SHORT COMMUNICATIONS

MEASUREMENT OF POLARIZATION RESISTANCE AND DOUBLE-LAYER CAPACITY OF CORROSION SYSTEM BY EXPONENTIAL LINEAR RELAXATION TECHNIQUE

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AN exponential linear relaxation technique for measurement of kinetic parameters of electrochemical systems was proposed by Rangarajan[1]. It was demonstrated that this method could be used to measure the double-layer capacitance as well[2]. In this paper we show that this linear relaxation technique can be used to measure the polarization resistance and double-layer capacitance of corrosion systems.

When an exponentially decaying current input of a small magnitude is applied to a corrosion system which is purely under activation control, the linearized current-potential relationship takes the form,

$$-C_d\frac{d\eta}{dt}-\frac{(\alpha_c+\beta_a)nF\eta\, i_{corr}}{RT}=i=\Delta I\exp(-t/\tau), \quad (1)$$

where $\Delta I\exp(-t/\tau)$ represents the current input, C_d is the double-layer capacitance of the corrosion system, α_c and β_a are respectively the transfer coefficients of the cathodic and anodic conjugate reactions of corrosion and i_{corr} is the corrosion rate.

The solution of (1) is given by,

$$\eta=\frac{\Delta I R_p\tau_d}{(\tau_d-1)}[\exp(-t/\tau)-\exp(-\tau_d t/\tau)] \quad (2)$$

where $R_p=\dfrac{RT}{(\alpha_c+\beta_a)nF\, i_{corr}}$ and $\tau_d=\dfrac{\tau}{R_pC_d}$.

It can be seen from (2) that the potential-time transient exhibits a maximum. This is essentially due to a time lag in overpotential (η) following current (i). For a corrosion system under activation control, the double-layer charging current ($= -C_d(d\eta/dt)$) is zero at the maximum point and the entire current is purely faradaic. Utilising this fact it can be shown,

$$R_p=\frac{-\eta_{max}}{\Delta I\exp(-t_{max}/\tau)} \quad (3)$$

where η_{max} and t_{max} are the co-ordinates of the maximum of $\eta-t$ transient.

For the same case, it can be shown from (2) that

$$(t_{max}/\tau)=\ln\tau_d/(\tau_d-1). \quad (4)$$

It is clear that using (3) and (4) R_p and C_d can be obtained from a single transient for a corrosion system which is under activation control.

A second method of getting R_p and C_d would be by fitting a curve, represented by (2), to the experimental data. A third method of obtaining R_p, is to plot η_{max} against i (corresponding to t_{max}) and evaluate $d\eta/di$ ($= R_p$). This method is a multitransient approach in contrast to the other two which employ only a single transient. It can be seen that all the three methods yield R_p values uncorrupted by double-layer charging.

The above expectations were verified by using the system, mildsteel (MS) in 1N sulphuric acid (deaerated), employing a galvanostat to impress the exponential current signal and recording the $\eta-t$ transient on a specially designed transient data recorder[3] the details of which will be published elsewhere.

Table 1 *Polarization resistance (R_p) of MS in 1N H_2SO_4 (deaerated) obtained by exponential linear relaxation technique*

	τ (m sec)	R_p from cathodic polarization (ohm.cm^2)	R_p from anodic polarization (ohm.cm^2)
Method 1	1	14.71	14.21
(by using eqn. (3))	1000	13.98	14.56
Method 2 (by curve fitting)	1	15.38	14.25
Method 3 (multitransient	1	14.85	14.52
approach	1000	13.72	13.85
Steady-state linear polarization	-	14.02	14.07

Table 2 *Double-layer capacitance (C_d) for the system, MS in 1N H_2SO_4 (deaerated) by the exponential linear relaxation method (τ = 1 m sec)*

	C_d from cathodic polarization ($\mu F/cm^2$)	C_d from anodic polarization ($\mu F/cm^2$)
(i) curve fitting	86.71	93.56
(ii) From η_{max} and t_{max} (using eqs. (3) and (4))	89.78	91.80

R_p values for this system obtained by all the three methods, described above, are shown in table 1. They are in good agreement with R_p values obtained by steady-state linear polarization technique. Thus, the exponential linear relaxation method of Rangarajan[1] could be considered as the transient analogue of linear polarization technique for measurement of corrosion rate but with a difference. The transient technique yields an additional information, namely C_d in the vicinity of corrosion potential.

For the system, mild steel in 1N sulphuric acid C_d value calculated from η_{max} and t_{max} using equations (3) and (4) as well as by curve fitting are shown in table 2. Donahue and Nobe[4] obtained a value of 55 ± 13 $\mu F/cm^2$ (at corrosion potential) for the interfacial capacitance of iron in deaerated 1N H_2SO_4, by galvanostatic charging technique. For the system MS in 0.5 N H_2SO_4 Devarajan and Balakrishnan[5] obtained (by small amplitude cyclic voltammetry) a C_d value of 166 $\mu F/cm^2$. This rather large value has been ascribed by them to be due to pseudocapacitance. Comparing the value given in this work with the reported values, it can be concluded that this method yields C_d data of the correct order of magnitude.

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ETHYNYLBENZENE: THE NEAR ULTRAVIOLET EMISSION SPECTRUM

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EMISSION spectra of polyatomic molecules, especially of aromatic hydrocarbons are very difficult to record. There is every probability of their dissociation before the excitation of the molecules takes place. It is also believed that generally the emission spectrum of a molecule yields more information of the ground electronic state than its absorption spectrum. With this in view an attempt was made to record and analyze the emission spectrum of ethynylbenzene.

The 2790 Å electronic absorption spectrum of ethynylbenzene in vapour phase has been studied earlier[1,2] under medium resolution and detailed work on this electronic spectrum was also carried out[3]. A detailed vibrational analysis of infrared and Raman spectra of this molecule has also been reported by King and So[4] who also attempted to record the emission spectrum of this molecule using different techniques of excitation but were not successful[3]. The present authors could record the emission spectrum of ethynylbenzene as explained below and in present note are given details of the investigation.

The excitation of the molecule was brought about by an uncondensed transformer discharge through the flowing vapour of the substance contained in a bulb attached to the conventional pyrex glass tube. The whitish blue discharge was maintained by controlling the output of the transformer at about 3000 volts. The substance used in the investigation was supplied by Light Chemical Company. The spectrum was photographed on Ilford R-40 plates using an Hilger medium quartz spectrograph with a slit width 0.03 mm. The spectra were recorded with different exposure times ranging from 5–10 hr. For comparison the near ultraviolet absorption spectrum of the ethynylbenzene in vapour phase was also recorded on the same spectrogram. The accuracy of measurements of the position of the bands is slightly better than ± 5 cm^{-1}.

The emission spectrum spreads in the region 2715 Å–3095 Å with a weak continuous background. The bands are sharp and degraded to the red. The emission spectrum observed here corresponds to the electronic transition $^1B_2 \leftarrow {}^1A_1$ under the C_{2v} symmetry of the molecule. A comparison of the emission spectrum