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2.5-Difuryl-N-Methylpyrrole as Corrosion Inhibitor for Steel in 1 M HCl

O. Krim[a], M. Bouachrine[b], B. Hammouti[*,a], A. Elidrissi[a], M. Hamidi[b]

[a] *Laboratoire de Chimie Appliquée et Environnement, Faculté des Sciences,B.P. 717, Oujda, Morocco*
[b] *Unité de Recherche sur les Macromolécules & Modélisation, Faculté des Sciences et Technique,_B.P. 509 Boutalamine, Errachidia, Morocco*

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Abstract

This work is a study of 2.5-difuryl-N-methylpyrrole (B1) compound on the corrosion of steel in HCl medium. The investigation was carried out using gravimetric and electrochemical polarisation measurements. The corrosion rate decreases continuously with concentration of the compound (B1) and the efficiency increases to reach 90 % at 10^{-3} M. Polarisation results indicate that B1 is a cathodic inhibitor. B1 is adsorbed on metal surface according to the Langmuir isotherm. Value of free enthalpy of adsorption obtained involves chemisorption between inhibitor molecules and metal surface.

Keywords: corrosion, inhibition, steel, acid, pyrrole, Langmuir.

Introduction

Inhibitors are often added in industrial processes to secure metal dissolution from acid solutions. Authors show that organic compounds containing O, S and/or N atoms act as effective inhibitors [1-3]. These organic compounds adsorb on metallic surface and then decrease the corrosion rate [4-7]. It has been observed that adsorption depends mainly on certain physico-chemical properties of the inhibitor group, like functional groups, electron density at the donor atom, π-orbital character, and the electronic structure of the molecule [8-10]. Among these various molecules, pyrrole and derivatives exhibit good protection against corrosion in acidic media [11-15]. Furthermore, the encouraging results obtained by the thiophene compounds [16-19] have incited us to test more synthesised heterocyclic compounds. This work is aimed to study the effect of a new

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[*] Corresponding author. E-mail address: hammoutib@yahoo.fr

compound based on pyrrole on the inhibition of the corrosion of steel in 1 M HCl. Weight loss and polarization methods were used.

Experimental details

The molecular structure of the studied compound is shown in Fig. 1.

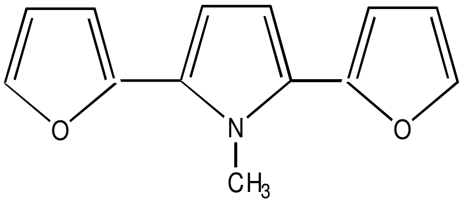

Figure 1. Molecular structure of 2.5-difuryl-N-methylpyrrole (B1).

The studied compound B1 (2.5-difuryl-N-methylpyrrole) was synthesized according the Stille reaction [20]: the cross coupling between 2.5-dibromo-N-methylpyrrole with 2-trimethylstannylfuran using 5% of $PdCl_2(P□_3)_2$. The trimethylstannylfuran is readily generated in excellent yield by quenching the □-lithio anion of the commercially available furan with trimethyl stannyl chloride [21].

Tests were performed on steel sheets of composition (0.09% P, 0.38% Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S and Fe balance). Steel coupons of size 2 cm × 2 cm were polished using a series of emery paper up to 1200 grit. The specimens are washed thoroughly with bidistilled water degreased and dried with acetone. The aggressive solution (1 M HCl) is prepared by dilution of analar grade 37% HCl.

Electrochemical measurements are carried out in a conventional three-electrode electrolysis cylindrical Pyrex glass cell. The working electrode (WE) had the form of a disc cut from a steel sheet. The exposed area to the corrosive solution is 1 cm^2. A saturated calomel electrode (SCE) and a platinum electrode are used, respectively as reference and auxiliary electrodes. Running on an IBM compatible personal computer, the 352 Soft Corr^{TM} III Software communicates with EG&G Instruments potentiostat-galvanostat model 263A at a scan rate of 20 mV/min. Before recording the polarisation curves, WE is firstly immersed into the test solution for 30 min to attain its free corrosion potential. The steel electrode is pre-polarized at -800 mV for 10 min. The polarisation curves are obtained from -800 mV to more positive values. To purchase oxygen from solution, the test solution is de-aerated with pure nitrogen and gas bubbling is maintained through the experiments. All potentials are given in the SCE scale. The cell is thermostated at 308 ± 0.5 K.

Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 100 cm^3. The steel specimens used have a rectangular form (2 cm × 2 cm × 0.05 cm). The immersion time for the weight loss is 4h.

In the case of the weight loss method, the relation determines the inhibition efficiency ($E_W\%$):

$$E_w\% = \left(1 - \frac{W_{corr}}{W^{\circ}_{corr}}\right) \times 100$$

W_{corr} and W°_{corr} are the corrosion rates of steel with and without inhibitor, respectively. For electrochemical measurements, the inhibition efficiency is calculated as follows:

$$E_I\% = \left(1 - \frac{I_{corr}}{I^{\circ}_{corr}}\right) \times 100$$

I_{corr} and I°_{corr} are the corrosion current density values with and without inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential.

In order to ensure reproducibility, all experiments are repeated three times. The evaluated inaccuracy does not exceed 10%.

Results and discussion

Polarisation measurements

Fig. 2 gathers the cathodic and anodic polarisation curves of steel in free acid and in the presence of B1 at different concentrations. The collected electrochemical parameters values of corrosion potentials E_{corr}, corrosion current I_{corr}, cathodic Tafel slope b_c, and inhibition efficiencies E%, are presented in Table 1.

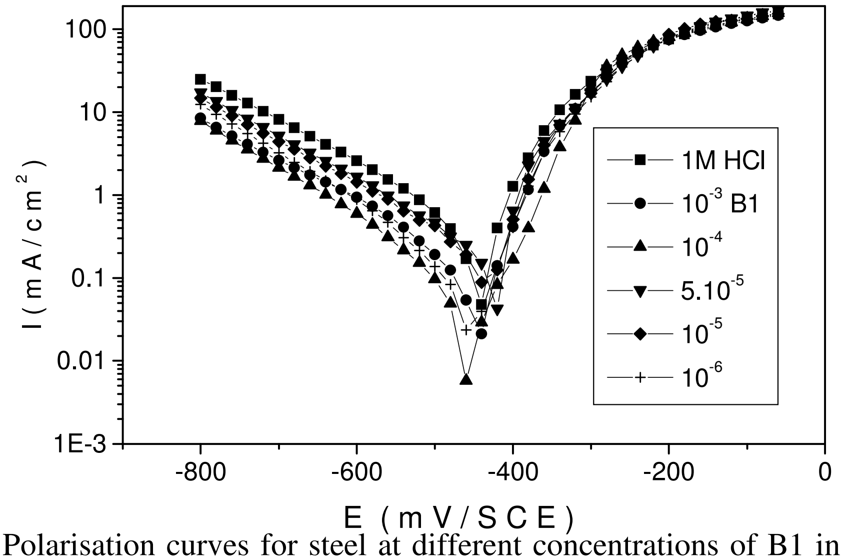

Figure 2. Polarisation curves for steel at different concentrations of B1 in deaerated 1 M HCl.

It is evident that the values of I_{corr} decrease with the concentration of inhibitor to attain the lowest value 85.8 μAcm^{-2} at 10^{-3} M. The cathodic Tafel slope and E_{corr} are almost constant when the inhibitor is added, showing that the inhibitor's presence does not modify the mechanism of the hydrogen reduction. In the anodic domain, no effect is observed at overvoltages higher than E_{corr} in the presence of B1. This result shows that the inhibition process of this inhibitor depends on the electrode potential. Then, the tested compound acts predominantly as a cathodic inhibitor.

Table 1. Electrochemical parameters and the corresponding inhibition efficiency of B1.

Concentration (M)	E_{corr} (mV/SCE)	b_c (mV/dec)	I_{corr} (µA/cm²)	E %
Free acid	-440	191	660	-
10^{-6}	-420	185	349.8	47
10^{-5}	-420	179	303.6	54
5.10^{-5}	-420	177	203	59
10^{-4}	-440	175	191.4	71
10^{-3}	-460	168	85.8	87

The limitation of inhibitory action on cathodic domain is found by different researchers [22–25]. In this case, the inhibition is generally interpreted by the formation of a protective layer of adsorbed inhibition species at the electrode surface [26]. At potentials higher than E_{corr}, the significant steel dissolution leads to desorption of the inhibiting film. In this domain, the desorption rate of the inhibitor preponderates over the adsorption rate.

Weight loss measurements

The weight loss of mild steel specimen in 1 M HCl solution, with and without different concentrations from the four sulfa drugs compounds, was determined after 6 h of immersion at 308 K. Obtained values of the inhibition efficiency (%I.E.) are given in Table 2. The inhibitor's presence reduces the corrosion rate of steel in hydrochloric acid. The inhibitory efficiency increases with the B1 concentration to reach 90% at 10^{-3} M, indicating that the pyrrole compound tested is a good inhibitor of steel in HCl solution. The corrosion inhibition is essentially due to the presence of electron donors groups (O, N) in the molecular structure of B1.

Table 2. Gravimetric parameters and the corresponding inhibition efficiency and surface coverage of B1.

Concentration (M)	W_{corr} (mg/cm²h)	E_w %	θ
Free acid	1.1	-	-
10^{-6}	0.866	21	0.21
10^{-5}	0.389	65	0.65
5.10^{-5}	0.307	72	0.72
10^{-4}	0.209	81	0.81
10^{-3}	0.114	90	0.90

Adsorption isotherm

The Langmuir [27] adsorption isotherm was found to be the best description of the adsorption behaviour of the studied inhibitor:

$$\frac{C}{\theta} = \frac{1}{k} + C$$

$$k = \frac{1}{55.5}\exp(-\frac{\Delta G°_{ads}}{RT})$$

C is B1 concentration, θ the fraction of the surface covered determined by E/100, k the equilibrium constant and $\Delta G°_{ads}$ the standard free energy of adsorption reaction.

Fig. 3 shows the dependence of the ratio C/θ as a function of C. The obtained plot is linear with a slope 1.10 to close to unity. The regression coefficient is R=0.99995. The intercept permit the calculation of the equilibrium constant *k* which is 1510745 M^{-1}. This result leads to evaluating $\Delta G°_{ads}$ = -40.82 kJ/mol.

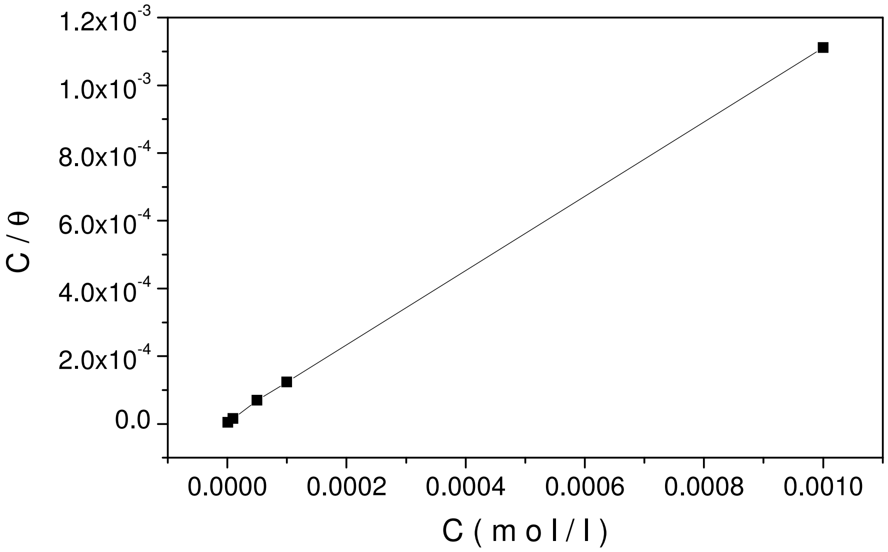

Figure 3. Langmuir isotherm adsorption of B1 on steel in 1 M HCl.

The negative value of ΔG_{ads} indicates that compound (B1) adsorbs spontaneously on the metal surface [28, 29]. Moreover, more information may be deduced from value of $\Delta G°_{ads}$. It is well known that values of $\Delta G°_{ads}$ of the order of -20 kJ mol^{-1} or lower predominate a physisorption; those of the order of -40 $kJmol^{-1}$ or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond [30]. In fact, in their study, Ashassi-Sorkhabi et al. [31] explained the role of substituents of some aminoacid compounds: the chemical adsorption has a fundamental role to coverage the corroded sites respect to physical adsorption. Although, in this concentration, amine group can protonated, but the presence of indole, pyrrole, or S–CH_3 group on the amino acids, decreases the stability of positive charge on the amino acids. However, it is well known that the presence of aromatic ring, hetero atoms, or long chain aliphatic groups on the inhibitor structure causes a significant increase in inhibition efficiencies [31]. Then, the value of $\Delta G°_{ads}$ obtained with B1 may introduce the chemisorption.

Conclusions

- Newly synthesised inhibitor is a good cathodic inhibitor for steel corrosion in 1 M HCl.
- Polarisation measurements show that B1 acts essentially as a cathodic inhibitor. The inhibition efficiency increases with the increase of concentration.
- The inhibitor efficiencies determined by polarisation and by gravimetric methods are in good agreement.
- B1 studied adsorption on the steel surface obeys the Langmuir isotherm model according to chemisorption.

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