Corrosion Science 92 (2015) 104–117

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Experimental and computational investigation on the corrosion inhibition characteristics of mild steel by some novel synthesized imines in hydrochloric acid solutions

Hany M. Abd El-Lateef *

Chemistry Department, Faculty of Science, Sohag University, 82524 Sohag, Egypt

ARTICLE INFO

Article history:
Received 28 June 2014
Accepted 26 November 2014
Available online 4 December 2014

Keywords:
A. Acid solutions
A. Mild steel
B. EIS
B. SEM
C. Acid inhibition

ABSTRACT

Two novel imines were synthesized and their inhibitive properties on mild steel corrosion in HCl were investigated using potentiodynamic polarization, electrochemical impedance spectroscopy and linear polarization resistance corrosion rate. Polarization curves indicate that all studied compounds were acting as mixed type inhibitors. All measurements showed that, inhibition efficiencies increase with increasing inhibitor concentration. Adsorption of these inhibitors follows Langmuir adsorption isotherm. The potential of zero charge in inhibited solution was studied, and a mechanism for the adsorption process was proposed. Theoretical calculations have been used to provide the correlation between the inhibition efficiencies of studied inhibitors and their molecular structure.

1. Introduction

Mild steel is used in mass amounts in marine applications, chemical processing, petroleum production and refining, construction and metal processing equipment [1–4], despite it has a relatively high cost. These applications usually induce serious corrosive effects on equipment's, tubes and pipelines made of iron and its alloys [5–7]. Hydrochloric acid is the most difficult of the common acids to handle from the standpoints of corrosion and materials of constructions. Extreme care is required in the selection of materials to handle the acid by itself, even in relatively dilute concentrations or in process solutions containing appreciable amount of hydrochloric acid. This acid is very corrosive to most of the common metals and alloys [8].

The use of chemical inhibitors has been acknowledged as one, and a very practical and most economical, method of combating corrosion [9–11]. The inhibiting molecule retards the rate of corrosion by acting at the metal–corrosive medium interface. Most of acid corrosion inhibitors are organic compounds containing electronegative atoms (such as, N, S, P, and O), the unsaturated bonds (such as, double bonds or triple bonds) and the plane conjugated systems including all kinds of aromatic cycles [12–15]. Schiff-bases are considered as a very important class of organic compounds having general formula R′—C=N—R″ where R′ and R″ are aryl, alkyl or cycloalkyl or heterocyclic groups formed by the condensation of an amine and a carbonyl group, having wide applications in many biological aspects, proteins, visual pigments, enzymic aldolization and decarboxylation reactions [16,17]. An interesting application of Schiff's bases is their use as effective corrosion inhibitors, which is based on their ability to spontaneously form a monolayer on the surface to be protected [18]. Several Schiff bases have also been investigated as corrosion inhibitors for different metals and alloys in acidic media [19–22]. Due to the presence of the —C=N— group, an electron cloud on the aromatic ring, the electronegative nitrogen, oxygen and sulfur atoms in the molecule, Schiff bases should be good corrosion inhibitors [23].

The quantum chemical calculations have been widely used to study the reaction mechanisms and to interpret the experimental results as well as to solve chemical ambiguities [24]. The use of theoretical parameters presents two main advantages:

I. The compounds and their various fragments and substituents can be directly characterized based on their molecular structure only.
II. The proposed mechanism of action can be directly accounted for in terms of the chemical reactivity of the compounds under study [25].

The present study was undertaken to assess the adsorption behavior and inhibition effect of sodium 3-[{[1-carboxy-3-(methylthio) propyl] imino} methyl]-4-hydroxybenzenesulfonate

---

* Tel.: +20 12 28 137 103; fax: +20 93 4601159.
E-mail address: Hany_shubra@yahoo.co.uk

http://dx.doi.org/10.1016/j.corsci.2014.11.040

(**S$_I$**) and sodium 3-{[(1-carboxy-2-phenylethyl) imino] methyl}-4-hydroxybenzenesulfonate (**S$_{II}$**) on the corrosion of mild steel in 1.0 M HCl solution at 50 °C using electrochemical techniques as well as to clarify the inhibition mechanism. The relation between the inhibition efficiency of used Schiff bases in the investigated acidic solution and some quantum chemical parameters (such as HOMO, LUMO energies and dipole moment) have been also studied.

2. Experimental procedure

2.1. Reagents and instrumentation

All the used amino acids in the present study are of analytical grade purchased from Sigma Aldrich and used as received without further purification, sodium 2-hydroxybenzaldehyde-5-sulfonate was prepared according to the literature [26]. Conductivity measurements were made at 25 °C on Jenway conductivity meter 4320 using bidistilled water as a solvent. The electronic spectra of the compounds were monitored using matched 1.0 cm silica cells on Perkin Elmer Lambda 35 spectrophotometer and IR spectra of the prepared compounds recorded over the 400–4000 cm^{-1} range on a Shimadzu FTIR-8101 Fourier transform infrared spectrophotometer using KBr disks. The ^{1}H NMR and ^{13}C NMR spectra were recorded from a Bruker Advance DPX-200 spectrometer. Elemental analyses were carried out at the micro analytical center, Cairo University, Egypt.

2.2. Synthesis of Schiff base compounds

4 mmol (0.896 g) of sodium 2-hydroxybenzaldehyde-5-sulfonate (pink) in 20 cm^3 de-ionized water was added drop wise to an equimolar aqueous solution of amino acid (**S$_I$**, 0.596 g DL-methionine in 15 ml de-ionized water; **S$_{II}$**, 0.33 g L-phenylalanine in 15 ml de-ionized water) then the mixture was stirred at 80 °C for 3 h to give yellow color (first observation indicated the formation of Schiff base). The obtained solution was evaporated under room temperature. The solid obtained was filtered-off, washed several times with ether, and then recrystallized from ethanol–water mixture (3:1). The two compounds were prepared by similar procedure. Melting point for all compounds is more than 350 °C but for aldehyde 263 °C. The structures of the prepared compounds are listed in Table 1.

2.3. Chemical composition of mild steel alloy

The working electrode made of C1018 mild steel, which is representative of a pipeline material. The cylindrical shaped working electrode has a diameter of 0.5 cm, length of 3.0 cm and 4.55 cm^2 exposed area to fluid. The chemical composition (wt%) of mild steel alloy used in this study was given in Table 2. The data was provided by European Corrosion Supplies Ltd. and was confirmed by energy dispersive X-ray fluorescence.

Table 2
Chemical composition of mild steel alloy.

Elements	Analysis (wt%)
C	0.18
Si	0.17
Ni	0.01
Mn	0.70
P	0.011
S	0.03
Cr	0.01
Fe	Rest

2.4. Preparation of solutions

The aggressive solutions used were made of AR grade (BDH) HCl. Appropriate concentration (1.0 M) of the acid was prepared using de-ionized water. The concentration range of inhibitors employed was 0.01–1.0 mM in 1.0 M HCl. All the Schiff base inhibitors are soluble in bidistilled water and in some organic solvents (ethanol and methanol), but partially soluble in acetone and insoluble in ether.

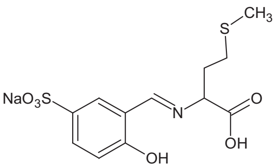
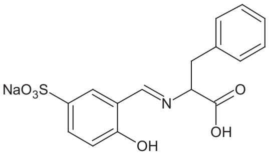
2.5. Corrosion measurements

All the experiments were performed at atmospheric pressure in a one liter glass cell. It consisted of a typical three electrode configuration where a mild steel was used as working electrode (A = 4.55 cm^2). This electrode was used for one time, a concentric platinum wire was used as a counter electrode and a saturated calomel electrode (SCE) electrode served as reference. The glass cell was filled with the prepared 1.0 M HCl solution. Then this cell was thermostated at 50 °C for 1 h before beginning the experiment. To remove any surface contamination and air formed oxide, the working electrode was kept at −1500 mV (SCE) for 5 min in the tested solution, disconnected shaken free of adsorbed hydrogen bubbles and then cathodic and anodic polarization was recorded. VersaSTAT4 potentiostat/galvanostat and ACM Gill AC instruments connected with a personal computer were used for the measurements.

2.5.1. Potentiodynamic measurements

The extrapolation of cathodic and anodic Tafel lines was carried out in a potential range ±250 mV vs. the corrosion potential (E_{corr})

Table 1
List of the synthesized Schiff base compounds include, code number, name and structure.

Code number of the Schiff base compounds	Name	Structure	Molecular weight (g mol^{-1})
S$_I$	Sodium 3-[{[1-carboxy-3-(methylthio) propyl] imino} methyl]-4-hydroxybenzenesulfonate		355.36
S$_{II}$	Sodium 3-{[(1-carboxy-2-phenylethyl) imino] methyl}-4-hydroxybenzenesulfonate		371.34