$$j/j_1^o = \frac{2m_2e^{\alpha f\eta}}{\left[\theta_{II}^e - (1 - \theta_I^e - \theta_{II}^e)m_2e^{-f\eta}\right]} \left\{ \frac{\left[m_3 + m_2e^{-(1-\alpha)f\eta} + m_2m_3e^{-f\eta}\right]}{\left(1 - \theta_I^e - \theta_{II}^e\right)\left[m_2m_3 + m_2e^{-(2-\alpha)f\eta} + m_3e^{-f\eta}\right]} + \frac{\left[\theta_{II}^e - \theta_I^e e^{-f\eta} + (1 - \theta_I^e - \theta_{II}^e)e^{-2f\eta}\right]}{\theta_I^e \left[m_3 + m_2e^{-(1-\alpha)f\eta} + m_2m_3e^{-f\eta}\right] + \theta_{II}^e \left[m_2m_3 + m_2e^{\alpha f\eta} + m_3e^{-f\eta}\right]} - e^{-f\eta} \right\}, \quad (13)$$

where $j_1^o = Fv_1^o$. Eq. (13) verify the condition $\lim_{\eta \rightarrow 0} j/j_1^o = 0$. The following anodic and cathodic limiting behaviour are also obtained:

$$\lim_{\eta \rightarrow \infty} j/j_1^o = \frac{2m_3}{\theta_{II}^e}, \quad \lim_{\eta \rightarrow -\infty} j/j_1^o = -\frac{2m_3}{(1 - \theta_I^e - \theta_{II}^e)}. \quad (14)$$

2.4. Simulations of $j(\eta)$, $\theta_I(\eta)$ and $\theta_{II}(\eta)$ dependencies

The simulation of the dependencies $\log j/j_1^o$, θ_I and θ_{II} on overpotential were carried out for both anodic and cathodic directions at 298 K and for $\alpha = 0.5$. The range of values of the kinetic parameters of the elementary steps used in the simulations were $10^{-8} \leq \theta_i^e \leq 0.99999$ ($i = I, II$) and $10^{-10} \leq m_j \leq 10^6$ ($j = 2, 3$). The results obtained indicate that there are numerous Tafelian regions and combinations of them. They are summarised in Table 1, with the corresponding ranges of the parameters θ_i^e ($i = I, II$) and m_i ($i = 1, 2$) values. It should be noticed that most of them cannot be derived from an approximated analysis of the kinetic mechanism. The most significant dependencies are illustrated in Fig. 1 and Fig. 2, with the Tafel slope values ($b/2.3026$) indicated on each region. Related to the dependencies of the surface coverage of the adsorbed intermediates on overpotential, it can be observed the existence of extreme (maximum and minimum).

3. Discussion

The dependence of the reaction rate on overpotential for the chlorine electrode reaction was established without kinetic approximations for the mechanism of Volmer–Krishtalic. The results obtained put into evidence the limitations of the use of kinetic approximations on the analysis of the descriptive capability of the reaction mechanism. In this particular case, one of the most important consequences is the possibility of describing limiting anodic current densities of kinetic nature without the supposition of barrierless processes. Furthermore, it can be observed the existence of limiting current densities, with the exception of the cathodic reaction when $\theta_I^e = (1 - \theta_{II}^e)$. In this case, two Tafel regions are clearly distinguished, which slope values are RT/F and $2RT/F$, respectively (see the asterisks in Table 1).

Another important aspect that should be considered is the behaviour exhibited by the surface coverage of the adsorbed reaction intermediates, $Cl_{(a)}$ and $Cl_{(a)}^+$, on overpotential. Such behaviour is different from that observed by the surface coverage in the Volmer–Heyrovsky–Tafel mechanism [9,10], where the rigorous resolution gives a monotonically increasing (or decreasing) variation of $\theta(\eta)$. Conversely, extreme points were observed in the present case. It is verified also that the existence of Tafelian domains is related to overpotential regions where the surface coverage of both adsorbed intermediates are constant or vary slightly on overpotential ($\partial\theta_i/\partial\eta \leq 10^{-3} \text{ V}^{-1}$). These results are in agreement with those obtained for the Volmer–Heyrovsky–Tafel mechanism [9,10].

Another important aspect to be taken into account in the kinetic study of the CIER is the design of the experiments in order to minimise the number of factors that could cause interference in the determination of the kinetic parameters from the equations derived. In the case of porous electrodes [11], such factors are current distribution, concentration gradients of reactants and products, occlusion of gases, etc. These factors are very difficult, if not impossible, to model adequately and therefore it should be more reasonable to use smooth electrodes. This could be a problem for when the electrode material is an oxide film, but there are for example studies of the CIER on monocrystalline RuO_2 [4], where the reaction mechanism could be appropriately analysed. Therefore, it should be bear in mind that the combination of the study of the CIER on porous electrodes and the use of approximated kinetic equations cannot give acceptable results.

It can be concluded that the chlorine electrode reaction will be verified on a given substrate through the mechanism of Volmer–Krishtalic (or another) in the case that it can describe the experimental dependence $\ln j$ versus η in the whole

region of overpotentials, free of interference such that diffusional control, porous electrode, etc. In order to elucidate this matter, the experimental results should be analysed on the light of this complete treatment in place of the usual approximated kinetic equations.

Acknowledgements

The financial support of UNL, CONICET and ANCYPT is gratefully acknowledged.

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