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Review article

A novel imidazoline derivative as corrosion inhibitor for P110 carbon steel in hydrochloric acid environment

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ABSTRACT

A novel imidazoline derivative, 2-methyl-4-phenyl-1-tosyl-4, 5-dihydro-1H-imidazole (IMI), was prepared and investigated as corrosion inhibitor for P110 carbon steel in 1.0 M HCl solution by weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests. The inhibition efficiency increased with the rising concentration of IMI inhibitor. The test results and fitting data indicated that the IMI behaved as a mixed-type inhibitor and obeys the Langmuir adsorption isotherm. Scanning electron microscopy (SEM) was carried out to investigate the surface of carbon steel specimens, showing great protection from aggressive solution. Finally, inhibition mechanism of IMI on metal surface was further discussed.

1. Introduction

To improve the productivity in the oil and gas industry, acidic stimulation techniques such as matrix acidizing and acid fracturing are widely used. In these process, large amount of highly concentrated acid, such as hydrochloric acid (HCl) and hydrofluoric acid (HF), is used to dissolve carbonate minerals [1].

However, the application of acid fluids in development of oil and gas fields can easily lead to severe corrosion on metal equipment including downhole tools, metal tubular and drill pipes. As a consequence, the costs of equipment maintenance and the security risks both increase dramatically, which contributes to the great economic losses and decline of production efficiency.

To protect the metal tools exposed to acid medium in petroleum industry, several methods such as anti-corrosion coatings, corrosion inhibitors and corrosion resistant steel, have been developed. Among them inhibitor is one of the most effective process. In consideration of efficiency and cost, adding efficient inhibitors to corrosive media is one of the most important and valid methods to protect metal equipment in petroleum industry. Because it can dramatically reduce the corrosion rate even at a low concentration varying from 10 mg/L to 5000 mg/L [1].

The most widely used inhibitors in petroleum industry are imidazoline derivatives. In previous literature some efficient imidazoline inhibitors have been reported [2–5]. We have prepared IMI inhibitor at room temperature using cationic Br as initiator [6]. Then the target product was gained simply by heating the reaction system at reflux for 4 h (Scheme 1). The inhibitory performance of IMI as corrosion inhibitor for P110 carbon steel in 1.0M hydrochloric acid solution was investigated, using weight loss method, electrochemical technique. Scanning electron microscopy (SEM) was employed to analyze the protection behavior of IMI on the surface of P110 carbon steel.

Abbreviations: IMI, 2-methyl-4-phenyl-1-tosyl-45-dihydro-1H-imidazole; EIS, electrochemical impedance spectroscopy; SEM, Scanning electron microscopy; AE, auxiliary electrode; SCE, saturated calomel electrodeb; RE, reference electrode; WE, working electrode; OCP, open-circuit potential.

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2. Experimental

2.1. Reagents and materials

All chemicals used in this study were analytical reagent grade and purchased from Kelong Chemical Reagent Factory (Chengdu, China).

The corrosion test samples were P110 carbon steel containing (wt%): 0.26C, 0.19 Si, 1.37 Mn, 0.004 P, 0.004S, 0.148Cr, 0.028 Ni, 0.019 Cu, 0.013 Mo, 0.006 V, 0.062 Al and balanced Fe. The surfaces of these steel specimens were polished with different grades of emery papers and degreased in ethanol, rinsed with distilled water and then dried at room temperature. The aggressive solution of 1.0 M HCl prepared by the dilution of analytical grade HCl (37 wt%) with deionized water was used as a blank solution.

2.2. .Synthesis and characterization of IMI

The imidazoline inhibitor IMI was synthesized according to the improved path (Scheme 1). The initial experiment was performed using styrene, NBS, acetonitrile, and tosyl ammonia at 25 °C.Then the intermediate was converted to imidazoline by heating the reaction system to 85 °C at reflux for 4 h. After the reaction was complete, saturated $Na_2S_2O_3$ (50 mL) and $NaHCO_3$ (50 mL) were added to quench it. The product was purified by flash column chromatography (dichloromethane/MeOH = 40:1) and then investigated by FT-IR and NMR spectroscopy.

2.3. Weight loss measurements

Triplicate specimens (22 mm × 12 mm × 2 mm) were immersed in 500 mL corrosive solution (1.0 M HCl solution) with varied concentration of IMI inhibitor at 60 °C for 72 h. After the test was completed, the samples were dipped in ethanol and washed with ultrasonic cleaner for several times followed by reweighting. The tests were performed in duplicate to guarantee the reliability of the results and the mean value of the weight loss was reported in 1–2% data errors.

2.4. Electrochemical measurements

Electrochemical measurements were carried out with a computer-controlled system CS310 (CorrTest Company, Wuhan, China) equipped with a standard three-electrode compartment. A saturated calomel electrode (SCE) coupled to a Luggin capillary were used as a reference electrode (RE), along with a platinum counter electrode as the auxiliary electrode (AE). The carefully treated P110 carbon steel was used as a working electrode (WE).

Before each EIS and polarization measurement, WE was immersed in 1.0 M HCl solution at 60 °C with and without different concentrations of inhibitors for 30 min to insure a steady open-circuit potential (OCP). In this situation, the response to the electrical excitation was determined only by the condition of the solid/liquid interface without any impact of electrode quality or other factors. All electrochemical measurements were repeated at least three times under the same condition so that repeatable data were guaranteed.

2.4.1. Potentiodynamic polarization measurements

With a scan rate of 1 mV/s, the potentiodynamic polarization curves were carried out in the potential range from −250 mV to 250 mV with reference to SCE at a steady open-circuit potential. The potentiodynamic current potential curves (Tafel curves) were simultaneously developed.

2.4.2. Electrochemical impedance spectroscopy measurements (EIS)

EIS measurements were performed at OCP in the wide frequency range from 100 kHz to 0.01 Hz at alternating current amplitude of 5 mV sine wave. Nyquist and Bode plots were analyzed to interpret the corrosion characteristics. A ZView3.0 version software was used to analyze and fit the impedance data.

2.5. Scanning electron microscope

The morphology of tested sample surfaces were carried out by SEM (JSM-7500F, Japan). The test was performed after the specimens was exposed to 1.0 M HCl solution for 72 h in the absence and presence of inhibitor IMI.

3. Results and discussion

3.1. FT-IR and NMR measurements

In order to characterize and confirm the product structure, FT-IR and ^1H NMR spectroscopy test was performed.

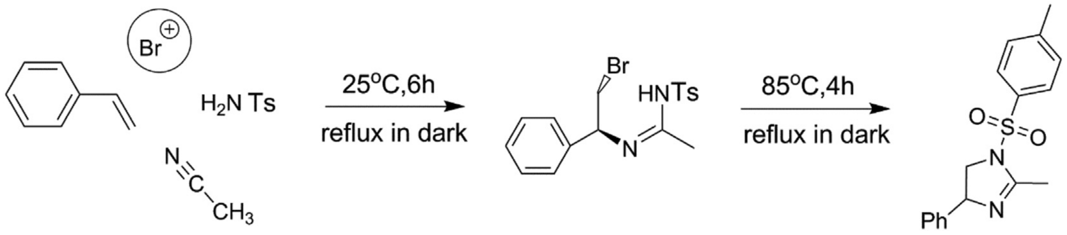
As shown in Fig. 1a and b, IR (cm^{-1}): 3275 (N–H), 2941 and 2876 ($-CH_2-$), 1656 and 1328 (C–N and C=N (imidazole ring)), 3063 and 814 (C–H (in benzene ring)), 1157 ($C-SO_2-N$). ^1H NMR (400 MHz,$CDCl_3$): δ = 7.83 (d, 2H, benzene-H), 7.71 (d, 2H, benzene-H), 7.32 (m, 3H, benzene-H), 7.21 (d, 2H, benzene-H), 5.04 (dd,1H, imidazole-H), 3.29 (ddm,2H, imidazole-H), 2.04 (s, 3H, benzene-CH_3), 1.61 (s, 3H, benzene-CH_3).

3.2. Weight loss measurements

The results of weight loss measurements for the corrosion of carbon steel in 1.0 M HCl with and without different inhibitor concentrations at 60 °C are shown in Table 1.

The corrosion rate (v) was calculated by the following equation:

$$v = \frac{W}{St} \tag{1}$$



Scheme 1. The synthesis of imidazoline derivative IMI.