

CORROSION OF IRON IN SULPHURIC ACID—AN ACCELERATED TAFEL STUDY

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(Received 16 November 1981)

The system $\text{Fe}/\text{H}_2\text{SO}_4$ enjoys the unique distinction of being the most widely studied system from the point of view of understanding the kinetics and mechanism of a corroding reaction. Corrosion current measurements have been reported on this system using a variety of techniques, both electrochemical and non-electrochemical.

A new technique termed 'Accelerated Tafel plots' has been reported earlier from these laboratories which was shown to be a useful tool for the acquisition of kinetic data of slow electrode reactions rapidly and reliably. The present paper describes the results of our experimental investigations involving the application of the accelerated Tafel technique to the study of the constituent redox reactions of iron corrosion in sulphuric acid with a view to assess the potentialities of this new technique for the rapid measurement of corrosion currents.

An exponentially decaying current pulse generator coupled with a potentiostat was used to generate the galvanostatic pulses of the desired time constants (1-100m sec) that were used as input signals. Recordings of overpotential time transients (accelerated Tafel plots) were done using a Tektronix Oscilloscope with an attached camera. A three electrode cell containing the iron sample in 1N H_2SO_4 , a platinum counter electrode and a mercury-mercurous sulphate reference electrode was employed. Both cathodic and anodic transient response of the corroding system under wide potential excursion conditions has been studied as a function of pulse width of the input signal and the magnitude of the initial current of the pulse.

Results of these detailed investigations are presented and discussed in the paper.

Keywords : Corrosion; Accelerated Tafel Plot; $\text{Fe}/\text{H}_2\text{SO}_4$ System; Redox Reactions; Potentiostat; Tektronix Oscilloscope

INTRODUCTION

THE Accelerated Tafel plot (ATP) technique reported earlier from these laboratories (Prabhakara Rao & Rangarajan, 1974; and Prabhakara Rao *et al.*, 1977) constitutes a simple, reliable and rapid technique for the evaluation of the Tafel parameters (kinetic parameters) for charge-transfer controlled electrode reactions by a transient method. Corrosion systems which comprise normally of slow component redox reactions appear to be the ideal systems for the application of this ATP technique. Further ATP technique being a transient method does not seriously alter the surface

state of the electrode during the actual polarization—a draw-back associated with the steady state methods of logarithmic polarization. The present paper describes the results of our experimental investigations involving the application of the ATP technique to the study of the corrosion of iron in semimolar sulphuric acid, which are carried out to ascertain the potentialities of this new technique for obtaining the instantaneous corrosion rates. The system of iron in sulphuric acid has been chosen considering the fact that it is the most widely studied corrosion system from the point of view of obtaining the corrosion kinetic parameters by a variety of techniques as well as understanding its mechanism.

THE METHOD

The ATP method consists of applying an exponentially decaying current pulse of suitable time-constant as given by eqn. (1) to the electrochemical system and recording the resulting potential-time response on an oscilloscope screen.

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

where Δi is the initial current, and τ is the time constant of the pulse. The resulting overpotential-time (η vs. t) transient for an activation controlled reaction is given as

$$\eta = \frac{RT}{\alpha n F} \left(-\frac{t}{\tau}\right) + \frac{RT}{\alpha n F} \ln\left(\frac{\Delta i}{i_0}\right) \quad \dots(2)$$

under Tafel conditions i.e., when backward reaction's contribution to η can be neglected. The values of slope and intercept of the resulting straight line are made use of in evaluating the kinetic parameters i_0 (i_{corr} in the case of a corrosion system) and α .

EXPERIMENTAL

Iron wire of Riedel AR quality was used. The test electrode was prepared by embedding the iron wire inside a teflon sleeve attached to a glass tube. A small length of the wire of known area was exposed to the corroding electrolyte. Platinized platinum gauze electrode and a Hg/Hg₂SO₄, 0.5M H₂SO₄ electrode were used as counter and reference electrodes respectively. A typical all-glass cell (Prabhakara Rao & Rangarajan, 1973) of three electrode configuration was used. The electrolyte viz., semimolar sulphuric acid was obtained from 'Rechem' pure sulphuric acid. Electrolyte solution was deaerated with nitrogen and the experiments were carried out at 25±1 °C. The test electrodes were abraded with 1/0, 2/0, 3/0 and 4/0 emery papers, degreased with trichloroethylene, dried and then wetted with conductivity water. The electrode was immediately after the pretreatment introduced into the electrolyte solution.

The electrical circuit for generating the exponential input pulses was the same as described elsewhere (Prabhakara Rao & Rangarajan, 1974). The $\eta-t$ transients

(including both anodic and cathodic responses) were recorded on a Tektronix 535A oscilloscope with type D-plug in amplifier and camera attachment. Enlarged prints of the transients were used for data analysis.

Linear polarization resistance measurements were also carried out for the same system with a view to get comparative data on corrosion current using a steady state potentiostatic method (Fig. 1).

RESULTS AND DISCUSSIONS

As pointed out in the introduction, the ATP method is based on the analysis of slope and intercept of the $\eta-t$ linear plot traced on the oscilloscope screen. Experimental data accumulated under anodic and cathodic perturbation conditions employing pulses of different τ 's and Δi 's have revealed interesting features for the $\eta-t$ transients apart from yielding the expected linear behaviour. These are discussed below. We shall first present the cathodic polarization data, which is known (Beetge & Robinson, 1977) to give better and more consistent kinetic data for the system under consideration.

Cathodic ATP's

Good linear response of η with time was observed under varied conditions of magnitude of inputs (Δi 's) and pulse time (τ 's). Typical ATP's are seen in Fig. 2(a). Based on the measured values of slope and intercept of such transients (using eqn. 2) i_{corr} and b_c parameters have been easily evaluated. A critical analysis of the data

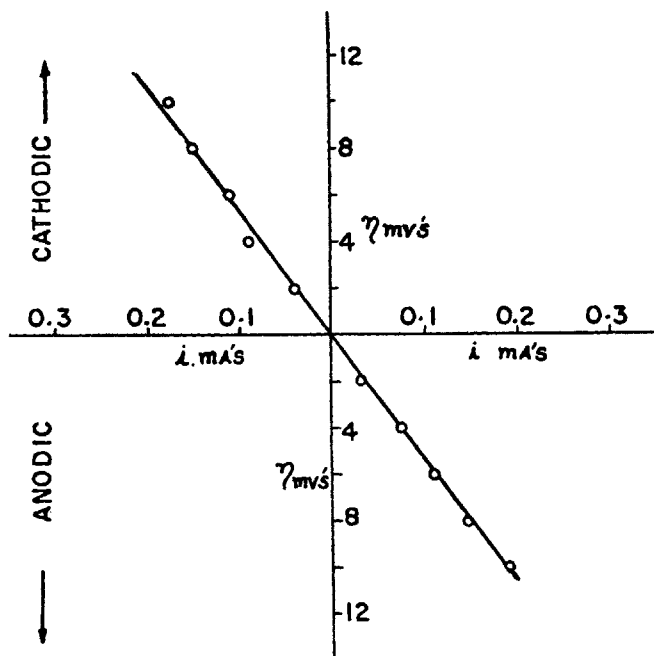


FIG. 1. Linear polarization plot for iron/semi molar sulphuric acid.

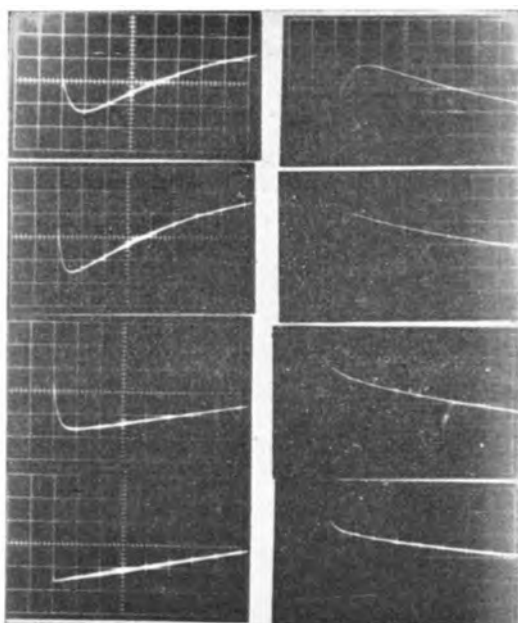


FIG. 2. ATP's for iron/semi molar sulphuric acid

| | | | |
|--------------|--|------------|--|
| (a) Cathodic | From top to bottom | (b) Anodic | From top to bottom |
| (i) | X-axis = 0.5m.sec/cm Y-axis = 50mV's/cm $\tau = 1$ m.sec. | (i) | X-axis = 0.2m.sec/cm Y-axis = 50mV/cm $\tau = 1$ m.sec. |
| (ii) | X-axis = 2.0m.sec/cm Y-axis = 50mV's/cm $\tau = 5$ m.sec. | (ii) | X-axis = 0.5m.sec/cm Y-axis = 50mV/cm $\tau = 5$ m.sec. |
| (iii) | X-axis = 2.0m.sec/cm Y-axis = 50mV's/cm $\tau = 20$ m.sec. | (iii) | X-axis = 2.0m.sec/cm Y-axis = 50mV's/cm $\tau = 20$ m.sec. |
| (iv) | X-axis = 50m.sec/cm Y-axis = 50mV's/cm $\tau = 500$ m.sec. | (iv) | X-axis = 5.0m.sec/cm Y-axis = 50mV/cm $\tau = 100$ m.sec. |

so obtained revealed a dependence of the kinetic parameters both on ' Δi ' and ' τ '. Table I presents data obtained from ATP's employing different Δi 's at constant τ (= 5m. sec) while Table II presents data on the effect of ' τ ' (keeping nearly constant $\eta_t = 0$).

From the observed dependence of both ' i_{corr} ' and ' b_e ' on ' Δi ' (Table I), it may be concluded that the reaction mechanism (hydrogen evolution in this case) probably is not same under the varied overpotential regimes that are experienced by the system when different Δi 's were used as inputs. It would therefore be of interest to study the corrosion parameters under controlled potential regime (thereby reducing the possibility of a mechanism change with potential) by this technique.

TABLE I

Effect of Δi on corrosion parameters at $\tau = 5m.sec.$

| Δi amp | slope mV/Decade | Intercept mV | i_{corr} amp/cm ² |
|--------------------------|-----------------|--------------|--------------------------------|
| 7.0071×10^{-3} | 138 | 151 | 5.8037×10^{-3} |
| 8.6731×10^{-3} | 151 | 173 | 6.3777×10^{-3} |
| 12.8381×10^{-3} | 173 | 206 | 8.4499×10^{-3} |
| 15.7781×10^{-3} | 178 | 224 | 8.9962×10^{-3} |

TABLE II

Effect of τ on corrosion parameters

| τ Milli second | Slope mV/Decade | Intercept mV | i_{corr} amp/cm ² |
|---------------------|-----------------|--------------|--------------------------------|
| 1 | 112 | 197 | 2.8266×10^{-3} |
| 5 | 155 | 195 | 5.5633×10^{-3} |
| 20 | 176 | 193 | 8.0785×10^{-3} |
| 100 | 193 | 185 | 10.9080×10^{-3} |
| 500 | 202 | 181 | 11.8654×10^{-3} |
| 2000 | 218 | 184 | 12.8131×10^{-3} |

Note: Δi values are adjusted to give nearly same over potentials at various τ 's.

This is precisely what is attempted in the results presented in Table II. Here we have incorporated the influence of ' τ ' on the corrosion parameters.

These results led us to conclude that the time of polarization (τ) has a profound influence on both ' i_{corr} ' and b_c values. It is of interest, to note that the i_{corr} value obtained from ATP using $\tau = 1m. sec.$ corresponds approximately to those obtained by the linear polarization resistance experiment. However, typically larger i_{corr} values as compared to steady state values for corrosion systems by transient techniques are reported in literature (Rajagopalan & Muralidharan, 1978). The data obtained in the present study are in conformity with the above observations.

Two points clearly emerge out from the foregoing. The cathodic Tafel regime of a corroding iron in sulphuric acid, when probed by a transient technique reveals complexity in the mechanism of hydrogen evolution and the Tafel slopes (b_c values) obtained from the transient data are variable and higher compared to steady state b_c values (viz. about 120mV's/decade). It would be of importance to understand the significance of these observations in the light of what is known about the system so far. Results obtained from steady state Tafel work involving the cathodic polarisation of Fe/H₂SO₄ rarely showed by complexity of the hydrogen evolution reaction on iron. This is apparent from the fact that most of the workers reported obtaining the theoretically expected value of $b_c \approx 120mV/decade$. However, recent work carried out employing such techniques as the impedance measurements, linear polarization experiments involving variable sweep rates and transient techniques has brought to light the complexity of the mechanism of hydrogen evolution on iron.

Epelboin *et al.* (1966) has illustrated clearly the evidence for a mechanism change with frequency of the input signal from the impedance data of a corroding iron in H_2SO_4 taken at various cathodic potential regimes. Beetge and Robinson have shown by steady state polarization experiments (using a slow sweep rate of 500mV/hour) that b_e values ranging from 175 to 240mV's can be obtained for a corroding carbon steel in sulphuric acid. The latter authors try to explain this in terms of transfer coefft. assuming value far from 0.5. These authors also report high i_{corr} values from their transient experiments. A change of charge transfer mechanism from the 'Heyrovsky' to 'Volmer' with increasing cathodic potentials was envisaged by Hackermann and Laengle (1971) from their galvanostatic polarization studies on iron in 2N hydrochloric acid.

The variation of ' i_{corr} ' with the frequency of the probing signal is revealed in a number of cases as reported by several workers. Epelboin *et al.* (1966) recommends obtaining the charge transfer resistance (R_t) from the impedance data of a freely corroding sample (iron in sulphuric acid) at high frequencies to get rid of contributions due to adsorption terms. Again Takenouti *et al.* (1979) encountered the problem of variation of ' R_p ' values with frequency of the triangular waveforms used for scanning in their linear polarization experiments which suggested clearly the need for a more complex equivalent circuit for the corroding iron in sulphuric acid. Prazak and Barton (1967) during their studies employing rectangular wave forms for obtaining the polarization resistance, observed a similar dependence on frequency of the wave form.

It can be seen from the above discussion that the results obtained in the present study are in conformity with the expectations based on a more complex scheme for the hydrogen evolution reaction. The present results obtained with varying time-constants covering varied overpotential regimes are perhaps more exhaustive in helping to illustrate the complexity. It may be remarked here that in none of the earlier works involving transient response measurements the kinetic parameters for corrosion of iron in sulphuric acid have been studied as a function of the pulse width. Finally, it is interesting to note that our observation viz., i_{corr} obtained with ATP using $\tau = 1\text{m. sec.}$ agrees closely with the i_{corr} data from linear polarization, is more akin to Epelboin's finding about the 'R.' measurement at high frequencies to obtain the true i_{corr} .

Anodic ATP's

Fig. 2(b) given typical $\eta-t$ transients for various τ 's (1, 5, 20, 100m seconds). In contrast to the cathodic ATP's, linearity of the $\eta-t$ could be obtained only at low time-constants for the input signal ($< 5\text{m sec}$) as can be seen from the figure. At these τ 's the ATP's allow us to compute the i_{corr} and b_a values by the usual intercept-slope method. Values of i_{corr} so obtained are found to be considerably higher than those obtained from the cathodic ATP's. The b_a values are found to be higher compared to the steady state values reported in the literature. Comparative data on i_{corr} from cathodic, anodic ATP's and linear polarization resistance method are given in Table III.

TABLE III
Comparison of i_{corr} , in amp/cm²

| From linear polarization method | From accelerated Tafel plot at $\tau = 1\text{m. sec.}$ | |
|---------------------------------|---|-------------------------|
| | Cathodic | Anodic |
| 2.0933×10^{-3} | 2.8266×10^{-3} | 1.9823×10^{-3} |

The important aspect to be noted however from the anodic ATP's is that the mechanism of dissolution of iron in sulphuric acid is shown to involve a more complicated scheme. This can be inferred from the absence of a simple linear plot of $\eta-t$ at τ 's greater than 5m sec. (see Fig. 2(b)). The indication of a more complex mechanism operating for iron dissolution from ATP's is fully in accordance with the observations of various authors who studied this system critically using a variety of experimental techniques in recent years. Essentially, the occurrence of consecutive electron transfer reactions with the possible participation by the adsorbed intermediates has been identified as the source for yielding the complicated mechanism by a number of workers including Epelboin *et al.*(1975), Lorenz *et al.*(1971) and Bech-Nielsen (1975), Kolotyркиn *et al.* (1967) have reviewed the results of anodic polarization of iron both by steady state and non steady state methods and comment on the reported divergence of b_a values over a wide range, attributing this to a complicated mechanism during anodic polarization, arising out of experimental conditions such as, electrode surface, its structure and pretreatment and electrolyte composition.

CONCLUSION

From this study, the following conclusions may be drawn :

1. Good ATP's showing the expected linear response of η with time over the entire range of τ 's studied are obtained in the cathodic polarization of iron in semi-molar sulphuric acid.
2. Values of i_{corr} obtained from cathodic ATP's approach the i_{corr} value obtained from steady state linear polarization data only under $\tau = 1\text{m sec.}$ conditions.
3. Variation of kinetic parameters with τ and η suggest a more complex mechanism, rather than a simple charge transfer reaction for the evolution of hydrogen on iron.
4. The anodic ATP's do yield a linear response of ' η vs. t ' under very restricted conditions viz., at time constants less than 5m sec and the i_{corr} obtained under these conditions turns out to be higher compared to the value obtained from cathodic ATP's.
5. The anodic ATP's obtained with $\tau > 5\text{m sec}$ by their very nature suggest a complicated mechanism for the anodic dissolution of iron.

6. All the above conclusions find support from the experimental data collected by other workers who investigated the Fe/H₂SO₄ system by different techniques in recent years.

ACKNOWLEDGEMENT

The authors express their sincere gratitude to Dr H. V. K. Udupa, Director for his permission to carry out these investigations and his keen interest.

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Discussion

V. S. BAGOTSKY (*The Institute of Electrochemistry of the Academy of Sciences of USSR, Moscow*): In your experimental conditions $\Delta\varphi$ changes linearly with time, i.e. $\frac{d\Delta\varphi}{dt}$ const. and the charging current does not diminish with time. Is there a possible effect on the measured Tafel-slope?

G. PRABHAKARA RAO: It is true that the charging current does not get entirely eliminated with time. However, the magnitude of this quantity could be computed accurately and an estimate of its influence could be arrived at easily. This will be done by us.

HIRA LAL (*Indian Institute of Technology, Bombay*): What is the surface treatment given to your electrodes before the experiment?

G. PRABHAKARA RAO: The electrodes are degreased with Trichlore-ethylene washed and used. Stable and reproducible open circuit potentials are obtained and are used as criteria for starting the polarization work.