Linear Polarisation Resistance Technique to Evaluate Alkaloids as Inhibitors for Corrosion of Mild Steel in Hydrochloric Acid

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LINEAR polarisation resistance technique is mainly employed to study the behaviour of three alkaloids viz cinchonine, quinine sulphate and brucine, as inhibitors for the corrosion of mild steel in 11% (v/v) and 0.1 N hydrochloric acids. In 11% acid solution brucine is found to be most efficient in inhibiting the corrosion while in dilute acid brucine provided better inhibition than cinchonine. These alkaloids have shown remarkable inhibition and a mechanism is proposed for their inhibition action.

It is known that compounds containing nitrogen, oxygen and sulphur retard corrosion of metals in acid media[1,2] and that alkaloids behave as inhibitors for corrosion of metals in acids[3–5], as for zinc corroding in dilute acids[6]. Recently, quinoline derivatives also are evaluated as inhibitors for the corrosion of mild steel in acid by linear polarisation resistance and Tafel extrapolation methods[7].

In the present work, mainly linear polarisation resistance (LPR) technique to monitor the corrosion rates of mild steel in HCl of 11% (v/v) and 0.1 N concentrations has been used. The effect of cinchonine, quinine sulphate and brucine is investigated as inhibitors in these media. The main advantages of this technique developed by Stern[8] are : the electrode surface is not disturbed, as the electrode is polarised only to about ± 10mV from the corrosion potential (E_k), secondly, this method can be used for quick measurement of the low corrosion currents. As HCl is extensively used in pickling baths and for descaling[9], it has been considered appropriate to study these alkaloids as inhibitors for it.

EXPERIMENTAL

The experimental set-up is as described earlier[10]. Two auxiliary electrodes (cylindrical) of pure platinum are placed on either side of the working electrode of mild steel in order to provide uniform current flux. The multineck polarisation cell is as described by Greene[11]. The constant potential source used is assembled in the Electronics laboratory of this college using operational amplifier circuitry. This, in combination with variable precision decade resistance box, is used to provide the constant current necessary for the galvanostatic polarisation studies.

The working electrode is a mild steel sample supplied by N. M. L. (Jamshedpur) analysing C = 0.13%, Mn = 0.50%, P = 0.065%, S = 0.03% and Si = 0.05%. The sample is carefully cut to cylindrical shape. After thorough pretreatment[12] and subsequent measurement of area, this working electrode is mounted on the glass holder as described by Stern and Makrides[13]. The electrode is cleaned with lukewarm mild detergent solution, washed repeatedly with double distilled water and immediately exposed to the acid/acid-inhibitor environment in the polarisation cell. A.R. grade chemicals were used and the experiments are at temperature of 25 ± 2° C.

PROCEDURE

The corrosion potential is recorded after about one hour of immersion in acid solutions, but in the presence of alkaloids about two hours waiting time is required for the system to attain steady-state conditions and to obtain the constant corrosion potential. The constant current steps for LPR measurements are applied galvanostatically by changing applied voltage from the constant potential source and/or the magnitude of precision resistance introduced in the circuit. After applying a predetermined magnitude of current, the potential of the working electrode is measured using an electrometer-potentiometer circuit drawing minimum current through this circuit while measuring potential, using SCE as reference electrode.

As applied currents used in the LPR measurements are low, it takes considerable time for working electrode to atttain a steady-state potential[14]. In order to overcome this difficulty

and hasten the measurements with fair degree of accuracy, the transient linear polarisation resistance technique is adopted: exactly equal increments of constant current are applied and corresponding potentials of the working electrode are recorded in transient condition after a lapse of equal intervals of time. This eliminates the need to wait for a long period required for attainment of steady-state conditions.

The working electrode is polarised cathodically upto a maximum of 30mV though it is reported that theoretically the electrode should be polarised at only ± 10 mV[8]. This is observed to be beneficial as larger number of observations could be made with this extended range and the linear current-voltage relationship is observed even upto this 30mV limit. After obtaining the LPR values for each set of acid/inhibitor concentration, a full cathodic polarisation curve is run in some cases to determine cathodic Tafel constant b_c and then extrapolated to the corresponding E_t in order to obtain corrosion current. After completion of each set of experiments the working electrode is polished, cleaned, washed for reuse. Studies are first in the presence of inhibitors and at the end blanks are run, to defer to the end, possible damage to the electrode surface and appreciable reduction in its area when it is exposed to acid alone.

TABLE I

Inhibitive Effect of Cinchonine, Quinine Sulphate and Brucine on Corrosion of Mild Steel in 11%(v/v) HCl.

(Temp. 25 ± 2° C)

Inhibitor	Inhibitor Concentration (%)	Corrosion Current Density (I_k (mA/cm^2)	Linear Polarisation Resistance R (Ohm/cm^2)	Inhibitor Efficiency I.E (%) LPR Method	Tafel Extrapolation
Blank	—	13.50	00.70	—	—
Cinchonine	0.06	1.10	13.50	94.81	91.85
	0.10	0.42	34.44	97.96	96.88
	0.15	0.24	56.00	98.92	98.22
Quinine	0.0050	—	4.57	84.68	—
sulphate	0.0075	1.05	53 33	93.82	88.88
	0.01	0.03	63.33	98.69	97.77
	0.02	—	116.00	99.10	—
	0 04	0.16	120.00	99.41	98.81
	0 05	0 12	160.00	99.56	99.11
Brucine	0.00075	—	2.28	69.29	—
	0.001	—	11.00	93.63	—
	0.005	—	20.00	96.50	—

RESULTS AND DISCUSSIONS

The LPR values and other parameters obtained for different concentrations of acid and alkaloids are recorded in Tables I and II. The value of E_k for mild steel in 11% HCl is about -0.475 V Vs SCE and remained almost unchanged in the presence of alkaloids. Similarly, the value of E_k for mild steel in 0.1N HCl is −0.525 V Vs SCE and remained constant in presence of the alkaloids while the value of b_c is 0.03 V/decade in the former and slightly higher at 0.100 V/decade in the latter. Inhibitor efficiency (I.E.) is calculated using LPR values as follows :

$$\text{Percentage I.E.} = R' - R/R' \times 100$$

where R' and R are the LPR values in presence and absence of alkaloids respectively. When Tafel extrapolation method is used, percentage I.E. is calculated as follows :

$$\text{Percentage I.E.} = (I_k - I'_k)/I_k \times 100$$

where I_k and I'_k is corrosion current density in absence and the presence of alkaloids. Interrelationship between these two factors for calculating I.E. is based on the observed fact that the term $(b_a \times b_c)/2.3(b_a + b_c)$ of the Stern-Geary equation is reasonably constant.

Overall behaviour of cinchonine, quinine sulphate and brucine in 11% HCl as inhibitors for mild steel are compared in Table-I. It can be seen from the table that the corrosion current density (I_k) of mild steel in 11% HCl appreciably decreases from 13.5 mA/cm² to 1.1 mA/cm² in presence of 0.05% cinchonine and to only 0.12 mA/cm² with 0.05% quinine sulphate. The LRP value of 0.7 Ohm/cm² of mild steel in the acid alone increases to 13.5 Ohm/cm² and 160 Ohm/cm² in the presence of cinchonine and quinine sulphate respectively when in such small concentrations as 0.05%. Quinine sulphate proves to be more effective in comparision to cinchonine as inhibitor for mild steel in 11% acid. It can also be seen that the concentration of brucine for similar protection is comparatively low, being 0.001% indicating as the most efficient of the three alkaloids.

Table-II shows the LPR values and the other parameters for mild steel in 0.1N HCl. Comparatively small concentrations of inhibitors are required for inhibition in contrast to the much higher concentrations required in more concentrated acids, as seen from tables I and II for cinchonine and brucine. For example, while for 97 to 99% I.E. in 11% HCl, 0.15% of cinchonine is only 0.015%

TABLE II

Inhibitive Effect of Cinchonine and Brucine on Corrosion of Mild Steel in 0.1 N Hydrochloric Acid

(Temp. 25 ± 2° C)

Inhibitor	Inhibitor Concentration (%)	Linear Polarisation Resistance R (Ohm/cm²)	Corrosion Current Density I_k (mA/cm²)	Inhibitor Efficiency I.E (%) LPR Method	Tafel Extrapolation
Blank	–	2.90	5.000	–	–
Cinchonine	0.005	16.66	1.000	80.18	80.00
	0.010	22.14	0.825	86.90	93.50
	0.015	99.99	0.175	97.09	96.05
Brucine	0.001	123.33	–	97.64	–
	0.005	145.00	–	98.00	–

is required in 0.1N HCl. Similar is the case with brucine. Brucine though most effective, being poisonous proper care is required in handling. Because of this, the other two alkaloids may find better favour though slightly less efficient.

MECHANISM OF INHIBITION

The I.E. of these three alkaloids appears to be related to the methoxy groups present in the molecule. Cinchonine, the least effective one has no methoxy group, quinine sulphate with one methoxy group shows a much higher efficiency. Brucine with two methoxy groups exhibits the highest I.E. The mechanism through which these methoxy groups influence the inhibiting properties of the alkaloids is under study. Though the highest I.E. observed in case of brucine can be explained to a certain extent on the basis of its large structure and high molecular weight, it is possibe that the presence of the two methoxy groups in this molecule reinforces the basic inhibitive property attributable to compounds of this type. Also all the three alkaloids are optically active and this activity differs in each compound. The differences in the degree in inhibition appear to be closely related to the optical activity displayed by them. Basically the inhibition displayed by these molecules is explained by the fact that they get chemisorbed on the metal surface and retard the cathodic reaction of hydrogen evolution. The presence of hetero-nitrogen atoms helps such chemisorption at the reaction centres. Methoxy groups add to the inhibition-efficiency, presumably through synergestic action.

CONCLUSIONS

Linear polarisation resistance technique could successfully be employed to evaluate alkaloids as inhibitors of corrosion of mild steel in 11% (v/v) and in 0.1N HCl. The order of inhibitor efficiency as follows :

Brucine > Quinine sulphate > Cinchonine

The presence of methoxy group in the molecule adds significantly to the efficiency of inhibition.

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