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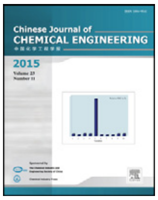

Research Note

N-methyl-2-(2-nitrobenzylidene) hydrazine carbothioamide — A new corrosion inhibitor for mild steel in 1 mol·L^{-1} hydrochloric acid

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ABSTRACT

The corrosion inhibition of mild steel in 1 mol·L^{-1} hydrochloric acid by *N*-methyl-2-(2-nitrobenzylidene) hydrazine carbothioamide (MNBHC) was studied using weight loss and electrochemical studies. Results obtained indicate that the inhibitor is effective in hydrochloric acid medium and the efficiency decreases with increase in temperature. Added halide additives improve the efficiency of the inhibitor. The AC impedance studies reveal that the process of inhibition is through charge transfer. Polarization studies indicate the mixed nature of the inhibitor. From the thermodynamic, spectral and surface analyses the nature of adsorption has been found out. The adsorption of the inhibitor on mild steel follows the Langmuir isotherm.

1. Introduction

Corrosion inhibition of metals is an important process in metal finishing industries. The treatment of inhibitor increases the life period of metal utensils. Several efforts have been made to control or reduce corrosion and out of numerous methods, the use of inhibitors is one of the most practical methods for the prevention of corrosion particularly in acidic media [1–3]. A number of organic and inorganic compounds are known to act as corrosion inhibitors for metals in various environments. Compounds containing nitrogen, sulfur and oxygen atoms adsorb on the metal surface and block the active sites and thereby decrease the corrosion rate. The efficiency of these compounds depends upon electron density present around the hetero atoms, number of adsorption active centers in the molecule, their charge density, molecular size, mode of adsorption and formation of metallic complexes [4–6]. Compounds with π-bonds generally exhibit good inhibitive properties due to interaction of π-electrons with metal surface. Schiff bases are one of the widely used corrosion inhibitors due to their ability to form protective layer on the metal surface. The presence of >C═N– group in the molecules of schiff bases makes these compounds effective corrosion inhibitors. Many corrosion protection works have been studied with the use of synthetic compounds especially organic compounds [7–9]. In the present study an attempt has been made to study the adsorption and inhibition effect *N*-methyl-2-(2-nitrobenzylidene) hydrazine carbothioamide (MNBHC) as a new inhibitor for the corrosion of mild steel in 1 mol·L^{-1} HCl using mass loss and electrochemical methods.

2. Materials and Methods

2.1. Materials preparation

The mild steel (MS) specimen of dimension 1 cm × 5 cm × 0.2 cm with an area of 12.3 cm^2 was used for the mass loss study and the specimen with an exposed area of 0.95 cm^2 was used for electrochemical study. The surface of the specimens was mechanically polished with different grades (600, 800 and 1000) of emery papers and then degreased with acetone and stored in a desicator. The composition (by mass) of MS is: C 0.14, Mn 0.57, Al 0.05, Cr 0.03, Si 0.02, Cu 0.01 and balance is Fe. The inhibitor MNBHC was prepared according to the reported procedure of Sampath *et al.* [10]. The product so obtained was taken for the investigation of corrosion inhibition study. Fig. 1 shows the molecular structure of the examined compound MNBHC.

2.2. Mass loss method

The pre-cleaned and pre-weighed MS specimens in triplicate were suspended in 100 ml test solution with and without inhibitor at different concentrations (4–32 mol·L^{-1}) of MNBHC in 1 mol·L^{-1} HCl for a period of 1 to 48 h. After that, the specimens were taken out, washed with distilled water, dried, and weighed. From the mass loss data, percentage inhibition efficiency (IE, %) was calculated and the optimum concentration of the inhibitor was established. To study the influence

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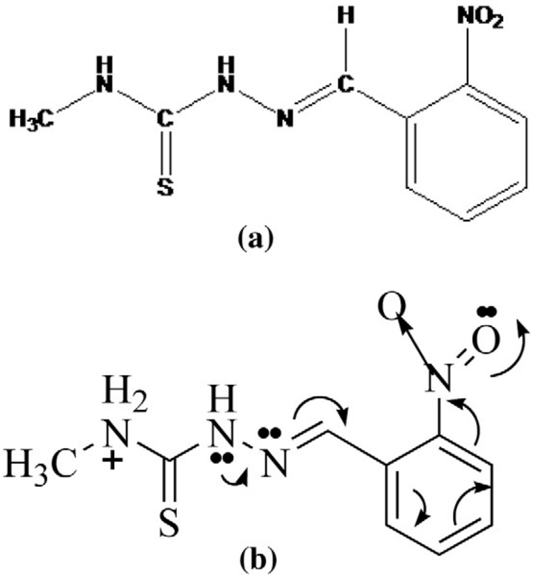

Fig. 1. (a) Chemical structure of studied schiff base *N*-methyl-2-(2-nitrobenzylidene) hydrazine carbothioamide. (b) Direction of electron movements in the chain of studied schiff base *N*-methyl-2-(2-nitrobenzylidene) hydrazine carbothioamide.

of the concentration of the acid on the effectiveness of the inhibitor, mass loss experiments were carried out in 1–3 mol·L^{-1} HCl. The inhibitor concentration was kept constant at 32 mol·L^{-1} in the test solution. The synergistic influence of halide ions was studied by adding the halide additives (1 mol·L^{-1}of KCl, KBr and KI) to MNBHC. All these studies were carried out at (303 ± 1) K. The influence of temperature on the corrosion behavior of MS in the presence of MNBHC was studied in the range of 303–333 K. The inhibiting power was calculated using the following equation.

$$\mathrm{IE} = [(W_\mathrm{B} - W_\mathrm{I})/W_\mathrm{B}] \times 100 \tag{1}$$

where, W_B and W_I are the mass loss of the MS specimens in the absence and in the presence of inhibitor respectively. The corrosion rate (CR, mm·a^{-1}) was calculated employing the equation,

$$\mathrm{CR} = 87.6W/\rho At \tag{2}$$

where, W is the mass loss of the specimen (mg), ρ is the density of the specimen (g·cm^{-3}), A is the area of specimen (cm^2), and t is the exposure time (h).

2.3. Electrochemical method

Electrochemical studies were carried out using Electrochemical Analyzer of HCH Instruments (Model 608D). The experiments were carried out in a three electrode cell assembly with a platinum wire mesh electrode and a saturated calomel electrode used as auxiliary and reference electrodes respectively. MS specimen was used as the working electrode. AC impendence studies were conducted in the frequency range of 10,000–1 Hz at the rest potential using 0.02 V sine wave as the excitation signal. R_ct and C_dl values were obtained from the Nyquist plots. The IE (%) was calculated from the following equation,

$$\mathrm{IE} = \left[\left(R^\mathrm{i}{}_\mathrm{ct} - R^\mathrm{o}{}_\mathrm{ct}\right)/R^\mathrm{i}{}_\mathrm{ct}\right] \times 100 \tag{3}$$

where $R^\mathrm{o}{}_\mathrm{ct}$ and $R^\mathrm{i}{}_\mathrm{ct}$ are the charge transfer resistance values in the absence and in the presence of inhibitor respectively. Potentiodynamic polarization studies were carried out in the potential range from −0.750 to −0.250 V at a scan rate of 0.01 V·s^{-1}. The electrochemical parameters such as corrosion current density (I_corr), corrosion potential (E_corr), anodic and cathodic slopes (b_a and b_c) were obtained from Tafel plots and the IE was determined using the formula,

$$\mathrm{IE} = \left[\left(I^\mathrm{o}{}_\mathrm{corr} - I^\mathrm{I}{}_\mathrm{corr}\right)/I^\mathrm{o}\right] \times 100 \tag{4}$$

where $I^\mathrm{o}{}_\mathrm{corr}$ and $I^\mathrm{i}{}_\mathrm{corr}$ are the corrosion current densities in absence and in presence of inhibitor respectively.

Table 1
Effect of concentration of MNBHC and immersion time on the corrosion inhibition of MS in 1 mol·L^{-1} HCl at room temperature

Conc. of MNBHC/mol·L^{-1}	1 h		24 h		48 h	
	IE/%	CR/mm·a^{-1}	IE/%	CR/mm·a^{-1}	IE/%	CR/mm·a^{-1}
Blank		21.4		20.5		17.7
4	48.7	11.0	46.2	11.0	37.5	11.1
8	65.3	7.4	55.5	9.1	41.8	10.3
16	66.5	7.2	64.0	7.4	72.8	4.8
24	72.5	5.9	76.8	4.7	85.1	2.6
32	73.3	5.7	83.6	3.4	89.2	1.9

Table 2
Effect of concentration of HCl on the corrosion inhibition of MS with 32 mol·L^{-1} MNBHC at room temperature

Conc. of acid/mol·L^{-1}	Conc. of MNBHC/mol·L^{-1}	IE/%	CR/mm·a^{-1}
1	0	–	21.4
	32	73.3	5.7
2	0	–	26.9
	32	71.3	7.7
3	0	–	29.0
	32	69.1	9.0

2.4. Surface analysis

Surface morphology of the MS for fresh, inhibited and uninhibited specimens were also examined using scanning electron microscope (SEM) of JOEL model (JSM 6390). Fourier transform infra-red (FT-IR) spectra were recorded using Perkin Elmer Spectrophotometer to study the characteristic adsorption of the functional groups present in the inhibitor on to the metal surface. FT-IR was recorded for the inhibitor MNBHC and the material obtained by scrapping the specimens after the immersion experiment.

Table 3
Effect of addition of halide additives (1 mol·L^{-1}) on the corrosion inhibition of MS in 1 mol·L^{-1} HCl with different concentrations of MNBHC

Conc. of MNBHC/mol·L^{-1}	Conc. of halide ions/mol·L^{-1}	IE/%	CR/mm·a^{-1}
0	–	–	21.4
4	–	48.7	11.0
4	KCl	65.3	7.4
4	KBr	80.5	4.2
4	KI	86.0	3.0
16	–	66.5	7.2
16	KCl	77.5	4.8
16	KBr	82.2	3.8
16	KI	86.9	2.8
32	–	73.3	5.7
32	KCl	78.0	4.7
32	KBr	82.6	3.7
32	KI	90.7	2.0