



Physicochemical interactions of chiral Schiff bases on high carbon steel surface: Corrosion inhibition in acidic media



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ARTICLE INFO

Article history:

Received 6 March 2013

Received in revised form 16 May 2013

Accepted 6 June 2013

Available online 9 July 2013

Keywords:

Chiral Schiff bases

High carbon steel

Corrosion inhibition

Electrochemical studies

SEM–EDS

ABSTRACT

(S)1-N-(1-hydroxy-1,1-diphenyl-3-methylbut-2-yl)-2-hydroxybenzaldimine (DPV) and (S)1-N-(1-hydroxy-3-methylbut-2-yl)-2-hydroxybenzaldimine (LV) were synthesized and investigated as inhibitors for the corrosion of the high carbon steel (HCS) in 1.0 M HCl by electrochemical measurements. According to the electrochemical methods, inhibitor DPV showed higher efficiency in comparison to that of LV. The Tafel polarization method revealed the mixed-mode inhibition of chiral Schiff bases with predominant control of the anodic reaction. The adsorption of the inhibitor molecules onto the HCS surface was found to follow the Langmuir adsorption isotherm. The values of the Gibbs free energy of adsorption strongly supported spontaneous physicochemical adsorption of inhibitor molecules on the HCS surface. The adsorption mechanism for inhibition was supported by Fourier transforms infrared (FTIR), wide-angle X-ray diffraction (WAXD), scanning electron microscopy–energy-dispersive X-ray (SEM–EDS) spectroscopic methods, and adsorption isotherms.

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1. Introduction

High carbon (or mild) steel (HCS) is one of the most commonly used constructional material in various chemical industries owing to its low cost [1], good tensile strength [2] and availability [3]. Also, the uses of acid solutions in chemical industries, such as acid pickling of metals [4], oil well acidification [5], ore production [6] and chemical cleaning and processing are indispensable [7]. Therefore so, the protection of HCS from acid corrosion is an important topic among the researchers due to its wide range of industrial applications [8]. Several attempts have been made to synthesize various organic and inorganic compounds containing electronegative functional groups (C=O, N–H, O–H and C=S) and electron rich aromatic systems [9–12] and investigated as inhibitors for the corrosion of carbon steel [13–15]. Among them benzimidazole derivatives, thiourea derivatives and Schiff bases have been widely considered as inhibitors for the corrosion of mild/carbon steel in acid solutions by many authors [16–21]. However, they possess limitation due to its high cost, high operational hazard, low solubility and their difficulty in preparation methods [17–20,22]. To overcome these issues, instead of toxic inhibitors, there are several environment friendly green inhibitors have been developed [23–26]. Abdel-Gaber et al. [27] investigated corrosion inhibition of mild steel using various plant extracts and found that the plant

extracts are effective against the corrosion of steel. Chauhan and Gunasekaran [28] have studied corrosion inhibition of mild steel using various environmental friendly green inhibitors and found that the extracts are effective corrosion inhibitors. However, they are limited due to its less effectiveness at lower concentrations as well as at elevated temperatures [29,30]. Hence, continuous efforts have been made to search for effective, environmental friendly and stable corrosion inhibitors for the inhibition of carbon steel. Recently, chiral amino acid derivatives have attracted much attention owing to its non-toxicity, less cost and possess high solubility in organic solvents [31,32]. Previously, it has been reported that the presence of electronegative atoms such as N and O in amino acid derivatives can effectively block the active corrosion sites on the metal surface by forming protective layer [13,15]. Hence, we believe that the amino acid derived ligands could act as effective inhibitors for the corrosion of carbon steel. So far, there is no report on the chiral amino acid derivatives for the corrosion of high carbon steel in hydrochloric acid medium.

Thus, we have planned to synthesize chiral Schiff bases ligands and focused to study their corrosion inhibition property of HCS in 1.0 M HCl. The prepared Schiff base ligands were well characterized by ¹H NMR, ¹³C NMR and FT-IR spectra. The inhibitive action of chiral Schiff bases toward the corrosion of HCS was investigated by electrochemical methods. Thermodynamic parameters were calculated to explain the modes of interaction of chiral Schiff bases on the HCS surface at different concentrations. In order to investigate the inhibition mechanism of chiral Schiff base ligands, HCS scraped were analyzed by FT-IR, WAXD and SEM–EDS analysis.

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2. Experimental details

2.1. Materials, specimen and electrolyte

L-Valine (Himedia), salicylaldehyde (Merck), ammonium chloride (Rankem), thionylchloride (Merck), Methanol (Finar), bromobenzene (Merck), magnesium turnings, iodine (Merck), sodium borohydride (Merck), hexane (Merck), tetrahydrofuran (Rankem), ethanol (Merck) were used as received. Tetrahydrofuran was used only after distillation with sodium metal and benzophenone. HCS specimens containing C = 13.97%, Mn = 0.66%, Si = 0.72%, Al = 0.16%, K = 0.23%, F = 2.29% and Fe = 81.14% were used for the study. AR-grade HCl (Merck) and doubly distilled water were used to prepare 1.0 M HCl solution for all experiments.

2.2. Synthesis of inhibitors

(S)1-N-(1-hydroxy-1,1-diphenyl-3-methylbut-2-yl)-2-hydroxybenzaldimine (DPV) and (S)1-N-(1-hydroxy-3-methylbut-2-yl)-2-hydroxybenzaldimine (LV) were synthesized according to the previously reported procedures [33,34]. The prepared chiral Schiff bases were characterized by ¹H NMR, ¹³C NMR and FT-IR. The chemical structures of the inhibitors are shown in Fig. 1.

2.2.1. DPV

Melting point: 170–172 °C, [α]_D²⁵ +77.8 (*c* = 1, CHCl₃) [Lit.11 [α]_D²⁵ +80.7 (*c* = 1, CHCl₃)]. FTIR (cm⁻¹) 3258, 2960, 1630, 1276. ¹H NMR (DMSO-d₆ δ ppm): 0.81 (d, ³J = 6.8 Hz, 3H, -CH₃), 0.91 (d, ³J = 6.8 Hz, 3H, -CH₃), 2.08 (m, ³J = 2.0 Hz, 1H, -CH), 3.89 (s, 1H, -OH), 4.01 (d, ³J = 2.0 Hz, 1H, -CH), 5.22 (s, 1H, -OH), 6.78 (m, ³J = 7.2 Hz, 1H, phenyl), 6.84 (d, ³J = 8.4 Hz, 1H, phenyl), 7.08 (t, ³J = 1.2 Hz, 1H, phenyl), 7.10 (t, ³J = 6.4 Hz, 1H, phenyl), 7.13 (m, ³J = 8.0 Hz, 3H, phenyl), 7.21 (t, ³J = 13.6 Hz, 1H, aromatic proton), 7.26 (t, ³J = 8.0 Hz, 2H, aromatic proton), 7.38 (d, ³J = 7.6 Hz, 2H, aromatic proton), 7.50 (d, ³J = 7.2 Hz, 2H, aromatic proton), 8.11 (s, 1H, -CH=N). ¹³C NMR (DMSO-D₆, δ ppm): 17.93, 22.57, 28.95, 80.4, 116.97, 118.54, 118.69, 125.79, 125.92, 126.75, 126.81, 128.23, 128.27, 131.68, 132.61, 144.31, 146.14, 160.91, 166.77.

2.2.2. LV

Melting point: 99–102 °C, [α]_D²⁵ = -24.1° (*c* = 1, CH₃OH) [Lit.11 [α]_D²⁴ = -26.2° (*c* = 1, CH₃OH)]. FTIR (cm⁻¹) 3580, 2962, 1628, 1278. ¹H NMR (CDCl₃, δ ppm): 0.88 (dd, ³J = 1.2 Hz, 6H, -(CH₃)₂), 1.87 (m, ³J = 6.4 Hz, 1H, -CH), 2.99 (m, ³J = 2.8 Hz, 1H, -CH), 3.69 (dd, ³J = 2.4 Hz, 1H, -CH), 3.76 (dd, ³J = 3.6 Hz, 1H, -CH), 5.04 (s, 1H, OH), 6.82 (t, ³J = 6.4 Hz, 1H, -phenyl), 6.88 (d, ³J = 8.4 Hz, 1H, phenyl), 7.19 (t, ³J = 7.6 Hz, 1H, phenyl), 7.25 (d, ³J = 7.2 Hz, 1H, phenyl), 8.29 (s, 1H, -C=N), 7.8 (s, 1H, -OH). ¹³C NMR (CDCl₃, δ ppm): 17.85, 32.15, 62.1, 79.81, 117.3, 120.5, 123.7, 130.1, 133.6, 151.4, 161.53.

2.3. Electrochemical measurements

Electrochemical measurements were carried out in a conventional three-electrode system, using a CH electrochemical analyzer model 604B electrochemical workstation maintained at

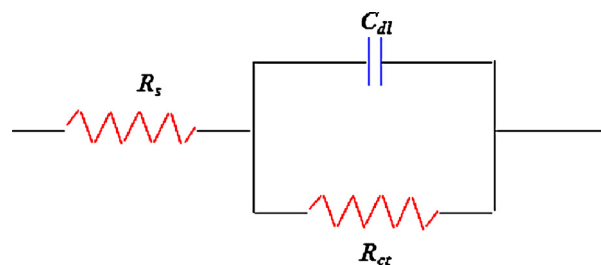


Fig. 2. Equivalent circuit model for electrochemical impedance measurements. In the given electrical equivalent circuit, R_s is the solution resistance, R_{ct} is the charge-transfer resistance, and C_{dl} is the double layer capacitance.

a temperature of 300 K. Pt and SCE were used as auxiliary and reference electrodes respectively. The working electrode was in the form of a square cut from HCS with surface area of 1.0 cm². Prior to the electrochemical measurements, HCS specimens are abraded with a series of emery papers from 400 to 1200 grade. Then the HCS specimens are washed carefully with distilled water, degreased with acetone and dried under vacuum. All tests have been performed with freshly abraded electrode in deaerated test solution and the temperature was kept at 300 ± 1 K.

In the electrochemical polarization technique, the linear Tafel segments of the anodic and cathodic curves were extrapolated to the corrosion potential to obtain the corrosion current densities. The anodic and cathodic polarization curves (b_a and b_c) were recorded by a sweep rate of 0.5 mV s⁻¹. Inhibition efficiency (IE%) values were calculated from I_{corr} as follows,

$$IE(\%) = \frac{(I'_{corr} - I_{corr})}{I_{corr}} \times 100 \quad (1)$$

where I'_{corr} and I_{corr} are corrosion current densities in the absence and presence of inhibitor.

AC impedance measurements were carried out at the range from 100 kHz to 10 MHz at amplitude of 10 mV. The impedance diagrams are given in Nyquist representation. The impedance spectra for the Nyquist plots were examined by fitting to the equivalent circuit model shown in Fig. 2, which has been used previously to model the mild steel/acid interface [35]. Inhibition efficiency values were calculated using Eq. (2):

$$IE(\%) = \frac{R_{ct} - R'_{ct}}{R_{ct}} \times 100 \quad (2)$$

where R_{ct} and R'_{ct} are corrosion current densities in the absence and presence of inhibitor.

2.4. Adsorption isotherm

In order to investigate the mechanism of inhibition, various adsorption isotherm models such as Langmuir, Frumkin and Temkin were tested. For this purpose, the degree of the surface coverage (θ) for different concentrations of inhibitors has been calculated from electrochemical data. Then these calculated values were used to determine empirically, which adsorption isotherm best fits the surface coverage data. The degree of surface coverage (θ) and the adsorption models are given as follows [36]:

$$\theta = \frac{IE}{100} \quad (3)$$

$$\text{Langmuir model: } K_{ads}C = \frac{\theta}{1 - \theta} \quad (4)$$

$$\text{Temkin model: } K_{ads}C = e^{\theta} \quad (5)$$

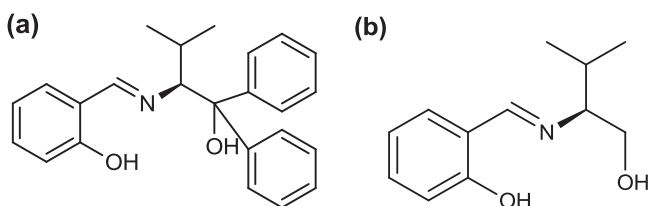


Fig. 1. Chemical structure of (a) DPV and (b) LV.

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