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Application of the accelerated Tafel plot technique to corrosion kinetics: role of double layer through simulation

V. YEGNARAMAN, C. AHMED BASHA, G. PRABHAKARA RAO

Central Electrochemical Research Institute, Karaikudi-623 006, India

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Results on the simulated η–t transient response of an 'actively' corroding system under accelerated Tafel plot (ATP) conditions have revealed the influence of input parameters (Δi, τ) and system parameters (C_{dl}, i_{corr} and b) and explained the observed dependence of kinetic parameters (arrived at on the basis of the intercept–slope method) on τ in certain time domains. New improved methods, which eliminate such dependence and give uniform corrosion rate data over all time domains, are described in the paper.

Nomenclature

ATP	accelerated Tafel plot
α	transfer coefficient
b	Tafel slope (V)
C_d	double layer capacitance (μF cm^{-2})
Δi	initial value of the exponentially decaying current (A)
E_c	corrosion potential (V)
η	overpotential (V)
η_m	overpotential corresponding to maximum in η–t transient (V)
F	Faraday constant (C mol^{-1})
i_{corr}	corrosion current density (A cm^{-2})
n	number of electrons involved in charge transfer step
p	intercept of ATP (V)
R	gas constant (J K^{-1} mol^{-1})
R_p	polarization resistance (Ω cm^2)
S	slope of ATP, i.e. $\tau d\eta/dt$ (V)
S_{av}	average of the S values at $\tau > \tau_{el}$ (V)
S_{meas}	slope of the linear η–t region, i.e. $d\eta/dt$ (V s^{-1})
T	temperature (K)
t	time (s)
t_m	time corresponding to η_m in the η–t transient (s)
τ	time constant of the exponentially decaying current pulse (s)
τ_{el}	electrode time constant given by R_pC_d (s)

1. Introduction

A new class of relaxation techniques employing an exponential current input has been reported [1] from these laboratories. Of these, the accelerated Tafel plot (ATP) method [2] is an elegant transient technique that allows the rapid acquisition of kinetic data for electrochemical systems under activation control. The chief advantage of the ATP method over the classical Tafel procedure lies in that the tedium of point-by-point scanning is eliminated and the kinetic data are obtained from a single transient. Further, the duration of polarization is very short (of the order of ms), thereby causing minimum, if not nil, damage to the electrode surface. This latter aspect is of vital significance for corroding systems whose instantaneous corrosion rates can also be determined by the ATP method.

The utility of the ATP technique for successful evaluation of kinetic parameters of a redox system [2] has been reported earlier. Efforts to employ this technique for the evaluation of kinetic parameters of corrosion reactions were partially successful as revealed from the results [3] of our experiments employing varied input time constants (τ). While the kinetic data acquired using high τ were satisfactory and consistent with data obtained by other methods, results obtained using low τ were not only different from the above, but also varied with the τ in this regime. Hence a detailed analysis of the simulated η–t response obtained under varied conditions of the input parameters (τ and Δi) as well as system parameters (the kinetic parameters i_{corr}, Tafel slope and double layer capacitance) was undertaken to investigate the factors responsible for the observed τ effects on the kinetic data and is reported here.

2. ATP method [2]

The method consists of applying an exponentially decaying current pulse described by Equation 1 and recording the resulting η–t response on an oscilloscopic screen

$$i(t) = \Delta i \exp\left(-\frac{t}{\tau}\right) \tag{1}$$

The resulting η–t transient for an activation-controlled reaction under Tafel conditions is given by

$$\eta = \frac{RT}{\alpha nF}\left(-\frac{t}{\tau}\right) + \frac{RT}{\alpha nF}\ln\left(\frac{\Delta i}{i_0}\right) \tag{2}$$

The slope (S) and intercept (p) values of the resulting straight line (plot of η vs t described by Equation 2) are made use of in evaluating the kinetic parameters (i_0 and α) through the following equations

$$i_0 = \Delta i \exp(-p/S) \tag{3}$$

$$\alpha = \frac{RT}{nF}\frac{1}{S} \tag{4}$$

Extension of the ATP method to a corroding system whose polarization behaviour can be described [4] by Equation 5

$$i = i_{corr}\left[\exp\left(\frac{2.3\eta}{b_a}\right) - \exp\left(\frac{-2.3\eta}{b_c}\right)\right] \tag{5}$$

where $\eta = E - E_c$ and b is the Tafel parameter given by $2.3\,RT/\alpha nF$, yields an η–t response (considering cathodic Tafel polarization) that can be represented as

$$\eta = \frac{b_c}{2.3}\left(\frac{t}{\tau}\right) - \frac{b_c}{2.3}\ln\left(\frac{\Delta i}{i_{corr}}\right) \tag{6}$$

Equation 6 enables the calculation of i_{corr} and the Tafel parameter from the knowledge of the slope and intercept values of the η–t transient.

3. Genesis of the problem

Experimental data allowed recognition of two regimes of τ for each corroding system studied — a low τ regime and a high τ regime — these being categorized with respect to electrode time constant, τ_{el} (τ_{el} is given by $R_p C_d$ where R_p is the polarization resistance and C_d is the double layer capacitance). The values of i_{corr} and b_c calculated from ATP slope and intercept values tend to become constant at $\tau > \tau_{el}$ (i.e. high τ regime) while they are found to increase with increase of τ at $\tau < \tau_{el}$ (i.e. low τ regime).

The dependence of i_{corr} and b_c on τ in the low τ regime observed from these results assumes importance in the light of variation in i_{corr} with time-dependent input signals reported in the literature. Variation of i_{corr} with the frequency of the probing signal has been reported in the case of a.c. [5] and rectangular [6] waveform inputs. Again during linear polarization with triangular [7–13] waveforms (under small amplitude cyclic voltammetry conditions) the measured polarization resistance is found to vary with the potential sweep rate. According to these results, an increase in i_{corr} results with increase of sweep rate. On the contrary, ATP results reveal a decrease of i_{corr} with decrease of τ or with increase of sweep rate. This reversal in the trend of results is intriguing. Of course, the ATP results were obtained under Tafel polarization conditions while the above results reported in the literature were taken under linear polarization conditions. That this difference in polarization range may not be responsible for the observed reversal in the trend involving sweep rate effect (or time constant effect) has been confirmed by obtaining i_{corr} values from the Tafel plots constructed from the linear sweep voltammograms recorded at different sweep rates under Tafel polarization conditions [3, 14] which are consistent with data under linear polarization conditions.

3.1. *Effect of double layer (dl)*

One may recall that in the formalism for the ATP technique presented above, the electrochemical system was assumed to involve only a simple faradaic charge transfer reaction and the influence of dl charging has been considered negligible. In transient measurements the latter assumption will not be rigorously valid under all conditions since the electrode also has a characteristic time constant (τ_{el}) whose value is governed by C_d and R_p. Because of this, dl charging during transient measurements will assume importance. The choice of a proper 'time window' for extracting kinetic parameters of an electrode reaction through transient techniques has been emphasized by studies [15] using computer curve-fitting procedures. At short times, dl charging tends to predominate. Hence the present observation of τ dependence of i_{corr} and b_c may probably originate from the neglect of dl charging. To investigate this aspect further and to understand the implications of dl charging on the corrosion parameters calculated at different time constants, a model involving a faradaic charge transfer reaction and dl charging has been assumed for the corrosion system and its theoretical transient response to an exponentially decaying current pulse under Tafel conditions has been simulated with systematic variation of the different parameters and the help of a personal computer.

4. Model and simulation

The corrosion system is assumed to involve a faradaic charge transfer reaction and dl charging. The current input i to such a system can be written as

$$i = i_d + i_f \tag{7}$$

where i_d and i_f are the currents utilized for dl charging and faradaic reaction, respectively. If the system is under activation control experiencing Tafel polarization conditions, then its η–t response to an input described by Equation 1 can be represented as

$$\Delta i \exp\left(-\frac{t}{\tau}\right) = C_d\frac{d\eta}{dt} + i_{corr}\exp\left(\frac{2.3\eta}{b}\right) \tag{8}$$

In Equation 8 the first term on the right hand side corresponds to dl charging current and the second term to faradaic current. Equation 8 involving five

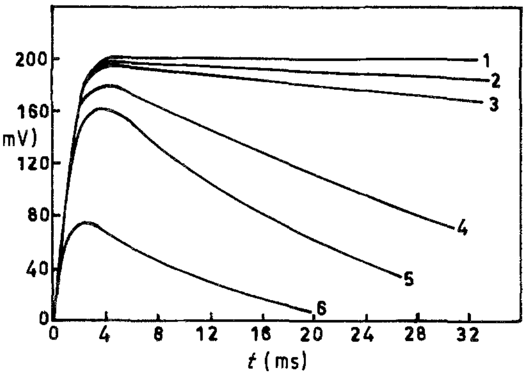

Fig. 1. Effect of τ on η–t transients at fixed values of $C_d = 50\,\mu F\,cm^{-2}$, $i_{corr} = 1 \times 10^{-4}\,A\,cm^{-2}$, $\alpha = 0.5$ and $\Delta i = 5 \times 10^{-3}\,A$ used for simulating the transient response. (1) $\tau = 1000\,ms$; (2) $\tau = 100\,ms$; (3) $\tau = 50\,ms$; (4) $\tau = 10\,ms$; (5) $\tau = 5\,ms$; (6) $\tau = 1\,ms$.

parameters, *viz.* C_d, i_{corr}, b, Δi and τ, is non-linear and can be solved numerically by a fourth order Runge–Kutta method using a personal computer (CASIO Model PB-300). Values of η and $d\eta/dt$ are computed at suitable intervals of time by assigning plausible values for the five parameters in Equation 8. From the data so generated, η–t profiles are constructed to yield the simulated transient.

The parameters involved in Equation 8 are of two types: (i) system parameters which characterize the system and are beyond experimental control (C_d, i_{corr} and b belong to this category); (ii) input parameters Δi and τ determine the electrical input characteristics and can be easily controlled and manipulated by the experimenter. Variation of Δi will facilitate polarizing the system to different extents while the variation of τ will enable the understanding of the system behaviour *vis-à-vis* its own time constant τ_{el}. Simulation studies have been carried out by systematic variation of the five parameters described above. In these studies ohmic drop normally arising due to high solution resistance or the presence of passive films on the electrode is assumed to be absent.

4.1. *Effect of input parameters*

In these studies the system parameters C_d and i_{corr} are assumed to be $50\,\mu F\,cm^{-2}$ and $1 \times 10^{-4}\,A\,cm^{-2}$, respectively. For the third system parameter b which is given by $2.3\,RT/\alpha nF$, α, n and T are assumed to be 0.5, 1 and 25° C, respectively while R and F have their usual significance. Since the ATP technique requires the system to be under activation control a low value of $1 \times 10^{-4}\,A\,cm^{-2}$ for i_{corr} has been chosen. The C_d value is chosen to be $50\,\mu F\,cm^{-2}$ since many of the electrochemical systems are known to have C_d around this value. For the system parameters assumed above, τ_{el} works out* to 12.8 ms. The influence of variation of Δi and τ individually is described below.

4.1.1. Effect of τ. The influence of τ variation covering 1 to 1000 ms on the η–t response has been studied by keeping Δi constant at 5×10^{-3} A. The resulting η–t transients computed using Equation 8 and the values of i_{corr}, C_d, b, Δi and τ described above are given in Fig. 1. The simulated transients appear similar to the experimental η–t transients [3, 14] exhibiting initially a steep increase in η followed by a maximum η_m corresponding to a time t_m beyond which a linear region exists so long as the polarization is in the Tafel range. In subsequent discussions, this region is referred to as the 'linear region' which corresponds to ATP.

The transients show that the extent of polarization (η_m) increases steeply as τ is raised from 1 to 10 ms, i.e. in the low τ regime. Then the increase in η_m tends to be marginal as τ varies from 50 to 1000 ms, i.e. in the high τ regime. The variation of t_m is only gradual with increase in τ.

It is found that the measured slope†, S_{meas}, of the ATPs decreases as τ increases and can be expected to reach zero as τ tends to infinity when the technique becomes a current step method.

The values of the ATP slope S become practically constant in the high τ regime. Values of α computed using these S are in good agreement with the value assumed for generating the η–t profiles. On the other hand, S values obtained in the low τ regime are smaller, thereby yielding higher α values. The observed high α values and low η_m values in the low τ regime (i.e. at $\tau < \tau_{el}$) clearly demonstrate the influence of dl charging on the measurements.

4.1.2. Effect of Δi. The simulated η–t transients obtained from the variation of Δi over 3×10^{-3} to 7×10^{-3} A at a typically constant τ of 100 ms are depicted in Fig. 2. The system parameters employed for generating the transients are the same as described in Section 4.1.1.

As can be seen from Fig. 2, the simulated transients show that the slope of the linear region remains unaffected by Δi variation. Further, with increase in Δi, η_m increases while t_m decreases.

4.2. *Effect of system parameters*

To consider the effect of varying the system parameters on the η–t transient, the input parameters are kept constant at $\Delta i = 5 \times 10^{-3}$ A and $\tau = 100$ ms. The three system parameters i_{corr}, C_d and b are varied keeping two of them constant at a time and the results are as follows.

4.2.1. Effect of b. In order to understand the influence of varying the b value which is given by $2.3RT/\alpha nF$,

* τ_{el} corresponds to R_pC_d and the value of the polarization resistance, R_p which is given by $b_ab_c/2.3(b_a + b_c)$. i_{corr} is obtained by assuming $b_a = b_c$. Accordingly for the chosen values of $\alpha = 0.5$, $n = 1$ and $i_{corr} = 1 \times 10^{-4}\,A\,cm^{-2}$, R_p is $256.5\,\Omega\,cm^2$.

† It may be noted that S_{meas} denotes the slope $d\eta/dt$ of the linear region of the ATP transient and it is measured in $V\,s^{-1}$. This can be distinguished from the ATP slope designated as S which is obtained by rationalization of S_{meas} with respect to τ and is expressed in V. They are related as

$$S_{meas} \times \tau = S = \frac{RT}{\alpha nF} = \frac{b}{2.3}$$

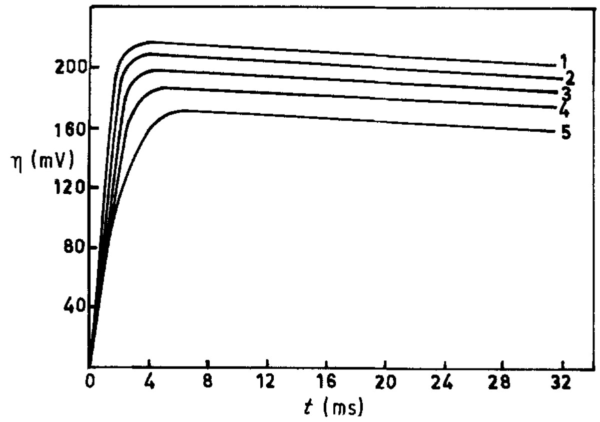

Fig. 2. Effect of Δi on η–t transients at fixed values of C_d = 50 μF cm^{-2}, i_{corr} = 1 × 10^{-4} A cm^{-2}, α = 0.5 and τ = 100 ms used for simulating the transient response. (1) Δi = 7 × 10^{-3} A; (2) Δi = 6 × 10^{-3} A; (3) Δi = 5 × 10^{-3} A; (4) Δi = 4 × 10^{-3} A; (5) Δi = 3 × 10^{-3} A.

the effect of α variation on η–t response is studied, other factors being constant for a given situation. Accordingly α is varied from 0.3 to 0.6 and the resulting η–t transients are presented in Fig. 3. C_d and i_{corr} are kept constant at 50 μF cm^{-2} and 1 × 10^{-4} A cm^{-2}, respectively. It may be seen from the figure that decrease in α (or increase in b) results in appreciable increase of η values at a given time in the transient response.

4.2.2. Effect of i_{corr}. The influence of i_{corr} variation on η–t transients is presented in Fig. 4. Values of C_d and α are kept constant at 50 μF cm^{-2} and 0.5, respectively.

It can be seen from the figure that the decrease in i_{corr} is found to increase η appreciably at a given time, which can readily be understood in terms of the relative polarizability of the system. The slope remains unaffected by i_{corr} variation. These transients point out the necessity of resorting to high Δi values in the case of systems characterized by high i_{corr} for taking the system in to Tafel region. However, while doing so, it has to be ensured that the system is still under activation polarization and concentration polarization does not set in.

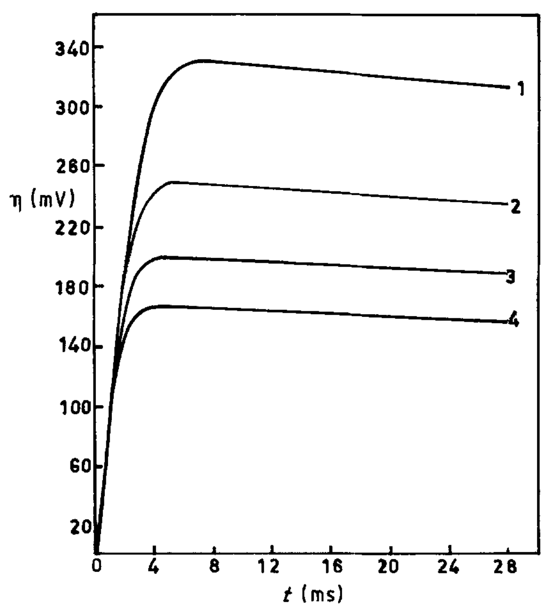

Fig. 3. Effect of α on η–t transients at fixed values of C_d = 50 μF cm^{-2}, i_{corr} = 1 × 10^{-4} A cm^{-2}, Δi = 5 × 10^{-3} A and τ = 100 ms used for simulating the transient response. (1) α = 0.3; (2) α = 0.4; (3) α = 0.5; (4) α = 0.6.

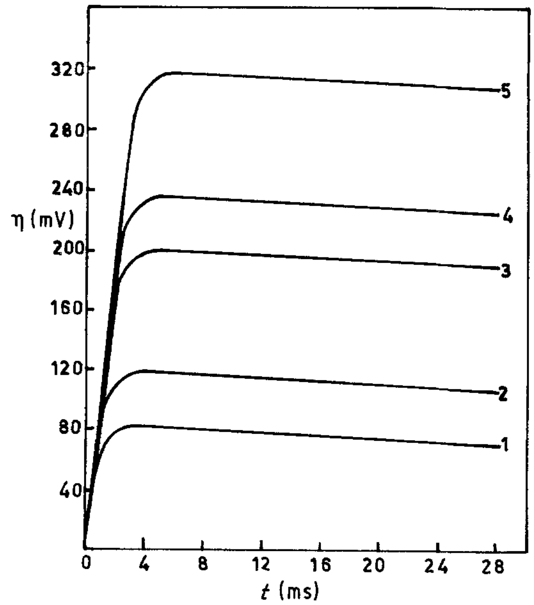

Fig. 4. Effect of i_{corr} on η–t transients at fixed values of C_d = 50 μF cm^{-2}, α = 0.5, Δi = 5 × 10^{-3} A and τ = 100 ms used for simulating the transient response. (1) i_{corr} = 1 × 10^{-3} A cm^{-2}; (2) i_{corr} = 5 × 10^{-4} A cm^{-2}; (3) i_{corr} = 1 × 10^{-4} A cm^{-2}; (4) i_{corr} = 5 × 10^{-5} A cm^{-2}; (5) i_{corr} = 1 × 10^{-5} A cm^{-2}.

4.2.3. Effect of C_d. The η–t transients obtained as a result of varying C_d from 30 to 200 μF cm^{-2} are shown in Fig. 5. The values of i_{corr} and α are maintained constant at 1 × 10^{-4} A cm^{-2} and 0.5, respectively.

It can be observed that increase of C_d raises t_m while η_m and the slope of the linear portion remain practically constant. Thus the increase of C_d is only found to delay the attainment of the maximum.

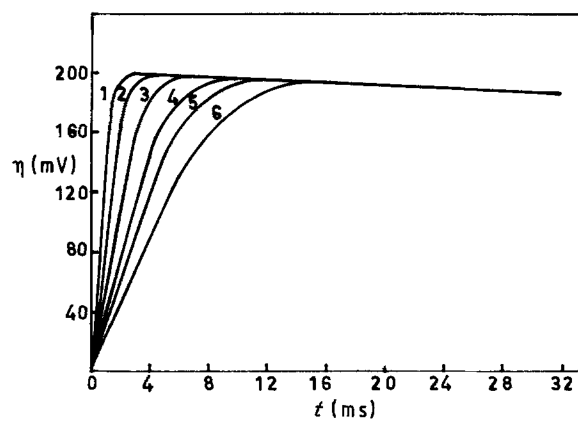

Fig. 5. Effect of C_d on η–t transients at fixed values of α = 0.5, i_{corr} = 1 × 10^{-4} A cm^{-2}, Δi = 5 × 10^{-3} A and τ = 100 ms used for simulating the transient response. (1) C_d = 30 μF cm^{-2}; (2) C_d = 50 μF cm^{-2}; (3) C_d = 80 μF cm^{-2}; (4) C_d = 120 μF cm^{-2}; (5) C_d = 150 μF cm^{-2}; (6) C_d = 200 μF cm^{-2}.

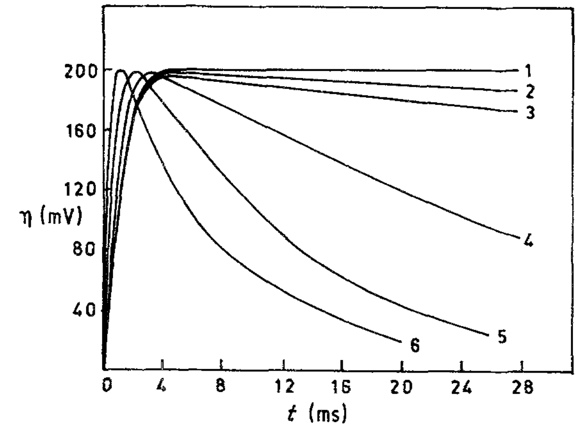

Fig. 6. Effect of Δi and τ on η–t transients at fixed values of C_d = 50 μF cm^{-2}, i_{corr} = 1 × 10^{-4} A cm^{-2} and α = 0.5 used for simulating the transient response to constant η_m (≈200 mV). (1) τ = 1000 ms, Δi = 5 × 10^{-3} A; (2) τ = 100 ms, Δi = 5 × 10^{-3} A; (3) τ = 50 ms, Δi = 5 × 10^{-3} A; (4) τ = 10 ms, Δi = 6.5 × 10^{-3} A; (5) τ = 3 ms, Δi = 1 × 10^{-2} A; (6) τ = 1 ms, Δi = 1.9 × 10^{-2} A.

4.3. *Simulation at same overpotential regime*

The tendency for η to decrease as τ decreases (cf. Fig. 1) necessitates the use of larger Δi values at low τ in order that the system passes through Tafel polarization conditions. This is acheived during experiments by manipulating both the input parameters (Δi and τ) so that nearly the same η range in the Tafel region is obtained under a given set of experimental conditions. Simulated η–t transients obtained at different Δi, τ combinations so as to give $\eta_m \approx$ 200 mV are given in Fig. 6. System parameters C_d, i_{corr} and α are assumed to be 50 μF cm^{-2}, 1 × 10^{-4} A cm^{-2} and 0.5, respectively.

The extent of the linear portion of the transient becomes smaller as τ decreases. These η–t transients are analysed by different methods for obtaining kinetic parameters and the details are given in the following section.

5. Evaluation of kinetic parameters (i_{corr} and Tafel slope)

5.1. *Intercept–slope method*

This is essentially a single transient analysis already discussed in Section 2. The method is simple and the calculation does not involve any assumptions.

The η–t transients in Fig. 6 have been analysed by this method and the results are presented in Table 1. S values of the different transients are seen to be practically constant as τ decreases from 1000 to 50 ms and thereafter it starts decreasing with decrease of τ. Correspondingly the values of α calculated from S in the τ range of 1000 to 50 ms remain constant and agree with the assumed value and deviations in the value of α from the assumed value increase with decreasing τ.

Again, i_{corr} data calculated in the τ range of 1000 to 50 ms are nearly constant and the values are in good agreement with the assumed value of 1 × 10^{-4} A cm^{-2} (within ±5%). But the data obtained from the low τ regime show that i_{corr} exhibits a decreasing trend as τ decreases and in fact at τ values of 1 and 3 ms, the situation is really worse and misleading.

The simulated results described in the foregoing paragraphs are seen to be in conformity with the experimental observations on the corrosion of metals in acids reported previously [3, 14] and discussed briefly in Section 3.

The role of dl in yielding two time domains (*viz.* τ range over which kinetic data are independent of τ and that in which kinetic data vary with τ described earlier) is revealed from the simulated data as follows. The magnitudes of both the charging and faradaic currents at typical τ in the τ regimes of interest have been computed and compared. For this purpose, taking typical τ of 1000 and 1 ms, the dl charging currents (given by $C_d\, d\eta/dt$) have been computed to be 2.5 × 10^{-6} A and 1.45 × 10^{-3} A, respectively (employing C_d = 50 μF cm^{-2} and $d\eta/dt$ taken from the simulated transients). Similarly the computation of faradaic currents [given by $i_{corr} \exp(2.3\eta/b)$] for the same system is seen to yield a value of 5 × 10^{-3} A (for assumed values of η = 0.2 V, α = 0.5 and i_{corr} = 1 × 10^{-4} A cm^{-2}). Comparison of the magnitudes of the charging and the faradaic currents at the two τ, 1 and 1000 ms reveals that they are comparable at the low τ (*viz.* 1 ms) while at high τ (*viz.* 1000 ms) the charging current is about three orders less than the faradaic current.

Now the role of τ_{el} in influencing the response characteristics of the system can be substantiated as follows using the simulated data. The τ_{el} for the simulated system works out to 12.8 ms (Section 4.1) which approximately demarcates the τ domain into the two regimes under consideration (cf. Table 1).

Table 1. Analysis of the simulated η–t transients

τ (ms)	$\Delta i \times 10^3$ (A)	Slope (S) (V)	Intercept (P) (V)	η_m (V)	t_m (ms)	η (V)	t (ms)	α (from S)	$i_{corr} \times 10^4$ A cm^{-2} Intercept–slope method	Method based on (η_m, t_m)	Method based on (η, t)
1	19	0.029	0.251	0.2048	1.25	0.161	3	0.886	0.033	1.011	1.019
3	10	0.039	0.234	0.2001	2.00	0.180	4	0.659	0.247	1.044	0.963
10	6.5	0.046	0.215	0.1980	3.00	0.178	8	0.558	0.606	1.021	0.968
50	5	0.051	0.202	0.1964	4.50	0.191	10	0.504	0.952	0.9991	0.980
100	5	0.051	0.201	0.1985	4.75	0.196	10	0.504	0.971	1.001	0.975
1000	5	0.051	0.201	0.2007	6.00	0.200	16	0.504	0.971	0.9994	0.975

It is thus clear that one should adopt τ that are higher than τ_{el} for obtaining reliable kinetic information practically free from dl charging effects. It is interesting to point out that dl interferences were not observed in the kinetic data obtained earlier for the quinone–hydroquinone system [2], obviously because the τ range employed was much higher than the τ_{el} for the system.

5.2. *Method based on* (η_m, t_m)

This method [3] is based on the basic Equation 8 which simplifies to

$$\Delta i \exp\left(-\frac{t_m}{\tau}\right) = i_{corr} \exp\left(\frac{2.3\eta_m}{b}\right) \qquad (9)$$

when the point of maximum (η_m, t_m) in the η–t transient is considered. Equation 9 can be rearranged to give

$$i_{corr} = \Delta i \exp\left[-\left(\frac{t_m}{\tau} + \frac{2.3\eta_m}{b}\right)\right] \qquad (10)$$

Thus i_{corr} can be evaluated from the knowledge of Δi and τ and experimentally measured η_m, t_m values. The value of b is derived from the slope S which corresponds to $b/2.3$. For this purpose the mean (S_{av}) of the S values that are found to be nearly independent of τ at τ greater than τ_{el}, is employed. Alternatively b can be taken from steady-state Tafel slope values available from the literature. This method is simple and makes no assumptions regarding the system.

The simulated η–t transients in Fig. 6 have been analysed and the results are presented in Table 1. It is instructive to note that at all the τ employed, the calculated i_{corr} values are in excellent agreement with the assumed value of 1×10^{-4} A cm^{-2}.

An important feature of this method of analysis is its ability to give correct values of i_{corr} even at τ less than τ_{el} due to the fact that η_m data employed in this analysis are free from dl influence. This can be easily seen from the comparative data presented in Table 1 at values of 1, 3 and 10 ms.

5.3. *Method based on* (η, t)

This is another direct method [3] based again on Equation 8 which can be rearranged to give

$$i_{corr} = \left[\Delta i \exp\left(-\frac{t}{\tau}\right) - C_d \frac{d\eta}{dt}\right] \exp\left(\frac{-2.3\eta}{b}\right) \qquad (11)$$

where (η, t) correspond to the coordinates of any point in the linear region whose S_{meas} is represented by $d\eta/dt$ in Equation 11. The b value is derived from S_{av} as described in Section 5.2. Employing the literature data or making a judicious assumption for the C_d value and with the knowledge of input parameters Δi and τ, i_{corr} can be computed with the help of Equation 11. Using this approach, η–t transients in Fig. 6 have been analysed and the data presented in Table 1. A value of $50\,\mu$F cm^{-2} for C_d has been employed in the above computations.

The calculated i_{corr} values are seen to be independent of τ and are in good agreement with the assumed value, *viz.* 1×10^{-4} A cm^{-2} at all τ employed in the study. The main advantage of this method over the one based on (η_m, t_m) is that (η, t) can be very precisely determined.

However, the need to employ C_d values from available literature or by judicious assumption may be an inherent disadvantage for this technique. To throw light on this aspect, i_{corr} values have been computed for assumed values of C_d ranging from 20 to 200 μF cm^{-2} using a typical set of data, *viz.* $\tau = 100$ ms, $\Delta i = 5 \times 10^{-3}$ A, $S = 0.051$ V, $\eta = 0.196$ V and $t = 10$ ms. The variation in values of i_{corr} computed is practically nil (0.972–0.991×10^{-4} A cm^{-2}) thereby indicating that the influence of C_d variation is negligible.

5.4 *Multi-transient analysis*

The kinetic parameters can be estimated by analysing the (η_m, t_m) data pooled from a number of transients obtained by variation of Δi and τ. This multi-transient analysis developed earlier [2] takes into account dl charging. Equation 9 can be rearranged to give

$$\eta_m = \frac{b}{2.3}\left(\ln \Delta i - \frac{t_m}{\tau}\right) - \frac{b}{2.3} \ln i_{corr} \qquad (12)$$

A plot of η_m vs $(\ln \Delta i - t_m/\tau)$ should yield a straight line whose intercept and slope will enable the calculation of i_{corr} and b.

For the model system whose C_d, i_{corr} and α are $50\,\mu$F cm^{-2}, 1×10^{-4} A cm^{-2} and 0.5, respectively, the η–t transients have been generated at different τ ranging from 1 to 1000 ms, by simulation experiments. The simulated data are subjected to the above analysis. The resulting plot of η_m vs $(\ln \Delta i - t_m/\tau)$ as shown in Fig. 7 yields a good straight line as expected. The values of α and i_{corr} obtained from the slope and intercept of the above straight line plot are 0.514 and 0.898×10^{-4} A cm^{-2}, respectively, which are in fair agreement with the assumed values, considering that the data is pooled from individual transients.

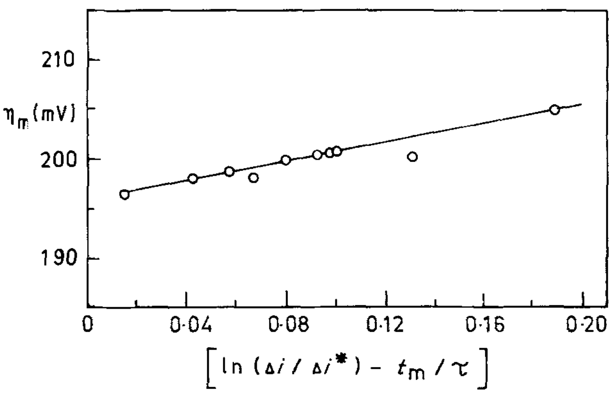

Fig. 7. Plot of η_m vs $[\ln(\Delta i/\Delta i^*) - t_m/\tau]$ based on data pooled from η–t transients simulated at fixed values of $C_d = 50\,\mu$F cm^{-2}, $i_{corr} = 1 \times 10^{-4}$ A cm^{-2} and $\alpha = 0.5$. Δi^*: dummy parameter = 0.0045 A.

The multi-transient analysis with 'pooled-up' data from ATPs obtained under varied conditions of input parameters on the same system is thus seen to be a valuable and independent method for cross-checking the kinetic data.

6. Discussion

The results (cf. Table 1) show that, for the simulated system, the two new methods of analysis which account for dl charging effects, yield constant i_{corr} values at all τ employed. On the other hand, the intercept–slope method of analysis gives constant i_{corr} at $\tau > \tau_{el}$ while at $\tau < \tau_{el}$ i_{corr} increases with increase in τ. This observation conforms to the behaviour exhibited by real corroding systems when subjected to intercept–slope analysis (cf. Section 3). Hence it is obvious that the intercept–slope analysis, which neglects dl charging effects, is mainly responsible for the trend in variation of i_{corr} with τ observed at low τ regime.

Besides, the application of the two new methods of analysis to the ATP data from real corroding systems has revealed [3] that i_{corr} remains practically constant in the high τ regime while in the low τ regime i_{corr} decreases with increase in τ. This variation of i_{corr} with τ in the low τ regime conforms to the trend of variation reported in the literature [5–13] and also discussed earlier in Section 3. Thus the intercept–slope method of analysis, which neglects dl influence, is seen to be responsible for the contradiction observed in the trend of i_{corr} variation with τ (and sweep rate).

However, it is relevant to note that the two new methods of analysis still yield a variation in i_{corr} with τ in the low τ regime for the corrosion systems while the same analysis gives, for the simulated system, constant i_{corr} values at all τ. This suggests that besides the dl influence, a possible kinetic complication arising out of the reduction of surface films may be responsible for the noted i_{corr} variation; this needs to be substantiated by further work.

7. Conclusions

Simulation studies with a model corroding system involving a faradaic charge transfer reaction and double layer (dl) charging under accelerated Tafel plot (ATP) conditions have revealed: (i) the marked influence of the dl on the calculated kinetic parameters under conditions of $\tau < \tau_{el}$ and the intercept–slope method of analysis which does not take dl charging into account, is seen to yield reliable kinetic data only at $\tau > \tau_{el}$; (ii) the two new methods of analysis based on (η_m, t_m) and on (η, t) yield i_{corr} data which are in good agreement with the assumed value at τ that are above and below τ_{el}; (iii) the multi-transient analysis based on (η_m, t_m) data pooled from a number of individual transients obtained at different (Δi, τ) combinations on a given system gives kinetic data in close agreement with those resulting from single-transient analysis, thereby providing a valuable cross-check for data analysis.

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