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Electrochemical and theoretical quantum approaches on the inhibition of C1018 carbon steel corrosion in acidic medium containing chloride using some newly synthesized phenolic Schiff bases compounds

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ABSTRACT

Two novel Schiff bases, 5-bromo-2-[(*E*)-(pyridin-3-ylimino)methyl]phenol (HBSAP) and 5-bromo-2-[(E)-(quinolin-8-ylimino)methyl]phenol (HBSAQ) have been synthesized. They have been characterized by elemental analysis and spectroscopic techniques (UV–Vis, IR and NMR). Moreover, the molecular structure of HBSAP and HBSAQ compounds are determined by single crystal X-ray diffraction technique. The inhibition activity of HBSAP and HBSAQ for carbon steel in 3.5% NaCl + 0.1 M HCl for both short and long immersion time, at different temperatures (20–50 °C), was investigated using electrochemistry and surface characterization. The potentiodynamic polarization shows that, the inhibitors molecule is more adsorbed on the cathodic sites. Its efficiency increases with increasing inhibitor concentrations (92.8% at the optimal concentration of 10^{-3} M for HBSAQ). Adsorption of the inhibitors on the carbon steel surface was found to obey Langmuir's adsorption isotherm with physical/chemical nature of the adsorption, as it is shown also by scanning electron microscopy. Further, the electronic structural calculations using quantum chemical methods were found to be in a good agreement with the results of the experimental studies.

1. Introduction

One of the main problems in the industrial process is corrosion of metals leading to increase in manufacturing costs, thereby production costs. Carbon steel has been one of the most important and widely used materials, playing a central role as basic material for the metallurgical industries. There are various techniques to protect carbon steel against corrosion in rough environments [1–3]. The use of corrosion inhibitors is one of the most economical and practical method to reduce the corrosive attack of the environment on carbon steel surface [4]. Corrosion inhibitors are commonly added in small amounts to corrosive environments to control corrosion. The inhibitors act at the interphase created by corrosion product between the metal and aqueous aggressive solution and their interaction with the corroding metal surface, through adsorption process, often leads to a change in the surface available to the process or in either the mechanism of the electrochemical process at the double layer [5].

In the literature, several Schiff bases have reported as effective corrosion inhibitors for different metals and alloys in acidic media [6–9]. Increasing popularity of Schiff bases in the field of corrosion inhibition science based on the ease of synthesis from relatively inexpensive starting materials and their eco-friendly or low toxic properties [10,11]. Due to the presence of the —C=N— group, electronegative nitrogen, sulfur and/or oxygen atoms in the molecule, Schiff bases should be good corrosion inhibitors. The action of such inhibitors depends on the specific interaction between the functional groups and the metal surface [12,13]. These molecules normally form a very thin and persistent adsorbed film that lead to decrease in the corrosion rate due to the slowing down of anodic, cathodic reaction or both [14,15]. Chloride containing acidic medium was used extensively in chemical and several industrial processes [16,17]. Therefore, the protection efficiency of inhibitors in this medium is very important.

Theoretical computational chemistry has been used recently to explain the mechanism of corrosion inhibition [3]. Electronic

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structural calculations using quantum chemical methods have been proved to be a very powerful tool for studying the electronic properties of the system and from here to discuss or elucidate a possible mechanism [3]. In this approach, the electronic properties relevant to the inhibiting action are calculated [18–20]. Ashassi-Sorkhabi et al. [21] investigated the possible application of benzylidene-pyridine-2-yl-amine, (4-benzylidene)-pyridine-2-yl-amine and (4-chloro-benzylidene)-pyridine-2-yl-amine as the corrosion inhibitors for mild steel in 1 M HCl solution. The experimental analysis shows that (4-chloro-benzylidene)-pyridine-2-yl-amine has better performance than the other inhibitors, which is supported by theoretical calculations [21]. In this study, synthesis, characterization, theoretical parameters and the inhibiting properties of two novel Schiff bases namely 5-bromo-2-[(*E*)-(pyridin-3-ylimino)methyl]phenol (HBSAP) and 5-bromo-2-[(E)-(quinolin-8-ylimino)methyl]phenol (HBSAQ) for carbon steel protection in 3.5% NaCl + 0.1 M HCl have been investigated. Electrochemical measurements have been performed and the adsorption mechanism was elucidated. The effect of temperature, inhibitor concentration and immersion time on the inhibition efficiency of carbon steel was also studied. The surface morphology of the carbon steel was examined with a scanning electron microscope (SEM) in the presence and absence of HBSAQ. In addition, the energies of the highest occupied molecular orbital (E_{HOMO}), the lowest unoccupied molecular orbital (E_{LUMO}), the energy gap (ΔE) and charge density distribution on the atoms were calculated.

2. Materials and methods

2.1. Synthesis of Schiff base compounds

Starting materials were purchased from Aldrich and all manipulations and used directly without further purification in the preparation of the Schiff bases compounds.

2.1.1. Synthesis of 5-bromo-2-[(E)-(pyridin-3-ylimino)methyl]phenol (HBSAP) compound

Suitable orange crystals were obtained directly from the synthesis of HBSAP compound. A solution of 4.04 g of 5-bromosalicylaldehyde (20 mmol) were dissolved in 60 ml of ethanol and heated to reflux. On the other hand, 3-aminopyridine (1.89 g, 20 mmol) was dissolved in 50 ml of ethanol. The mixture of both solutions was refluxed for 3 h. Yield: 90%. IR (cm^{-1}) 1615 s, 1560 m, 1474 s, 1354 s, 1273 s, 1181 s, 977 w, 915 w, 809 s, 699 m, 563 w, 451 w. Elemental analysis calculation for HBSAP ($C_{12}H_9N_2OBr$): C, 51.96; H, 3.24; N, 10.10%. Found: C, 51.77; H, 3.11; N, 10.11%. ^{1}H NMR (400 MHz, DMSO-d_6): d(ppm) 6.81 (d, 1H), 7.41 (d, 1H), 7.8 (s, 1H), 7.34 (t, 1H), 8.31 (s, 1H), 8.45(d, 1H), 7.71 (s, 1H), 8.59 (s, 1H), 13.48 (s, 1H).

2.1.2. Synthesis of 5-bromo-2-[(E)-(quinolin-8-ylimino)methyl]phenol (HBSAQ) compound

Suitable bright-red crystals were obtained directly from the synthesis of the HBSAQ compound. A solution of 4.04 g of 5-bromosalicylaldehyde (20 mmol) were dissolved in 60 ml of ethanol and heated to reflux. On the other hand, 8-aminoquinoline (5.76 g, 20 mmol) was dissolved in 50 ml of ethanol. The mixture of both solutions was under reflux for 3 h. Yield: 87%. IR (cm^{-1}) 1617 s, 1474 m, 1382 w, 1283 m, 1186 m, 964 w, 828 m, 792 s, 753 m, 589 m, 482 m. Elemental analysis calculation for HBSAQ ($C_{16}H_{10}N_2OBr$): C, 58.68; H, 3.06; N, 8.56. Found: C, 58.89; H, 3.15; N, 8.42%. ^{1}H NMR (400 MHz, DMSO-d_6): d(ppm) 6.97 (d, 1H), 6.99 (d, 1H), 7.89 (d, 4H), 7.94 (d, 1H), 8.43 (d, 1H), 8.46 (d, 1H), 8.98 (s, 1H), 9.11 (s, 1H), 14.08 (s, 1H).

2.2. Structure determination

C, H and N analyses were performed with a Perkin–Elmer 2400 series II analyzer. Infrared spectra (4000–400 cm^{-1}) were recorded from KBr pellets on a Bruker IFS-125 FT-IR spectrophotometer. NMR spectra were measured and recorded in the Central Lab., Chemistry Department, Faculty of Science, Sohag University at 25 °C on a multinuclear FT-NMR spectrometer Bruker ARX400 at 400.1 (1H) and 100.6 (13C and dept) MHz. The 1H and 13C chemical shifts δ are given in ppm absorption spectra were recorded with 1 nm resolution for all cases on a Cary 100 Bio UV–spectrophotometer.

2.3. Crystal structure determination

Single crystal diffraction data for HBSAP and HBSAQ were collected on a yellow plate on a Bruker APEXII SMART diffractometer at the Facultat de Química, Universitat de Barcelona, using a microfocus Molybdenum k_α radiationsource. The crystal was kept at 101.0 K during data collection. Using Olex2 [22], the structure was solved with the ShelXS-2013 [23] structure solution program using Direct Methods and refined with the olex2.refine [24] refinement package using Gauss–Newton minimization.

2.4. Chemical composition of carbon steel alloy

The chemical composition (wt%) of carbon steel C1018 electrodes used in this study was C 0.18%, Si 0.17%, Mn 0.70%, P 0.011%, S 0.03%, Ni 0.01%, Cr 0.01% and Fe balance. The data were provided by European Corrosion Supplies Ltd.

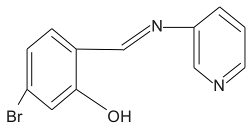
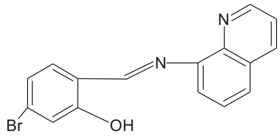
2.5. Test solution

The aggressive solution 3.5% NaCl + 0.1 M HCl (pH = 1.29), 3.5% NaCl (E. Merck), was prepared by dissolving of analytical grade NaCl in deionized water. Appropriate volume (0.1 M) of the acid was added to NaCl solution. The concentration range of inhibitors employed was 1×10^{-5} to 1×10^{-3} M in 3.5% NaCl + 0.1 M HCl. All the Schiff bases inhibitors (as sodium salt) are soluble in bidistilled water. The scheme of the structures of HBSAP and HBSAQ compounds is shown in Table 1.

2.6. 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 carbon 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

Table 1
List of the synthesized Schiff base compounds includes abbreviation, name, M. wt and structure.

Compound name	Abbreviation	Structure	M. wt
5-Bromo-2-[(E)-(pyridin-3-ylimino) methyl] phenol	HBSAP		277.12
5-Bromo-2-[(E)-(quinolin-8-ylimino) methyl] phenol	HBSAQ		327.18