

*Use of impedance measurements for the determination of the instant rate of metal corrosion**

I. EPELBOIN, M. KEDDAM AND H. TAKENOUTI

Laboratoire de Physique des Liquides et d'Electrochimie, Groupe de Recherche du C.N.R.S., associé à l'Université de Paris 11, quai St-Bernard, Paris, France

Received 3 August 1971

The various methods of evaluating corrosion rate and charge transfer resistance have been critically reviewed on the basis of the recent developments on the measurement and interpretation of faradaic impedances. It is demonstrated that the entity which is most accurately correlated with corrosion rate is the transfer resistance, the limit of the faradaic impedance at infinite frequency. In the case of iron, with and without inhibitor (propargylic alcohol), it has been ascertained, under various experimental conditions, that the measurement of this resistance constitutes nowadays the best electrochemical test for corrosion, and allows the *a priori* calculation of corrosion rate.

Introduction

The corrosion rate of a metal in an electrolytic medium has long been determined by methods involving the use of sinusoidal or alternating square-wave signals. These techniques are more or less explicitly based on the hypothesis that the impedance of the metal-electrolyte interface is equivalent to the polarization resistance R_p , i.e. the slope of the steady-state current-potential curve ($R_p = dV/dI$). It is generally considered that R_p is inversely proportional to I_{corr} , i.e. the current which is equivalent to the corrosion rate. Some authors have tentatively accounted for the efficiency of corrosion inhibitors, i.e. the adsorption coverage at the interface, by measuring the electrochemical double-layer capacity.

In this paper, we shall present a critical survey of the various techniques which are commonly described in the literature. To this end, we shall refer to the recent information concerning the origin and meaning of the interface impedance.

* This paper constitutes a chapter of H. Takenouti's University thesis, which was presented in Paris on June 25, 1971 [1]

This will lead to a novel method of using impedance in order to predict the corrosion rate. We shall illustrate our method by studying a typical case of corrosion and corrosion inhibition.

1. Different methods of estimating corrosion rate

The corrosion rate of a metal is defined by the weight-loss per unit of time and per unit of surface in contact with the corrosive medium. This constitutes a direct method of measurement which has two advantages: it is always applicable and gives valuable information on the real conditions for the use of a given material since it requires no hypothesis on the corrosion mechanism. However, direct measurement being sometimes unwieldy or even impossible, other methods, based on electrochemical techniques, have been elaborated in order to test or evaluate quantitatively the behaviour of a metal towards corrosion.

1.1. Method based on plotting of current-potential curves

The first of these methods is directly deduced from the determination of the exchange current

of a redox couple: the anodic $I_a(V)$ and cathodic $I_c(V)$ current-potential characteristics [2] are extrapolated up to their intersection at a point whose coordinates are I_{corr} and V_{corr} ; the characteristics are, of course, both considered as Tafel lines. This method is widely used, but it can fail when the potential variation is coupled with a variation of the area on which the anodic, or cathodic, reaction takes place. This is precisely the case of iron in acidic medium, as we have already shown [3], [4]. Moreover, the value of V_{corr} determined by this method often differs from the real value as measured by the direct method.

It seems that these problems are solved by a recent method which relates the corrosion rate to the slope of the over-all current-potential curve $I = f(V)$ taken at the corrosion potential V_{corr} itself. As early as 1938, Wagner and Traud [5] assumed that there exists a proportionality relationship between these two entities. In 1951, Bonhoeffer and Jena [6] applied this idea to the study of a series of iron samples of different purities, and introduced, following a suggestion by Lange, the term polarization resistance, R_p , for the entity $(dV/dI)_{I=0}$. Eventually, numerous theories tried to account for this method, all of them leading to expressions for R_p of the form $R_p = (K/I_{\text{corr}})$ whether the rates of the anodic and cathodic processes are determined by activation [7] or mass transfer [8] phenomena. However, all the possible expressions for the coefficient K show that it depends not only on I_{corr} but also on the nature of the electrochemical processes [7], the concentration of the compounds implied in the reactions [9], and on how the reactions distribute themselves on the surface [10]. For this reason, it is difficult to accept that R_p and I_{corr} are rigorously inversely proportional. Besides, several papers describe an experimental variation of K with I_{corr} . According to Brauns and Schwenk [11], this variation could be empirically represented by a relationship of the form

$$R_p = K' + \frac{K''}{I_{\text{corr}}}$$

1.2. Methods involving alternating current

(a) *Measurement of R_p .* In order to study the variation of R_p or to simplify its determination,

some authors have already used techniques which impose on the electrode undergoing study a sinusoidal [12] or square-wave [13], [14] alternating current. We have elucidated the advantages of this method in a previous paper [15]; in particular, we have shown, in the case of the corrosion of iron in acidic media, the role of dissolved oxygen in the solution and also that of the manner of adding the inhibitors. Our results have been recently confirmed by the study of the current-potential curves (see §1.1) [16]. Most authors consider R_p as equal to the modulus $[Z]$ of the electrode, as measured at only one frequency (often 50 Hz). An empirical relationship can thus be established between $[Z]$ and I_{corr} but it has been shown [14] that this relationship also depends on the frequency of measurement. As a matter of fact, as shown by our study on the variation of $[Z]$ with frequency [15], the polarization resistance can be considered as the limiting value of the impedance when frequency tends towards zero; it is of course absolutely necessary to take into account the ohmic resistance of the electrolyte which can be of the same magnitude as R_p when corrosion is important.

Consequently, considering the complexity of the frequency-dependence of impedance, we can understand why only an accurate experimental study can allow us to choose the experimental conditions for each particular case.

(b) *Measurement of the double-layer capacity.* Certain investigators [17] tried to use impedance measurements in quite a different way, in particular to evaluate the efficiency of corrosion inhibitors. It can indeed be admitted that this efficiency is proportional to the coverage fraction by the inhibitor (θ_{inh}) provided that the double-layer capacity depends linearly on θ_{inh} . If C_{d_s} denotes the capacity corresponding to a completely covered surface, C_{d_o} to an uncovered surface, and C_d to the surface to be studied, then the inhibitor efficiency can be defined as:

$$H_{C_d} (\%) = \frac{C_{d_s} - C_d}{C_{d_o} - C_{d_s}} \times 100. \quad (1)$$

Considering how difficult it is to define and measure the double-layer capacity for soluble electrodes [18], one may wonder what is the real meaning of a H_{C_d} value determined by this

method. Consequently, if this method is to be more than a mere empirical test, it should be completed by a study of the frequency-dependence of the impedance.

(c) *Measurement of the faradaic impedance at the corrosion potential.* The main objection against the two above-mentioned techniques (§(a) and (b)) arises from the use of only one measurement frequency. As a matter of fact, further information can be provided from measurements carried out over a wide frequency range. In order to illustrate this point, we give in Fig. 1 an example of an impedance diagram recorded at the corrosion potential itself. This diagram was obtained under the following conditions: a Holzer-type iron,* a 0.2 cm² surface, a 1M H₂SO₄ solution. This diagram is evidently very similar to those obtained for the dissolution of iron at low anodic over-voltage [19]. This similarity confirms the idea that the corrosion potential has no particular property from an electrochemical point of view. At high frequencies, there always appears a double-layer capacity whereas, at low frequencies, two inductive terms can still be separated, one of them corresponding to iron dissolution [18] and the other to hydrogen evolution [4]. Consequently, it seems quite reasonable to adopt here, at least from a qualitative point of view, the mixed kinetic model [4] which accounts for the phenomena occurring at the anode and cathode. In this paper, we shall use this model to determine the corrosion rate of iron.

2. Corrosion rate and electrode impedance relationship

2.1. General considerations

What we know about the nature of the impedance frequency-dependence [4] [18], allows us to wonder whether the limit at zero frequency (R_p) is actually the best entity to be correlated with corrosion rate. Although R_p is measured at the corrosion potential itself, we understand

* This iron sample was denoted as iron II in reference [4]. Its composition was: C.A.F.L. (114 AV) standardized at 900°C under vacuum. Main impurities: Si = 0.33%; Mn = 0.06%; S = 0.018%; C = 0.003%.

that, though it actually gives information on the rates of the anodic and cathodic reactions, and hence on I_{corr} , it also contains information arising from other phenomena such as the variation of the coverage of adsorbates with potential [4]. Since we are dealing with impedances, hence with linear responses, we may not expect any improvement of this situation by merely decreasing the level of the alternating signal.

We are thus led intuitively to the conclusion that the measurement of the impedance may provide data more directly related to the corrosion process, if, of course, the frequency is sufficiently high so that the coverage of the adsorbates does not vary with the potential. This last condition is satisfied by the use of the transfer resistance R_t , i.e. the limit of the faradaic impedance at infinite frequency. This is not surprising since the faradaic impedance theory predicts that R_t is actually the entity which is related to the direct current by the simplest equations, whether impedance is a reaction impedance or a diffusion impedance [18]. The product $R_t I$ remains indeed constant provided that certain conditions, which can easily be expressed, are satisfied.

2.2. Justification of the choice of the transfer resistance

The former reasoning can be justified from a theoretical point of view, as we shall see in the following paragraphs.

(a) *Reaction impedance.* It is generally admitted that the anodic and cathodic reactions follow Tafel's laws, with exponents b_a and b_c , and take place on fractions θ_a and θ_c of the surface, respectively. In this paper, subscripts a and b correspond to the anodic and cathodic processes, respectively. The current I and the current densities J are related by:

$$I_a = \theta_a J_a \text{ and } I_c = \theta_c J_c$$

the over-all current being:

$$I = I_a + I_c$$

Consequently

$$\frac{1}{R_p} = \theta_a \frac{dJ_a(V)}{dV} + J_a \frac{d\theta_a}{dV} + \theta_c \frac{dJ_c(V)}{dV} + J_c \frac{d\theta_c}{dV} \quad (2)$$

If neither θ_a nor θ_c varies with V near V_{corr} , then equation (2) is reduced to equation (3):

$$\frac{1}{R_p} = \theta_a J_a b_a - \theta_c J_c b_c = I_{\text{corr}} (b_a + b_c) \quad (3)$$

Note that Stern's second method [2] is based on this last equation.

On the other hand, if the derivatives $d\theta_a/dV$ and $d\theta_c/dV$ are not equal to zero, equation (2) takes a more complex form:

$$\frac{1}{R_p} = I_{\text{corr}} \left(b_a + b_c + \frac{1}{\theta_a} \frac{d\theta_a}{dV} - \frac{1}{\theta_c} \frac{d\theta_c}{dV} \right) \quad (4)$$

In fact, the fractions θ_a and θ_c vary at finite rates which obey relationships of the form:

$$\frac{d\theta}{dV} = \frac{1}{1+j\omega}$$

It is always possible to find a sufficiently high frequency so that neither θ_a nor θ_c varies with potential. In that case, impedance is reduced to a resistance R_t , called transfer resistance, which is the limit of the faradaic impedance at infinite frequency; consequently, equation (4) can also be written as:

$$\frac{1}{R_t} = I_{\text{corr}} (b_a + b_c). \quad (5)$$

Equation (5), which is analogous to the expression which generally relates transfer resistance to current, is only valid if all the reactions are irreversible.

It is evident that equation (3) is only a particular case of equation (5), for when the faradaic impedance is purely resistive we have:

$$Z_f = R_t = R_p.$$

We can understand why the use of R_t rather than R_p is far more promising, by comparing equations (4) and (5). In fact, the coefficient relating resistance and corrosion current should depend on the least number of parameters possible and remain constant over a wide range of experimental conditions, which is the case when R_t is used.

(b) *Diffusion impedance.* The corrosion rate is limited by mass transfer only in exceptional cases. However, mass transfer may have an influence, for instance in the presence of dissolved oxygen [1], [15] or when the cathodic reaction is very fast [9].

If we assume that the rate of one of the reactions, for instance the cathodic, is limited by mass transfer, then

$$\frac{dI_c}{dV} = 0$$

and:

$$\frac{1}{R_p} = I_{\text{corr}} b_a. \quad (6)$$

This expression remains valid only as long as the cathodic current is a limiting current I_{lim} .

Now, in most cases, the process is only partially controlled by mass transfer and:

$$\frac{1}{R_p} = \frac{dI_a}{dV} + \left(\frac{dV}{dI_c} \right)^{-1} = I_a b_a - (R_{t_c} + R_d)^{-1}. \quad (7)$$

It can be demonstrated [20] that the diffusion resistance R_d is an increasing function of the ratio I_c/I_{lim} , its form being $1/(1-I_c/I_{\text{lim}})$. Consequently, in this case, there no longer exists a simple relation between R_p and I_{corr} , but only between R_t and I_{corr} , and:

Fig. 1. Impedance diagram for the spontaneous corrosion of iron in a 1 M H_2SO_4 aerated solution (air bubbling). (Parameter: frequency in Hz.)

Fig. 2. Impedance diagram for the spontaneous corrosion of iron in a 0.5 M H_2SO_4 solution. (Atmosphere: air; parameter: frequency in Hz.)

Fig. 3. Impedance diagram for the spontaneous corrosion of iron in a 0.5 M $\text{H}_2\text{SO}_4 + 0.1 \times 10^{-3}$ M $\text{CH}\equiv\text{C}-\text{CH}_2\text{OH}$ solution. (Atmosphere: air; parameter: frequency in Hz.)

Fig. 4. Impedance diagram for the spontaneous corrosion of iron in a 0.5 M $\text{H}_2\text{SO}_4 + 0.2 \times 10^{-3}$ M $\text{CH}\equiv\text{C}-\text{CH}_2\text{OH}$ solution. (Atmosphere: air; parameter: frequency in Hz.)

Fig. 5. Impedance diagram for the spontaneous corrosion of iron in a 0.5 M $\text{H}_2\text{SO}_4 + 0.5 \times 10^{-3}$ M $\text{CH}\equiv\text{C}-\text{CH}_2\text{OH}$ solution. (Atmosphere: air; parameter: frequency in Hz.)

Fig. 6. Impedance diagram for the spontaneous corrosion of iron in a 0.5 M $\text{H}_2\text{SO}_4 + 2.10^{-3}$ M $\text{CH}\equiv\text{C}-\text{CH}_2\text{OH}$ solution. (Atmosphere: air; parameter: frequency in Hz.)

Fig. 7. Impedance diagram for the spontaneous corrosion of iron in a 0.5 M $\text{H}_2\text{SO}_4 + 5.10^{-3}$ M $\text{CH}\equiv\text{C}-\text{CH}_2\text{OH}$ solution. (Atmosphere: air; parameter: frequency in Hz.)

Fig. 8. Impedance diagram for the spontaneous corrosion of iron in a 0.5 M $\text{H}_2\text{SO}_4 + 20.10^{-3}$ M $\text{CH}\equiv\text{C}-\text{CH}_2\text{OH}$ solution. (Atmosphere: air; parameter: frequency in Hz.)

$$\frac{1}{R_t} = I_{\text{corr}}(b_a + b_c)$$

which is identical to equation (5).

It is evident that equation (6) is only a particularly fortunate case of equation (7) when R_d tends towards infinity if the process is totally controlled by mass transfer.

In conclusion, the existence of an inverse proportionality relationship between the polarization resistance R_p and the corrosion rate of a metal is related to highly restrictive conditions. This confers on the use of R_p a rather limited interest. *This relationship is only a particular case of an analogous law which involves the transfer resistance R_t instead of R_p .* The expression of the coefficient relating R_t and I_{corr} contains only the exponents of the activation laws (Tafel coefficients) even in the presence of a coverage process and a concentration gradient. This coefficient can consequently be considered as being constant over a wide range of experimental conditions as long as the nature of the electrochemical reactions remains unchanged. Thus, not only is R_t rather easy to determine experimentally, but it can also be regarded from a theoretical point of view as being the most adequate entity to be employed in the electrochemical determination of corrosion rate. We shall now apply these considerations to the example of a typical case of corrosion and corrosion inhibition, namely that of iron.

3. Application to the corrosion inhibition of iron

3.1. Inhibiting effectiveness of propargylic alcohol

It is well known in the literature that acetylenic alcohols inhibit the corrosion of iron. We have already studied the influence of one of the best known of these inhibitors, namely the 2-butyne 1,4-diol, on the mechanisms of the cathodic, then the anodic reactions at the surface of this metal in sulphuric acid medium [3, 4, 19]. Propargylic alcohol, $\text{CH}\equiv\text{C}-\text{CH}_2-\text{OH}$, is known to have an inhibiting efficiency of the same magnitude as that of 2-butyne 1,4-diol. As in the case of this last inhibitor, this efficiency is related to the appearance of an hysteresis in the current-potential curve obtained by a potentiokinetic

plot and, as we shall see below, the relaxation of the inhibiting coverage introduces an inductive term in the faradaic impedance. Consequently, these two alcohols have quite similar behaviours, this similarity being apparently a property of the triple acetylenic bond.

However, it has recently been stated that if propargylic alcohol is sufficiently pure, it has no inhibiting effect [21, 22]. In order to check this, we studied the inhibiting effect of highly pure propargylic alcohol obtained by preparative chromatography. We measured directly this effect by weight-loss [23], and determined, at the same time, the impedance of the sample at the corrosion potential. We have thus been able to compare the various techniques of evaluating corrosion rate with each other and with the direct method.

(a) *Weight-loss.* The iron sample used here has the same chemical composition as that the Holzer-type iron which was described above. However, a different thermal treatment conferred larger grains on this sample and a corrosion rate about 2.5 times lower in a molar sulphuric acid solution.

Weight-loss experiments have been carried out under the following conditions: duration: 24 hours; atmosphere: air; temperature: 25°C; medium: 0.5 M H_2SO_4 pure or containing propargylic alcohol at the following concentrations: 0.1, 0.2, 0.5, 2, 5 and 20.10⁻³ M. The obtained results are summarized in Table 1. The efficiency of the inhibitor can be directly calculated from weight-loss measurements:

$$H_{\text{dir}} = \frac{100(x_0 - x)}{x_0} \quad (8)$$

where x_0 = weight-loss in the absence of inhibitor and x = in the presence of inhibitor.

The inhibiting efficiency thus measured goes through a maximum at an alcohol concentration of 0.5 × 10⁻³ M. At this point, the corrosion rate is divided by 10. A higher concentration of inhibitor increases the corrosion rate, as already mentioned in the literature.

(b) *Impedance measurements.* Impedance diagrams (Figs. 2–8) have been recorded 2 hr after immersing the electrode, since experi-

Table 1. Inhibitor efficiency of propargylic alcohol as determined by weight-loss in a 0.5 M H₂SO₄ solution.

Concentrations (10 ⁻³ M)	0	0.1	0.2	0.5	2	5	20
x (mg cm ⁻² h ⁻¹)	0.8	0.144	0.129	0.09	0.165	0.280	0.280
H_{dir} (%)	0	82	84	89	79	74	74

x : weight-loss

H_{dir} : inhibitor efficiency by direct measurement.

mental conditions are then sufficiently steady to allow accurate measurements. They correspond to the same concentrations of inhibitor as above. They were obtained with a galvanostat built in our laboratory by C. Gabrielli, and a transfer function analyser (Solartron JM 1600 A).

The diagrams show the second inductive loop we mentioned above (§ 1.2.c). This loop becomes more and more important as the inhibitor concentration increases. For this reason, R_p diminishes more rapidly than R_t . Table 2 summarizes the values of R_p and R_t as determined from the diagrams. We can see that the values of R_p and R_t obtained do pass through a maximum for a 0.5×10^{-3} M solution and decrease beyond this concentration. If we assume that the corrosion rate is inversely proportional to the resistance (either R_p or R_t), we can calculate the inhibitor efficiency from the values of R_p or R_t using a relationship analogous to equation (8). Values of this novel inhibitor efficiency calculated from R_p (denoted H_{Rp}) and R_t (H_{Rt}) are listed in Table 2.

We also tried to calculate the inhibitor efficiency from the double-layer capacity as determined from the diagrams in Figs. 2–8. The time-constant related to this capacity being clearly distributed [18], we chose the apparent values of C_d measured at 1 kHz. We could not find any saturation effect as a function of concentration; actually, the capacity goes through a minimum at an inhibitor concentration of 0.5×10^{-3} M at which concentration the efficiency of the inhibitor is maximal. In accordance with [24], we adopt a relation of a different form than equation (1):

$$H_{Ca} = K_1 \left(1 - \frac{C_d}{C_{d_0}} \right) \times 100. \quad (9)$$

The coefficient K_1 can be determined by direct measurement, without knowing C_{d_0} .

The obtained values of H_{Ca} are given in the last column of Table 2. Coefficient K_1 was chosen so that H_{Ca} is standardized by $H_{Ca} = H_{dir}$ at a concentration of 0.5×10^{-3} M.

The results listed in Table 2 can lead to the following conclusions:

—The values of H_{Rt} are in agreement with those of H_{dir} , except at very high concentrations of inhibitor when indications become pessimistic.

—The values of H_{Rp} can be considered as acceptable, but beyond an inhibitor concentration of $2 \cdot 10^{-3}$ M, they predict a negative inhibitor effectiveness, i.e. a marked acceleration of corrosion which is in complete disagreement with direct measurements. This disagreement could be predicted both from the theoretical considerations described above and the change of the impedance diagrams with inhibitor concentration. The increasing importance of the L.F. inductive term, which is caused by the relaxation of the inhibitor coverage, enhances the weight of the terms in $d\theta_\omega/dV$ (equation (4) and at the same time the difference between R_t and R_p . Note (Fig. 8) that at the highest concentration of propargylic alcohol there appears a third reactive term which might be due to a *new* reaction occurring at the electrode and involving the inhibitor itself.

—The values of H_{Ca} , when standardized by comparison with the direct measurements, are close to those of H_{Rp} . They show the same type of errors as H_{Rp} at high concentrations of inhibitor. Besides, neither in [17] nor in [24] have the authors satisfactorily checked the generality of the relations between corrosion rate and capacity they used. As a matter of fact, these relations imply that the inhibitor may cover

Table 2. Calculated inhibitor efficiency of propargylic alcohol in a 0.5 M H₂SO₄ solution

Concentrations (10 ⁻³ M)	H _{d1r} (%)	R _t (Ω)	H _{Rt} (%)	R _p (Ω)	H _{Rp} (%)	C _d (μF)	H _{Cd} (%)
0	0	163	0	148	0	21	0
0.1	82	540	70	360	59	13	59
0.2	84	800	80	526	72	10.3	77
0.5	89	1300	88	800	82	8.6	89
2	79	1105	85	500	79	8.9	87
5	74	473	66	25	-490	21	0
20	74	250	36	36	-310	48	-193

R_t: transfer resistance

H_{Rt}: inhibitor efficiency from R_t measurements

R_p: polarization resistance

H_{Rp}: inhibitor efficiency from R_p measurements

C_d: double-layer capacity

H_{Cd}: inhibitor efficiency from C_d measurements

A negative value for H implies an increase of the corrosion rate.

completely the electrode and that this leads to the total cancelling of corrosion rate. These conditions are evidently satisfied only for exceptional cases.

We confirmed the inhibitor efficiency of highly pure propargylic alcohol. However, an excess of inhibitor turns out to be useless or even harmful.

The most reliable of the various electrochemical techniques we compared seems to be that based on the transfer resistance measurement. We can therefore understand why some authors [14], thinking they were dealing with R_p, obtained a very satisfying agreement between corrosion rate and measured resistance by using frequencies varying between some Hz to a few ten Hz. This can easily be explained since, in reality, the impedance modulus at these frequencies is closer to R_t than R_p, under the usual concentration and temperature conditions of the electrolyte.

However, this is only a method allowing a comparative study after the coefficient relating R_t and I_{corr} is determined by direct measurement. It may seem illusive to determine this coefficient from R_p, and of course impossible from C_d, but we can calculate it *a priori* by our method and predict the absolute corrosion rate.

3.2. Theoretical estimation of the corrosion rate

To this end, it is sufficient to calculate the co-

efficient $K = R_t I_{\text{corr}}$. If we accept that the anodic and cathodic reactions both occur in two consecutive steps (denoted 1 and 2), assumed irreversible, we can write:

$$K = \frac{2}{(b_{a,1} + b_{a,2}) + (b_{c,1} + b_{c,2})} \quad (10)$$

Constants *b* are determined from current-potential curves or impedance diagrams obtained at high anodic and cathodic polarizations [4], [18]. In the case of the iron sample we studied here:

$$(b_{a,1} + b_{a,2}) = 47 \text{ V}^{-1}$$

$$(b_{c,1} + b_{c,2}) = 35.4 \text{ V}^{-1}$$

This leads to a value $K = 24.9 \text{ mV}$ and a corrosion rate, on the basis of a valency 2 for iron, equal to $0.78 \text{ mg cm}^{-2} \text{ h}^{-1}$. Direct measurement leads to a value of $0.8 \text{ mg cm}^{-2} \text{ h}^{-1}$ for the corrosion rate. For the Holzer-type iron sample described at the beginning of this paper, we found a value of 2 by direct measurement and a value of $2.1 \text{ mg cm}^{-2} \text{ h}^{-1}$ from R_t values.

Consequently, provided that the Tafel constants are known for the anodic and cathodic reactions, measurement of R_t allows the *a priori* calculation of the corrosion rate even for complex processes involving coverage relaxation.

Conclusion

The accurate knowledge of the impedance at the

corrosion potential led us to examine critically, then perfect, certain methods of evaluating corrosion rate from electrochemical measurements. Regarding corrosion as a particular case of mixed electrochemical kinetics, we have been able to establish the expression for impedance at the corrosion potential. We hence showed that the entity which is most 'intimately' correlated with corrosion rate is the *transfer resistance* (limit of the faradaic impedance at infinite frequency) and *not* the polarization resistance (limit of the faradaic impedance at zero frequency) as generally stated.

We established, under various conditions, that measurement of the charge-transfer resistance not only constitutes an accurate test for resistance to corrosion but also allows the *a priori* calculation of the rate of this process.

References

- [1] H. Takenouti, 'Utilisation des mesures d'impédance faradique à l'étude du mécanisme électrochimique de la corrosion du fer et de son inhibition', *Thèse d'Université* presented at the University of Paris VI, 1971.
- [2] M. Stern and A. L. Geary, *J. Electrochem. Soc.*, **104** (1957) 56.
- [3] I. Epelboin, Ph. Morel, and H. Takenouti, Third European Symposium on Corrosion Inhibitors (Ferrara, Italy, 1970); idem, *Annali Univ. Ferrara*, N.S., Sez. V, Suppl. No. 5, **23** (1971).
- [4] I. Epelboin, Ph. Morel and H. Takenouti, *J. Electrochem. Soc.*, **118** (1971) 1282.
- [5] C. Wagner and W. Traud, *Z. Elektrochem.*, **44** (1938) 391.
- [6] K. Bonhoeffer and W. Jena, *Z. Elektrochem.*, **59** (1951) 151.
- [7] M. Stern and E. D. Weisert, *Proc. Amer. Soc. Test. Mater.*, **59** (1959) 1280.
- [8] L. I. Antropov, M. A. Gerasimenko and Ju. S. Gerasimenko, *Zashita Metallov*, **2** (1966) 115.
- [9] P. J. Gellings, Third Symposium of the European Federation of Corrosion (Brussels, Belgium, 1963).
- [10] M. Stern, *Corrosion N.A.C.E.*, **14** (1958) 43.
- [11] E. Brauns and W. Schwenk, *Werkst. und Korr.*, **12** (1961) 73.
- [12] W. Schwenk and H. E. Buhler, *Corrosion Science*, **3** (1963) 261.
- [13] J. C. Rowland and M. N. Bentley, *Brit. Corrosion J.*, **2** (1967) 92.
- [14] M. Prazak and K. Barton, *Corrosion Science*, **7** (1967) 159.
- [15] I. Epelboin, M. Keddad and H. Takenouti, 17th C.I.T.C.E. meeting, Tokyo, 1966.
- [16] D. Raux, 'Contribution à l'étude de l'inhibition de la corrosion du fer en milieu acide par l'alcool propargylique', 'Thèse de 3e Cycle', Paris 1970.
- [17] B. Dus and Z. Szklarska-Smialowska, *Corrosion N.A.C.E.*, **25** (1969) 69.
- [18] I. Epelboin and M. Keddad, *J. Electrochem. Soc.*, **117** (1970) 1052.
- [19] I. Epelboin, M. Keddad and H. Takenouti, Third European Symposium on Corrosion Inhibitors (Ferrara, Italy, 1970); idem., *Annali Univ. Ferrara* (1971), N.S., Sez. V, Suppl. No. 5, 237.
- [20] C. Deslouis, I. Epelboin, M. Keddad and J. C. Lestrade, *J. Electroanal. Chem.*, **28** (1970) 57.
- [21] M. Mabile, 'Influence de la pureté de l'alcool propargylique sur son aptitude à l'inhibition de la corrosion du fer en milieu acide', 'Thèse de 3e Cycle', Paris, 1967.
- [22] M. Mabile and J. Talbot, *C.R. Acad. Sci.*, Paris, **264 C** (1967) 855.
- [23] S. Czernecki, M. Froment, C. Georgoulis, Ph. Morel and H. Takenouti, *J. Chim. Phys.*, **64** (1967) 1821.
- [24] T. Murakawa, S. Nagaura and N. Hackermann, *Corrosion Science*, **7** (1967) 79.