

## SMALL AMPLITUDE CYCLIC VOLTAMMETRY—A TECHNIQUE FOR SCREENING PICKLING INHIBITORS

G DEVARAJAN

Sri Paramakalyani College, Alwarkurichi-627 412

and K BALAKRISHNAN

Central Electrochemical Research Institute, Karaikudi-623 006

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In this paper the usefulness of small amplitude cyclic voltammetry (S.A.C.V.) for the evaluation of acid inhibitors for mild steel in three different acids, viz. hydrochloric, sulphuric and perchloric acids has been examined in terms of the role played by scan rate and the number of cycles. The results are compared with those obtained by Tafel extrapolation methods and weight loss method. A number of aromatic aldehydes, furfuraldehyde and crotonaldehyde have been studied.

**Key Words:** Small amplitude cyclic voltammetry, mild steel, acid inhibitor, Tafel extrapolation, double layer capacitance

## INTRODUCTION

Among the various electrochemical methods 'Linear polarisation method' has been used widely to investigate the corrosion mechanism. This method has also been used to screen various acid inhibitors. Cyclic voltammetric studies have also been used for estimating polarisation resistance at corrosion potential [1] and also for determining corrosion rates in presence of inhibitors [2]. The small amplitude cyclic voltammetry (SACV) is used extensively in corrosion research for estimating polarisation resistance of a metal solution interface [3]. In this technique a triangular voltage of 10-20 mV peak-to-peak is imposed on the corroding electrode and the current response is recorded for one or more cycles. The slope of current-voltage curve  $\Delta E / \Delta I$  at the corrosion potential is used for estimating the polarisation resistance. Nonlinear response in the current-voltage curves has been reported and discussed [3]. The hysteresis in the current vs potential curves in SACV has recently been analysed in terms of the impedance of an equivalent electrical circuit [4]. It is shown that the degree of hysteresis is sensitive to the potential sweep rate, and that the observed current response can be used to estimate values for the resistances and capacitances at the interface. A similar mathematical approach to the relationship between the electrode impedance and the response to the linear disturbance has been attempted [5]. A simple and yet elegant Fourier synthesis approach to the problem of SACV was reported [6].

In the present work small amplitude voltammograms have been recorded for mild steel in different acids like HCl, H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> with and without aldehydes as inhibitors. Polarisation resistance and double layer capacitance have also been calculated [4]. Linear sweep voltammetry has been employed for calculating corrosion currents in these media by Tafel extrapolation method.

## EXPERIMENTAL

Mild steel specimens of 3 × 1 × 0.04 cm were spot welded to steel rods. The specimens were masked with araldite exposing 1 cm<sup>2</sup> area only. The exposed area was polished with 1/0, 2/0, 3/0 and 4/0 emery papers successively degreased with trichloroethylene and used.

The SACV measurements were performed using a low current potentiostat incorporating a summing amplifier to increase the

accuracy. A voltage scan generator in conjunction with a X-Y recorder was used. The circuit diagram of SACV set up is shown in Fig. 1.

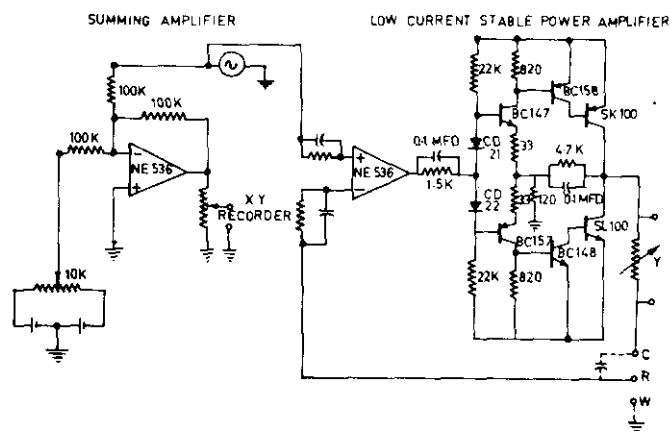


Fig. 1: Circuit diagram for SACV set up

The potentiostat was tested using a dummy cell containing a parallel combination of a capacitance (500  $\mu$ F) and a resistance 350 ohms) with a series resistance of 10 ohms. The current-voltage characteristics of the dummy cell for various scan rates are shown in Fig. 2.

The specimens were introduced into the acid solution (with or without inhibitors) which was previously deaerated with nitrogen. After keeping in the acid solution with continuous deaeration, the potential was adjusted to zero current and a triangular scan of -10 mV to +10 mV was applied and the current voltage curves were recorded. During recording nitrogen atmosphere was maintained over the solution.

Linear sweep voltammetric studies were carried out in both anodic and cathodic regions from corrosion potential independently at a sweep rate of 200 mV/min. These results were made use of for plotting the polarisation characteristics and for

calculating the corrosion current by extrapolation of Tafel lines.

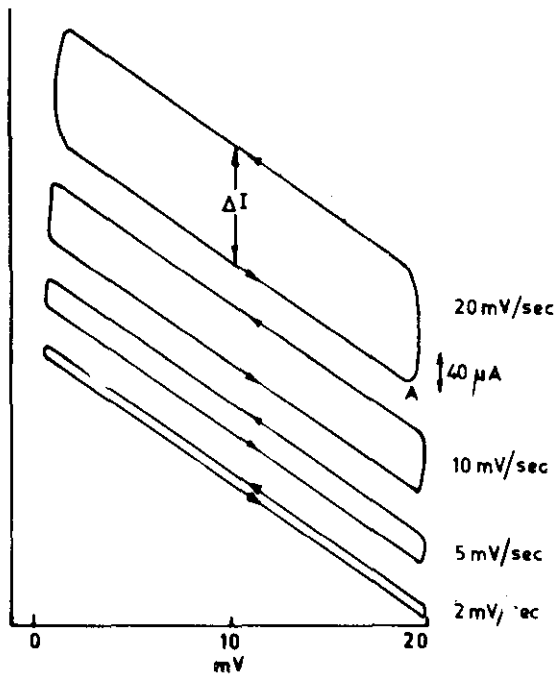


Fig. 2. Cyclic voltammograms for the electrical equivalent circuit shown in Fig. 1 (a) as a function of voltage sweep rate.  $R = 10\Omega$ ;  $R = 350\Omega$ ;  $C = 500\mu\text{f}$ ;  $E_m = 20\text{mV}$

### RESULTS AND DISCUSSION

The typical current-voltage behaviour of mild steel in acid solution is shown in Fig. 3.

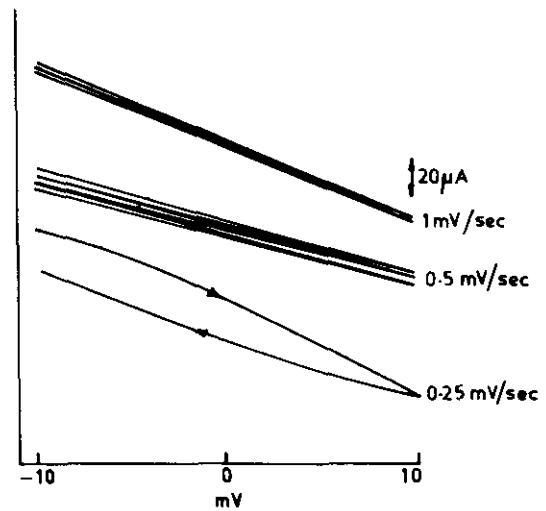
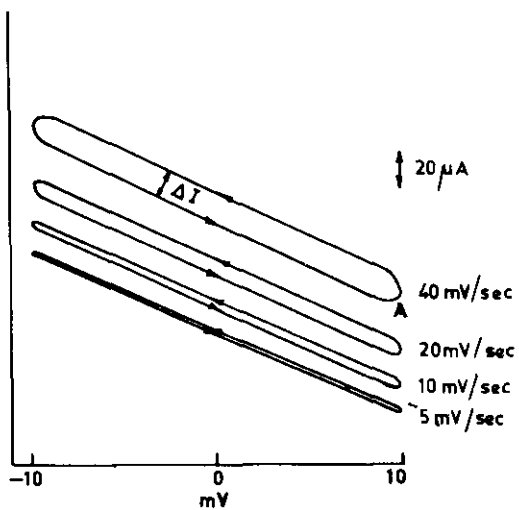
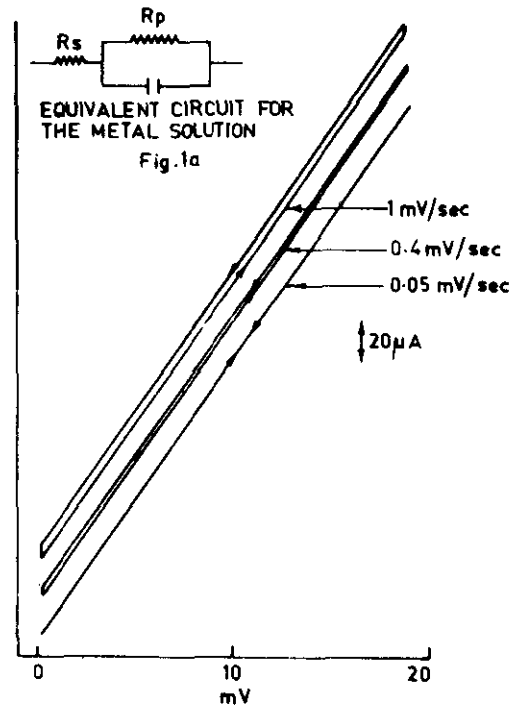


Fig. 3: typical small amplitude cyclic voltammograms for mild steel in 0.5N acid solution

When these voltammograms are compared with that of the dummy cell, the differences in the salient features are quite clear. The voltammograms of the dummy cell are more or less parallelograms with sharp changes in current at the reversal points, i.e. they show exponential type of relaxation phenomenon at the start of the scans

in both directions. Moreover, the only difference that can be observed with voltammograms at different scan rates is the decrease in hysteresis current with decrease in scan rate. At very low scan rates the hysteresis current becomes negligibly small and the forward and reverse voltammograms superimpose to form a straight line.

The voltammograms of the metal/acid system on the other hand have more or less an elongated elliptical shape without sharp changes in current at scan reversal points even at higher scan rates. In many cases at and below 1 mV/sec. the current direction is changed and the corrosion potential also gets shifted with reverse sweep at every cycle. The shift increases with decrease in scan rate. In presence of aldehydes also similar behaviour is observed with decrease in magnitude of current. The hysteresis current also decreases with the addition of aldehydes.

The peculiar behaviour observed in the system of mild steel in acid solution is the change in corrosion potential at lower scan rates below 1 mV/sec during the reverse scan of first cycle and the subsequent cycles. So the completion of hysteresis loop at applied potential limit is not observed. The shift in corrosion potential may be attributed to the surface changes taking place due to active dissolution of mild steel in acid. The similar type of behaviour is also observed in presence of aldehydes but the shift in the corrosion potential is on the negative side uniformly.

#### Effect of scan rate on the slope of the current-voltage curve

The slope of the current voltage curve is not changed very much with scan rate. But considerable change in the slope of current-voltage curve with scan rate has been reported in the case of Cu-Ni alloy in sea water and stainless steel in sodium fluoride solution. The results obtained were confirmed by repeating the experiments in the present experimental set up for stainless steel in sodium fluoride solution [7]. Hence, it is to be concluded that the dependence of the slope of E-I curve on the scan rate varies with the system.

#### Comparison of corrosion currents obtained by different methods

In order to determine the utility of SACV for measuring corrosion rate, first the linear polarisation resistance of mild steel in pure acid and in presence of different concentrations of aldehydes have been calculated by determining the slope of current-voltage curve ( $\Delta E / \Delta I$ ) at the lowest scan rate of 0.05 mV/sec. At this lowest scan rate, a steady state can be assumed and the polarisation resistance can be considered as equal to true d.c. polarisation resistance.

Secondly, in order to obtain the true polarisation resistance values, the  $R_p$  values (calculated from the first cycle forward scan) are plotted against scan rate and extrapolated to zero scan rate and the true polarisation resistance at zero scan rate is taken for the calculation of corrosion current.

Thirdly, the  $1/R_d$  values ( $R_d$  is the diagonal resistance) for scan rates 40, 20, 10 and 5 mV/sec are plotted against scan rate and extrapolated to zero scan rate and the  $1/R_d$  value at zero scan rate is taken as  $1/R_p$  assuming  $1/R_s$  (solution resistance) as negligible in highly conducting solutions in the equation  $\frac{1}{R_d} = \frac{1}{R_p + R_s}$ . The true polarisation resistance values determined by extrapolation methods are calculated for pure acid containing 10 mM of inhibitor for comparison. Invariably for pure acid solutions the extrapolation of  $R_p$  to zero scan rate

gives higher values than the other two methods. In presence of 10 mM aldehydes, currents obtained by all the three methods are almost the same in most of the cases. This may be due to very slight change in the slope of current voltage curve with scan rates. In systems where there is large change in slope with scan rate the extrapolation of  $1/R_d$  values to zero scan rate may give better values than the other two.

#### Measurement of double layer capacitance

The hysteresis current observed is used to calculate the double layer capacitance using the relation

$$\Delta I = \frac{2 R_p^2 C}{(R_p + R_s)^2}$$

where  $\Delta I$  is the hysteresis current. At highly conducting solutions  $R_s$  will be small and can be neglected compared to  $R_p$  and  $\Delta I$  will be equal to  $2C$  where  $C$  is the capacitance of the double layer. The capacity values (Table-I) are considerably decreased by the addition of aldehydes although the decrease is not proportional to their inhibition efficiencies. The decrease in capacity values indicate the absorption of aldehydes on iron surface. It may be seen that the capacity values are considerably larger indicative of pseudo capacitance. However, these values agree fairly well with the values obtained by charging technique [8]. The higher values for corroding systems have also been reported for Cu/Ni alloy in seawater [9].

Table I: Double layer capacitance ( $\mu\text{F}/\text{cm}^2$ ) of mild steel in 0.5N acids containing 10 mM aldehydes calculated by SACV method

Aldehydes	HCl	H <sub>2</sub> SO <sub>4</sub>	HClO <sub>4</sub>
Blank	172	166	128
Benzaldehyde	106	200	93
Salicylaldehyde	117	73	100
p-Hydroxybenzaldehyde	142	145	66
o-Tolualdehyde	82	114	66
p-Tolualdehyde	126	113	80
Anisaldehyde	113	153	75
Vanillin	145	133	106
Cinnamaldehyde	128	53	50
Crotonaldehyde	120	133	93
Furfuraldehyde	121	113	106

#### Linear sweep voltammetry

From the polarisation behaviour of mild steel in acid and acid containing inhibitors it is observed that the corrosion potential in HCl and HClO<sub>4</sub> are shifted to more positive values in presence of inhibitors indicating anodic polarisation. On the other hand in H<sub>2</sub>SO<sub>4</sub> the shift of corrosion potential to more negative values indicates cathodic polarisation. At high anodic potentials all aldehydes show depolarisation. In HCl and HClO<sub>4</sub> the anodic Tafel slopes are not changed very much in presence of aldehydes. But in H<sub>2</sub>SO<sub>4</sub>, significant changes in anodic Tafel slopes are noted. However, the values of cathodic Tafel slopes do not change in presence of aldehydes. The corrosion currents calculated by

extrapolation of Tafel slopes indicate that in presence of aldehydes the corrosion currents are reduced considerably in all the three acids.

#### Comparison of SACV with other methods

The corrosion rates of mild steel in various acids obtained by SACV, and linear sweep voltammetric method are compared with weight loss method (for 30 minutes) duration in Table II.

Table II: Comparison of corrosion rates of mild steel ( $\mu\text{A}/\text{cm}^2$ ) calculated by different methods in 0.5N acids

Time: 30 Min.

Temp.:  $30 \pm 2^\circ\text{C}$

Acid	Weight loss	Tafel extrapolation	LPR	SACV
<i>Deaerated</i>				
HCl	408.0	120.0	65.4	66.2
H <sub>2</sub> SO <sub>4</sub>	288.0	220.0	145.0	147.0
HClO <sub>4</sub>	216.0	100.0	107.0	110.0
<i>Aerated</i>				
HCl	414.0	—	—	—
H <sub>2</sub> SO <sub>4</sub>	366.0	—	—	—
HClO <sub>4</sub>	342.0	—	—	—

The equivalent corrosion current density obtained from weight loss method in 3 to 5 times higher than the values directly obtained by other two methods. This may be due to the fact that the weight loss method is the average value over the duration of 30 minutes and includes the effect of changes in the true area of the surface. The electrochemical methods give instantaneous value only.

It may be further seen that the electrochemical method indicates that the sulphuric acid is more corrosive than hydrochloric acid as indicated by the higher corrosion currents. This is in contradiction with the results obtained by weight loss method. This difference in HCl and H<sub>2</sub>SO<sub>4</sub> is reflected in the values of linear polarisation resistance indicating that it is not due to the change in the values of Tafel slopes assumed in the calculation

Table III: Comparison of inhibition efficiencies of 10 mM aldehydes in 0.5 N acids calculated by different methods

Aldehydes	Weight loss			Polarisation			L.P.R.			$R_p \rightarrow 0$			$\frac{1}{R_d} \rightarrow 0$		
	HCl	H <sub>2</sub> SO <sub>4</sub>	HClO <sub>4</sub>	HCl	H <sub>2</sub> SO <sub>4</sub>	HClO <sub>4</sub>	HCl	H <sub>2</sub> SO <sub>4</sub>	HClO <sub>4</sub>	HCl	H <sub>2</sub> SO <sub>4</sub>	HClO <sub>4</sub>	HCl	H <sub>2</sub> SO <sub>4</sub>	HClO <sub>4</sub>
Benzaldehyde	36	47	47	22	41	64	50	51	64	51	52	64	52	21	58
Salicylaldehyde	33	34	41	25	48	63	41	63	60	40	76	60	30	77	58
p-Hydroxybenzaldehyde	61	50	60	73	43	70	37	31	47	37	20	46	31	13	30
o-Tolualdehyde	72	53	58	77	—	65	67	67	73	67	68	74	68	66	69
p-Tolualdehyde	62	62	58	58	48	85	52	67	76	53	67	76	53	49	75
Anisaldehyde	74	66	60	73	36	81	48	35	68	48	31	68	54	41	71
Vanillin	71	51	48	50	41	61	22	48	60	43	47	62	40	47	49
Cinnamaldehyde	94	84	88.5	73	71	80	54	84	87	50	84	87	57	86	84
Crotonaldehyde	78	55	52	15	23	44	33	44	49	32	46	61	49	49	50
Furfuraldehyde	48	56	48	17	55	32	37	48	50	37	46	55	43	49	44

of corrosion current. The order of corrosivity is also tested by repeating the experiments in air saturated solution using corrosion console (EG and G PARC Model 350-A Console). This also indicates higher corrosivity for sulphuric acid than hydrochloric acid. The difference in the order of corrosivity between weight loss method and electrochemical method are difficult to explain.

The inhibition efficiencies of 10 mM aldehydes determined by different methods are compared in Table III. In sulphuric acid solutions also weight loss shows higher efficiency except in salicylaldehyde and ortho and para tolualdehydes. In perchloric acid solutions electrochemical methods show higher efficiency than weight loss methods.

Interestingly cinnamaldehyde which gives the maximum inhibition efficiency in the weight loss method gives a considerably lower efficiency in HCl in electrochemical methods. However cinnamaldehyde shows higher inhibition efficiency only over longer duration tests. This is interpreted as due to the fact that the inhibition by cinnamaldehyde is mainly caused by the slow formation of film on the surface. Since the time involved in electrochemical measurements is comparatively small, inhibition efficiency is low due to incomplete coverage of the surface by the film. The fact that a film consisting of a new type of corrosion product incorporating cinnamaldehyde has been formed, is confirmed by visual and IR spectra also.

#### CONCLUSION

SACV method is a simple elegant method for studying corrosion systems. In addition to polarisation resistance values, it is also possible to calculate the capacitance at metal solution interface from the hysteresis current. SACV method can be satisfactorily used for screening inhibitors in acid medium. The advantage of SACV method over Tafel extrapolation method is that it involves less perturbation of electrode surface. Calculation of capacitance from hysteresis current for metal in acid solutions has to be taken with some reservation since adsorbed hydrogen on the metal surface can also give rise to hysteresis. With all the above said facts SACV is a useful technique for corrosion research with its experimental simplicity and for many systems the SACV response at low voltage sweep is almost entirely resistive in character.

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