ANALYSIS OF THE ANODIC PROCESSES OF 8-HYDROXYQUINOLINE IN AcOH–AcONa BUFFER ON MERCURY

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Polarographic current–potential characteristics for the anodic behaviour of 8-hydroxyquinoline (QH) in a pH ~ 5 aqueous AcOH–AcONa buffer have been examined in detail at low concentrations. The electrode reaction is $2\ Hg + 2\ QH \rightleftharpoons Hg_2Q_2 + 2\ H^+ + 2\ e$. The study of the polarographic wave has been performed introducing the Frumkin isotherm in the treatment of adsorption. Also, the inhibition of electrode process due to the films formed on electrode surface has been discussed.

In previous papers on the anodic behaviour of mercury electrode in 8-hydroxyquinoline (QH) aqueous solutions[1–4], strong adsorption of depolarizer and organometallic compound formed in the electrode process has been observed. Moreover, precipitation processes at high concentrations have been detected. This behaviour has also been observed with other anodic depolarizers of mercury[5–11].

The analysis of the system at low QH concentrations using the Langmuir isotherm does not give good results[4]. It is the goal of this paper to show that these differences can be explained by taking into account the interaction forces between the adsorbed molecules. So, we have introduced in mathematical treatment of polarographic waves a Frumkin type isotherm to describe the adsorption of our compounds. Finally, the inhibition of electrode process due to the films formed on electrode surface has been discussed.

EXPERIMENTAL

Polarograms were recorded with the multipolarograph Amel 471, and the $i = f(t)$ curves were obtained by means of a Tacussel Potenciostat PRT 20-2X and an oscilloscope Tektronix 5103-N D15. The working electrode was a capillary Tacussel ($m = 0{\cdot}97$ mg/s at $h = 50$ cm) and the drop time (t_1) was 2 s. The potential values were taken in reference to the aqueous Hg/Hg_2SO_4 electrode, saturated with K_2SO_4. Voltammograms were recorded with a PAR polarographic analyzer 174A and a recorder Linseys LY 1800, using a SMDE PAR model 303 as a working electrode.

Chemicals were of analytical reagent grade. Tridistilled water was used for preparing solutions and all mercury was doubly distilled before use. Buffer mixture was prepared by mixing 1M-AcOH and AcONa solutions. The experiments were carried out at constant temperature $25 \pm 0{\cdot}1$°C and at 0·2M ionic strength.

RESULTS AND DISCUSSION

D.c. and a.c. phase sensitive polarograms of QH are shown in Fig. 1. The wave appearing at more anodic potentials (Wave I) has the properties of an adsorption wave. At QH concentrations lower than $5 \cdot 10^{-5}$ mol dm^{-3}, the limiting current is proportional to concentration, $h_{corr}^{1/2}$ and $t_1^{1/6}$. At QH concentration higher than $5 \cdot 10^{-5}$ mol dm^{-3} the limiting current remains constant and proportional to h_{corr} and $t_1^{-1/3}$.

The wave II, visible at depolarizer concentration higher than 10^{-4} mol dm^{-3} (Fig. 2) does not have the characteristics of a "normal wave". $i_{lim,\,I+II}$ shows anomalous dependences on the depolarizer concentration (Fig. 2), h_{corr} and t_1. Such behaviour is due to the precipitation process already studied[4,12].

REACTION PRODUCT AND NUMBER OF ELECTRONS

To identify the product formed in the electrode process, electrolysis at constant potential on the plateau of the wave II has been performed. A yellow precipitate appears. Its elemental analysis agrees with 1 : 1 QH : Hg ratio for the compound: theoretical % C: 31·4, N: 4·1, H: 1·75; experimental % (two samples): C: 30·85, 30·74; N: 4·00, 3·94; H: 1·91, 1·90. On the other hand, its IR spectrum shows the bands of C—O at 1 115 cm^{-1} and metal-O at 490 cm^{-1} and 735 cm^{-1} which are characteristic of 8-hydroxyquinoline chelates[13–15]. So, we propose the formula $(C_9H_6NO)_2 . Hg_2$ for the product of the electrode process[16].

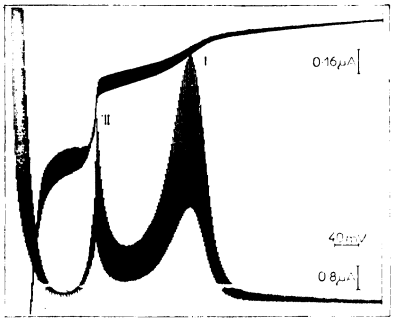

FIG. 1

Polarograms d.c. and a.c. phase sensitive (75 Hz and 5 mV r.m.s.) of 8-hydroxyquinoline in AcOH–AcONa buffer. pH 5·28, $c_r^* = 4 \cdot 10^{-4}$ mol dm^{-3}, $v_f = -0{\cdot}6$ V

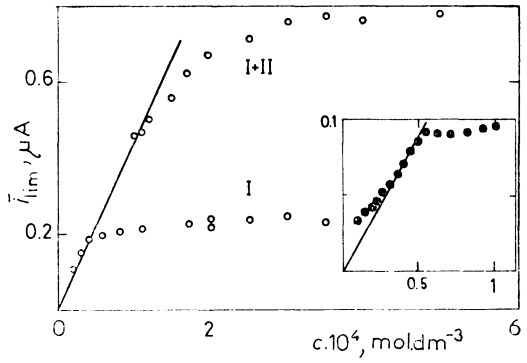

FIG. 2

Plot of i_{lim} *vs* concentration of 8-hydroxyquinoline at pH 5·3

Coulometric measurements and calculations performed in the linear zone of the polarographic $i_{lim} - c$ graph show the transfer of one electron per QH molecule, in good agreement with the proposed product.

According to these experimental results, the mechanism of the electrode process could be:

$$2\,Hg \rightleftharpoons Hg_2^{2+} + 2\,e \qquad (A)$$

$$Hg_2^{2+} + 2\,QH(r) \rightleftharpoons Q_2Hg_2(o) + 2\,H^+ . \qquad (B)$$

However, at very low concentrations (less than $2 . 10^{-5}$ mol dm^{-8}) when the coverage is lower than 0·5, we observe a gradual increase of the number of electrons towards two (Fig. 2).

ANALYSIS OF THE POLAROGRAPHIC WAVES

Wave I

Taking into account the strong adsorption of both depolarizer and product (electrocapillary curves, voltammetry, polarography, ...) we have analyzed the wave I at $c < 5 . 10^{-5}$ mol dm^{-3} according to the hypothesis proposed by Laviron[17] and and introducing the Frumkin isotherm

$$b_o c_o(0, t) = (\Theta_o/n_o(1 - \Theta_o - \Theta_r)^{n_o}) \exp(-2a_o n_o \Theta_o - 2a_{or} n_o \Theta_r) \qquad (1)$$

$$b_r c_r(0, t) = (\Theta_r/n_r(1 - \Theta_o - \Theta_r)^{n_r}) \exp(-2a_r n_r \Theta_r - 2a_{or} n_r \Theta_r)$$

being Θ_o, Θ_r the coverages, b_o, b_r the adsorption coefficients; n_o, n_r the number of water molecules (or clusters of water molecules) displaced by one molecule of o or r, and a_o, a_r and a_{or} the constants of interaction.

The saturation value of surface concentration Γ_m of product from polarographic adsorption current is $\Gamma_{m,o} = 7 . 10^{-11}$ mol/cm^2 (in ref.[4], $\Gamma_{m,o}$ is given in mol/cm^2 per electron). On the other hand, if we calculate Γ_r for the depolarizer using Koryta equation[18] at $c_r^* = 5 . 10^{-5}$ mol dm^{-3} (QH concentration for which $\Theta_o = 1$), a value of $1{\cdot}4 . 10^{-10}$ mol/cm^2 is obtained. The ratio $\Gamma_{r,Koryta}/\Gamma_{m,o} = 2$ agrees with the stoichiometry of the product of the electrode process.

The simulation of the wave I is made following the procedure due to Laviron[17]. The above results allow us to assume that

$$2\Gamma_o + \Gamma_r = \Gamma_T = 0{\cdot}74 D_r^{1/2} t_1^{1/2} c_r^* \qquad (2)$$

and if we supose $n_0 = 2n_r$, the resolution of the system of equations gives the relation $i - E$:

$$\exp\left(\frac{2F}{RT}(E - E^{0\prime})\right) = \frac{b_r^2}{b_0}\frac{n^0}{8\sigma\xi^2}\frac{\Theta}{(1-\Theta)^2}\exp\left(\sigma n_0(G\Theta + J)\right), \qquad (3)$$

where

$$E^{0\prime} = E^0 + \frac{RT}{2F}\ln\frac{[H^+]^2}{K},$$

being K the equilibrium constant of Eq. (*B*);

$$\Theta = \bar{i}/\bar{i}_{lim}; \quad \sigma = \Gamma_T/\Gamma_{m,0} = 0{\cdot}74D_r^{1/2}c_r^* t_1^{1/2}/\Gamma_{m,0}\,; \quad \xi = \Gamma_{m,0}/\Gamma_{m,r}$$

and

$$G = a_{0r}(1 + 2\xi) - a_0 - 2\xi a_r\,, \quad J = 2\xi a_r - 2\xi a_{0r}\,.$$

The half-wave potential is

$$E_{1/2} = E^{0\prime} + \frac{RT}{2F}\ln\frac{b_r^2 n_0}{b_0 4\sigma\xi^2} + \frac{RT}{2F}\left[\sigma n_0\left(\frac{1}{2}G + J\right)\right]. \qquad (4)$$

Introducing this value in equation (*3*), we obtain

$$E = E_{1/2} + \frac{RT}{2F}\left\{\ln\frac{\Theta}{2(1-\Theta)^2} + \sigma n_0\left[G\left(\Theta - \frac{1}{2}\right)\right]\right\}; \qquad (5)$$

that implies a linear plot

$$E\ vs\left(\ln\frac{\bar{i}}{(\bar{i}_{lim} - \bar{i})^2} + \sigma n_0 G\frac{\bar{i}}{\bar{i}_{lim}}\right)$$

with a dependence of $RT/2F = 12{\cdot}8$ mV at 25°C.

The dependences of $E_{1/2}$ with depolarizer concentration and drop time are

$$E_{1/2} = \text{const.} + \frac{RT}{2F}\,\mathrm{A}kc_r^* - \frac{RT}{2F}\ln c_r^* \text{ with } k = \frac{0{\cdot}74D_r^{1/2}t_1^{1/2}}{\Gamma_{m,0}} \qquad (6)$$

$$E_{1/2} = \text{const.} + \mathrm{A}k' t_1^{1/2} - \frac{RT}{4F}\ln t_1 \text{ with } k' = \frac{0{\cdot}74D_r^{1/2}c_r^*}{\Gamma_{m,0}} \qquad (7)$$

being $A = n_0\left[a_{0r}\left(\frac{1}{2} - \xi\right) - \frac{1}{2}a_0 + \xi a_r\right]$.

The experimental plots agree with the proposed equations. From the slopes of the plots $E_{1/2} + \boldsymbol{RT}/2\boldsymbol{F} \ln c_r^*$ *vs* c_r^* and $E_{1/2} + \boldsymbol{RT}/4\boldsymbol{F} \ln t_1$ *vs* $t_1^{1/2}$ we calculate a value of 0·75 ± 0·06 for A.

The values of $E_{3/4} - E_{1/4}$ may be obtained from Eq. (*3*)

$$E_{3/4} - E_{1/4} = \frac{\boldsymbol{RT}}{2\boldsymbol{F}} \ln 27 + \frac{1}{2} \sigma n_0 G \,. \qquad (8)$$

There is a slight increase of the experimental value of $E_{3/4} - E_{1/4}$ when the concentration of QH decreases (76 mV at $5 \cdot 10^{-5}$ mol dm^{-3} to 85 mV at 10^{-5} mol dm^{-3}) although a decrease of $E_{3/4} - E_{1/4}$ towards the value of an adsorption process without interactions ($\boldsymbol{RT}/2\boldsymbol{F}$ ln 27 mV)[17] should be expected according to Eq. (*8*).

The interaction parameter G can be obtained from the Eq. (*5*). The plots E *vs* $f(i)$ (Fig. 3) are linear with slopes of 12–14 mV for values of $G = 0{\cdot}65 \pm 0{\cdot}05$ in all cases, except at very low concentrations.

According to Parsons[19], for the determination of n_0 a cluster of water molecules occupying an area of 30 to 40 Å^2 has to be considered. In this case, the area of a molecule of product of the electrode process is 230 Å^2 aprox. Accordingly n_0 has to be 6.

The representation of the simulated polarigraphic waves, obtained taking G equal to 0·65, agrees well with the experimental ones (Fig. 4). Their shapes are in good agreement with theoretical ones obtained by Laviron using interaction parameters similar to ours (Fig. 2 ref.[17]).

We can observe that results obtained from Eqs (*3*)–(*7*) are in good agreement with experimental data (Figs 3, 4). Moreover, the transfer of two electrons per QH molecule observed at low QH concentrations and the „anomalous" $E_{3/4} - E_{1/4}$ values may be explained assuming the formation of a 1 : 1 QH : Hg derivative.

As pointed out by Vlček[7] in the analysis of the anodic behaviour of chlorides, the first step of the electrode process can be the arrangement of a molecule of QH on the electrode surface with the formation of a QHg derivative. Moreover, it is true that the probability of the existence of such compound increases when the coverage of electrode surface diminishes. So, we can assume that at concentrations lower than $2{\cdot}5 \cdot 10^{-5}$ mol cm^{-3} ($\Theta < 0{\cdot}5$) and in the potential range corresponding to the foot of the wave, the current has values higher than those calculated from Eq. (*3*), as observed experimentally in these conditions (Figs 2 and 4). Also, the animalous behaviour of the foot of the wave may affect the $E_{1/4}$ and therefore the $E_{3/4} - E_{1/4}$ values. In this sense, we can see that there is a better agreement of the calculated values at high coverages:

$$c = 3{\cdot}5 \cdot 10^{-5} \text{ mol dm}^{-3}\,, \quad E_{calc} = 80 \text{ mV}\,, \quad E_{exp} = 76 \text{ mV}\,;$$
$$c = 4 \cdot 10^{-5} \text{ mol dm}^{-3}\,, \quad E_{calc} = 76 \text{ mV}\,, \quad E_{exp} = 74 \text{ mV}\,.$$

Wave II

The behaviour at high depolarizer concentrations and the results achieved by Guidelli in the study of methylene blue[20] are similar: *a*) In the concentration range $1{\cdot}7 \cdot 10^{-4}$ . . mol dm^{-3} – $3 \cdot 10^{-4}$ mol dm^{-3} the wave II consists of two separate steps (Fig. 5). At higher concentraitons, this behaviour cannot be observed due to the change in the shape of this wave (Fig. 1). *b*) Dependence of $E_{1/2}$ of waves I and II with concentration (Fig. 6 and Fig. 2 in ref.[20]). *c*) The shape of the potenciostatic $i = f(t)$ curves However, neither the dependence of $E_{3/4} - E_{1/4}$ on depolarizer concentration (Fig. 3, ref.[20]) agrees with that proposed by the author[20], nor the „normal" voltammetric peak is splitted in two peaks[4]. These results suggest that the two layer model[20] could be useful at high depolarizer concentrations.

INHIBITION PROCESSES

A qualitative analysis of the system shows an inhibition effect due to both the first adsorption film of the organomercury derivative (wave I and voltammetric peak I) and

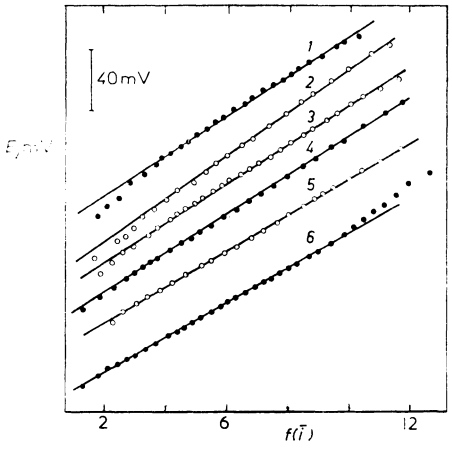

FIG. 3

Plot of E *vs* ln $[\bar{i}/(i_e - \bar{i})^2] + \sigma n_0 G(\bar{i}/i_e)$; pH = 5·3 c_r^* mol dm^{-3}): *1* $2 \cdot 10^{-5}$; *2* $2{\cdot}5 \cdot 10^{-5}$; *3* $3 \cdot 10^{-5}$; *4* $3{\cdot}5 \cdot 10^{-5}$; *5* $4 \cdot 10^{-5}$; *6* $4{\cdot}5 \cdot 10^{-5}$

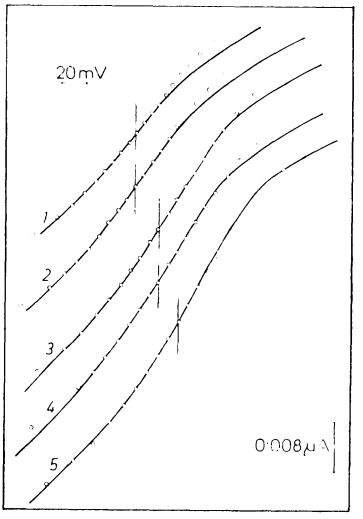

FIG. 4

Polarograms ($E - E_{1/2}$ *vs* $\bar{i}$) of 8-hydroxyquinoline. Concentration (mol dm^{-3}): *1* $2 \cdot 10^{-5}$; *2* $3 \cdot 10^{-5}$; *3* $3{\cdot}5 \cdot 10^{-5}$; *4* $4 \cdot 10^{-5}$; *5* $4{\cdot}5 \cdot 10^{-5}$. The vertical line of each curve refers to 0V. Solid curves are experimental. circles were calculated from Eq. (5) with $D = 7{\cdot}5 \cdot 10^{-6}$ cm^2/s, $t_1 = 2s$ $n_0 = 6$ and $G = 0{\cdot}65$

the film formed by precipitation at high concentrations (wave II and voltammetric peak II).

The first one is indicated by the following facts:

1) The existence if a sharp increase of current of wave II at high concentrations. Moreover, the negative branch of the corresponding a.c. polarographic peak occurs at potentials without current in d.c. polarographic conditions. This means that a capacitive process takes place immediatly before wave II, and it could be the loss of the inhibitory properties of the film due to a structural change or to its desorption (Figs 1 and 5).

2) In voltammetric study of the system, the inversion of the potential sweep at potentials corresponding to the negative branch of peak II leads to the appearance of oxidation peaks in the cathodic sweep (Fig. 7).

3) If the potential is stopped during 15 s at potentials more cathodic than peak potential of peak II (Fig. 8), we can observe: *a*) a decrease of current; *b*) a slow increase of current and *c*) a decrease of current to zero.

The same charges are obtained for the reduction peaks when the hold-up is long enough (Fig. 8) and when the inversion potential is more anodic than peak II (Fig. 7). This means at the electrode process takes place at more cathodic potentials when the inhibition has been broken.

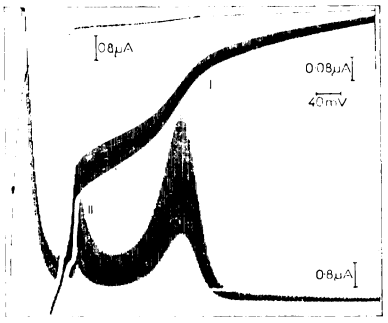

FIG. 5

Polarograms d.c. and a.c. phase sensitive (75 Hz and 5 mV r.m.s.) of 8-hydroxyquinoline. pH 5·26, $c_r^* = 2 \cdot 10^{-4}$ mol dm^{-3}

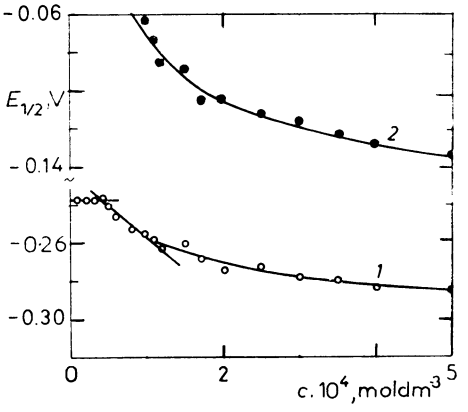

FIG. 6

Relationship between $E_{1/2}$ *vs* c_r^* at pH = = 5·3. *1* Wave I; *2* wave II

The inhibition due to the precipitation film is clearly observed by the decrease of current to zero at more anodic potentials than peak II (ref.[4]), an by the presence of penetration currents in polarography[12].

The characteristics of the process and the shape of $i = f(t)$ curves (sharp decrease of current in t_m – time required for unity of product coverage) show that the inhibition does not imply a current function of coverage for the „adsorption process" of wave I, and only takes place when the film recoverying the electrode surface becomes compact, *i.e.* at t_m (ref.[21,22]). So, before t_m, the current is equal to the normal value in absence of inhibition and it does not affect in any way the theoretical analysis of the wave that we have made at low concentrations. The dependence of t_m on potential agrees with an inhibition produced by the product of a chemical reaction following the charge transfer[22] (linear plot ln t_m *vs* E. Calculated slope 78 n; experimental slope aprox. 180) in good concordance with the proposed mechanism.

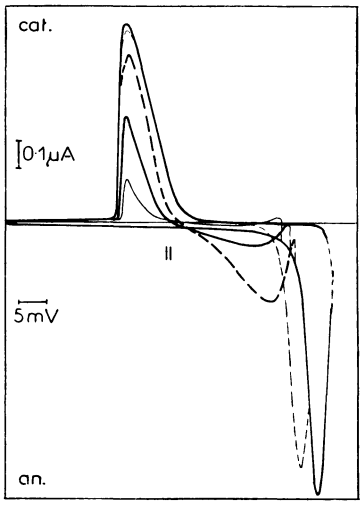

FIG. 7

Cyclic voltammograms. Analysis of „normal" peak. pH 5·21, $c_r^* = 7{\cdot}5 \cdot 10^{-4}$ mol . . dm^{-3}. Sweep rate 2 mV/s, $V_f = 0{\cdot}15$ V. Initial stabilization time: 30 s. Study of influence of switching potential on cathodic scan. Reference electrode Ag/AgCl (KCl sat.)

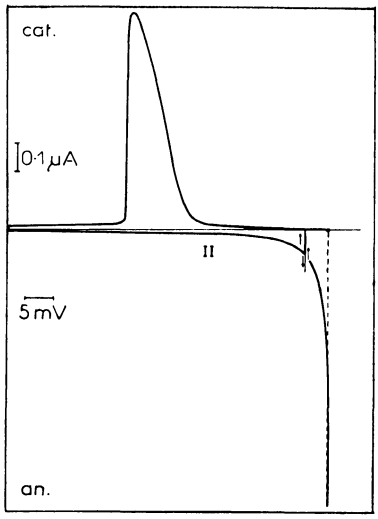

FIG. 8

Cyclic voltammograms. A 15 s hold at different potentials. Experimental conditions of Fig. 7

REFERENCES

1. Breyer B.: Aust. J. Sci. *23*, 225 (1961).
2. Nomura J.: Nagoya Daigaku Gakuho *24*, 97 (1972).
3. Fujinaga T., Izutsu K., Okazaki S., Sawamoto H.: J. Electroanal. Chem. Interfacial Electrochem. *21*, 187 (1969).
4. Muller C., Claret J., Feliu J. M., Virgili J.: Electrochim. Acta *27*, 1003 (1982).
5. Koryta J., Zuman P.: This Journal *18*, 197 (1953).
6. Armstrong R. D., Fleischmann M., Koryta J.: This Journal *30*, 4342 (1965).
7. Vlček A. A.: This Journal *19*, 221 (1954).
8. Zuman P., Koryta J., Kalvoda R.: This Journal *18*, 350 (1953).
9. Biegler T.: *J. Electroanal. Chem. Interfacial Electrochem. 6*, 357 (1964).
10. Bewick A., Fleischmann M. in the book: *Topics in Surface Chemistry* (E. Kay, P. S. Bagus Eds). Plenum Press, New York 1978.
11. Virgili J., Muller C., Feliu J. M., Claret J.: An. Quim. *78*, 220 (1982).
12. Biegler T.: J. Electroanal. Chem. Interfacial Electrochem. *4*, 317 (1962).
13. Bellamy L. G.: *Infra-red Spectra of Complex Molecules*, 2nd Ed. Methuen, London 1962.
14. Aly H. F., Abdel Kerim F. M., Kandil A. T.: J. Inorg. Nucl. Chem. *33*, 4344 (1971).
15. Magee R. J., Gordon L.: Talanta *10*, 851, 961 (1963).
16. Faraglia G., Roncucci L., Barbieri R.: Gazz. Chim. Ital. *93*, 1413 (1963).
17. Laviron E.: J. Electroanal. Chem. Interfacial Electrochem. *63*, 245 (1975).
18. Koryta J.: This Journal *18*, 206 (1953).
19. Parsons R.: J. Electroanal. Chem. Interfacial Electrochem. *8*, 93 (1964).
20. Piccardi G., Pergola F., Foresti M., Guidelli R.: J. Electroanal. Chem. Interfacial Electrochem. *84*, 235 (1977).
21. Laviron E., Degrand C.: Bull. Soc. Chim. Fr. *4566* (1970).
22. Laviron E., Degrand C.: Bull. Soc. Chim. Fr. *2194* (1966).