STUDY OF THE EE MECHANISM WITH ADSORPTION OF THE INTERMEDIATE AT SPHERICAL AND PLANAR ELECTRODES FOLLOWING A LANGMUIR'S ISOTHERM

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

The theory for the EE mechanism with adsorption of the intermediate following Langmuir's isotherm has been developed for the expanding sphere with any power law electrode model. The equations obtained with this model are general and can be applied, for example, to a stationary plane electrode, to a stationary sphere electrode, and to the two models of dropping mercury electrode (DME), expanding plane and expanding sphere. The influence exerted by the sphericity of the electrode on the current–potential (I/E) curves and the characteristics of these curves are discussed.

The study of the electrode processes complicated by the adsorption of reactants and/or products has received special attention in the literature[1-3]. Most of the theoretical work on these systems has been focussed mainly on the response of a single charge transfer reaction at a stationary plane electrode or at a DME. In turn, the theory concerning the response of an EE mechanism with adsorption of the intermediate has received much less attention[4-10]. Thus, for this mechanism it has been only possible to obtain analytical expressions for the current and the surface concentrations when the adsorption process follows Henry's isotherm. However, no rigorous solution has been found for the case of langmuirian adsorption. For this isotherm, Lovric[8] has reported an approximate treatment that uses numerical methods to solve the integral equations obtained when the Laplace transformation method is applied to this system. In addition, this approximate solution is restricted to a stationary plane electrode and so, it cannot be applied to describe rigorously the corresponding responses at a DME or at an SMDE. In this paper we have used a unified electrode model recently reported[11], the expanding sphere with any power law, which includes, among others: (a) stationary plane; (b) stationary sphere; (c) expanding plane; and (d) expanding sphere. This procedure allows us to obtain the response for this mechanism without performing a separate derivation for each one of these models. Thus, this general solution allows us to analyze the cases (b), (c) and (d) which had not been previously described in the literature.

THEORETICAL

For the expanding sphere with any power law electrode model[11], the electrode area, $A(t)$, and the operator for mass transport, $\mathbf{D}_i$, are defined by:

$$A(t) = 4\pi r_0^2 = A_0 t^z \quad (z \geqq 0) \tag{1}$$

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

Hence, the mass transport and the boundary value problem for the mechanism

$$\mathrm{A} + \mathrm{e} \rightleftharpoons \mathrm{B} + \mathrm{e} \rightleftharpoons \mathrm{C}$$

where species B is adsorbed following a Langmuir's adsorption isotherm at this electrode model are given by the equations

$$\mathbf{D}_A C_A = \mathbf{D}_B C_B = 0 \tag{2}$$

$$t = 0: \quad C_A = C_A^*; \quad C_B = C_B^*; \quad C_C = C_C^*; \quad \Gamma_B = 0 \tag{3}$$

$$t > 0, \quad r \to \infty: \quad C_A \to C_A^*; \quad C_B \to C_B^*; \quad C_C \to C_C^* \tag{4}$$

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

$$D_A\left(\frac{\partial C_A}{\partial r}\right)_{r_0} = \frac{i_1}{nF\,A(t)} \tag{5}$$

$$D_B\left(\frac{\partial C_B}{\partial r}\right)_{r_0} = \frac{i_2}{FA(t)} - \frac{i_1}{FA(t)} + \frac{z}{t}\Gamma_B + \frac{\mathrm{d}\Gamma_B}{\mathrm{d}t} \tag{6}$$

$$D_C\left(\frac{\partial C_C}{\partial r}\right)_{r_0} = -\frac{i_2}{FA(t)} \tag{7}$$

$$C_A(0, t) = \mathrm{e}^{J_1} C_B(0, t) \tag{8}$$

$$C_B(0, t) = \mathrm{e}^{J_2} C_C(0, t) \tag{9}$$

$$\Gamma_B = \frac{\Gamma_{S,B}\beta_B C_B(0, t)}{1 + \beta_B C_B(0, t)}, \tag{10}$$

where

$$J_i = \frac{F}{RT}(E - E_i^0) \quad (i = 1, 2)\,. \tag{11}$$

Other definitions are conventional.

Note that Eq. (*1*), which defines the electrode area expanding law, includes 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 introducing the transformations

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

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

$$\chi = \mathscr{A}_0 \sqrt{[(2z + 1)\, D_B t]}\,, \tag{12}$$

where

$$\mathscr{A}_0 = \frac{C_T(\beta_1 A_1 + A_2 + \beta_2 A_3)}{\Gamma_{S,B}} \tag{13}$$

$$A_1 = \frac{C_A^*}{C_T}\,; \quad A_2 = \frac{C_B^*}{C_T}\,; \quad A_3 = \frac{C_C^*}{C_T}\,; \quad C_T = C_A^* + C_B^* + C_C^* \tag{14}$$

$$\beta_1 = (D_A/D_B)^{1/2}\,; \quad \beta_2 = (D_C/D_B)^{1/2} \tag{15}$$

by assuming for simplicity $D_A = D_B = D_C = D$, and by using established procedures[9–14] we find that the surface excess, $\Gamma_B(t)$, and the surface concentration, $C_B(0, t)$, are given by

$$\frac{\Gamma_B(t)}{\Gamma_{S,B}} = \sum_{j=1} v_j \chi^j + \xi \sum_{j=1} t_j \chi^j \tag{16}$$

$$\frac{C_B(0, t)}{C_T} = \frac{1}{1 + e^{J_1} + e^{-J_2}}\left(\sum_{j=1} w_j \chi^j + \xi \sum_{j=1} y_j \chi^j\right). \tag{17}$$

In turn, expressions for normalized currents are defined by

$$I_j = \frac{i_j}{i_{d,e}(1)} \quad (j = 1, 2); \quad I = \frac{i}{i_{d,e}(2)} = \frac{I_1 + I_2}{2} \tag{18}$$

with

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

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

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

$$p_{j,i}(z) = p_{[j+(1-z)i]/(2z+1)}; \quad p_x = \frac{2\Gamma(1 + x/2)}{\Gamma[(1 + x)/2]} \tag{19}$$

$$I_1 = A_1 - \frac{e^{J_1}}{1 + e^{J_1} + e^{-J_2}} S_e \tag{20}$$

$$I_2 = -A_3 + \frac{e^{-J_2}}{1 + e^{J_1} + e^{-J_2}} S_e . \tag{21}$$

In these expressions the v_j, t_j, w_j and y_j coefficients and the S_e series are identical to those obtained in Appendix A of reference[14] with $B_3 = 1$. In short, Eqs (*16*)–(*18*) and (*20*)–(*21*) describe the response for the EE mechanism with adsorption of the intermediate at the expanding sphere with any power law electrode model and they can be applied easily to the following electrode models: (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 ($z = 2/3$, $\xi \neq 0$).

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the I/E curves on the spherical correction parameter, ξ, for strong adsorption of the intermediate at a DME. In these curves ΔE ($= E_2^0 - E_1^0$) = 0 V (unstable intermediate) so that the corresponding polarogram shows a single wave in absence of adsorption (curves 1). Conversely, and due to the adsorption process, the single wave splits and two new waves, A and B, appear. Waves A and B are related, respectively, to the *prewave* and *postwave* observed for a single charge transfer process in the cases corresponding to strong adsorption of the product and the reactant. The influence exerted by the curvature of the electrode is more significant for the limiting currents of the main wave and the *postwave* than for the limiting current of the *prewave*, and this effect is analogous to that observed for an E mechanism[14]. In addition, under these conditions of strong ad-

sorption of the intermediate we have (for $A_1 = 1$, i.e., when only species A is present in the bulk solution)

$$\frac{i_{1,1}}{i_{d,p}(2)} \simeq \sqrt{\left(\frac{\pi}{21Dt}\right)} \frac{\Gamma_{S,B}}{C_A^*} \tag{22}$$

$$\frac{i_{1,2}}{i_{d,p}(2)} \simeq 1 + \Theta\xi - \sqrt{\left(\frac{\pi}{21Dt}\right)} \frac{\Gamma_{S,B}}{C_A^*}, \tag{23}$$

where $i_{1,1}$ and $i_{1,2}$ are the values of the current at the plateau of separation between the main wave and the *prewave* or the *postwave*, respectively. These equations are also valid for a stable intermediate, although in this case the *prewave* appears preceding the first wave whereas the *postwave* is observed at potentials more negative than the limiting current for the second step of charge transfer. It is interesting to show that according to Eq. (*22*) $i_{1,1}$ decreases as $C_A^*/\Gamma_{S,B}$ becomes greater, so that in the limit case, i.e. for $C_A^*/\Gamma_{S,B} \gg 1$ (this situation corresponds to $t \gg t_m$ (ref.[14]) – t_m is equivalent to Koryta's maximum coverage time[15]), the *prewave* disappears. Under these conditions, the *postwave* also disappears and the main wave shows

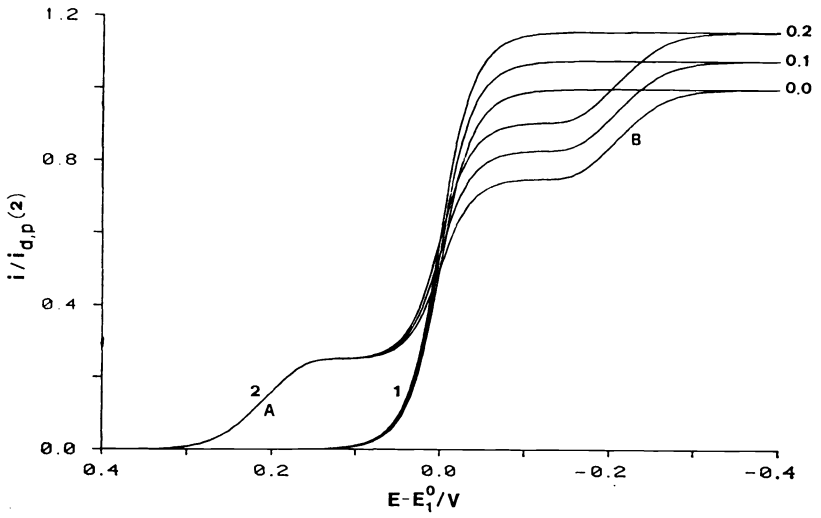

FIG. 1

Unnormalized current–potential curves for a DME with $\beta_B = 10^4$ m^3 mol^{-1}, $\Gamma_{S,B} = 10^{-5}$ mol m^{-2}, $C_A^* = 0{\cdot}5$ mol m^{-3}, $\Delta E = 0$ V, $T = 298$ K, $A_1 = 1$, $\beta_1 = \beta_2 = 1$, $t = 1$ s, and $D = 10^{-9}$ m^2 s^{-1} (curves 2). The corresponding curves obtained in absence of adsorption have also been included (curves 1); ξ-values shown on the curves

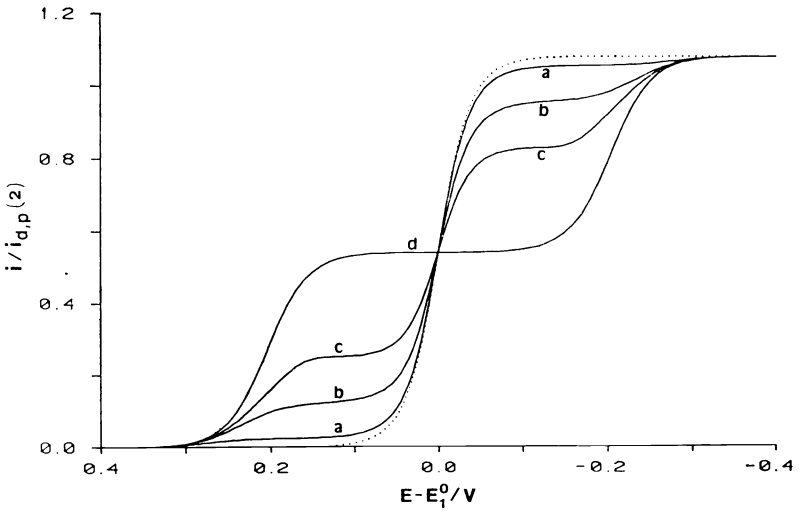

FIG. 2

Dependence of $i/i_{d,p}$ (2) on E for a DME with $\xi = 0{\cdot}1$ and C_A^* (mol m^{-3}): a 5, b 1, c 0·5, d 1·0. The situation corresponding to a diffusion-controlled process has also been represented (...); other conditions as in Fig. 1

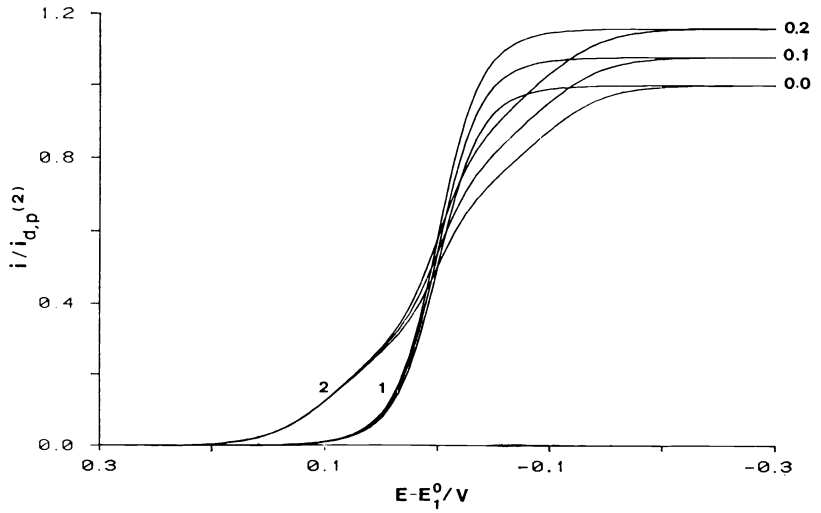

FIG. 3

Current–potential curves for a DME with $\beta_B = 100$ m^3 mol^{-1} (curves 2). ξ-Values shown on the curves. The corresponding curves obtained in absence of adsorption have also been included (curves 1); Other conditions as in Fig. 1

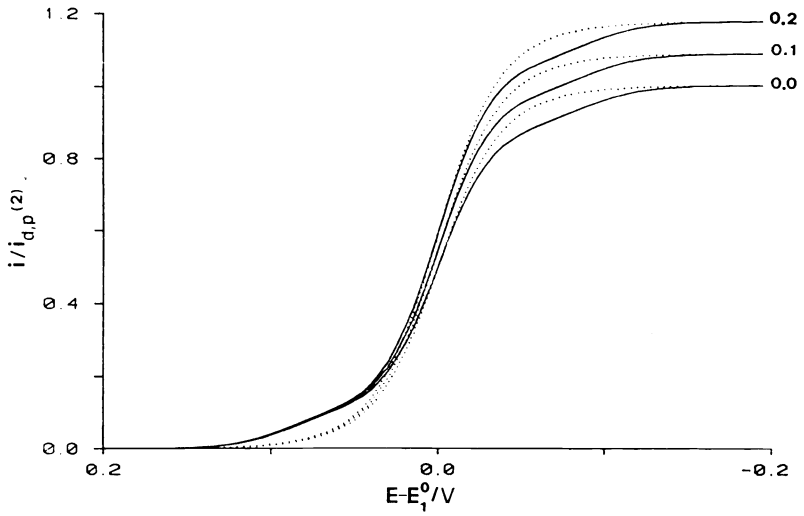

FIG. 4

Dependence of $i/i_{d,p}$ (2) on E for an SMDE with $C_A^* = 0{\cdot}3$ 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

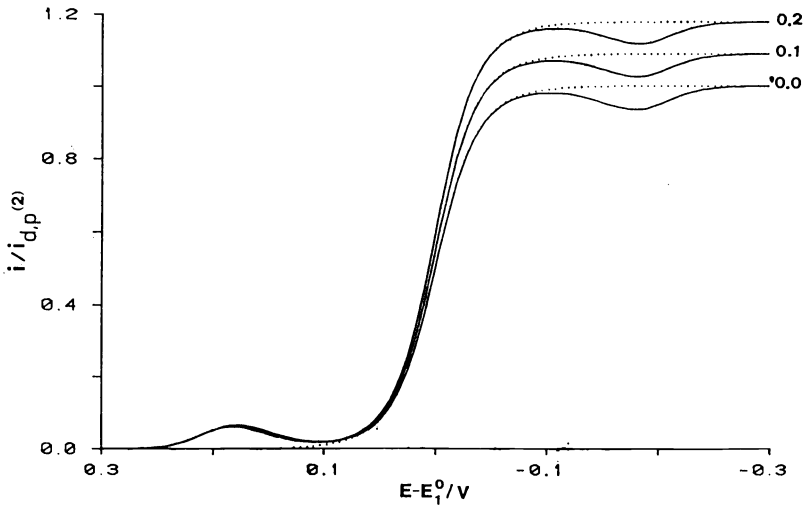

FIG. 5

Current–potential curves for an SMDE with $\beta_B = 100$ m^3 mol^{-1}. ξ-Values shown on the curves. The situation corresponding to a diffusion-controlled process has also been represented (...); other conditions as in Fig. 1

a behaviour which is similar to that found in absence of adsorption. In addition, as $C_A^*/\Gamma_{S,B}$ decreases it follows that $i_{1,1} \to i_{1,2}$ and in the limit case for $t \gg t_m$ the single wave corresponding to a diffusion-controlled process splits in two waves (i.e., Henry's linear approximation[9]). This effect can be useful to detect the intermediate adsorption on the electrode and it is illustrated in Fig. 2.

In turn, the situation for weaker adsorption is illustrated in Fig. 3 for the case of an unstable intermediate. The I/E curves plotted under these conditions show a distorted shape, which is less pronounced as β_B decreases. On the other hand, if the intermediate adsorbed is stable, a shift of the two waves towards more positive and negative potentials, respectively, and which is associated to the two steps of charge transfer, is observed.

Regarding the I/E curves obtained for an SMDE, they are shown in Figs 4–5 for $\beta_B = 10\,000$ and $100\ m^3\ mol^{-1}$ and different values of ξ. Note that the plateau obtained at a DME for the case of strong adsorption of the intermediate disappears (Fig. 4) and, instead, a maximum is observed. (This effect is analogous to that found for an E mechanism[14]). Finally, if the adsorption is weaker (Fig. 5) the polarogram shows a distorted shape which is similar to that obtained for a DME (Fig. 3).

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