EFFECTS OF LANGMUIRIAN ADSORPTION ON THE POTENTIOSTATIC RESPONSE AT SPHERICAL AND PLANAR ELECTRODES

María-Luisa ALCARAZ and Jesús GÁLVEZ*

Laboratory of Physical Chemistry, Faculty of Science, 30100 Murcia, Spain

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Dedicated to the memory of Prof. J. Heyrovský on the occasion of his centenary.

Equations for a potentiostatic reaction with an adsorption process following Langmuir's isotherm have been derived for the expanding sphere with any power law electrode model. This model is very general and includes, among others, the following ones: (a) stationary plane; (b) stationary sphere; (c) expanding plane; and (d) expanding sphere. Characteristics of these solutions and the behavior of the corresponding asymptotic solutions are discussed. A comparison of the results obtained for plane and spherical electrodes has also been performed.

Many electrode reactions are influenced by adsorption of reactants and/or products, and special attention has been devoted to the theoretical and experimental study of these electrode processes[1-15]. Unfortunately, rigorous mathematical treatments are complex, specially in those cases described by non-linear adsorption isotherms. Thus, several approximate treatments have been reported in the literature for the case of a Langmuirian adsorption[5-12,16-33]. The diffusion-layer model, based on the Brdička's[16] assumption of the stationary state, has been used by Guidelli[17] and Sluyters and co-workers[20] in order to explain the polarographic curves obtained experimentally. However, this simplified model gives no information on the surface concentrations and the corresponding excesses of the adsorbing species because they are assumed independent on time. In turn, Laviron[8-10] has developed other model, which uses the Koryta's[26] hypothesis of maximum flux, although this model is only valid for the case of strong adsorption. Also, there have been reported treatments[27-28] that use numerical methods to solve the integral equations obtained when the Laplace transformation method is applied to these systems. These methods do not provide analytical expressions for the current and the surface excesses of the adsorbing species.

In addtion to these approximate methods, Reinmuth and Balasubramanian[5,6,33] obtained rigorous solutions for the stationary and expanding plane electrode models which were given in the form of power series. However, these solutions can only be

used at short times. In order to solve this problem, Sluyters[22] proposed an asymptotic solution based on the expansion in negative powers fo the dimensionless time parameter for the surface excess of the adsorbing species. This solution can be applied at long times but it is restricted to the expanding plane electrode model. These authors also obtained the corresponding solution for the stationary plane electrode model, although in this case only the first coefficient (i.e., for $j = 0$) of the asymptotic expansion could be determined. Hence, this solution is not complete and cannot be used for computation purposes.

In any case, we wish to point out that all methods above described to deal with adsorption processes carry out separate derivations for each electrode model. In this paper we have used a unified electrode model recently reported[35], the expanding sphere with any power law, which includes, among others, the following: (a) stationary plane; (b) stationary sphere; (c) expanding plane; and (d) expanding sphere. This procedure has the advantage that in order to obtain the response for a given system we do not need to consider a separate derivation for each one of them and so, for example, the equations published previously by Reinmuth and Balasubramanian are only particular cases of this general solution (cases (a) and (c)). In addition, when our general solution is applied to the stationary plane electrode model it provides the coefficients of the asymptotic solution of the surface excesses for $j = 0$ to $j = 2$, and the corresponding ones of the current for $j = 0$ to $j = 3$. Finally, the general solution also allows us to take into account the influence exerted by the sphericity of the electrode both in an SMDE and in a DME (cases (b) and (d)) which had not been previously described in the literature. Thus, a comparison of the responses obtained for the expanding and stationary plane electrode models can be performed.

THEORETICAL

The mass transport and the boundary value problem for the mechanism

$$A + ne \rightleftharpoons B$$

when both species A and B are adsorbed following Langmuir's isotherm on an expanding sphere with any power law electrode model[35] are defined by the equations

$$\mathbf{D}_A C_A = \mathbf{D}_B C_B = 0 \tag{1}$$

$$t = 0: \quad C_A = C_A^*; \quad C_B = C_B^*; \quad \Gamma_A = \Gamma_B = 0 \tag{2}$$

$$t > 0, \; r \to \infty: \quad C_A \to C_A^*; \quad C_B \to C_B^* \tag{3}$$

$t > 0$, $r = r_0$:

$$D_A\left(\frac{\partial C_A}{\partial r}\right)_{r_0} = \frac{i}{nF\,A(t)} + \frac{z}{t}\Gamma_A + \frac{\mathrm{d}\Gamma_A}{\mathrm{d}t} \tag{4}$$

$$D_B\left(\frac{\partial C_B}{\partial r}\right)_{r_0} = -\frac{i}{nF\,A(t)} + \frac{z}{t}\Gamma_B + \frac{\mathrm{d}\Gamma_B}{\mathrm{d}t} \tag{5}$$

$$C_A(0, t) = \mathrm{e}^J C_B(0, t) \tag{6}$$

$$\Gamma_i = \frac{\Gamma_{S,i}\beta_i C_i(0, t)}{1 + \beta_A C_A(0, t) + \beta_B C_B(0, t)} \quad (i = A, B) \tag{7}$$

with

$$J = \frac{nF}{RT}(E - E^0) \tag{8}$$

$$A(t) = 4\pi r_0^2 = \mathscr{A}_0 t^z \quad (z \geqq 0)\,. \tag{9}$$

In these expressions $\mathbf{D}_i$ is the operator defined by[35]

$$\mathbf{D}_i = \frac{\partial}{\partial t} - D_i\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{z r_0^3 r}{2r^2 t}\frac{\partial}{\partial r}$$

where r is the distance from the centre of the sphere and r_0 the electrode radius. Note that Eq. (9), which defines the electrode area expanding law, is quite general and embraces as particular cases the following types of electrodes: (a) stationary plane ($z = 0$, $r_0 \to \infty$); (b) stationary mercury drop electrode (SMDE) ($z = 0$, $0 < r_0 < \infty$); (c) DME, expanding plane electrode model ($z = 2/3$, $r_0 \to \infty$); (d) DME, expanding sphere electrode model ($z = 2/3$, $0 < r_0 < \infty$).

By using the transformations

$$s_i = \sqrt{\left(\frac{2z + 1}{4D_i t}\right)}(r - r_0)$$

$$\xi_i = \sqrt{\left(\frac{4D_i t}{2z + 1}\right)}\frac{1}{r_0}$$

$$\chi = A_0\sqrt{[D_A(2z + 1)\,t]}\,, \tag{10}$$

where

$$A_0 = \frac{C_T(A_1 + A_1\gamma^{-1})}{\Gamma_{S,A}(1 + \sigma_1)} \tag{11}$$

$$\gamma = (D_A/D_B)^{1/2} \tag{12}$$

$$A_1 = C_A^*/C_T\,; \quad A_2 = C_B^*/C_T\,; \quad C_T = C_A^* + C_B^* \tag{13}$$

$$\sigma_1 = \Gamma_{S,B}/\Gamma_{S,A}\,, \tag{14}$$

and if C_A, C_B, $\Gamma(= \Gamma_A + \Gamma_B)$ and Γ_A adopt the form

$$\begin{aligned} C_A(s_A, \xi_A, \chi) &= \sum_{i,j} \varrho_{i,j}(s_A)\, \xi_A^i \chi^j \\ C_B(s_B, \xi_B, \chi) &= \sum_{i,j} \phi_{i,j}(s_B)\, \xi_B^i \chi^j \\ \Gamma(\xi_A, \chi) &= \sum_{i,j} \gamma_{i,j} \xi_A^i \chi^j \\ \Gamma_A(\xi_A, \chi) &= \sum_{i,j} \gamma_{i,j}^A \xi_A^i \chi^j\,, \end{aligned} \tag{15}$$

Eqs (*1*) become

$$\varrho''_{i,j}(s_A) + 2s_A\, \varrho'_{i,j}(s_A) - \frac{2}{2z+1}\left[(1-z)\, i + j\right] \varrho_{i,j}(s_A) = \sum_{l=0}^{i-1} e_l(s_A)\, \varrho'_{i-l-1,j}(s_A)$$

$$\phi''_{i,j}(s_B) + 2s_B\, \phi'_{i,j}(s_B) - \frac{2}{2z+1}\left[(1-z)\, i + j\right] \phi_{i,j}(s_B) = -\sum_{l=0}^{i-1} e_l(s_B)\, \phi'_{i-l-1,j}(s_B) \tag{16}$$

with

$$e_l(s_i) = 2(-1)^l s_i^l \left[1 - \frac{z}{2z+1}(l+3)\, s_i^2\right] \tag{17}$$

and the initial and boundary conditions (Eqs (*2*)–(*7*))

$$\begin{aligned} s_i \to \infty: \quad & \varrho_{0,0} = C_A^*\,; \quad \varrho_{i,j} = 0 \quad \text{unless} \quad i = j = 0 \\ & \phi_{0,0} = C_B^*\,; \quad \phi_{i,j} = 0 \quad \text{unless} \quad i = j = 0 \end{aligned} \tag{18}$$

$s_i = 0$:

$$\varrho'_{i,j}(0) + \frac{\phi'_{i,j}(0)}{\gamma^{i+1}} = A_0\left[j + 1 + 2z + (1-z)\, i\right] \gamma_{i,j+1}\,; \quad i, j \geqq 0 \tag{19}$$

$$\varrho_{i,j}(0) = \mathrm{e}^J \phi_{i,j}(0)\,; \quad i, j \geqq 0 \tag{20}$$

$$\varrho_{i,0}(0) = \gamma_{i,0}^A = 0\,; \quad i \geqq 0 \tag{21}$$

$$\gamma^{A}_{i,j} = \beta_A[\Gamma_{S,A}\varrho_{i,j}(0) - B_1 \sum_{k=0}^{i} (\sum_{l=1}^{j-1} \gamma^{A}_{k,l}\, \varrho_{i-k,j-l}(0)] \quad ; \; i \geqq 0\,, \quad j \geqq 1 \tag{22}$$

$$\gamma_{i,j} = B_2 \gamma^{A}_{i,j}\,; \quad i, j \geqq 0\,, \tag{23}$$

where

$$B_1 = \frac{e^J + \sigma_0}{e^J} \tag{24}$$

$$B_2 = \frac{e^J + \sigma}{e^J} \tag{25}$$

$$\sigma = \sigma_0 \sigma_1\,; \quad \sigma_0 = \beta_B/\beta_A\,. \tag{26}$$

The $\varrho_{i,j}(s_A)$ and $\phi_{i,j}(s_B)$ functions which are the solution of the problem can be obtained by following an analogous derivational pattern to that described in references[36-37]. Thus, if we assume for simplicity $D_A = D_B = D$, we find

$$\frac{\Gamma_A(t)}{\Gamma_{S,A}} = \frac{e^J(1 + \sigma_1)}{e^J + \sigma} (\sum_{j=1} v_j \chi^j + \xi \sum_{j=1} t_j \chi^j) \tag{27}$$

$$\frac{\Gamma_B(t)}{\Gamma_{S,B}} = \frac{\sigma_0(1 + \sigma_1)}{e^J + \sigma} (\sum_{j=1} v_j \chi^j + \xi \sum_{j=1} t_j \chi^j) \tag{28}$$

$$\frac{C_A(0, t)}{C_T} = \frac{e^J}{1 + e^J} (\sum_{j=1} w_j \chi^j + \xi \sum_{j=1} y_j \chi^j) \tag{29}$$

$$\frac{i}{i_{d,e}} = \frac{A_1\sigma - A_2 e^J}{e^J + \sigma} + \frac{(1 - \sigma)\, e^J}{(1 + e^J)(e^J + \sigma)} S_e \tag{30}$$

with

$$i_{d,e} = i_{d,p}(1 + \Theta\xi)$$

$$i_{d,p} = nF\, A(t) \left(\frac{D_A(2z + 1)}{\pi t}\right)^{1/2} C_T$$

$$\Theta(z) = \frac{2(1 + 2z)}{4 + 5z}\, p_{0,1}(z)$$

$$p_{j,i}(z) = p_{[j+(1-z)i[/(1+2z)}\,; \quad p_x = \frac{2\Gamma(1 + x/2)}{\Gamma((1 + x)/2)} \tag{31}$$

and where the v_j, t_j, w_j, and y_j coefficients and the S_e series are defined in the Appendix A.

In short, Eqs (*27*)–(*30*) are the general solution for the expanding sphere with any power law electrode model, and they include as particular cases the following ones: (a) stationary plane ($z = 0$, $\xi = 0$); (b) stationary sphere ($z = 0$, $\xi \neq 0$); (c) expanding plane ($z = 2/3$, $\xi = 0$); and (d) expanding sphere ($z = 2/3$, $\xi \neq 0$). The corresponding asymptotic solutions for the series in the expressions (*27*)–(*30*) are shown in the Appendix B.

RESULTS AND DISCUSSION

Table I shows the Γ/Γ_S-values computed from Eqs (*27*), (*I*)–(*II*) (Appendix A) and (*I*), (*VI*) and (*XV*) (Appendix B) for a diffusion-controlled process (i.e. $E \to \infty$ and $C_B^* = 0$). The values corresponding to the two different types of plane electrodes (stationary and expanding models) have been reported and compared with those obtained by Sluyters[22]. Our results coincide with those found by Sluyters for a DME (expanding plane model) although, they differ for the case of a stationary plane electrode. This is due to the fact that we have included in the asymptotic expansion the coefficients for $j = 0$ to $j = 3$ while in the solution reported by Sluyters et al.[22] only the coefficient for $j = 0$ was determined.

Regarding the influence exerted by the sphericity of the electrode on Γ/Γ_S-values, which has not been described previously in the literature, this is shown in Table II both for an SMDE and for a DME. Note that Γ/Γ_S increases with ξ, although, in agreement with Eqs (*27*), (*I*)–(*II*) (Appendix A) and (*I*)–(*II*),(*VI*)–(*VII*) and (*XV*)–(*XVI*) (Appendix B), the influence of the sphericity disappears for $\chi \to 0$ and $\chi \to \infty$. This effect is analogous to that found for an adsorption process following Henry's isotherm[4].

Characteristics of the *I–E* curves are illustrated in Figs 1 and 2 where, for simplicity, the assumption $A_2 = 0$ (i.e. no product B is present in the bulk solution) has been made. These figures show the dependence of the unnormalized *I–E* curves on the spherical correction parameter, ξ, for strong adsorption at a DME when the reactant (Fig. 1), or the product of the reaction (Fig. 2), is adsorbed. Note that when the reactant is adsorbed the influence exerted by the sphericity of the electrode is significant enough, and becomes maximum for the limiting currents. Under these conditions, the limiting current corresponding to the first wave is given by

$$\frac{i_{l,1}}{i_{d,p}} \simeq 1 + \Theta\xi - 2\sqrt{\left(\frac{\pi}{21\,Dt}\right)}\frac{\Gamma_{S,A}}{C_A^*} \qquad (32)$$

while the limiting current, i_l, for the main wave coincides with that found for

a diffusion-controlled process

$$\frac{i_1}{i_{d,p}} = 1 + \Theta\xi \,. \tag{33}$$

TABLE I

Comparison between Γ/Γ_S-values obtained from Eqs (27) and (I)–(II) (Appendix A), and those found by Sluyters for a diffussion-controlled process at a stationary and an expanding plane electrodes. Values of z given as: (a) 2/3 (expanding plane); (b) 0 (stationary plane)

$\beta_A C_A^*$	χ	Γ/Γ_S(a)	Γ/Γ_S(a)[a]	Γ/Γ_S(b)	Γ/Γ_S(b)[a]
0·1	0·1	0·0345	0·0345	0·0465	0·0909
	0·2	0·0497	0·0497	0·0692	0·0909
	1.0	0·0789	0·0789	0·0866	0·0909
	2·0	0·0846	0·0846	0·0888	0·0909
	5·0	0·0883	0·0883	0·0901	0 0909
0·5	0·1	0·0447	0·0447	0·0958	0·0958
	0·2	0·0839	0·0839	0·168	0·168
	1·0	0·223	0·223	0·289	0·333
	2·0	0·272	0·272	0·312	0·333
	5·0	0·308	0·308	0·325	0·333
2·0	0·1	0·0474	0·0474	0·108	0·108
	0·2	0·0931	0·0931	0·207	0·207
	0·5	0·222	0·222	0·458	0·458
	1.0	0·407	0·407	0·562	0·667
	2·0	0·510	0·510	0·620	0·667
	5·0	0·610	0·610	0·649	0·667
10·0	0·1	0·0482	0·0482	0·112	0·112
	0·2	0·0960	0·0960	0·222	0·222
	0·5	0·237	0·237	0·534	0·534
	1·0	0·462	0·462	0·847	0·909
	2·0	0·735	0·735	0·883	0·909
	5·0	0·873	0·873	0·900	0·909
100·0	0·1	0·0483	0·0483	0·113	0·113
	0·2	0·0966	0·0966	0·225	0·225
	0·5	0·241	0·241	0·561	0·561
	1·0	0·481	0·481	0·982	0·990
	2·0	0·923	0·923	0·987	0·990
	5·0	0·985	0·985	0·989	0·990

[a] Results obtained by Sluyters.

In contrast, if the product of the reaction is adsorbed the effect exerted by the curvature of the electrode is less significant but becomes maximum for the limiting current of the main wave. In this case, the approximate expression for the limiting current of the *prewave* does not depend on the spherical correction parameter, ξ

TABLE II

Dependence of Γ/Γ_S vs χ on the sphericity of the electrode computed from Eqs (*27*) and (*I*)–(*II*) (Appendix A) for a diffusion-controlled process. The ξ-values are: (1) 0·1 and (2) 0·2

$\beta_A C_A^*$	χ	DME		SMDE	
		$\Gamma/\Gamma_S(1)$	$\Gamma/\Gamma_S(2)$	$\Gamma/\Gamma_S(1)$	$\Gamma/\Gamma_S(2)$
0·1	0·1	0·0363	0·0381	0·0503	0·0541
	0·2	0·0507	0·0517	0·0711	0·0730
	1·0	0·0795	0·0801	0·0870	0·0874
	2·0	0·0849	0·0853	0·0890	0·0892
	5·0	0·0884	0·0886	0·0901	0·0902
0·5	0·1	0·0476	0·0505	0·0996	0·103
	0·2	0·0890	0·0940	0·174	0·180
	1·0	0·226	0·228	0·293	0·296
	2·0	0·275	0·278	0·314	0·315
	5·0	0·309	0·311	0·326	0·326
2·0	0·1	0·0506	0·0538	0·113	0·117
	0·2	0·0993	0·105	0·216	0·224
	0·5	0·236	0·250	0·474	0·490
	1·0	0·430	0·453	0·569	0·577
	2·0	0·517	0·525	0·623	0·627
	5·0	0·613	0·616	0·651	0·652
10·0	0·1	0·0515	0·0548	0·177	0·122
	0·2	0·102	0·109	0·231	0·241
	0·5	0·253	0·269	0·556	0·578
	1·0	0·492	0·522	0·851	0·854
	2·0	0·760	0·785	0·885	0·887
	5·0	0·876	0·879	0·901	0·901
100·0	0·1	0·0517	0·0550	0·183	0·123
	0·2	0·103	0·110	0·235	0·245
	0·5	0·258	0·274	0·585	0·610
	1·0	0·514	0·547	0·982	0·983
	2·0	0·961	0·968	0·987	0·987
	5·0	0·985	0·986	0·989	0·989

$$\frac{i_{1,1}}{i_{d,p}} \simeq 2\sqrt{\left(\frac{\pi}{21Dt}\right)}\frac{\Gamma_{S,B}}{C_A^*} \tag{34}$$

while, as expected, the total limiting current is identical to that corresponding to a diffusion-controlled process (Eq. (*33*)). Deviations obtained with Eqs (*32*) and (*34*) are less than 5% in those cases in which an appreciable separation between the waves is observed. In addition, from Eqs (*32*) and (*34*) it follows that a suitable modification of the values of C_A^* and t allows us to find the conditions in which the *postwave* or *prewave* are defined, and this is an useful criterion to detect the reactant or product adsorption on the electrode. Thus, for the particular case of strong adsorption and values of $t > t_m$, where t_m is equivalent to Koryta's maximum coverage time[26], the polarogram shows a *postwave* or a *prewave*, which, however, disappears when $t \gg t_m$. The t_m-value for this new electrode model is given by the general expression,

$$t_m = \frac{(2z + 1)\pi}{4D}\left(\frac{\Gamma_S}{C_A^*(1 + \bar{\Theta}(z)\xi)}\right)^2$$

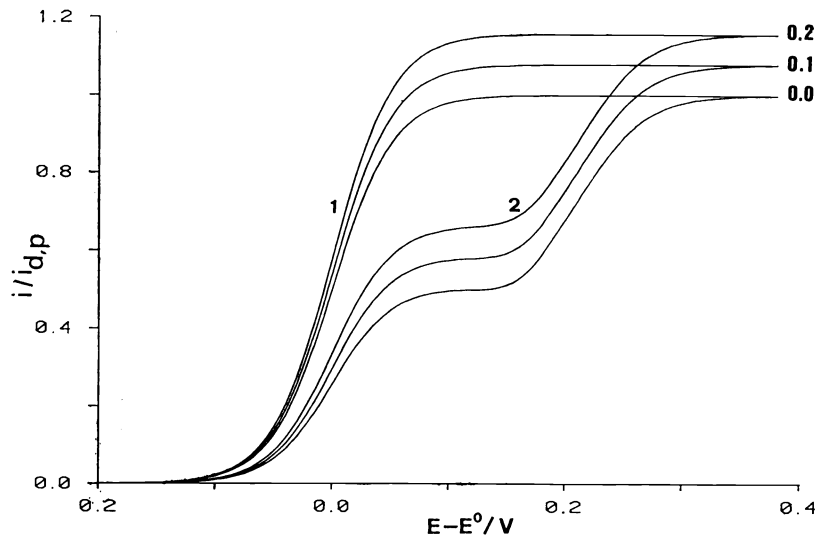

FIG. 1

Unnormalized current–potential curves in a DME for $n = 1$, $T \simeq 298$ K, $\beta_A = 10^4$ m^3 mol^{-1}, $\Gamma_{S,A} = 10^{-5}$ mol m^{-2}, $C_A^* = 0{\cdot}5$ mol m^{-3}, $A_1 = 1$, $\gamma = 1$, $t = 1$ s, $D = 10^{-9}$ m^2 s^{-1} and $\sigma = 0$ (curves 2). The corresponding curves obtained in absence of adsorption have also been included (curves 1). ξ-values shown on the curves

$$\bar{\Theta}(z) = \frac{2z + 1}{z + 2} \Theta(z) \tag{35}$$

which contributes of the influence exerted by the sphericity of the electrode.

In the cases corresponding to a weaker adsorption, the *I–E* curves show a distorted shape which may be similar to that found for an irreversible charge reaction.

On the other hand, if both species are adsorbed strongly on the electrode, the polarogram shows a *prewave* or a *postwave* depending on $\sigma > 10^3$ or $\sigma < 10^{-3}$, respectively. In these cases, the characteristics of the *I–E* curves are analogous to those found for $\sigma = 0$ (i.e. adsorption of the reactant) and $\sigma \to \infty$ (i.e. adsorption of the product). In addition, if $\sigma = 1$ and $D_A = D_B = D$, Eq. (*30*) becomes identical to that obtained for a reversible charge transfer reaction and therefore it is not possible to detect the influence exerted by the adsorption process on the *I–E* curves. This effect is similar to that found in the case corresponding to a Henry's adsorption isotherm[4].

Regarding the *I–E* curves obtained for an SMDE, they are shown in Figs 3–4 for the cases of strong reactant and product adsorption and different values of ζ. Note that in both figures the plateau obtained at a DME disappears and, instead,

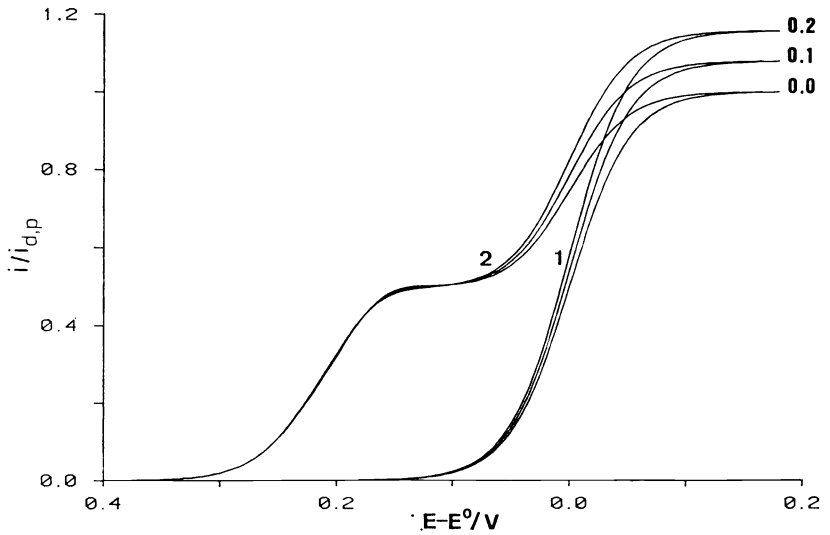

FIG. 2

Current–potential curves in a DME for $\sigma \to \infty$, $\beta_B = 10^4$ m^3 mol^{-1} and $\Gamma_{S,B} = 10^{-5}$ mol m^{-2} (curves 2). The corresponding curves obtained in absence of adsorption have also been included (curves 1). ξ-values shown on the curves. Other conditions as in Fig. 1

a maximum is observed. For strong adsorption of the reactant the potential at which the maximum appears and the corresponding value of the current are given by

$$E_{max} \simeq E^0 + \frac{RT}{nF} \ln\left[\frac{B + \sqrt{(B(1 + \Theta\zeta))}}{1 + \Theta\zeta - B}\right] \tag{36}$$

$$\frac{i_{max}}{i_{d,p}} \simeq (\sqrt{(1 + \Theta\zeta)} - \sqrt{B})^2 , \tag{37}$$

where

$$B = \frac{1}{2\beta_A C_A^* D t (C_A^*/\Gamma_S)^2} . \tag{38}$$

For $\beta_A \Gamma_{S,A} = 0{\cdot}1$ m, $C_A^*/\Gamma_{S,A} = 3 \cdot 10^4$ m^{-1} and $\xi = 0{\cdot}2$, deviations obtained with the approximate Eqs (*35*) and (*36*) are of 2% and 1%, respectively.

APPENDIX A

The v_j, t_j, w_j and y_j coefficients and the S_c series in Eqs (*27*)–(*30*) are defined by

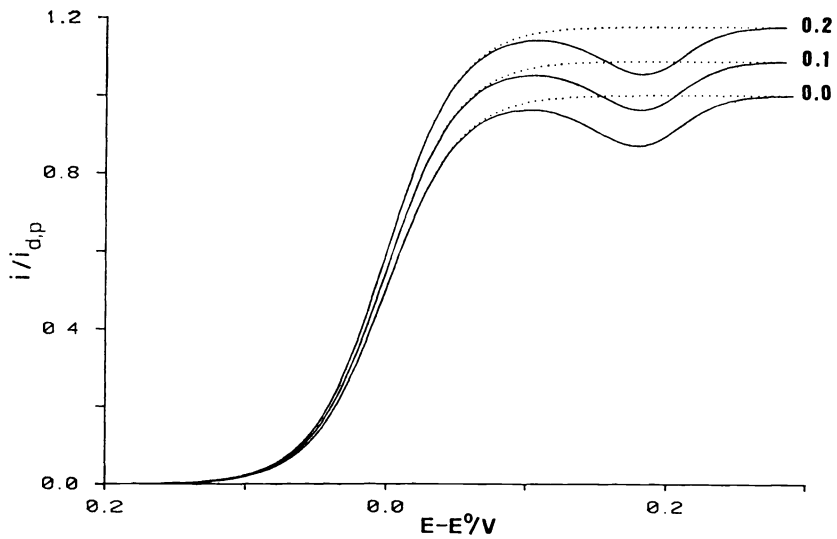

FIG. 3

Dependence of $i/i_{d,p}$ on E in an SMDE for $\sigma = 0$ and $C_A^* = 0{\cdot}3$ mol m^{-3}. ξ-values shown on the curves. The situation corresponding to a diffusion-controlled process has also been represented (...). Other conditions as in Fig. 1

the expressions

$$v_1 = \frac{p_0}{1 + 2z}$$

$$v_j = -\frac{\delta_0 p_{j-1,0}(z)}{j + 2z} v_{j-1} + B_3 \cdot \sum_{i=1}^{j-2} v_i v_{j-1} \frac{j - i + 2z}{j + 2z} \frac{p_{j-1,0}(z)}{p_{j-i-1,0}(z)}; \quad j \geqq 2 \qquad (I)$$

$$t_1 = \frac{p_0 \Theta}{2 + z}$$

$$t_j = -\frac{p_{j-1,1}(z)}{j + 1 + z} \left\{ \delta_0 t_{j-1} + \frac{v_j u_{j-1}(z)(j + 2z)}{p_{j-1,0}(z)\, p_{j-1,1}(z)} - \right.$$

$$- B_3 \left[\sum_{i=1}^{j-2} \frac{t_i v_{j-i}(j - i + 2z)}{p_{j-i-1,0}(z)} + \sum_{i=1}^{j-2} \frac{v_i}{p_{j-i-1,1}(z)} \cdot \right.$$

$$\left. \left. \cdot \left(\frac{(j - i + 2z)\, v_{j-i} u_{j-i-1}(z)}{p_{j-i-1,0}(z)} + (j - i + 1 + z)\, t_{j-i} \right) \right] \right\}; \quad j \geqq 2 \qquad (II)$$

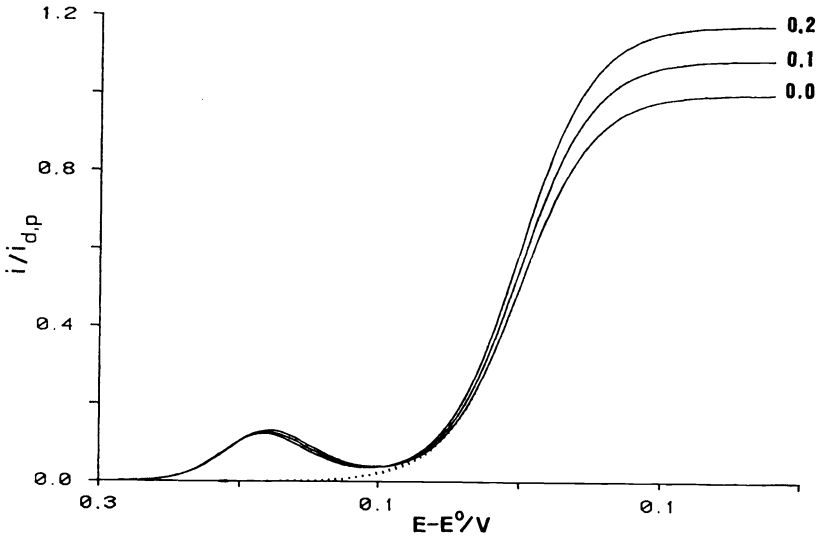

FIG. 4

Current–potential curves in an SMDE for $\sigma \to \infty$, $\beta_B = 10^4$ m^3 mol^{-1}, $\Gamma_{S,B} = 10^{-5}$ mol m^{-2} and $C_A^* = 0{\cdot}3$ mol m^{-3}. ξ-values shown on the curves. The situation corresponding to a diffusion-controlled process has also been represented (...). Other conditions as in Fig. 1

$$w_1 = \frac{p_0 \delta_0}{1 + 2z}$$

$$w_j = \left(\frac{B_3 p_0}{1 + 2z} - \frac{\delta_0 p_{j-1,0}(z)}{j + 2z} \right) w_{j-1} - B_3 \sum_{i=2}^{j-1} \frac{w_{i-1} w_{j-i} p_{i-1,0}(z)}{i + 2z}; \quad j \geqq 2 \qquad (III)$$

$$y_1 = \frac{p_0 \Theta \delta_0}{2 + z}$$

$$y_j = \left(\frac{B_3 p_0}{1 + 2z} - \frac{\delta_0 p_{j-1,1}(z)}{j + 1 + z} \right) y_{j-1} + \left(\frac{\delta_0}{j + 1 + z} u_{j-1}(z) + \frac{B_3 p_0 \Theta}{2 + z} \right) w_{j-1} +$$

$$+ B_3 \left(\sum_{i=2}^{j-1} \frac{w_{i-1} u_{i-1}(z) - y_{i-1} p_{i-1,1}(z)}{i + 1 + z} w_{j-i} - \sum_{i=2}^{j-1} \frac{w_{i-1} p_{i-1,0}(z)\, y_{j-i}}{i + 2z} \right); \quad j \geqq 2 \qquad (IV)$$

$$S_e = \frac{1}{1 + \Theta \xi} (S_1 + \xi Z) \qquad (V)$$

$$S = \sum_{j=1} E_j \chi^j$$

$$E_1 = \frac{p_{1,0}(z)\, \delta_0}{1 + 2z}$$

$$E_j = \left(\frac{B_3 p_0}{1 + 2z} - \frac{\delta_0 p_{j-1,0}(z)}{j + 2z} \right) \frac{p_{j,0}(z)}{p_{j-1,0}(z)} E_{j-1} -$$

$$- B_3 p_0 \sum_{i=2}^{j-1} \frac{E_{i-1} E_{j-i} p_{j,0}(z)}{(i + 2z)\, p_{j-i,0}(z)}; \quad j \geqq 2 \qquad (VI)$$

$$Z = \sum_{j=1} z_j \chi^j$$

$$z_1 = - \frac{E_1 u_1(z)}{p_{1,0}(z)} + \frac{\Theta \delta_0 p_{1,1}(z)}{2 + z}$$

$$z_j = p_{j,1}(z) \left[\left(\frac{B_3 p_0}{1 + 2z} \frac{1}{p_{j-1,1}(z)} - \frac{\delta_0}{j + 1 + z} \right) z_{j-1} \right.$$

$$- \frac{E_j u_j(z)}{p_{j,0}(z)\, p_{j,1}(z)} + \left(\frac{u_{j-1}(z)}{(1 + 2z)\, p_{j-1,1}(z)} + \frac{\Theta}{2 + z} \right) -$$

$$\frac{B_3 p_0 E_{j-1}}{p_{j-1,0}(z)} - B_3 p_0 \left(\sum_{i=2}^{j-1} \frac{E_{i-1}}{i + 2z} \frac{E_{j-i} u_{j-i}(z) / p_{j-i,0}(z) + z_{j-i}}{p_{j-i,1}(z)} + \right.$$

$$+\sum_{i=2}^{j-1}\frac{z_{i-1}E_{j-i}}{(i+1+z)\,p_{j-i,0}(z)}\Bigg)\Bigg]\,;\quad j\geqq 2\,, \tag{VII}$$

where

$$B_3=\frac{B_1}{B_2}(1+\sigma_1) \tag{VIII}$$

$$\delta_0=\delta_1(1+\sigma_1)$$

$$\delta_1=\frac{1+\mathrm{e}^J}{\beta_A B_2 C_T \mathrm{e}^J} \tag{IX}$$

$$u_j(z)=\frac{2}{(2+z)(4+5z)}\left[4j(z+2+j)-(1+2z)(z+2+2j)\,p_{j,0}(z)\,p_{j,1}(z)\right] \tag{X}$$

APPENDIX B

If $\chi \gg 1$ we can obtain an asymptotic solution for the series in the Eqs (*27*)–(*30*) by expanding Eqs (*15*) in negative powers of χ and proceeding as previously for the expansion in positive powers of χ. Thus, we have

$$\sum_{j=1} v_j\chi^j \to \frac{1}{\delta_0+B_4}+\sum_{j=1} v_j\chi^{-j}\,;\quad \chi\gg 1 \tag{I}$$

$$\sum_{j=1} t_j\chi^j \to \sum_{j=0}\tau_j\chi^{-j}\,;\quad \chi\gg 1 \tag{II}$$

$$\sum_{j=1} w_j\chi^j \to 1+\sum_{j=1}\varpi_j\chi^{-j}\,;\quad \chi\gg 1 \tag{III}$$

$$\sum_{j=1} y_j\chi^j \to \sum_{j=0}\eta_j\chi^{-j}\,;\quad \chi\gg 1 \tag{IV}$$

$$S_e \to 1+S_e^*\,;\quad \chi\gg 1\,, \tag{V}$$

where

$$v_0=\frac{1}{\delta_0+B_4}$$

$$v_j=\frac{\delta_0}{(\delta_0+B_4)^2}\,\frac{j-1-2z}{p_{-j,0}(z)}\,v_{j-1}-\frac{B_4}{\delta_0+B_4}\sum_{i=1}^{j-1}v_i v_{j-i-1}\,\frac{j-i-1-2z}{p_{-(j-i),0}(z)}\,;\quad j\geqq 1 \tag{VI}$$

$$\tau_0 = 0$$

$$\tau_j = \frac{1}{\delta_0 + B_4}\left\{\left[\frac{(j-1-2z)\,v_{j-1}\,u_j^*(z)}{p_{-j,0}(z)} + (j-2-2z)\,\tau_{j-1}\right]\frac{\delta_0}{\delta_0 + B_4}\,\frac{1}{p_{-j,1}(z)} - \right.$$

$$- B_4\left[\sum_{j-1}^{i=1}\frac{v_i}{p_{-(j-i),1}(z)}\left(\frac{(j-i-1-2z)\,v_{j-i-1}u_{j-1}^*(z)}{p_{-(j-i),0}(z)} + \right.\right.$$

$$\left.\left.\left. + (j-i-2-z)\tau_{j-i-1}\right) + \sum_{i=1}^{j-1}\frac{\tau_i v_{j-i-1}(j-i-1-2z)}{p_{(j-i),0}(z)}\right]\right\};\quad j \geqq 1 \qquad (VII)$$

$$\bar{\omega}_1 = -\frac{2z}{p_{-1,0}(z)\,(\delta_0 + B_4)}$$

$$\bar{\omega}_j = \frac{\delta_0}{(\delta_0 + B_4)^2}\,\frac{j-1-2z}{p_{-j,0}(z)}\,\bar{\omega}_{j-1} - \frac{B_4}{\delta_0 + B_4}\cdot$$

$$\cdot\sum_{i=2}^{j-1}\frac{\bar{\omega}_i\bar{\omega}_{j-i}p_{-i,0}(z)\,(j-1-2z)}{p_{-j,0}(z)\,(i-1-2z)};\quad j \geqq 2 \qquad (VIII)$$

$$\eta_0 = 0$$

$$\eta_1 = \frac{1}{p_{-1,1}(z)}\,\bar{\omega}_1\,u_1^*(z)$$

$$\eta_j = \frac{j-2-z}{p_{-j,1}(z)}\left\{\frac{\delta_0}{(\delta_0 + B_4)^2}\,\eta_{j-1} + \frac{u_j^*(z)\,\bar{\omega}_j}{j-2-z} - \right.$$

$$\left. - \frac{B_4}{\delta_0 + B_4}\left[\sum_{i=2}^{j-1}\frac{\bar{\omega}_i\eta_{j-i}\,p_{-i,0}(z)}{i-1-2z} - \sum_{i=2}^{j-1}\frac{\bar{\omega}_{j-i}[\bar{\omega}_i\,u_i^*(z) - \eta_i p_{-i,1}(z)]}{i-2-z}\right]\right\};\quad j \geqq 2 \qquad (IX)$$

$$S_e^* = \frac{1}{1 + \Theta\xi}\,[S^* + \xi Z^*] \qquad (X)$$

$$S^* = \sum_{j=1}\varepsilon_j\chi^{-j}$$

$$\varepsilon_1 = -\frac{2z}{p_0(\delta_0 + B_4)}$$

$$\varepsilon_j = \frac{\delta_0}{(\delta_0 + B_4)^2}\,\frac{j-1-2z}{p_{-(j-1),0}(z)}\,\varepsilon_{j-1} - \frac{B_4 p_0}{\delta_0 + B_4}\sum_{i=2}^{j-1}\frac{\varepsilon_i\varepsilon_{j-i}(j-1-2z)}{p_{-(j-i),0}(z)\,(i-1-2z)};\quad j \geqq 2$$

$$(XI)$$

$$Z^* = \sum_{j=1} z_j^* \chi^{-j}$$

$$z_1^* = 0$$

$$z_j^* = (j - 2 - z)\left\{\left[\frac{\varepsilon_{j-1}\, u_{j-1}^*(z)}{p_{-(j-1),0}(z)} + z_{j-1}^*\right]\frac{\delta_0}{(\delta_0 + B_4)^2}\cdot\right.$$

$$\cdot\frac{1}{p_{-(j-1),1}(z)} - \frac{B_4 p_0}{\delta_0 + B_4}\left[\sum_{i=2}^{j-1}\frac{\varepsilon_i}{(i - 1 - 2z)\, p_{-(j-i),1}(z)}\cdot\right.$$

$$\left.\left.\cdot\left(\frac{\varepsilon_{j-i}\, u_{j-i}^*(z)}{p_{-(j-i),0}(z)} + z_{j-i}^*\right) + \sum_{i=2}^{j-1}\frac{z_i^*\varepsilon_{j-i}}{(i - 2 - z)\, p_{-(j-i),0}(z)}\right]\right\};\quad j \geqq 2 \qquad \text{(XII)}$$

$$B_4 = \frac{e^J + \sigma_0}{e^J + \sigma}(1 + \sigma_1) \qquad (XIII)$$

$$u_j^*(z) = \frac{2}{(2 + z)(4 + 5z)}\left[-4j(z + 2 - j) - (1 + 2z)\cdot\right.$$

$$\left.\cdot(z + 2 - 2j)\, p_{-j,0}(z)\, p_{-j,1}(z)\right] \qquad (XIV)$$

For the particular case corresponding to a stationary electrode ($z = 0$), we need to solve the 0/0 type indeterminations which are shown in Eqs (*VI*)–(*IX*) and (*XI*)–(*XII*) when $j \geqq 1$. Under these conditions, those equations may be rewritten in this way

$$v_1 = -\frac{\delta_0}{(\delta_0 + B_4)^3}\frac{p_0}{2}$$

$$v_2 = -\frac{B_4\delta_0 p_0^2}{4(\delta_0 + B_4)^5} \qquad (XV)$$

$$\tau_0 = 0$$

$$\tau_1 = \frac{\delta_0}{2(\delta_0 + B_4)^3} \qquad (XVI)$$

$$\varpi_1 = -\frac{p_0}{2(\delta_0 + B_4)}$$

$$\varpi_2 = 0 \qquad (XVII)$$

$$\eta_0 = 0$$

$$\eta_1 = -\frac{\bar{\omega}_1}{p_0}$$

$$\eta_2 = -\frac{p_0\delta_0}{2(\delta_0 + B_4)^2}\left(\frac{1}{2(\delta_0 + B_4)} + \eta_1\right)$$

$$\eta_3 = -\frac{B_4\delta_0\bar{\omega}_1^2}{2(\delta_0 + B_4)^3} \qquad (XVIII)$$

$$S^* = \sum_{j=1}^{3} \varepsilon_j \chi^{-j}$$

$$\varepsilon_1 = 0$$

$$\varepsilon_2 = -\frac{\delta_0}{2(\delta_0 + B_4)^3}$$

$$\varepsilon_3 = -\frac{\delta_0 B_4 p_0}{2(\delta_0 + B_4)^5} \qquad (XIX)$$

$$Z^* = \sum_{j=0}^{4} z_j^* \chi^{-j}$$

$$z_0^* = \frac{\sqrt{\pi}}{2}$$

$$z_1^* = 0$$

$$z_2^* = 0$$

$$z_3^* = \frac{\delta_0 - B_4}{2(\delta_0 + B_4)^2}\left(\varepsilon_2 - \frac{\delta_0}{2(\delta_0 + B_4)^3}\right)$$

$$z_4^* = \frac{1}{\delta_0 + B_4}\left\{\frac{\delta_0 - B_4}{2(\delta_0 + B_4)} N_3 + B_4 p_0 \left[\left(\frac{\delta_0}{2(\delta_0 + B_4)^3} - N_2\right) N_2 + \frac{z_3^*}{\delta_0 + B_4}\right]\right\} \qquad (XX)$$

Note that in the asymptotic series expansions only are determined the coefficients for $j \leqq 1$ (Eq. (*XVI*)), $j \leqq 2$ (Eqs (*XV*) and (*XVII*)), $j \leqq 3$ (Eqs (*XVIII*)–(*XIX*)) and $j \leqq 4$ (Eq. (*XX*)).

REFERENCES

1. Holub K.: Collect. Czech. Chem. Commun. *31*, 1461 (1966).
2. Holub K.: J. Electroanal. Chem. *16*, 433 (1968).
3. Guidelli R.: J. Electroanal. Chem. *18*, 5 (1968).
4. Gálvez J., Alcaraz M. L., Park S-M.: J. Electroanal. Chem. *247*, 99 (1988).
5. Reinmuth W. H., Balasubramanian K.: J. Electroanal. Chem. *38*, 79 (1972).
6. Reinmuth W. H., Balasubramanian K.: J. Electroanal. Chem. *38*, 271 (1972).
7. Mas F., Puy J., Sanz F., Virgili J.: J. Electroanal. Chem. *158*, 217 (1983).
8. Laviron E.: Bull. Soc. Chim. Fr. *1969*, 1798.
9. Laviron E.: J. Electroanal. Chem. *52*, 355 (1974).
10. Laviron E.: J. Electroanal. Chem. *63*, 245 (1975).
11. Picardi G., Pergola F., Alosi G., Guidelli R.: J. Electroanal. Chem. *48*, 235 (1977).
12. Foresti M. L., Pergola F., Alosi G., Guidelli R.: J. Electroanal. Chem. *137*, 341 (1982).
13. van Leeuwen H. P., Sluyters-Rehbach M., Holub K.: J. Electroanal. Chem. *135*, 13 (1982).
14. van Leeuwen H. P.: J. Electroanal. Chem. *162*, 67 (1984).
15. Gálvez J., Park S-M.: J. Electroanal. Chem. *263*, 257 (1989).
16. Brdička R.: Z. Elektrochem. *48*, 278 (1942).
17. Guidelli R.: J. Phys. Chem. *74*, 95 (1970).
18. Guidelli R., Pezzatini G.: J. Electroanal. Chem. *84*, 211 (1977).
19. Guidelli R., Pergola F.: J. Electroanal. Chem. *84*, 255 (1977).
20. Sluyters-Rehbach M., Wijnhorst C. A., Sluyters J. H.: J. Electroanal. Chem. *74*, 3 (1976).
21. Sluyters-Rehbach M., Sluyters J. H.: J. Electroanal. Chem. *75*, 371 (1977).
22. Sluyters-Rehbach M., Sluyters J. H.: J. Electroanal. Chem. *81*, 211 (1977).
23. van Leeuwen H. P., Sluyters-Rehbach M., Holub K.: J. Electroanal. Chem. *191*, 293 (1985).
24. Laviron E.: J. Electroanal. Chem. *124*, 19 (1981).
25. Laviron E.: J. Electroanal. Chem. *140*, 247 (1982).
26. Koryta J.: Collect. Czech. Chem. Commun. *18*, 206 (1953).
27. Levich V. G., Khaikin B. I., Belokolos E. D.: Elektrokhimiya *1*, 1273 (1965); English translation in Sov. Electrochem. *1*, 1137 (1965).
28. Puy J., Mas F., Sanz F., Virgili J.: J. Electroanal. Chem. *158*, 231 (1983).
29. Mas F., Puy J., Sanz F., Virgili J.: J. Electroanal. Chem. *183*, 41 (1985).
30. Sanz F., Puy J., Mas F., Virgili J.: J. Electroanal. Chem. *183*, 57 (1985).
31. Mas F., Puy J., Sanz F., Virgili J.: J. Electroanal. Chem. *183*, 73 (1985).
32. Guaus E., Mas F., Puy J., Sanz F.: J. Electroanal. Chem. *224*, 1 (1987).
33. Reinmuth W. H.: J. Phys. Chem. *65*, 473 (1961).
34. Nicholson R. S., Olmstead M. L. in: *Electrochemistry, Calculations, Simulation, and Instrumentation*, Part I (J. S. Mattson, H. B. Mark, Jr. and H. C. MacDonald, Eds). Dekker, New York 1972.
35. Gálvez J., Park S-M.: J. Electroanal. Chem. *259*, 21 (1989).
36. Gálvez J., Saura R., Molina A.: J. Electroanal. Chem. *147*, 53 (1983).
37. Gálvez J., Molina A., Fuente T.: J. Electroanal. Chem. *107*, 217 (1980).
38. Koutecký J.: Czech. J. Phys. *2*, 50 (1953).
39. Brinkman A. A. M. M., Los J. M.: J. Electroanal. Chem. *7*, 171 (1964).
40. Gálvez J.: *Thesis*. Universidad de Murcia, Murcia 1973.