

STUDY OF THE RATE OF CORROSION OF METALS BY A FARADAIC DISTORTION METHOD, I

J. DÉVAY and L. MÉSZÁROS

(Research Group of Electrochemistry of the Hungarian
Academy of Sciences, Veszprém)

Received June 30, 1978

Accepted for publication August 8, 1978

A method based on faradaic distortion is presented for the study of the kinetics of corrosion processes for the case when the current-voltage characteristics of both the anodic and the cathodic reactions can be expressed by Tafel's equation. The harmonic components of the current flowing through the electrode under the effect of a sinusoidal alternating voltage superimposed on the polarizing direct voltage are examined as functions of the time-average value of the polarizing direct voltage and the amplitude of the alternating voltage. The corrosion current and the Tafel slopes of the anodic and cathodic reactions can be determined by measuring the first, second and third harmonic components of the faradaic current at one potential in each of the anodic and cathodic Tafel ranges. The evaluation of the corrosion current and of the Tafel's slopes from the harmonic component of the current measured at the corrosion potential is also presented. Simple relationships are obtained if the amplitude of the alternating voltage is small.

Introduction

The current-voltage characteristics of electrode-solution interface *i.e.* the polarization curve is generally nonlinear mainly as a consequence of the nonlinearity of the faradaic impedance. (The nonlinearity *i.e.* the potential dependence of the capacity of the double-layer is an additional cause of the above effect.) It follows from the above fact that current rectification is observed when the electrode is polarized by a nondistorted sinusoidal alternating voltage and the current is distorted as compared to the applied voltage *i.e.* the current contains higher harmonic components in addition to the one having the same frequency as the polarizing voltage. The latter phenomenon is termed faradaic distortion while the former is the faradaic rectification. Consider as an example of this phenomenon a current-voltage characteristics given by an expression of second order

$$I = AU + BU^2 \quad (1)$$

substituting voltage U by $U_0 \sin \omega t$ (where U_0 is the amplitude and ω the angular frequency of the alternating voltage) current I will be given by the following formula:

$$I = AU_0 \sin \omega t + BU_0^2 \sin^2 \omega t = \frac{BU_0^2}{2} + AU_0 \sin \omega t + \frac{BU_0^2}{2} \cos 2\omega t. \quad (2)$$

Thus, in addition to the component having frequency ω the current is composed of a d.c. component $\frac{BU_0^2}{2}$ and a second harmonic component having frequency 2ω and amplitude $\frac{BU_0^2}{2}$. Both rectification and distortion originate from term BU^2 containing the second power of U and causing the nonlinearity. When the current-voltage characteristics is described by an expression containing higher powers of U (e.g. by a transcendent integer function defined by a power series) the current also contains higher harmonic components of frequency $k\omega$ ($k = 1, 2, 3 \dots$). The parameters of the current-voltage characteristics (A and B in the above example) appear in the amplitudes of both the rectified current and the harmonic components consequently these parameters can be evaluated if the amplitudes are known.

The above considerations also apply to the case of the polarization by alternating current of an electrode having a nonlinear current-voltage characteristics. In this case the potential of the electrode exhibits faradaic distortion and faradaic rectification.

A similar approach is valid for the case when an alternating voltage or alternating current is superimposed on the direct voltage or direct current, respectively, polarizing the electrode. In this case the d.c. polarization curve observed in the absence of a.c. current is modified by the faradaic rectification component, and the harmonic components of the current or those of the potential can be studied as a function of the polarizing direct voltage or direct current, respectively. Thus valuable information is obtained on the kinetics of the electrode reaction.

Faradaic rectification has been studied first by DOSS and AGARWAL [1, 2] in the audio-frequency range. These authors applied the above method for the study of the kinetics of redox processes near the reversible potential. BARKER [3, 4, 5] employed radio-frequency signals for the investigation of rapid electrode processes. Later several authors studied the details of the method. DELAHAY *et al.* [6] studied the rectification and distortion effects caused by the nonlinear current-voltage characteristics of redox processes in the case of simultaneous diffusion and charge transfer polarizations in the vicinity of the reversible potential.

VAN CAKENBERGHE [7] has suggested the use of the second harmonic component generated by faradaic distortion for the determination of the transfer coefficient. This method has been developed further by BAUER and ELVING [8]. Several authors have derived expressions for diffusion and charge transfer polarization [9, 10, 11]. The potential dependence of the second harmonic current component was mainly studied from a polarographic point of view aiming at kinetic investigations [12 through 19] or at analytical determinations [11, 20, 21].

An extremely lucid summary of the effect related to faradaic impedance, faradaic rectification and distortion has been presented by DEVANATHAN [22] for the case of redox reactions in the vicinity of the reversible potential. DEVANATHAN *et al.* [23] determined the kinetic parameters of some redox reactions by the measurement of faradaic distortion at radio-frequency signals (100 kHz to 1 MHz).

RANGARAJAN [24, 25, 26] has developed an operator method for the mathematical evaluation of the non-linear response of the faradaic impedance. This method is applicable in the case of any current or voltage perturbations.

In recent years some attempts have been presented regarding the use of faradaic rectification and distortion in the study of corrosion processes. SANTHYARAYANA [27, 28] determined the rate of corrosion by faradaic rectification measurement at the electrode polarized by sinusoidal alternating voltage in the vicinity of the corrosion potential. This method can only be applied if the Tafel slope of at least one of the partial processes is known. SANTHYARAYANA and SRINIVASAN [29] have derived a relation for the determination of the corrosion current from the potential shift caused by faradaic rectification for such cases when the corrosion potential does not considerably differ from the reversible potential of the metal electrode. The Tafel slopes of the partial electrode processes must be known also in this case. Experimental evidence of the above mentioned relationship has also been presented [30]. PRABHAKARA RAO and MISRA [31] have studied the potential dependence of the first and second harmonic a.c. and that of the intermodulation current components generated by a small amplitude alternating voltage superimposed on the direct voltage. These authors confined their study to the vicinity of the corrosion potential assuming that the polarization curve could be considered linear with respect to d.c. in this potential range and they substituted the exponential expressions relating to the a.c. component with fourth order Taylor polynomials. This method permits the determination of the corrosion current and that of the Tafel slopes as well.

In our previous work we have considered the effect of alternating current on electrode reactions and corrosion processes having various current-voltage characteristics [32 through 40]. It has been shown that the polarization curve of the electrode and consequently the rate of corrosion were altered by a.c. to an extent depending on the amplitude and the frequency of the latter. The effect of the double-layer capacity has also been considered.

In this communication a new a.c. method will be presented for the determination of the electrochemical rate of corrosion of metals. The potential dependence of the harmonic components of the current is examined in the case of the polarization of the electrode by an alternating voltage superimposed on the direct voltage which permits the evaluation of the kinetic parameters (corrosion current, Tafel slopes) of the corrosion process. It was assumed that both

the cathodic and the anodic reactions of the corrosion process can be represented by a Tafel-type current-voltage characteristics and the reversible potential of the two partial processes sufficiently differ from the corrosion potential.

Harmonic components of the faradaic current

In the present case the polarization curve of the electrode is expressed by the following equation :

$$j = j_K \left(e^{\frac{\Delta E}{\beta_a}} - e^{-\frac{\Delta E}{\beta_c}} \right), \quad (3)$$

where j is the current density, j_K the corrosion current density, $\Delta E = E - E_K$ is the polarization *i.e.* the difference of the actual potential and the corrosion potential while β_a and β_c are parameters proportional to Tafel slopes b_a and b_c of the anodic and cathodic processes, respectively :

$$\beta_a = \frac{b_a}{\ln 10} \quad \text{and} \quad \beta_c = \frac{b_c}{\ln 10}.$$

If the electrode is polarized by a sinusoidal voltage having angular frequency ω and amplitude U_0 superimposed on the direct voltage $\overline{\Delta E}$

$$\Delta E = \overline{\Delta E} + U_0 \sin \omega t \quad (4)$$

the current density can be calculated by the following equation

$$j = j_K \left(e^{\frac{\overline{\Delta E} + U_0 \sin \omega t}{\beta_a}} - e^{-\frac{\overline{\Delta E} + U_0 \sin \omega t}{\beta_c}} \right) + C \frac{d(\Delta E)}{dt}. \quad (5)$$

The first term of equation (5) is faradaic current density j while the second term represents the capacitive current density, C being the double layer capacity referred to the unit area of the electrode. The capacity of the double layer is assumed to be independent of the frequency [41] and of the potential in the potential range used in the investigation. The resistance of the solution between the working electrode and the reference electrode is disregarded in the theoretical derivation. The effect of the nonlinearity of the double layer capacity and the influence of the solution resistance will be considered in a future publication. Note that amplitude U_0 of the alternating voltage is not limited except in so far as it is assumed that in the potential range $\Delta E = \overline{\Delta E} + U_0 \sin \omega t$ only one cathodic reaction (*e.g.* H_2 evolution) takes place in addition to the anodic reaction consisting of metal dissolution.

We examine the faradaic current density

$$\mathbf{j}_F = \mathbf{j}_K \left(e^{\frac{\overline{\Delta E} + U_0 \sin \omega t}{\beta_a}} - e^{-\frac{\overline{\Delta E} + U_0 \sin \omega t}{\beta_c}} \right), \quad (6)$$

the capacitive current density

$$C \frac{d(\Delta E)}{dt} = \omega C U_0 \cos \omega t \quad (7)$$

will be considered later.

The exponential terms of equation (6) can be written in the form of products and thus the factors depending on the time average value of $\overline{\Delta E}$ are separated and the following relation is obtained

$$\mathbf{j}_F = \mathbf{j}_K \left(e^{\frac{\overline{\Delta E}}{\beta_a}} \cdot e^{\frac{U_0 \sin \omega t}{\beta_a}} - e^{-\frac{\overline{\Delta E}}{\beta_c}} \cdot e^{-\frac{U_0 \sin \omega t}{\beta_c}} \right). \quad (8)$$

The faradaic current density has a distorted sinusoidal form because of the non-linear (exponential) characteristics of the anodic and cathodic charge transfer reactions and thus in addition to the fundamental harmonic having frequency ω , higher harmonics of frequency $k\omega$ ($k = 1, 2, 3 \dots$) are also present in the current. The harmonic components of the current density can be obtained by developing the exponential terms

$$e^{\frac{U_0 \sin \omega t}{\beta_a}} \quad \text{and} \quad e^{-\frac{U_0 \sin \omega t}{\beta_c}}$$

in Fourier series [37]

$$\begin{aligned} \mathbf{j}_F = \mathbf{j}_K \left\{ \left[I_0 \left(\frac{U_0}{\beta_a} \right) + 2 \sum_{k=1}^{\infty} (-1)^k I_{2k+1} \left(\frac{U_0}{\beta_a} \right) \sin (2k+1) \omega t + \right. \right. \\ \left. \left. + 2 \sum_{k=1}^{\infty} (-1)^k I_{2k} \left(\frac{U_0}{\beta_a} \right) \cos 2k \omega t \right] e^{\frac{\overline{\Delta E}}{\beta_a}} - \right. \\ \left. - \left[I_0 \left(\frac{U_0}{\beta_c} \right) - 2 \sum_{k=0}^{\infty} (-1)^k I_{2k+1} \left(\frac{U_0}{\beta_c} \right) \sin (2k+1) \omega t + \right. \right. \\ \left. \left. + 2 \sum_{k=1}^{\infty} (-1)^k I_{2k} \left(\frac{U_0}{\beta_c} \right) \cos 2k \omega t \right] e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\}, \quad (9) \end{aligned}$$

where I_n ($n = 0, 1, 2 \dots$) are modified Bessel functions of the first kind. However, it is sufficient to substitute the faradaic current density by a third order Fourier polynomial as the measurement of harmonic components higher

than the third one is burdened with difficulty and inaccuracy. The amplitudes of the higher harmonic components are so small as to be commensurable with the noise level of the measuring system. Thus, by rearranging the terms having identical frequencies one obtains

$$\begin{aligned} \mathbf{j}_F = & \mathbf{j}_k \left\{ I_0 \left(\frac{U_0}{\beta_a} \right) e^{\frac{\overline{\Delta E}}{\beta_a}} - I_0 \left(\frac{U_0}{\beta_c} \right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} + \\ & + 2\mathbf{j}_k \left\{ I_1 \left(\frac{U_0}{\beta_a} \right) e^{\frac{\overline{\Delta E}}{\beta_a}} + I_1 \left(\frac{U_0}{\beta_c} \right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \sin \omega t - \\ & - 2\mathbf{j}_k \left\{ I_2 \left(\frac{U_0}{\beta_a} \right) e^{\frac{\overline{\Delta E}}{\beta_a}} - I_2 \left(\frac{U_0}{\beta_c} \right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \cos \omega t - \\ & - 2\mathbf{j}_k \left\{ I_3 \left(\frac{U_0}{\beta_a} \right) e^{\frac{\overline{\Delta E}}{\beta_a}} + I_3 \left(\frac{U_0}{\beta_c} \right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \sin 3\omega t. \end{aligned} \quad (10)$$

The first term of equation (10) is the time average of the current density, $\bar{\mathbf{j}}$ (d.c. component) while the second, third and fourth terms are the first, second and third harmonic components, respectively. The latter terms can be measured by a frequency selective measuring receiver. Thus the d.c. component is given by the following formula

$$\bar{\mathbf{j}} = \mathbf{j}_k \left\{ I_0 \left(\frac{U_0}{\beta_a} \right) e^{\frac{\overline{\Delta E}}{\beta_a}} - I_0 \left(\frac{U_0}{\beta_c} \right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\}, \quad (11)$$

while the faradaic rectification term is

$$\begin{aligned} \overline{\Delta \mathbf{j}} &= \mathbf{j}_k \left\{ I_0 \left(\frac{U_0}{\beta_a} \right) e^{\frac{\overline{\Delta E}}{\beta_a}} - I_0 \left(\frac{U_0}{\beta_c} \right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} - \mathbf{j}_k \left\{ e^{\frac{\overline{\Delta E}}{\beta_a}} - e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} = \\ &= \mathbf{j}_k \left\{ \left(I_0 \left(\frac{U_0}{\beta_a} \right) - 1 \right) e^{\frac{\overline{\Delta E}}{\beta_a}} - \left(I_0 \left(\frac{U_0}{\beta_c} \right) - 1 \right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\}, \end{aligned} \quad (12)$$

and the amplitudes of the harmonic components relating from faradaic distortion are

$$\mathbf{j}_1 = 2\mathbf{j}_k \left\{ I_1 \left(\frac{U_0}{\beta_a} \right) e^{\frac{\overline{\Delta E}}{\beta_a}} + I_1 \left(\frac{U_0}{\beta_c} \right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\}, \quad (13)$$

$$\mathbf{j}_2 = 2\mathbf{j}_k \left| I_2 \left(\frac{U_0}{\beta_a} \right) e^{\frac{\overline{\Delta E}}{\beta_a}} - I_2 \left(\frac{U_0}{\beta_c} \right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right|, \quad (14)$$

$$\mathbf{j}_3 = 2\mathbf{j}_k \left\{ I_3 \left(\frac{U_0}{\beta_a} \right) e^{\frac{\overline{\Delta E}}{\beta_a}} + I_3 \left(\frac{U_0}{\beta_c} \right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\}. \quad (15)$$

Note that the signs in equation (10) were neglected in expression (14) and (15), similarly the phase reversal of the second harmonic is not indicated either because the amplitudes are defined as positive quantities. Thus the faradaic rectification component and the amplitudes of the first, second and third harmonic components generated by faradaic distortion are related to the polarizing direct voltage and the amplitude of the alternating voltage by equations (12) through (15).

The above relationship do not contain any restriction regarding the amplitude of the alternating voltage. However, much simpler expressions can be obtained if the amplitude of the alternating voltage is reduced to an extent permitting the substitution of the Bessel functions by the first or first and second terms of their Taylor polynomials.

The approximate value of the Bessel function used in the above equation are the following

$$I_0(x) \cong 1 + \left(\frac{x}{2}\right)^2, \quad (16)$$

$$I_1(x) \cong \frac{x}{2}, \quad (17)$$

$$I_2(x) \cong \frac{1}{2} \left(\frac{x}{2}\right)^2, \quad (18)$$

$$I_3(x) \cong \frac{1}{6} \left(\frac{x}{2}\right)^3. \quad (19)$$

The error caused by the above approximation when $x = \frac{U_0}{\beta} = 1$ amounts to 10 per cent approximately and it can be reduced further by decreasing amplitude U_0 . The error becomes negligible as compared to the inaccuracies of the measuring method when the amplitude is 5 to 10 mV. Equations (12) through (15) are simplified to the following formulas by substituting the approximate values of the Bessel functions:

$$\bar{A}j = j_k \left(\frac{1}{\beta_a^2} e^{\frac{\Delta E}{\beta_a}} - \frac{1}{\beta_c^2} e^{-\frac{\Delta E}{\beta_c}} \right) \frac{U_0^2}{4}, \quad (20)$$

$$\bar{j}_1 = j_k \left(\frac{1}{\beta_a} e^{\frac{\Delta E}{\beta_a}} + \frac{1}{\beta_c} e^{-\frac{\Delta E}{\beta_c}} \right) U_0, \quad (21)$$

$$\bar{j}_2 = j_k \left| \frac{1}{\beta_a^2} e^{\frac{\Delta E}{\beta_a}} - \frac{1}{\beta_c^2} e^{-\frac{\Delta E}{\beta_c}} \right| \frac{U_0^2}{4}, \quad (22)$$

$$\bar{j}_3 = j_k \left(\frac{1}{\beta_a^3} e^{\frac{\Delta E}{\beta_a}} + \frac{1}{\beta_c^3} e^{-\frac{\Delta E}{\beta_c}} \right) \frac{U_0^3}{24}. \quad (23)$$

Faradaic rectification current component $\overline{\Delta j}$ is represented in Fig. 1 as a function of the time average value of polarizing voltage $\overline{\Delta E}$, while the potential dependence of the amplitude of the fundamental harmonic component and that of the higher harmonic components generated by faradaic distortion are shown in Figs 2 through 4, respectively. The curves shown in the figures were calculated according to equations (20) through (23) with the following parameters: $U_0 = 0.010$ V, $\beta_a = \beta_c = 0.050$ V and $\beta_a = 0.025$ V and $\beta_c = 0.050$ V, respectively. The difference between the data calculated with exact formulas (12) through (15) and approximate equations (20) through (23), respectively, are shown in Figs 5 through 8 as functions of amplitude U_0 of the alternating voltage for the case when $\Delta E = 0$ i.e. at the corrosion potential while Figs 9 through 12 represent the same relationship for the case of polarization $\Delta E = 0.100$ V. The parameters used in this calculation were the following $\beta_a = 0.025$ and $\beta_c = 0.050$ V.

Determination of the corrosion current and of the Tafel slopes

The kinetic parameters of the corrosion process (j_k, β_a, β_c) can be evaluated from data obtained in measurements made with an electrode either polarized in the range of the validity of Tafel's equation or maintained at the corrosion potential using either exact equations (13) through (15) or approximate formulas (21) through (23).

The harmonic components of the faradaic current are given by the following formulas deduced from equations (13) through (15) for the case of measurements with an anodically polarized electrode at a sufficiently large polarization ($\frac{\Delta E_a}{\beta_a} > 1$) in the range of the validity of Tafel's equation.

$$\hat{j}_{1a} = 2j_k I_1 \left(\frac{U_0}{\beta_a} \right) e^{\frac{\Delta E_a}{\beta_a}}, \quad (24)$$

$$\hat{j}_{2a} = 2j_k I_2 \left(\frac{U_0}{\beta_a} \right) e^{\frac{\Delta E_a}{\beta_a}}, \quad (25)$$

$$\hat{j}_{3a} = 2j_k I_3 \left(\frac{U_0}{\beta_a} \right) e^{\frac{\Delta E_a}{\beta_a}}. \quad (26)$$

The quotients of the amplitudes of the harmonic components measured at the same potential $\overline{\Delta E_a}$ namely

$$\frac{\hat{j}_{1a}}{\hat{j}_{2a}} = \frac{I_1 \left(\frac{U_0}{\beta_a} \right)}{I_2 \left(\frac{U_0}{\beta_a} \right)}, \quad (27)$$

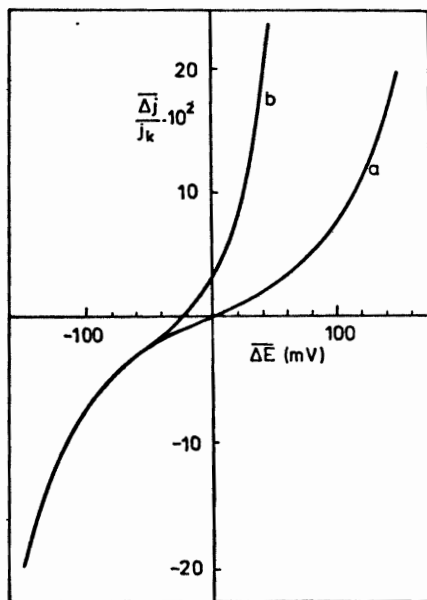


Fig. 1. Faradaic rectification component plotted as a function of polarization $\overline{\Delta E}$; $U_0 = 10$ mV; a: $\beta_a = \beta_c = 50$ mV; b: $\beta_a = 25$ mV, $\beta_c = 50$ mV

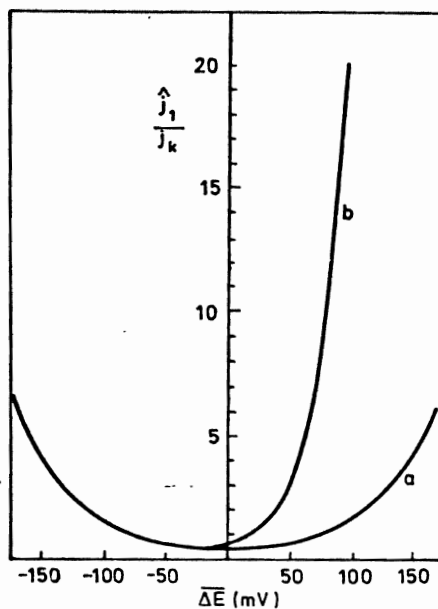


Fig. 2. Amplitude of the fundamental harmonic component plotted as a function of polarization. $U_0 = 10$ mV; a: $\beta_a = \beta_c = 50$ mV; b: $\beta_a = 25$ mV, $\beta_c = 50$ mV

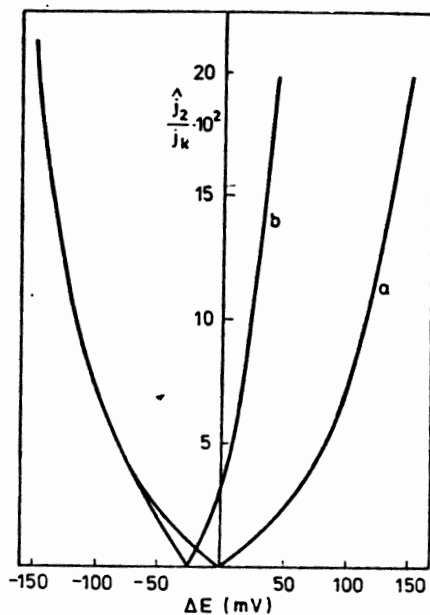


Fig. 3. Amplitude of the second harmonic current plotted as a function of polarization. $U_0 = 10$ mV. a: $\beta_a = \beta_c = 50$ mV; b: $\beta_a = 25$ mV; $\beta_c = 50$ mV

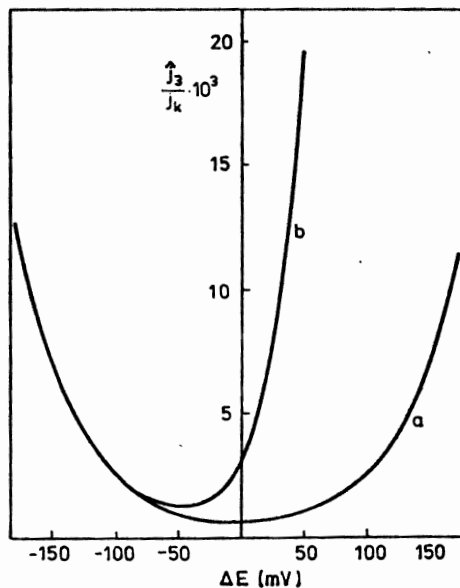


Fig. 4. Amplitude of the third harmonic component plotted as a function of polarization. $U_0 = 10$ mV. a: $\beta_a = \beta_c = 50$ mV; b: $\beta_a = 25$ mV, $\beta_c = 50$ mV

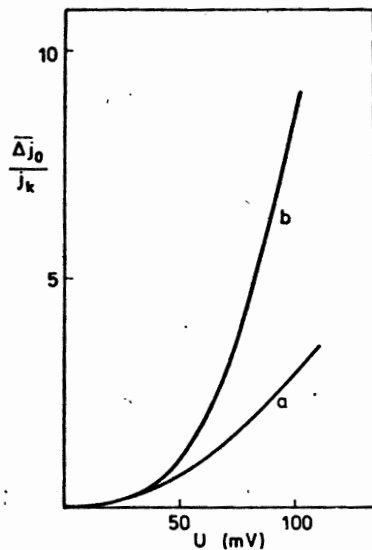


Fig. 5. Faradaic rectification component plotted as a function of amplitude U_0 of the alternating voltage at the corrosion potential $\overline{\Delta E} = 0$; $\beta_a = 25$ mV, $\beta_c = 50$ mV. *a*: calculated with approximate formula (20); *b*: calculated with exact formula (12)

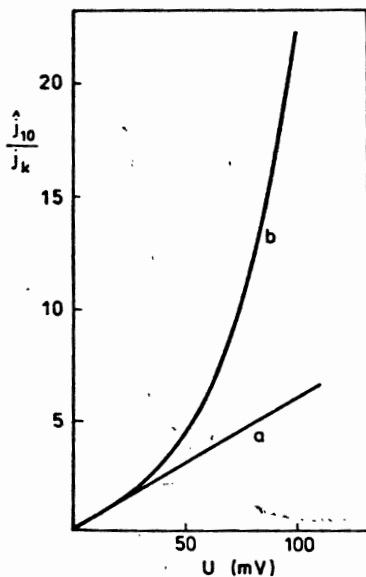


Fig. 6. Amplitude of the fundamental harmonic component plotted as a function of amplitude U_0 of the alternating voltage at the corrosion potential $\overline{\Delta E} = 0$, $\beta_a = 25$ mV, $\beta_c = 50$ mV. *a*: calculated with approximate formula (21), *b*: calculated with exact formula (13)

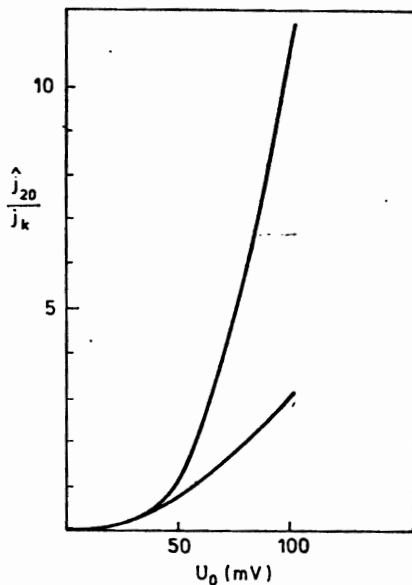


Fig. 7. Amplitude of the second harmonic component plotted as a function of amplitude U_0 of the alternating voltage at the corrosion potential $\overline{\Delta E} = 0$; $\beta_a = 25$ mV, $\beta_c = 50$ mV; a: calculated with approximate formula (22); b: calculated with exact formula (14)

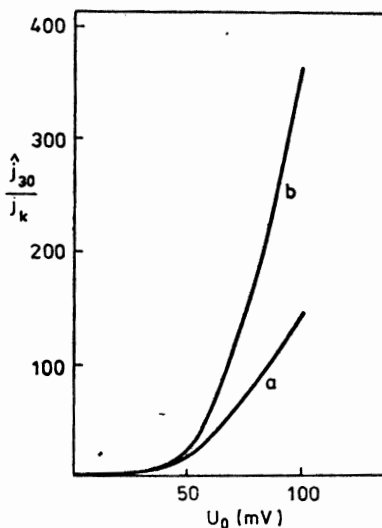


Fig. 8. Amplitude of the third harmonic component plotted as a function of amplitude U_0 of the alternating voltage at the corrosion potential $\overline{\Delta E} = 0$; $\beta_a = 25$ mV, $\beta_c = 50$ mV. a: calculated with approximate formula (23); b: calculated with exact formula (15)

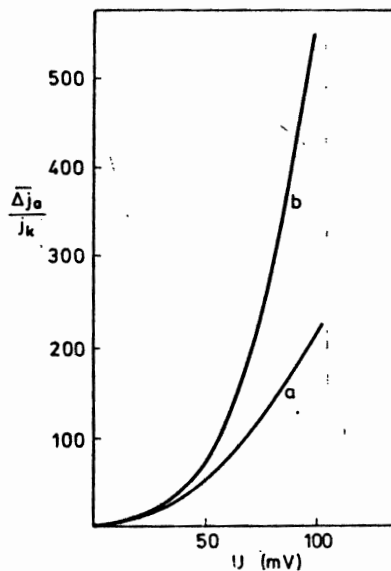


Fig. 9. Faradaic rectification component plotted as a function of amplitude U_0 of the alternating voltage at anodic polarization $\overline{\Delta E} = 100$ mV. $\beta_a = 20$ mV. $\beta_c = 50$ mV. *a*: calculated with approximate formula (20); *b*: calculated with exact formula (19)

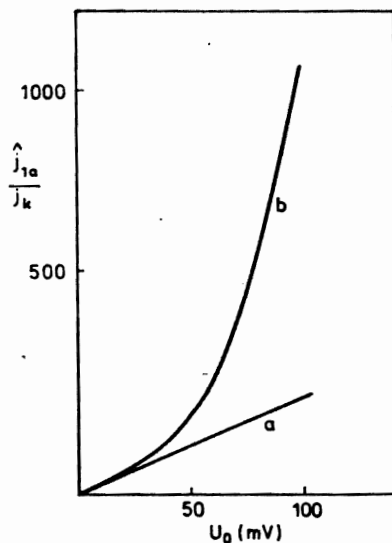


Fig. 10. Amplitude of the fundamental harmonic component plotted as a function of amplitude U_0 of the alternating voltage at anodic polarization $\overline{\Delta E} = 100$ mV. $\beta_a = 25$ mV, $\beta_c = 50$ mV; *a*: calculated with approximate formula (21); *b*: calculated with exact formula (13)

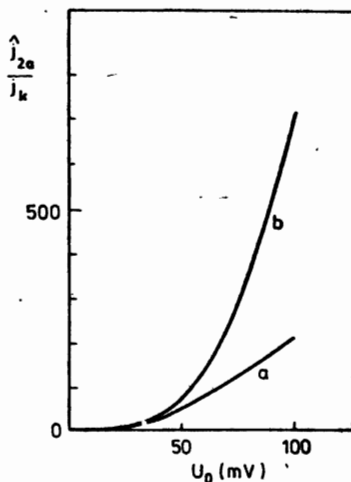


Fig. 11. Amplitude of the second harmonic component plotted as a function of amplitude U_0 of the alternating voltage at anodic polarization $\overline{\Delta E} = 100$ mV. $\beta_a = 25$ mV, $\beta_c = 50$ mV. a: calculated with approximative formula (22); b: calculated with exact formula (14)

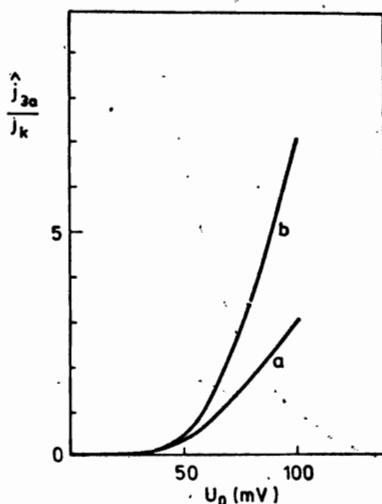


Fig. 12. Amplitude of the third harmonic component plotted as a function of amplitude U_0 of the alternating voltage at anodic polarization $\overline{\Delta E} = 100$ mV. $\beta_a = 25$ mV, $\beta_c = 50$ mV. a: calculated with approximative formula (23); b: calculated with exact formula (15)

and

$$\frac{j_{2a}}{j_{3a}} = \frac{I_2\left(\frac{U_0}{\beta_a}\right)}{I_3\left(\frac{U_0}{\beta_a}\right)} \quad (28)$$

respectively, permit the evaluation of β_a by successive approximation using mathematical tables.

β_a can be obtained also by a simpler method without resorting to successive approximations if one employs recursion formulas [42] valid for modified Bessel functions of the first kind.

$$\frac{2n}{x} I_n(x) = I_{n-1}(x) - I_{n+1}(x). \quad (29)$$

Equation (29) yields for $n = 2$

$$\frac{4}{x} I_2(x) = I_1(x) - I_3(x), \quad (30)$$

whence one obtains by substitution of $x = \frac{U_0}{\beta_a}$ and rearrangement

$$\beta_a = \frac{U_0}{4} \left[\frac{I_1\left(\frac{U_0}{\beta_a}\right)}{I_2\left(\frac{U_0}{\beta_a}\right)} - \frac{I_3\left(\frac{U_0}{\beta_a}\right)}{I_2\left(\frac{U_0}{\beta_a}\right)} \right]. \quad (31)$$

Substitution of equations (27) and (28) in equation (31) gives

$$\beta_a = \frac{U_0}{4} \frac{j_{1a} - j_{3a}}{j_{2a}}. \quad (32)$$

Thus parameter β_a can be determined from measurement data of the amplitudes of the first, second and third harmonic current component, respectively, at one potential $\overline{\Delta E}_a$ in the range of validity of Tafel's equation.

When

$$j_{3a} \ll j_{1a},$$

equation (32) can be simplified to yield

$$\beta_a \approx \frac{U_0}{4} \frac{j_{1a}}{j_{2a}}. \quad (33)$$

Parameter β_c relating to the cathodic reaction $\left(-\frac{\overline{\Delta E}_c}{\beta_c} > 1\right)$ can be obtained by a similar procedure.

Namely

$$\hat{j}_{1c} = 2j_k I_1 \left(\frac{U_0}{\beta_c} \right) e^{-\frac{\Delta E_c}{\beta_c}}, \quad (34)$$

$$\hat{j}_{2c} = 2j_k I_2 \left(\frac{U_0}{\beta_c} \right) e^{-\frac{\Delta E_c}{\beta_c}}, \quad (35)$$

$$\hat{j}_{3c} = 2j_k I_3 \left(\frac{U_0}{\beta_c} \right) e^{-\frac{\Delta E_c}{\beta_c}}, \quad (36)$$

thus

$$\frac{\hat{j}_{1c}}{\hat{j}_{2c}} = \frac{I_1 \left(\frac{U_0}{\beta_c} \right)}{I_2 \left(\frac{U_0}{\beta_c} \right)}, \quad (37)$$

and

$$\frac{\hat{j}_{2c}}{\hat{j}_{3c}} = \frac{I_2 \left(\frac{U_0}{\beta_c} \right)}{I_3 \left(\frac{U_0}{\beta_c} \right)}. \quad (38)$$

Parameter β_c is given by the following expressions from equations (37) and (38) using recursion formula (29).

$$\beta_c = \frac{U_0}{4} \frac{\hat{j}_{1c} - \hat{j}_{3c}}{\hat{j}_{2c}}, \quad (39)$$

or

$$\beta_c \approx \frac{U_0}{4} \frac{\hat{j}_{1c}}{\hat{j}_{2c}}, \quad (40)$$

where \hat{j}_{1c} , \hat{j}_{2c} and \hat{j}_{3c} are the amplitudes of the harmonic components measured at potential ΔE_c corresponding to a cathodic polarization in the range of the validity of Tafel's equation.

The corrosion current density can be calculated using anyone among equations (24) through (26) and equations (34) through (36) knowing β_a or β_c and polarization ΔE_a and ΔE_c employed during the measurement of \hat{j}_{1a} , \hat{j}_{2a} and \hat{j}_{3a} as well as \hat{j}_{1c} , \hat{j}_{2c} and \hat{j}_{3c} respectively.

$$\begin{aligned} j_k &= \frac{\hat{j}_{1a}}{2I_1 \left(\frac{U_0}{\beta_a} \right)} e^{-\frac{\Delta E_a}{\beta_a}} = \frac{\hat{j}_{2a}}{2I_2 \left(\frac{U_0}{\beta_a} \right)} e^{-\frac{\Delta E_a}{\beta_a}} = \frac{\hat{j}_{3a}}{2I_3 \left(\frac{U_0}{\beta_a} \right)} e^{-\frac{\Delta E_a}{\beta_a}} = \\ &= \frac{\hat{j}_{1c}}{2I_1 \left(\frac{U_0}{\beta_c} \right)} e^{-\frac{\Delta E_c}{\beta_c}} = \frac{\hat{j}_{2c}}{2I_2 \left(\frac{U_0}{\beta_c} \right)} e^{-\frac{\Delta E_c}{\beta_c}} = \frac{\hat{j}_{3c}}{2I_3 \left(\frac{U_0}{\beta_c} \right)} e^{-\frac{\Delta E_c}{\beta_c}}. \end{aligned} \quad (41)$$

The above formulas can be used also when a small amplitude alternating voltage ($U_0 \leq 10$ mV) is superimposed on the polarizing direct voltage, however, simpler expressions can be obtained if one takes into account the approximate formulas (17) through (19) derived by developing Bessel's functions in Taylor series. Parameters β_a and β_c can be calculated using the following formulas

$$\beta_a = \frac{U_0}{4} \frac{j_{1a}}{j_{2a}} = \frac{U_0}{6} \frac{j_{2a}}{j_{3a}}, \quad (42)$$

and

$$\beta_c = \frac{U_0}{4} \frac{j_{1c}}{j_{2c}} = \frac{U_0}{6} \frac{j_{2c}}{j_{3c}}, \quad (43)$$

respectively. Equations (42) and (43) were obtained by substituting equations (17) through (19) in equations (27), (28) and (37), (38), respectively. Equations (41) relating to the corrosion current density can also be rewritten in the simpler form

$$\begin{aligned} j_k &= j_{1a} \frac{\beta_a}{U_0} e^{-\frac{\overline{\Delta E}_a}}{\beta_a} = j_{2a} \frac{4\beta_a^2}{U_0^2} e^{-\frac{\overline{\Delta E}_a}}{\beta_a} = j_{3a} \frac{24\beta_a^3}{U_0^3} e^{-\frac{\overline{\Delta E}_a}}{\beta_a} = \\ &= j_{1c} \frac{\beta_c}{U_0} e^{\frac{\overline{\Delta E}_c}}{\beta_c} = j_{2c} \frac{4\beta_c^2}{U_0^2} e^{\frac{\overline{\Delta E}_c}}{\beta_c} = j_{3c} \frac{24\beta_c^3}{U_0^3} e^{\frac{\overline{\Delta E}_c}}{\beta_c}. \end{aligned} \quad (44)$$

We note that parameters β_a and β_c as well as corrosion current j_k can also be evaluated by the well-known Tafel's extrapolation method *i.e.* by plotting the logarithm of the harmonic components of the faradaic current as a function of polarization $\overline{\Delta E}$ according to equations (13) through (15) or according to equations (21) through (23) when $U_0 \leq 10$ mV. However, the advantage of our method as compared to Tafel's extrapolation technique consists in the fact that it is sufficient to measure the amplitude of the harmonic components at one potential either ΔE_a in the anodic Tafel range or ΔE_c in the cathodic Tafel range and it is not necessary to plot the complete polarization curve.

Parameters β_a and β_c as well as corrosion current density j_k can also be evaluated from the data of harmonic components j_{10} , j_{20} and j_{30} measured at the corrosion potential ($\overline{\Delta E} = 0$). In fact, substituting $\overline{\Delta E} = 0$ in equations (13) through (15) one obtains

$$j_{10} = 2j_k \left\{ I_1 \left(\frac{U_0}{\beta_a} \right) + I_1 \left(\frac{U_0}{\beta_c} \right) \right\}, \quad (45)$$

$$j_{20} = 2j_k \left| I_2 \left(\frac{U_0}{\beta_a} \right) - I_2 \left(\frac{U_0}{\beta_c} \right) \right|, \quad (46)$$

$$j_{30} = 2j_k \left\{ I_3 \left(\frac{U_0}{\beta_a} \right) + I_3 \left(\frac{U_0}{\beta_c} \right) \right\}, \quad (47)$$

and corrosion current density j_k can be evaluated if β_a and β_c are *a priori* known.

It is noteworthy that equation (46) is not applicable if $\beta_a = \beta_c$ as in this case $j_{20} = 0$. Faradaic rectification component Δj_0 can also be employed for the evaluation of the corrosion current density if $\beta_a \neq \beta_c$ as equation (12) can be rewritten in the following form for the case when $\overline{\Delta E} = 0$.

$$\overline{\Delta j_0} = j_k \left\{ I_0 \left(\frac{U_0}{\beta_a} \right) - I_0 \left(\frac{U_0}{\beta_c} \right) \right\}. \quad (48)$$

It is not essential to know parameters β_a and β_c *a priori* for the evaluation of the corrosion current density if three data among j_{10} , j_{20} , j_{30} and Δj_0 are simultaneously measured at corrosion potential $\overline{\Delta E} = 0$ as any three formulas among expressions (45) through (48) form an independent linear equation system for the evaluation of β_a , β_c and j_k . The equation system can be solved by a suitable computer program.

A much simpler set of equations is obtained when a small amplitude alternating voltage ($U_0 \leq 10$ mV) is employed in the measurements. In this case equation (20) through (23) yield the following expressions by substituting $\overline{\Delta E} = 0$.

$$\overline{\Delta j_0} = j_k \left(\frac{1}{\beta_a^2} - \frac{1}{\beta_c^2} \right) \frac{U_0^2}{4}, \quad (49)$$

$$j_{10} = j_k \left(\frac{1}{\beta_a} + \frac{1}{\beta_c} \right) U_0, \quad (50)$$

$$j_{20} = j_k \left| \frac{1}{\beta_a^2} - \frac{1}{\beta_c^2} \right| \frac{U_0^2}{4}, \quad (51)$$

$$j_{30} = j_k \left(\frac{1}{\beta_a^3} + \frac{1}{\beta_c^3} \right) \frac{U_0^3}{24}. \quad (52)$$

Solving set of equations (50) through (52) the corrosion current density can be evaluated according to the following formula

$$j_k = \frac{j_{10}^2}{\sqrt{48} \sqrt{2j_{10}j_{30} - j_{20}^2}}. \quad (53)$$

Comparing equations (49) and (51) we observe that

$$j_{20}^2 = (\overline{\Delta j_0})^2, \quad (54)$$

thus the second harmonic amplitude in equation (53) can be substituted by faradaic rectification $\overline{\Delta j_0}$ whence

$$j_k = \frac{j_{10}^2}{\sqrt{48} \sqrt{2j_{10}j_{30} - (\overline{\Delta j_0})^2}}. \quad (55)$$

β_a and β_c can be expressed from equations (49) and (50) or (50) and (51) if corrosion current density j_k is known.

Thus from equations (49) and (50)

$$\frac{1}{\beta_a} = \frac{1}{2U_0} \left(\frac{j_{10}}{j_k} + 4 \frac{\Delta j_0}{j_{10}} \right), \quad (56)$$

$$\frac{1}{\beta_c} = \frac{1}{2U_0} \left(\frac{j_{10}}{j_k} - 4 \frac{\Delta j_0}{j_{10}} \right); \quad (57)$$

while from equations (50) and (51), if $\beta_a < \beta_c$:

$$\frac{1}{\beta_a} = \frac{1}{2U_0} \left(\frac{j_{10}}{j_k} + 4 \frac{j_{20}}{j_{10}} \right), \quad (58)$$

$$\frac{1}{\beta_c} = \frac{1}{2U_0} \left(\frac{j_{10}}{j_k} - 4 \frac{j_{20}}{j_{10}} \right); \quad (59)$$

or if $\beta_a > \beta_c$

$$\frac{1}{\beta_a} = \frac{1}{2U_0} \left(\frac{j_{10}}{j_k} - 4 \frac{j_{20}}{j_{10}} \right), \quad (60)$$

$$\frac{1}{\beta_c} = \frac{1}{2U_0} \left(\frac{j_{10}}{j_k} + 4 \frac{j_{20}}{j_{10}} \right). \quad (61)$$

The sign of Δj_0 permits to decide whether equations (58) and (59) or equation (60) and (61) have to be used as $\Delta j_0 > 0$ in the case of $\beta_a < \beta_c$, while $\Delta j_0 < 0$ in the case of $\beta_a > \beta_c$ according to equation (49); $\beta_a = \beta_c$ if $\Delta j_0 = 0$ (and in this case $j_{20} = 0$).

Thus the above method permits the determination of the corrosion current density and parameters β_a and β_c proportional to the Tafel's slope from measurements made at the corrosion potential only. The advantage of this method as compared to the well-known "linear polarization" technique and its various modifications [43] consists in the fact that d.c. polarization is not involved and thus any shift in the corrosion potential caused by polarization can be avoided or at least decreased. It is well-known that change in the corrosion potential can considerably alter the slope of the polarization curve and thus the corrosion current density evaluated from the latter.

The relations derived in this paper refer to the faradaic current components only. The effect of the double layer capacity connected parallelly to the faradaic impedance and the possibility of the elimination of the capacitive current will be dealt with in a subsequent paper as well as the effect of the ohmic drop on the solution resistance between the working electrode and the reference electrode. The experimental verification of the above theoretical relations will also be presented in the next future.

- [1] DOSS, K. S., AGARWAL, H. P.: Proc. Indian Acad. Sci. 34 A, 263 (1951)
 [2] DOSS, K. S., AGARWAL, H. P.: Proc. Indian Acad. Sci. 35 A, 45 (1952)
 [3] BARKER, G., in CHARLOT, G. Ed., Modern Electroanalytical Methods, Elsevier, Amsterdam, 1958. p. 122
 [4] BARKER, G. C., in YEAGER, E. Ed., Transactions of the Symposium on Electrode Processes Wiley, New York, 1961. pp. 325-365
 [5] BARKER, G. C., FAIRELOTH, R. L., GARDNER, A. W.: Nature, 181, 247 (1958)
 [6] DELAHAY, P., SENDA, M., WELS, C. H.: J. Am. Chem. Soc. 83, 312 (1961)
 [7] VAN CAKENBERGHE, J.: Bull. Soc. Chim. Belges 60, 3 (1951)
 [8] BAUER, H. H., ELVING, P. J.: Anal. Chem., 30, 334 (1958)
 [9] BAUER, H. H.: Australian J. Chem. 17, 591 (1964)
 [10] BAUER, H. H.: Australian J. Chem. 17, 715 (1964)
 [11] SMITH, D. E., REINMUTH, W.: Anal. Chem. 33, 482 (1961)
 [12] BAUER, H. H., Foo, D.: Australian J. Chem., 19, 1103 (1966)
 [13] KOOLJMAN, D., SLUYTERS, J. H.: Rec. Trav. Chim., 83, 587 (1964)
 [14] McCORD, T. G., SMITH, D. E.: Anal. Chem., 40, 1959 (1968)
 [15] McCORD, T. G., SMITH, D. E.: Anal. Chem., 41, 115, 131 (1969)
 [16] DÉVAY, J., MÉSZÁROS, L., GARAI, T.: Magy. Kém. Folyóirat 74, 403 (1969); Acta Chim. Acad. Sci. Hung. 18, 141 (1968)
 [17] McCORD, T. G., SMITH, D. E.: Anal. Chem., 42, 2 (1970)
 [18] McCORD, T. G., SMITH, D. E.: Anal. Chem., 42, 126 (1970)
 [19] RANGLES, J. E. B., WITHOUSE, D. R.: Trans. Faraday Soc., 64, 1376 (1968)
 [20] NEEB, R.: Z. Anal. Chem. 186, 53 (1962); 181, 401 (1962)
 [21] DÉVAY, J., GARAI, T., MÉSZÁROS, L., PALÁGYI-FÉNYES, B.: Magy. Kém. Folyóirat, 75, 460 (1969); Hung. Sci. Instr. 15, 1 (1969)
 [22] DEVANATHAN, M. A. V.: Electrochimica Acta, 17, 1755 (1972)
 [23] DEVANATHAN, M. A. V.: J. Electroanal. Chem. 62, 195 (1975)
 [24] RANGARAJAN, S. K.: J. Electroanal. Chem. 56, 1 (1974)
 [25] RANGARAJAN, S. K.: J. Electroanal. Chem. 56, 27 (1974)
 [26] RANGARAJAN, S. K.: J. Electroanal. Chem. 62, 31 (1975)
 [27] SATHYANARAYANA, S.: J. Electroanal. Chem. 50, 411 (1974)
 [28] SATHYANARAYANA, S.: J. Electroanal. Chem. 62, 209 (1975)
 [29] SATHYANARAYANA, S., SRINIVASAN, R.: Br. Corros. J., 12, 217 (1977)
 [30] SRINIVASAN, R., SAHYANARAYANA, S.: Br. Corros. J. 12, 228 (1977)
 [31] PRABHAKARA RAO, G., MISHRA, A. K.: J. Electroanal. Chem. 77, 121 (1977)
 [32] ERDEY-GRUZ, T., DÉVAY, J., HORÁNYI, GY., VAJASDY, I., MÉSZÁROS, L.: Magy. Kém. Folyóirat, 67, 378 (1961); Acta Chim. Acad. Sci. Hung. 30, 431 (1962)
 [33] ERDEY-GRUZ, T., DÉVAY, J., VAJASDY, I., HORÁNYI, GY., MÉSZÁROS, L.: Magy. Kém. Folyóirat, 67, 446 (1961); Acta Chim. Acad. Sci. Hung. 32, 363 (1962)
 [34] ERDEY-GRUZ, T., DÉVAY, J., VAJASDY, I.: Magy. Kém. Folyóirat, 68, 185 (1962); Acta Chim. Acad. Sci. Hung., 37, 251 (1963)
 [35] ERDEY-GRUZ, T., DÉVAY, J., HORÁNYI, GY., VAJASDY, I.: Magy. Kém. Folyóirat, 67, 244 (1961); Acta Chim. Acad. Sci. Hung. 30, 29 (1962)
 [36] ERDEY-GRUZ, T., DÉVAY, J., VAJASDY, I., HORÁNYI, GY.: Magy. Kém. Folyóirat, 67, 244 (1961); Acta Chim. Acad. Sci. Hung. 30, 29 (1962)
 [37] DÉVAY, J., MÉSZÁROS, L.: Magy. Kém. Folyóirat, 71, 68 (1965); Acta Chim. Acad. Sci. Hung. 43, 25 (1965)
 [38] DÉVAY, J., MÉSZÁROS, L.: Magy. Kém. Folyóirat, 71, 238 (1965); Acta Chim. Acad. Sci. Hung. 45, 119 (1965)
 [39] DÉVAY, J., MÉSZÁROS, L.: Magy. Kém. Folyóirat 71, 240 (1965); Acta Chim. Acad. Sci. Hung. 45, 119 (1965)
 [40] DÉVAY, J., MÉSZÁROS, L.: Magy. Kém. Folyóirat 71, 277 (1965); Acta Chim. Acad. Sci. Hung. 45, 37 (1965)
 [41] ARMSTRONG, R. D., RACE, W. P.: J. Electroanal. Chem. 33, 285 (1971)
 [42] ANGOT, A.: Compléments de Mathématiques. Editions de la Revue d'Optique, Paris 1952
 [43] MANSFELD, F.: The Polarization Resistance Technique for Measuring Corrosion Currents; in FONTANA, M. G. and STAELE, R. W. Ed.: Advances in Corrosion Science and Technology. vol. 6., Plenum 1976

József DÉVAY

Lajos MÉSZÁROS

H-8200 Veszprém, Schönherz Z. u. 10.

MTA. Szervetlen Kémiai

Kutató Laboratórium

Acta Chim. Acad. Sci. Hung. 100, 1079

H 1112 Budapest, Budaörsi-út. 45.