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ORIGINAL ARTICLE

Thermodynamic, chemical and electrochemical investigations of 2-mercapto benzimidazole as corrosion inhibitor for mild steel in hydrochloric acid solutions

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Abstract The inhibiting action of 2-mercapto benzimidazole (2MBI) on mild steel in 1.0 M hydrochloric acid has been investigated at 308 K using weight loss measurements and electrochemical techniques (impedance spectroscopy and potentiodynamic polarisation). Inhibition efficiency increases with 2MBI concentration to attain 98% at 10^{-3} M. Polarisation curves indicate that 2MBI acts as a mixed-type inhibitor. Inhibition efficiency values obtained from various methods were in good agreement. EIS measurements showed an increase of the transfer resistance with the inhibitor concentration. The temperature effect on the corrosion behaviour of steel in 1.0 M HCl without and with the 2MBI at various concentrations was studied in the temperature range from 308 to 353 K. Thermodynamic parameters such as heat of adsorption (ΔH°_{ads}), entropy of adsorption (ΔS°_{ads}) and adsorption free energy (ΔG°_{ads}) have been calculated. Kinetic parameters for the corrosion reaction at different concentrations of 2MBI were determined. Adsorption of 2MBI on the mild steel surface in 1.0 M HCl follows the Langmuir isotherm model.

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1. Introduction

Hydrochloric acid is a strong inorganic acid that is used in many industrial processes. The most important areas of applications are acid pickling, acid descaling and oil well acidizing. During these processes, metal such as steel is subjected to serious acid corrosion and inhibitors are often needed to reduce corrosion rates in this media.

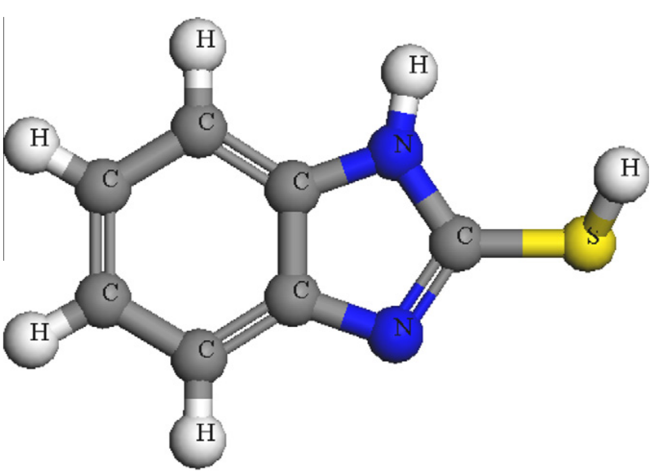
Most of the efficient inhibitors used in industry are organic compounds having multiple bonds in their molecules, which mainly contain nitrogen and sulphur. Nitrogen-containing compounds are more effectively in HCl (Bentiss et al., 2000; Abd El-Maksoud, 2003), whereas sulphur-containing compounds are preferred for H_2SO_4. These compounds can adsorb on metal surface and block the cathodic and/or anodic sites on the metal surface which lead to decrease the corrosion rate (Fisher, 1972; Riggs Jr., 1974). The mode of adsorption depends mainly on the chemical structure of the inhibitor, the chemical composition of the solution, the nature of the metal surface and the electrochemical potential of the metal-solution interface (Ita and Offiong, 1997a,b; Lukovits et al., 2001).

A survey of literature shows that nitrogen-containing organic compounds, such as amines, heterocyclic compounds (Ousslim et al., 2009; Sykes, 1984; Tang et al., 2003; Mernari et al., 1998; Bentiss et al., 2000; Walker, 1975; Xue et al., 1991; Wang et al., 2002; Kertit and Hammouti, 1996) and imidazole derivatives (Stupnicek-Lisac et al., 2002; Sivaraju et al., 2008; Khaled and Amin, 2009; Zhang et al., 2004; Christov and Popova, 2004; Khaled, 2003) offer good protection of metallic materials in acidic solutions. The encouraging results obtained with 2-mercapto benzimidazole (Wang et al., 2003; Popova et al., 2003; Trachli et al., 2002; Wang, 2001; Aljourani et al., 2009; Amar et al., 2007; Khaled and Fadl-Allah, 2009) have incited us to extend its use in the corrosion-inhibiting action on mild steel in HCl solution.

The aim of this work is to study the effect of 2-mercapto benzimidazole (2MBI) on the corrosion inhibition of mild steel in molar hydrochloric acid solution. The behaviour of steel in 1.0 M HCl with and without inhibitor is studied using gravimetric, potentiodynamic and EIS measurements. The thermodynamic parameters for the adsorption process and activation parameters for steel dissolution reactions are determined and discussed.

2. Experimental

2-Mercapto benzimidazole (2MBI) was analytical grade. The molecular structure is shown below:



Chemical structure of 2-mercapto benzimidazole.

The aggressive solution (1.0 M HCl) was prepared by dilution of analytical grade 37% HCl solution with double-distilled water. Prior to all measurements, the steel samples with the following composition (0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and the remainder iron) were abraded with different emery papers up to 1200 grade, washed thoroughly with double-distilled water, degreased with AR grade ethanol, acetone and drying at room temperature.

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 ml. The steel specimens used had a rectangular form (2.5 cm × 2 cm × 0.05 cm). The immersion time for the weight loss was 6 h at 308 K and 1 h at the other temperatures. After the corrosion test, the specimens of steel were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Triplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in mg cm^{-2} h^{-1}.

Electrochemical measurements were carried out in a conventional three-electrode electrolysis cylindrical Pyrex glass cell. The working electrode (WE) in the form of disc cut from steel has a geometric area of 1 cm^2 and is embedded in polytetrafluoroethylene (PTFE). A saturated calomel electrode (SCE) and a disc platinum electrode were used as reference and auxiliary electrodes, respectively. The temperature was thermostatically controlled at 308 ± 1 K. The working electrode, WE was abraded with silicon carbide paper (grade P1200), degreased with acetone and rinsed with double-distilled water before use.

Running on a personal computer, the 352 Soft Corr™ III software communicates with EG&G Instruments potentiostat–galvanostat model 263 A at a scan rate of 0.5 mV s^{-1}. Before recording the cathodic polarisation curves, the steel electrode is polarised at −800 mV for 10 min. For anodic curves, the potential of the electrode is swept from its corrosion potential after 30 min at free corrosion potential, to more positive values. The test solution is deaerated with pure nitrogen. Gas bubbling is maintained through the experiments.

The electrochemical impedance spectroscopy (EIS) measurements were carried out with the electrochemical system (Tacussel) which included a digital potentiostat model Voltalab PGZ 100 computer at E_{corr} after immersion in solution without bubbling, the circular surface of steel exposing of 1 cm^2 to the solution were used as working electrode. After the determination of steady-state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure. The impedance diagrams are given in the Nyquist representation. Values of R_t and C_{dl} were obtained from Nyquist plots.

3. Results and discussion

3.1. Weight loss tests

Gravimetric measurements of steel were investigated in 1.0 M HCl in the absence and presence of various 2MBI concentrations at 6 h of immersion and at 308 K. The inhibition efficiency (α%) was calculated by the following relation:

$$\alpha\% = \frac{W_{corr} - W_{corr(inh)}}{W_{corr}} \times 100 \quad (1)$$