SHORT COMMUNICATIONS

MEASUREMENT OF CORROSION RATE AND DOUBLE-LAYER CAPACITY BY LARGE AMPLITUDE EXPONENTIAL RELAXATION TECHNIQUE

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PRABHAKARA Rao and Rangarajan[1] have shown that the potential-time $(\eta - t)$ transient obtained by impressing an exponentially decaying current of sufficiently large magnitude to an electrochemical system corresponds to an accelerated Tafel plot. They applied this technique to the system, hydroquinone-quinone/Pt and demonstrated that this method can be successfully used for the determination of kinetic parameters. This technique was applied to corrosion rate (i_{corr}) measurement by Prabhakara Rao and Yegnaraman[2]. However, their results showed that the measured i_{corr} was dependent on τ.

In this communication we show that this method can be used to measure i_{corr}, Tafel slopes and $C_d(E)$ of the corrosion systems under activation control.

When a current input of the form $\Delta I \exp(-t/\tau)$, where ΔI is sufficiently large to keep the system in the Tafel region, is applied to a corrosion system under activation control, the resulting current-potential relationship can be shown to be,

$$i = \Delta I \exp(-t/\tau) = -C_d \frac{d\eta}{dt} + i_{corr} \exp(-2.303\eta/b_c)$$

(1)

or

$$i = \Delta I \exp(-t/\tau) = -C_d \frac{d\eta}{dt} - i_{corr} \exp(2.303\eta/b_a),$$

(2)

where b_c and b_a are Tafel slopes of cathodic and anodic reactions of the corrosion system. If the charging current $(= -C_d(d\eta/dt))$ is zero, then (1) and (2) become

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*Ref. 6 gives a similar equation in a different context.

Tafel relations. Under such conditions $\eta - t$ transient will be a straight line and an accelerated Tafel plot is obtained. However, charging current is generally not negligible except when τ is very large compared to the time required for charging the double layer. Even under conditions where double-layer charging current cannot be neglected, it can be easily corrected for corrosion systems under activation control by using the elegant approach suggested by Rangarajan[1,3].

When charging and activation are both present, $\eta - t$ transient exhibits a maximum. At t_{max}, the current is entirely faradaic because $(d\eta/dt)$ is zero at that instant. Hence a Tafel plot uncorrupted by double-layer charging can easily be got by using the η_{max} and i at t_{max} of several transients obtained by varying ΔI keeping τ constant. Getting i_{corr}, b_a and b_c from the Tafel plot is straightforward.

A second approach is to correct a single transient for double-layer charging by the procedure described below. At each η value, the total current is equal to the sum of faradaic current (i_F) and non-faradaic current (i_{nF}). For every η (excepting η_{max}) there are two values of current; one in the rising portion (i_{t1}) and another in the falling portion (i_{t2}). However, i_F will be the same both in the rising and falling portions at constant η. Therefore it is easy to show that

$$(i_F)_{t1} = (i_{t1}) + C_d(d\eta/dt)_{t1},$$

(3)

where

$$C_d = \frac{(i_{t2}) - (i_{t1})}{(d\eta/dt)_{t1} - (d\eta/dt)_{t2}}.$$

(4)*

At each η, i_F can be calculated by (3). By plotting these values of i_F against the corresponding values of η in the semilog paper, i_{corr} and Tafel slopes can be found. Incidentally, $C_d = f(E)$ is recovered from (4).

Employing the system, mildsteel in 1N sulphuric acid (deaerated) and using a measurement set up consisting of galvanostat and transient data recorder[4] the conclusions drawn above were verified.

The values of i_{corr} obtained after correcting for charging current by multitransient and single transient methods are shown in table 1 and are in good agreement with the steady-state logarithmic polarization value. It is clear from the present result that double-layer charging current correction leads to the measurement of true corrosion rate. No variation of

Table 1 I_{corr} of MS in $1N$ H_2SO_4 (deaerated) obtained at various τ values after correcting for double-layer charging current

	τ (m sec)	i_{corr} cathodic polarization (mA/cm^2)	i_{corr} anodic polarization (mA/cm^2)	b_c (mV)	b_a (mV)
Method 1	1	1.45	1.30	93	76
(by using η_{max}	10	1.40	1.35	96	83
and i at t_{max};	100	1.40	1.35	99	83
multitransient	500	1.40	1.30	99	76
method)	1000	1.35	1.35	99	83
Method 2	5	1.40	1.40	103	83
(using single	7.5	1.50	1.40	103	86
transient corrected for	10	1.40	1.45	96	86
double-layer charging)	50	1.40	1.40	96	83

Note: Steady-state logarithmic polarization data i_{corr} (from cathodic and anodic Tafel plots) = 1.35 mA/cm^2; b_c = 96.3 mV; b_a = 83 mV.
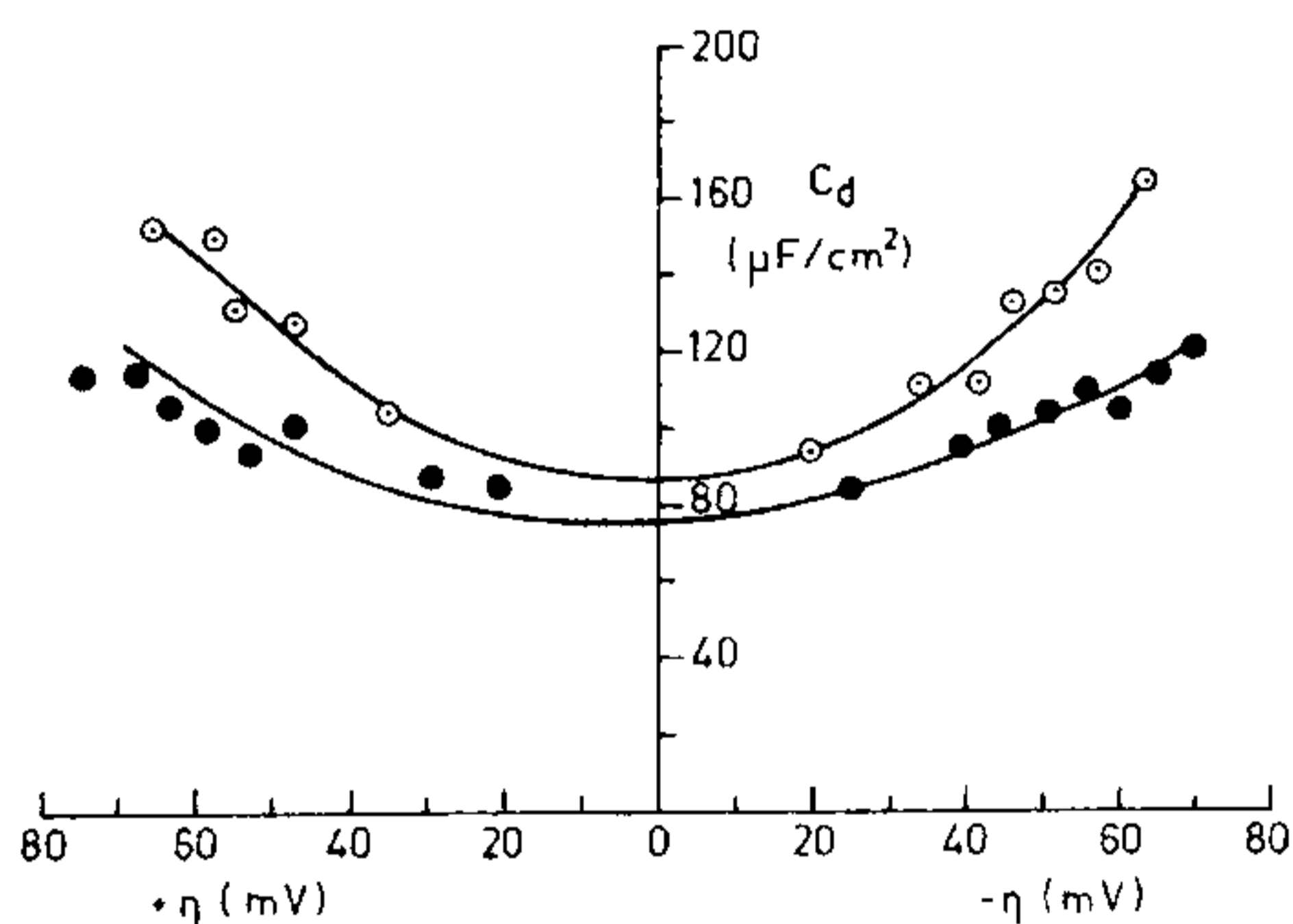

Figure 1. Variation of C_d with overpotential for MS in $1N$ H_2SO_4 (deaerated) with and without hexamine inhibitor. o without inhibitor; • with 10 mM hexamine inhibitor.

i_{corr} with τ is seen. Obviously, the results obtained by Prabhakara Rao and Yegnaraman[2] showed variation of i_{corr} with τ essentially due to the neglect of double-layer charging current.

A plot of C_d vs η for MS in $1N$ H_2SO_4 (deaerated) obtained from a single transient recorded at τ = 50 m sec is shown in figure 1. The effect of adding hexamine (10 mM) as inhibitor is also shown in the same figure. The decrease in double-layer capacity brought about by the adsorption of the inhibitor is evident from the plot.

The value of i_{corr} obtained with a single $\eta - t$ transient at τ = 50 m sec with and without inhibitor is shown in table 2. The values obtained by the two methods show an excellent consistency.

Since C_d is proportional to area it is possible to measure changes in the area of corroding system with time by this technique. Figure 2(a) shows corrosion rate of MS in $1N$ H_2SO_4 as a function of time. It is seen that the corrosion rate increases with time. A similar trend was reported by Mansfeld[5] for the system of iron in $1N$ H_2SO_4. We investigated to find out whether such an increase is due to change in area of the electrode with time. From figure 2(b) it can be seen that C_d increases by about 20% showing that the area changes only by 20% in 3 hr. However, the corrosion rate increases by nearly three times during the same period. From this it is evident that increase in corrosion rate cannot be solely attributed to increase in area.

The exponential relaxation which was called as accelerated Tafel plot by Rangarajan and Prabhakara Rao[1] can be considered as nonlinear relaxation technique as distinct from linear relaxation technique[3]. It has been demonstrated in this paper that the exponential nonlinear relaxation technique can be used for corrosion systems under activation control to get (i) corrosion rate and Tafel slopes (ii) C_d values as a function of potential and (iii) area changes with time of corrosion systems. It is shown that the correction for double-layer charging is essential to obtain true corrosion rate. Such a correction can be accomplished easily. Neglecting the charging current contribution could

Table 2 *Corrosion rates of MS in 1N H_2SO_4 (deaerated) obtained from single and multitransient methods with and without hexamine inhibitor $\tau = 50\,msec$*

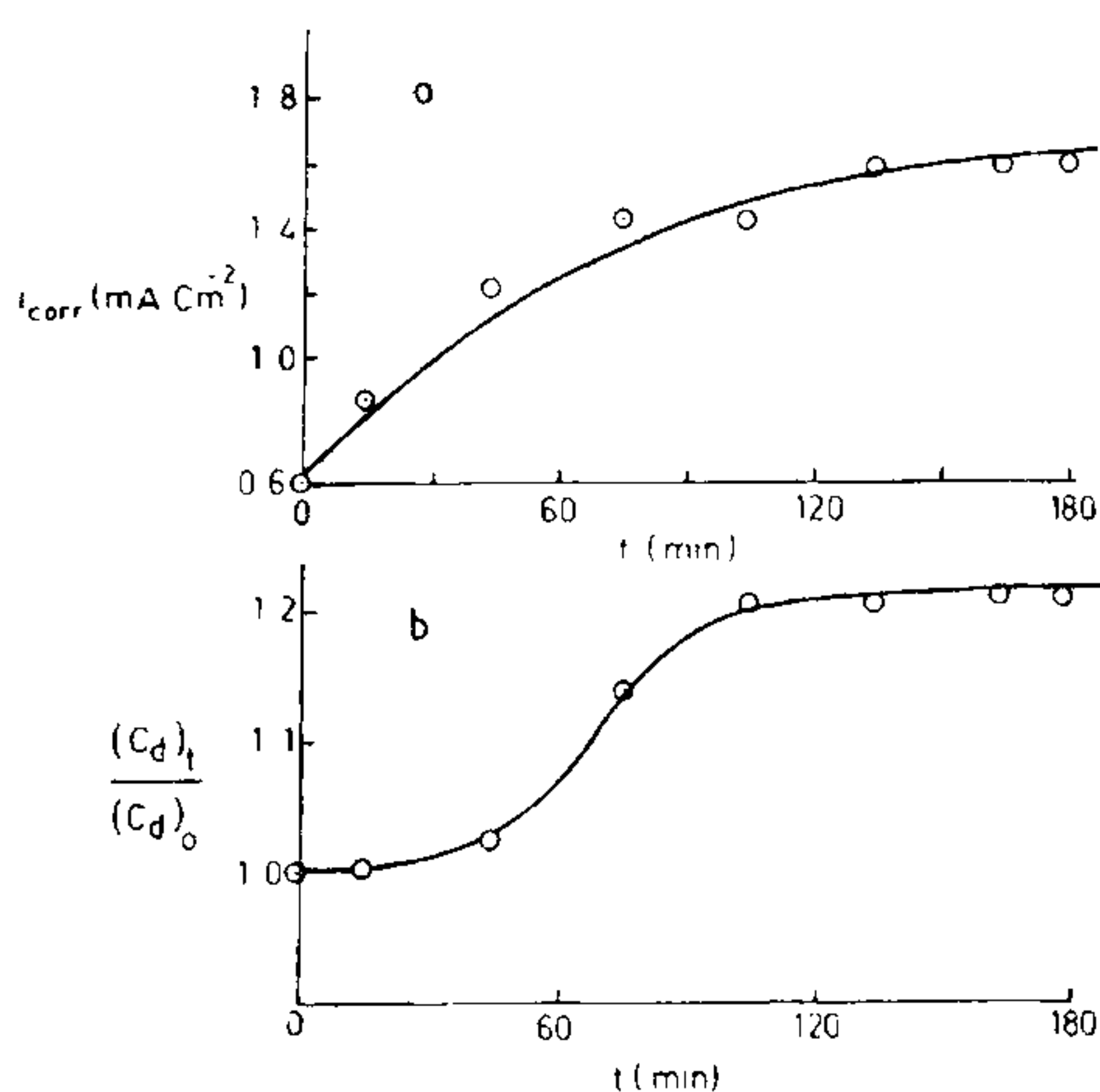|	I_{corr} (mA/cm^2)			
	Single transient method		Multitransient method	
Concentration of hexamine (mM)	Cathodic polarization	Anodic polarization	Cathodic polarization	Anodic polarization
0	1.393	1.428	1.428	1.428
10	0.385	0.385	0.385	0.400

Figure 2. Time dependence of (a) i_{corr} and (b) area of the electrode.

lead to such artefacts as variation of i_{corr} with time constant τ.

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EFFECT OF PHOTOPROTECTION OF UV IRRADIATED *ESCHERICHIA COLI* ON THE INDUCTION OF L-ARABINOSE ISOMERASE

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It was reported from this laboratory that catabolite repression mediated via cyclic AMP is partially responsible for causing the inhibition of L-arabinose isomerase induction in *Escherichia coli* B/r irradiated with UV light[1,2]. It was also shown that the enzyme synthesizing system is released from UV light induced catabolite repression when the cells recover from the damage[3]. Swenson[4] showed that illumination of cells by near UV light prior to far UV irradiation protected them from the inhibition of β-galactosidase induction. The aim of the present study was to find out whether similar photoprotective effect is observed in L-arabinose isomerase synthesizing system.

L-arabinose isomerase was induced and assayed in the same way as described earlier[5]. The methods of tris-EDTA treatment of the cells and UV light irradiation have also been described previously[2]. Before irradiating with 540 ergs/mm^2 of UV light (peak output at 254 nm) at room temperature, tris-EDTA treated cells in minimal medium containing casamino acids (0.025%) were held at 5°C and il-