

ORIGINAL ARTICLE

An experimental and theoretical investigation on adsorption properties of some diphenolic Schiff bases as corrosion inhibitors at acidic solution/mild steel interface



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Abstract The effect of novel synthesized three Schiff bases, namely, 1,3-bis[2-(2-hydroxy benzylidenamino) phenoxy] propane (P1), 1,3-bis[2-(5-chloro-2-hydroxybenzylidenamino) phenoxy] propane (P2), and 1,3-bis[2-(5-bromo-2-hydroxybenzylidenamino) phenoxy] propane (P3), on the corrosion of mild steel in 0.1 M HCl was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy methods. Polarization measurements suggest that P1 acts as mixed type inhibitor while P2 and P3 behave as mainly cathodic inhibitors for acidic corrosion of steel. All electrochemical measurements show that inhibition efficiencies increase with increase in inhibitor concentration. This reveals that inhibitive actions of inhibitors were mainly due to adsorption on steel surface. Adsorption of these inhibitors follows Temkin adsorption isotherm. The correlation between the adsorption ability of inhibitors and their molecular structures has been investigated using quantum chemical parameters obtained by MNDO semi-empirical method. Calculated quantum chemical parameters indicate that Schiff bases adsorbed on steel surface by chemical mechanism.

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1. Introduction

Steel is extensively used in various industrial operations and the study of its corrosion inhibition in pickling bath is of great importance. The use of inhibitors is one of the practical methods for protection against corrosion in especially acidic media (Nathan, 1977; TrabANELLI, 1991; Bahrami et al., 2010; Fouda and Ellithy, 2009). Most of the effective inhibitors are organic compounds combining nitrogen, oxygen, phosphorous and sulphur in their structures (Clubby, 1990; Stupnisek-Lisac

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and Ademovic, 1995; Özcan et al., 2004; Moretti et al., 1996). The inhibiting actions of organic compounds are usually attributed to their interactions with the metal surface via their adsorption. These compounds in general are adsorbed on the metal surface, blocking the active corrosion sites. Four types of adsorption may take place by organic molecules at metal/solution interface: (1) electrostatic attraction between the charged molecules and the charged metal, (2) interaction of unshared electron pairs in the molecule with the metal, (3) interaction of π electrons with the metal and (4) combination of (1) and (3) (Shokry et al., 1998).

The adsorption ability of inhibitors onto metal surface depends on the nature and surface charge of metal, the chemical composition of electrolytes, and the molecular structure and electronic characteristics of inhibitor molecules. Organic compounds containing functional electronegative groups and π -electrons in triple or conjugated double bonds are usually good inhibitors (Yurt et al., 2004; Ju et al., 2008; Ahamad et al., 2010a). Schiff bases, with $RC=NR'$ as general formula, have both the features combined with their structure which may then give rise to particularly potential inhibitors.

Schiff bases are condensation products of an amine and a ketone or aldehyde. The greatest advantage of Schiff bases is that they can be easily synthesized from relatively inexpensive materials. Some Schiff bases have been recently reported as effective corrosion inhibitors for steel, aluminium and copper in acidic media (Bain et al., 1989; Emregül et al., 2003; Gomma and Wahdan, 1995; Yurt et al., 2006; Li et al., 1999a,b; Negm and Zaki, 2008).

The purpose of the present study is to investigate the effect of 1,3-bis[2-(2-hydroxybenzylidenamino)phenoxy]propane, 1,3-bis[2-(5-chloro-2-hydroxybenzylidenamino)phenoxy]propane, and 1,3-bis[2-(5-bromo-2-hydroxybenzylidenamino)phenoxy]propane on the electrochemical behaviour of mild steel in 0.1 M HCl solution using electrochemical techniques. In order to investigate the relationship between inhibition efficiency and the structure of studied Schiff bases, some quantum chemical parameters such as HOMO and LUMO energies, charge density of adsorption centres, dihedral angles

and dipole moment have also been calculated. Theoretical approaches provide means of analyzing metal-inhibitor interactions and there are many reports related with this area (Yurt et al., 2005a,b; Bentiss et al., 2002).

2. Experimental

2.1. Materials and sample preparation

The Schiff base compounds used were synthesized by condensation reaction between 1.9 mmol 1,3-bis(*o*-aminophenoxy)-3-oxopropane and the corresponding aldehydes (3.8 mmol) in 50 mL methanol and recrystallized in methanol-THF mixture. The aldehyde compounds used were salicylaldehyde, 5-chlorosalicylaldehyde and 5-bromosalicylaldehyde. All chemicals were purchased from Merck and were not purified further. The structures of all synthesized salicylaldehyde Schiff bases, 1,3-bis[2-(2-hydroxybenzylidenamino)phenoxy]propane (P1), 1,3-bis[2-(5-chloro-2-hydroxybenzylidenamino)phenoxy]propane (P2), and 1,3-bis[2-(5-bromo-2-hydroxybenzylidenamino)phenoxy]propane (P3), were characterized by using elementary analyses, FT-IR, ^{13}C NMR and 1H NMR spectroscopy techniques. The general structure of these inhibitors is given by Fig. 1.

2.2. Electrochemical experiments

Electrochemical experiments were performed using mild steel specimen with the following composition: 0.134% C, 0.0514% Ni, 0.555% Mn, 0.0117% P, 0.200% Si, 0.0258% S and balance Fe. A cylindrical steel rod (whose exposed surface area was 0.1963 cm²) was inserted into a Teflon tube so that only the flat surface was in contact with test solution. Before each experiment, the electrode was polished with a sequence of emery papers of different grades (600, 800 and 1200), washed with double distilled water and degreased with acetone.

Electrochemical impedance (EIS) and potentiodynamic polarization (PP) studies were carried out using a Gamry PC3/600 potentiostat/galvanostat/ZRA system (Wilmington, USA). Electrochemical experiments were performed in a conventional three-electrode cell at 25 °C with a platinum counter electrode and silver-silver chloride (Ag|AgCl|Cl⁻) electrode as reference electrode. Solutions were prepared with double distilled water and deaerated by bubbling ultra pure nitrogen gas for 30 minutes before use and continued during tests. Working electrode was first immersed into the test solution for 30 min to establish a steady state open circuit potential. EIS measurements were performed at corrosion potentials (E_{corr}) over a frequency range of 0.05–10⁵ Hz with a signal amplitude perturbation of 5 mV. Potentiodynamic polarization studies were performed with a scan rate of 0.5 mV/s in the potential range from -400 to +400 mV relative to the corrosion potential. Experiments were always repeated at least three times.

2.3. Quantum chemical calculations

Theoretical calculations were carried out at the restricted Hartree-Fock Level (RHF) using MNDO, semi-empirical SCF-MO methods in the HyperChem Release 8.0 packet program

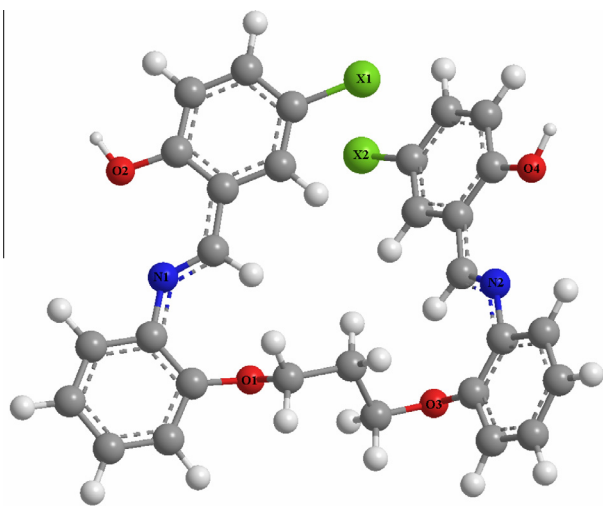


Figure 1 Molecular structure of investigated Schiff bases (P1; X = H, P2; X = Cl, P3; X = Br).

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