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ORIGINAL ARTICLE

Experimental, Monte Carlo and molecular dynamics simulations to investigate corrosion inhibition of mild steel in hydrochloric acid solutions

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Abstract The efficiency of three furan derivatives, namely 2-(*p*-toluidinylmethyl)-5-methyl furan (Inh. A), 2-(*p*-toluidinylmethyl)-5-nitro furan (Inh. B) and 2-(*p*-toluidinylmethyl)-5-bromo furan (Inh. C), as possible corrosion inhibitors for mild steel in 1.0 M HCl, has been determined by weight loss and electrochemical measurements. These compounds inhibit corrosion even at very low concentrations, and 2-(*p*-toluidinylmethyl)-5-methyl furan (Inh. A) is the best inhibitor. Polarization curves indicate that all compounds are mixed-type inhibitors, affecting both cathodic and anodic corrosion currents. Adsorption of furan derivatives on the mild steel surface follows the Langmuir adsorption isotherm, and the calculated Gibbs free energy values confirm the chemical nature of the adsorption. Monte Carlo simulations technique incorporating molecular mechanics and molecular dynamics can be used to simulate the adsorption of furan derivatives on mild steel surface in 1.0 M HCl.

1. Introduction

The study of corrosion of mild steel and iron is a matter of tremendous theoretical and practical concern and as such has received a considerable amount of interest (Uhlig and Revie, 1985; Sastri, 1998).

Acid solutions, widely used in industrial acid cleaning, acid descaling, acid pickling, and oil well acidizing, require the use of corrosion inhibitors in order to restrain their corrosion attack on metallic materials. The use of organic compounds containing oxygen, sulfur and nitrogen to reduce corrosion attack on steel has been studied in some details (Sykes, 1990; Elachouri et al., 1995; Mernari et al., 1998). The existing data

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show that most organic inhibitors adsorb on the metal surface by displacing water molecules on the surface and forming a compact barrier film (Phani et al., 1995).

The interfacial behaviour of organic compounds can be modeled by modifying substituent and functional groups. Molecules that are otherwise only physically attached to the metal surface can be changed into chemically adsorbed entities. This is of particular significance in the field of corrosion inhibitors.

The correlation between the inhibitor efficiency and the molecular structure of organic compounds has been extensively investigated (Kuron et al., 1985; Edwards et al., 1994; Sastri and Perumareddi, 1994; Stupniek-Lisac et al., 1995).

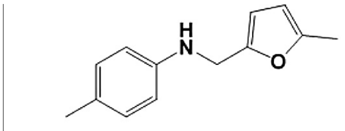
Availability of non-bonded (lone pair) and π-electrons in inhibitor molecules facilitates electron transfer from the inhibitor to the metal. A coordinate covalent bond involving transfer of electrons from inhibitor to the metal surface may be formed (Hackerman and Hurd, 1962). The strength of the chemisorption bond depends upon the electron density on the donor atom of the functional group and also upon the polarizability of the group.

The present work involves an extensive investigation of the three furan derivatives, which have been chosen to evaluate the effect of systematic changes in the molecular structure and the polar function of the compound. This is achieved by changing the substituents with respect to the oxygen hetero-atom in the furan ring, using one type of substituent.

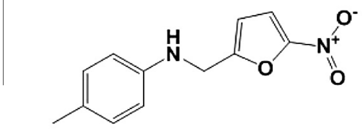
This study aims to continue our pervious investigation of furan derivatives as possible corrosion inhibitors (Khaled, 2010a) for mild steel in 1.0 M HCl solutions. Measurements were conducted using several corrosion monitoring techniques, such as weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy, EIS. It is also the purpose of this paper to elucidate the adsorption behaviour of some furan derivatives at the mild steel surface using molecular dynamics simulations.

2. Experimental details

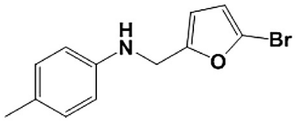
The furan derivatives investigated as corrosion inhibitors in hydrochloric acid are presented in Fig. 1. All furan derivatives were prepared by sodium borohydride reduction of corresponding azomethynes according to reported procedure (Klepo and Jakopi, 1985, 1987; Hansal et al., 1955).



2-(p-toluidinylmethyl)-5-methyl furan (A)



2-(p-toluidinylmethyl)-5-nitro furan (B)



2-(p-toluidinylmethyl)-5-bromo furan (C)

Figure 1 Investigated furan derivatives.

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 paper up to 4/0 grit size, washed thoroughly with double-distilled water, degreased with AR grade ethanol, acetone and dried at room temperature.

Weight loss 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 30 ± 1 °C. 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 $\text{mg cm}^{-2}\,\text{h}^{-1}$.

The electrochemical measurements were performed in a typical three-compartment glass cell consisted of the mild steel specimen as working electrode (WE), platinum counter electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode. The counter electrode was separated from the working electrode compartment by fritted glass. The reference electrode was connected to a Luggin capillary to minimize IR drop. Solutions were prepared from bidistilled water of resistivity 13 MΩ cm.

The electrode potential was allowed to stabilize 60 min before starting the measurements. All experiments were conducted at 30 ± 1 °C. Measurements were performed using Gamry Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry Framework system based on the ESA400, Gamry applications that include dc105 for dc corrosion measurements, EIS300 for electrochemical impedance spectroscopy measurements along with a computer for collecting data. Echem Analyst 5.58 software was used for plotting, graphing and fitting data.

Tafel polarization curves were obtained by changing the electrode potential automatically from (-750 to $-300\ \text{mV}_{\text{SCE}}$) at open circuit potential with scan rate of $1.0\ \text{mV s}^{-1}$. Impedance measurements were carried out in frequency range from 10 kHz to 20.0 mHz with an amplitude of 10 mV peak-to-peak using ac signals at open circuit potential.

The values of inhibition efficiency from corrosion current density and charge transfer resistance were calculated using Eqs. (1) and (2), respectively.

$$\sigma_{\text{p}}\% = \frac{j^{\text{o}}_{\text{corr}} - j_{\text{corr}}}{j^{\text{o}}_{\text{corr}}} \times 100 \qquad (1)$$

where $j^{\text{o}}_{\text{corr}}$ and j_{corr} are corrosion current densities obtained in the absence and presence of inhibitor, respectively:

$$\sigma_{\text{EIS}}\% = \frac{R_{\text{ct}} - R^{\text{o}}_{\text{ct}}}{R_{\text{ct}}} \times 100 \qquad (2)$$

where R_{ct} and R^{o}_{ct} are charge transfer resistances in the presence and absence of inhibitor, respectively.