CORROSION INHIBITION OF STEEL IN ACIDIC MEDIA BY BENZIMIDAZOLE DERIVATIVES

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Abstract - In connection with the use of substituted benzimidazoles as inhibitors of acid corrosion of mild steel, attention was turned to the influence of structure and composition of homologous series of benzimidazole derivatives. The protective effects of substituted benzimidazoles on the corrosion of mild steel in 1M HCl were studied using weight loss and polarisation techniques. The results of the investigation show that all investigated benzimidazole derivatives have fairly good inhibiting properties for steel corrosion in hydrochloric acid. The compound 2,2'-Octamethylenebis-benzimidazole (III) is the best inhibitor and its inhibition efficiency reaches (94%) at 10^{-4} M in 1M acid concentration.
Keywords – Corrosion; Inhibition; Benzimidazole derivatives; Mild steel

1. INTRODUCTION

The corrosion of iron and mild steel is a fundamental academic and industrial concern that has received a considerable amount for attention [1]. Aqueous solution of acids is among the most corrosive media. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [2]. The progress in this field has been phenomenal in recent years and is borne out by the out put of literature [3].

Acid solution are widely used in industry, the most important fields of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. Because of the general aggressivity of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulphur, oxygen, phosphorous, sulfer and aromatic ring or triple bonds. It has been reported that the inhibition efficiency increases in the order: $O < N < S < P$ [4-7].

Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal. The extent of adsorption depends of the nature of the metal, the metal surface conditions, the mode of adsorption, the chemical structure of inhibitors and the type of corrosive media [8]. Most of commercial inhibitors are toxic compounds and should be replaced with new environmentally friendly inhibitors.

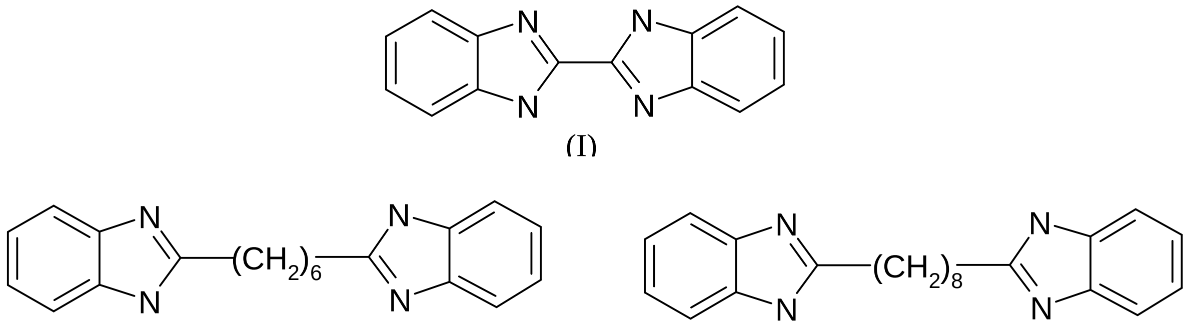
This paper focuses on the efficiency of non-toxic benzimidazole derivatives as steel corrosion inhibitors in hydrochloric acid. Benzimidazoles are organic compounds with two nitrogen atoms in the heterocyclic ring. One of the nitrogen atoms is of pyrrole type, and the other is a pyridine-like nitrogen atom. The benzimidazole molecule shows two anchoring sites suitable for surface bonding: the nitrogen atom with its lonely sp^2 electron pair and the aromatic ring.

The influence of the structure and composition of homologous benzimidazole derivatives on the inhibiting efficiency of steel corrosion in hydrochloric acid was studied using electrochemical method and gravimetric method.

2. EXPERIMENTAL SECTION

2.1. Material preparation

Corrosion tests were performed on a mild steel of the following percentage composition:
0.21 C, 0.38 Si, 0.09 P, 0.05 Mn, 0.05 S, 0.01 Al and the remainder iron. For the gravimetric and electrochemical measurements, pre-treatment of the surface of specimens was carried out, by grinding with paper of 600-1200 grit, rinsing with bidistilled water, ultrasonic degreasing in ethanol, and dried at room temperature before use. The aggressive solution 1M HCl, were prepared by dilution of analytical grade 37% with bidistilled water. The molecular formulas of the tested inhibitors are shown in Figure 1.



(I)

(II)

(III)

Figure 1: Chemical structure of the investigated benzimidazole derivatives

2.2. Methods

2.2.1. Weight loss study

Gravimetric experiments were carried out a double glass cell equipped with a thermostated cooling condenser. The solution volume was 100 ml. The used steel specimens had rectangular form (length = 2 cm, width = 1 cm, thickness = 0.06 cm). Maximum duration of tests was 24 h at 30°C in non-de-aerated solution. At the end of tests the specimens were carefully washed in ethanol under ultrasound, and then weighed. Duplicate experiments were performed in each case and the mean value of the weight loss has been reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in mg $cm^{-2}h^{-1}$.

2.2.2. Electrochemical studies

Experiments were carried out in pyrex cell, which has three compartments. A graphite rod was used as the counter electrode and a sutured calomel electrode (SCE) served as reference electrode. All potentials reported here were referred to the SCE. Measurements were obtained using a combined system containing potentiostat Model Amel 551, Voltage scan generator Model Amel 568 and recorder type Kipp-Zonen/BD 9. All tests have been performed in de-aerated solution under continuously stirred conditions at room temperature. Before recording the polarisation curves, the open-circuit potential was stable within 30 mn. The cathodic branch was always determined first; the open-circuit potential was then re-established and the anodic branch determined. The anodic and cathodic polarisation curves was recorded by a constant sweep rate 0.5mV/s. Inhibition efficiencies were determined from corrosion currents calculated by Tafel extrapolation method.

3. RESULTS AND DISCUSSION

3.1. Gravimetric measurements

Different experimental techniques can be used to evaluate inhibition efficiency of the benzimidazole derivatives. Gravimetry is one of the simplest. Determination of the weight loss allows the calculation of the inhibition efficiency, E(%):

$$E\ \% = \left(\frac{W_{corr} - W_{corr(inh)}}{W_{corr}} \right) X\ 100 \qquad (1)$$

Where W_{corr} and $W_{corr(inh)}$ are the corrosion rates of mild steel in the absence and presence of organic compound, respectively. Table 1 gives the data of the weight loss determinations for different concentrations of compounds in 1 M HCl at 30°C. Measurements for different concentrations of compounds (I), (II) and (III) show that theses inhibitors inhibit the corrosion of mild steel. Corrosion rate values of mild steel decrease when the inhibitors concentration increase.

Table 1: Corrosion rate of mild steel and inhibition efficiency for various concentrations of benzimidazole derivatives (I, II and III) for the corrosion of mild steel in 1M HCl obtained from weight loss measurements.

Inhibitor	**Concentration (10^{-5}mol.l^{-1})**	**Corrosion rate (10^{-3}mg.cm^{-2}.h^{-1})**	**E (%)**
Blanc	___	157.5	___
	1	53.8	65.8
	5	45.3	71.2
I	10	29.4	81.3
	100	28.2	82.1
	1	36.8	76.6
	5	27.7	82.4
II	10	17.6	88.8
	100	16.5	89.5
	1	28.0	82.2
	5	16.9	89.2
III	10	15.3	90.2
	100	12.9	91.8

E(%) increases with increasing inhibitor concentration. At 10^{-3} M for each inhibitor studied, the inhibition efficiency attains 82.1%, 89% and 91.8% respectively for compounds (I, II and III). Further increases of inhibitor concentration provide a lower degree of protection. The concentration 10^{-3} M was found to be the optimum concentration for the inhibitors. From weight loss measurements, we can conclude that the efficiency of the three tested benzimidazole derivative follow the order: III > II > I (Table 1). Therefore, 2,2'-Octaméthylène-bis-benzimidazole (III) is most effective inhibition for mild steel in 1 M HCl solution.

3.2. Polarisation measurements

Anodic and cathodic polarized potentials were measured in the absence and presence of inhibitors. Figure 2 shows the anodic and cathodic polarisation curves for mild steel in 1 M HCl in the presence and absence of inhibitors at optimized concentration.

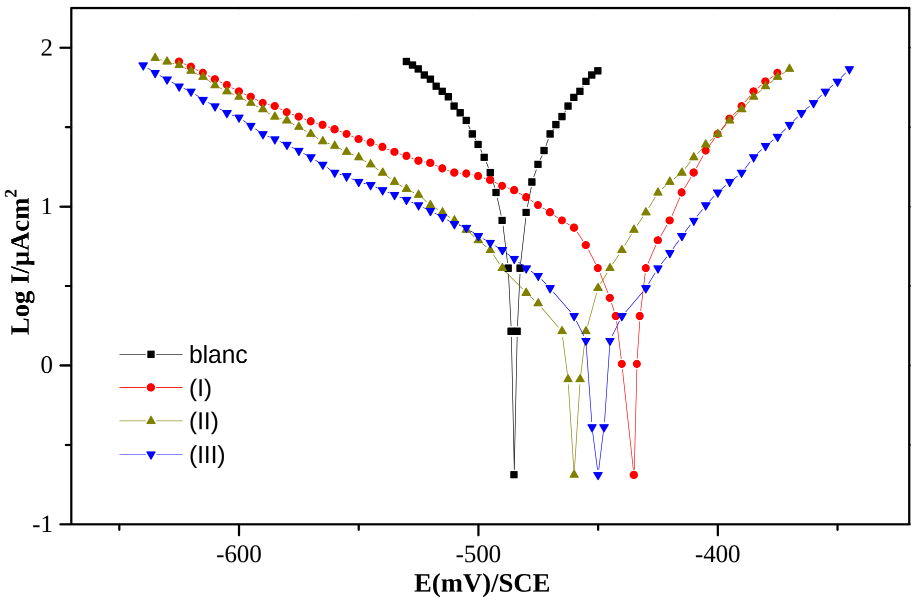


Figure 2: Potentiodynamic polarisation curves for mild steel in 1 M HCl containing different inhibitors

Values of corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (b_c) and corrosion inhibition efficiency (E%) for different inhibitors in HCl 1M are given in Table 2. The inhibition efficiency is defined as:

$$E\ \% = \left(\frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \right) \text{x } 100 \qquad (2)$$

Where I_{corr} and $I_{corr(inh)}$ are the corrosion current density values without and with inhibitors, respectively, determined by extrapolation of cathodic and anodicTafel lines to the corrosion potential.

Table 2: Potentiodynamic polarisation parameters for the corrosion of mild steel in 1 M HCl containing different benzimidazole derivatives

Inhibitors	E_{cor} (mV/SCE)	I_{cor} (μA/cm^{-2})	b_c (mV/dec)	E (%)
Blanc	-485	13.9	44	_____
I	-435	2.1	163	84
II	-460	1.5	114	88
III	-450	1.4	129	90

From this result, it can be concluded that:

- the values of corrosion current density (I_{corr}) of mild steel in the inhibited solution were smaller than those for the inhibitor-free solution,
- addition of benzimidazole derivatives does not change the value of b_c
- the results obtained from the polarisation curves correspond to those from the corrosion weight loss test.

It is evident from Figure 2 that the cathodic reaction (hydrogen evolution) is inhibited. Tafel lines of nearly equal slopes were obtained. The constancy of this cathodic slope can indicate that the mechanism of proton discharge reaction does not change by addition of the benzimidazole derivatives to the acidic media.

In anodic domain, we notice that E_{corr} has shifted to more positive potentials compared to the uninhibited solution. It's also clear that the addition of benzimidazole derivative have an effect on the anodic branch of the potentiodynamic scan. This result indicates that a bezimidazole derivative exhibits both cathodic and anodic inhibition effects. Therefore they can be classified as inhibitors of relatively mixed effect (anodic/cathodic inhibition) in 1M HCl.

4. CONCLUSION

The three studied compounds inhibit the corrosion of mild steel in 1 M HCl media. Comparative study of these inhibitors shows that 2,2'-Octaméthylène-bis-benzimidazole (III) is the best inhibitor. Polarisation curves recording have shown that the addition of benzimidazole derivatives does not change the proton reduction mechanism. They act as mixed type inhibitors in acidic media. The inhibition efficiency value increases with the inhibitors concentration and reaches a maximum at 10^{-3}M. The corrosion inhibition of benzimidazole derivatives can be interpreted by a simple blocked fraction of the electrode surface related to the adsorption of the inhibitor species on the steel surface. The results obtained from polarisation curves and the weight loss are in reasonably good agreement.

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