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

DETERMINATION OF THE KINETIC PARAMETERS OF THE CORROSION PROCESS BY INTERMODULATION DISTORTION

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An intermodulation technique based on faradaic distortion has been developed for the study of the kinetics of corrosion processes if both the anodic and the cathodic reaction have Tafel type current-potential characteristics. Formulas have been derived for the harmonic components (having frequencies ω_1, ω_2, $2\omega_1$, $2\omega_2$, $3\omega_1$, $3\omega_2$) and the intermodulation components (having frequencies $\omega_1 \pm \omega_2$, $\omega_1 \pm 2\omega_2$, $\omega_2 \pm 2\omega_1$) of the current flowing through the electrode polarized by the sum of two different sinusoidal alternating voltages superimposed on the polarizing direct voltage as functions of the direct voltage and the amplitudes of the alternating voltages.

The corrosion current and the Tafel slopes can be determined from data of the harmonic and intermodulation components at one potential in the cathodic and anodic Tafel ranges, respectively. A method has been developed for the determination of the kinetic parameters of the corrosion process by the measurement of the harmonic and/or intermodulation current components at the corrosion potential. The equations can be considerably simplified if a small amplitude alternating voltage is employed. The measurement of the intermodulation components is more advantageous than that of the harmonic components as the distortion of the sine-wave generators does not interfere.

In our previous communication [1] a new a.c. method has been presented for the determination of the rate of electrochemical corrosion of metals. The potential dependence of the harmonic components of the current flowing through the electrode under the effect of a sinusoidal voltage has been studied in order to determine the kinetic parameters of the corrosion process. Both the anodic and the cathodic reactions of the corrosion process have been assumed to exhibit Tafel type current-voltage characteristics. Relationships have been established between the kinetic parameters of the corrosion process (corrosion current density, Tafel slopes) and the harmonic components of the a.c. On the basis of these relationships, the kinetic parameters of the corrosion process can be determined by means of the measurement of the harmonic components at a single potential namely either at the corrosion potential or at one potential of the anodic or cathodic Tafel ranges of the polarization curves.

The present communication is related to the study of the components of the current flowing through the non-linear faradaic impedance under the effect of intermodulation distortion. Intermodulation distortion is observed when two or more alternating voltages of different angular frequencies (ω_1, ω_2, ...) are simultaneously connected to a circuit having non-linear current-voltage characteristics. In this case intermodulation components having $n_1\omega_1 \pm n_2\omega_2 \pm \ldots$ (n_1, $n_2 = 1, 2, 3, 4, \ldots$) frequencies also appear in the current in addition to the fundamental harmonic and higher harmonic components, having $\omega_1, \omega_2, \ldots$ and $n_1\omega_1, n_2\omega_2, \ldots$ frequencies, respectively. The intermodulation components, similarly to the harmonic components, depend on the parameters of the non-linear current-voltage characteristics. This phenomenon can be illustrated by the example of current-voltage characteristics of second degree:

$$I = AU + BU^2. \tag{1}$$

If voltage U is

$$U = U_1 \sin \omega_1 t + U_2 \sin \omega_2 t \tag{1a}$$

where U_1 and U_2 are the amplitudes of the alternating voltages and ω_1 and ω_2 are the corresponding angular frequencies, current I is

$$I = A(U_1 \sin \omega_1 t + U_2 \sin \omega_2 t) + B(U_1 \sin \omega_1 t + U_2 \sin \omega_2 t)^2. \tag{2}$$

Taking into account well-known trigonometric identities, Eq. (2) can be written in the form

$$I = \frac{B}{2}(U_1^2 + U_2^2) + A(U_1 \sin \omega_1 t + U_2 \sin \omega_2 t) - \tag{3}$$
$$- \frac{B}{2}(U_1^2 \cos 2\omega_1 t + U_2^2 \cos 2\omega_2 t) + BU_1U_2(\cos(\omega_1 - \omega_2)t - \cos(\omega_1 + \omega_2)t).$$

It is apparent that the current contains the intermodulation components of frequencies $\omega_1 \pm \omega_2$ in addition to the fundamental harmonic components of frequencies ω_1 and ω_2 as well as the d.c. component $\frac{B}{2}(U_1^2 + U_2^2)$ generated by rectification and the second harmonic components. When the current-voltage characteristics is a polynomial composed of higher powers of U or an exponential function of U, the current contains higher harmonic components and also intermodulation components having frequencies $n_1\omega_1 \pm n_2\omega_2$ ($n_1, n_2 = 1, 2, 3, \ldots$).

The parameters (A, B) of the current-voltage characteristics can be determined if the amplitudes of the harmonic and intermodulation components are known , as the former parameters appear in the latter.

The above considerations also apply to the case when the circuit having non-linear current voltage characteristics is supplied with a.c. having two or more different frequencies. In this case rectification and distortion is observed in the voltage appearing across the circuit.

Similar effects are encountered also in such cases when the non-linear circuit is supplied with the sum of alternating voltages or of a.c. having frequencies $\omega_1, \omega_2, \ldots$ superimposed on direct voltage or d.c.

However, the current-voltage characteristics observed in the absence of a.c. are altered by the rectification current. The study of the harmonic and of the intermodulation components as functions of the direct voltage or current respectively, offer valuable information on the parameters of the non-linear current-voltage characteristics.

NEEB [2, 3] has introduced the measurement of intermodulation distortion, namely the measurement of current components having $n_1\omega_1 \pm n_2\omega_2$ frequencies in a.c. polarography and tensammetry.

RANGARAJAN [4] has developed an operator method for the study of the non-stationary behaviour of non-linear systems. This method has been applied for the special cases of sinusoidal alternating voltages of ω frequency and amplitude modulated alternating voltages [5]. PRABHAKARA RAO and MISHRA [6] have studied the potential dependence of the fundamental and second harmonic components as well as that of the intermodulation components of $\omega_1 \pm \omega_2$ frequencies flowing through the electrode polarized by a small amplitude alternating voltage, superimposed on the direct voltage in the vicinity of the corrosion potential. The polarization curve has been assumed to be linear with respect to d.c. in the vicinity of the corrosion potential, while it was substituted by a fourth order Taylor polynomial with respect to a.c. The above method permitted the determination of both the corrosion current and the Tafel slopes.

A more detailed consideration of the intermodulation distortion observed on the faradaic impedance permits the determination of the kinetic characteristics of the corrosion process. The intermodulation technique can be regarded as a new possibility for kinetic investigations since in our previous communication [1] only a method based on harmonic distortion has been presented. In the present communication we examined the potential dependence of the a.c. components flowing through the electrode polarized by the sum of sinusoidal alternating voltages of amplitudes U_1 and U_2 and frequencies ω_1 and ω_2, respectively, superimposed on the direct voltage. The effect of the amplitudes of the alternating voltages will also be considered.

Similarly to the assumption already made in our previous communication [1], both the anodic and cathodic reaction of the corrosion process are assumed to exhibit Tafel type current-voltage characteristics and the reversible potentials of the reactions are assumed to differ to a great extent from the corrosion potential.

Harmonic and Intermodulation Components of the Faradaic Current

The polarization curve of the electrode can be given in the present case by the following equation

$$\mathrm{j} = \mathrm{j}_k\left(e^{\frac{\Delta E}{\beta_a}} - e^{-\frac{\Delta E}{\beta_c}}\right), \qquad (4)$$

where j is the current density, j_k is 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 the Tafel slopes, b_a and b_c, of the anodic and cathodic processes respectively

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

When the electrode is polarized by alternating voltages of amplitudes U_1 and U_2 and angular frequencies ω_1 and ω_2 respectively, superimposed on direct voltage $\overline{\Delta E}$, having the form

$$\Delta E = \overline{\Delta E} + U_1 \sin \omega_1 t + U_2 \sin \omega_2 t \tag{5}$$

the faradaic current density is given by the following expression

$$\mathbf{j}_F = \mathbf{j}_k\left(e^{\frac{\overline{\Delta E} + U_1 \sin \omega_1 t + U_2 \sin \omega_2 t}{\beta_a}} - e^{-\frac{\overline{\Delta E} + U_1 \sin \omega_1 t + U_2 \sin \omega_2 t}{\beta_c}}\right) \tag{6}$$

(the non-faradaic current flowing through the double layer capacity will be considered later).

Separating the exponential expressions of Eq (6) to products the trigonometric terms can be expanded into Fourier series or can be substituted by their third order Fourier polynomials as shown in a previous communication [1]

$$\begin{aligned}
\mathbf{j}_F = {} & \mathbf{j}_k\left(e^{\frac{\overline{\Delta E}}{\beta_a}} \cdot e^{\frac{U_1 \sin \omega_1 t}{\beta_a}} \cdot e^{\frac{U_2 \sin \omega_2 t}{\beta_a}} - e^{-\frac{\overline{\Delta E}}{\beta_c}} \cdot e^{-\frac{U_1 \sin \omega_1 t}{\beta_c}} \cdot e^{-\frac{U_2 \sin \omega_2 t}{\beta_c}}\right) = \\
= {} & \mathbf{j}_k\left\{e^{\frac{\overline{\Delta E}}{\beta_a}}\left[I_0\left(\frac{U_1}{\beta_a}\right) + 2I_1\left(\frac{U_1}{\beta_a}\right)\sin \omega_1 t - 2I_2\left(\frac{U_1}{\beta_a}\right)\cos 2\omega_1 t - 2I_3\left(\frac{U_1}{\beta_a}\right)\sin 3\omega_1 t\right]\cdot\right. \\
& \cdot\left[I_0\left(\frac{U_2}{\beta_a}\right) + 2I_1\left(\frac{U_2}{\beta_a}\right)\sin \omega_2 t - 2I_2\left(\frac{U_2}{\beta_a}\right)\cos 2\omega_2 t - 2I_3\left(\frac{U_2}{\beta_a}\right)\sin 3\omega_2 t\right] - \\
& - e^{-\frac{\overline{\Delta E}}{\beta_c}}\left[I_0\left(\frac{U_1}{\beta_c}\right) - 2I_1\left(\frac{U_1}{\beta_c}\right)\sin \omega_1 t - 2I_2\left(\frac{U_1}{\beta_c}\right)\cos 2\omega_1 t + 2I_3\left(\frac{U_1}{\beta_c}\right)\sin 3\omega_1 t\right]\cdot \\
& \left.\cdot\left[I_0\left(\frac{U_2}{\beta_c}\right) - 2I_1\left(\frac{U_2}{\beta_c}\right)\sin \omega_2 t - 2I_2\left(\frac{U_2}{\beta_c}\right)\cos 2\omega_2 t + 2I_3\left(\frac{U_2}{\beta_c}\right)\sin 3\omega_2 t\right]\right\}.
\end{aligned} \tag{7}$$

By executing the multiplications in the Fourier polynomials and employing the trigonometrical identities

$$\sin\alpha \cdot \sin\beta = \frac{1}{2}[\cos(\alpha - \beta) - \cos(\alpha + \beta)],$$

and

$$\sin\alpha \cdot \cos\beta = \frac{1}{2}[\sin(\alpha + \beta) + \sin(\alpha - \beta)],$$

the faradaic current is obtained in the following form:

$$
\begin{aligned}
\mathrm{j}_F = \mathrm{j}_k & \left\{ I_0\left(\frac{U_1}{\beta_a}\right) I_0\left(\frac{U_2}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} - I_0\left(\frac{U_1}{\beta_c}\right) I_0\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} + \\
+ 2\mathrm{j}_k & \left\{ I_0\left(\frac{U_2}{\beta_a}\right) I_1\left(\frac{U_1}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} + I_0\left(\frac{U_2}{\beta_c}\right) I_1\left(\frac{U_1}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \sin \omega_1 t + \\
+ 2\mathrm{j}_k & \left\{ I_0\left(\frac{U_1}{\beta_a}\right) I_1\left(\frac{U_2}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} + I_0\left(\frac{U_1}{\beta_c}\right) I_1\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \sin \omega_2 t - \\
- 2\mathrm{j}_k & \left\{ I_0\left(\frac{U_2}{\beta_a}\right) I_2\left(\frac{U_1}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} - I_0\left(\frac{U_2}{\beta_c}\right) I_2\left(\frac{U_1}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \cos 2\omega_1 t - \\
- 2\mathrm{j}_k & \left\{ I_0\left(\frac{U_1}{\beta_a}\right) I_2\left(\frac{U_2}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} - I_0\left(\frac{U_1}{\beta_c}\right) I_0\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \cos 2\omega_2 t + \\
+ 2\mathrm{j}_k & \left\{ I_0\left(\frac{U_2}{\beta_a}\right) I_3\left(\frac{U_1}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} + I_0\left(\frac{U_2}{\beta_c}\right) I_3\left(\frac{U_1}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \sin 3\omega_1 t - \\
- 2\mathrm{j}_k & \left\{ I_0\left(\frac{U_1}{\beta_a}\right) I_3\left(\frac{U_2}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} + I_0\left(\frac{U_1}{\beta_c}\right) I_3\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \sin 3\omega_2 t + \\
- 2\mathrm{j}_k & \left\{ I_1\left(\frac{U_1}{\beta_a}\right) I_1\left(\frac{U_2}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} - I_1\left(\frac{U_1}{\beta_c}\right) I_1\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \cos(\omega_1 - \omega_2) t - \\
- 2\mathrm{j}_k & \left\{ I_1\left(\frac{U_1}{\beta_a}\right) I_1\left(\frac{U_2}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} - I_1\left(\frac{U_1}{\beta_c}\right) I_1\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \cos(\omega_1 + \omega_2) t - \\
- 2\mathrm{j}_k & \left\{ I_1\left(\frac{U_1}{\beta_a}\right) I_2\left(\frac{U_2}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} + I_1\left(\frac{U_1}{\beta_c}\right) I_2\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \sin(\omega_1 + 2\omega_2) t - \\
- 2\mathrm{j}_k & \left\{ I_1\left(\frac{U_1}{\beta_a}\right) I_2\left(\frac{U_2}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} + I_1\left(\frac{U_1}{\beta_c}\right) I_2\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right) \sin(\omega_1 - 2\omega_2) t - \\
- 2\mathrm{j}_k & \left\{ I_1\left(\frac{U_2}{\beta_a}\right) I_2\left(\frac{U_1}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} + I_1\left(\frac{U_2}{\beta_c}\right) I_2\left(\frac{U_1}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \sin(\omega_2 + 2\omega_1) t - \\
- 2\mathrm{j}_k & \left\{ I_1\left(\frac{U_2}{\beta_a}\right) I_2\left(\frac{U_1}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} + I_1\left(\frac{U_2}{\beta_c}\right) I_2\left(\frac{U_1}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \sin(\omega_2 - 2\omega_1) t . \qquad (8)
\end{aligned}
$$

The first term of Eq. (8) yields d.c. component $\bar{\mathrm{j}}$ of the faradaic current

$$
\bar{\mathrm{j}} = \mathrm{j}_k \left\{ I_0\left(\frac{U_1}{\beta_a}\right) I_0\left(\frac{U_2}{\beta_a}\right) e^{\frac{\overline{\Delta E}}{\beta_a}} - I_0\left(\frac{U_1}{\beta_c}\right) I_0\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\}, \qquad (9)
$$

while the faradaic rectification term, $\overline{\Delta \mathrm{j}}$, is

$$\overline{\Delta \mathrm{j}} = \mathrm{j}_k \left\{ \left[I_0\left(\frac{U_1}{\beta_a}\right) I_0\left(\frac{U_2}{\beta_a}\right) - 1 \right] e^{\frac{\Delta E}{\beta_a}} - \left[I_0\left(\frac{U_1}{\beta_c}\right) I_0\left(\frac{U_2}{\beta_c}\right) - 1 \right] e^{-\frac{\Delta E}{\beta_c}} \right\}. \quad (10)$$

The next six terms of Eq. (8) correspond to the two fundamental frequencies (ω_1 and ω_2) and to the higher harmonic ones ($2\omega_1, 2\omega_2, 3\omega_1, 3\omega_2$). The amplitudes of the harmonic components are denoted by $\hat{\mathrm{j}}$:

$$\hat{\mathrm{j}}(\omega_1) = 2\mathrm{j}_k \left\{ I_0\left(\frac{U_2}{\beta_a}\right) I_1\left(\frac{U_1}{\beta_a}\right) e^{\frac{\Delta E}{\beta_a}} + I_0\left(\frac{U_2}{\beta_c}\right) I_1\left(\frac{U_1}{\beta_c}\right) e^{-\frac{\Delta E}{\beta_c}} \right\}, \quad (11)$$

$$\hat{\mathrm{j}}(\omega_2) = 2\mathrm{j}_k \left\{ I_0\left(\frac{U_1}{\beta_a}\right) I_1\left(\frac{U_2}{\beta_a}\right) e^{\frac{\Delta E}{\beta_a}} + I_0\left(\frac{U_1}{\beta_c}\right) I_1\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\Delta E}{\beta_c}} \right\}, \quad (12)$$

$$\hat{\mathrm{j}}(2\omega_1) = 2\mathrm{j}_k \left| I_0\left(\frac{U_2}{\beta_a}\right) I_2\left(\frac{U_1}{\beta_a}\right) e^{\frac{\Delta E}{\beta_a}} - I_0\left(\frac{U_2}{\beta_c}\right) I_2\left(\frac{U_1}{\beta_c}\right) e^{-\frac{\Delta E}{\beta_c}} \right|, \quad (13)$$

$$\hat{\mathrm{j}}(2\omega_2) = 2\mathrm{j}_k \left| I_0\left(\frac{U_1}{\beta_a}\right) I_2\left(\frac{U_2}{\beta_a}\right) e^{\frac{\Delta E}{\beta_a}} - I_0\left(\frac{U_1}{\beta_c}\right) I_2\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\Delta E}{\beta_c}} \right|, \quad (14)$$

$$\hat{\mathrm{j}}(3\omega_1) = 2\mathrm{j}_k \left\{ I_0\left(\frac{U_2}{\beta_a}\right) I_3\left(\frac{U_1}{\beta_a}\right) e^{\frac{\Delta E}{\beta_a}} + I_0\left(\frac{U_2}{\beta_c}\right) I_3\left(\frac{U_1}{\beta_c}\right) e^{-\frac{\Delta E}{\beta_c}} \right\}, \quad (15)$$

$$\hat{\mathrm{j}}(3\omega_2) = 2\mathrm{j}_k \left\{ I_0\left(\frac{U_1}{\beta_a}\right) I_3\left(\frac{U_2}{\beta_a}\right) e^{\frac{\Delta E}{\beta_a}} + I_0\left(\frac{U_1}{\beta_c}\right) I_3\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\Delta E}{\beta_c}} \right\}. \quad (16)$$

The components having fequencies $\omega_1 \pm \omega_2$, $\omega_1 \pm 2\omega_2$ and $\omega_2 \pm 2\omega_1$ respectively, correspond to six other terms of Eq. (8) however, the amplitudes of these components are identical in pairs and can be written in a concise form

$$\hat{\mathrm{j}}(\omega_1 \pm \omega_2) = 2\mathrm{j}_k \left| I_1\left(\frac{U_1}{\beta_a}\right) I_1\left(\frac{U_2}{\beta_a}\right) e^{\frac{\Delta E}{\beta_a}} - I_1\left(\frac{U_1}{\beta_c}\right) I_1\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\Delta E}{\beta_c}} \right|, \quad (17)$$

$$\mathrm{j}(\omega_1 \pm 2\omega_2) = 2\mathrm{j}_k \left\{ I_1\left(\frac{U_1}{\beta_a}\right) I_2\left(\frac{U_2}{\beta_a}\right) e^{\frac{\Delta E}{\beta_a}} + I_1\left(\frac{U_1}{\beta_c}\right) I_2\left(\frac{U_2}{\beta_c}\right) e^{-\frac{\Delta E}{\beta_c}} \right\}, \quad (18)$$

$$\mathrm{j}(\omega_2 \pm 2\omega_1) = 2\mathrm{j}_k \left\{ I_1\left(\frac{U_2}{\beta_a}\right) I_2\left(\frac{U_1}{\beta_a}\right) e^{\frac{\Delta E}{\beta_a}} + I_1\left(\frac{U_2}{\beta_c}\right) I_2\left(\frac{U_1}{\beta_c}\right) e^{-\frac{\Delta E}{\beta_c}} \right\}. \quad (19)$$

The signs indicated in Eq. (8) are disregarded in Eqs (13)—(17), as is the phase reversal of the second harmonic components and that of the intermodulation components of frequencies $\omega_1 \pm \omega_2$ since the amplitudes are defined as positive quantities.

Simpler relationships are obtained if we confine our investigations to small amplitudes U_1 and U_2, permitting to substitute the Bessel functions in the above equations by the first term or the first two ones of the respective Taylor polynomials.

Using the approximate expressions derived in our previous communication [1] Eqs (9)–(19) can be rewritten in simpler forms:

$$\bar{j} = j_k \left\{ \left[1 + \frac{U_1^2 + U_2^2}{4\beta_a^2} \right] e^{\frac{\overline{\Delta E}}{\beta_a}} - \left[1 + \frac{U_1^2 + U_2^2}{4\beta_c^2} \right] e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\}, \tag{20}$$

$$\Delta\bar{j} = j_k \left\{ \frac{1}{\beta_a^2} e^{\frac{\overline{\Delta E}}{\beta_a}} - \frac{1}{\beta_c^2} e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \frac{U_1^2 + U_2^2}{4}, \tag{21}$$

$$\hat{j}(\omega_1) = j_k \left\{ \left[1 + \left(\frac{U_2}{2\beta_a} \right)^2 \right] \frac{1}{\beta_a} e^{\frac{\overline{\Delta E}}{\beta_a}} + \left[1 + \left(\frac{U_2}{2\beta_c} \right)^2 \right] \frac{1}{\beta_c} e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} U_1, \tag{22}$$

$$\hat{j}(\omega_2) = j_k \left\{ \left[1 + \left(\frac{U_1}{2\beta_a} \right)^2 \right] \frac{1}{\beta_a} e^{\frac{\overline{\Delta E}}{\beta_a}} + \left[1 + \left(\frac{U_1}{\beta_c} \right)^2 \right] \frac{1}{\beta_c} e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} U_2, \tag{23}$$

$$\hat{j}(2\omega_1) = j_k \left\| \left[1 + \left(\frac{U_2}{2\beta_a} \right)^2 \right] \frac{1}{\beta_a^2} e^{\frac{\overline{\Delta E}}{\beta_a}} - \left[1 + \left(\frac{U_2}{\beta_c} \right)^2 \right] \frac{1}{\beta_c^2} e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\| \frac{U_1^2}{4}, \tag{24}$$

$$\hat{j}(2\omega_2) = j_k \left\| \left[1 + \left(\frac{U_1}{2\beta_a} \right)^2 \right] \frac{1}{\beta_a^2} e^{\frac{\overline{\Delta E}}{\beta_a}} - \left[1 + \left(\frac{U_1}{2\beta_c} \right)^2 \right] \frac{1}{\beta_c^2} e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\| \frac{U_2^2}{4}, \tag{25}$$

$$\hat{j}(3\omega_1) = j_k \left\{ \left[1 + \left(\frac{U_2}{2\beta_a} \right)^2 \right] \frac{1}{\beta_a^3} e^{\frac{\overline{\Delta E}}{\beta_a}} + \left[1 + \left(\frac{U_2}{2\beta_c} \right)^2 \right] \frac{1}{\beta_c^3} e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \frac{U_1^3}{24}, \tag{26}$$

$$\hat{j}(3\omega_1) = j_k \left\{ \left[1 + \left(\frac{U_1}{2\beta_a} \right)^2 \right] \frac{1}{\beta_a^3} e^{\frac{\overline{\Delta E}}{\beta_a}} + \left[1 + \left(\frac{U_1}{2\beta_c} \right)^2 \right] \frac{1}{\beta_c^3} e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \frac{U_2^3}{24}, \tag{27}$$

$$\hat{j}(\omega_1 \pm \omega_2) = j_k \left| \frac{1}{\beta_a^2} e^{\frac{\overline{\Delta E}}{\beta_a}} - \frac{1}{\beta_c^2} e^{-\frac{\overline{\Delta E}}{\beta_c}} \right| \frac{U_1 U_2}{2}, \tag{28}$$

$$\hat{j}(\omega_1 \pm 2\omega_2) = j_k \left\{ \frac{1}{\beta_a^3} e^{\frac{\overline{\Delta E}}{\beta_a}} + \frac{1}{\beta_c^3} e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \frac{U_1 U_2^2}{8}, \tag{29}$$

$$\hat{j}(\omega_2 \pm 2\omega_1) = j_k \left\{ \frac{1}{\beta_a^3} e^{\frac{\overline{\Delta E}}{\beta_a}} + \frac{1}{\beta_c^3} e^{-\frac{\overline{\Delta E}}{\beta_c}} \right\} \frac{U_1^2 U_2}{8}. \tag{30}$$

Thus we obtained the d.c. components, the amplitudes of the harmonic and intermodulation components of the faradaic current flowing through the electrode polarized by the sum of the alternating voltages having amplitudes U_1 and U_2 and angular frequencies ω_1 and ω_2, respectively, superimposed on direct voltage $\overline{\Delta E}$. The equations represent the components of the current as functions of the direct voltage $\overline{\Delta E}$ and amplitudes U_1 and U_2 of the alternating voltages. It is noteworthy that the above equations relate to the faradaic current exempt from a capacitive component and they can be applied only in such cases when the ohmic drop on the resistance of the solution is compensated by an adequate potentiostat, *i.e.* $\overline{\Delta E}$, U_1 and U_2 are the voltages actually branched to the electrode impedance proper as mentioned in a previous communication [7]. The capacity of the double layer can be considered as a linear circuit element, thus it causes neither harmonic nor intermodulation distortion. Capacitive current is only observed in the fundamental harmonic components. In our previous communication [7] the method of the elimination of the capacitive current has also been reported.

Determination of the Corrosion Current and the Tafel Slopes

The kinetic parameters of the corrosion process (j_k, β_a, β_a) can be determined by the intermodulation method in much the same manner as in the case of harmonic distortion, reported in a previous communication [1]. However, the intermodulation effect offers also a new possibility for the determination of the kinetic parameters since both the harmonic and the intermodulation current components depend on the amplitudes of both alternating voltages and thus the independent variation of the latter provides further information.

Let us consider first the application of the methods reported in a previous communication [1] to intermodulation distortion.

The following equations are related to the harmonic and intermodulation components of the faradaic current observed on the electrode polarized in the range of validity of Tafel's equation for the anodic reaction in the case of an anodic polarization sufficiently large as to have $\frac{\overline{\Delta E}_a}{\beta_a} > 1$ according to Eqs (11)—(19).

$$\hat{\mathrm{j}}_a(\omega_1) = 2\mathrm{j}_k I_0\left(\frac{U_2}{\beta_a}\right) I_1\left(\frac{U_1}{\beta_a}\right) e^{\frac{\overline{\Delta E}_a}{\beta_a}}, \qquad (31)$$

$$\hat{\mathrm{j}}_a(\omega_2) = 2\mathrm{j}_k I_0\left(\frac{U_1}{\beta_a}\right) I_1\left(\frac{U_2}{\beta_a}\right) e^{\frac{\overline{\Delta E}_a}{\beta_a}}, \qquad (32)$$

$$\hat{\mathbf{j}}_a(2\omega_1) = 2\mathbf{j}_k I_0\left(\frac{U_2}{\beta_a}\right) I_2\left(\frac{U_1}{\beta_a}\right) e^{\frac{\Delta E}{\beta_a}}, \tag{33}$$

$$\hat{\mathbf{j}}_a(2\omega_2) = 2\mathbf{j}_k I_0\left(\frac{U_1}{\beta_a}\right) I_2\left(\frac{U_2}{\beta_a}\right) e^{\frac{\Delta E_a}{\beta_a}}, \tag{34}$$

$$\hat{\mathbf{j}}_a(3\omega_1) = 2\mathbf{j}_k I_0\left(\frac{U_2}{\beta_a}\right) I_3\left(\frac{U_1}{\beta_a}\right) e^{\frac{\Delta E_a}{\beta_a}}, \tag{35}$$

$$\hat{\mathbf{j}}_a(3\omega_2) = 2\mathbf{j}_k I_0\left(\frac{U_1}{\beta_a}\right) I_3\left(\frac{U_2}{\beta_a}\right) e^{\frac{\Delta E_a}{\beta_a}}, \tag{36}$$

$$\hat{\mathbf{j}}_a(\omega_1 \pm \omega_2) = 2\mathbf{j}_k I_1\left(\frac{U_1}{\beta_a}\right) I_1\left(\frac{U_2}{\beta_a}\right) e^{\frac{\Delta E_a}{\beta_a}}, \tag{37}$$

$$\hat{\mathbf{j}}_a(\omega_1 \pm 2\omega_2) = 2\mathbf{j}_k I_1\left(\frac{U_1}{\beta_a}\right) I_2\left(\frac{U_2}{\beta_a}\right) e^{\frac{\Delta E_a}{\beta_a}}, \tag{38}$$

$$\hat{\mathbf{j}}_a(\omega_2 \pm 2\omega_1) = 2\mathbf{j}_k I_1\left(\frac{U_2}{\beta_a}\right) I_2\left(\frac{U_1}{\beta_a}\right) e^{\frac{\Delta E_a}{\beta_a}}. \tag{39}$$

Parameter β_a can be determined by successive approximation from one of the following quotients

$$\frac{\hat{\mathbf{j}}_a(\omega_i)}{\hat{\mathbf{j}}_a(2\omega_i)} = \frac{I_1\left(\frac{U_i}{\beta_a}\right)}{I_2\left(\frac{U_i}{\beta_a}\right)}, \qquad (i = 1, 2) \tag{40}$$

$$\frac{\hat{\mathbf{j}}_a(2\omega_i)}{\hat{\mathbf{j}}_a(3\omega_i)} = \frac{I_2\left(\frac{U_i}{\beta_a}\right)}{I_3\left(\frac{U_i}{\beta_a}\right)}, \qquad (i = 1, 2) \tag{41}$$

$$\frac{\hat{\mathbf{j}}_a(\omega_1 \pm \omega_2)}{\hat{\mathbf{j}}_a(\omega_1 \pm 2\omega_2)} = \frac{I_1\left(\frac{U_2}{\beta_a}\right)}{I_2\left(\frac{U_2}{\beta_a}\right)}, \tag{42}$$

$$\frac{\hat{\mathbf{j}}_a(\omega_1 \pm \omega_2)}{\hat{\mathbf{j}}_a(\omega_2 \pm 2\omega_1)} = \frac{I_1\left(\frac{U_1}{\beta_a}\right)}{I_2\left(\frac{U_1}{\beta_a}\right)}, \tag{43}$$

However, successive approximation can be avoided by applying the recursion formula

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

valid for modified first order Bessel Functions for the case of $n = 2$ and $x = \frac{U_i}{\beta_a}$ $(i = 1, 2)$ (*Cf.* [1]). Thus β_a can be expressed by the amplitudes of the harmonic and intermodulation components

$$\beta_a = \frac{U_i}{4}\left(\frac{I_1\left(\frac{U_i}{\beta_a}\right)}{I_2\left(\frac{U_i}{\beta_a}\right)} - \frac{I_3\left(\frac{U_i}{\beta_a}\right)}{I_2\left(\frac{U_i}{\beta_a}\right)}\right), \qquad (i = 1, 2), \tag{45}$$

or

$$\beta_a = \frac{U_1}{4}\left(\frac{\hat{\mathrm{j}}_a(\omega_1)}{\hat{\mathrm{j}}_a(2\omega_1)} - \frac{\hat{\mathrm{j}}_a(3\omega_1)}{\hat{\mathrm{j}}_a(2\omega_1)}\right) = \frac{U_2}{4}\left(\frac{\hat{\mathrm{j}}_a(\omega_2)}{\hat{\mathrm{j}}_a(2\omega_2)} - \frac{\hat{\mathrm{j}}_a(3\omega_2)}{\hat{\mathrm{j}}_a(2\omega_2)}\right) =$$

$$= \frac{U_1}{4}\left(\frac{\hat{\mathrm{j}}_a(\omega_1 \pm \omega_2)}{\hat{\mathrm{j}}_a(\omega_2 \pm 2\omega_1)} - \frac{\hat{\mathrm{j}}_a(3\omega_1)}{\hat{\mathrm{j}}_a(2\omega_1)}\right) = \frac{U_2}{4}\left(\frac{\hat{\mathrm{j}}_a(\omega_1 \pm \omega_2)}{\hat{\mathrm{j}}_a(\omega_1 \pm 2\omega_2)} - \frac{\hat{\mathrm{j}}_a(3\omega_2)}{\hat{\mathrm{j}}_a(2\omega_2)}\right). \tag{46}$$

It is noteworthy that the last two terms of identities (46) only contain intermodulation and higher harmonic components. The latter can be determined by direct measurement as they are exempt from capacitive current contrary to the fundamental harmonic components having frequencies ω_1 and ω_2, respectively, which can only be substituted in expression (46) after the elimination of the capacitive current by extrapolation [7].

If amplitudes U_1 and U_2 are sufficiently small as to permit to neglect I_3 in comparison to I_1, $\left(I_3\left(\frac{U_i}{\beta_a}\right) \ll I_1\left(\frac{U_i}{\beta_a}\right);\ i = 1, 2\right)$ Eq. (46) is obtained in a simplified form

$$\beta_a \simeq \frac{U_1}{4}\,\frac{\hat{\mathrm{j}}_a(\omega_1)}{\hat{\mathrm{j}}_a(2\omega_1)} = \frac{U_2}{4}\,\frac{\hat{\mathrm{j}}_a(\omega_2)}{\hat{\mathrm{j}}_a(2\omega_2)} = \frac{U_1}{4}\,\frac{\hat{\mathrm{j}}_a(\omega_1 \pm \omega_2)}{\hat{\mathrm{j}}_a(\omega_2 \pm 2\omega_1)} = \frac{U_2}{4}\,\frac{\hat{\mathrm{j}}_a(\omega_1 \pm \omega_2)}{\hat{\mathrm{j}}_a(\omega_1 \pm 2\omega_2)}. \tag{47}$$

Corrosion current density j_k can be determined by any one of Eqs (31)—(39) if β_a is known.

Parameter β_c and corrosion current density j_k can similarly be determined by applying the above considerations to the cathodic reaction in the case when $-\frac{\overline{\Delta E_c}}{\beta_c} > 1$, *i.e.* the measurement is performed at a potential $\overline{\Delta E_c}$ in the cathodic Tafel range. The equations relating to cathodic polarization are identical to Eqs (31)—(34) and (45)—(47) except for the subscripts.

The equations can considerably be simplified if quotients (40)—(43) are calculated by employing relations (22)—(30) for the case of anodic $\left(\frac{\overline{\Delta E_a}}{\beta_a} > 1\right)$ and cathodic $\left(-\frac{\overline{\Delta E_c}}{\beta_c} > 1\right)$ polarization, respectively, since successive approximation on the basis of Eqs (40)—(43) can be avoided and β_a or β_c can be expressed directly by the amplitudes of the harmonic and intermodulation components.

$$\beta_a = \frac{U_i}{4}\frac{\hat{\mathbf{j}}_a(\omega_i)}{\hat{\mathbf{j}}_a(2\omega_i)}, \qquad (i = 1, 2) \tag{48}$$

$$\beta_a = \frac{U_i}{6}\frac{\hat{\mathbf{j}}_a(2\omega_i)}{\hat{\mathbf{j}}_a(3\omega_i)}, \tag{49}$$

$$\beta_a = \frac{U_2}{4}\frac{\hat{\mathbf{j}}_a(\omega_1 \pm \omega_2)}{\hat{\mathbf{j}}_a(\omega_1 \pm 2\omega_2)} = \frac{U_1}{4}\frac{\hat{\mathbf{j}}_a(\omega_1 \pm \omega_2)}{\hat{\mathbf{j}}_a(\omega_2 \pm 2\omega_1)}. \tag{50}$$

Similar relationships are obtained for the parameters of the cathodic reaction when the harmonic and intermodulation components are measured at potential $\overline{\Delta E_c}$ in the cathodic Tafel range.

$$\beta_c = \frac{U_i}{4}\frac{\hat{\mathbf{j}}_c(\omega_i)}{\hat{\mathbf{j}}_c(2\omega_i)}, \qquad (i = 1, 2) \tag{51}$$

$$\beta_c = \frac{U_i}{6}\frac{\hat{\mathbf{j}}_c(2\omega_i)}{\hat{\mathbf{j}}_c(3\omega_i)} \qquad (i = 1, 2) \tag{52}$$

$$\beta_c = \frac{U_2}{4}\frac{\hat{\mathbf{j}}_c(\omega_1 \pm \omega_2)}{\hat{\mathbf{j}}_c(\omega_1 \pm 2\omega_2)} = \frac{U_1}{4}\frac{\hat{\mathbf{j}}_c(\omega_1 \pm \omega_2)}{\hat{\mathbf{j}}_c(\omega_2 \pm 2\omega_1)}. \tag{53}$$

Corrosion current density $\mathbf{j}_k$ can be expressed from one of Eqs (22)—(30) applied for the case when $\frac{\overline{\Delta E_a}}{\beta_a} > 1$, or $-\frac{\overline{\Delta E_c}}{\beta_c} > 1$, if β_a or β_c, respectively, have been determined from the above equations.

$$\mathbf{j}_k = \frac{\hat{\mathbf{j}}_a(\omega_1)\,\beta_a}{\left[1 + \left(\frac{U_2}{2\beta_a}\right)^2\right] U_1} e^{-\frac{\overline{\Delta E_a}}{\beta_a}} = \frac{\hat{\mathbf{j}}_a(\omega_2)\,\beta_a}{\left[1 + \left(\frac{U_1}{2\beta_a}\right)^2\right] U_2} e^{-\frac{\overline{\Delta E_a}}{\beta_a}} =$$

$$= \frac{4\hat{\mathbf{j}}_a(2\omega_1)\,\beta_a^2}{\left[1 + \left(\frac{U_2}{2\beta_a}\right)^2\right] U_1^2} e^{-\frac{\overline{\Delta E_a}}{\beta_a}} = \frac{4\hat{\mathbf{j}}_a(2\omega_2)\,\beta_a^2}{\left[1 + \left(\frac{U_1}{2\beta_a}\right)^2\right] U_2^2} e^{-\frac{\overline{\Delta E_a}}{\beta_a}} =$$

$$= \frac{24\hat{j}_a(3\omega_1)\,\beta_a^3}{\left[1+\left(\frac{U_2}{2\beta_a}\right)^2\right]U_1^3}\, e^{-\frac{\overline{\Delta E_a}}{\beta_a}} = \frac{24\hat{j}_a(3\omega_2)\,\beta_a^3}{\left[1+\left(\frac{U_1}{2\beta_a}\right)^2\right]U_2^3}\, e^{-\frac{\overline{\Delta E_a}}{\beta_a}} =$$

$$= \frac{2\hat{j}_a(\omega_1 \pm \omega_2)\,\beta_a^2}{U_1 U_2}\, e^{-\frac{\overline{\Delta E_a}}{\beta_a}} = \frac{8\hat{j}_a(\omega_1 \pm 2\omega_2)\,\beta_a^3}{U_1 U_2^2}\, e^{-\frac{\overline{\Delta E_a}}{\beta_a}} =$$

$$= \frac{8\hat{j}_a(\omega_2 \pm 2\omega_1)\,\beta_a^3}{U_1^2 U_2}\, e^{-\frac{\overline{\Delta E_a}}{\beta_a}} . \tag{54}$$

In the case of cathodic polarization $\left(-\frac{\overline{\Delta E_c}}{\beta_c} > 1\right)$ subscript c is used in Eq. (54) and $-\overline{\Delta E_c}$ is inserted instead of $\overline{\Delta E_a}$.

Thus it can be concluded that parameters β_a and β_c as well as corrosion current density j_k can also be determined by the intermodulation technique from data obtained at potentials $\overline{\Delta E_a}$ and $\overline{\Delta E_c}$ in the validity range of Tafel's equation for the anodic and cathodic reaction, respectively.

The extrapolation to $\omega = 0$ for the elimination of the capacitive current (observed in the fundamental harmonic current components) can be avoided if the higher harmonic and/or the intermodulation components are only employed for the evaluation of the kinetic parameters.

Corrosion current density j_k and parameters β_a and β_c can also be calculated from data at corrosion potential $\overline{\Delta E} = 0$ by introducing $\overline{\Delta E} = 0$ in Eqs (10)—(19).

$$\overline{\Delta j_0} = j_k \left\{ I_0\left(\frac{U_1}{\beta_a}\right) I_0\left(\frac{U_2}{\beta_a}\right) - I_0\left(\frac{U_1}{\beta_c}\right) I_0\left(\frac{U_2}{\beta_c}\right) \right\}, \tag{55}$$

$$\hat{j}_0(\omega_1) = 2j_k \left\{ I_0\left(\frac{U_2}{\beta_a}\right) I_1\left(\frac{U_1}{\beta_a}\right) + I_0\left(\frac{U_2}{\beta_c}\right) I_1\left(\frac{U_1}{\beta_c}\right) \right\}, \tag{56}$$

$$\hat{j}_0(\omega_2) = 2j_k \left\{ I_0\left(\frac{U_1}{\beta_a}\right) I_1\left(\frac{U_2}{\beta_a}\right) + I_0\left(\frac{U_1}{\beta_c}\right) I_1\left(\frac{U_2}{\beta_c}\right) \right\}, \tag{57}$$

$$\hat{j}_0(2\omega_1) = 2j_k \left| I_0\left(\frac{U_2}{\beta_a}\right) I_2\left(\frac{U_1}{\beta_a}\right) - I_0\left(\frac{U_2}{\beta_c}\right) I_2\left(\frac{U_1}{\beta_c}\right) \right|, \tag{58}$$

$$\hat{j}_0(2\omega_2) = 2j_k \left| I_0\left(\frac{U_1}{\beta_a}\right) I_2\left(\frac{U_2}{\beta_a}\right) - I_0\left(\frac{U_1}{\beta_c}\right) I_2\left(\frac{U_2}{\beta_c}\right) \right|, \tag{59}$$

$$\hat{j}_0(3\omega_1) = 2j_k \left\{ I_0\left(\frac{U_2}{\beta_a}\right) I_3\left(\frac{U_1}{\beta_a}\right) + I_0\left(\frac{U_2}{\beta_c}\right) I_3\left(\frac{U_1}{\beta_c}\right) \right\}, \tag{60}$$

$$\hat{j}_0(3\omega_2) = 2j_k \left\{ I_0\left(\frac{U_1}{\beta_a}\right) I_3\left(\frac{U_2}{\beta_a}\right) + I_0\left(\frac{U_1}{\beta_c}\right) I_3\left(\frac{U_2}{\beta_c}\right) \right\}, \tag{61}$$

$$\hat{\mathbf{j}}_0(\omega_1 \pm \omega_2) = 2\mathbf{j}_k \left| I_1\left(\frac{U_1}{\beta_a}\right) I_1\left(\frac{U_2}{\beta_a}\right) - I_1\left(\frac{U_1}{\beta_c}\right) I_1\left(\frac{U_2}{\beta_c}\right)\right|, \tag{62}$$

$$\hat{\mathbf{j}}_0(\omega_1 \pm 2\omega_2) = 2\mathbf{j}_k \left\{ I_1\left(\frac{U_1}{\beta_a}\right) I_2\left(\frac{U_2}{\beta_a}\right) + I_1\left(\frac{U_1}{\beta_c}\right) I_2\left(\frac{U_2}{\beta_c}\right)\right\}, \tag{63}$$

$$\hat{\mathbf{j}}_0(\omega_2 \pm 2\omega_1) = 2\mathbf{j}_k \left\{ I_1\left(\frac{U_2}{\beta_a}\right) I_2\left(\frac{U_1}{\beta_a}\right) + I_1\left(\frac{U_2}{\beta_c}\right) I_2\left(\frac{U_1}{\beta_c}\right)\right\}. \tag{64}$$

The corrosion current density can readily be expressed from any one of the above equations if β_a and β_c are known. It is noteworthy that Eqs (55), (58), (59) and (62) can only be used if $\overline{\Delta \mathbf{j}_0}$, $\hat{\mathbf{j}}_0(2\omega_1)$, $\hat{\mathbf{j}}_0(2\omega_2)$ and $\hat{\mathbf{j}}_0(\omega_1 \pm \omega_2)$, respectively, differ from zero.

However β_a, β_c and $\mathbf{j}_k$ can also be calculated by using three linearly independent equations from among Eqs (45)—(64) and writing a suitable computer program.

β_a and β_c and $\mathbf{j}_k$ can also be expressed in an explicit form if small amplitude alternating voltages are employed. In this case Eqs (21)—(30) are utilized by introducing $\overline{\Delta E} = 0$:

$$\overline{\Delta \mathbf{j}_0} = \mathbf{j}_k \left\{\frac{1}{\beta_a^2} - \frac{1}{\beta_c^2}\right\} \frac{U_1^2 + U_2^2}{4}, \tag{65}$$

$$\hat{\mathbf{j}}_0(\omega_1) = \mathbf{j}_k \left\{\left[1 + \left(\frac{U_2}{2\beta_a}\right)^2\right]\frac{1}{\beta_a} + \left[1 + \left(\frac{U_2}{2\beta_c}\right)^2\right]\frac{1}{\beta_c}\right\} U_1, \tag{66}$$

$$\hat{\mathbf{j}}_0(\omega_2) = \mathbf{j}_k \left\{\left[1 + \left(\frac{U_1}{2\beta_a}\right)^2\right]\frac{1}{\beta_a} + \left[1 + \left(\frac{U_1}{2\beta_c}\right)^2\right]\frac{1}{\beta_c}\right\} U_2, \tag{67}$$

$$\hat{\mathbf{j}}_0(2\omega_1) = \mathbf{j}_k \left|\left[1 + \left(\frac{U_2}{2\beta_a}\right)^2\right]\frac{1}{\beta_a^2} - \left[1 + \left(\frac{U_2}{2\beta_c}\right)^2\right]\frac{1}{\beta_c^2}\right| \frac{U_1^2}{4}, \tag{68}$$

$$\hat{\mathbf{j}}_0(2\omega_2) = \mathbf{j}_k \left|\left[1 + \left(\frac{U_1}{2\beta_a}\right)^2\right]\frac{1}{\beta_a^2} - \left[1 + \left(\frac{U_1}{2\beta_c}\right)^2\right]\frac{1}{\beta_c^2}\right| \frac{U_2^2}{4}, \tag{69}$$

$$\hat{\mathbf{j}}_0(3\omega_1) = \mathbf{j}_k \left\{\left[1 + \left(\frac{U_2}{2\beta_a}\right)^2\right]\frac{1}{\beta_a^3} + \left[1 + \left(\frac{U_2}{2\beta_c}\right)\right]\frac{1}{\beta_c^3}\right\} \frac{U_1^3}{24}, \tag{70}$$

$$\hat{\mathbf{j}}_0(3\omega_2) = \mathbf{j}_k \left\{\left[1 + \left(\frac{U_1}{2\beta_a}\right)^2\right]\frac{1}{\beta_a^3} + \left[1 + \left(\frac{U_1}{2\beta_c}\right)^2\right]\frac{1}{\beta_c^3}\right\} \frac{U_2^3}{24}, \tag{71}$$

$$\hat{\mathbf{j}}_0(\omega_1 \pm \omega_2) = \mathbf{j}_k \left|\frac{1}{\beta_a^2} - \frac{1}{\beta_c^2}\right| \frac{U_1 U_2}{2}, \tag{72}$$

$$\hat{\mathbf{j}}_0(\omega_1 \pm 2\omega_2) = \mathbf{j}_k \left\{\frac{1}{\beta_a^3} + \frac{1}{\beta_c^3}\right\} \frac{U_1 U_2^2}{8}, \tag{73}$$

$$\hat{\mathbf{j}}_0(\omega_2 \pm 2\omega_1) = \mathbf{j}_k \left\{\frac{1}{\beta_a^3} + \frac{1}{\beta_c^3}\right\} \frac{U_1^2 U_2}{8}. \tag{74}$$

The expressions related to the amplitudes of the harmonic components assume the simple forms given by Eqs (50)—(52) of our previous communication [1] if the bracketed expressions of Eqs (66)—(71) are approximately equal to unity. The latter condition is fulfilled if the amplitudes of the alternating voltages are properly selected. In this case corrosion current density j_k and parameters β_a and β_c can be calculated using Eqs (53), (58), (59), (60) and (61) given in our previous communication [1]. Equations (72)—(74) relating to the intermodulation components can readily be employed in the expressions used for the calculation of β_a and β_c and the corrosion current density, instead of Eqs (68)—(71) relating to the higher harmonic components since in the case if $1+\left(\frac{U}{2\beta}\right)^2 \approx 1$

$$\hat{\mathrm{j}}_0(2\omega_1)=\frac{U_1}{2U_2}\,\hat{\mathrm{j}}_0(\omega_1\pm\omega_2)\,, \tag{75}$$

$$\hat{\mathrm{j}}_0(2\omega_2)=\frac{U_2}{2U_1}\,\hat{\mathrm{j}}_0(\omega_1\pm\omega_2)\,, \tag{76}$$

$$\hat{\mathrm{j}}_0(3\omega_1)=\frac{U_1^2}{3U_2^2}\,\hat{\mathrm{j}}_0(\omega_1\pm2\omega_2)\,, \tag{77}$$

$$\hat{\mathrm{j}}_0(3\omega_2)=\frac{U_2^2}{3U_1^2}\,\hat{\mathrm{j}}_0(\omega_2\pm2\omega_1)\,. \tag{78}$$

Thus the kinetic parameters of the corrosion process are given by the following relationships containing the harmonic and intermodulation components of the faradaic current measured at the corrosion potential:

$$\begin{aligned}
\mathrm{j}_k &= \frac{\hat{\mathrm{j}}_0^2(\omega_1)}{\sqrt{48}\sqrt{2\hat{\mathrm{j}}_0(\omega_1)\,\hat{\mathrm{j}}_0(3\omega_1)-\hat{\mathrm{j}}_0^2(2\omega_1)}}=\frac{\hat{\mathrm{j}}_0^2(\omega_2)}{\sqrt{48}\sqrt{2\hat{\mathrm{j}}_0(\omega_2)\,\hat{\mathrm{j}}_0(3\omega_2)-\hat{\mathrm{j}}_0^2(2\omega_2)}}=\\
&=\frac{U_2}{U_1}\,\frac{\hat{\mathrm{j}}_0^2(\omega_1)}{2\sqrt{8\hat{\mathrm{j}}_0(\omega_1)\,\hat{\mathrm{j}}_0(\omega_1\pm2\omega_2)-3\hat{\mathrm{j}}_0^2(\omega_1\pm\omega_2)}}=\\
&=\frac{U_1}{U_2}\,\frac{\hat{\mathrm{j}}_0^2(\omega_2)}{2\sqrt{8\hat{\mathrm{j}}_0(\omega_2)\hat{\mathrm{j}}_0(\omega_2\pm2\omega_1)-3\hat{\mathrm{j}}_0^2(\omega_1\pm\omega_2)}}\,,
\end{aligned} \tag{79}$$

$$\begin{aligned}
\frac{1}{\beta_a} &= \frac{1}{2U_1}\left(\frac{\hat{\mathrm{j}}_0(\omega_1)}{\mathrm{j}_k}\pm4\,\frac{\hat{\mathrm{j}}_0(2\omega_1)}{\hat{\mathrm{j}}_0(\omega_1)}\right)=\frac{1}{2U_2}\left(\frac{\hat{\mathrm{j}}_0(\omega_2)}{\mathrm{j}_k}\pm4\,\frac{\hat{\mathrm{j}}_0(2\omega_2)}{\hat{\mathrm{j}}_0(\omega_2)}\right)=\\
&=\frac{1}{2U_1}\left(\frac{\hat{\mathrm{j}}_0(\omega_1)}{\mathrm{j}_k}\pm2\,\frac{U_1}{U_2}\,\frac{\hat{\mathrm{j}}_0(\omega_1\pm\omega_2)}{\hat{\mathrm{j}}_0(\omega_1)}\right)=\\
&=\frac{1}{2U_2}\left(\frac{\hat{\mathrm{j}}_0(\omega_2)}{\mathrm{j}_k}\pm2\,\frac{U_2}{U_1}\,\frac{\hat{\mathrm{j}}_0(\omega_1\pm\omega_2)}{\hat{\mathrm{j}}_0(\omega_2)}\right),
\end{aligned} \tag{80}$$

$$\frac{1}{\beta_c} = \frac{1}{2U_1}\left(\frac{\hat{\mathbf{j}}_0(\omega_1)}{\mathbf{j}_k} \mp 4\frac{\hat{\mathbf{j}}(2\omega_1)}{\hat{\mathbf{j}}_0(\omega_1)}\right) = \frac{1}{2U_2}\left(\frac{\hat{\mathbf{j}}_0(\omega_2)}{\mathbf{j}_k} \mp 4\frac{\hat{\mathbf{j}}(2\omega_2)}{\hat{\mathbf{j}}_0(\omega_2)}\right) =$$

$$= \frac{1}{2U_1}\left(\frac{\hat{\mathbf{j}}_0(\omega_1)}{\mathbf{j}_k} \mp 2\frac{U_1}{U_2}\frac{\hat{\mathbf{j}}_0(\omega_1 \pm \omega_2)}{\hat{\mathbf{j}}_0(\omega_1)}\right) =$$

$$= \frac{1}{2U_2}\left(\frac{\hat{\mathbf{j}}_0(\omega_2)}{\mathbf{j}_k} \mp 2\frac{U_2}{U_1}\frac{\hat{\mathbf{j}}_0(\omega_1 \pm \omega_2)}{\hat{\mathbf{j}}_0(\omega_2)}\right). \tag{81}$$

The upper signs of Eqs (80) and (81) refer to the case when $\beta_a < \beta_c$, while the lower signs are valid when $\beta_a > \beta_c$. $\beta_a < \beta_c$ when $\overline{\Delta \mathbf{j}_0} > 0$, according to Eq. (65), while $\beta_a > \beta_c$ when $\overline{\Delta \mathbf{j}_0} < 0$, when $\overline{\Delta \mathbf{j}_0} = 0$. $\beta_a = \beta_c$ and can be calculated using any one of Eqs (66), (67), (70), (71), (73) and (74).

Except for minor modifications, the above method can be considered essentially identical to the method based solely on harmonic distortion as presented in a previous report [1] However, the intermodulation effect offers new possibilities for the determination of the kinetic parameters of the corrosion process which are based on the fact that amplitudes U_1 and U_2 of the alternating voltages, having different frequencies, can be varied independently from one another and the amplitudes of the harmonic components of the current are affected by both U_1 and U_2. (This effect is also encountered in the case of intermodulation components but it does not lead to a new evaluation method.).

The dependence of the harmonic components of the current on amplitudes U_1 and U_2 of the alternating voltages are given by Eqs (31)—(36) at a polarizing potential $\overline{\Delta E_a}$ in the anodic Tafel range where $\frac{\overline{\Delta E_a}}{\beta_a} > 1$. The following ratios permit to calculate β_a using tables of Bessel functions when the current components of frequency ω_1, $2\omega_1$, $3\omega_1$ and ω_2, $2\omega_2$, $3\omega_2$ are also measured in the case of $U_2 = 0$ and $U_1 \neq 0$ or $U_1 = 0$ and $U_2 \neq 0$, respectively:

$$\frac{\hat{\mathbf{j}}_a(\omega_1)}{[\hat{\mathbf{j}}_a(\omega_1)]_{U_2=0}} = \frac{\hat{\mathbf{j}}_a(2\omega_1)}{[\hat{\mathbf{j}}_a(2\omega_1)]_{U_2=0}} = \frac{\hat{\mathbf{j}}_a(3\omega_1)}{[\hat{\mathbf{j}}_a(3\omega_1)]_{U_2=0}} = I_0\left(\frac{U_2}{\beta_a}\right), \tag{82}$$

$$\frac{\hat{\mathbf{j}}_a(\omega_1)}{[\hat{\mathbf{j}}_a(\omega_2)]_{U_1=0}} = \frac{\hat{\mathbf{j}}_a(2\omega_2)}{[\hat{\mathbf{j}}_a(2\omega_2)]_{U_1=0}} = \frac{\hat{\mathbf{j}}_a(3\omega_2)}{[\hat{\mathbf{j}}_a(3\omega_2)]_{U_1=0}} = I_0\left(\frac{U_1}{\beta_a}\right). \tag{83}$$

[Note that $I_0(0) = 1$].

The approximation $I_0(x) \approx 1 + \frac{x^2}{2}$ can be employed when the amplitudes of the alternating voltages are small and β_a can be expressed from Eqs

(83) and (82) by algebraic calculation

$$\frac{1}{\beta_a^2} = \frac{4}{U_2^2}\left(\frac{\hat{j}_a(\omega_1)}{[\hat{j}_a(\omega_1)]_{U_2=0}} - 1\right) = \frac{4}{U_2^2}\left(\frac{\hat{j}_a(2\omega_1)}{[\hat{j}_a(2\omega_1)]_{U_2=0}} - 1\right) =$$
$$= \frac{4}{U_2^2}\left(\frac{\hat{j}_a(3\omega_1)}{[\hat{j}_a(3\omega_1)]_{U_2=0}} - 1\right), \tag{84}$$

$$\frac{1}{\beta_a^2} = \frac{4}{U_1^2}\left(\frac{\hat{j}_a(\omega_2)}{[\hat{j}_a(\omega_2)]_{U_1=0}} - 1\right) = \frac{4}{U_1^2}\left(\frac{\hat{j}_a(2\omega_2)}{[\hat{j}_a(2\omega_2)]_{U_1=0}} - 1\right) =$$
$$= \frac{4}{U_1^2}\left(\frac{\hat{j}_a(3\omega_2)}{[\hat{j}_a(3\omega_2)]_{U_1=0}} - 1\right). \tag{85}$$

We note that voltage U_2 of frequency ω_2 has to be small in Eq. (84) while this applies to voltage U_1 of frequency ω_1 in Eq. (85).

The corrosion current density can be expressed from one of Eqs (31)—(39) if β_a has been determined in the above manner.

Similar relationships are obtained using the harmonic components of the current measured on an electrode polarized to potential $\overline{\Delta E_c}$ in the cathodic Tafel range, where $-\frac{\overline{\Delta E_c}}{\beta_c} > 1$. In this case Eqs (82)—(85) are modified by changing subscripts a to c.

Thus it can be concluded that the kinetic parameters of a corrosion process characterized by Tafel type cathodic and anodic reactions can be determined by the study of harmonic and intermodulation distortion caused by the non-linearity of the faradaic impedance. The methods presented in this communication permit the determination of the kinetic parameters on the basis of the measurement of the harmonic and/or intermodulation components at one potential (at one potential either in the cathodic or the anodic Tafel range or at the corrosion potential).

The intermodulation effect has another advantage in addition to those mentioned in the first report of this series [1]. Namely, frequencies $\omega_1 \pm \omega_2$ $\omega_2 \pm 2\omega_1$ and $\omega_1 \pm 2\omega_2$ of the intermodulation components do not coincide with the higher harmonics of fundamental frequencies ω_1 and ω_2 if the latter are properly selected and thus the distortion of the signal generators producing the fundamental harmonic voltages does not interfere in the measurement of the intermodulation components. However, the distortion of the signal generators can affect the measurement of the higher harmonic components and consequently, in the latter case it is advisable to use generators having very small distortion.

The experimental verification of the above methods will be presented in a later communication.

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