

**CORROSION INHIBITION OF STEEL BY SELECTED  
IMIDAZOLE SERIES: SPECTROSCOPIC,  
ELECTROCHEMICAL AND MECHANISTIC STUDIES**

**BY**

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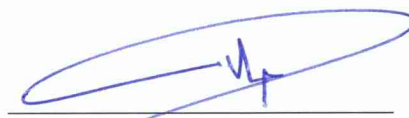


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[Dedicated to my family ]

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## LIST OF ABBREVIATIONS

|       |   |                                                               |
|-------|---|---------------------------------------------------------------|
| AC    | : | Alternating current                                           |
| AFM   | : | Atomic force microscopy                                       |
| API   | : | 4-(1H-imidazol-1-yl)aniline                                   |
| BI    | : | Benzimidazole                                                 |
| B3LYP | : | Becke, 3-parameter, Lee-Yang-Parr                             |
| BPW91 | : | Becke, Perdew, Wang 1991 local correlation                    |
| CR    | : | Corrosion rate                                                |
| CPI   | : | 4-(4-chlorophenyl)imidazole                                   |
| DC    | : | Direct current                                                |
| DFT   | : | Density functional theory                                     |
| EIS   | : | Electrochemical impedance spectroscopy                        |
| EDX   | : | Energy dispersive x-ray spectroscopy                          |
| FESEM | : | Field-emission scanning electron microscopy                   |
| FTIR  | : | Fourier transformed infra-red spectroscopy                    |
| HIP   | : | 1,1'-(hexane-1,6-diyl)bis(3-(3-(1H-imidazol-1-yl)propyl)urea) |

|          |   |                                                                              |
|----------|---|------------------------------------------------------------------------------|
| HOMO     | : | Highest occupied molecular orbital                                           |
| Imz      | : | Imidazole                                                                    |
| LPR      | : | Linear polarization resistance                                               |
| LUMO     | : | Lowest un-occupied molecular orbital                                         |
| Mpy      | : | Mils per year                                                                |
| Mmpy     | : | Millimeter per year                                                          |
| MD       | : | Molecular dynamics                                                           |
| NMR      | : | Nuclear magnetic resonance spectroscopy                                      |
| NVT      | : | Number of moles, volume, temperature                                         |
| OCP      | : | Open circuit potential                                                       |
| PBE      | : | Perdew-Burke-Ernzerhof                                                       |
| PDP      | : | Potentiodynamic polarization                                                 |
| PIP      | : | 1,1'-(4-methyl-1,3-phenylene)bis(3-(3-(1 <i>H</i> -imidazol-1-yl)propyl)urea |
| PUCorr-1 | : | Polyurea corrosion inhibitor-1                                               |
| PUCorr-2 | : | Polyurea corrosion inhibitor-2                                               |
| QSAR     | : | Quantitative structure-activity relationship                                 |
| VASP     | : | Vienna <i>Ab-initio</i> simulation package                                   |

## ABSTRACT

Full Name : [Ismail Abdulazeez]

Thesis Title : [Corrosion Inhibition of Steel by Selected Imidazole Series:  
Spectroscopic, Electrochemical and Mechanistic Studies]

Major Field : [Chemistry]

Date of Degree : [April 2019]

[Obtaining a detailed insight into the mechanism of the protective action of various organic corrosion inhibitors on mild steel has remained an active area of research over the years. Organic corrosion inhibitors are molecules containing heteroatoms such as oxygen, nitrogen, sulfur and phosphorus which have high electron density and are capable of forming a protective film on the metal. Despite the general belief that such molecules adsorb on the metal by displacing water molecules on the surface leading to the formation of a compact barrier which in turn reduces corrosion attack on the metal, not much detailed mechanistic study have been reported on how such adsorption takes place and the contribution of substituent groups present in the molecules on their corrosion inhibitive performance. The use of computational chemistry as a tool in this aspect have greatly enhanced the prediction of the inhibition efficiencies of these inhibitors based on their electronic and molecular properties and reactivity indices, which are subsequently corroborated by experimental measurements. In the present study, mechanistic studies on the inhibition of mild steel corrosion by a series of imidazole derivatives starting from simple molecules to bulky ones was conducted. DFT studies, spectroscopic and electrochemical studies were conducted on the molecules and the mechanisms of action of the molecules in the inhibition of mild steel corrosion were investigated. ]

## ملخص الرسالة

الاسم الكامل: إسماعيل عبدالعزيز

عنوان الرسالة: تآكل الصلب المثبط من خلال سلسلة مختارة من الإيميدازول: دراسة طيفية وكهروكيميائية وميكانيكية

التخصص: الكيمياء

تاريخ الدرجة العلمية: أبريل 2019

ظل الحصول على فكرة مُفصلة عن آلية العمل الوقائي لمختلف مثبطات التآكل العضوي للفولاذ الطري مجالاً نشطاً للبحث على مر السنين. مثبطات التآكل العضوي هي جزيئات تحتوي على ذرات غير متجانسة مثل الأوكسجين والنيتروجين و الكبريت والفسفور وهي ذات كثافة إلكترونية عالية وقادرة على تشكيل طبقة واقية على المعدن. على الرغم من الاعتقاد السائد بأن مثل هذه الجزيئات تُمتص على المعدن من خلال إزاحة جزيئات الماء على السطح مما يؤدي إلى تشكيل حاجز مدمج مما يقلل بدوره من هجوم التآكل على المعدن، إلا أنه لم يتم الإفصاح عن دراسة ميكانيكية تفصيلية حول كيفية حدوث هذا الامتزاز (الامتصاص) ومساهمة المجموعات البديلة الموجودة في هذه الجزيئات على أدائها المثبط للتآكل. إن استخدام الكيمياء الحاسوبية كأداة في هذا الجانب قد عزز بشكل كبير التنبؤ بكفاءة تثبيط هذه المواد المثبطة بناءً على خواصها الإلكترونية والجزيئية ومؤشرات التفاعل، والتي تدعمها بعد ذلك القياسات التجريبية.

في الدراسة الحالية، أجرينا دراسة آلية منهجية حول تثبيط تآكل الفولاذ الطري من خلال سلسلة من مشتقات الإيميدازول بدءاً من الجزيئات البسيطة إلى الجزيئات الضخمة. أجريت دراسات DFT والدراسات الطيفية والكهروكيميائية على سلسلة من المركبات وتم التوصل للتفسير المنطقي و الفهم الكامل لآلية عمل الجزيئات في تثبيط تآكل الفولاذ الطري.



# CHAPTER 1

## INTRODUCTION

### 1.1 Corrosion overview

Corrosion is a natural phenomenon which leads to surface deterioration of metals as a result of interaction with their environment. Metallic corrosion occurs because virtually all metals are unstable (having high energy) and have the tendency to revert back to their more stable original states (having lower energy) by combining with elements present in their environment. Corrosion processes are mainly responsible for numerous losses in the industries and has become a major challenge for such industries who are continuously striving on ways to tackle this menace. Over 50% of the various incidences leading to pipeline failures in the oil and gas industries have been linked to corrosion [1]. In most of the reported cases, corrosion is caused by fluids flowing through the pipeline containing organic acids, brine and gases such as hydrogen sulfide and carbon dioxide [2, 3]. Deterioration of pipeline due to corrosion often leads to severe economic and environmental consequences and sometimes leads to shutdown of oil production facilities. According to a study reported in 2016 the global cost of corrosion was estimated at \$ 2.5 trillion (USD) annually equivalent to 3.4% of global annual GDP [4]. The study also found that implementing corrosion prevention best practices could result in annual global savings of \$ 375 – 875 billion (USD). Moreover, appropriate corrosion

control measures help avoid many potential disasters which often times lead to loss of life, negative social impacts and pollution of water resource and the environment [5].

Corrosion is an electrochemical process involving the reaction of the metal with its environment, usually catalyzed by moisture and oxygen. The basic electrochemical mechanism of aqueous corrosion involves the occurrence of an anodic reaction and a simultaneous cathodic reaction. These two reactions are always coupled together to form a complete electrode process. As illustrated in Fig. 1.1 for the corrosion of iron, the first step in the process is the anodic oxidation of Fe to  $\text{Fe}^{2+}$  ions from the metal surface which goes into the bulk of the solution. At the same time a simultaneous cathodic reaction occurs where pair of electrons released from the metallic anode is accepted by oxygen molecules. These processes could lead to uniform corrosion if the surface deteriorates uniformly, or other forms of corrosion such as crevice, pitting, galvanic stress corrosion etc. As shown in Fig. 1.1, formation of rust continues until the entire mass of the metal has been totally degraded depending on a number of environmental factors [6].

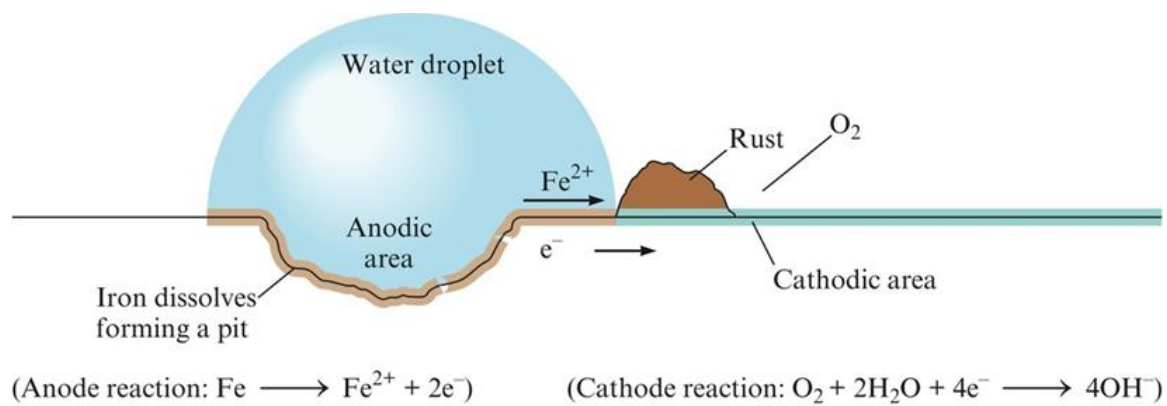


Figure 1.1 Mechanism of iron corrosion

## **1.2 Corrosion inhibition**

Mild steel despite its low resistance to corrosion, is greatly used in the oil and gas industries mainly because of its availability, strength and cost effectiveness [7]. The role of mild steel in this environment is to transport gases and liquids through pipelines from their sources to the consumers over a long distance [8]. During normal pipeline operations (Fig. 1.2), warm petroleum products with small amounts of salt and water travel through the pipeline. Factors which include: nutrients (nitrite; phosphate), oxygen, chloride and bacteria also contribute significantly to internal corrosion in petroleum transporting pipelines [8]. In oil-transporting pipelines, stagnation of water occurs due to the slopes in the landscape, and this acts as a breeding ground for bacteria. Under this condition, a good inhibitor is needed for preventing pipeline corrosion. It has also been estimated that 40% of all internal corrosion of pipelines in the oil and gas industry can be attributed to microbial corrosion. Different methods are used for protecting petroleum product pipelines from corrosion [9]. Application of a protective surface coating is one of these methods. This is an expensive procedure, and it is impossible to coat the pipeline when it is already corroded and filled with petroleum product. One of the efficient and cost-effective approaches to mitigate this problem is thus the application of corrosion inhibitors. A corrosion inhibitor is a chemical substance which, when added in small concentrations to an aggressive environment, minimizes or prevents corrosion [10].

### **1.2.1 Classification of corrosion inhibitors**

Corrosion inhibitors can be classified on the basis of;

- I. Their chemical nature as organic or inorganic inhibitors,
- II. Their mode of action as anodic-type, cathodic-type, mixed-type and adsorption-type inhibitors.

A general scheme showing the classification of these molecules is shown in Fig. 1.3.

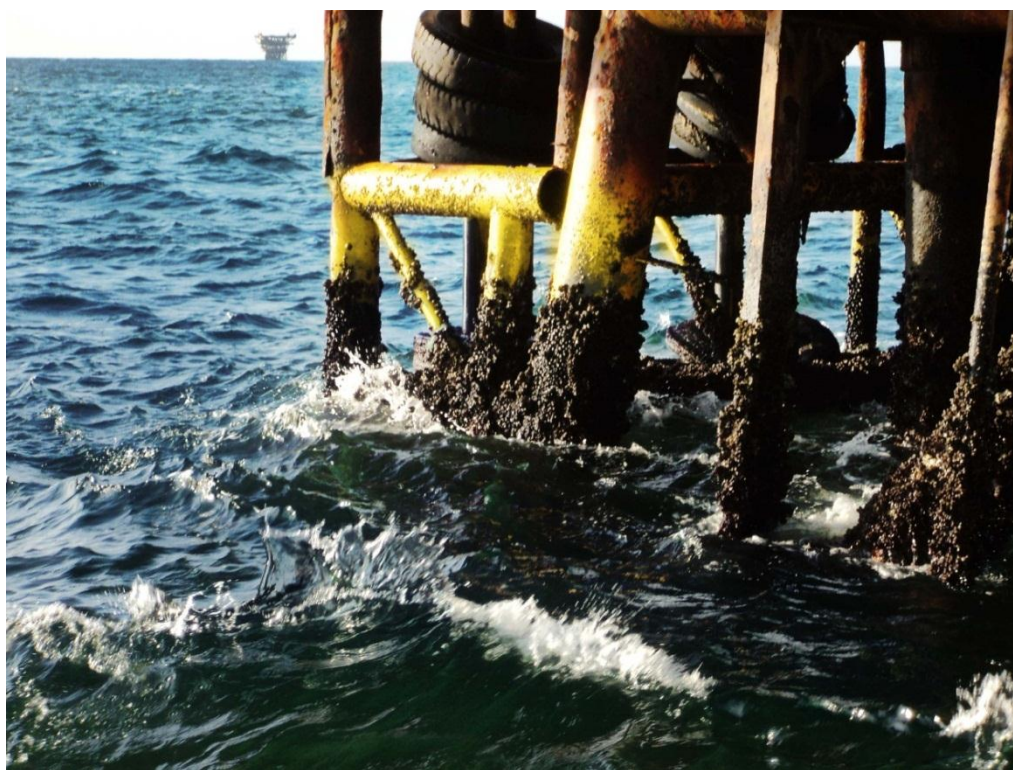
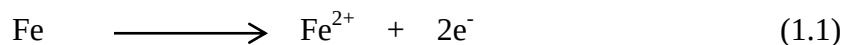


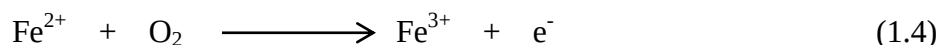
Figure 1.2 A portion of mild steel exposed to corrosive environment

### 1.2.2 Mechanism of action of inhibitors

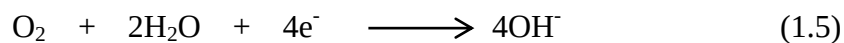
The series of reactions leading to mild steel corrosion are summarized as follows. First, upon contact with the corrosive medium, Fe undergoes oxidation to form  $\text{Fe}^{2+}$  as follows [11];



The  $\text{Fe}^{2+}$  generated in the process combines with the chloride ions in the medium and later with water molecules and oxygen atoms in a series of reactions as follows;



The cathodic reaction which completes the electrochemical process is represented as follows;



From the combined anodic and cathodic reactions, precipitates of  $\text{Fe(OH)}_2$  are formed which gradually accumulates on the metal surface and further reacts with dissolved oxygen giving complex corrosion products [12]. Although a detailed mechanism of how inhibitors accomplish the inhibition of corrosion is not well documented, it is generally believed that the inhibition occurs through either of the following ways [13]:

1. The inhibitor adsorb chemically on the metal surface thereby forming a thin protective film which is capable of preventing corrosion attack (chemisorption). Examples are organic molecules containing heteroatoms with non-bonding electrons such as imidazole and its derivatives [14];
2. The inhibitor adsorbs physically on the metal surface through electrostatic attraction between the metal and electron rich sites in the inhibitor forming a

protective barrier (physisorption). Examples are charge carrying molecules such as surfactants [15];

3. The inhibitor accelerates the formation of an oxide layer on the metal which passivates the metal and prevents corrosion attack (passivation). Examples are salts of ions such as chromate [16] and nitrite [17];
4. The inhibitor reacts with a potential corrosive component present in aqueous media leading to the formation of a complex product and at the same time preventing corrosion attack on the metal (scavenging). Examples are hydrazine and sodium sulfite [18].

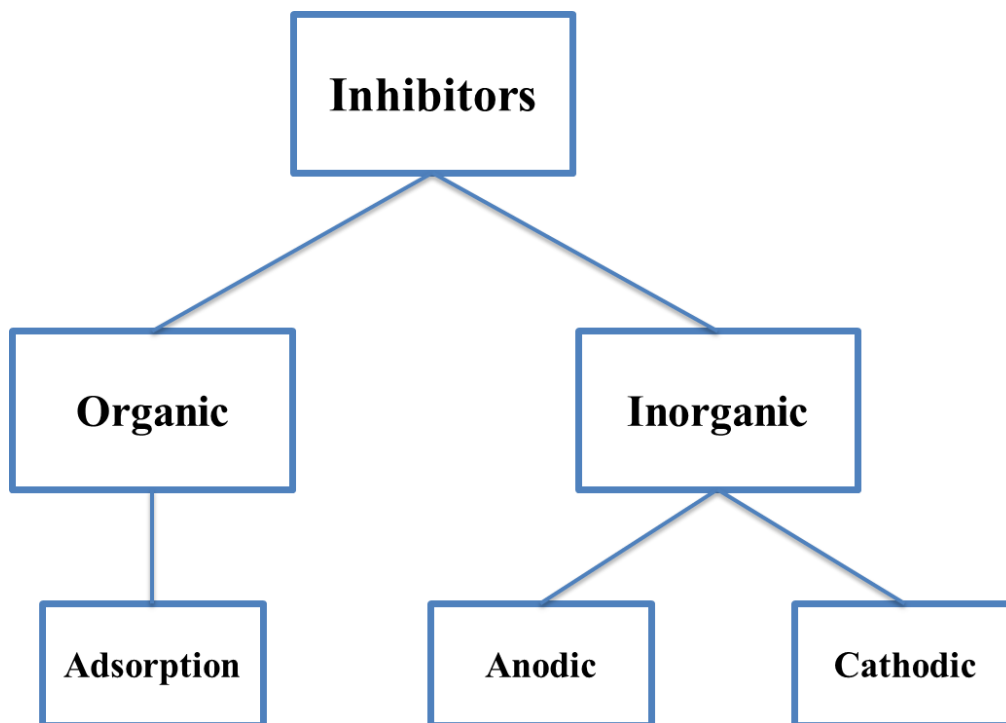


Figure 1.3 Inhibitor classification scheme

## 1.3 Methods of monitoring corrosion

### 1.3.1 Gravimetric method

Gravimetric (weight loss) measurement is the simplest and oldest established method of corrosion rate measurement. In this method, a weighed specimen (coupon) of the metal or alloy under study with an accurately known area is immersed into the corrosive solution and allowed to stand for a reasonable time interval. Thereafter the specimen is removed, cleaned of all corrosion products and dried. The loss in weight is converted to corrosion rate (CR) using the equation [19]:

$$CR = \frac{\text{weight loss} \times K}{\text{metal density (gcm}^{-3}\text{)} \times \text{exposed area (A)} \times \text{exposure time (hr)}} \quad (1.6)$$

Where K = constant and a function of the desired unit of corrosion rate. Examples of corrosion rates units along with their corresponding area and K values are given in Table 1.1.

Table 1.1 Gravimetric corrosion rate K-values

| Corrosion rate unit    | Area unit (A)   | K-value                |
|------------------------|-----------------|------------------------|
| Mils/year (mpy)        | cm <sup>2</sup> | 3.45 x 10 <sup>6</sup> |
| Mils/year (mpy)        | in <sup>2</sup> | 5.34 x 10 <sup>5</sup> |
| Millimeters/year (mmy) | cm <sup>2</sup> | 8.75 x 10 <sup>4</sup> |

This technique is a simple technique that requires no complex or sophisticated instrumentation. It provides direct corrosion rates without any theoretical approximations and is applicable to all corrosive media and all forms of metals or alloys.

### **1.3.2 Electroanalytical methods**

#### **1.3.2.1 DC techniques**

In these techniques, a fixed potential is applied to a metal substrate and the resulting current response is measured. Although dc techniques have been effective in corrosion monitoring, they are often stricken with inevitable interferences such as stray currents from nearby aligning structures, power stations, etc. Examples of dc-based techniques are [19]; dc voltage gradient measurement, close potential survey, cathodic protection current and coating conductance measurements.

#### **1.3.2.2 AC techniques**

In ac techniques, attenuations or voltage drop caused by applied current is measured. Examples of ac-based techniques are [19]; ac voltage gradient measurement, trans wave system, Pearson survey and electromagnetic current attenuation and the commonly used electrochemical impedance spectroscopy (EIS).

Electrochemical impedance spectroscopy (EIS) is a powerful ac technique used in corrosion and other surface and electrochemical studies. It is a less intrusive technique and can provide information about a given process in a reaction without disturbing the reaction too much, by applying small amplitude sinusoidal perturbation to the system. Due to its ability to reveal the mechanism of film formation on the surface of a given metal and the persistence or otherwise of such films, it is a generally adopted technique in

corrosion inhibition studies. Other applications where EIS has found use are: corrosion protection coatings, film formation on metals and corrosion product analysis [5]. This technique yields information like interfacial properties of a metal where basic microscopic reactions take place and from these properties electrochemical parameters of an electrically conducting surface are extracted.

In EIS, impedance of a metal specimen is measured by applying an AC potential (sinusoidal) and measuring the current flowing through. Impedance is represented as a complex variable as follows:

$$Z(\omega) = \frac{E}{I} = Z_o \exp(j\phi) = Z_o(\cos\phi + j\sin\phi) \quad (1.7)$$

Where;

$$E = E_o \exp(j\omega t) \quad (1.8)$$

And 
$$I = I_o \exp(j\omega t) \quad (1.9)$$

EIS data are presented either in the form of Nyquist or Bode plots as shown in Fig. 1.4 and Fig. 1.5.

From these plots, EIS parameters such as electrolyte's resistance to polarization ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ), specimen's resistance to polarization ( $R_p$ ) and double layer capacitance ( $C_{dl}$ ) are determined, and using the expression for the charge transfer resistance (equation 1.10), corrosion exchange current density can be calculated.

$$R_{ct} = \frac{RT}{nFi_o} \quad (1.10)$$

Where  $R$  = gas constant,  $T$  is temperature,  $n$  is number of transferred electrons and  $F$  is Faraday's constant.

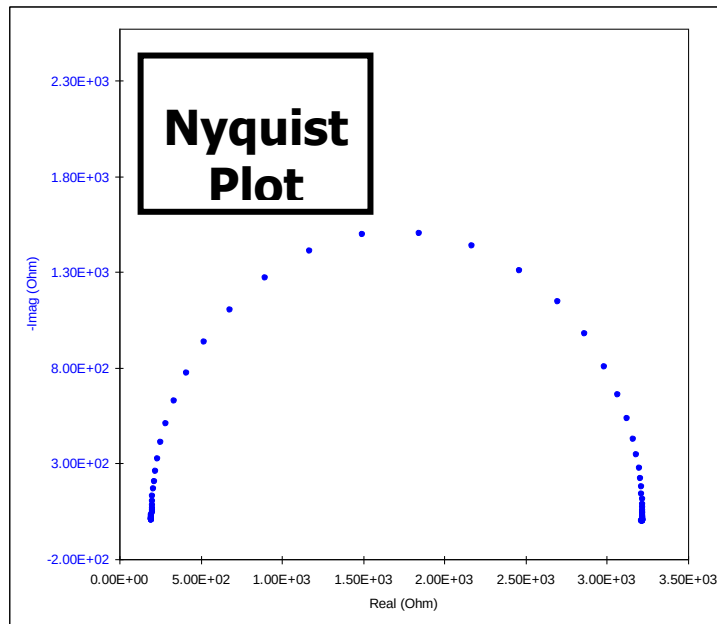


Figure 1.4 Example of Nyquist plot

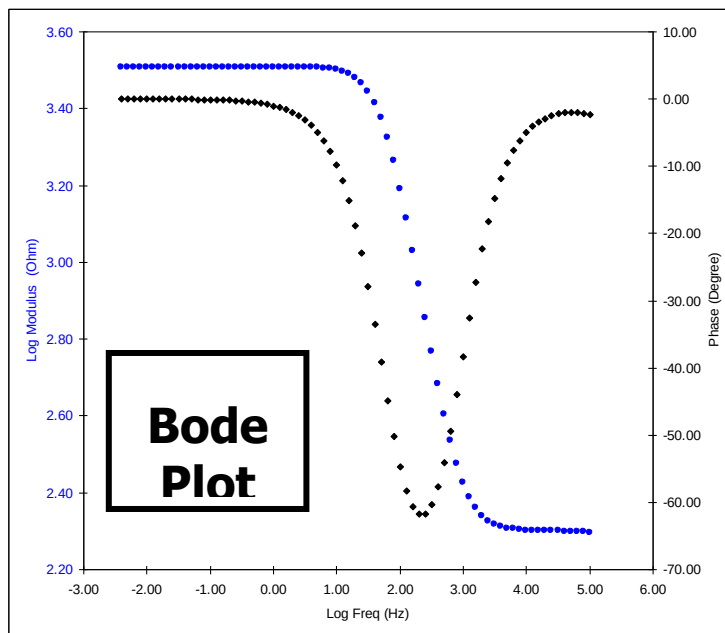


Figure 1.5 Example of Bode plot

### 1.3.2.3 Other techniques

Other electroanalytical techniques used in corrosion monitoring include; linear polarization resistance (LPR), potentiodynamic polarization (PDP), galvanic monitoring, cathodic shielding and electrical resistance measurements.

LPR is a non-destructive technique in which the metal specimen is polarized, typically in the order of  $\pm 10$  mV relative to its open circuit potential. As a result current flows between the working and counter electrodes, and the specimen's resistance to polarization is measured from the slope of potential vs current curve. From the polarization resistance,  $R_p$  corrosion current can be obtained using the Stern-Geary equation as follows [20];

$$i_{corr} = \frac{1}{2.303 R_p} \left( \frac{\beta_a \times \beta_c}{\beta_a + \beta_c} \right) \quad (1.11)$$

Where  $R_p$  = polarization resistance;  $i_{corr}$  corrosion current;  $\beta_a$  the anodic slope and  $\beta_c$  the cathodic slope. From the corrosion current, corrosion rate can be obtained using the equation:

$$CR = \frac{i_{corr} \times K \times EW}{d \times A} \quad (1.12)$$

Where K is a constant, EW the equivalent weight in grams/equivalent, d is the density in  $\text{g/cm}^3$  and A is the sample area in  $\text{cm}^2$ .

In PDP, the potential of the metal is varied at a selected rate by the application of current. The potential is scanned anodically and cathodically and from the resulting Tafel polarization curve (Fig. 1.6), information on the corrosion rate, pitting susceptibility,

passivity, etc. of the material under investigation can be obtained. Once the anodic and cathodic slopes are established, the current density at the point where the anodic and cathodic reaction rates are equivalent is the corrosion current ( $i_{\text{corr}}$ ) and corrosion potential ( $E_{\text{corr}}$ ). Corrosion rate can be found using equation 1.12.

Galvanic monitoring, (zero resistance ammetry) involves the use of two dissimilar metal electrodes immersed in the corrosive electrolyte to monitor potential between them. In this technique, corrosion rate is directly related to the current generated in the process.

In cathodic shielding, the protective current from the cathode is shielded from the anodic metal by means of resistive films, while in electrical resistance measurements, electrical resistance probes are used in measuring in situ mass loss of a metal when exposed to the corrosive electrolyte. The resultant electrical resistance is then linked with the length and cross sectional area of the metal from which corrosion rate can be deduced.

#### **1.4 Applications of DFT in corrosion studies**

In recent years, the use of computational tools in the design of effective organic corrosion inhibitors has received great attentions due to its ability to predict reactivities of the molecules from their structural and molecular properties. Computational approach using density functional theory (DFT) is one of the most important theoretical methods used in the study of interaction of solid surfaces with organic molecules. Traditionally, corrosion inhibitive performances of molecules are evaluated through weight loss assessments and electrochemical measurements. These methods are however costly, time consuming and most times are not sufficient to predict the mechanism of action of the inhibitor molecules. Since the introduction of quantum chemical methods in corrosion studies in

1971 [21], researchers are now able to predict reactivities of molecules towards corrosion inhibition at a low cost and shorter time through calculation of quantum chemical parameters of the molecules [22, 23]. DFT calculations of isolated molecules were used to estimate molecular properties such as the HOMO-LUMO energies ( $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ ), dipole moment ( $\mu$ ), electronegativity ( $\chi$ ), electrophilicity ( $\omega$ ) and hardness ( $\eta$ ) which are correlated with the corrosion inhibition efficiency of the potential corrosion inhibitors through the Quantitative Structure-Activity Relationship (QSAR) model [24, 25].

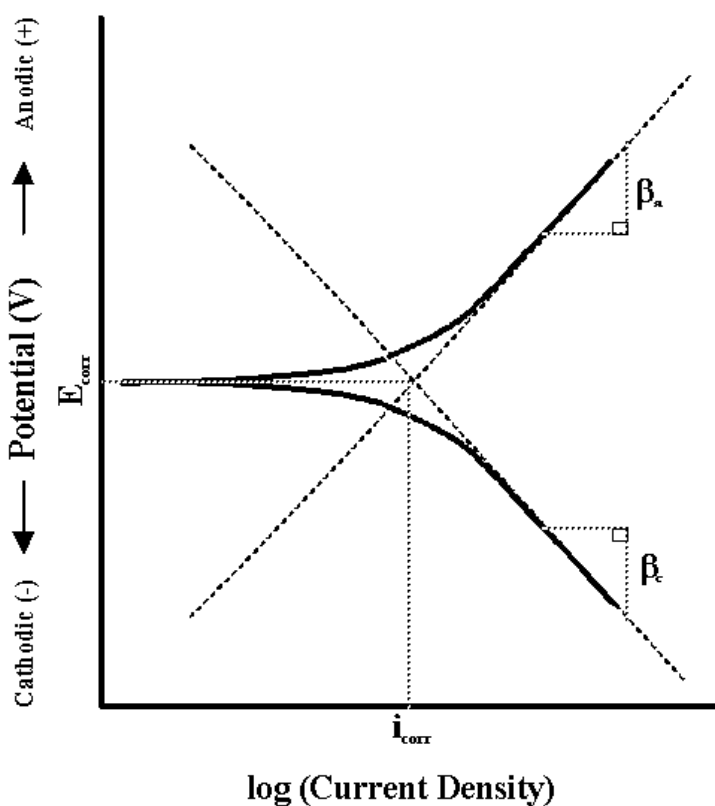


Figure 1.6 Example of Tafel polarization curve

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Organic molecules in anti-corrosion studies

Organic molecules having electron-rich heteroatoms, such as sulfur, nitrogen and oxygen, aromatic fragments or multiple bonds are commonly used for anti-corrosion applications due to their ability to adsorb and displace water molecules on the surface of the metal to form protective barriers against corrosion [26-29]. The presence of non-bonding electrons on the heteroatoms facilitates their interaction with the metal through the formation of coordinate covalent bond. The strength of this bond depends on the electron density on the heteroatom and the polarizability of such atom or group of atoms. With increasing carbon chain, it has been observed that the tendency to inhibit corrosion of organic molecules decreases as a result of a decrease in solubility of such molecules in aqueous solution with increasing hydrocarbon chain. Hence to increase the solubility of these molecules, various hydrophilic substituent groups such as  $-\text{NH}_2$ ,  $-\text{NO}_2$ ,  $-\text{CHO}$ ,  $-\text{COOH}$ , are incorporated into the molecules with a consequent increase in corrosion inhibition efficiency.

The efficiency of organic corrosion inhibitors depend on the following factors:

- I. Chemical structure of the molecule;
- II. Presence of conjugated pi-bonds'
- III. The presence of non-bonding electrons in the molecule;

- IV. Nature and charge of the metal;
- V. The presence of steric hindrance along adsorption sites of the molecule;
- VI. Type of medium in which they are applied.

## **2.2 Imidazole and its derivatives**

Several organic molecules having imidazole [30, 31], pyridine [32], histidine [33], triazole [34], benzimidazole [35], quinoline [36], piperazine [37], hydrazine [38], pyrimidine [39], tetrazoles [40], cationic ammonium salts [41] and schiff bases [42] moieties have been reported for anti-corrosion applications. Among these molecules, imidazole and its derivatives have received greater attention over the years due to its low toxicity, environmental friendliness and excellent oil and water solubility [43]. It is generally believed that the presence of quaternary nitrogen atoms and the aromatic character in these molecules play significant role in enhancing their corrosion inhibitive properties. Furthermore, their ability to accept back-donation of electrons from atoms of the metal enhances their adsorption capabilities, leading to formation of stable protective layers which protect the metal from corrosion attack.

A number of studies have been reported on the corrosion inhibitive properties of imidazole and its derivatives in various corrosive media. Zhang et al. [44] reported the corrosion inhibitive performance of self-assembled films of imidazole and five of its derivatives as follows: imidazole (IMZ), 1-benzyl-1H-imidazole (BZIM), (E)-3-(4-((1H-imidazol-1-yl) methyl) phenyl) acrylic acid (IMMP), 1-butyl-1H-imidazole (BTIM), 1-tosyl-1H-imidazole (TSIM) and (E)-methyl-3-(4-((1H-imidazol-1-yl) methyl) phenyl) acrylate (MIMMP) in 0.5 M HCl using electrochemical impedance spectroscopy and

polarization techniques. It was found that inhibition efficiency increases with immersion time, the optimum immersion time being 24 h at 25 °C in the order IMZ < BTIM < BZIM < TSIM < IMMP < MIMMP. Corrosion inhibitive performance of benzimidazole and its derivatives; 2-methyl benzimidazole and 2-mercapto benzimidazole in 1.0 M HCl were reported by Aljourani et al. [14]. It was found that the compounds adsorb physically on the metal, thereby retarding both the anodic and cathodic processes. The influence of pH on the corrosion inhibition efficiency of two imidazole derivatives; 4-methyl-1(p-tolyl) imidazole (TMI) and 4-methyl-1-phenyl imidazole (PMI) on metallic copper was studied by Curkovic et al [45]. Polarization and impedance studies were carried out at various solution pH (0.3 – 5.6) in both acidic and alkaline media. It was found from this study that the inhibition efficiency of both compounds studied was enhanced with an increase in solution pH, from around 20% in 0.5 M HCl to 92% in 0.5 M NaCl at 1 h immersion. The enhancement was attributed to the ability of the molecules to form strong inhibitor-Cu complex which serves as a protective layer on the surface of the metal. El-Haddad et al reported the corrosion inhibitive properties of imidazole derivatives in acidic medium [46]. Electrochemical measurements showed that methyl imidazole performs better compared to imidazole, perhaps due to the presence of electron donating methyl group on the compound. The corrosion inhibition potentials of vinyl imidazole (VI) and allyl imidazole (AI) for carbon steel in 1 M HCl at 25 °C was studied by Obot et al [47] theoretically and experimentally. Quantum chemical calculations using density functional theory (DFT) were carried out on the two compounds studied and it was found that VI adsorbed better on the steel surface compared to its allyl counterpart. In addition, equilibrium adsorption behavior of VI and AI molecules on Fe<sub>2</sub>O<sub>3</sub> (010) surface was

investigated using molecular dynamics (MD) simulations and the adsorption energies were found to follow the order VI > AI. Gopi et al carried out the experimental and theoretical investigations of mild steel corrosion in groundwater using some synthesized bipodal (BIDM) and tripodal (TITM) derivatives of imidazole [28]. Results from gravimetric and electrochemical measurements showed that both compounds possess the ability to inhibit the corrosion of mild steel in groundwater with the TITM having the highest inhibition efficiency.

Zhang et al reported the electrochemical corrosion evaluation of two imidazole derivatives on P110 carbon steel in acid medium [48]. Obayes et al. [49] conducted the quantum chemical assessment of derivatives of benzimidazole containing  $-\text{NO}_2$ ,  $-\text{SH}$  and  $-\text{CH}_3$  substituents at  $\text{C}_4$ ,  $\text{C}_5$ ,  $\text{C}_6$  and  $\text{C}_7$  and relates their molecular structures to the theoretical inhibition efficiencies. Electrochemical and quantum chemical evaluation of newly synthesized benzimidazole derivatives containing  $-\text{NH}_2$  and  $-\text{OH}$  moieties in acidic medium was studied by Ochoa et al. [50] Hernandez and co-workers [51] reported the quantum chemical and electrochemical assessments of bis-benzimidazole derivative containing amine linkages in acidic medium. Theoretical and electrochemical evaluation of the corrosion inhibition potentials of newly synthesized long chain alkyl-substituted benzimidazole in acidic medium was reported by Zhang et al. [52]. Gutierrez et al. reported the electrochemical corrosion inhibitive performance of imidazole and benzimidazole having electron-releasing and electron-withdrawing substituents in acid medium [53]. Electrochemical corrosion tests supported with DFT calculations revealed that halogen substituted molecules displayed higher inhibitive efficiency. A

representative summary of the corrosion inhibition studies reported on imidazole molecules is presented in Table 2.1.

## **2.3 Identification of research problem**

The application of organic molecules either as simple molecules or in polymeric forms as corrosion inhibitors has proven to be an efficient means of the inhibition of mild steel corrosion both in acidic and saline media as evidenced by the number of publications appearing in the literature on this subject over the years. These molecules are generally believed to inhibit corrosion by adsorbing on the surface of the metal through their electron-rich sites and the vacant d-orbital of the metal ions, forming a protective hydrophobic film which shields the metal from corrosion attack. However, very little efforts are dedicated to understanding the underlying mechanistic behaviors of these molecules at the molecular level leading to the observed corrosion inhibitive properties. This is so because the molecules depending on several environmental factors could exist in different forms, exhibiting different properties. Hence to fully understand the mechanism of action of the molecules, there is the need to conduct a detailed mechanistic study on their adsorption properties as this will pave the way for the design of effective corrosion inhibitors.

To address this issue, we conducted a detailed quantum chemical and periodic slab DFT studies supported with spectroscopic and electrochemical corrosion measurements on a series of selected imidazole molecules, starting from simple to large complex molecules, with the aim of providing a rationale behind their corrosion inhibitive properties. It is believed that with the proper implementation of DFT-based electronic methods, the

chemical reactivity and structural features of organic inhibitors can be fairly predicted [21], and theoretical results from such calculations when properly correlated with experimental observations shall provide useful insights in rationalizing observed corrosion inhibitive properties [6, 55, 56].

## **2.4 Research objectives**

The objective of this research is to conduct a detailed mechanistic study on the corrosion inhibition mechanism of organic molecules using DFT, spectroscopic and electrochemical approach. Specifically, the proposed research aimed to achieve the following objectives:

1. To conduct a detailed DFT study of a series of selected imidazole series and polymeric molecules to correlate their structural properties with their corrosion inhibitive properties.
2. To carry out spectroscopic studies of the molecules using NMR, Raman, and FT-IR techniques to understand their modes of adsorption on iron and how this affects their inhibitive performance.
3. To carry out electrochemical corrosion studies using DC polarization and AC impedance techniques to observe how the presence of the inhibitor molecules affects the corrosion of mild steel in acid and saline media and under various conditions.
4. To utilize surface characterization techniques such as XPS, SEM, EDX and AFM to understand the mode of surface coverage of the proposed molecules on mild

steel and come up with a detailed mechanism of adsorption of the molecules under various conditions.

Table 2. 1 Summary of reported imidazole derivatives

| S/N | Inhibitors                                                                                                                       | Inhibitor Concentration | Specimen               | Electrochemical Technique | Max. % Inhibition Efficiency | Ref  |
|-----|----------------------------------------------------------------------------------------------------------------------------------|-------------------------|------------------------|---------------------------|------------------------------|------|
| 1   | Imidazole and 5 of its derivatives                                                                                               | 1 mM – 1 M              | Iron sheet             | EIS, PDP                  | 86.8                         | [44] |
| 2   | Benzimidazole, 2-methyl benzimidazole, 2-mercapto benzimidazole                                                                  | 50 – 250 ppm            | Mild steel             | EIS, PDP                  | 90.4                         | [14] |
| 3   | 4-methyl-1(p-tolyl) imidazole (TMI),<br>4-methyl-1-phenyl imidazole (PMI)                                                        | 1 – 5 mM                | Copper cylindrical rod | EQCM, EIS, PDP            | 93.0                         | [45] |
| 4   | 2-amino methyl benzimidazole (ABI)<br><br>Bis (2-benzimidazolyl) amine (BBIA)<br><br>Tris (2-benzimidazolyl methyl) amine (TBIA) | 0.1 – 2 mM              | Mild steel             | EIS, PDP                  | 94.14                        | [54] |

Table 2.2 Summary of reported imidazole derivatives (cont'd)

| S/N | Inhibitors                                                      | Inhibitor Concentration                          | Specimen          | Electrochemical Technique | Max. % Inhibition Efficiency | Ref  |
|-----|-----------------------------------------------------------------|--------------------------------------------------|-------------------|---------------------------|------------------------------|------|
| 5   | Imidazole, Methyl imidazole                                     | $3 \times 10^{-5} - 18 \times 10^{-5} \text{ M}$ | Aluminum          | EIS, PDP, EFM             | 76.0                         | [46] |
| 6   | Vinyl imidazole (VI), Allyl imidazole (AI)                      | 1 – 10 mM                                        | Mild steel        | EIS, PDP, LPR             | 82.3                         | [47] |
| 7   | 1,4-bis(N-imidazolyl methyl)-2,5-dimethoxy benzene (BIDM)       | 0.17 – 1.01 mM                                   | Mild steel        | EIS, PDP                  | 90.0                         | [28] |
|     | 1,3,5-tris(N-imidazolyl methyl)-2,4,6-trimethoxy benzene (TITM) | 0.12 – 0.74 mM                                   |                   |                           |                              |      |
| 8   | 2-methyl-4-phenyl-1-tosyl-4,5-dihydrido-1H-imidazole (IMI)      | 50 – 300 mg/L                                    | P110 carbon steel | EID, PDP                  | 94.64                        | [48] |
| 9   | Imidazole and benzimidazole derivatives                         | 0.1 – 10 mM                                      | AISI 1018         | EIS, PDP                  | 90.5                         | [53] |

## **CHAPTER 3**

# **IMPACT OF ELECTRON-WITHDRAWING AND ELECTRON DONATING SUBSTITUENTS ON THE CORROSION INHIBITIVE PROPERTIES OF BENZIMIDAZOLE DERIVATIVES: A QUANTUM CHEMICAL STUDY**

### **3.1 A brief overview**

The role of substituents in the enhancement of corrosion inhibition effectiveness in some organic compounds has been the subject of several studies in recent years. Understanding the relationship between corrosion inhibition performance and electronic properties of the molecule shall facilitate the design of efficient inhibitors and reduce the burden of experimental trials involved. In this study, quantum chemical calculations using density functional theory (DFT) method were performed on benzimidazole and its derivatives involving various electron-withdrawing and electron-releasing substituents. Several reactivity indicators, such as frontier orbitals, energy gaps, electronegativity, electrophilicity and global hardness were calculated and correlated with available experimental data. Frontier orbital energy gap predicted 2-nitrobenzimidazole to possess higher anti-corrosion properties, while electronegativity, electrophilicity and global hardness predicted 2-aminobenzimidazole to exhibit higher corrosion inhibition tendency. Results of molecular level interaction studies predicted that the adsorption of the molecules over the iron surface would take place preferentially through the nitrogen

atoms of the imidazole ring and the carbon atoms of the benzene ring, resulting in the formation of Fe-N and Fe-C bonds with 2.00 – 2.40 Å bond distances which lie within the range of the chemisorption interaction.

### 3.2 Computational procedure

Molecular structures of the isolated inhibitor molecules were optimized using density functional theory (DFT) and the exchange correlation were treated using the hybrid functional, B3LYP and BPW91 [57, 58]. The BPW91 functional was used for calculations involving iron clusters since it provides an accurate description of such clusters [59], whereas the 6-31g(d) basis set was used for C, H and N, and other lighter atoms. A full structural optimization and vibrational analysis of the optimized structures was carried out to determine whether they correspond to a maximum or minimum on the potential energy curve. In order to simulate aqueous medium in which the inhibitor molecules are commonly used, Tomasi's polarized continuum model-self-consistent reaction field (PCM-SCRF) [60] was applied with the solvent chosen as water. Similar calculations were carried out on the protonated forms of the molecules which are the common state of the molecules in acidic medium. 2-NH<sub>2</sub>-BI, 2-SH-BI and 2-OH-BI contain two sites prone to protonation in acidic medium based on Mulliken charge distribution; hence protonated forms of these molecules were studied with two protons attached.

Global reactivity descriptors were estimated following the DFT-Koopman's theorem relating the energy of highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) and lowest unoccupied

molecular orbital ( $E_{\text{LUMO}}$ ) of the molecules as shown in Table 3.1 [61]. Where  $A$  is electron affinity,  $I$  is ionization potential and  $\eta$  global hardness of the molecules, respectively. Others are  $\omega$  representing global electrophilicity index and  $\chi$  the electronegativities of the molecules which is the measure of the power of the molecules to attract electrons towards themselves when chemically combined with other molecules. Fraction of electrons transferred during the interaction of the inhibitor molecules and Fe atoms ( $\Delta N$ ) was calculated with theoretical values of 0 and 7.0 eV assigned for  $\eta_{\text{Fe}}$  and  $\chi_{\text{Fe}}$ , respectively [62] .

Molecular level adsorption studies were carried out using the cluster model and the interaction energies of the molecules with  $\text{Fe}_4$  cluster were calculated. According to this model, interaction of an inhibitor molecule with metal surface is considered local. Hence, quantum chemical study is restricted to the calculation of interaction energy between the inhibitor and metallic atoms upon which the adsorption is directly taking place [63]. Interaction free energies of the inhibitor-cluster complexes were calculated according to the following equations:

$$E_{\text{interaction}} = -E_{\text{binding}} \quad (3.1)$$

$$E_{\text{binding}} = E_{\text{complex}} - (E_{\text{cluster}} + E_{\text{inhibitor}}) \quad (3.2)$$

Where  $E_{\text{complex}}$ ,  $E_{\text{cluster}}$  and  $E_{\text{inhibitor}}$  represents the free energies of the inhibitor-Fe complex, metal cluster and the isolated inhibitor molecules, respectively. All calculations were carried out on Gaussian 09 software suite [64].

### 3.3 Results and discussion

The chemical structures of the studied molecules are presented in Table 3.2. While the optimized molecular structures representing the lowest energy conformers of the non-protonated and protonated molecules using hybrid DFT functional, B3LYP/6-31G(d) are shown in Fig. 3.1. The corresponding quantum chemical reactivity descriptors are given in Table 3.2 and Table 3.3.

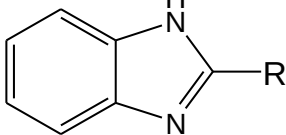
Table 3.1 Quantum chemical parameters and their equations

| Quantum parameter                 | Symbol     | Equation                                                      |
|-----------------------------------|------------|---------------------------------------------------------------|
| Electron affinity                 | A          | $-E_{HOMO}$                                                   |
| Ionization potential              | I          | $-E_{LUMO}$                                                   |
| Global hardness                   | $\eta$     | $\frac{I - A}{2}$                                             |
| Electrophilicity index            | $\omega$   | $\frac{\mu^2}{2\eta}$                                         |
| Electronegativity                 | $\chi$     | $\frac{I + A}{2}$                                             |
| Fraction of transferred electrons | $\Delta N$ | $\frac{[\chi_{Fe} - \chi_{inh}]}{2 (\eta_{Fe} - \eta_{inh})}$ |

According to the molecular orbital theory, effectiveness of interaction between two reacting molecules is dependent on the interaction between their frontier orbitals (HOMO/LUMO) [65]. Thus, to understand the adsorption and consequent corrosion inhibitive effectiveness of the studied molecules, the distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as well

as the energy gap between them were investigated. Frontier orbital distribution of the molecules (Fig 3.2) showed that the HOMO and LUMO are well distributed over the heterocyclic benzimidazole ring and the respective substituents. These indicates the propensity of the molecules to donate charges from the electron-rich centers into unoccupied d-orbitals of the metal and are capable of electron back-acceptance from the occupied orbitals to form strong adsorbed films which shield the metal from corrosion attacks.

Table 3.2 Chemical structures of studied molecules

|  |                         |                                   |
|-----------------------------------------------------------------------------------|-------------------------|-----------------------------------|
| R                                                                                 | Molecule                | Abbreviation                      |
| H                                                                                 | Benzimidazole           | BI                                |
| NH <sub>2</sub>                                                                   | 2-Aminobenzimidazole    | NH <sub>2</sub> -BI               |
| C <sub>6</sub> H <sub>5</sub>                                                     | 2-Phenylbenzimidazole   | C <sub>6</sub> H <sub>5</sub> -BI |
| COOH                                                                              | 2-Carboxylbenzimidazole | COOH-BI                           |
| SH                                                                                | 2-Thiobenzimidazole     | SH-BI                             |
| OCH <sub>3</sub>                                                                  | 2-Methoxybenzimidazole  | OCH <sub>3</sub> -BI              |
| OH                                                                                | 2-Hydroxybenzimidazole  | OH-BI                             |
| Br                                                                                | 2-Bromobenzimidazole    | Br-BI                             |
| Cl                                                                                | 2-Chlorobenzimidazole   | Cl-BI                             |
| F                                                                                 | 2-Fluorobenzimidazole   | F-BI                              |
| CH <sub>3</sub>                                                                   | 2-Methylbenzimidazole   | CH <sub>3</sub> -BI               |
| CN                                                                                | 2-Cyanobenzimidazole    | CN-BI                             |
| NO <sub>2</sub>                                                                   | 2-Nitrobenzimidazole    | NO <sub>2</sub> -BI               |

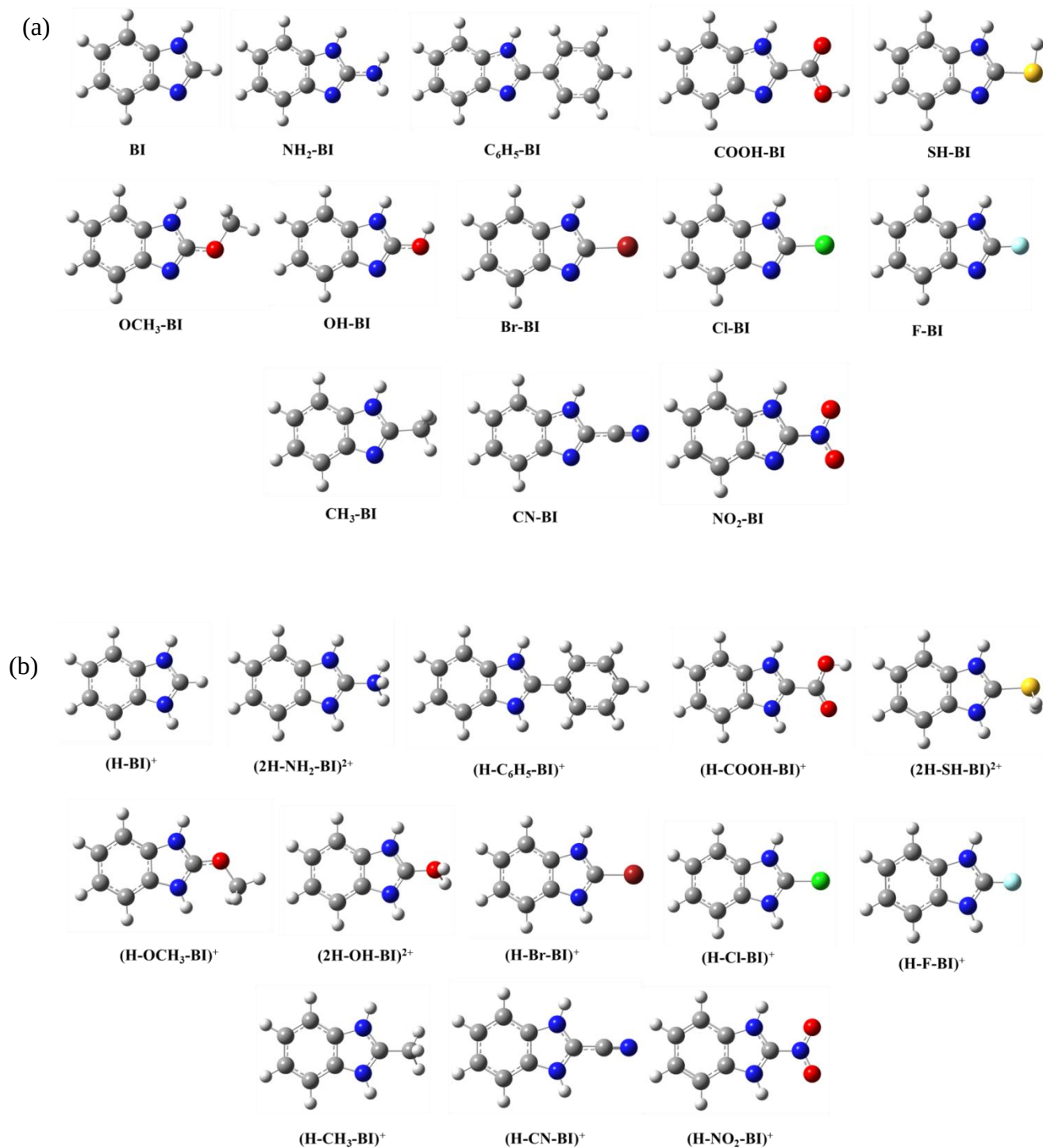


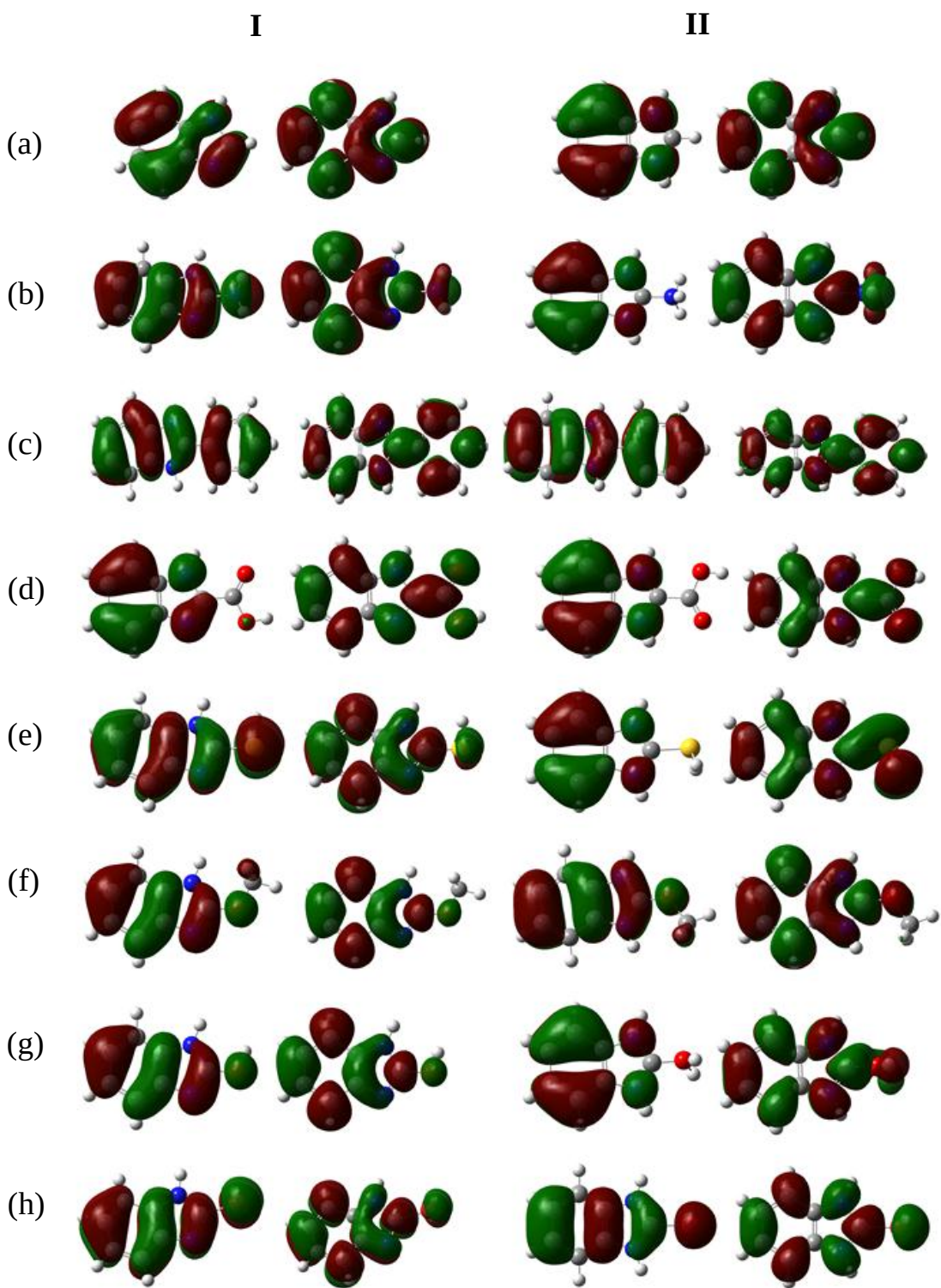
Figure 3.1 Optimized geometries representing lowest energy conformers of (a) non-protonated and (b) protonated molecules at B3LYP/6-31G(d)

Table 3.3 Quantum chemical descriptors of non-protonated molecules at B3LYP/6-31G(d) in aqueous medium

| Neutral molecules (aqueous)       |                        |                        |         |        |        |        |           |       |
|-----------------------------------|------------------------|------------------------|---------|--------|--------|--------|-----------|-------|
| Molecule                          | E <sub>HOMO</sub> (eV) | E <sub>LUMO</sub> (eV) | ΔE (eV) | χ (eV) | η (eV) | ω (eV) | μ (debye) | ΔN    |
| BI                                | -6.129                 | -0.377                 | 5.752   | 3.253  | 2.876  | 1.839  | 5.022     | 0.652 |
| NH <sub>2</sub> -BI               | -5.457                 | 0.005                  | 5.462   | 2.726  | 2.731  | 1.360  | 6.239     | 0.782 |
| C <sub>6</sub> H <sub>5</sub> -BI | -5.804                 | -1.175                 | 4.629   | 3.489  | 2.314  | 2.630  | 5.104     | 0.758 |
| COOH-BI                           | -6.365                 | -1.699                 | 4.666   | 4.032  | 2.333  | 3.483  | 2.893     | 0.636 |
| SH-BI                             | -5.878                 | -0.405                 | 5.473   | 3.141  | 2.737  | 1.803  | 6.107     | 0.705 |
| OCH <sub>3</sub> -BI              | -5.758                 | -0.118                 | 5.640   | 2.938  | 2.820  | 1.530  | 7.360     | 0.720 |
| OH-BI                             | -5.808                 | -0.099                 | 5.709   | 2.954  | 2.854  | 1.528  | 7.160     | 0.709 |
| Br-BI                             | -6.238                 | -0.583                 | 5.655   | 3.410  | 2.828  | 2.057  | 4.723     | 0.635 |
| Cl-BI                             | -6.262                 | -0.547                 | 5.714   | 3.405  | 2.857  | 2.028  | 4.920     | 0.629 |
| F-BI                              | -6.194                 | -0.293                 | 5.901   | 3.243  | 2.951  | 1.783  | 4.933     | 0.637 |
| CH <sub>3</sub> -BI               | -6.003                 | -0.304                 | 5.700   | 3.154  | 2.850  | 1.745  | 5.282     | 0.675 |
| CN-BI                             | -6.450                 | -1.634                 | 4.816   | 4.042  | 2.408  | 3.392  | 7.095     | 0.614 |
| NO <sub>2</sub> -BI               | -6.600                 | -2.997                 | 3.603   | 4.798  | 1.802  | 6.389  | 7.986     | 0.611 |

Table 3.4 Quantum chemical descriptors of protonated molecules at B3LYP/6-31G(d) in aqueous medium

| Protonated molecules (aqueous)    |                        |                        |         |        |        |        |           |       |
|-----------------------------------|------------------------|------------------------|---------|--------|--------|--------|-----------|-------|
| Molecule                          | E <sub>HOMO</sub> (eV) | E <sub>LUMO</sub> (eV) | ΔE (eV) | χ (eV) | η (eV) | ω (eV) | μ (debye) | ΔN    |
| BI                                | -7.000                 | -1.352                 | 5.648   | 4.176  | 2.824  | 3.087  | 7.202     | 0.500 |
| NH <sub>2</sub> -BI               | -7.288                 | -2.012                 | 5.277   | 4.650  | 2.638  | 4.098  | 19.125    | 0.445 |
| C <sub>6</sub> H <sub>5</sub> -BI | -6.590                 | -1.988                 | 4.602   | 4.289  | 2.301  | 3.997  | 0.023     | 0.589 |
| COOH-BI                           | -7.156                 | -2.662                 | 4.493   | 4.909  | 2.247  | 5.363  | 2.241     | 0.465 |
| SH-BI                             | -7.446                 | -3.117                 | 4.329   | 5.282  | 2.165  | 6.444  | 13.832    | 0.397 |
| OCH <sub>3</sub> -BI              | -6.680                 | -0.847                 | 5.834   | 3.763  | 2.917  | 2.428  | 5.700     | 0.555 |
| OH-BI                             | -7.338                 | -2.081                 | 5.257   | 4.710  | 2.629  | 4.219  | 18.332    | 0.436 |
| Br-BI                             | -7.166                 | -1.808                 | 5.358   | 4.487  | 2.679  | 3.758  | 1.174     | 0.469 |
| Cl-BI                             | -7.128                 | -1.663                 | 5.465   | 4.395  | 2.732  | 3.535  | 1.851     | 0.477 |
| F-BI                              | -7.096                 | -1.217                 | 5.880   | 4.156  | 2.940  | 2.938  | 3.729     | 0.484 |
| CH <sub>3</sub> -BI               | -6.906                 | -1.204                 | 5.702   | 4.055  | 2.851  | 2.884  | 6.430     | 0.516 |
| CN-BI                             | -7.243                 | -2.789                 | 4.454   | 5.016  | 2.227  | 5.648  | 1.765     | 0.446 |
| NO <sub>2</sub> -BI               | -7.355                 | -3.847                 | 3.508   | 5.601  | 1.754  | 8.943  | 4.517     | 0.399 |



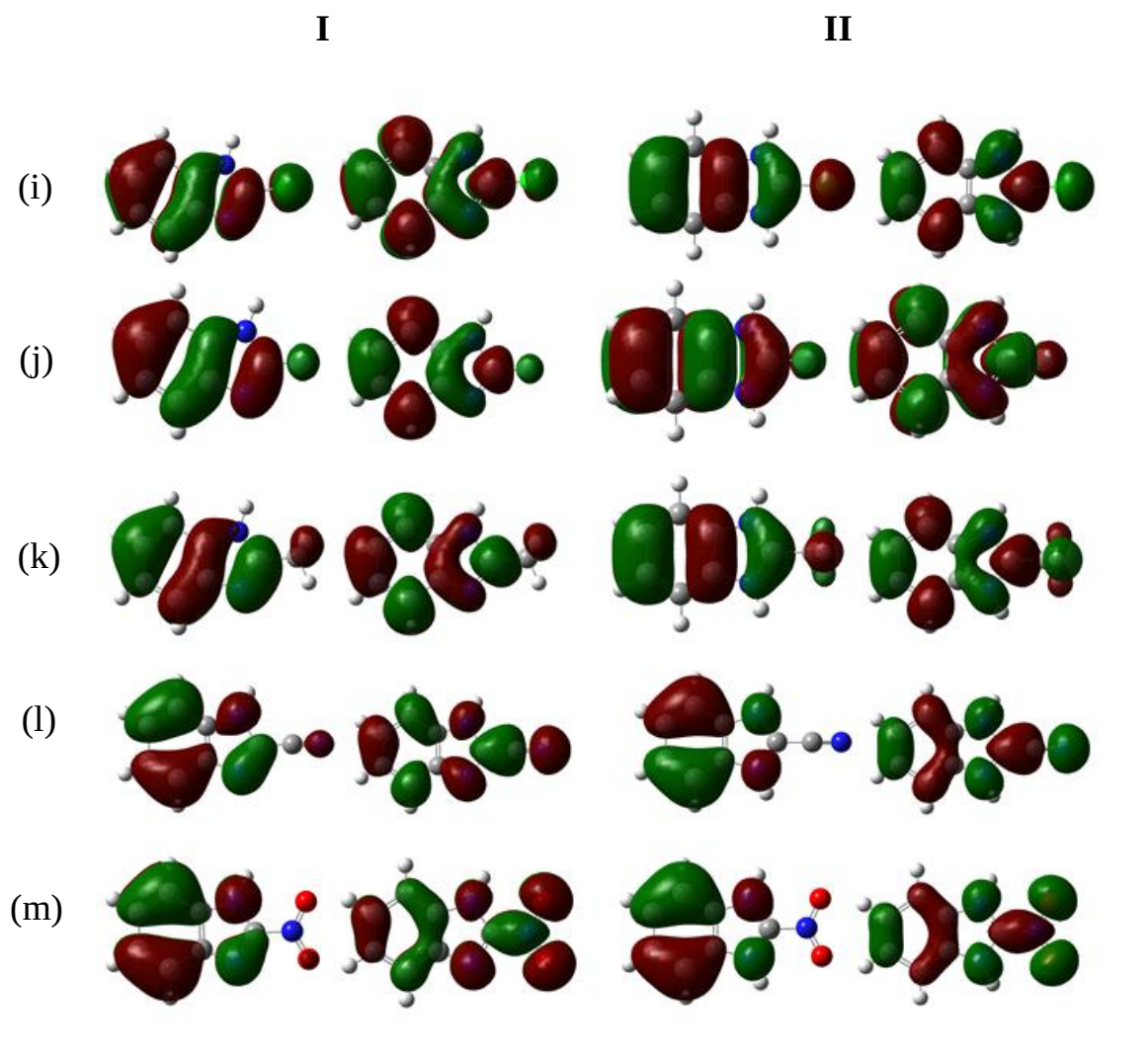


Figure 3.2 Frontier orbital distribution of (I) neutral and (II) protonated molecules: (a) BI, (b)  $\text{NH}_2\text{-BI}$ , (c)  $\text{C}_6\text{H}_5\text{-BI}$ , (d)  $\text{COOH-BI}$ , (e)  $\text{SH-BI}$ , (f)  $\text{OCH}_3\text{-BI}$ , (g)  $\text{OH-BI}$ , (h)  $\text{Br-BI}$ , (i)  $\text{Cl-BI}$ , (j)  $\text{F-BI}$ , (k)  $\text{CH}_3\text{-BI}$ , (l)  $\text{CN-BI}$ , (m)  $\text{NO}_2\text{-BI}$

The energy gap between the HOMO-LUMO molecular orbitals ( $\Delta E$ ) is another important feature which determines the adsorption of molecules on metallic surfaces. As  $\Delta E$  decreases, reactivity of the molecules towards corrosion inhibition increases. Comparison of  $\Delta E$  of the studied molecules (neutral and protonated) in aqueous and gaseous media is

presented in Fig. 3.3 and Fig. 3.4. Notably from Fig. 3.3, NO<sub>2</sub>-BI has the least energy gap and is predicted to possess greater corrosion inhibitive properties in aqueous medium. Whereas in vacuum where the effect of solvation is neglected (Fig. 3.4), SH-BI was found to possess the lowest energy gap when protonated, hence is regarded to possess higher tendency towards inhibition of metallic corrosion. Popova et al [66] have reported the effects of substituent groups and molecular geometry on the adsorption and corrosion inhibitive properties of benzimidazole in acidic medium using gravimetric and electrochemical techniques. Substituents studied include –CH<sub>3</sub>, –NH<sub>2</sub>, –SH, –CH<sub>2</sub>OH and –CH<sub>2</sub>CN at C<sub>2</sub> and –NO<sub>2</sub> and –CO<sub>2</sub>H at C<sub>5</sub> of benzimidazole molecules. The trend of inhibition efficiencies obtained for C2 substituted molecules (SH-BI > NH<sub>2</sub>-BI > CH<sub>3</sub>-BI) followed similar trend as the theoretical values of  $\Delta E$  obtained in the present study. Therefore upon interaction with the metal surface, a molecule having lower energy gap possess a greater propensity for interaction to form a protective layer against corrosion attack. There was no report on the corrosion inhibitive studies of 2-nitrobenzimidazole (NO<sub>2</sub>-BI) so far in the literature. However, based on  $\Delta E$  values calculated in the present study this molecule is expected to have better corrosion protection in aqueous medium.

Electronegativity ( $\chi$ ) expresses the electron attracting power of a molecule. It is a useful quantum chemical reactivity descriptor which indicates the likelihood of a molecule to serve as an effective corrosion inhibitor. According to Sanderson's principle [67], molecules with high electronegativities attains rapid equalization when in contact with metallic surface (due to small difference in electronegativity) and as such possess low corrosion inhibitive performance. An efficient corrosion inhibitor is therefore a molecule having in addition to low energy gap ( $\Delta E$ ), a low  $\chi$  value. Notably from Tables 3.3 & 3.4

(and Fig. 3.3, Fig. 3.4), neutral molecules exhibit lower  $\chi$  values in both aqueous and gaseous media, with  $\text{NH}_2\text{-BI}$  having the least value in both media. For the protonated molecules however,  $\text{OCH}_3\text{-BI}$  exhibit the least value. Variation in  $\chi$  values of the molecules are attributed to the nature of the substituents where  $-\text{NH}_2$ ,  $-\text{OCH}_3$ ,  $-\text{OH}$  are regarded as strong ring activators (electron-releasing) while  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{COOH}$  among others are strong deactivators (electron-withdrawing). Ghanbari et al. [68] reported the electrochemical corrosion inhibitive performance of benzimidazole and its derivatives ( $2\text{-CH}_3\text{-BI}$  and  $2\text{-NH}_2\text{-BI}$ ) in acidic medium. The corrosion inhibition efficiencies recorded in 1.0 M phosphoric acid at 50 mM inhibitor concentrations are in the order  $2\text{-NH}_2\text{-BI} > \text{BI} > 2\text{-CH}_3\text{-BI}$ . Aljourani et al. [14] studied the corrosion inhibitive performance of benzimidazole and its derivatives ( $2\text{-CH}_3\text{-BI}$  and  $2\text{-SH-BI}$ ) in acidic medium using electrochemical techniques. Inhibition efficiencies recorded at 250 ppm concentrations followed the order  $2\text{-SH-BI} > 2\text{-CH}_3\text{-BI} > \text{BI}$ . A closer look at  $\chi$  values of the molecules revealed that the order does not correlate with those of experimental studies. It therefore follows that although lower  $\chi$  values implies higher tendency to donate charges, this factor alone does not translate to higher corrosion inhibition efficiencies. Hence, for effective protection against corrosion, an inhibitor molecule should possess minimal  $\chi$  in addition to low  $\Delta E$ .

Hardness ( $\eta$ ) measures the resistance of a molecule to electron density distortion. It is an important feature which expresses the tendency of a molecule to donate its non-bonding electrons when interacting with another. In accordance with hard-soft acid-base (HSAB) theory, molecules having high hardness are usually less reactive due to their lower tendency to donate electrons. Whereas soft molecules (those having lower hardness)

possess greater electron-donating capacities and as such are predicted as effective corrosion inhibitors [69, 70]. Results of hardness obtained in the present study followed similar order as experimental data reported by Popova et al. [66] and shows the significance of  $\eta$  in predicting the corrosion inhibitive performance of a molecule.

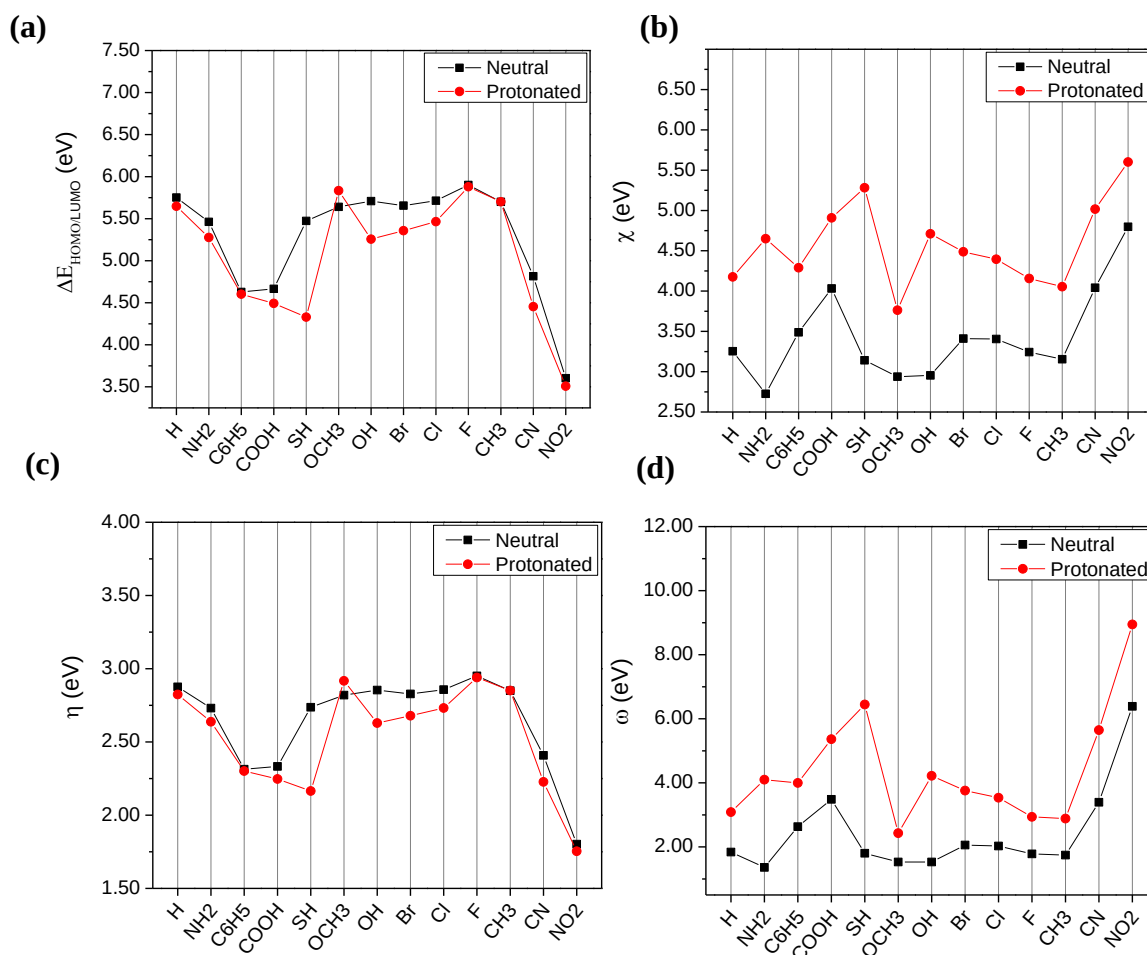


Figure 3.3 (a) HOMO/LUMO energy gap, (b) electronegativities, (c) global hardness and (d) electrophilicities of the non-protonated and protonated molecules in aqueous medium

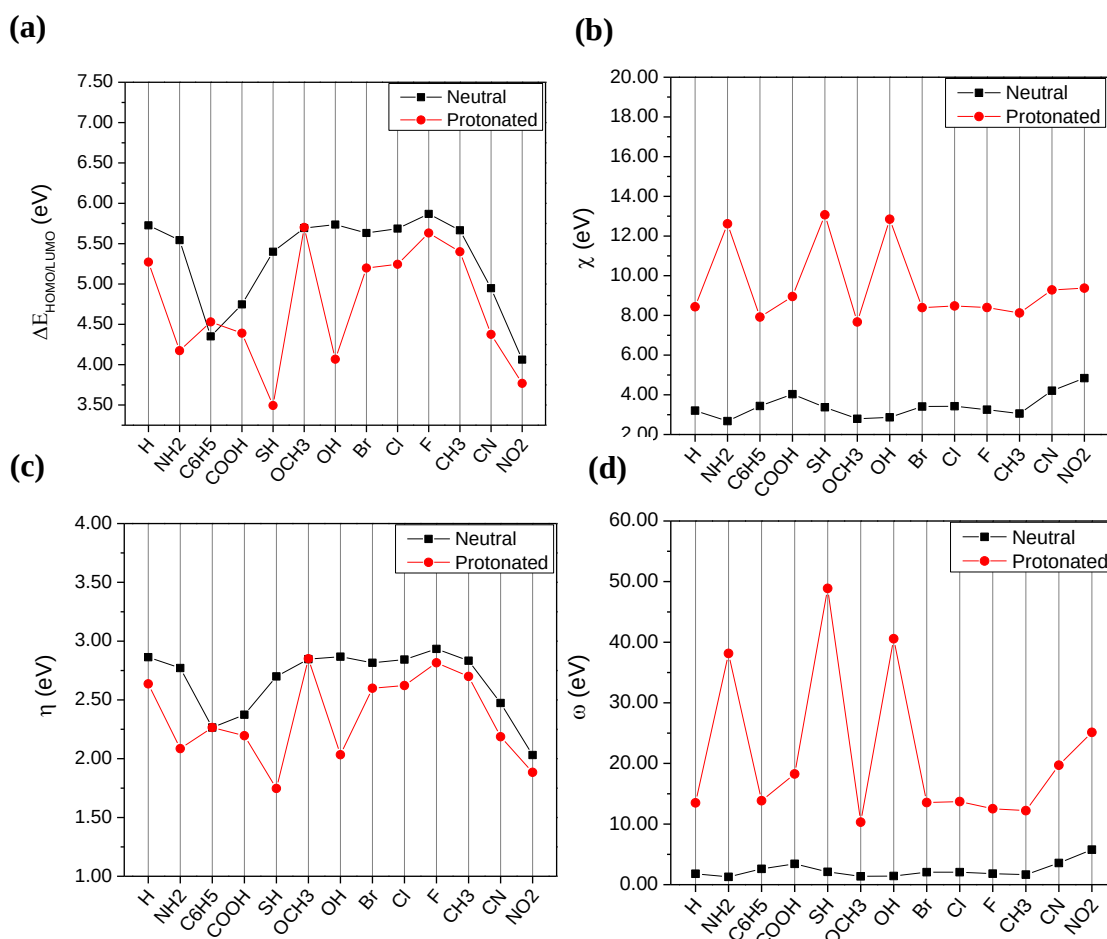


Figure 3.4 (a) HOMO/LUMO energy gap, (b) electronegativities, (c) global hardness and (d) electrophilicities of the non-protonated and protonated molecules in vacuum

Electrophilicity index ( $\omega$ ) expresses the stabilization energy of a molecule upon receiving electrons [71]. It indicates the electrophilicity or nucleophilicity of a molecule as molecules having higher values of  $\omega$  are usually regarded as strong electrophiles and such molecules do not form strong interactions with metal surfaces. Adsorption of corrosion inhibitors onto metallic surfaces usually involve electron pair transfer from the inhibitor molecules to the un-occupied orbitals of the metal atoms and a back-donation of electrons

from the metal atoms to the inhibitor molecules giving rise to a strong metal-inhibitor complexes. This implies that to achieve maximum protection against corrosion, a molecule should possess minimal  $\omega$ . Electrophilicity values obtained for the studied molecules in this study showed that protonated molecules possess higher values of  $\omega$  compared to un-protonated ones. This could be due to an increase in atomic sites prone to nucleophilic attacks within the molecules. In addition, since protonation imparts positive charges on the molecules, this will decrease their propensity towards electron donation as they become electrophilic in nature. Although the order of  $\omega$  for the protonated and un-protonated molecules does not follow the same order as reported experimental data [14, 66, 68], it is an important reactivity descriptor which expresses the charge donation capability of an inhibitor molecule.

Dipole moment ( $\mu$ ) describes the charge separation within an inhibitor molecule. High values of  $\mu$  implies high intra-molecular interactions within an inhibitor molecule leading to formation of strong adsorbed layers on the metal surface [34]. No specific order relating dipole moment with corrosion inhibition efficiencies has been established yet in the literature. However, it can be used to estimate the total surface coverage of an inhibitor molecule on metallic surfaces. Hence a molecule having higher  $\mu$  will exhibit large surface coverage when adsorbed on the metal surface leading to an increase in inhibition efficiency. The order of  $\mu$  of the studied molecules were found to follow similar order as inhibition efficiencies reported by Aljourani et al.[14] for the non-protonated molecules, while for the protonated molecules the order was found to correlate with experimental data reported by Ghanbari et al [68].

During interaction of the inhibitor molecules with metal atoms on the surface, electron are usually transferred from the less electronegative inhibitor molecules to the more electronegative metal atoms until equilibration is achieved. The fraction of transferred electrons,  $\Delta N$  is usually used to indicate the direction of electron flow within the system. Positive values of  $\Delta N$  implies that the inhibitor molecules donates electrons to the metal atoms, while negative values implies the reverse [72]. As reported by Lukovits [73], corrosion inhibition efficiencies of molecules having  $\Delta N < 3$  usually increases with increasing electron donation capacity. Values of  $\Delta N$  for protonated and non-protonated molecules in aqueous medium (Tables 3.3 & 3.4) predicts that the inhibitor molecules can donate electrons to the atoms of the metal.

To further study the molecular level adsorption of the inhibitor molecules over the metal surface, structural optimization with  $\text{Fe}_4$  cluster was carried out.  $\text{Fe}_4$  cluster gave a ground state distorted tetrahedron with bond distances of 2.22 Å at the corners and 2.40 Å at the edges which are similar to the nearest neighbor distance (nnd) of bulk bcc iron (2.48 Å) [74] as shown in Fig. 3.5. The mode of interaction between the iron cluster and the molecules was similar for both the non-protonated and protonated molecules (Table 3.5) resulting in the formation of  $\text{Fe-N}_{\text{benz}}$  and  $\text{Fe-C}_{\text{benz}}$  bonds in the range 2.00 – 2.40 Å which is within the range of chemisorption distances (2.83 – 3.0 Å) [75-77]. This confirms the formation of adsorbed layer of inhibitor molecules over the metal surface. In addition, interaction of the protonated molecules especially in BI was more effective than the un-protonated molecule with a difference of interaction energy of the order approx. 2.0 kcal/mol. This is because protonation generates delocalized region  $\text{N}_1=\text{C}=\text{N}_3$  which anchors over the metal surface [24]. Furthermore, interaction of the molecules with  $\text{Fe}_4$

cluster was investigated by analyzing the changes in Mulliken charges upon interaction and the results (Table 3.6) further confirms that electrons were transferred from the inhibitor molecules to  $\text{Fe}_4$  in both protonated and non-protonated systems except in CN-BI where the reverse effect was found. The order of interaction energies partially correlates with experimental data reported by Popova et al. [66], and demonstrated the significance of DFT cluster modeling in the rationalization of mechanism of action of corrosion inhibitors on metallic surfaces [24, 74].

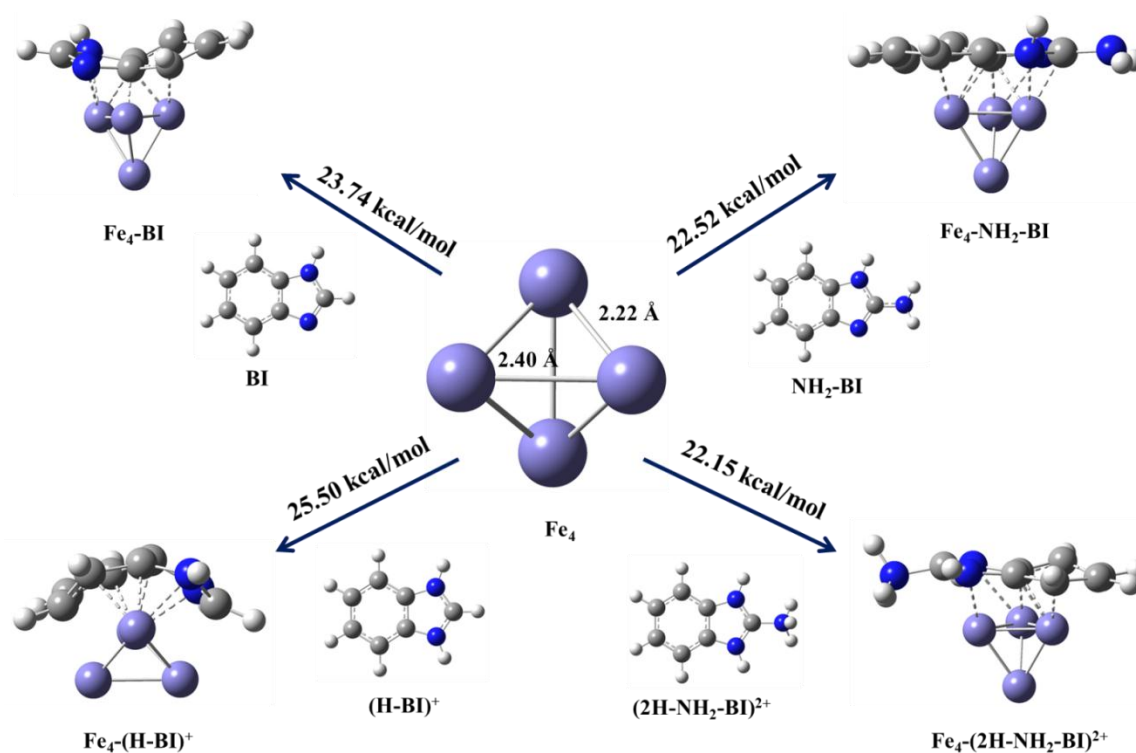


Figure 3.5 Interaction of  $\text{Fe}_4$  cluster with non-protonated and protonated molecules

Table 3.5 Molecular level adsorption of non-protonated and protonated molecules on Fe<sub>4</sub> cluster

| Molecule                          | Neutral | Protonated |
|-----------------------------------|---------|------------|
| C <sub>6</sub> H <sub>5</sub> -BI |         |            |
| COOH-BI                           |         |            |
| SH-BI                             |         |            |
| OCH <sub>3</sub> -BI              |         |            |
| OH-BI                             |         |            |
| Br-BI                             |         |            |
| Cl-BI                             |         |            |
| F-BI                              |         |            |

Table 3.5 continued

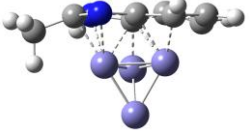
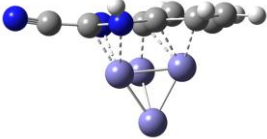
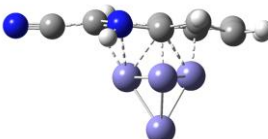
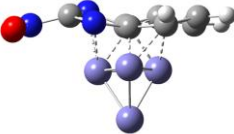
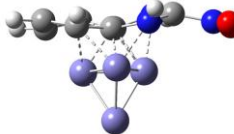
| Molecule            | Neutral                                                                           | Protonated                                                                         |
|---------------------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| CH <sub>3</sub> -BI |  |  |
| CN-BI               |  |  |
| NO <sub>2</sub> -BI |  |  |

Table 3.6 Sum of Mulliken charges of the molecules before and after complexation and interaction energies

| Sum of Mulliken charges           |         |                   |            |                   | Interaction energies<br>(Kcal/mol) |            |
|-----------------------------------|---------|-------------------|------------|-------------------|------------------------------------|------------|
| Compound                          | Neutral |                   | Protonated |                   |                                    |            |
|                                   | Free    | Upon complexation | Free       | Upon complexation | Neutral                            | Protonated |
| Fe <sub>4</sub>                   | 0.000   | -0.164            | 0.000      | -0.119            | 23.741                             | 25.503     |
| BI                                | 0.000   | 0.164             | 1.000      | 1.119             |                                    |            |
| Fe <sub>4</sub>                   | 0.000   | -0.148            | 0.000      | -0.005            | 22.524                             | 22.148     |
| NH <sub>2</sub> -BI               | 0.000   | 0.148             | 2.000      | 2.005             |                                    |            |
| Fe <sub>4</sub>                   | 0.000   | -0.263            | 0.000      | -0.273            | 23.189                             | 23.877     |
| C <sub>6</sub> H <sub>5</sub> -BI | 0.000   | 0.263             | 1.000      | 1.273             |                                    |            |
| Fe <sub>4</sub>                   | 0.000   | -0.090            | 0.000      | -0.163            | 24.199                             | 24.718     |
| COOH-BI                           | 0.000   | 0.090             | 1.000      | 1.163             |                                    |            |
| Fe <sub>4</sub>                   | 0.000   | -0.149            | 0.000      | -0.007            | 24.563                             | 23.938     |
| SH-BI                             | 0.000   | 0.149             | 2.000      | 2.007             |                                    |            |
| Fe <sub>4</sub>                   | 0.000   | -0.183            | 0.000      | -0.160            | 25.808                             | 25.550     |
| OCH <sub>3</sub> -BI              | 0.000   | 0.183             | 1.000      | 1.160             |                                    |            |
| Fe <sub>4</sub>                   | 0.000   | -0.169            | 0.000      | -0.095            | 24.640                             | 23.210     |
| OH-BI                             | 0.000   | 0.169             | 2.000      | 2.095             |                                    |            |
| Fe <sub>4</sub>                   | 0.000   | -0.164            | 0.000      | -0.005            | 24.175                             | 21.761     |
| Br-BI                             | 0.000   | 0.164             | 1.000      | 1.005             |                                    |            |
| Fe <sub>4</sub>                   | 0.000   | -0.162            | 0.000      | -0.140            | 24.470                             | 24.937     |
| Cl-BI                             | 0.000   | 0.162             | 1.000      | 1.140             |                                    |            |
| Fe <sub>4</sub>                   | 0.000   | -0.173            | 0.000      | -0.101            | 24.177                             | 24.906     |
| F-BI                              | 0.000   | 0.173             | 1.000      | 1.101             |                                    |            |
| Fe <sub>4</sub>                   | 0.000   | -0.031            | 0.000      | -0.133            | 23.287                             | 24.395     |
| CH <sub>3</sub> -BI               | 0.000   | 0.031             | 1.000      | 1.133             |                                    |            |
| Fe <sub>4</sub>                   | 0.000   | -0.010            | 0.000      | 0.046             | 25.428                             | 21.645     |
| CN-BI                             | 0.000   | 0.010             | 1.000      | 0.954             |                                    |            |
| Fe <sub>4</sub>                   | 0.000   | -0.056            | 0.000      | -0.001            | 24.502                             | 24.297     |
| NO <sub>2</sub> -BI               | 0.000   | 0.056             | 1.000      | 1.001             |                                    |            |

### 3.4 Summary

DFT-based quantum chemical calculations were carried out on benzimidazole and its derivatives containing various electron-withdrawing and electron-releasing substituents in order to understand the effects of electronic properties in the design of effective inhibitors of metallic corrosion. Analysis of the HOMO/LUMO energy gap ( $\Delta E$ ), electronegativity ( $\chi$ ), electrophilicity ( $\omega$ ), dipole moment ( $\mu$ ) and fraction of transferred electrons ( $\Delta$ ) revealed that although not all reactivity descriptors follow similar order as experimental data, they are sufficient to predict the corrosion inhibitive efficiencies of simple organic molecules. Molecular level interaction studies further revealed that adsorption of the molecules over iron surface would take place preferentially through the nitrogen atoms of the imidazole ring and carbon atoms of the benzene ring, resulting in the formation of Fe-N and Fe-C bonds in the range 2.00 – 2.40 Å which is within the range of chemisorption distance. The significance of DFT-based quantum chemical calculations in the design of effective inhibitors of metallic corrosion is hereby demonstrated in the present study.

## **CHAPTER 4**

# **MECHANISTIC EVALUATION OF THE INFLUENCE OF HALOGEN SUBSTITUENTS ON THE CORROSION INHIBITIVE EFFICIENCY OF SIMPLE IMIDAZOLE MOLECULES: A SYNERGISTIC THEORETICAL AND EXPERIMENTAL APPROACH**

### **4.1 A brief overview**

Obtaining a detailed insight into the mechanism of the protective action of various organic corrosion inhibitors on mild steel corrosion has remained an active area of research over the years. The use of computational chemistry as a tool in this aspect have greatly enhanced the prediction of the inhibition efficiencies of these inhibitors based on their electronic and molecular properties and reactivity indices, which are subsequently corroborated by experimental measurements. The present study reports the adsorption behavior and corrosion inhibition mechanism of imidazole and its C2-halogenated analogues (with the halogen atoms being Cl, Br or I) on Fe(100) surface using DFT-based molecular dynamics (MD) simulations and electrochemical techniques. MD simulations revealed that C2-halogenated imidazoles adopt the tilted conformation on Fe surface with a significantly lengthened C–halogen bond and readily undergo facile dissociation at the halo-substitution with calculated adsorption energies -3.95, -3.76 and -3.48 eV for 2-I-Imz, 2-Br-Imz and 2-Cl-Imz, respectively. Electrochemical evaluations supported with surface characterization studies showed that the inhibitor molecules

adsorb onto mild steel with 2-I-Imz having the highest inhibition efficiency of 83.5%. The order of inhibition efficiencies correlates with adsorption energies and kinetic behavior predicted by the MD approach. The strength of adsorption is in the order  $I > Br > Cl$ . The present study therefore provides a thorough mechanistic understanding of the role halogen substituents could play on the corrosion inhibitive performance of small organic systems.

## **4.2 Experimental and computational procedure**

### **4.2.1 Reagents and solutions**

All reagents used in this study were of standard purity and of analytical grade (Sigma-Aldrich) and were used as-received without further purifications. Solutions of imidazole and its derivatives were prepared by dissolving the respective reagents, namely imidazole (Imz), 2-bromo-1*H*-imidazole (2-Br-Imz), 2-chloro-1*H*-imidazole (2-Cl-Imz) and 2-iodo-1*H*-imidazole (2-I-Imz), in 1.0 M HCl (fluka) using double distilled water.

### **4.2.2 Electrochemical methods**

Electrochemical measurements were performed in a 250-ml jacketed electrochemical cell kit with three-electrode compartments (Gamry). Mild steel bar AISI 1018 with the following compositions; C, 0.15 – 0.20%; Mn, 0.60 – 0.90%; P, 0.04%; S, 0.05% and balance Fe was used as the sample specimen, saturated calomel electrode (SCE) and carbon graphite as the reference and counter electrodes, respectively. The sample specimen was polished sequentially using silicon carbide emery papers of different grit size (120 – 800), rinsed with distilled water, placed in an ultrasonic acetone bath to remove possible residue due to polishing, rinsed with acetone, dried in warm air, and

stored in a desiccator before use. Gamry potentiostat/galvanostat/ZRA (Reference 600) equipped with a Gamry framework interface was used for electrochemical studies. Gamry Echem Analyst version 6.03 was used for data analysis and fittings. All experiments were conducted at room temperature. Open circuit potential measurements were carried out during two hours of immersion in 5.0 mM freshly prepared solutions of the molecules in 1.0 M HCl. Electrochemical impedance spectroscopy measurements (EIS) were carried out at open circuit potential ( $E_{ocp}$  vs SCE) in 250 ml of 1.0 M acid solution in the absence and presence of inhibitor molecules in the frequency range 100 KHz to 100 mHz, with an amplitude of perturbation 10 mV r.m.s. Polarization (Tafel) curves were obtained by scanning the potential at 0.5 mV/s in the range +250 mV to -250 mV against the open circuit potential ( $E_{ocp}$ ). Corrosion potential ( $E_{corr}$  /V vs SCE) and corrosion current density ( $i_{corr}$ , A cm<sup>-2</sup>) were obtained by extrapolation of anodic ( $\beta_a$ ) and cathodic ( $\beta_c$ ) branches of the Tafel curves. All electrochemical tests were carried out in triplicates; the average of which was reported.

#### **4.2.3 Spectroscopic methods**

Samples for XPS, SEM and AFM experiments were iron sheets with dimensions 1 cm x 1 cm x 0.2 cm. Samples were immersed in 50 ml of 1.0 M HCl with and without inhibitors for 24 h, rinsed with anhydrous ethanol and ultra-pure water and dried in a stream of nitrogen. AFM was carried out on Agilent 5100 SPM system, interfaced with a controller PicoScan (Agilent Technologies, Tempe AZ, USA). All measurements were made by scanning sample's surface at a rate of 1 – 3 line per second and were conducted at room temperature using the tapping mode. Probe tip (Bruker AFM probes Co.) with radius 10 nm and specific force constant 40 N/m was used with maximum resonance frequency of

320 KHz. SEM micrographs were recorded using TESCAN LYRA 3 (Czech Republic) field emission scanning electron microscopy (FESEM) equipped with energy-dispersive X-ray spectroscopy (EDX) detector. XPS analysis was conducted using X-ray photoelectron spectrometer (Thermo Scientific ESCALAB 250 Xi).

#### 4.2.4 Computational details

Adsorption of imidazole molecules on iron surface were performed with Vienna *Ab Initio* Simulation Package (VASP) 5.4.1 [78-81]. The kinetic energy cut-off used for the plane wave is 400 eV. A 1000 eV cut-off for plane wave representation of the augmentation charges is used, together with an additional supported grid for the augmented charge is used. Projector Augment-wave (PAW) pseudopotential [82, 83] from VASP for Perdew-Burke-Ernzerhof (PBE) functional [58] was used for the slab calculations. First order smearing via the method of Methfessel-Paxton (MP) [84] was used. The width for smearing is 0.1 eV. Dipole correction along the Z-axis (normal to the slab) is applied. Ionic relaxation was performed with a convergence criterion based on force per atom. A cut-off of 0.01 eV/Å was used. K-point meshes of  $(4 \times 4 \times 1)$  for  $(2 \times 2)$  and  $\begin{pmatrix} 2 & 1 \\ 0 & 2 \end{pmatrix}$  supercell,  $(3 \times 3 \times 1)$  for  $(3 \times 3)$  supercell and  $(2 \times 2 \times 1)$  for  $(4 \times 4)$  supercell were generated by Monkhorst-Pack (MP) scheme [85]. An electronic degree of freedom convergence criterion of  $10^{-8}$  eV was specified. The computed equilibrium lattice constant of alpha iron at our level of theory is 2.84 Å. This was employed to model the bulk layers of the slabs. The adsorption energies ( $E_{\text{ads}}$ ) were calculated by the following expression:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{Fe}(100)} - E_{\text{iso}} \quad (4.1)$$

where  $E_{\text{total}}$  is the total energy of the system,  $E_{\text{Fe}(100)}$  is the energy associated to the isolated surface, and  $E_{\text{iso}}$  corresponds to the energy of the isolated imidazole species. The *nudged elastic band (NEB) method* [86] was employed to locate the transition states and minimum energy paths between known reactants and products. Activation energy ( $E_a$ ) is defined as the difference between the energy of the transition state ( $E_{\text{TS}}$ ) and the energy of the reactant ( $E_{\text{reactant}}$ )

$$E_a = E_{\text{TS}} - E_{\text{reactant}} \quad (4.2)$$

Molecular dynamic (MD) simulations were performed with VASP 5.4.1 via MDALGO = 2 using an NVT ensemble regulated with a Nose-Hoover thermostat. The Nose mass was set to 0.05 via the SMASS keyword. A time step of 0.5 femtoseconds was used. The velocities were set randomly according to a Maxwell-Boltzmann distribution at the initial temperature specified. The temperature was maintained at 300 K or 1500 K via Nose-Hoover thermostat. For the MD simulation, the slab used consists of four layers. The bottom two layers are frozen. A minimal of 10 self-consistent steps was performed at each cycle. Other parameters are identical to those presented in the preceding paragraph, except for the MD simulation of four imidazole molecules on a (4×4) Fe 100 slab where a kinetic energy cut-off used for the plane wave was 350 eV and the electronic degree of freedom convergence criterion was  $10^{-7}$  eV. Free molecule was calculated at the gamma point only in a  $25 \text{ \AA} \times 25 \text{ \AA} \times 25 \text{ \AA}$  box. The gamma point only version of VASP 5.4.1 was used with the aid of Gaussian smearing method.

## 4.3 Results and discussion

### 4.3.1 Electrochemical measurements

To determine the appropriate immersion time before carrying out each experiment, open circuit potential vs time ( $E_{ocp}$ ) measurements were performed in 250 ml solutions of 1.0 M HCl in the absence and presence (5.0 mM) of the inhibitors (Fig. 4.1).  $E_{ocp}$  is the potential measured when a metal is allowed to corrode naturally without applying an external force in a corrosive medium, which provides an idea on the tendency of the metal to corrode in such a medium. This information serves as a starting point for the application of electrochemical methods of corrosion measurements [12, 87, 88].

Notably from Figure 4.1, the  $E_{ocp}$  of the inhibitor-free solution (blank) continuously decreased as a result of continuous dissolution of the metal. However, on introduction of the inhibitors the potential shifted to noble values and became almost stable after about 30 min of immersion, which is an indicative of the attainment of steady state corrosion potential. The shift to noble values is in the order 2-I-Imz > 2-Br-Imz > Imz > 2-Cl-Imz which implies an increase in the thermodynamic stability of the surface corrosion product film and hence corrosion inhibitive performance of the molecules follow the same order. The observed order may be attributed to the ability of the dissociated halogen substituents to bind to  $Fe^{2+}$  species on mild steel in addition to the adsorbed organic molecules which shield the metal from further corrosion (see subsequent theoretical section). This was true for all C2-halo substituted imidazoles studied except with 2-Cl-Imz where the dissociated chloride ions tend to attack the metal surface leading to more corrosion [89].

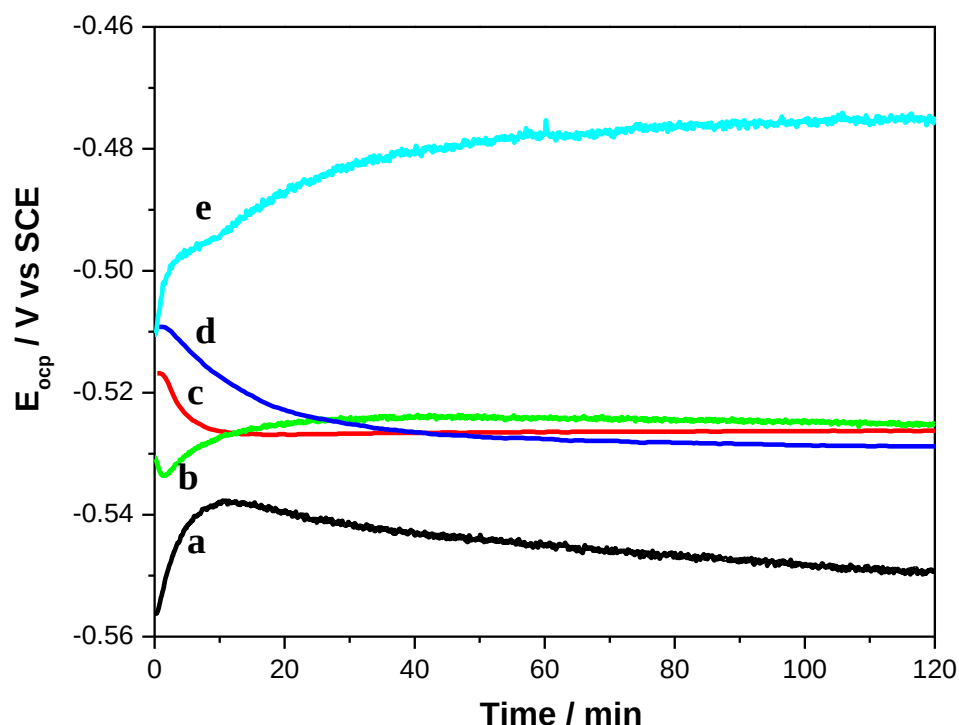


Figure 4.1 Open circuit potential ( $E_{ocp}$  vs SCE) – time curves of mild steel specimen in (a) 1.0 M HCl without and with 5.0 mM concentrations of (b) 2-Br-Imz, (c) Imz, (d) 2-Cl-Imz, and (e) 2-I-Imz.

Tafel polarization measurements were further carried out in 1.0 M HCl in the absence and presence of the inhibitor molecules at 25 °C. Table 4.1 gives a summary of data obtained by extrapolation of anodic and cathodic branches of the Tafel plots. Electrochemical data which include corrosion potential ( $E_{corr}$ ), corrosion rate ( $C_{rate}$ ), corrosion current density ( $i_{corr}$ ), anodic Tafel slopes ( $\beta_a$ ) and cathodic Tafel slopes ( $\beta_c$ ) are presented in the table. Inhibition efficiencies of the molecules were calculated using the equation:

$$\eta (\%) = \left( \frac{i_{corr}^{\circ} - i_{corr}}{i_{corr}^{\circ}} \right) \times 100 \quad (4.3)$$

where  $i_{corr}^{\circ}$  and  $i_{corr}$  are corrosion current density values in the absence and presence of the inhibitors respectively [53].

Table 4.1 Tafel polarization data of inhibitors in 1.0 M HCl

| Inhibitor                        | C <sub>inhibitor</sub><br>(mM) | E <sub>corr</sub> (V<br>vs SCE) | β <sub>a</sub> (V/dec) | -β <sub>c</sub> (V/dec) | i <sub>corr</sub> (x10 <sup>-4</sup><br>A.cm <sup>-2</sup> ) | C <sub>rate</sub><br>(mpy) | η (%) |
|----------------------------------|--------------------------------|---------------------------------|------------------------|-------------------------|--------------------------------------------------------------|----------------------------|-------|
| <b>Blank<br/>(1.0 M<br/>HCl)</b> | 0                              | -0.52                           | 0.80                   | 0.11                    | 2.3                                                          | 104.5                      | -     |
| <b>2-Cl-Imz</b>                  | 0.5                            | -0.53                           | 0.88                   | 0.96                    | 2.2                                                          | 100.8                      | 3.5   |
| <b>Imz</b>                       | 0.5                            | -0.53                           | 0.82                   | 0.10                    | 2.1                                                          | 96.7                       | 7.3   |
| <b>2-Br-Imz</b>                  | 0.5                            | -0.52                           | 0.66                   | 0.98                    | 1.5                                                          | 69.3                       | 33.7  |
| <b>4-Ph-Imz</b>                  | 0.5                            | -0.54                           | 0.28                   | 0.31                    | 1.4                                                          | 63.3                       | 39.8  |
| <b>2-I-Imz</b>                   | 0.5                            | -0.48                           | 0.13                   | 0.14                    | 1.1                                                          | 50.5                       | 51.9  |

The results in Table 4.1 revealed that the selected inhibitors may not be practical corrosion inhibitors due to their structural features. Structural properties such as long alkyl chains, volume and aromaticity have been listed as important features in corrosion inhibition studies [90, 91]. However, understanding the mechanism of corrosion protection by these molecules will pave the way for understanding of more complex and efficient molecules. To further study the inhibitive performance of the molecules, Tafel

polarization measurements were carried out by varying the inhibitor concentrations. Figure 4.2 shows representative plots of the least and most efficient molecules according to Table 4.1. The corresponding Tafel extrapolated data is shown in Table 4.2.

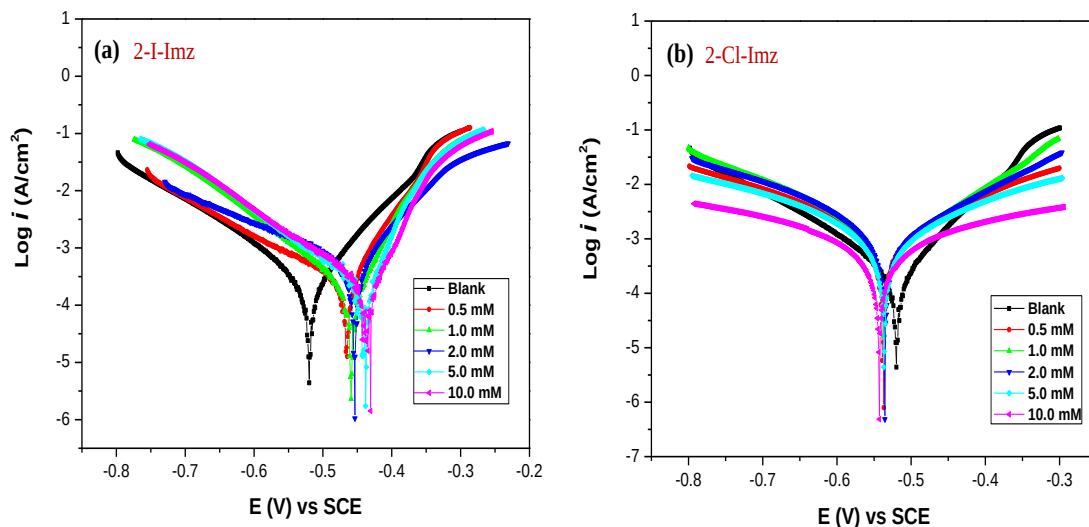


Figure 4.2 Tafel polarization curves in 1.0 M HCl with various concentrations of inhibitors (a) 2-iodo-1H-imidazole and (b) 2-chloro-1H-imidazole

From Figure 4.2 and the data in Table 4.2, a corresponding decrease in corrosion current is observed with an increase in inhibitor concentrations due to an increase in surface coverage with an inhibition efficiency of 80% at 10 mM concentration of 2-I-Imz. There was also a continuous shift of the corrosion potential ( $E_{\text{corr}}$ ) towards more positive values, an indication that 2-I-Imz acts mainly as anodic-type corrosion inhibitor [22]. It is well known that anodic-type inhibitors spread and block the active sites on metals preventing further dissolution of the metal. Thus, we would expect that the inhibition efficiency of

these molecules to increase with increasing concentration due to enhancement in surface coverage.

Table 4.2 Tafel polarization data of 2-I-Imz and 2-Cl-Imz in 1.0 M HCl

| Inhibitor                        | C <sub>inhibitor</sub><br>(mM) | E <sub>corr</sub> (V<br>vs SCE) | β <sub>a</sub> (V/dec) | -β <sub>c</sub> (V/dec) | i <sub>corr</sub> (x10 <sup>-4</sup><br>A.cm <sup>-2</sup> ) | C <sub>rate</sub><br>(mpy) | η (%) |
|----------------------------------|--------------------------------|---------------------------------|------------------------|-------------------------|--------------------------------------------------------------|----------------------------|-------|
| <b>blank<br/>(1.0 M<br/>HCl)</b> | 0                              | -0.52                           | 0.80                   | 0.11                    | 2.3                                                          | 104.5                      | -     |
|                                  | 0.5                            | -0.54                           | 0.15                   | 0.11                    | 2.1                                                          | 102.2                      | 6.5   |
|                                  | 1.0                            | -0.54                           | 0.14                   | 0.12                    | 2.0                                                          | 99.6                       | 11.9  |
|                                  | 2.0                            | -0.54                           | 0.91                   | 0.76                    | 1.8                                                          | 97.2                       | 19.2  |
| <b>2-Cl-Imz</b>                  | 5.0                            | -0.54                           | 0.23                   | 0.22                    | 1.0                                                          | 82.4                       | 55.2  |
|                                  | 10.0                           | -0.54                           | 0.80                   | 0.11                    | 0.6                                                          | 68.5                       | 72.5  |
|                                  | 0.5                            | -0.46                           | 0.64                   | 0.24                    | 1.8                                                          | 90.5                       | 19.2  |
|                                  | 1.0                            | -0.46                           | 0.50                   | 0.83                    | 1.2                                                          | 56.7                       | 45.9  |
|                                  | 2.0                            | -0.45                           | 0.61                   | 0.12                    | 1.0                                                          | 52.8                       | 57.1  |
| <b>2-I-Imz</b>                   | 5.0                            | -0.44                           | 0.28                   | 0.70                    | 0.8                                                          | 35.4                       | 66.3  |
|                                  | 10.0                           | -0.43                           | 0.23                   | 0.55                    | 0.4                                                          | 20.8                       | 80.2  |

To further elucidate the inhibitive mechanism of the halo-substituted imidazoles, electrochemical impedance measurements were carried out. Mild steel specimen was immersed in 1.0 M HCl with and without the inhibitors for 60 min prior to each experiment in order to attain a steady state potential. Experiments were conducted while stirring the solution and the inhibition efficiencies were calculated according to the following equation:

$$\eta (\%) = \left( \frac{R_p - R_p^0}{R_p} \right) \times 100 \quad (4.4)$$

where  $R_p$  and  $R_p^\circ$  are the polarization resistances in the presence and absence of the inhibitor molecules, respectively [53]. Figures 4.3 and 4.4 show the representative Nyquist and Bode plots of the inhibitor molecules at varying concentrations.

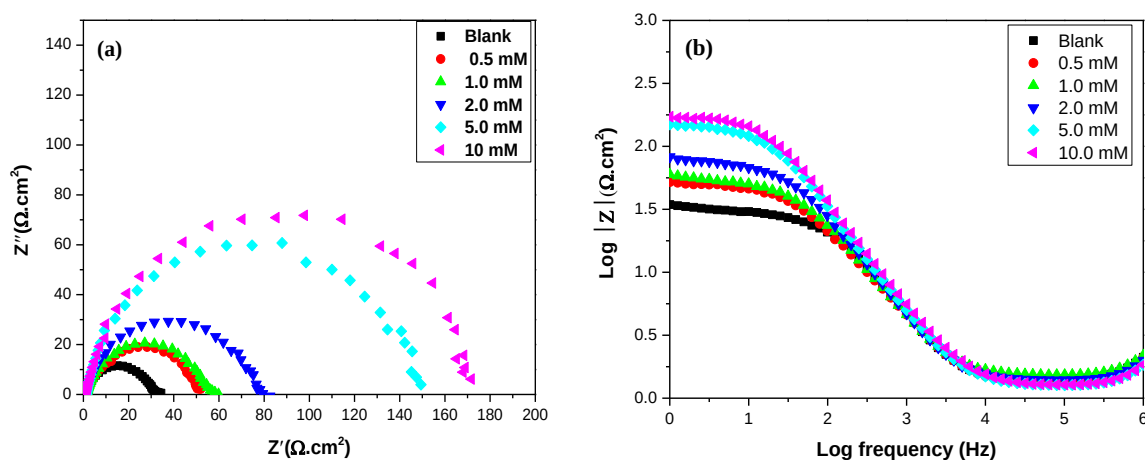


Figure 4.3 Nyquist (a) and Bode (b) plots of mild steel sample in 1.0 M HCl in the absence and presence of varying concentrations of 2-iodo-1H-imidazole (0.5 – 10.0 mM).

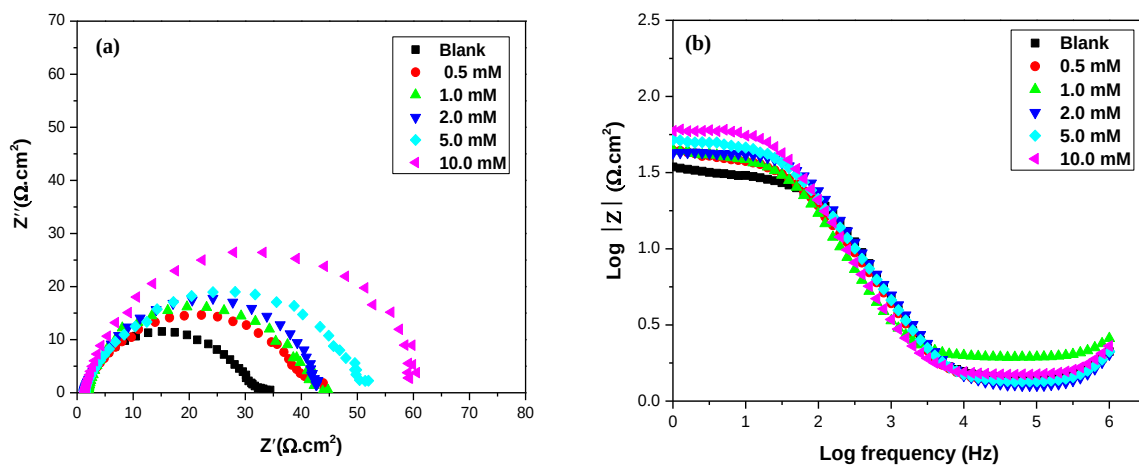


Figure 4.4 Nyquist (a) and Bode (b) plots of mild steel sample in 1.0 M HCl in the absence and presence of varying concentrations of 2-chloro-1H-imidazole (0.5 – 10.0 mM).

The Nyquist plots in both cases show a depressed semi-circle which indicates that there is only one time constant equivalent to the charge transfer process in the system [14]. Furthermore, the depressed capacitive loops are due to the dispersion effect which occurs as a result of the roughness and heterogeneity of the surface of mild steel, adsorption of inhibitor molecules and the existence of porous layers on the metal surface [92]. The presence of smaller capacitive loops at low frequency regions in the un-inhibited medium and lower inhibitor concentrations (0.5 mM and 1.0 mM) are due to diffusion of oxygen from the bulk of the solution to the surface of mild steel specimen. This implies that at these concentrations the corrosion of mild steel is diffusion controlled [93]. It is also observed from the Nyquist plots that the inhibited solutions display bigger capacitive loop diameters in the high frequency region compared to the inhibitor-free solution. This is an indication that corrosion of mild steel in acidic medium is slowed or prevented by the presence of the inhibitor molecules. In addition, the diameter of the high frequency loops continuously increases with an increase in concentration of the inhibitor molecules which are ascribed to an increase of surface coverage ( $\theta$ ) of the inhibitor molecules on mild steel surface with increasing concentration [94]. Bode plots in the absence and presence of inhibitor molecules show the effect of the corrosion inhibitor molecules at the low frequency impedance modulus. The low frequency impedance modulus ( $Z$ ) is observed to increase with increasing concentration of the inhibitor molecules, and this has been related to the adsorption of the inhibitors on the exposed steel surface [54]. Higher impedance values implies better inhibition efficiency and the results obtained for the two inhibitor molecules correlates with those obtained by Tafel polarization measurements.

Equivalent circuit constructed for fitting and extraction of EIS data (Table 4.3) is shown in Figure 4.5. It comprises of an arrangement of the polarization resistance,  $R_p$ , which is the resistance due to the mild steel polarization. The  $R_p$  is constructed in series with the Warburg impedance,  $W$ , which accounts for the diffusion process. Both  $R_p$  and  $W$  are in parallel with the constant phase element, CPE. The overall connection is set in series with the solution resistance,  $R_s$ . The inclusion of the CPE in the equivalent circuit model was to account for the local inhomogeneity in the dielectric material and the porosity in mass transport effect; which led to the observed depressed semi-circle in the Nyquist plots [95].

Impedance of the CPE is defined as follows:

$$Z_{CPE} = \frac{1}{Q(i\omega)^n} \quad (4.5)$$

where  $Q$  is the magnitude of the CPE,  $n$  the phase shift,  $\omega$  the angular frequency (defined by  $\omega = 2\pi f$ , where  $f$  is the frequency at which the imaginary part of impedance is the highest), and  $i$  an imaginary number. The phase shift  $n$  determines what CPE stands for;  $n = 0$  implies that CPE represents a resistance,  $n = 1$  a capacitance and  $n = -1$  an inductance.

In order to estimate the double layer capacitance,  $C_{dl}$  we use the relation:

$$C_{dl} = Y_o(2\pi f_{max})^{n-1} \quad (4.6)$$

where  $f_{max}$  represents the maximum frequency of the imaginary component of the impedance.

As evidenced from the EIS data in Table 4.3, there is a decrease in the double layer capacitance ( $C_{dl}$ ) for both inhibitor molecules which is due to an increase in the double layer thickness due to adsorption of the inhibitor molecules. This conforms to the mathematical expression of the Helmholtz model [40] given by the equation:

$$C_{dl} = \frac{\epsilon \epsilon_0 A}{d} \quad (4.7)$$

where  $d$  is the protective layer thickness,  $\epsilon$  the dielectric constant of the medium,  $\epsilon_0$  vacuum permittivity and  $A$  the effective surface area of the electrode.

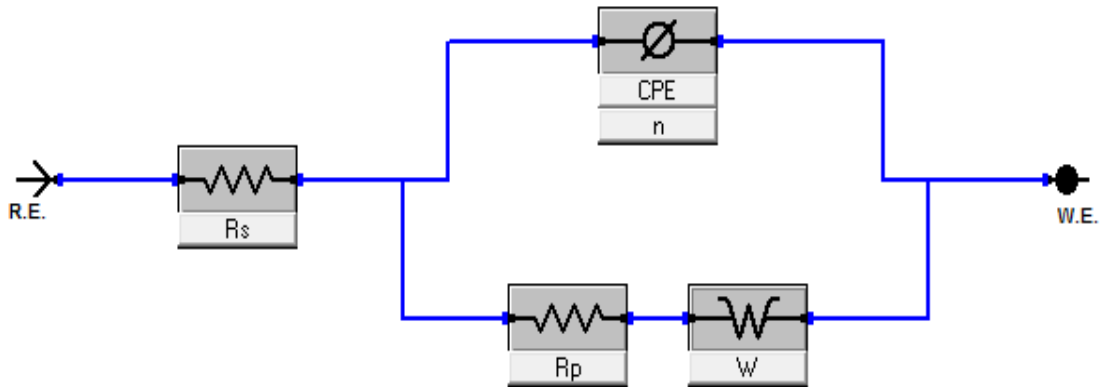


Figure 4.5 Equivalent circuit corresponding to fitted EIS data

Table 4.3 EIS data in the absence and presence of varying concentration of inhibitors

| Inhibitor | C <sub>inhibitor</sub><br>(mM) | R <sub>s</sub> (Ω.cm <sup>2</sup> ) | R <sub>p</sub><br>(Ω.cm <sup>2</sup> ) | C <sub>dl</sub><br>(μF cm <sup>-2</sup> ) | W (Ω cm <sup>2</sup><br>s <sup>1/2</sup> ) | n   | θ   | η %  | χ <sup>2</sup> (x10 <sup>-4</sup> ) |
|-----------|--------------------------------|-------------------------------------|----------------------------------------|-------------------------------------------|--------------------------------------------|-----|-----|------|-------------------------------------|
| blank     | 0                              | 1.4                                 | 29.4                                   | 64.4                                      | 86.0                                       | 0.9 | --  | --   | 2.7                                 |
| 2-I-Imz   | 0.5                            | 1.3                                 | 49.3                                   | 42.5                                      | 48.0                                       | 0.8 | 0.4 | 41.4 | 3.3                                 |
|           | 1.0                            | 1.5                                 | 53.3                                   | 47.3                                      | 40.2                                       | 0.9 | 0.4 | 46.2 | 2.5                                 |
|           | 2.0                            | 1.4                                 | 74.4                                   | 42.7                                      | 19.3                                       | 0.9 | 0.6 | 61.6 | 2.5                                 |
|           | 5.0                            | 1.3                                 | 145.9                                  | 43.5                                      | 15.6                                       | 0.9 | 0.8 | 80.6 | 2.5                                 |
|           | 10.0                           | 1.3                                 | 172.6                                  | 36.8                                      | 10.5                                       | 0.9 | 0.8 | 83.5 | 2.5                                 |
| 2-Cl-Imz  | 0.5                            | 1.3                                 | 39.0                                   | 12.2                                      | 61.2                                       | 0.8 | 0.2 | 24.6 | 3.3                                 |
|           | 1.0                            | 1.9                                 | 39.8                                   | 12.1                                      | 65.5                                       | 0.9 | 0.2 | 26.1 | 1.7                                 |
|           | 2.0                            | 1.3                                 | 42.3                                   | 11.1                                      | 24.8                                       | 0.9 | 0.3 | 30.5 | 3.2                                 |
|           | 5.0                            | 1.3                                 | 48.7                                   | 12.4                                      | 16.5                                       | 0.8 | 0.4 | 39.6 | 3.3                                 |
|           | 10.0                           | 1.5                                 | 59.7                                   | 13.0                                      | 16.6                                       | 0.9 | 0.5 | 51.7 | 2.8                                 |

The ability to adsorb on metal surfaces forming a protective layer is one of the important features of organic corrosion inhibitors. Adsorption is a surface phenomenon and a consequence of surface energy. The surface of solids is usually in a state of strain which results in unbalanced residual forces. These residual forces results in higher surface energy. As a result, the surfaces of solids always have a tendency to attract and retain molecular species which it comes in contact with. Adsorption could be through electrostatic interactions between charged molecules and the metal, otherwise known as physisorption or through sharing or transfer of electrons from molecules to the metal surface atoms to form a coordinate type of bond, known as chemisorption. Adsorption isotherms are used to provide information on the mechanism through which the inhibitor molecules interacts with the metal surface [53]. To obtain adsorption isotherms, we first determined the degree of surface coverage,  $\theta$  of the inhibitor molecules. This dimensionless parameter is a function of the changes in polarization resistances of the inhibitor molecules as follows:

$$\theta = \left( \frac{R_p - R_p^0}{R_p} \right) \quad (4.8)$$

Among the commonly used adsorption isotherms are the Langmuir, Frumkin and Temkin isotherms, each of which relates the surface coverage of a given adsorbate to its concentration  $C$  (M) according to the following equations [96]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad \text{Langmuir isotherm} \quad (4.9)$$

$$\log \left( \frac{\theta}{(1-\theta)c} \right) = \log K_{ads} + g\theta \quad \text{Frumkin isotherm} \quad (4.10)$$

$$\log \left( \frac{\theta}{c} \right) = \log K_{ads} - g\theta \quad \text{Temkin isotherm} \quad (4.11)$$

where  $K_{ads}$  is the adsorption equilibrium constant and  $g$  the molecular interaction parameter (Frumkin) or surface free energy parameter (Temkin).  $K_{ads}$  is related to the Gibbs free energy of adsorption,  $\Delta G_{ads}$  by the equation:

$$\Delta G_{ads} = -RT \ln(55.5 K_{ads}) \quad (4.12)$$

where  $R$  is the molar gas constant,  $T$  the absolute temperature and 55.5 the molar concentration of water.

Langmuir isotherm indicates that a given adsorbate only cover one substrate site. According to this model, the surface free energies of all the sites on the substrate are equal, and that no interaction occurs between the species. However, once the concentration of the adsorbed species is high to the extent that there is the possibility of attractive or repulsive interactions among the species, this model fails and it becomes necessary to fit using either the Frumkin or Temkin isotherm model. In the Frumkin model, the interaction between the adsorbed species was taken into consideration, and it was assumed that adsorption sites are uniform. While in the Temkin model it was assumed that although no molecular interaction between the adsorbed species, the surface free energy of the substrate vary with the extent of surface coverage,  $\theta$  [96, 97].

Experimental results were fitted into Langmuir ( $R^2$ , 0.998 and 0.983), Frumkin ( $R^2$ , 0.627 and 0.780) and Temkin ( $R^2$ , 0.925 and 0.850) models for 2-I-Imz and 2-Cl-Imz,

respectively. The results suggested that experimental data fit better with the Langmuir model. However, it can be noticed that the resulted slope is greater than unity for both molecules, which implies that each inhibitor specie occupies more than one adsorption site and interacts with other adsorbed species on the metal surface [98], factors which are not taken into consideration in the derivation of Langmuir isotherm. To account for these two factors, Villamil *et al.* [99] proposed a modified Langmuir model which takes into consideration the interactions between adsorbed species as follows;

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \quad (4.13)$$

where n is the slope and refers to the number of displaced water molecules from the metal surface as a result of adsorption of the inhibitor species [100-104]. Our experimental data therefore fits with the modified Langmuir isotherm with the corresponding adsorption parameters given in Table 4.4. Typical values of Gibbs free energy of adsorption,  $\Delta G_{ads} < -20$  kJ/mol are generally associated with electrostatic interactions (physisorption), while values  $> -40$  kJ/mol are associated with chemisorption [105]. The adsorption data of both inhibitor molecules (Table 4.4) falls between the two classifications indicating the possibility of undergoing both physical and chemical modes of adsorption.

Table 4.4 Langmuir adsorption data of 2-I-Imz and 2-Cl-Imz

| Inhibitor | $K_{ads} (x10^3 \text{ Lmol}^{-1})$ | $\Delta G_{ads} (\text{kJ/mol}^{-1})$ | $R^2$ |
|-----------|-------------------------------------|---------------------------------------|-------|
| 2-I-Imz   | 1.2                                 | -27.6                                 | 0.998 |
| 2-Cl-Imz  | 0.9                                 | -26.7                                 | 0.983 |

### 4.3.2 Adsorption properties and molecular dynamics simulations

To further shed light on the interaction between imidazole molecules and iron surface, namely Fe(100), quantum chemical periodic slab calculations and molecular dynamics simulation were carried out for the C2-halogenated imidazoles, namely 2-Cl-Imz, 2-Br-Imz and 2-I-Imz. Initially, we investigated various possible adsorption modes of imidazole on Fe(100) surface. The adsorption of the parent imidazole on Fe(100) has been reported in a DFT study by Kokalj with the PBE functional and ultrasoft pseudopotential [106]. Here, five possible conformations have been identified for imidazole on Fe(100), namely perpendicular, parallel, parallel-dissociated, tilted, and tilted-dissociated (Figure 4.6).

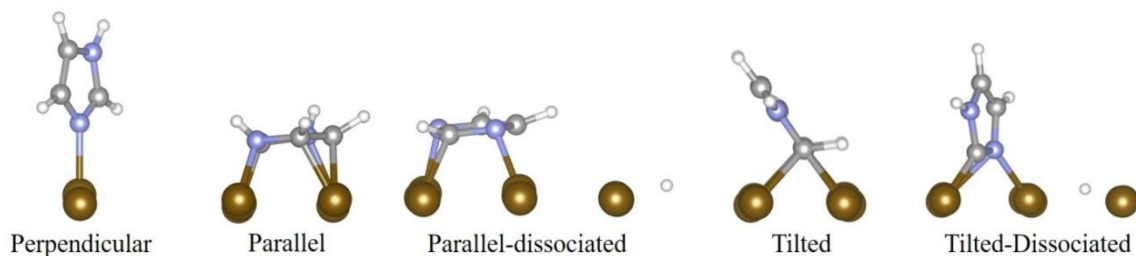


Figure 4.6 Various conformations of imidazole on Fe(100) surface.

It is instructive to first examine the molecular adsorption at various coverages, using a variety of different supercells (the coverage is defined as the inverse of the number of surface Fe atoms per imidazole molecule). Our calculations revealed a similar trend in adsorption energies ( $E_{\text{ads}}$ ) of perpendicular, parallel and tilted conformations with monolayer as reported by Kokalj [106] – the adsorption energies become more negative

with decreasing monolayer (Table 4.5), except in the case of the tilted-dissociated conformation. In addition, our calculations indicated that the parallel-dissociated conformation is the most stable adsorption conformation for intact imidazole at all the monolayer considered. At 1/9 monolayer, the tilted-dissociated conformation is the most stable conformation, followed by the parallel-dissociated conformation. At 1/16 monolayer, the situation is reversed, with the parallel-dissociated conformation being the most stable and the tilted-dissociated conformation having similar adsorption energy as the parallel conformation. This suggests possible repulsive interaction of the parallel conformation at 1/9 monolayer which is alleviated at 1/16 monolayer. On the contrary, the tilted-dissociated conformation suffered a decrease in the magnitude of the adsorption energy from 1/9 monolayer to 1/16 monolayer. This suggests the existence of attractive interactions is lost as the imidazole molecules spread further apart.

Table 4.5 Adsorption energies (E<sub>ads</sub>) of imidazole on Fe(100) surface at various monolayers for different conformations in the gas phase and aqueous medium<sup>a</sup>

| conformation         | $\frac{1}{4}$ (2x2) | $\frac{1}{4} \left( \begin{pmatrix} 2 & 1 \\ 0 & 2 \end{pmatrix} \right)$ | 1/9           | 1/16          |
|----------------------|---------------------|---------------------------------------------------------------------------|---------------|---------------|
| perpendicular        | -0.42 (-0.43)       | -0.44 (-0.54)                                                             | -0.62 (-0.68) | -0.67 (-0.68) |
| tilted               | -0.20 (+0.06)       | -0.20 (+0.10)                                                             | -0.45 (-0.27) | -0.49 (-0.71) |
| tilted-dissociated   | -1.37 (-1.06)       | -1.34 (-1.09)                                                             | -1.40 (-1.20) | -1.27 (-1.05) |
| parallel             | -0.73 (-0.49)       | -0.56 (-0.16)                                                             | -0.79 (-0.61) | -1.25 (-0.97) |
| parallel-dissociated | N/A                 | N/A                                                                       | -1.23 (-0.94) | -1.47 (-1.27) |

<sup>a</sup> Aqueous values in parenthesis.

The effect of water was modeled by a continuum solvation model as implemented in VASPsol [107]. In general, the magnitudes of the adsorption energies in aqueous medium

decrease relative to the gas-phase results (Table 4.5). The relative energies between various conformations remain virtually unchanged.

Although the energetic of the parallel conformation is more favorable than the tilted conformation, there is a substantial barrier of dissociation of +0.75 eV from the parallel to parallel-dissociated conformation at 1/9 monolayer according to our calculations (+0.90 eV is reported by Kokalj [106]). On the other hand, molecular dynamics simulation indicated that the tilted conformation is *meta*-stable and dissociates readily on Fe(100) surface within 200 femtoseconds (fs) (Figure 4.7). It thus appears that from a kinetic perspective, the rate of formation of parallel-dissociated conformation is not competitive to the formation of the tilted-dissociated conformation.

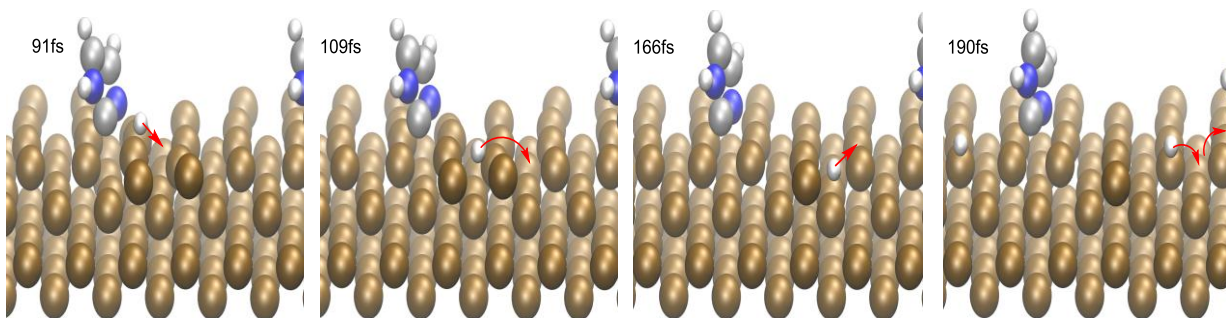


Figure 4.7 NVT MD simulation of tilted conformation at 300 K.

In order to have a better understanding of the kinetic behavior of imidazole on Fe(100) surface, we performed a high temperature MD simulation (NVT) with four imidazole molecules on a Fe(100) surface at 1500 K over a duration of 499 fs. The high temperature increases the probability of observing events such as diffusion and reactions which are unlikely to be observed in a simulation with a duration that lasts for picoseconds. Four different imidazole molecules in a (4x4) Fe(100) cell allowed conformations' freedom

that cannot be achieved in a (2x2) cell when the periodic boundary condition was imposed. We observed that at 275.5 fs, one of the imidazole adopted the parallel conformation. At 499 fs, two imidazole molecules were dissociated while the other two desorbed from the surface (Figure 4.8).

For the adsorption properties of series of C2-halogenated imidazoles, we began our calculations with the perpendicular conformation at 1/16 coverage. Apart from 2-Cl-Imz, the perpendicular conformation does not exist as the process of ionic relaxation inevitably resulted in the tilted-dissociated conformation. 2-Cl-Imz has weaker adsorption relative to imidazole. The tilted-dissociated conformations of these C2-halogenated imidazoles, however, adsorbed much more strongly to Fe(100) surface relative to imidazole (Table 4.6). The magnitude of the adsorption energies follow the trend  $X = \text{I} > \text{Br} > \text{Cl}$ . The main difference in the magnitude of the adsorption energy can be ascribed to the stronger interaction between halogen relative to hydrogen and the weaker C–X bond relative to a C–H bond.

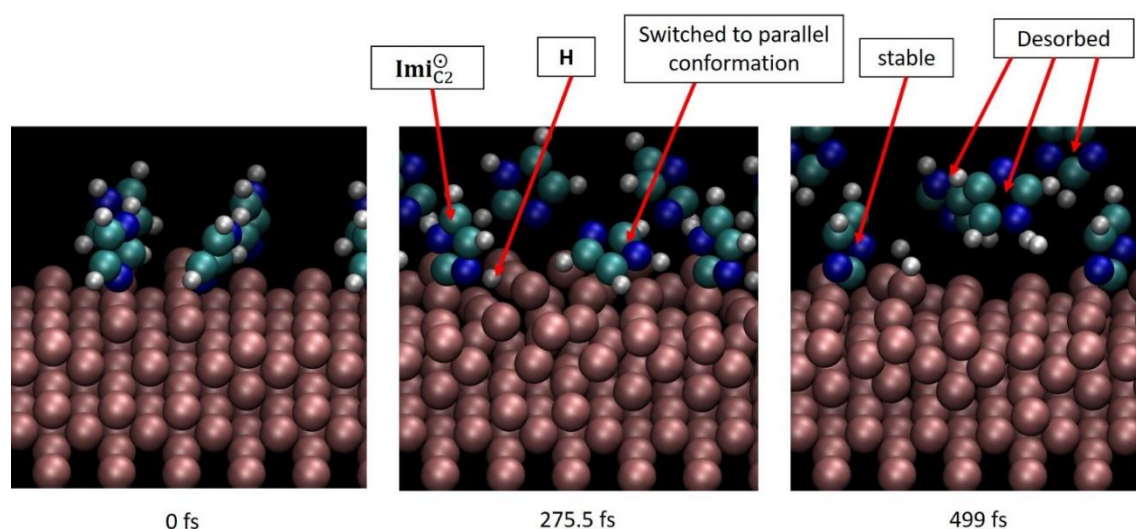


Figure 4.8 NVT MD simulation of 4 imidazole molecules on a (4x4) Fe(100) slab at 1500 K.

To gain further insight on the rate of dissociation of 2-I-Imz on Fe(100), we performed an NVT MD simulation on 2-I-Imz which was partially relaxed on Fe(100) slab described by a (4x4) supercell. Key moments of the molecular dynamic simulation are depicted in **Error! Reference source not found.**4.9. At 200 fs, dissociation of C–I bond was completed and the imidazole core began to adopt the tilted conformation. The process of adopting the tilted-dissociated conformation was virtually completed at 329 fs. This simulation suggests that 2-I-Imz is capable of forming a protective layer in its tilted-dissociated conformation upon contact with Fe(100) surface. We note that Kokalj hypothesized that this layer is responsible for the corrosion inhibition property of imidazole [106].

Table 4.6 Adsorption energies of various C2-halogenated imidazoles at 1/16 monolayer

| C2-halogenated<br>imidazole | adsorption energy / eV |                    |
|-----------------------------|------------------------|--------------------|
|                             | perpendicular          | tilted-dissociated |
| 2-Cl-Imz                    | -0.51                  | -3.48              |
| 2-Br-Imz                    | dissociate             | -3.76              |
| 2-I-Imz                     | dissociate             | -3.95              |

The facile dissociation of 2-I-Imz and its strong adsorption allude to its potential as a superior corrosion inhibitor relative to imidazole and other halo-substituted imidazoles. Overall, the magnitude of the calculated adsorption energies of the inhibitor molecules is in the order 2-I-Imz > 2-Br-Imz > Imz > 2-Cl-Imz. These computational results are in good accord with the experimentally determined inhibitive efficiencies of the molecules and shows that this method of MD simulation can be utilized as a powerful tool in the

investigation of corrosion inhibition of organic molecules, especially when the stability of the mode of adsorption of the molecules on the metal is a determining factor.

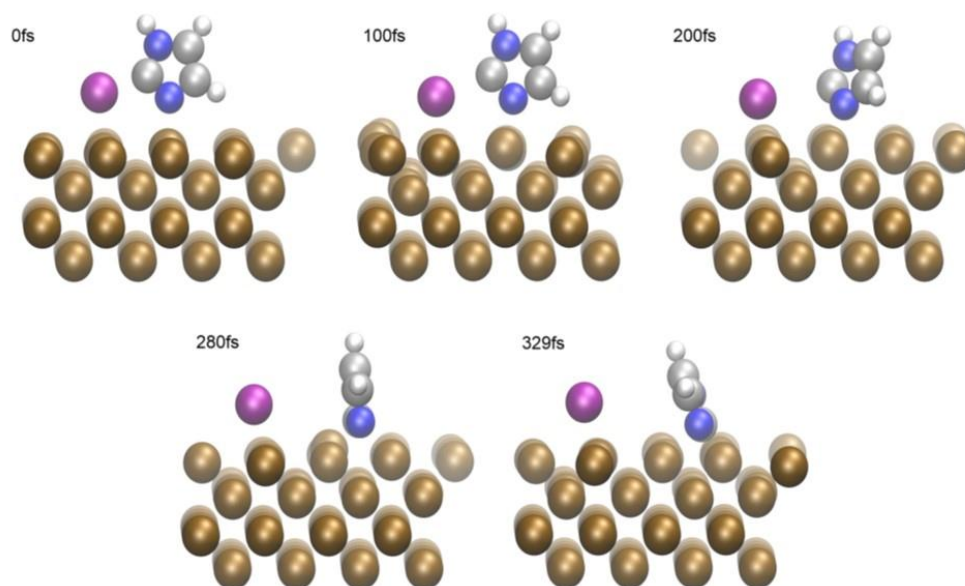


Figure 4.9 NVT MD simulation of 2-I-Imz on Fe(100) at 300 K.

The difference noticed between the calculated adsorption and Langmuir free energy values (Table 4.4) for the imidazole systems as well as in other similar studies [100, 108-113] is worth to be commented on. The adsorption energy refers to a molecular dynamic quantity that corresponds to the binding energy at 0 K. It gives an idea of the extent of adsorption of the inhibitor molecule on the metal surface in an ideal setting. On the other hand, the Gibbs free energy of adsorption is a thermodynamic parameter which was derived on experimental basis. Considering the difference in the theoretical and experimental basis of these two quantities and depending on the experimental conditions and the modeling parameters adopted, they could disagree even by a number of

magnitudes. In any case, the free energy here is helpful to predict the degree of spontaneity of the adsorption process being investigated.

### 4.3.3 Spectroscopic studies

SEM micrographs of mild steel specimen was taken after immersion in 1.0 M HCl in the absence and presence of 5.0 mM of the inhibitor molecules at 25 °C. The results are displayed in Figure 4.10. As shown in Figure 4.10a, the morphology of steel is clearly visible with the grain boundaries comprising ferrite and pearlite revealed [114, 115]. After immersion in 1.0 M HCl for 24 h there was a complete destruction of the steel microstructure with a consequent formation of massive pits as revealed in Figure 4.10b. However, upon addition of the inhibitor molecules (Figures 4.10c-g), the damage to the steel significantly reduced and a complete surface coverage were observed in the presence of 2-I-Imz molecule (Figure 4.10g). This is in agreement with other experimental results which show that 2-I-Imz molecule exhibits the best inhibitive performance among the halo-substituted imidazoles studied.

XPS analysis was carried out to investigate the adsorption of the molecules on the metal and to determine the composition of the films formed. A representative spectrum of 2-I-Imz is shown in Figure 4.11. The high resolution peaks for (a) C 1s, (b) O 1s, (c) Cl 2p<sub>1/2</sub> and 2p<sub>3/2</sub>, (d) N 1s and (e) Fe 2p<sub>1/2</sub> and 2p<sub>3/2</sub> are shown in the figure. The deconvoluted C 1s spectrum was fitted to three distinct peaks at 284.5, 284.7 and 286.1 eV (Figure 4.11a). The peak at 284.5 eV corresponds to sp<sup>2</sup> hybridized carbon of the imidazole rings while those at 284.7 and 286.1 eV were assigned to sp<sup>3</sup> hybridized and C-O carbon atoms which may have arisen due to atmospheric exposure of the steel sample leading to

contamination [116]. The spectrum of O 1s was fitted into three peaks as shown in Figure 4.11b. The peak observed at binding energy 530.8 eV is a characteristic peak of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> while that observed at around 531.0 eV was assigned to surface oxygen as a result of water chemisorption to form Fe-OH [117]. The peak at 533.0 eV represents loosely bound oxygen on the metal surface [118]. The Cl 2p spectrum shows two peaks after deconvolution appearing at around 198.0 eV for 2p<sub>3/2</sub> and 200.0 eV for 2p<sub>1/2</sub> as shown in Figure 4.11c. The peak at 198.0 eV represents inorganic chlorine which could be as a result of the formation of ferric chloride (FeCl<sub>3</sub>), while that at around 200.0 eV was due to organic chlorine which exist in the form of C-Cl bonds [119]. N 1s signal of the steel sample was fitted into three peaks located at around 397.0, 398.2 and 400.0 eV (Figure 4.11d), corresponding to pyridinic, pyrrolic and quaternary nitrogen atoms, respectively. The first component represents non-protonated sp<sup>2</sup> hybridized nitrogen atoms (=N-) present in the imidazole rings [120]. Component two having the highest contribution to the N1s signal is due to the coordinate nitrogen atoms in the imidazole ring which serves as the basic point of interaction between the imidazole and Fe on the steel surface (N-Fe) [54]. The third peak represents the oxidized form of nitrogen atoms which forms as a result of protonation of nitrogen atoms in the imidazole ring [54]. The Fe 2p spectrum (Figure 4.11e) shows three principal peaks which include Fe 2p<sub>3/2</sub> at 710.9 eV, Fe 2p<sub>1/2</sub> at 724.5 eV and a satellite peak at 718.5 eV consistent with the presence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [121]. Furthermore, the fitted Fe 2p peaks revealed the presence of Fe in the form of ferric (Fe<sup>3+</sup>) and ferrous (Fe<sup>2+</sup>) species with the dominant peak corresponding to the ferric specie. The presence of the ferric specie is associated to the oxidation of the ferrous specie during the course of corrosion of the steel sample. XPS results are in agreement

with other experimental results and confirm the adsorption of the inhibitor molecules on mild steel.

AFM was further utilized to investigate the topography of the steel specimen in the absence and presence of the inhibitor molecules (Figure 4.12). A significant decrease in surface roughness and increased surface coverage was observed in the sample treated with 2-I-Imz (Figure 4.12c) relative to the bare mild steel (Figure 4.12a) and that treated with 2-Cl-Imz (Figure 4.12b). This confirms the adsorption of 2-I-Imz and formation of a protective film on mild steel compared to the un-inhibited medium. In addition, the 2D topography analysis of sample treated with 2-Cl-Imz shows evidence of damage to the surface of mild steel as was observed in the SEM micrographs presented in Figure 4.10.

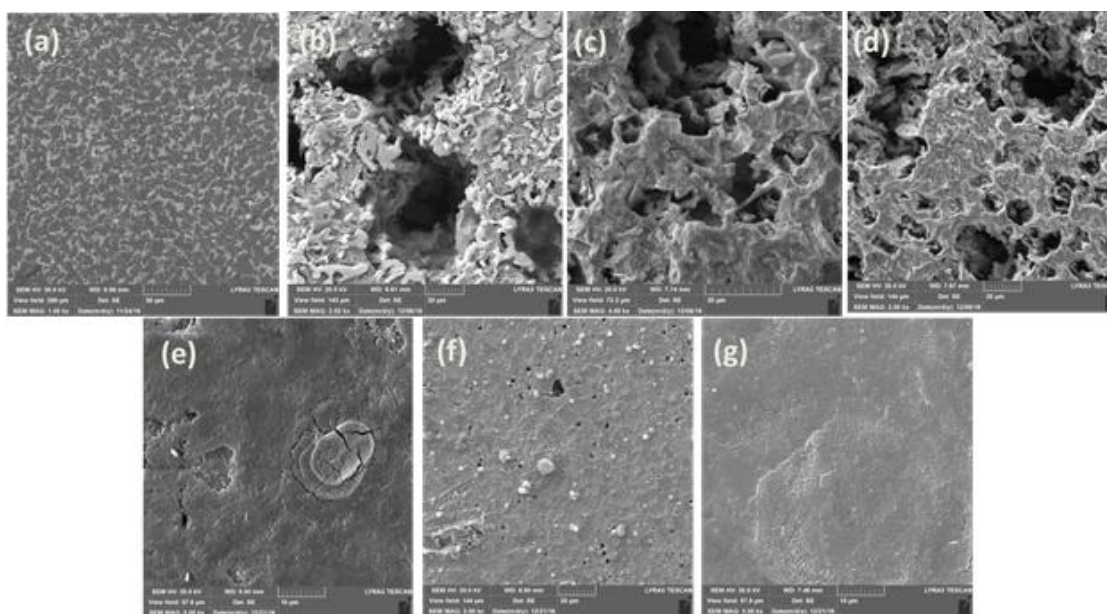


Figure 4.10 SEM micrographs of mild steel sample: (a) as received and after immersion in 1.0 M HCl solution in the absence (b) and presence of 5.0 mM 2-Cl-Imz (c), Imz (d), 2-Br-Imz (e) 4-Ph-Imz (f) and 2-I-Imz (g) for 24 h at 25 °C.

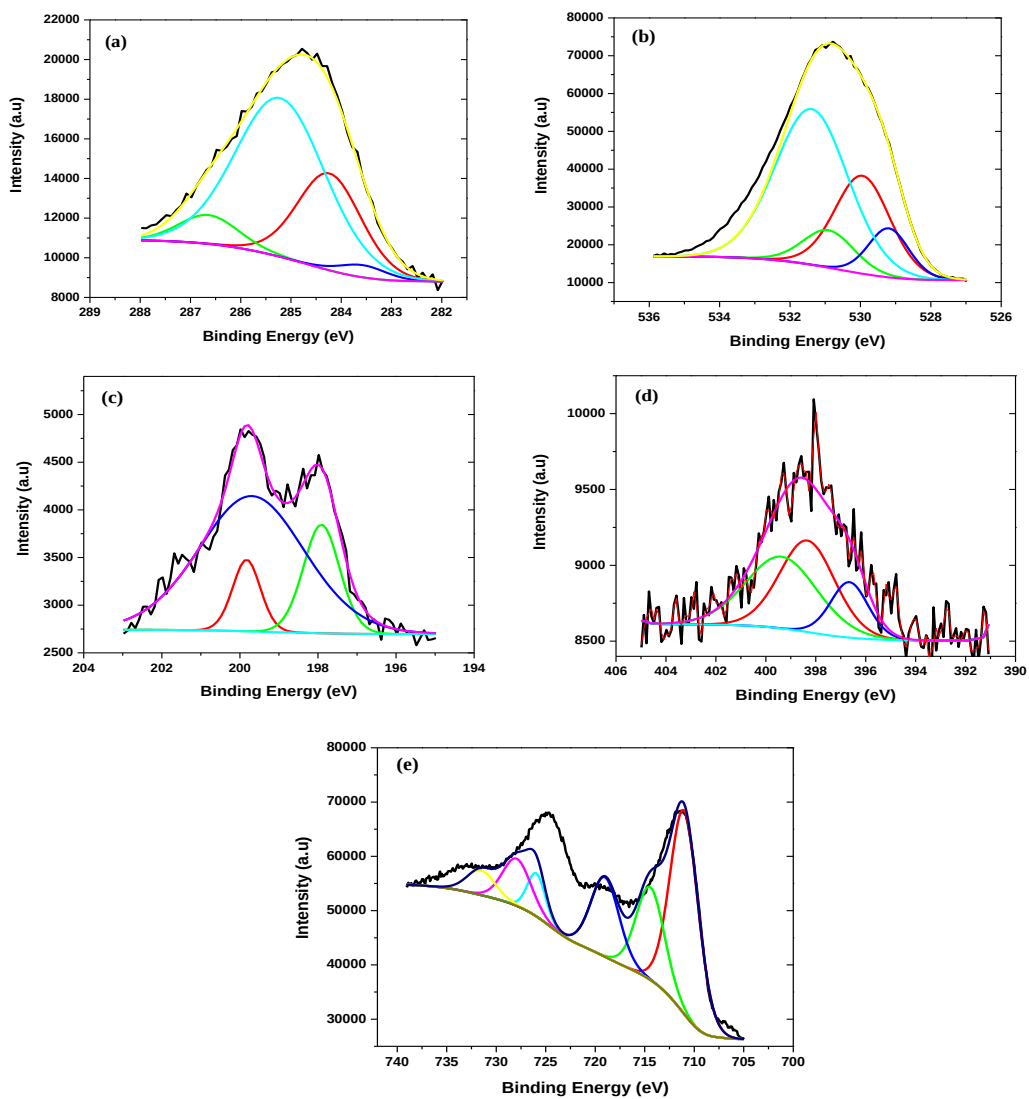


Figure 4.11 XPS spectra for mild steel sample in the presence of 5.0 mM 2-I-Imz showing peaks for (a) C 1s, (b) O 1s, (c) Cl 2p<sub>1/2</sub> and 2p<sub>3/2</sub>, (d) N 1s and (e) Fe 2p<sub>1/2</sub> and 2p<sub>3/2</sub>.

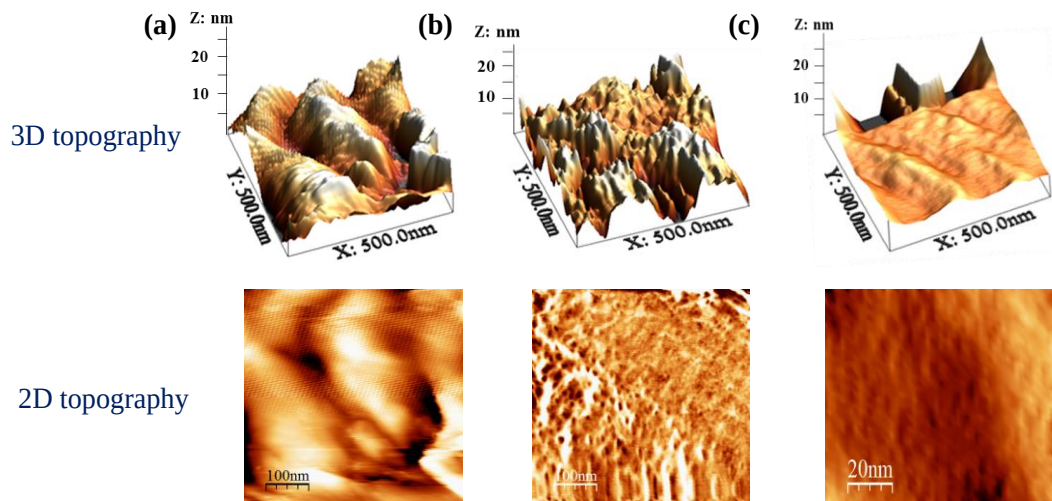


Figure 4.12 AFM images of (a) bare steel and after treatment with (b) 2-Cl-Imz and (c) 2-I-Imz

#### 4.4 Summary

The predictive corrosion inhibitive properties of C2-halogenated imidazoles have been investigated in comparison with experimental data. Molecular dynamics calculations predicted the adsorption of the molecules on Fe(100) surface to follow the order  $I > Br > Cl$  with calculated adsorption energies -3.98, -3.76 and -3.48 eV, respectively. Although the parallel conformation of the molecules was found to be more stable due to pi-metal stabilization, the tilted conformation was kinetically labile with the C-halogen bond readily fragmented. The dissociated products were predicted to firmly bind to the iron surface and, hence, are capable of forming a strongly adsorbed layer with properties depending on the halogen-metal interaction. This was elucidated experimentally where 2-I-Imz was shown to have the highest inhibition efficiency of 83.5%, in agreement with MD results and due to the well-known strong adsorption of iodine on electrode surfaces. Whereas,  $Cl^-$  and  $Br^-$  are well known for their corrosion attack through exchange with

oxygen in the matrix of the protective oxide surface film of the metal. This was shown clearly by AFM and FESEM where more pitting damage occurred on the metal surface in accordance with the literature with corrosion damage increasing from  $\text{Br}^-$  to  $\text{Cl}^-$  with chloride showing the most damaging properties of the studied molecules. Therefore, our predictive model is in accordance with all experimental results and demonstrated clearly that the theoretical approach adopted in this study can be further implemented in understanding the corrosion inhibition mechanism of more complex molecules.

## CHAPTER 5

# AROMATICITY AND SUBSTITUENT EFFECTS ON THE CORROSION INHIBITIVE PROPERTIES OF BENZIMIDAZOLE DERIVATIVES: AN ELECTROCHEMICAL AND QUANTUM CHEMICAL STUDY

### 5.1 A brief overview

Aromaticity is one of the major factors generally believed to influence the corrosion inhibitive properties of organic molecules. Along with this factor is also the contributing effect of electron-releasing and electron-withdrawing substituents. In the present study, the role of phenyl substituents and the influence of electron-releasing and electron-withdrawing substituents on the corrosion inhibition efficiency of imidazole were investigated using quantum chemical DFT calculations and electrochemical measurements. DFT calculations supported with Tafel polarization measurements revealed that the presence of phenyl substituent on imidazole greatly enhances its corrosion protection. Results of molecular level interaction studies predicted the adsorption of the molecules on the surface of iron to take place through chemisorption mechanism, yielding Fe-N and Fe-C bonds in the range 1.90 – 2.20 Å. An overall corrosion inhibition efficiencies of 95.5% and 96.0% were recorded for 4-(4-chlorophenyl)imidazole, 4-CPI and 4-(1H-imidazol-1-yl)aniline, 1-API, respectively.

## 5.2 Experimental and computational procedure

### 5.2.1 Reagents and solutions

All reagents used were of standard purity and of analytical grade (Sigma-Aldrich) and were used as-received without further purifications. Solutions of imidazole derivatives (Table 5.1) were prepared by dissolving the respective reagents in 1.0 M HCl (fluka) using double distilled water.

### 5.2.2 Electrochemical methods

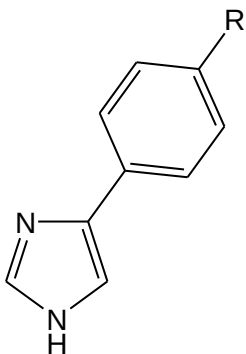
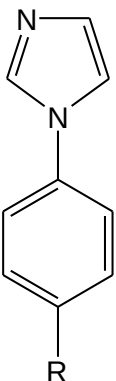
Electrochemical measurements were performed in a 250-ml jacketed electrochemical cell kit with three-electrode compartments (Gamry). Mild steel bar AISI 1018 with the following compositions; C, 0.15 – 0.20%; Mn, 0.60 – 0.90%; P, 0.04%; S, 0.05% and balance Fe was used as the sample specimen, saturated calomel electrode (SCE) and carbon graphite as the reference and counter electrodes, respectively. The sample specimen was polished sequentially using silicon carbide emery papers of different grit size (120 – 800), rinsed with distilled water, placed in an ultrasonic acetone bath to remove possible residue due to polishing, rinsed with acetone, dried in warm air, and stored in a desiccator before use. Gamry potentiostat/galvanostat/ZRA (Reference 600) equipped with a Gamry framework interface was used for electrochemical studies. Gamry Echem Analyst version 6.03 was used for data analysis and fittings. All experiments were conducted at room temperature. Tafel polarization measurements were carried out by scanning the potential at 0.5 mV/s in the range +250 mV to -250 mV against the open circuit potential ( $E_{ocp}$ ). Corrosion potential ( $E_{corr}$  /V vs SCE) and corrosion current density ( $i_{corr}$ , A cm<sup>-2</sup>) were obtained by extrapolation of anodic ( $\beta_a$ ) and cathodic ( $\beta_c$ )

branches of the Tafel curves. All electrochemical tests were carried out in triplicates; the average of which was reported. Inhibition efficiencies were calculated using equation:

$$\eta (\%) = \left( \frac{i_{corr}^{\circ} - i_{corr}}{i_{corr}^{\circ}} \right) \times 100 \quad (5.1)$$

where  $i_{corr}^{\circ}$  and  $i_{corr}$  are corrosion current density values in the absence and presence of the inhibitors obtained from Tafel polarization measurements, respectively.

Table 5.1 Chemical structures of inhibitor molecules

|   | Substituent (R)  | Name                             | Abbreviation |
|-------------------------------------------------------------------------------------|------------------|----------------------------------|--------------|
|                                                                                     | H                | 4-phenylimidazole                | 4-PI         |
|                                                                                     | F                | 4-(4-fluorophenyl)imidazole      | 4-FPI        |
|                                                                                     | Cl               | 4-(4-chlorophenyl)imidazole      | 4-CPI        |
|                                                                                     | Br               | 4-(4-bromophenyl)imidazole       | 4-BPI        |
|  | H                | 1-phenylimidazole                | 1-PI         |
|                                                                                     | OH               | 4-(imidazol-1-yl)phenol          | 1-HPI        |
|                                                                                     | OCH <sub>3</sub> | 1-(4-methoxyphenyl)-1H-imidazole | 1-MPI        |
|                                                                                     | NH <sub>2</sub>  | 4-(1H-imidazol-1-yl)aniline      | 1-API        |

### 5.2.3 Computational method

Full geometry optimization of the molecules was performed on Gaussian 09 package [64], using the hybrid-functional of the Becke three-parameters, Lee, Yang and Par (B3LYP) and the 6-31G(d) basis set for C, H, N and O, while BPW91 was used for iron cluster. Structural geometry optimization was carried out to the minima on potential energy surfaces without imposing any constraints. Reactivity descriptors such as global hardness ( $\eta$ ), electron affinity (A), ionization potential (I), electronegativity ( $\chi$ ), and fraction of transferred electrons ( $\Delta N$ ) were calculated. Molecular level adsorption studies were carried out using the cluster model and the interaction energies of the molecules with Fe<sub>4</sub> cluster were calculated. Interaction free energies of the inhibitor-cluster complexes were calculated according to the following equations:

$$E_{interaction} = -E_{binding} \quad (5.2)$$

$$E_{binding} = E_{complex} - (E_{cluster} + E_{inhibitor}) \quad (5.3)$$

Where  $E_{complex}$ ,  $E_{cluster}$  and  $E_{inhibitor}$  represents the free energies of the inhibitor-Fe complex, metal cluster and the isolated inhibitor molecules, respectively.

## 5.3 Results and discussion

### 5.3.1 Electrochemical measurements

Electrochemical behavior of the inhibitor molecules were studied using potentiodynamic polarization measurements on mild steel specimen in 1.0 M HCl in the absence and presence of the inhibitors. Fig. 5.1 and Fig. 5.2 shows the Tafel polarization curves, while

the corresponding extrapolated data are given in Tables 5.2 & 5.3. Notably from these data, the corrosion current density ( $i_{\text{corr}}$ ) decreases significantly with in the presence of the inhibitor molecules. This indicates that the molecules adsorb on the surface of the metal preventing corrosion attack. Furthermore, the polarization curves of the inhibited solutions showed a decrease in anodic and cathodic slopes compared to the un-inhibited solution. This implies that both the anodic and cathodic processes are inhibited. A shift in corrosion potential ( $E_{\text{corr}}$ ) was also observed with the increase in concentration of the inhibitors in a manner that suggests that they act as mixed-type corrosion inhibitors, inhibiting both anodic and cathodic processes [122, 123]. Overall corrosion inhibition efficiencies of 95.5% and 96.0% were recorded at 10 mM concentrations for 4-CPI and 1-API, respectively.

### 5.3.2 Computational studies

The optimized molecular structures representing the lowest energy conformers of the inhibitor molecules at hybrid DFT functional, B3LYP/6-31G(d) are presented in Fig. 5.3. The corresponding quantum chemical reactivity descriptors of the protonated and non-protonated forms of the molecules are given in Tables 5.4 and 5.5. Molecular electronic properties have been associated to the corrosion inhibitive efficiencies of various molecules [124-126]. Although not sufficient in most cases [125], these properties have been successfully used to predict the adsorption properties of inhibitor molecules on metallic surfaces. Frontier orbital distribution of the molecules showed that the highest occupied molecular orbital (HOMO) and the lowest un-occupied molecular orbitals (LUMO) orbitals are well distributed over the imidazole ring and the respective substituents. This shows the tendency of the molecules to donate charges to atoms of the

metal and show their propensity to serve as effective corrosion inhibitors. The HOMO-LUMO energy gap ( $\Delta E$ ) further revealed that moving down the halogen group the reactivity of the molecules towards inhibition of corrosion increases in agreement with their experimental corrosion inhibition efficiencies (Table 5.1). A similar result was obtained for 1-phenyl substituted molecules where the energy gap predicted 1-API to have greater tendency towards corrosion inhibition, which also corroborates the experimental data.

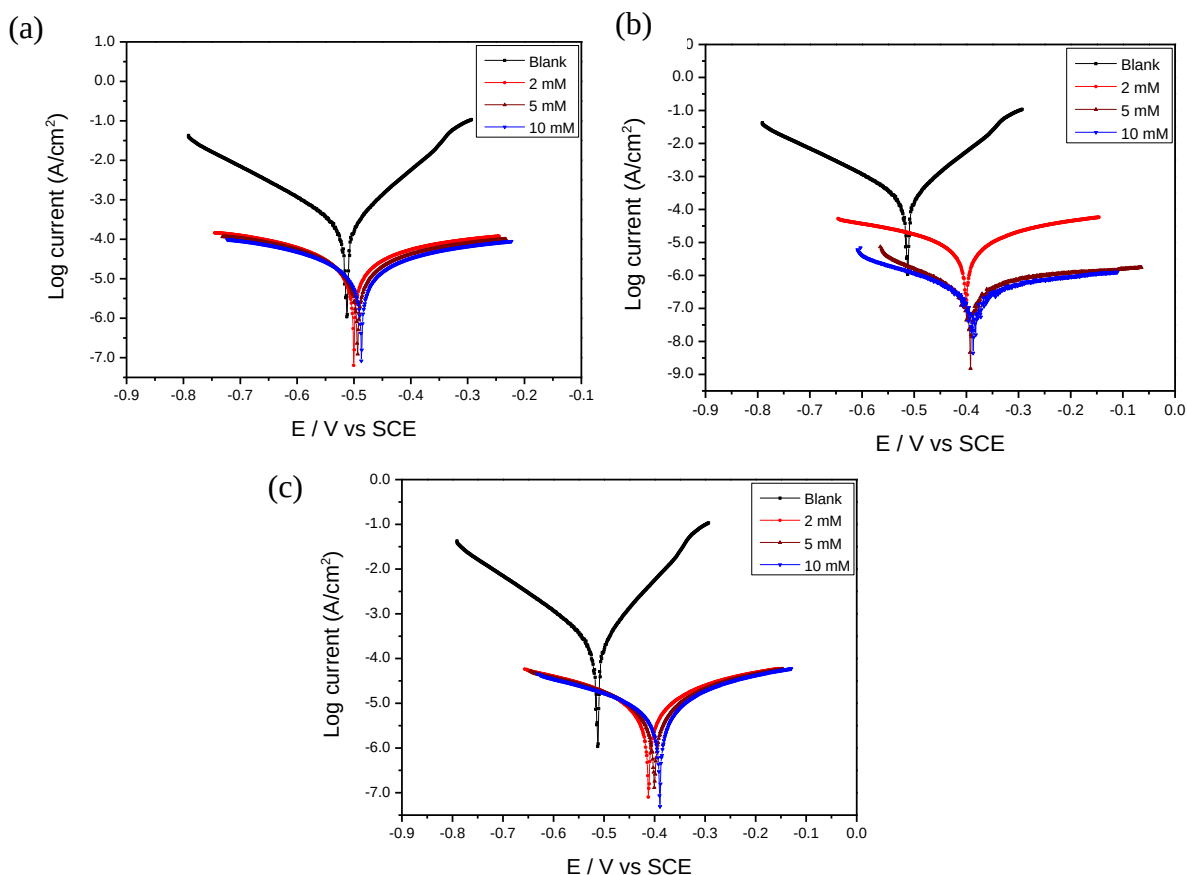


Figure 5.1 Tafel polarization curves of mild steel corrosion in 1.0 M HCl in the absence and presence of 2.0 – 10.0 mM concentrations of (a) 4-PI, (b) 4-FPI and (c) 4-CPI

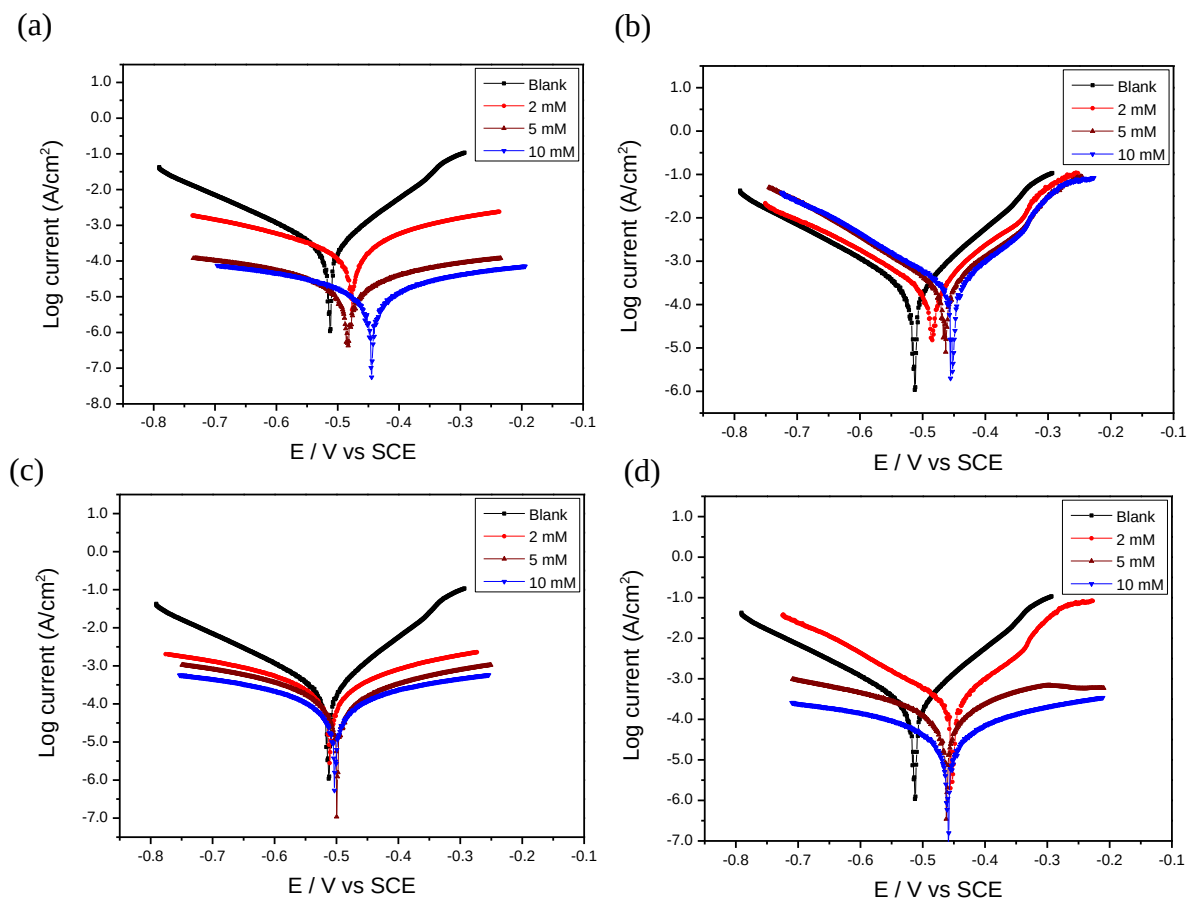


Figure 5.2 Tafel polarization curves of mild steel corrosion in 1.0 M HCl in the absence and presence of 2.0 – 10.0 mM concentrations of (a) 1-PI, (b) 1-MPI and (c) 1-HPI and (d) 1-API

Table 5.2 Tafel polarization data in 1.0 M HCl in the presence of 4-PI, 4-FPI and 4-CPI

| Medium | Inhibitor Conc. (mM) | $E_{\text{corr}} / \text{V vs SCE}$ | $i_{\text{corr}} (\mu\text{A.cm}^{-2})$ | Corrosion rate (mmpy) | $\theta$ | $\eta\%$ |
|--------|----------------------|-------------------------------------|-----------------------------------------|-----------------------|----------|----------|
| Blank  | 0                    | -0.512                              | 301.10                                  | 3.43                  | -        | -        |
| 4-PI   | 2.0                  | -0.501                              | 39.13                                   | 0.45                  | 0.87     | 87.0     |
|        | 5.0                  | -0.494                              | 33.12                                   | 0.37                  | 0.89     | 89.0     |
|        | 10.0                 | -0.487                              | 25.60                                   | 0.29                  | 0.91     | 91.5     |
| 4-FPI  | 2.0                  | -0.400                              | 33.12                                   | 0.37                  | 0.89     | 89.0     |
|        | 5.0                  | -0.392                              | 21.10                                   | 0.24                  | 0.93     | 92.9     |
|        | 10.0                 | -0.387                              | 19.57                                   | 0.22                  | 0.94     | 93.5     |
| 4-CPI  | 2.0                  | -0.412                              | 24.09                                   | 0.27                  | 0.92     | 91.9     |
|        | 5.0                  | -0.400                              | 18.66                                   | 0.21                  | 0.94     | 93.8     |
|        | 10.0                 | -0.390                              | 13.55                                   | 0.15                  | 0.95     | 95.5     |

Table 5.3 Tafel polarization data in 1.0 M HCl in the presence of 1-PI, 1-MPI, 1-HPI and 1-API

| Medium | Inhibitor Conc. (mM) | $E_{\text{corr}} / \text{V vs SCE}$ | $i_{\text{corr}} (\mu\text{A.cm}^{-2})$ | Corrosion rate (mmpy) | $\theta$ | $\eta\%$ |
|--------|----------------------|-------------------------------------|-----------------------------------------|-----------------------|----------|----------|
| Blank  | 0                    | -0.512                              | 301.10                                  | 3.43                  | -        | -        |
| 1-PI   | 2.0                  | -0.477                              | 45.14                                   | 0.52                  | 0.85     | 85.0     |
|        | 5.0                  | -0.484                              | 30.50                                   | 0.33                  | 0.89     | 89.9     |
|        | 10.0                 | -0.445                              | 24.09                                   | 0.27                  | 0.91     | 91.9     |
| 1-MPI  | 2.0                  | -0.485                              | 45.00                                   | 0.49                  | 0.85     | 85.0     |
|        | 5.0                  | -0.464                              | 21.00                                   | 0.24                  | 0.93     | 93.0     |
|        | 10.0                 | -0.454                              | 19.25                                   | 0.22                  | 0.93     | 93.6     |
| 1-HPI  | 2.0                  | -0.511                              | 49.10                                   | 0.57                  | 0.83     | 83.7     |
|        | 5.0                  | -0.500                              | 15.90                                   | 0.18                  | 0.94     | 94.7     |
|        | 10.0                 | -0.503                              | 15.65                                   | 0.18                  | 0.94     | 94.8     |
| 1-API  | 2.0                  | -0.454                              | 30.11                                   | 0.34                  | 0.90     | 90.0     |
|        | 5.0                  | -0.462                              | 22.05                                   | 0.26                  | 0.92     | 92.7     |
|        | 10.0                 | -0.459                              | 12.04                                   | 0.14                  | 0.96     | 96.0     |

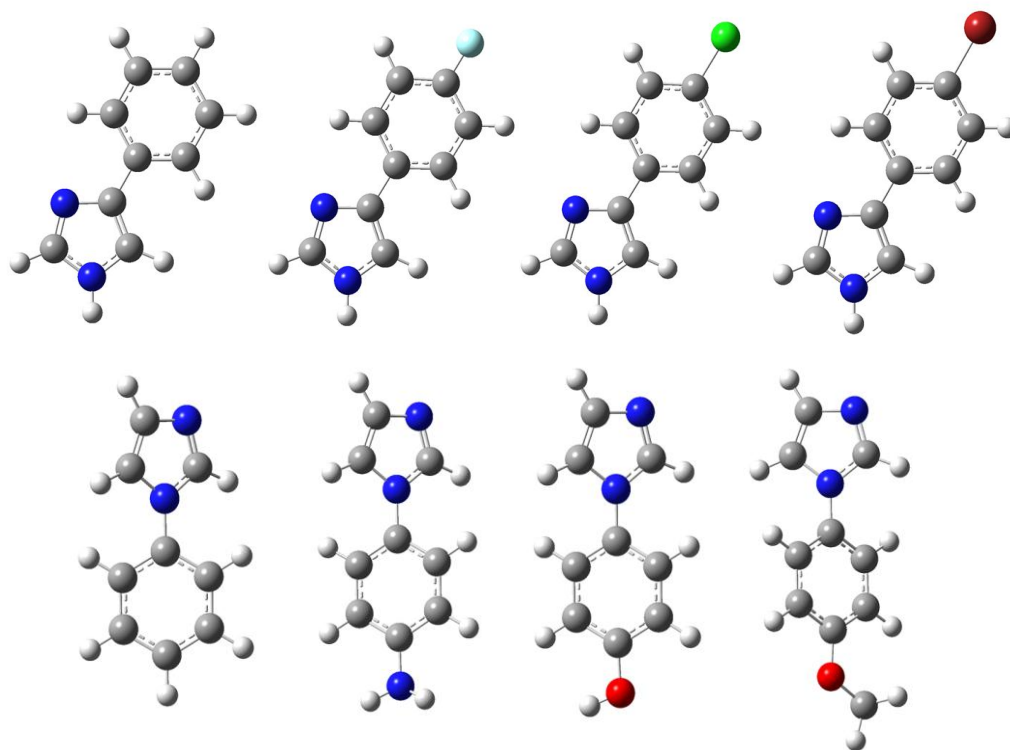


Figure 5.3 Optimized structures of inhibitor molecules at B3LYP/6-31G(d) level of theory

Table 5.4 Quantum chemical reactivity descriptors of 4-PI, 4-FPI, 4-CPI and 4-BPI

| Quantum Parameters     | Non-protonated molecules |        |        |        | Protonated molecules |        |        |        |
|------------------------|--------------------------|--------|--------|--------|----------------------|--------|--------|--------|
|                        | 4-PI                     | 4-BPI  | 4-CPI  | 4-FPI  | 4-PI                 | 4-BPI  | 4-CPI  | 4-FPI  |
| $E_{\text{HOMO}}$ (eV) | -5.596                   | -5.619 | -5.642 | -5.560 | -6.451               | -6.346 | -6.441 | -6.373 |
| $E_{\text{LUMO}}$ (eV) | -0.433                   | -0.648 | -0.639 | -0.375 | -1.077               | -1.343 | -1.262 | -1.037 |
| $\Delta E$ (eV)        | 5.163                    | 4.971  | 5.003  | 5.185  | 5.374                | 5.003  | 5.179  | 5.336  |
| $\chi$ (eV)            | 3.015                    | 3.134  | 3.140  | 2.967  | 3.764                | 3.845  | 3.852  | 3.705  |
| $\eta$ (eV)            | 2.581                    | 2.485  | 2.502  | 2.592  | 2.687                | 2.501  | 2.589  | 2.668  |
| $\omega$ (eV)          | 1.760                    | 1.976  | 1.971  | 1.698  | 2.636                | 2.954  | 2.865  | 2.572  |
| $\Delta N$             | 0.772                    | 0.778  | 0.771  | 0.778  | 0.602                | 0.631  | 0.608  | 0.617  |

Table 5.5 Quantum chemical reactivity descriptors of 1-PI, 1-MPI, 1-HPI and 1-API

| Quantum Parameters     | Non-protonated molecules |        |        |        | Protonated molecules |        |        |        |
|------------------------|--------------------------|--------|--------|--------|----------------------|--------|--------|--------|
|                        | 1-PI                     | 1-MPI  | 1-HPI  | 1-API  | 1-PI                 | 1-MPI  | 1-HPI  | 1-API  |
| $E_{\text{HOMO}}$ (eV) | -6.158                   | -5.825 | -5.850 | -5.402 | -6.996               | -6.248 | -6.303 | -5.688 |
| $E_{\text{LUMO}}$ (eV) | -0.461                   | -0.275 | -0.259 | -0.119 | -1.135               | -0.966 | -0.976 | -0.883 |
| $\Delta E$ (eV)        | 5.697                    | 5.550  | 5.592  | 5.283  | 5.860                | 5.282  | 5.328  | 4.805  |
| $\chi$ (eV)            | 3.310                    | 3.050  | 3.054  | 2.760  | 4.065                | 3.607  | 3.639  | 3.286  |
| $\eta$ (eV)            | 2.849                    | 2.775  | 2.796  | 2.641  | 2.930                | 2.641  | 2.664  | 2.402  |
| $\omega$ (eV)          | 1.923                    | 1.676  | 1.668  | 1.443  | 2.820                | 2.464  | 2.486  | 2.247  |
| $\Delta N$             | 0.648                    | 0.712  | 0.706  | 0.803  | 0.501                | 0.642  | 0.631  | 0.773  |

Other reactivity descriptors which include electronegativity ( $\chi$ ), electrophilicity ( $\omega$ ), hardness ( $\eta$ ) and fraction of transferred electrons ( $\Delta N$ ) were also calculated according to the DFT-Koopman's theorem relating the energy of highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) and lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ) as presented in Tables 5.4 & 5.5 [61].

Electronegativity ( $\chi$ ) expresses the electron attracting power of a molecule. According to Sanderson's principle of electronegativity equalization [67], interactions of inhibitor molecules with metal atoms occur such that electrons are transferred from the less electronegative inhibitor to the more electronegative metal atoms until equalization is achieved. Inhibitor molecules having high electronegativity attain rapid equalization with atoms of the metal and therefore display low corrosion inhibition efficiencies. This implies that for effective inhibition of corrosion, a molecule should possess minimal

electronegativity value. Electrophilicity index ( $\omega$ ) represents a measure of stabilization energy of a given system upon receiving electron [71]. It signifies the nucleophilicity or electrophilicity of a molecule as molecules having high  $\omega$  values are termed strong electrophiles. An inhibitor having low value of  $\omega$  would possess high propensity to accept back-donation of electrons from the atoms of the metal. Global hardness ( $\eta$ ), a measure of chemical reactivity of a molecule indicates the resistance of a molecule to electron density distortion. Molecules with high global hardness are usually less reactive and tend to adsorb less on the metal according to the hard-soft acid base (HSAB) theory [70]. Molecules with high global softness on the other hand are easily polarized and prone to acquire electronic charge. This in turn enhances their ability to adsorb on the metal surface, acting as corrosion inhibitors. The results of quantum chemical studies are in agreement with Tafel polarization data.

Furthermore, we carried out molecular level adsorption studies of the inhibitor molecules over the metal surface. Structural optimization of the molecules with  $\text{Fe}_4$  cluster was carried out on  $\text{Fe}_4$  cluster with a ground state distorted tetrahedron geometry and bond distances of 2.22 Å at the corners and 2.40 Å at the edges were conducted. The results (Fig. 5.4 and Fig. 5.5) revealed that the preferred mode of interactions between atoms of the metal and the inhibitor molecules was a parallel adsorption leading to formation of bonds  $\text{Fe-N}_{\text{benz}}$  and  $\text{Fe-C}_{\text{benz}}$  in the range 1.90 – 2.20 Å which falls within the range of chemisorption distances (2.83 – 3.0 Å) [75-77]. The order of interaction energies further corroborates the experimental data obtained from Tafel polarization measurements and shows the influence of aromaticity and substituent effects in enhancing the corrosion inhibitive properties of organic molecules.

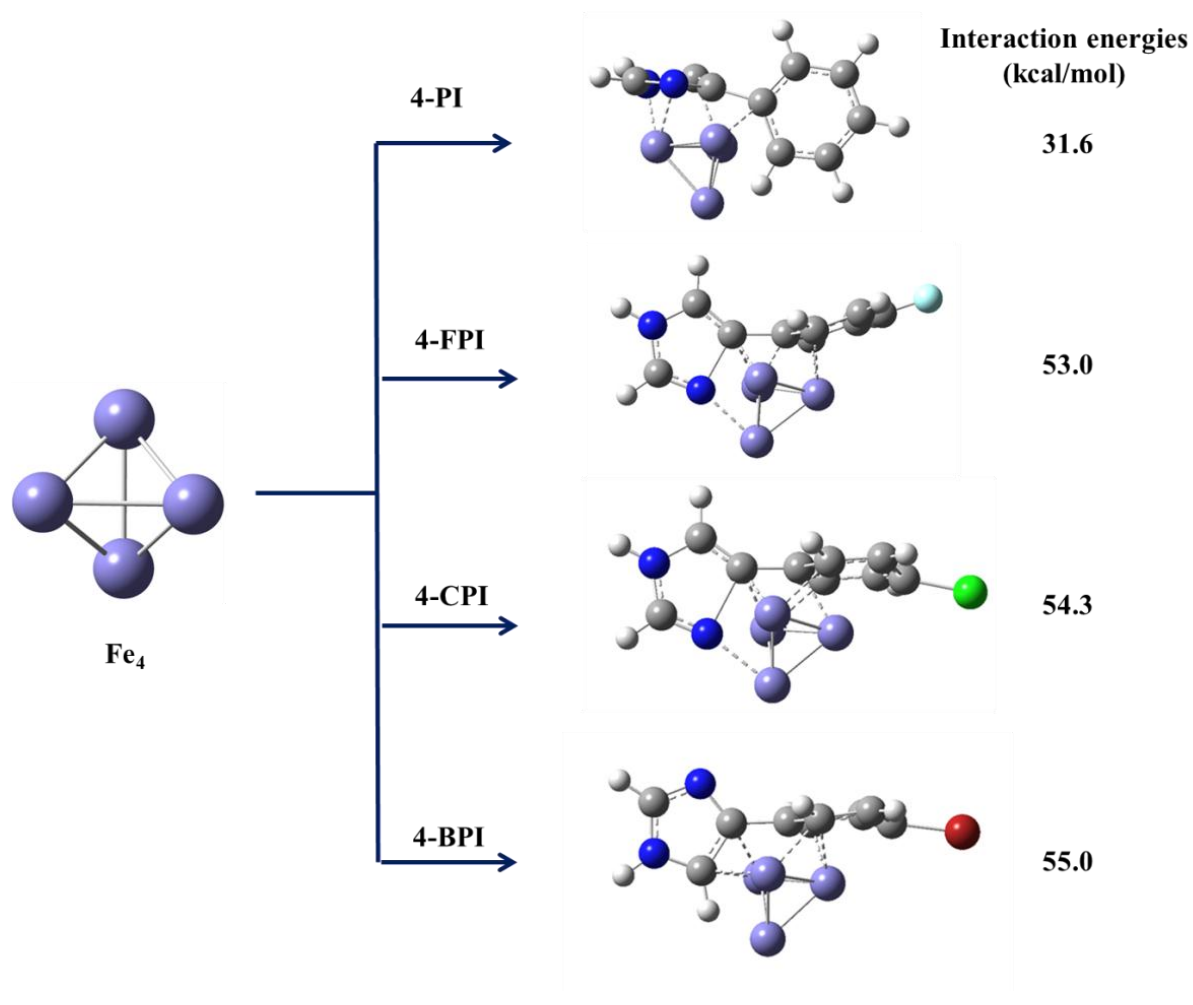


Figure 5.4 Molecular level interaction of Fe<sub>4</sub> cluster and 4-PI, 4-FPI, 4-CPI and 4-BPI

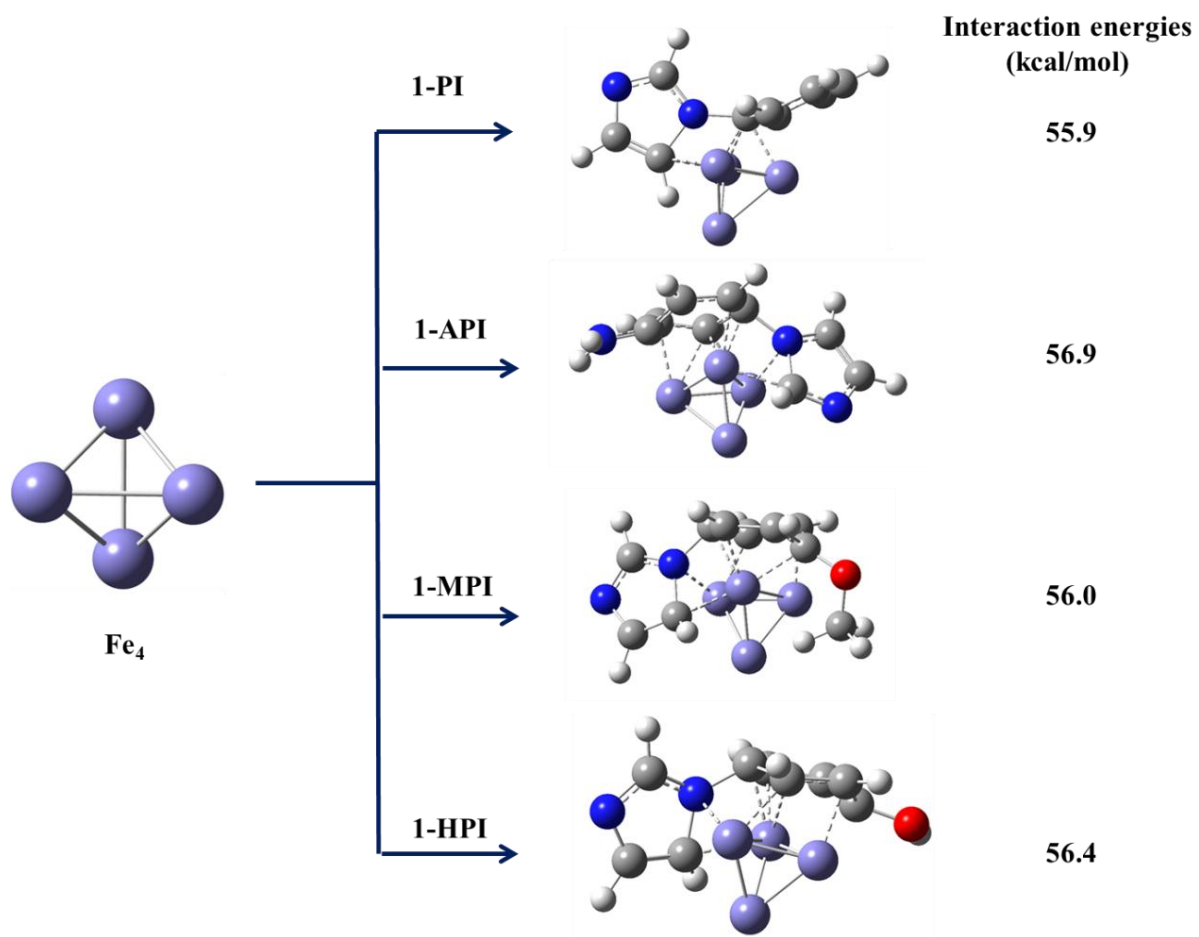


Figure 5.5 Molecular level interaction of Fe<sub>4</sub> cluster and 1-PI, 1-API, 1-MPI and 1-HPI

## 5.4 Summary

The role of phenyl substituents and influence of electron-releasing and electron-withdrawing substituents on the corrosion inhibitive properties of imidazole was successfully investigated using quantum chemical DFT calculations, supported with Tafel polarization measurements. Results of molecular level interaction studies predicted the adsorption of the molecules on the surface of iron to take place through chemisorption mechanism, yielding Fe-N and Fe-C bonds in the range 1.90 – 2.20 Å. Electrochemical corrosion measurements revealed that the inhibition efficiency of the molecules with increasing concentration due to increase in surface coverage, in agreement with DFT calculations. An overall corrosion inhibition efficiencies of 95.5% and 96.0% were recorded for 4-(4-chlorophenyl)imidazole, 4-CPI and 4-(1H-imidazol-1-yl)aniline, 1-API, respectively. This study therefore demonstrates the role of phenyl substituents in enhancing the corrosion inhibitive properties of organic molecules.

## CHAPTER 6

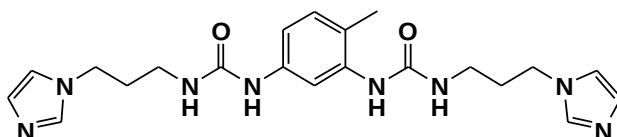
### NEW IMIDAZOLE DIMERS AS INHIBITORS OF MILD STEEL CORROSION IN ACID MEDIA

#### 6.1 A brief overview

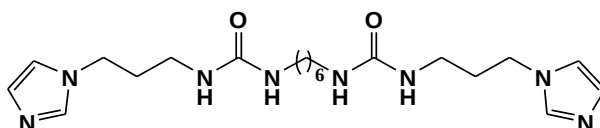
Imidazole derivatives have received greater attention in corrosion inhibition in recent years due to their non-toxicity, environmental friendliness as well as excellent water and oil solubility [29, 31, 46]. The presence of quaternary N atoms and aromatic character in these molecules significantly enhances their adsorption capabilities through charge donation, leading to formation of stable protective layers which prevents metals from corrosion attack. In the present study, we report the synthesis of two new imidazole derivatives namely: 1,1'-(4-methyl-1,3-phenylene)bis(3-(3-(1*H*-imidazol-1-yl)propyl)urea (PIP), and 1,1'-(hexane-1,6-diyl)bis(3-(3-(1*H*-imidazol-1-yl)propyl)urea) (HIP), and their corrosion inhibitive performance in 1.0 M HCl. Tafel polarization measurements suggests that PIP performed excellently acting as mixed-type corrosion inhibitor. EIS measurements showed a significant decrease in  $C_{dl}$  due to a decrease in dielectric constant between the metal and the electrolyte caused by adsorption of the inhibitors. Results of surface characterization using SEM and AFM, supported with DFT calculations confirm the adsorption of the inhibitors on the metal surface blocking the active corrosion sites, resulting with an overall inhibition efficiency of 98% at PIP concentration of 100 ppm.

## 6.2 Experimental

All chemicals utilized were of standard purity and were used without further purifications. PIP was synthesized by nucleophilic addition of 1-(3-aminopropyl)imidazole, 3-AP (1.25 g, 10 mmol) and toluene-2,4-diisocyanate, TDI (0.90 g, 5 mmol) in a round-bottomed flask containing 20 ml of acetonitrile at 60 °C for 6 h. At the end of 6 h, the product was filtered, washed in acetone and dried in a vacuum oven at 70 °C. Similar procedure was used to synthesize HIP substituting TDI with hexamethylene diisocyanate, HMDI (0.84 g, 5 mmol). Molecular structures of the new dimers are presented in Fig. 6.1.



1,1'-(4-methyl-1,3-phenylene)bis(3-(3-(1*H*-imidazol-1-yl)propyl)urea (PIP)



1,1'-(hexane-1,6-diyl)bis(3-(3-(1*H*-imidazol-1-yl)propyl)urea) (HIP)

Figure 6.1 Molecular structures of PIP and HIP imidazole dimers

### 6.2.1 Electrochemical measurements

Electrochemical experiments were conducted in a three-electrode Gamry electrochemical cell. Mild steel, AISI 1018 was used as the sample specimen, saturated calomel electrode and carbon graphite as the reference and auxiliary electrodes, respectively. Gamry potentiostat/galvanostat/ZRA (Reference 600) equipped with a Gamry framework interface was used for electrochemical studies. A stabilization period of 60 min was allowed for mild steel specimen in the electrolyte solution (1 M HCl) prior to all electrochemical measurements. Polarization curves were obtained by scanning the potential at 0.5 mV/s in the range +250 mV to -250 mV against the open circuit potential ( $E_{ocp}$ ). EIS measurements were performed at open circuit potential ( $E_{ocp}$  vs SCE) in the frequency range 100 KHz to 100 mHz, with an amplitude of perturbation 10 mV r.m.s. Inhibition efficiencies were calculated using equations (6.1) and (6.2), as follows:

$$\eta (\%) = \left( \frac{i_{corr}^{\circ} - i_{corr}}{i_{corr}^{\circ}} \right) \times 100 \quad (6.1)$$

where  $i_{corr}^{\circ}$  and  $i_{corr}$  are corrosion current density values in the absence and presence of the inhibitor obtained from Tafel polarization measurements, respectively, and

$$\eta (\%) = \left( \frac{R_p - R_p^{\circ}}{R_{ct}} \right) \times 100 \quad (6.2)$$

where  $R_p$  and  $R_p^{\circ}$  are the resistances to polarization in the presence and absence of the inhibitor as obtained from EIS measurements, respectively.

### 6.2.2 Surface characterization

SEM and AFM analysis were conducted on specimen with dimensions 1 cm x 1 cm x 0.2 cm. Specimen were immersed in 50 ml of 1.0 M HCl with and without the inhibitors for 24 h, rinsed with anhydrous ethanol and ultra-pure water and dried at room temperature. SEM micrographs were recorded using Genesis-2120 high performance scanning electron microscope equipped with energy-dispersive X-ray spectroscopy (EDX) detector. AFM was carried out on Agilent 5100 SPM system, interfaced with a controller PicoScan (Agilent Technologies, Tempe AZ, USA) and images were analyzed using WxSM ver5.1 software.

### 6.2.3 Quantum chemical DFT studies

Full geometry optimizations of the inhibitors were conducted on Gaussian 09 package, using the hybrid-functional, B3LYP and the 6-31G(d) basis set. Electronic reactivity descriptors such as global hardness ( $\eta$ ), electronegativity ( $\chi$ ), electrophilicity ( $\omega$ ) and fraction of transferred electrons during metal-inhibitor interactions ( $\Delta N$ ) were estimated following the DFT-Koopman's theorem relating the energy of highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) and lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ) of the molecules [25].

## 6.3 Results and discussion

### 6.3.1 Characterizations of PIP and HIP

$^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ) spectrum of PIP gave resonance peaks at  $\delta$  2.0 (m, 4H),  $\delta$  3.0 (t, 4H) and  $\delta$  3.9 (t, 4H) corresponding to methylene protons in 3-AP, in addition to the peak at  $\delta$  2.2 (s, 3H) representing methyl protons of TDI. The disappearance of the peak at  $\delta$  1.7 corresponding to primary amine protons ( $-\text{NH}_2$ ) in 3-AP and the subsequent appearance of a peak at  $\delta$  6.1 ppm corresponding to secondary amine ( $-\text{NH}$ ) protons confirms the formation of PIP. Others are resonance peaks at  $\delta$  6.9 (s, 2H),  $\delta$  7.2 (s, 2H),  $\delta$  7.6 (s, 2H) corresponding to imidazole protons while peaks at  $\delta$  7.5 (s, 1H),  $\delta$  7.7 (s, 1H) and  $\delta$  8.5 (s, 1H) represents aromatic protons.  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ ) of PIP gave peaks at  $\delta$  17.0,  $\delta$  32.5,  $\delta$  37.0 and  $\delta$  43.0 ppm representing the methyl carbon ( $-\text{CH}_3$ ) of TDI, and the methylene ( $-\text{CH}_2$ ) carbons of 3-AP, respectively. Aromatic carbons appeared in the range  $\delta$  100 – 140 ppm, while carbon atom of the urea carbonyl group ( $\text{C}=\text{O}$ ) appeared at  $\delta$  155 ppm. Similarly, HIP was characterized using  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR and all peaks were assigned accordingly.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of monomer (API) and both dimers (PIP and HIP) are presented in Fig. 6.2 & 6.3.

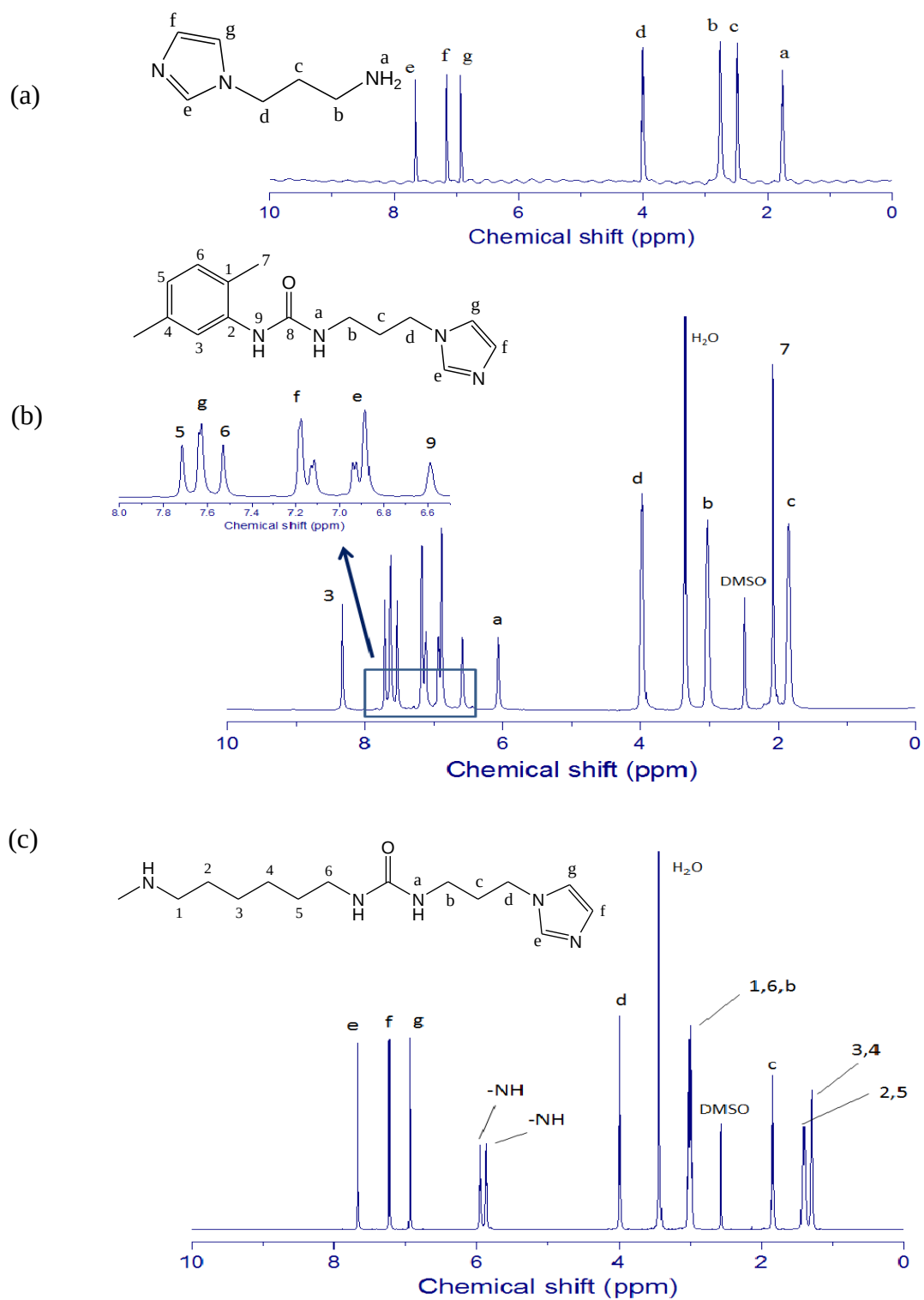


Figure 6.2  $^1\text{H}$  NMR spectra of (a) API, (b) PIP and (c) HIP

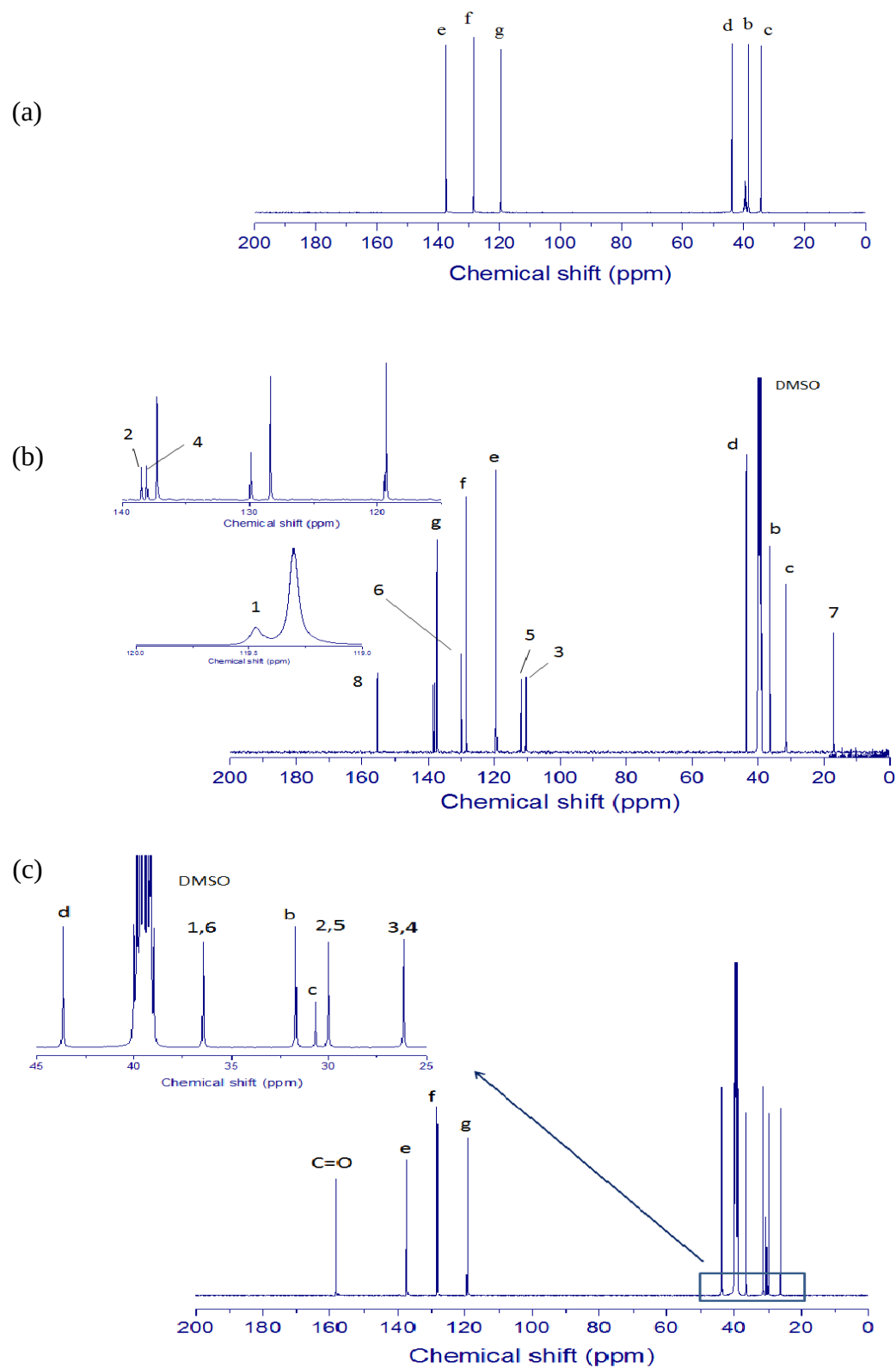


Figure 6.3  $^{13}\text{C}$  NMR spectra of (a) API, (b) PIP and (c) HIP

### 6.3.2 DFT results

As predicted from the molecular orbital theory, the effectiveness of interaction between two reacting molecules is dependent on the their frontier orbitals (HOMO/LUMO) distribution and the energy gap maintained within [65]. Frontier orbital analysis of the inhibitors (Fig. 6.4) showed that the HOMO and LUMO are well distributed over the  $\pi$  system in PIP and the imidazole fragment in HIP. These indicate the tendency of the molecules to donate charges from the electron-rich centers into un-occupied d-orbitals of the metal and their tendency to accept electron back-donation. The HOMO/LUMO energy gap (values in parenthesis represents protonated molecules) further revealed that PIP having the lowest energy gap will have the greater propensity to donate charges and is predicted as a superior inhibitor than HIP. Other reactivity descriptors (Table 6.1) such as global hardness ( $\eta$ ) which expresses the tendency of a molecule to donate its non-bonding electrons during interaction with another; electronegativity ( $\chi$ ) which expresses the electron attracting power of a molecule; electrophilicity index ( $\omega$ ) which expresses the stabilization energy of a molecule upon receiving charges and fraction of transferred electrons during metal-inhibitor interactions ( $\Delta N$ ) all predicted PIP having values:  $\eta$ , 2.57 eV;  $\chi$ , 3.08 eV;  $\omega$ , 1.85 eV and  $\Delta N$ , 0.76 as having better tendency to serve as effective corrosion inhibitor compared to HIP having values:  $\eta$ , 2.92 eV;  $\chi$ , 3.43 eV;  $\omega$ , 2.01 eV and  $\Delta N$ , 0.61.

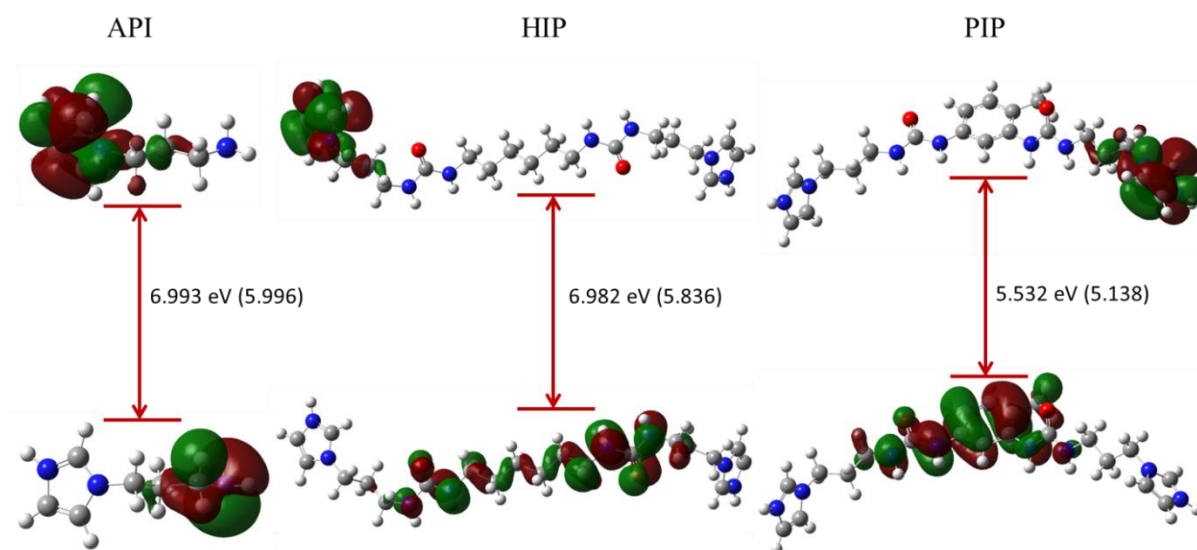


Figure 6.4 Frontier orbital distribution of API, HIP and PIP

Table 6.1 Quantum chemical reactivity descriptors of API, HIP and PIP

| Non-protonated |                        |                        |                 |             |             |               |            |
|----------------|------------------------|------------------------|-----------------|-------------|-------------|---------------|------------|
| Molecule       | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $\Delta E$ (eV) | $\chi$ (eV) | $\eta$ (eV) | $\omega$ (eV) | $\Delta N$ |
| API            | -6.07                  | 0.92                   | 6.99            | 2.57        | 3.50        | 0.95          | 0.63       |
| HIP            | -6.09                  | 0.90                   | 6.98            | 2.59        | 3.49        | 0.96          | 0.63       |
| PIP            | -5.62                  | -0.90                  | 5.53            | 2.85        | 2.76        | 1.47          | 0.75       |
| Protonated     |                        |                        |                 |             |             |               |            |
| Molecule       | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $\Delta E$ (eV) | $\chi$ (eV) | $\eta$ (eV) | $\omega$ (eV) | $\Delta N$ |
| API            | -6.47                  | -0.47                  | 5.60            | 3.47        | 3.00        | 2.01          | 0.59       |
| HIP            | -6.34                  | -0.51                  | 5.84            | 3.43        | 2.92        | 2.01          | 0.61       |
| PIP            | -5.65                  | -0.52                  | 5.14            | 3.08        | 2.57        | 1.85          | 0.76       |

### 6.3.3 Electrochemical corrosion tests

Potentiodynamic polarization measurements were conducted on mild steel specimen in 1.0 M HCl in the absence and presence of PIP and HIP (20 – 100 ppm). The resulting Tafel polarization curves for PIP are presented in Fig. 6.5a, while the extrapolated data are given in Table 6.2. In the absence of the inhibitors, mild steel specimen corroded severely in the acid medium resulting with high anodic ( $\beta_a$ ) and cathodic ( $\beta_c$ ) Tafel slopes, high corrosion current ( $i_{\text{corr}}$ ) and consequently high corrosion rate. In the presence of PIP however, a large suppression in anodic and cathodic reactions was observed with a significant decrease in  $i_{\text{corr}}$  value from 301  $\mu\text{A}/\text{cm}^2$  to 19.0  $\mu\text{A}/\text{cm}^2$  at 20 ppm PIP. In addition, a corresponding shift in corrosion potential ( $E_{\text{corr}}$ ) was observed with an increase in PIP concentration which suggests that the inhibitor acts by adsorbing onto the metal surface and blocking the active corrosion sites. The magnitude of the shift in  $E_{\text{corr}}$  was less than 85 mV, indicating that the inhibitor exhibits mixed-type behavior simultaneously impeding both anodic and cathodic processes [127]. The decrease in  $i_{\text{corr}}$  with an increase in PIP concentration therefore implies an increase in surface coverage by the adsorbed inhibitor molecules forming a protective layer which isolates the metal from acid solution. An overall inhibition efficiency of 99% was recorded at PIP concentration of 100 ppm, while an efficiency of 94% was recorded for HIP.

EIS measurement (Fig. 6.5b) further suggests the adsorption of the inhibitors onto mild steel with a significant decrease in double layer capacitance,  $C_{\text{dl}}$  (Table 6.2) due to a decrease in local dielectric constant between the metal and the electrolyte caused by adsorption of the inhibitors [127]. A single depressed capacitive loop was observed in the Nyquist plot due to surface heterogeneity caused by the adsorbed molecules.

Furthermore, an increase in diameter of the semi-circles with an increase in concentration of PIP was observed as a result of increasing surface coverage, resulting with large resistance to polarization,  $R_p$  and an efficiency of 96% at 100 ppm PIP (95% for HIP).

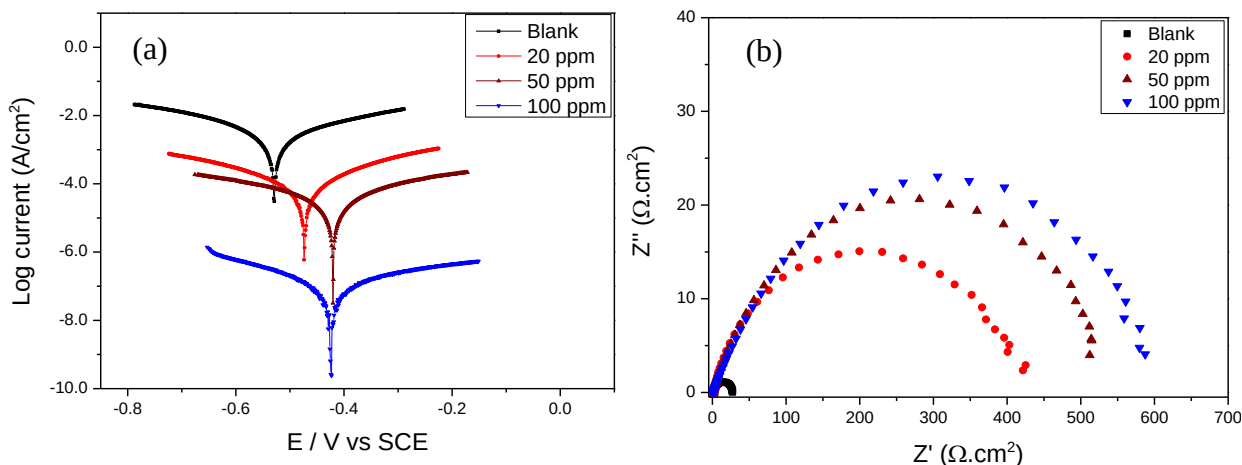


Figure 6.5 Tafel polarization curves and (b) Nyquist plots for mild steel corrosion in 1.0 M HCl in the absence and presence of 20 – 100 ppm of PIP

### 6.3.4 Surface characterization results

SEM micrographs and AFM 3D images of specimen immersed in 1.0 M HCl in the absence and presence of 100 ppm PIP are shown in Fig. 6.6. Compared to the inhibited medium, the specimen immersed in 1.0 M HCl showed evidence of pitting corrosion (Fig. 6.6a) which was minimized in the inhibited specimen (Fig. 6.6b). Furthermore, topography of specimen immersed in 1.0 M HCl (Fig. 6.6c) showed the presence of large peaks and valleys with an average roughness of  $\sim 400$  nm, compared to the inhibited

specimen (Fig. 6.6d) which shows a remarkable decrease in roughness  $\sim 120$  nm, confirming the adsorption of the inhibitor molecules which forms a protective layer that shields the metal from corrosion attack.

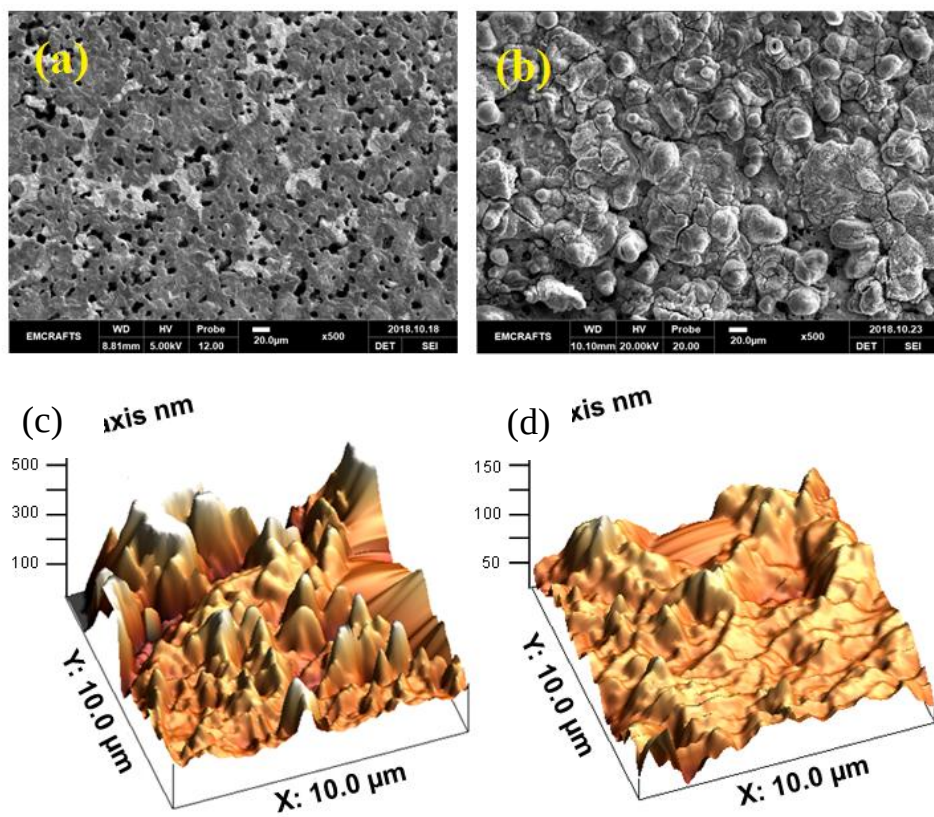


Figure 6.6 SEM micrographs (a & b) and AFM images (c & d) of specimen mild steel specimen immersed in 1.0 M HCl in the absence and presence of 100 ppm PIP for 24 h

Table 6.2 Tafel polarization and EIS data of mild steel corrosion in the presence of PIP

| <b>Tafel polarization data</b> |                       |                                |                                |                                           |                                                 |                           |          |
|--------------------------------|-----------------------|--------------------------------|--------------------------------|-------------------------------------------|-------------------------------------------------|---------------------------|----------|
| Medium                         | Inhibitor conc. (ppm) | $E_{\text{corr}}$ (V vs SCE)   | $\beta_a$ (V/dec)              | $-\beta_c$ (V/dec)                        | $i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ ) | Corr. rate (mmpy)         | $\eta\%$ |
| Blank                          | 0                     | -0.52                          | 0.42                           | 0.25                                      | 301                                             | 3.43                      | -        |
| PIP                            | 20                    | -0.47                          | 0.06                           | 0.07                                      | 19.0                                            | 0.22                      | 93.7     |
|                                | 50                    | -0.42                          | 0.05                           | 0.05                                      | 6.15                                            | 0.07                      | 97.9     |
|                                | 100                   | -0.42                          | 0.02                           | 0.01                                      | 0.67                                            | 0.01                      | 99.8     |
| <b>EIS data</b>                |                       |                                |                                |                                           |                                                 |                           |          |
| Medium                         | Inhibitor conc. (ppm) | $R_s$ ( $\Omega.\text{cm}^2$ ) | $R_p$ ( $\Omega.\text{cm}^2$ ) | $C_{\text{dl}}$ ( $\mu\text{F cm}^{-2}$ ) | n                                               | $\chi^2 (\times 10^{-4})$ | $\eta\%$ |
| Blank                          | 0                     | 1.81                           | 25.8                           | 123                                       | 0.9                                             | 3.0                       | -        |
| PIP                            | 20                    | 1.48                           | 421                            | 18.9                                      | 0.9                                             | 4.2                       | 93.8     |
|                                | 50                    | 1.42                           | 539                            | 19.6                                      | 0.8                                             | 4.4                       | 95.2     |
|                                | 100                   | 1.45                           | 610                            | 17.3                                      | 0.8                                             | 4.3                       | 96.0     |

## 6.4 Summary

Two newly synthesized imidazole derivatives, PIP and HIP were successfully evaluated as inhibitors of mild steel corrosion in 1.0 M HCl. DFT studies predicted PIP having frontier orbital distribution across the  $\pi$  system as having better tendency to serve as effective corrosion inhibitor. Tafel polarization and EIS measurements supported with surface characterization using SEM and AFM revealed that the inhibitors exhibit mixed-type behaviors, adsorbing on the metal surface to form a protective layer which shields the metal from corrosion attack. Overall an inhibition efficiency of 98% was achieved at PIP concentration of 100 ppm.

## **CHAPTER 7**

# **EXPERIMENTAL AND THEORETICAL EVALUATION OF THE CORROSION INHIBITION OF MILD STEEL IN AQUEOUS MEDIA BY NEW POLYUREA-BASED MATERIALS**

### **7.1 A brief overview**

Polyurea protective coatings have received considerable attention in recent years due to their high thermal and chemical resistance, water proofing properties, abrasion resistance and structural diversity. A major challenge in the application of these coatings especially in the industries is the cost involved, because it requires shutting down production facilities or prior to installation of the pipes. Moreover, it is practically impossible to coat the pipeline when it is already corroded and filled with petroleum products. Therefore, one of the best mitigation strategies is to design corrosion inhibitors that are soluble in aqueous medium and can be injected continuously into the flow streams to serve as protective barriers against the corrosive medium. In the present study, we report the corrosion inhibitive performance of two newly synthesized polyurea materials (PUCorr-1 and PUCorr-2) in acid and saline media using electrochemical, spectroscopic and DFT methods. Electrochemical studies supported with quantum chemical DFT calculations and surface characterization revealed that PUCorr-1 and PUCorr-2 adsorbs onto mild steel through a chemisorption mechanism yielding stable protective films. Corrosion resistance of mild steel in the presence of PUCorr-1 was observed to increase with

increasing temperature and inhibitor concentrations reaching an optimum efficiency of 99.9% at elevated temperature for both polymers. In the presence of CO<sub>2</sub> and H<sub>2</sub>S gases, PuCorr-1 exhibited excellent performance (> 94% efficiency) with current densities of 14.20  $\mu\text{A}/\text{cm}^2$  and 1.96  $\mu\text{A}/\text{cm}^2$ , respectively, while PUCorr-2 exhibited efficiency of 99% in CO<sub>2</sub> medium, making both polymers potential corrosion inhibitors in industrial processes CO<sub>2</sub> gas.

## **7.2 Materials and methods**

### **7.2.1 Synthesis of PUCorr-1 and PUCorr-2**

All chemicals utilized in this study were of standard purity and were used without further purifications. Toluene diisocyanate (TDI, a mixture of 2,4- (80%) and 2,6- (20%) – isomers used in the synthesis of PUCorr-1) was supplied by Fluka, 1,4-diaminobutane, DAB (Alfa Aesar), acetonitrile (Merck), hydrochloric acid, sodium sulfide, sodium chloride and glacial acetic acid (Fisher Scientific) and N-methyl-2-pyrrolidone (Riedel – de Haen). Others are toluene diisocyanate (TDI, 95% used in the synthesis of PUCorr-2), and piperazine (PPZ, 99%), (Sigma Aldrich). To enhance the dispersion of the polymers in the electrolyte solutions, N-methyl-2-pyrrolidone was added (100:1 v/v) in both blank solutions and solutions containing the inhibitor materials.

PUCorr-1 was synthesized according to the following procedure (scheme 7.1) [128]; Diaminobutane, DAB (0.88 g, 10 mmol), was added to 20 ml acetonitrile in a three-necked round bottomed flask and immersed in an oil bath at 60 °C until it dissolved completely. Thereafter, toluene diisocyanate, TDI (0.90 g, 5 mmol), was added-drop wise while stirring at 600 rpm, and the polymerization was allowed to continue for 6 h. At the

end of 6 h, the product was filtered, washed in acetone and dried up in a vacuum oven at 70 °C until a constant mass was reached. The resulting powder weighed 1.70 g (96% yield). FTIR; 3350 cm<sup>-1</sup> (s, NH stretch), 3000 cm<sup>-1</sup> (m, CH stretch), 1650 cm<sup>-1</sup> (s, C=O stretch), 1550 cm<sup>-1</sup> (s, NH bend), 1230 cm<sup>-1</sup> (s, CN bend), 700 cm<sup>-1</sup> (w, NH wag). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>); δ 1.3 (m, 2H, CH<sub>2</sub>), δ 2.1 (m, 2H, CH<sub>2</sub>), δ 3.1 (s, 3H, CH<sub>3</sub>), δ 6.0 (s, 1H, NH) and δ 6.3 – 8.5 (m, 3H, Ar-H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>); δ 12.50 and 18.5 (CH<sub>3</sub>), δ 28.0 and 32.0 (CH<sub>2</sub>), δ 110.8 – 138.5 (Ar-C) and δ 158.0 (C=O). Elemental analysis (EDX); C: 55.65 wt%, N: 22.81 wt% and O: 17.53 wt%.

A similar procedure was adopted for the synthesis of PUCorr-2 with PPZ in place of DAB (scheme 7.2). The resulting powder weighed 1.72 g (98% yields). FTIR; 3350 cm<sup>-1</sup> (s, NH stretch), 3000 cm<sup>-1</sup> (m, CH stretch), 1680 cm<sup>-1</sup> (vs, C=O stretch), 1550 cm<sup>-1</sup> (vs, NH bend, or C=C stretch), 1400 cm<sup>-1</sup> (vs, sp<sup>3</sup> CH bend), 1230 cm<sup>-1</sup> (vs, CN stretch), 950 cm<sup>-1</sup> (s, sp<sup>3</sup> C-C stretch), 650 cm<sup>-1</sup> (w, NH wag). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>); δ 1.9 (s, 1H, terminal NH), δ 2.1 (t, 4H, 2CH<sub>2</sub>), δ 2.2 (s, 3H, CH<sub>3</sub>), δ 2.7 (t, 4H, 2CH<sub>2</sub>), δ 7.0 – 7.5 (m, 3H, Ar-H) and δ 8.0 – 8.5 (s, 1H, each of urea NH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>); δ 18.0 (CH<sub>3</sub>), δ 44.0 and 46.0 (CH<sub>2</sub>), δ 115.0 – 140.0 (Ar-C) and δ 156.0 (C=O). Elemental analysis (EDX); C: 54.34 wt%, N: 27.92 wt% and O: 17.74 wt%.

### 7.2.2 Electrochemical measurements

Electrochemical measurements were conducted in a jacketed electrochemical cell kit with three-electrode compartments (Gamry). Mild steel bar AISI 1018 with the following compositions; C, 0.15 – 0.20%; Mn, 0.60 – 0.90%; P, 0.04%; S, 0.05% and balance Fe was used as the sample specimen, saturated calomel electrode (SCE) and carbon graphite

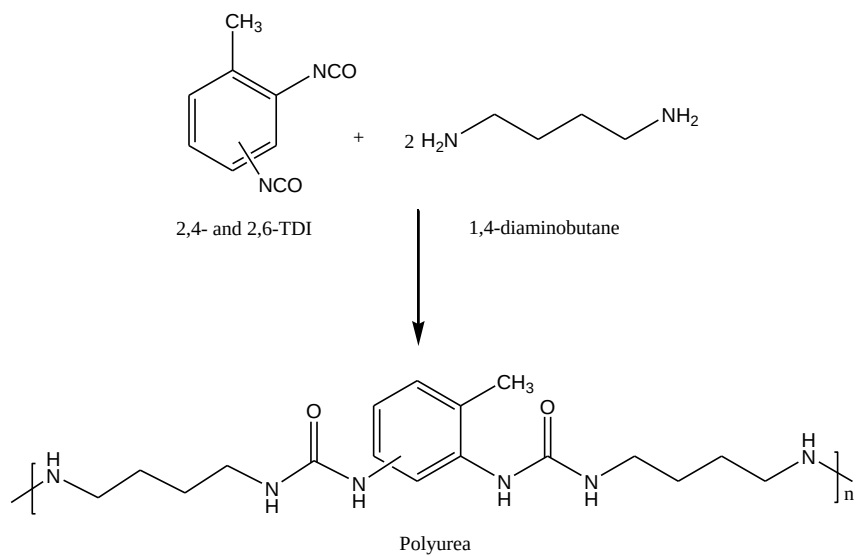
as the reference and counter electrodes, respectively. Gamry potentiostat/galvanostat/ZRA (Reference 600) equipped with a Gamry framework interface was used for electrochemical studies. Gamry Echem Analyst version 6.03 was used for data analysis and fittings. All measurements were carried out in triplicate and the average reported. Polarization curves were obtained by scanning the potential at 0.5 mV/s in the range +250 mV to -250 mV against the open circuit potential ( $E_{ocp}$ ). Electrochemical impedance spectroscopy measurements (EIS) were carried out to understand the characteristics of the electrochemical processes occurring at the steel/solution interface in the presence of the inhibitor molecule. EIS measurements were performed at an open circuit potential ( $E_{ocp}$  vs SCE) in the frequency range 100 KHz to 100 mHz, with an amplitude of perturbation 10 mV r.m.s. Inhibition efficiencies were calculated using equations (1) and (2), as follows:

$$\eta (\%) = \left( \frac{i_{corr}^{\circ} - i_{corr}}{i_{corr}^{\circ}} \right) \times 100 \quad (7.1)$$

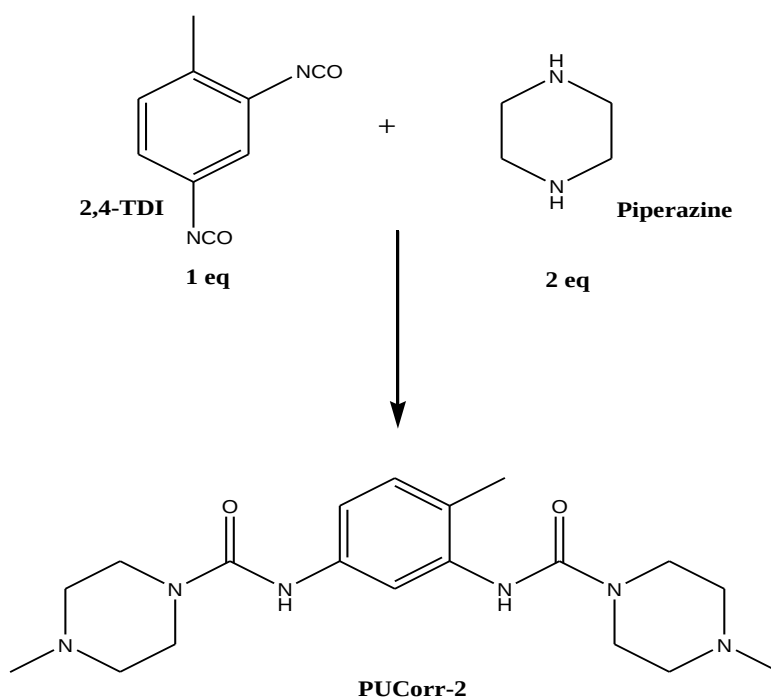
where  $i_{corr}^{\circ}$  and  $i_{corr}$  are corrosion current density values in the absence and presence of the inhibitor obtained from Tafel polarization measurements, respectively, and

$$\eta (\%) = \left( \frac{R_{ct} - R_{ct}^{\circ}}{R_{ct}} \right) \times 100 \quad (7.2)$$

where  $R_{ct}$  and  $R_{ct}^{\circ}$  are the charge transfer resistances in the presence and absence of the inhibitor as obtained from EIS measurements, respectively.



Scheme 7.1 Synthesis of PUCorr-1



Scheme 7.2 Synthesis of PUCorr-2

### 7.2.3 DFT procedure

Full geometry optimization of PUCorr-2 was performed on Gaussian 09 package [64], using the hybrid-functional of the Becke three-parameters, Lee, Yang and Par (B3LYP) and the 6-31G(d) basis set. Structural geometry optimizations of the various forms of the polymer were carried out to the minima on potential energy surfaces without imposing any constraints. Their relative stabilities and the total energies of the natural bonding orbitals were also computed. Reactivity descriptors such as global hardness ( $\eta$ ), electron affinity (A), ionization potential (I), electronegativity ( $\chi$ ), and fraction of transferred electrons ( $\Delta N$ ) were calculated. To check possible local reactivity sites on the molecules, condensed Fukui functions were calculated using the UCA-FUKUI v.1.0 software via the finite difference approximation method which provides good correlation with the frontier molecular orbital method [129].

## 7.3 Results and discussion

### 7.3.1 Characterization of PUCorr-1 and PUCorr-2

To check the successful synthesis and level of purity of the polymers,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR techniques were utilized. Similar tests were conducted on the monomers and the results for PUCorr-1 are presented in Figs. 7.1 & 7.2. Similar tests were conducted on PUCorr-2 and its monomers and the results are presented in Figs. 7.3 & 7.4. Detailed peak assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of PUCorr-1 are as follows:

From Fig. 7.1a, 1,4-diaminobutane is expected to have two resonance peaks in the  $^{13}\text{C}$  NMR which were both present at chemical shifts 30.98 ppm and 41.76 ppm

corresponding to the carbon atoms labeled as 1'' and 2'' respectively. In the case of TDI it consist of two isomers, 2,4- and 2,6- hence the observed multiple resonance peaks. Assignment of  $^{13}\text{C}$  NMR resonance peaks followed an already reported procedure[130] and are labeled as shown in Fig. 1a. In the case of PUCorr-1 (Fig. 7.1b), it can be seen that peaks assigned to carbon atoms attached to  $-\text{NCO}$  of TDI ( $\text{C}_2$ ,  $\text{C}_{2'}$ ,  $\text{C}_4$  and  $\text{C}_{6'}$ ) at 132.55 ppm and 132.83 ppm all disappeared in PUCorr-1 spectrum. Furthermore, peaks assigned to  $-\text{NCO}$  carbons ( $\text{C}_8$ ,  $\text{C}_9$  and  $\text{C}_{8'}$ ) at 131.30 ppm and 124.20 ppm were also absent. New peaks appeared at 155.27 ppm which have been assigned to characteristic resonances of carbonyl linkage ( $\text{C}=\text{O}$ ) in polyurea [130].

Notably from the  $^1\text{H}$  NMR spectrum of DAB (Fig. 7.2a), a broad peak was observed at chemical shift 1.45 ppm corresponding to the terminal amino hydrogen atoms. Likewise two additional peaks were observed at 1.33 ppm and 2.49 ppm assigned to protons labeled as 2'' and 1'', respectively. The proton resonance at 2.49 ppm is not clearly visible as it overlaps with that of residual solvent (DMSO) signal at 2.50 ppm. In the case of TDI, resonance peaks of the methyl groups ( $\text{H}_7$  and  $\text{H}_{7'}$ ) appeared at 2.51 ppm and also overlap with the solvent signal. Aromatic protons which appeared in the range of chemical shifts 6.0 – 8.0 ppm were also assigned as shown. For PUCorr-1 however, multiple peaks appeared between chemical shifts 1.30 ppm and 4.0 ppm and have been assigned to the protons in DAB (1'' and 2''), DMSO signal, and methyl protons ( $\text{H}_7$  and  $\text{H}_{7'}$ ) on TDI and residual water present in DMSO as shown in Fig. 7.2b. Furthermore, resonance peak of protons in the urea ( $-\text{NH}$ ) linkage appeared at 6.00 ppm, while those for aromatic protons gave a complicated splitting pattern in the range 6.30 – 8.55 ppm as have been previously assigned [130] due to the presence of two isomers of TDI.

The  $^{13}\text{C}$  resonance spectrum of toluene diisocyanate, TDI showed a single peak at chemical shift 18.0 ppm corresponding to the methyl carbon ( $\text{C}_7$ ) present on the molecule. Others are the aromatic and isocyanate carbon atoms labeled and identified accordingly as shown in Fig. 7.3a. The  $^{13}\text{C}$  NMR spectrum of piperazine, PPZ (Fig. 7.3b) gave a single peak at around 48.0 ppm corresponding to the four methylene carbon atoms in the molecule. Resonance peak of the compound appeared at the same chemical shift because all four carbon atoms have the same chemical environment. In the case of PUCorr-2 (Fig. 7.3c), it can be seen that while the methyl carbon atom of TDI ( $\text{C}_7$ ) appeared at the same chemical shift as in the monomer, the methylene carbon atoms in PPZ now have different chemical environments and appeared separately as  $\text{C}_a, \text{C}_b$  and  $\text{C}_c, \text{C}_d$  at 44.0 and 46.0 ppm, respectively. Furthermore, peaks assigned to  $-\text{NCO}$  carbons ( $\text{C}_8$  and  $\text{C}_8'$ ) at 123.0 and 125.0 ppm is now absent. In addition, peaks assigned to carbon atoms bearing the  $-\text{NCO}$  group ( $\text{C}_2$  and  $\text{C}_4$ ) both appeared shifted due to the formation of urea linkage. New peaks appeared at around chemical shift 155.5 ppm and have been assigned to characteristic resonances of the carbonyl ( $\text{C}=\text{O}$ ) linkage in polyurea.

From the  $^1\text{H}$  NMR spectrum of TDI (Fig. 7.4a), four distinct resonance peaks at chemical shifts 2.40, 6.76, 6.80 and 7.15 ppm were present corresponding to the methyl ( $\text{H}_7$ ) and aromatic proton atoms ( $\text{H}_3$ ,  $\text{H}_5$  and  $\text{H}_6$ ), respectively. The spectrum of PPZ on the other hand (Fig. 7.4b) gave two resonance peaks at 2.20 and 2.80 ppm corresponding to the  $-\text{NH}$  and methylene protons ( $\text{H}_a$ ,  $\text{H}_b$ ,  $\text{H}_c$  and  $\text{H}_d$ ), respectively.  $^1\text{H}$  NMR spectrum of PUCorr-2 showed a resonance peak at 1.90 ppm (singlet) corresponding to terminal  $-\text{NH}$  protons on the polymer. Others are resonance peaks at 2.10 ppm (triplet, 4H  $\text{H}_c$  and  $\text{H}_d$ ), 2.20 ppm (singlet, 3H,  $\text{H}_7$ ) and 2.70 ppm (triplet, 4H,  $\text{H}_a$  and  $\text{H}_b$ ). Solvent (DMSO) and

residual water peaks appeared at 2.55 and 3.50 ppm, respectively while aromatic protons ( $H_3$ ,  $H_5$  and  $H_6$ ) appeared in the region 7.00 – 7.50 ppm. Finally, -NH protons of the urea linkage appeared at 8.10 – 8.20 ppm due the difference in chemical environments.

FT-IR spectrum of PUCorr-1 (Fig. 7.5a) shows the presence of C=O stretching of the urea linkage at  $1650\text{ cm}^{-1}$ , and a substituted -NH stretching at  $3350\text{ cm}^{-1}$  [131]. The strong absorption band at  $1550\text{ cm}^{-1}$  represents the -NH bending while the -CH stretching band appeared around  $3000\text{ cm}^{-1}$  [130]. Others are the -NH wagging, -CH and -CN stretching modes at  $700\text{ cm}^{-1}$ ,  $2930\text{ cm}^{-1}$  and  $1230\text{ cm}^{-1}$ , respectively. TGA analysis (Fig. 7.5b) shows three major losses in weight. The first slow weight loss of 15% is due to the loss of water embedded inside the polyurea nearly at  $120\text{ }^{\circ}\text{C}$ , while the second and third losses approximately at  $300\text{ }^{\circ}\text{C}$  and  $550\text{ }^{\circ}\text{C}$  refer to the combustion of nitrogenous organic fractions present in the polymer with the release of  $\text{CO}_2$ ,  $\text{NO}_x$  and  $\text{H}_2\text{O}$  species [132].

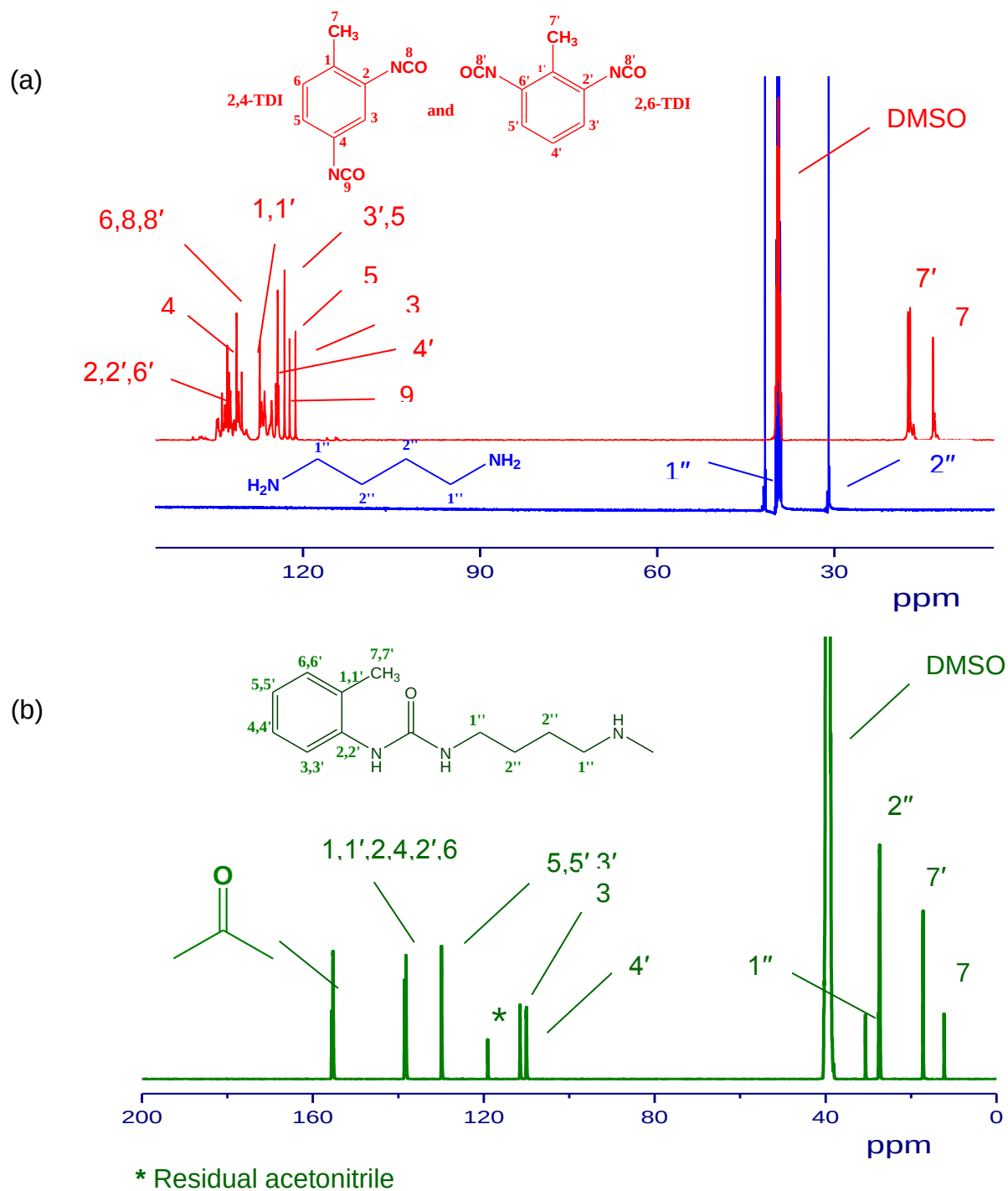


Figure 7.1  $^{13}\text{C}$  NMR spectra of (a) TDI and DAB monomers, and (b) PUCorr-1

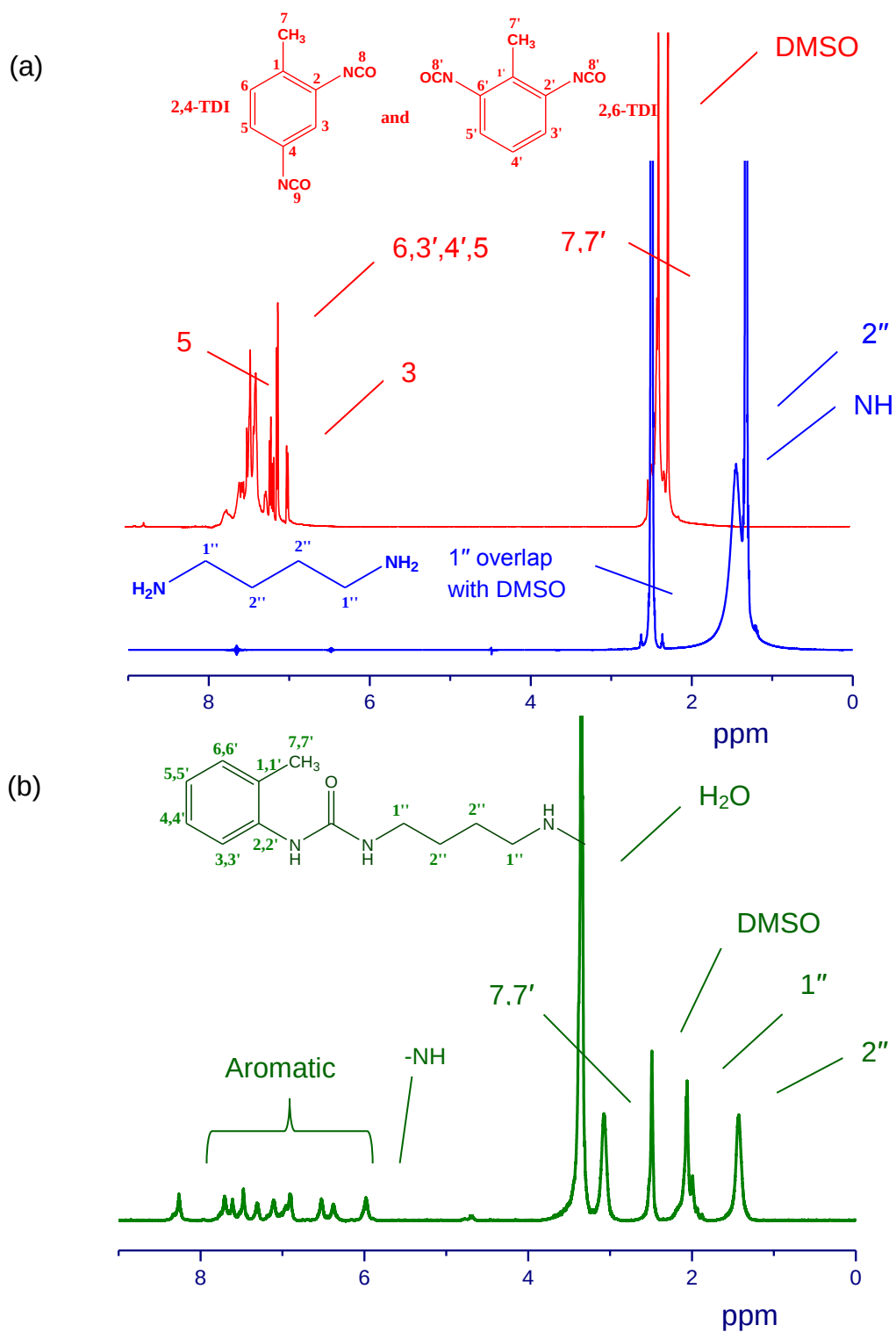


Figure 7.2 <sup>1</sup>H NMR spectra of (a) TDI and DAB monomers, and (b) PUCorr-1

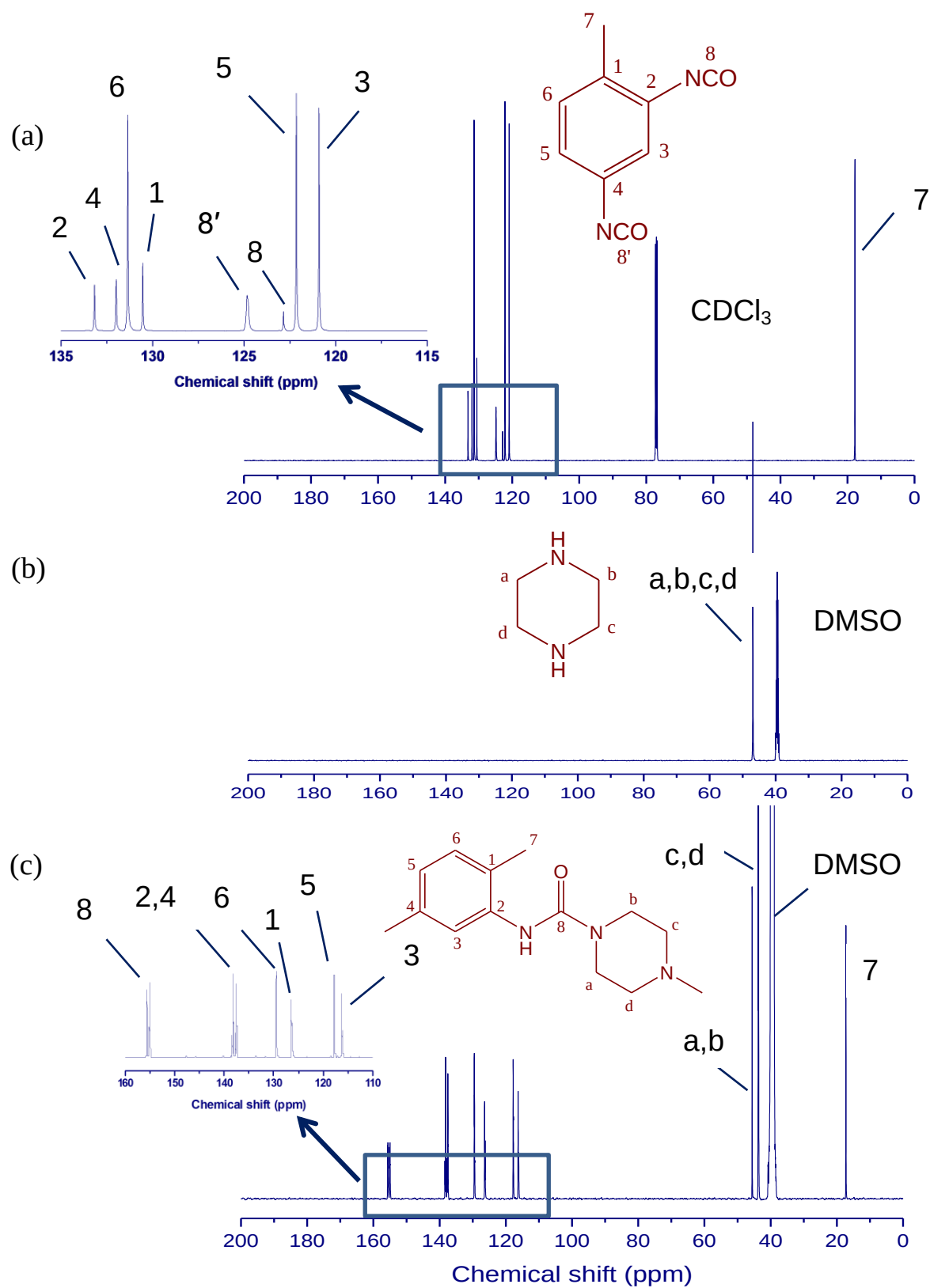


Figure 7.3 <sup>13</sup>C NMR spectra of (a) TDI, (b) PPZ, and (c) PUCorr-2

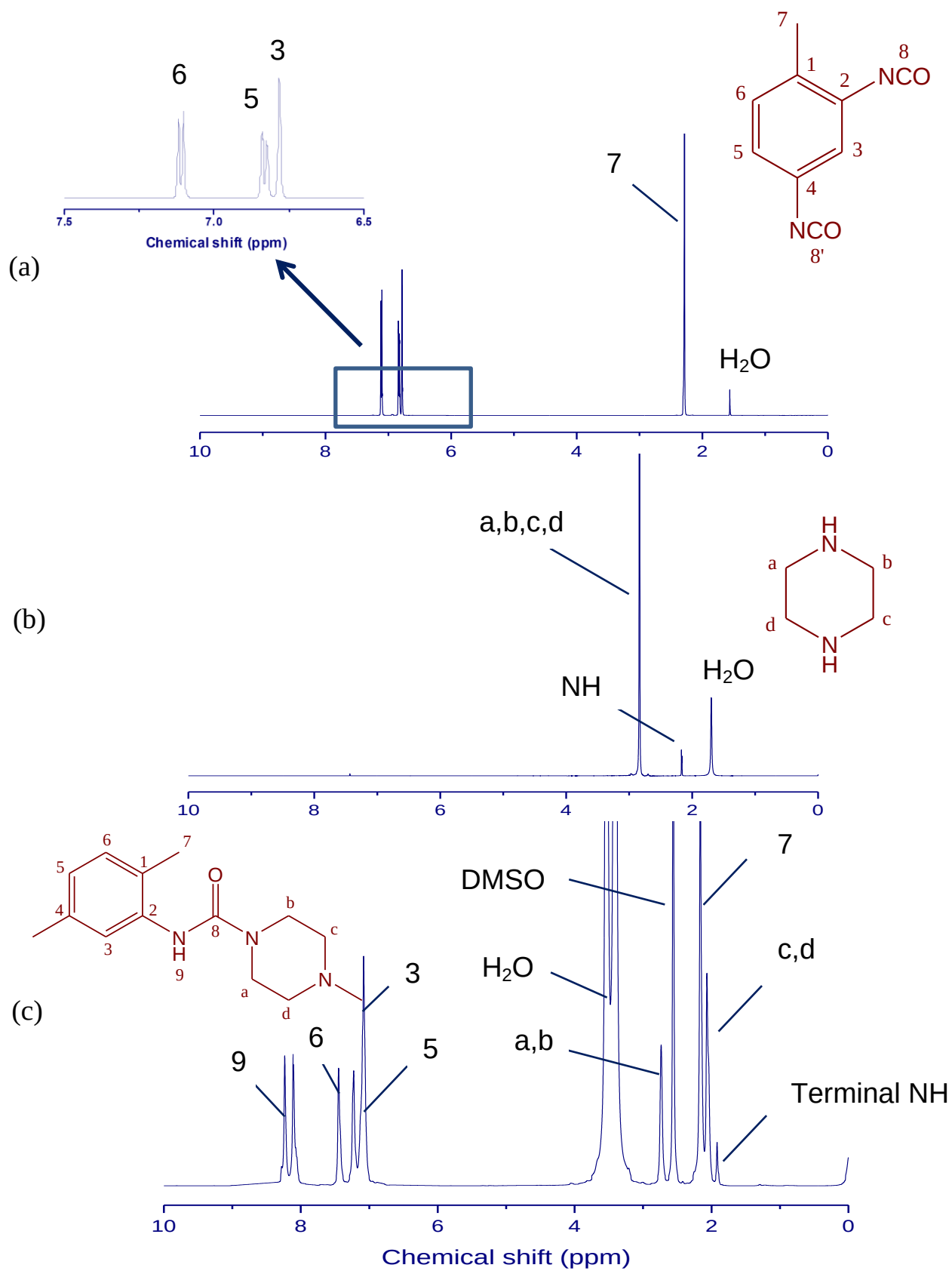


Figure 7.4 <sup>1</sup>H NMR spectra of (a) TDI, (b) PPZ, and (c) PUCorr-2

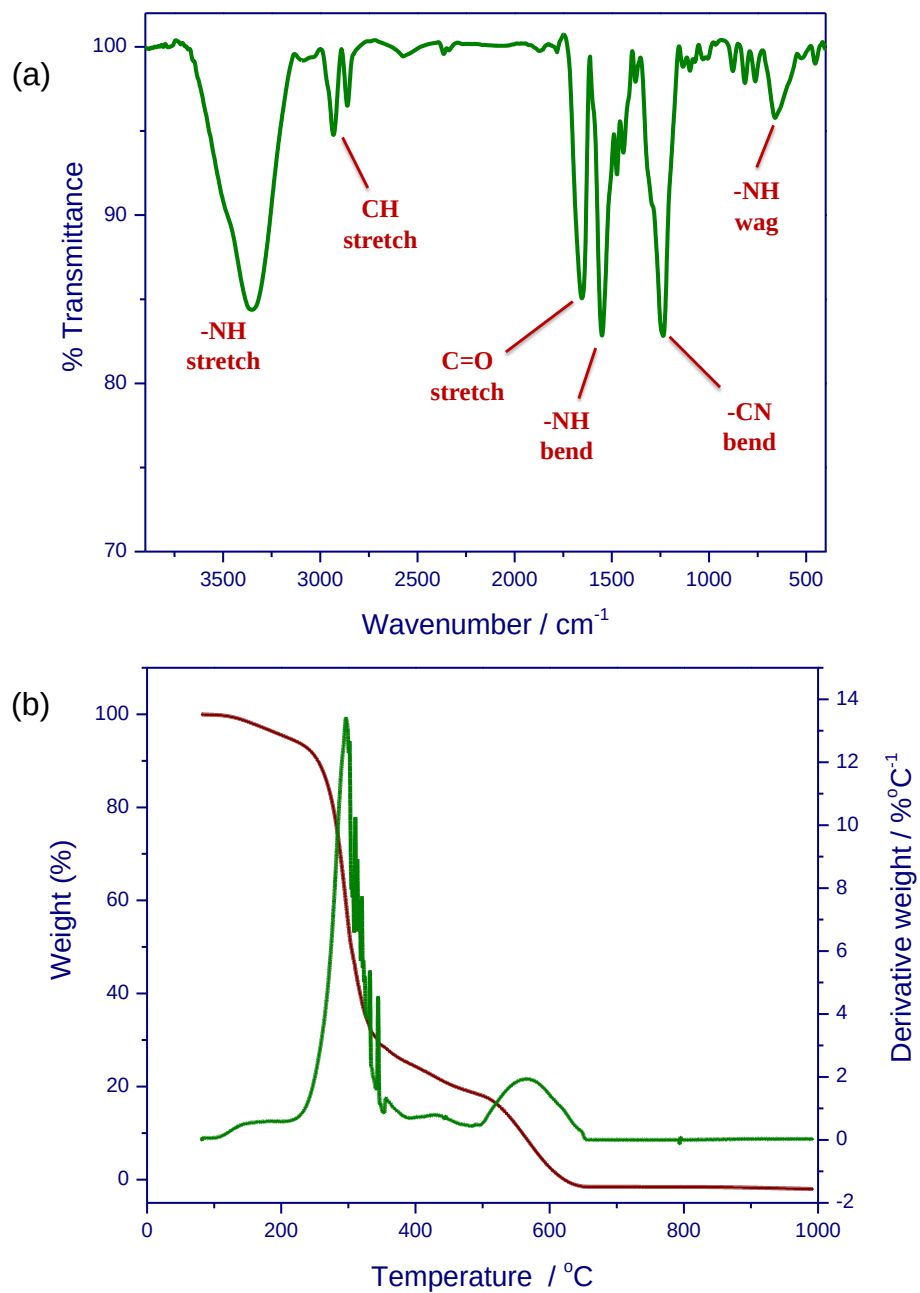


Figure 7.5 (a) FT-IR and (b) TGA spectra of PUCorr-1

The FT-IR spectrum of PUCorr-2 (Fig. 7.6a) shows a strong absorption band at  $3350\text{ cm}^{-1}$  corresponding to  $\text{-NH}$  vibrational stretch. The medium band at  $3000\text{ cm}^{-1}$  corresponds to  $\text{CH}$  vibrational stretch, while the very strong band at  $1680\text{ cm}^{-1}$  corresponds to the  $\text{C=O}$  stretch [131]. Others are  $\text{sp}^3\text{ CH}$  bend at  $1400\text{ cm}^{-1}$ ,  $\text{CN}$  stretch at  $1230\text{ cm}^{-1}$ ,  $\text{sp}^3\text{ C-C}$  stretch at  $950\text{ cm}^{-1}$  and  $\text{-NH}$  wag at  $650\text{ cm}^{-1}$ , respectively. A very strong absorption band appeared at  $1550\text{ cm}^{-1}$  and it could not be ascertained whether this band is due to  $\text{-NH}$  bend or  $\text{C=C}$  stretch as both bands occur in this region. Thermal degradation characteristics of PUCorr-2 were further investigated by TGA analysis. As shown in Fig. 7.6b two major losses in weight were recorded at  $300^\circ\text{C}$  and  $550^\circ\text{C}$  referring to the combustion of nitrogenous organic fractions present in the polymer with the release of  $\text{CO}_2$ ,  $\text{NO}_x$  and  $\text{H}_2\text{O}$  species [132], respectively.

Elemental analysis confirmed the composition of both materials to be C, N and O while x-ray diffraction pattern revealed a broad characteristic peak of amorphous materials for both polymers.

### **7.3.2 Electrochemical corrosion studies**

Electrochemical behavior of the corrosion inhibition process of PUCorr-1 was thoroughly investigated. Open circuit potential ( $E_{\text{ocp}}$ ) measurements (Fig. 7.7) showed that a steady state was reached nearly after 300 s of the immersion in the presence of PUCorr-1 with a corresponding shift to the nobler  $E_{\text{ocp}}$ ; an indication of an increasing surface coverage with the increase of the PUCorr-1 concentration, and resulting with a consequent decrease in the corrosion rate.

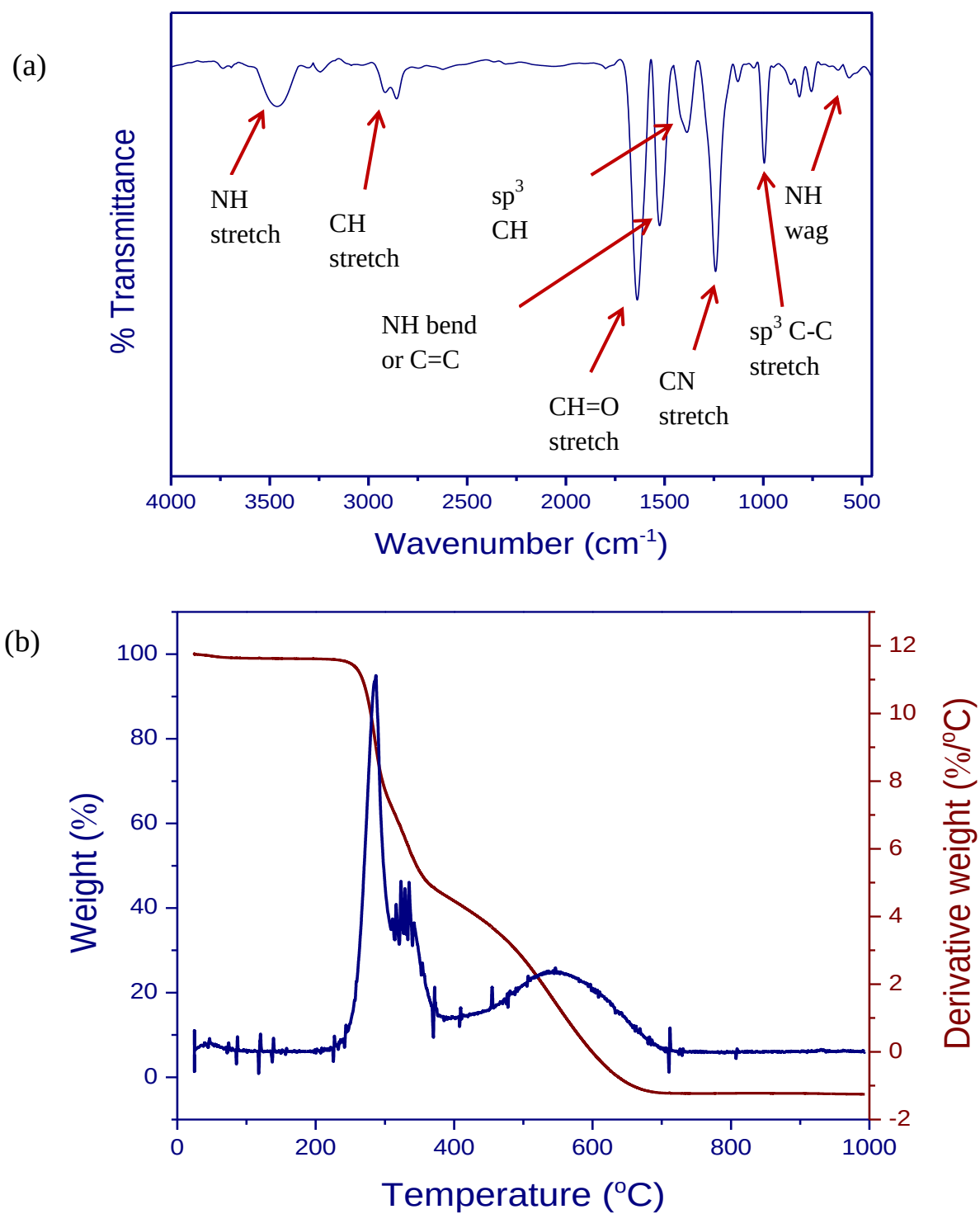


Figure 7.6 (a) FT-IR and (b) TGA spectra of PUCorr-2

The kinetics of the anodic and cathodic processes was evaluated using the potentiodynamic polarization (Tafel) approach. Tafel curves measured at different temperatures (25 °C – 50 °C) and inhibitor concentrations (20 ppm – 100 ppm) are presented in Fig. 7.8, while the corresponding extrapolated data are listed in Table 7.1. Blank measurements were carried out in a solution containing N-methyl-2-pyrrolidone with the ratio 100:1 v/v. The results revealed that the addition of the inhibitor significantly affects both anodic and cathodic processes as the curves shifted towards a lower corrosion current compared to the solution without the inhibitor. The shift in corrosion current densities appeared to be more significant for the anodic curves, suggesting that PUCorr-1 has a pronounced inhibitive effect on the anodic half-reaction [133]. With increasing temperature and upon the addition of the polymer, both corrosion current densities ( $i_{\text{corr}}$ ) and corrosion potential ( $E_{\text{corr}}$ ) shifted as compared to the blank solution. The shift in  $E_{\text{corr}}$  implies that PUCorr-1 acts as a mixed-type inhibitor with a predominant effect on the anodic process. Overall, an inhibition efficiency of 99.9% was recorded at 100 ppm and a temperature of 50 °C proposing PUCorr-1 as a promising inhibitor for mild steel corrosion in acidic environment (Fig. 7.9) [134, 135].

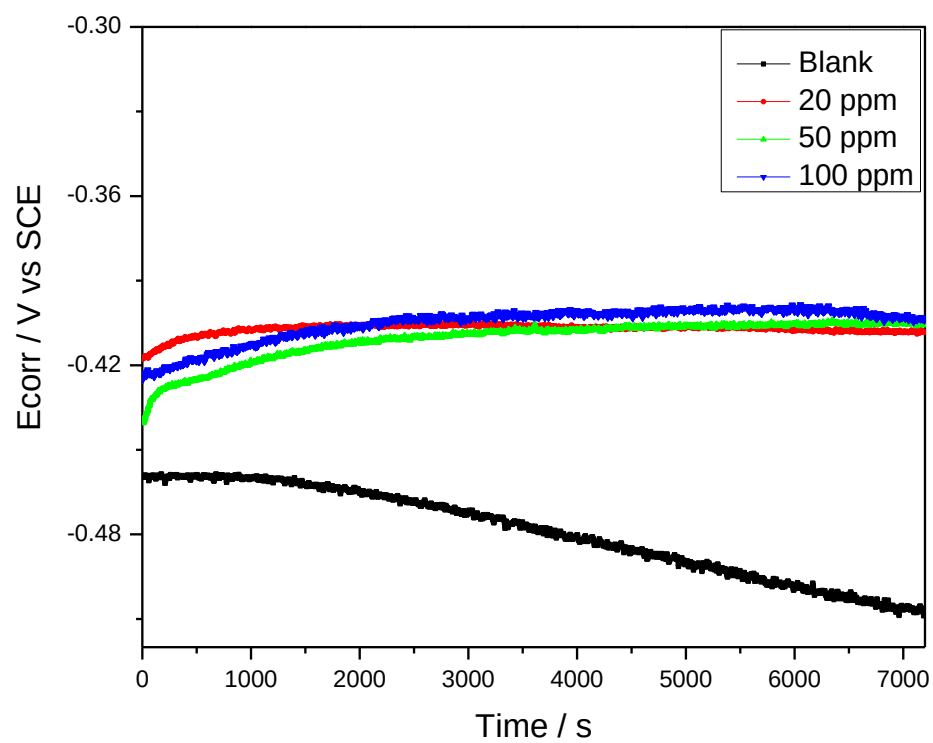


Figure 7.7 Open circuit vs time curves of mild steel in 1.0 M HCl in the absence and presence of PUCorr-1 at 25 °C

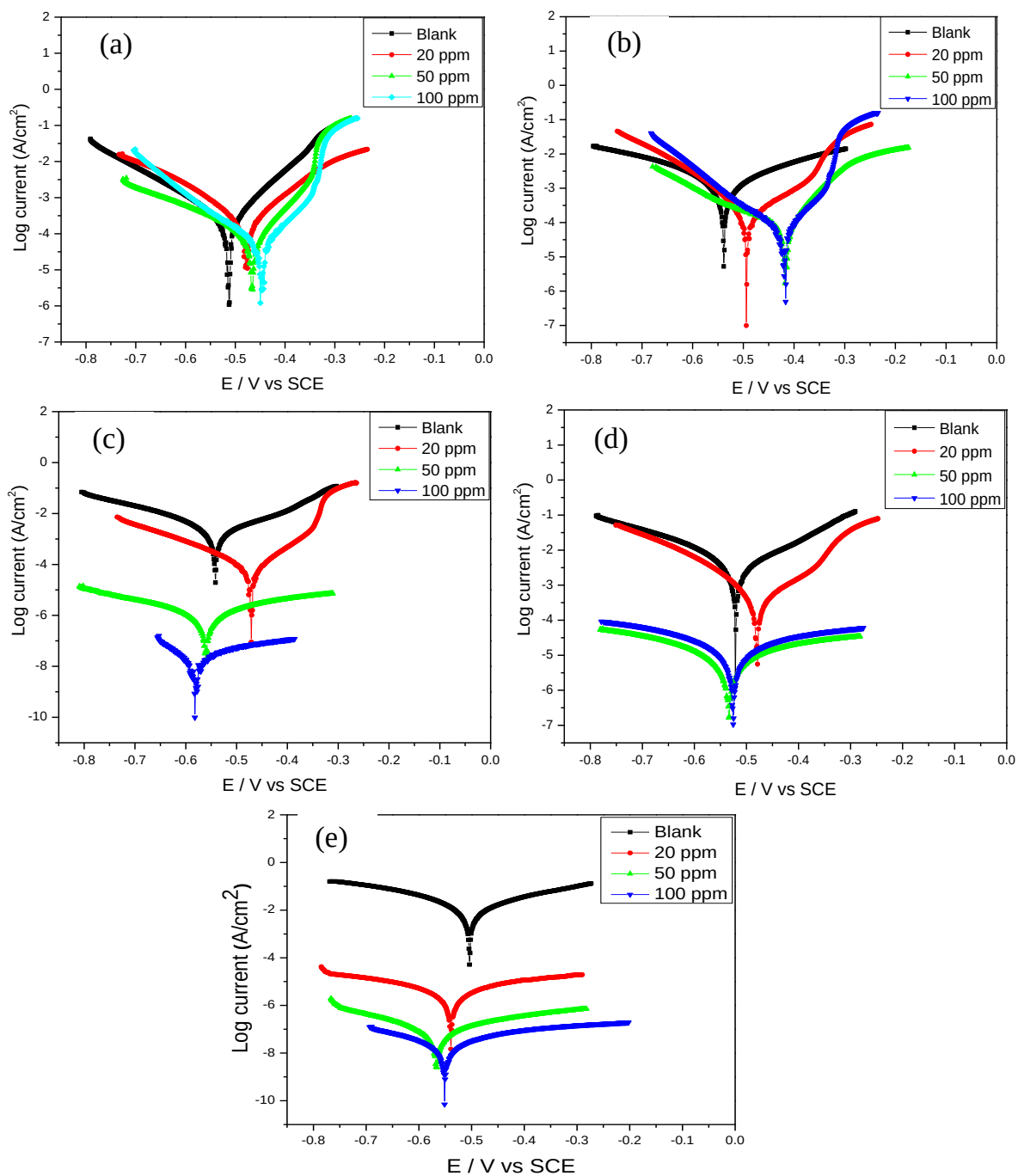


Figure 7.8 Tafel polarization curves of mild steel at (a) 298 K, (b) 303 K, (c) 308 K, (d) 313 K and (e) 323 K and varying concentrations of PUCorr-1; 20, 50 and 100 ppm in 1.0 M HCl

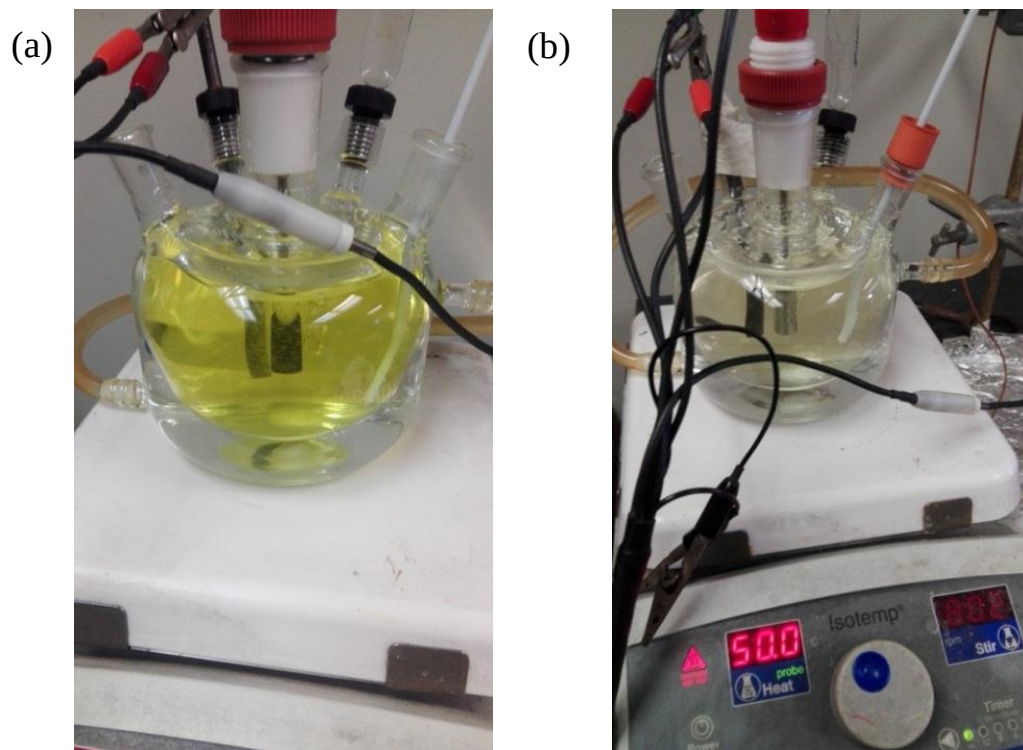


Figure 7.9 Corrosion medium of 1.0 M HCl in the absence (a) and presence (b) of 100 ppm PUCorr-1

Table 7.1 Tafel polarization data of mild steel at varying temperature and concentration

| Temperature (K) | Medium   | Inhibitor Conc. (ppm) | $E_{\text{corr}} / \text{V vs SCE}$ | $i_{\text{corr}} (\mu\text{A.cm}^{-2})$ | Corrosion rate (mmpy) | $\theta$ | $\eta\%$ |
|-----------------|----------|-----------------------|-------------------------------------|-----------------------------------------|-----------------------|----------|----------|
| 298             | Blank    | 0                     | -0.512                              | 301.1                                   | 3.43                  | -        | -        |
|                 | PUCorr-1 | 20                    | -0.420                              | 87.0                                    | 1.02                  | 0.703    | 70.3     |
|                 |          | 50                    | -0.420                              | 15.2                                    | 0.18                  | 0.948    | 94.8     |
|                 |          | 100                   | -0.402                              | 5.0                                     | 0.06                  | 0.983    | 98.3     |
| 303             | Blank    | 0                     | -0.539                              | 470.2                                   | 5.46                  | -        | -        |
|                 | PUCorr-1 | 20                    | -0.494                              | 28.1                                    | 0.33                  | 0.939    | 94.0     |
|                 |          | 50                    | -0.417                              | 17.0                                    | 0.20                  | 0.963    | 96.3     |
|                 |          | 100                   | -0.416                              | 1.2                                     | 0.02                  | 0.996    | 99.6     |
| 308             | Blank    | 0                     | -0.542                              | 3070.3                                  | 35.56                 | -        | -        |
|                 | PUCorr-1 | 20                    | -0.471                              | 2.0                                     | 0.02                  | 0.999    | 99.9     |
|                 |          | 50                    | -0.561                              | 0.1                                     | 0.01                  | 0.999    | 99.9     |
|                 |          | 100                   | -0.582                              | 0.1                                     | 0.01                  | 0.999    | 99.9     |
| 313             | Blank    | 0                     | -0.521                              | 4400.5                                  | 51.08                 | -        | -        |
|                 | PUCorr-1 | 20                    | -0.479                              | 31.3                                    | 0.36                  | 0.994    | 99.4     |
|                 |          | 50                    | -0.534                              | 11.1                                    | 0.13                  | 0.998    | 99.8     |
|                 |          | 100                   | -0.526                              | 3.6                                     | 0.03                  | 0.999    | 99.9     |
| 323             | Blank    | 0                     | -0.504                              | 8430.2                                  | 96.5                  | -        | -        |
|                 | PUCorr-1 | 20                    | -0.539                              | 2.2                                     | 0.02                  | 0.999    | 99.9     |
|                 |          | 50                    | -0.566                              | 0.6                                     | 0.01                  | 0.999    | 99.9     |
|                 |          | 100                   | -0.551                              | 0.3                                     | 0.01                  | 0.999    | 99.9     |

Kinetics and characteristics of the electrochemical processes occurring at the steel/solution interface in the presence of PUCorr-1 was further investigated using electrochemical impedance spectroscopy (EIS) technique. The dominating part in this process is believed to be a charge transfer reaction occurring at the metal/solution interface as implied by the Nyquist (Fig. 7.10a and Fig. 7.10b) and Bode (Fig. 7.10c and

7.10d) plots which are characterized by single depressed semi-circles [136]. In addition, a single capacitive loop was present indicating that PUCorr-1 acts primarily as an interface inhibitor through a surface coverage mechanism [137]. The diameter of the semi-circle was noticed to grow with increasing the inhibitor concentration due to the increase in the surface coverage by the inhibitor polymer. Bode plots also revealed the effect of the addition of the inhibitor at the lower frequency modulus as the low frequency impedance increases with the increase of the inhibitor concentration, which could be attributed to the adsorption of the inhibitor molecules onto the exposed steel surface [138]. In the absence of the inhibitor, the mild steel corroded freely in an acidic medium without a resistive barrier giving rise to a large double layer capacitance,  $C_{dl}$  and a lower charge transfer resistance,  $R_{ct}$  (Table 7.2). When the inhibitor was introduced, however, a significant drop in  $C_{dl}$  values and a corresponding increase in  $R_{ct}$  were noticed. This is because in the presence of the inhibitor, the charge transfer process leading to the corrosion of the metal was prevented by adsorbed films of the inhibitor molecules, thereby slowing down the corrosion rate [138]. Equivalent circuit model used for fitting and obtaining the EIS data is shown in Fig. 7.11. It comprises of a constant phase element, CPE in parallel with the charge transfer resistance,  $R_{ct}$ , both of which are in a series connection with the electrolyte resistance,  $R_s$ . Impedance of the constant phase element,  $Z_{CPE}$  is given as:

$$Z_{CPE} = Y_0^{-1}(i\omega)^{-n} \quad (7.3)$$

Where  $Y_0$  represents CPE constant,  $i^2$  an imaginary number (-1),  $\omega$  angular frequency ( $\text{rad s}^{-1}$ ) and  $n$  is CPE exponent. Values of  $n$  characterizes CPE, where  $n = 0$  implies that CPE = resistance;  $n = 1$ , CPE = capacitance;  $n = -1$ , CPE = inductance and  $n = 0.5$ , CPE

= Warburg impedance [139]. Double layer capacitance,  $C_{dl}$  was estimated using the equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (7.4)$$

where  $f_{max}$  represents the maximum frequency of the imaginary component of the impedance and  $R_{ct}$  the charge-transfer resistance.

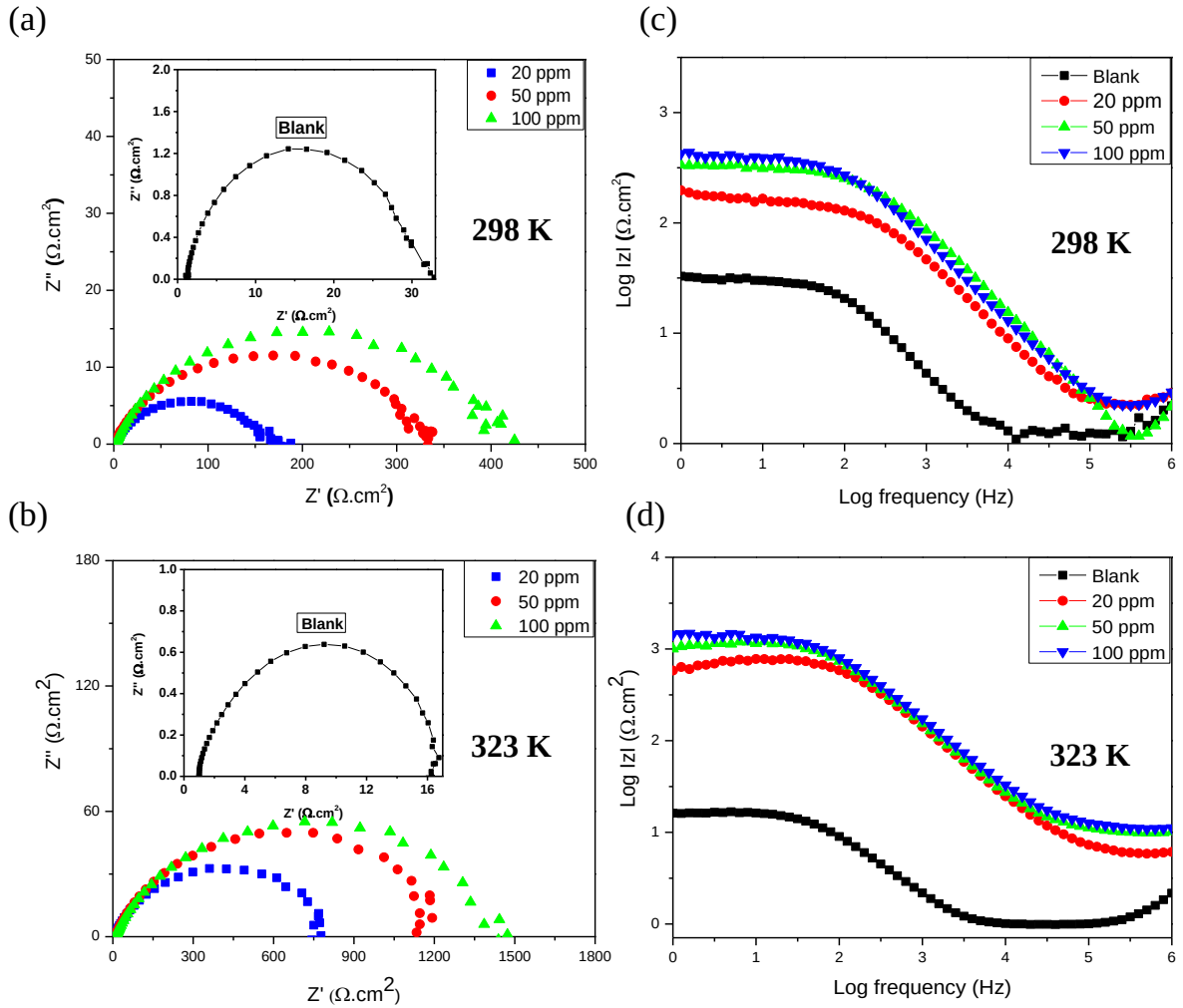


Figure 7.10 Nyquist plots (a),(b) and Bode plots (c),(d) of mild steel corrosion in 1.0 M HCl at 298 K and 323 K

Table 7.2 EIS data of mild steel corrosion in 1.0 M HCl with inhibitor molecules

| Temperature (K) | Medium   | Inhibitor conc. (ppm) | $R_s$ ( $\Omega.cm^2$ ) | $R_{ct}$ ( $\Omega.cm^2$ ) | $C_{dl}$ ( $\mu F.cm^{-2}$ ) | n    | $\eta\%$ |
|-----------------|----------|-----------------------|-------------------------|----------------------------|------------------------------|------|----------|
| 298             | Blank    | 0                     | 1.237                   | 29.54                      | 431.0                        | 0.91 | -        |
|                 | PUCorr-1 | 20                    | 2.165                   | 160.2                      | 31.5                         | 0.84 | 81.6     |
|                 |          | 50                    | 2.120                   | 313.4                      | 25.7                         | 0.82 | 90.6     |
|                 |          | 100                   | 2.104                   | 402.3                      | 25.1                         | 0.82 | 93.0     |
| 323             | Blank    | 0                     | 1.00                    | 15.56                      | 1296.3                       | 0.88 | -        |
|                 | PUCorr-1 | 20                    | 5.83                    | 722.4                      | 14.0                         | 0.85 | 97.9     |
|                 |          | 50                    | 9.86                    | 1163.0                     | 13.7                         | 0.85 | 98.7     |
|                 |          | 100                   | 10.76                   | 1430.0                     | 11.1                         | 0.82 | 98.9     |

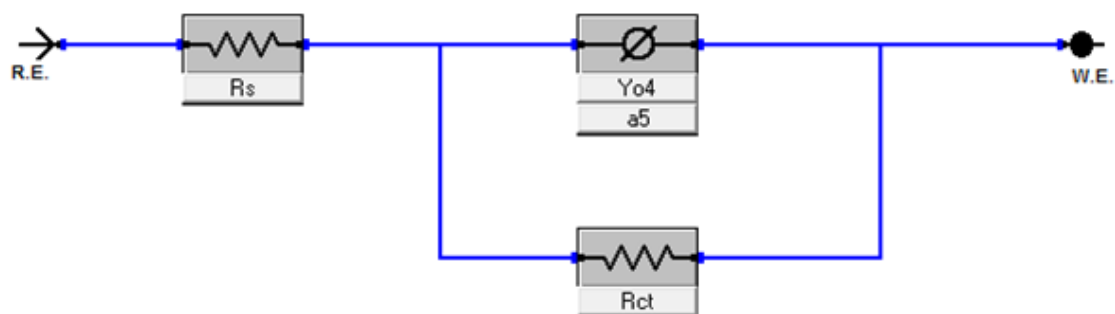


Figure 7.11 Equivalent circuit model used to fit EIS data

For PUCorr-2, a stabilization period of 60 min was allowed for mild steel specimen in both acid (1.0 M HCl) and saline (0.5 M NaCl) media prior to the electrochemical measurements with optimum concentration of 20 – 100 ppm as shown in Fig. 7.12. Tafel polarization measurements were carried out in both media in the absence and presence of the inhibitor. Figure 7.13 shows the Tafel polarization curves, while the corresponding extrapolated data are given in Table 7.3. Notably from these data, the corrosion current density ( $i_{\text{corr}}$ ) decreases with the presence of PUCorr-2. The variation in Tafel slope suggests that PUCorr-2 influences the kinetics of hydrogen evolution reaction leading to an increase in the energy barrier for proton discharge which subsequently results into less gas evolution [140]. A shift in corrosion potential ( $E_{\text{corr}}$ ) was also observed with the addition of PUCorr-2 and with increasing temperature in a manner that suggests that the adsorbed polymer films acted as mixed-type corrosion inhibitor, impeding both anodic and cathodic processes with more pronounced effects on the anodic reaction (metal dissolution) [122, 123]. An efficiency of 99.4% was achieved at 25 °C in the presence of 100 ppm PUCorr-2, while at elevated temperature (60 °C) where there is less dissolved oxygen, an efficiency of 99.9% was recorded at 100 ppm. Similar corrosion tests were conducted in saline medium (0.5 M NaCl) and the results shown in Fig. 7.14 and Table 7.4 further demonstrate the propensity of PUCorr-2 to serve as inhibitor of mild steel corrosion in both acidic and saline media.

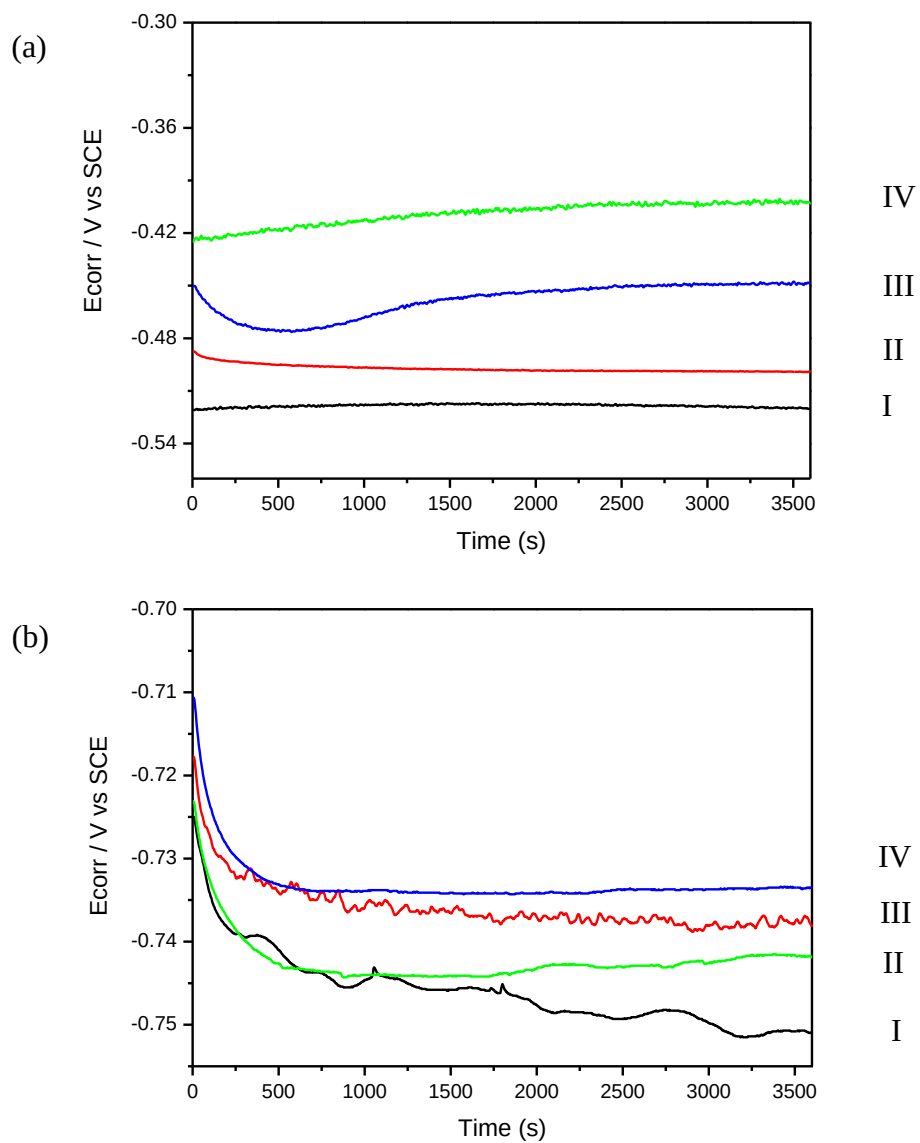


Figure 7.12 Open circuit potential plots of mild steel specimen immersed in (a) 1.0 M HCl and (b) 0.5 M NaCl in the absence of inhibitor (I) and presence of (II) 20 ppm, (III) 50 ppm and (IV) 100 ppm PUCorr-2 at 25 oC

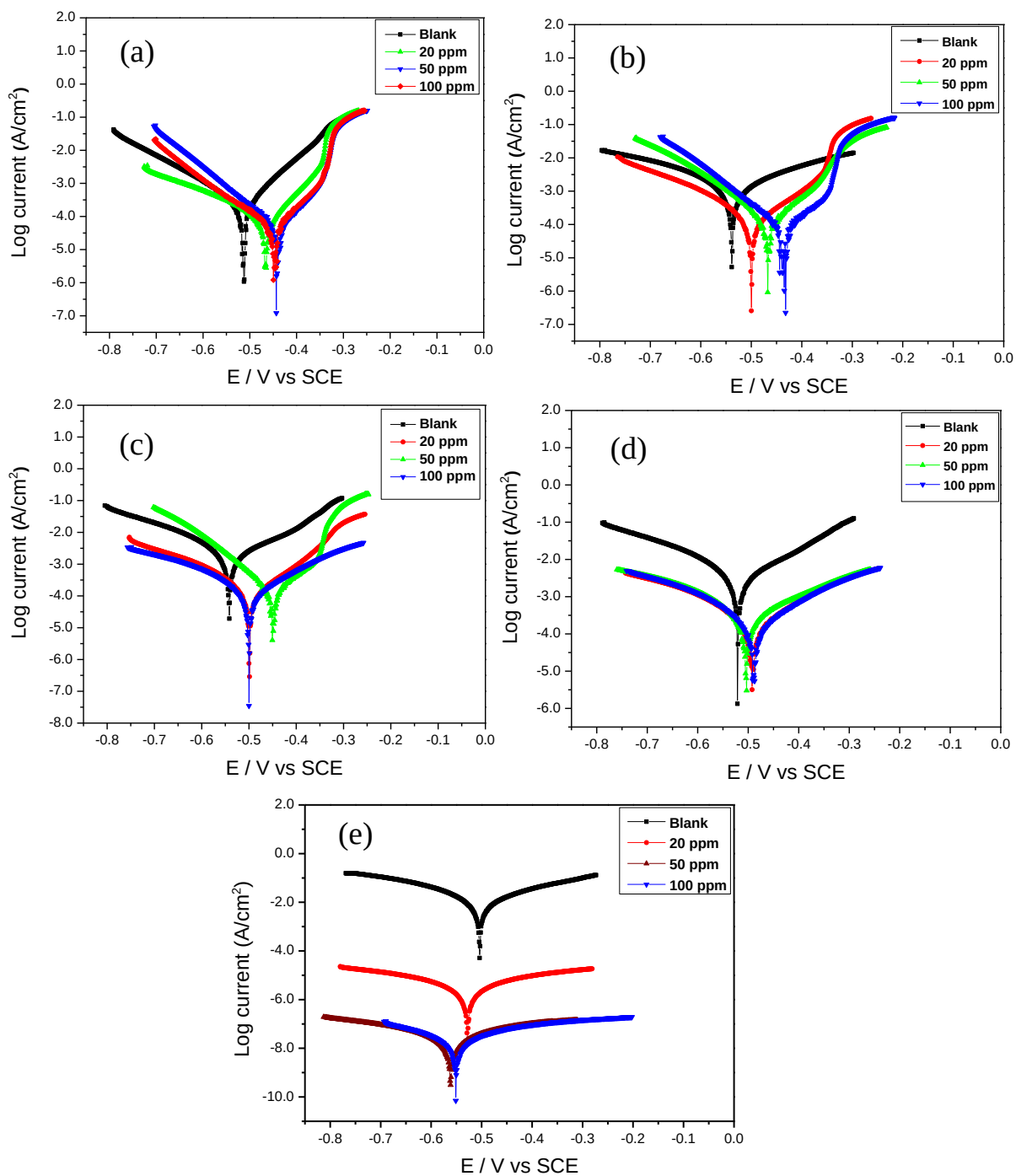


Figure 7.13 Tafel polarization curves of mild steel specimen in 1.0 M HCl in the absence (blank) and presence of PUCorr-2 (20 – 100 ppm) at (a) 298 K, (b) 303 K, (c) 313 K, (d) 323 K and (e) 333 K

Table 7.3 Tafel polarization data of mild steel in 1.0 M HCl

| Temperature (K) | Medium   | Inhibitor Conc. (ppm) | $E_{\text{corr}} / \text{V vs SCE}$ | $i_{\text{corr}} (\mu\text{A}.\text{cm}^{-2})$ | Corrosion rate (mmpy) | $\theta$ | $\eta\%$ |
|-----------------|----------|-----------------------|-------------------------------------|------------------------------------------------|-----------------------|----------|----------|
| 298             | Blank    | 0                     | -0.512                              | 301.1                                          | 3.43                  | -        | -        |
|                 | PUCorr-2 | 20                    | -0.466                              | 69.0                                           | 0.88                  | 0.771    | 77.1     |
|                 |          | 50                    | -0.443                              | 9.2                                            | 0.10                  | 0.969    | 97.1     |
|                 |          | 100                   | -0.449                              | 2.1                                            | 0.02                  | 0.993    | 99.3     |
| 303             | Blank    | 0                     | -0.539                              | 470.2                                          | 5.46                  | -        | -        |
|                 | PUCorr-2 | 20                    | -0.500                              | 18.2                                           | 0.22                  | 0.961    | 96.1     |
|                 |          | 50                    | -0.467                              | 13.3                                           | 0.16                  | 0.972    | 97.2     |
|                 |          | 100                   | -0.433                              | 1.2                                            | 0.05                  | 0.997    | 99.7     |
| 313             | Blank    | 0                     | -0.542                              | 3070.3                                         | 35.56                 | -        | -        |
|                 | PUCorr-2 | 20                    | -0.499                              | 8.5                                            | 0.08                  | 0.997    | 99.7     |
|                 |          | 50                    | -0.450                              | 5.1                                            | 0.06                  | 0.998    | 99.8     |
|                 |          | 100                   | -0.500                              | 5.0                                            | 0.06                  | 0.998    | 99.8     |
| 323             | Blank    | 0                     | -0.521                              | 4400.5                                         | 51.08                 | -        | -        |
|                 | PUCorr-2 | 20                    | -0.492                              | 28.5                                           | 0.32                  | 0.994    | 99.4     |
|                 |          | 50                    | -0.504                              | 21.3                                           | 0.25                  | 0.995    | 99.5     |
|                 |          | 100                   | -0.489                              | 5.2                                            | 0.07                  | 0.999    | 99.9     |
| 333             | Blank    | 0                     | -0.504                              | 8430.2                                         | 96.5                  | -        | -        |
|                 | PUCorr-2 | 20                    | -0.528                              | 10.6                                           | 0.04                  | 0.998    | 99.8     |
|                 |          | 50                    | -0.561                              | 1.5                                            | 0.01                  | 0.999    | 99.9     |
|                 |          | 100                   | -0.551                              | 1.5                                            | 0.01                  | 0.999    | 99.9     |

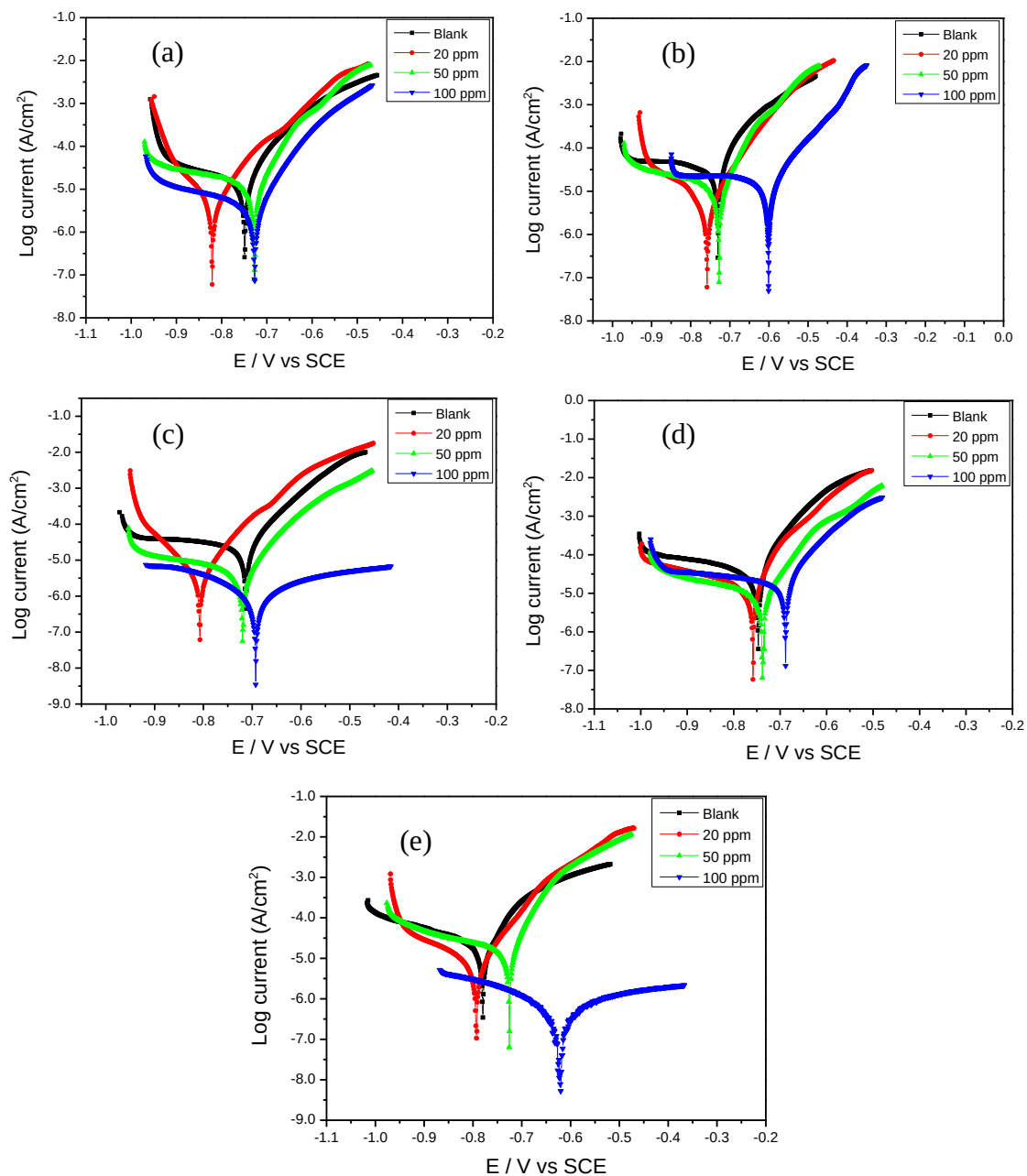


Figure 7.14 Tafel polarization curves of mild steel specimen in 0.5 M NaCl in the absence (blank) and presence of PUCorr-2 (20 – 100 ppm) at (a) 298 K, (b) 303 K, (c) 313 K, (d) 323 K and (e) 333 K

Table 7. 4 Tafel polarization data of mild steel in 0.5 M NaCl in the presence of PUCorr-2

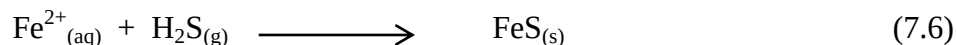
| Temperature (K) | Medium   | Inhibitor Conc. (ppm) | $E_{\text{corr}} / \text{V}$ vs SCE | $i_{\text{corr}}$ ( $\mu\text{A}.\text{cm}^{-2}$ ) | Corrosion rate (mmpy) | $\theta$ | $\eta\%$ |
|-----------------|----------|-----------------------|-------------------------------------|----------------------------------------------------|-----------------------|----------|----------|
| 298             | Blank    | 0                     | -0.749                              | 30.30                                              | 0.403                 | -        | -        |
|                 | PUCorr-2 | 20                    | -0.821                              | 5.98                                               | 0.069                 | 0.829    | 82.9     |
|                 |          | 50                    | -0.727                              | 3.37                                               | 0.039                 | 0.903    | 90.3     |
|                 |          | 100                   | -0.727                              | 3.05                                               | 0.022                 | 0.945    | 94.5     |
| 303             | Blank    | 0                     | -0.730                              | 45.40                                              | 0.527                 | -        | -        |
|                 | PUCorr-2 | 20                    | -0.758                              | 4.66                                               | 0.054                 | 0.898    | 89.8     |
|                 |          | 50                    | -0.727                              | 2.91                                               | 0.034                 | 0.935    | 93.5     |
|                 |          | 100                   | -0.601                              | 1.92                                               | 0.028                 | 0.947    | 94.7     |
| 313             | Blank    | 0                     | -0.713                              | 33.20                                              | 0.385                 | -        | -        |
|                 | PUCorr-2 | 20                    | -0.807                              | 4.25                                               | 0.049                 | 0.873    | 87.3     |
|                 |          | 50                    | -0.720                              | 2.11                                               | 0.024                 | 0.938    | 93.8     |
|                 |          | 100                   | -0.693                              | 1.97                                               | 0.022                 | 0.943    | 94.3     |
| 323             | Blank    | 0                     | -0.747                              | 39.70                                              | 0.461                 | -        | -        |
|                 | PUCorr-2 | 20                    | -0.759                              | 1.62                                               | 0.019                 | 0.959    | 95.9     |
|                 |          | 50                    | -0.738                              | 1.03                                               | 0.012                 | 0.974    | 97.4     |
|                 |          | 100                   | -0.688                              | 0.73                                               | 0.008                 | 0.983    | 98.3     |
| 333             | Blank    | 0                     | -0.780                              | 54.20                                              | 0.630                 | -        | -        |
|                 | PUCorr-2 | 20                    | -0.793                              | 3.18                                               | 0.037                 | 0.941    | 94.1     |
|                 |          | 50                    | -0.726                              | 1.63                                               | 0.019                 | 0.970    | 97.0     |
|                 |          | 100                   | -0.623                              | 0.45                                               | 0.005                 | 0.992    | 99.2     |

Electrochemical impedance spectroscopy (EIS) technique was further utilized to investigate the kinetics of the electrochemical process as shown in Fig. 7.15. The depressed single capacitive loop has been attributed to surface heterogeneity due to the adsorbed inhibitors through a surface coverage mechanism [137]. In the absence of the inhibitor, the mild steel specimen corroded freely without a resistive barrier giving rise to

a large double layer capacitance,  $C_{dl}$  and a lower polarization resistance,  $R_p$  (the resistance of the specimen to corrosion), as shown in Table 7.5. When the inhibitor was introduced, however, a drop in  $C_{dl}$  values and a corresponding increase in  $R_p$  were noticed. Values obtained from EIS measurements correlates with those obtained from Tafel polarization measurements.

Furthermore, the inhibitive performance of PUCorr-1 has been tested under simulated severe conditions in the presence of  $CO_2$  and  $H_2S$  gases. Such gases represent significant contributors in accelerating metallic corrosion in oil and gas industries, and hence testing the corrosion inhibitor under such conditions shall be more indicative of its aptness to be potentially used under industrially harsh conditions. The presence of  $H_2S$  further complicates the corrosion process leading to hydrogen induced cracking and sulfide stress corrosion [141]. To study the corrosion inhibitive performance of PuCorr-1 in the presence of  $CO_2$  and  $H_2S$  gases, Tafel polarization measurements were conducted in 0.5 M NaCl. Prior to the measurements,  $N_2$  gas (99.999%) was purged into the electrolyte solution (0.5 M NaCl) for 30 min to maintain an anoxic (oxygen-free) condition. This was followed by purging high purity  $CO_2$  gas (99.995%) for 30 min to remove all dissolved oxygen before commencement of measurements. The complete removal of oxygen and saturation of the solution with  $CO_2$  were achieved when an open circuit potential became stable and, thereafter, Tafel polarization measurements were carried out.  $H_2S$  corrosion studies were conducted by dissolving 25 mg  $Na_2S$  in 100 ml 5% acetic acid and the resulting gas passed into the electrolyte solution (0.5 M NaCl) for 30 min as shown in Fig 7.16 before conducting electrochemical measurements. Similar corrosion measurements were conducted in a 15% HCl (5.0 M) solution. In the presence of  $CO_2$

and H<sub>2</sub>S gases, mild steel undergoes corrosion leading predominantly to the formation [142] of FeCO<sub>3</sub> and FeS according to equations (7.5) and (7.6);



Since the rate of formation of Fe<sup>2+</sup> species precedes the above processes, it is apparent that the presence of adsorbed polymer films which block the active corrosion sites would lead to a corresponding decrease in the corrosion rate [143]. This can be noticed from the Tafel polarization curves (Fig. 7.17) and the corresponding extrapolated data (Table 7.6) that the addition of PUCorr-1 in saline solutions saturated with CO<sub>2</sub> and H<sub>2</sub>S has led to a decrease in the anodic current as well as an increase in the corrosion resistance of the mild steel specimen. Excellent inhibition efficiencies of 97.2% and 94.7% were achieved in saline media saturated with CO<sub>2</sub> and H<sub>2</sub>S gases, respectively, implying the potential of PUCorr-1 to be applied as an inhibitor of mild steel corrosion in harsh environments involving CO<sub>2</sub> and H<sub>2</sub>S gases

Corrosion inhibitive performance of PUCorr-2 was also investigated in the presence of CO<sub>2</sub> gas. The results (Fig. 7.18) and the corresponding extrapolated data (Table 7.7) revealed that the addition of PUCorr-2 in saline solutions saturated with CO<sub>2</sub> led to a decrease in the anodic current as well as an increase in the corrosion resistance of the mild steel specimen. Excellent inhibition efficiency of 99.5% was achieved in saline media saturated with CO<sub>2</sub> in the presence of 100 ppm PUCorr-2.

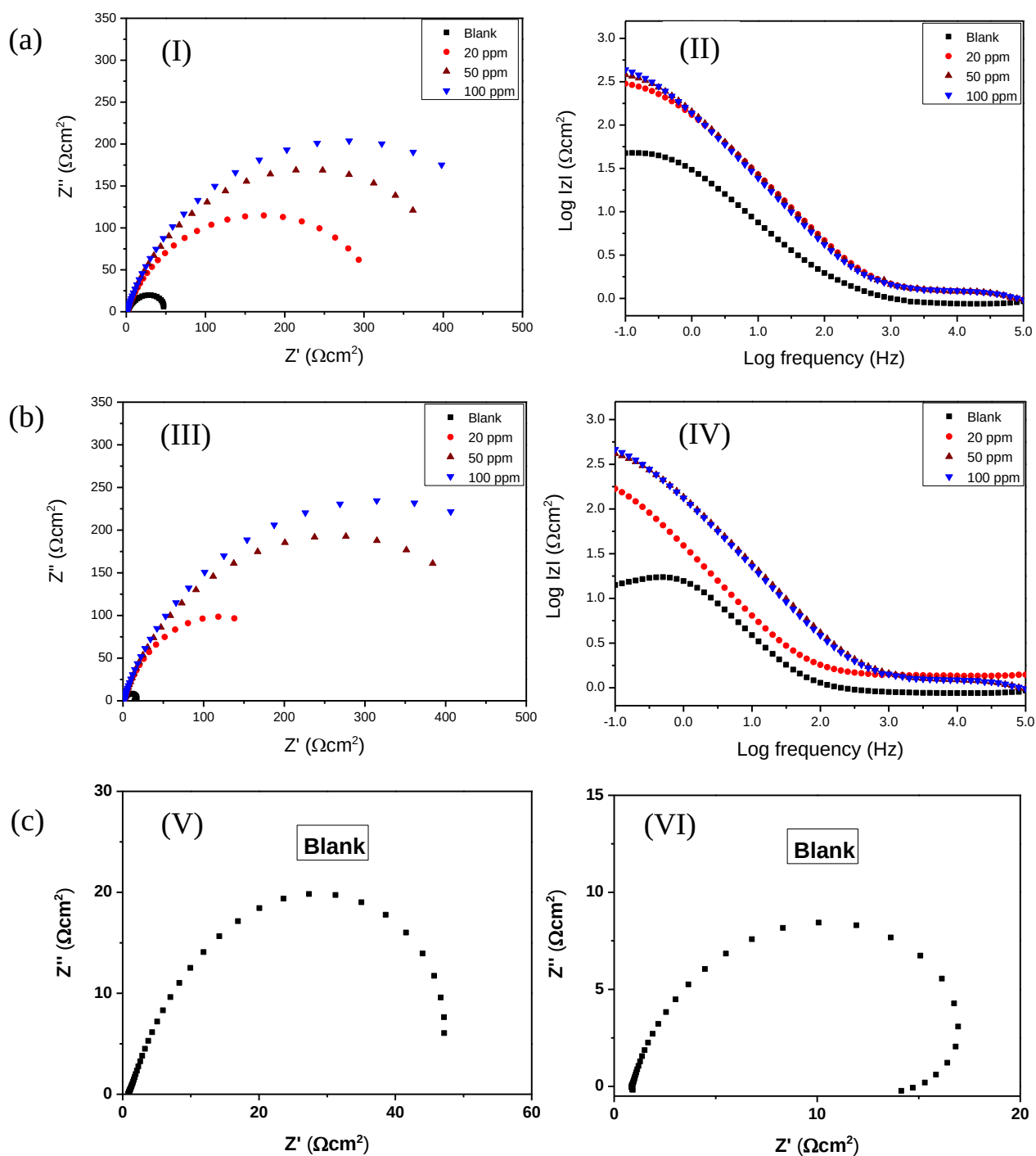


Figure 7.15 Nyquist (I) and (III) and Bode (II) and (IV) plots of mild steel specimen in 0.5 M NaCl in the absence and presence of 20 – 100 ppm PUCorr-2 at (a) 298 K and (b) 333 K. Plots (c) V and VI represents expanded Nyquist plots in blank solution at 298 K and 333 K, respectively

Table 7.5 EIS data of mild steel in 0.5 M NaCl in the absence and presence of PUCorr-2

| Temperature (K) | Medium   | Inhibitor conc. (ppm) | $R_s$ ( $\Omega.cm^2$ ) | $R_p$ ( $\Omega.cm^2$ ) | $C_{dl}$ ( $\mu F.cm^{-2}$ ) | n    | $\eta\%$ |
|-----------------|----------|-----------------------|-------------------------|-------------------------|------------------------------|------|----------|
| 298             | Blank    | 0                     | 0.869                   | 56.14                   | 28.30                        | 0.74 | -        |
|                 | PUCorr-2 | 20                    | 1.073                   | 326.20                  | 9.70                         | 0.79 | 82.8     |
|                 |          | 50                    | 1.081                   | 461.40                  | 11.50                        | 0.80 | 87.9     |
|                 |          | 100                   | 1.099                   | 561.20                  | 15.20                        | 0.80 | 90.0     |
| 333             | Blank    | 0                     | 0.890                   | 16.38                   | 48.80                        | 0.90 | -        |
|                 | PUCorr-2 | 20                    | 1.362                   | 261.4                   | 24.30                        | 0.83 | 93.7     |
|                 |          | 50                    | 1.099                   | 530.3                   | 7.69                         | 0.80 | 96.9     |
|                 |          | 100                   | 1.104                   | 635.0                   | 7.80                         | 0.80 | 97.4     |



Figure 7.16 Experimental set-up for  $H_2S$  corrosion measurement

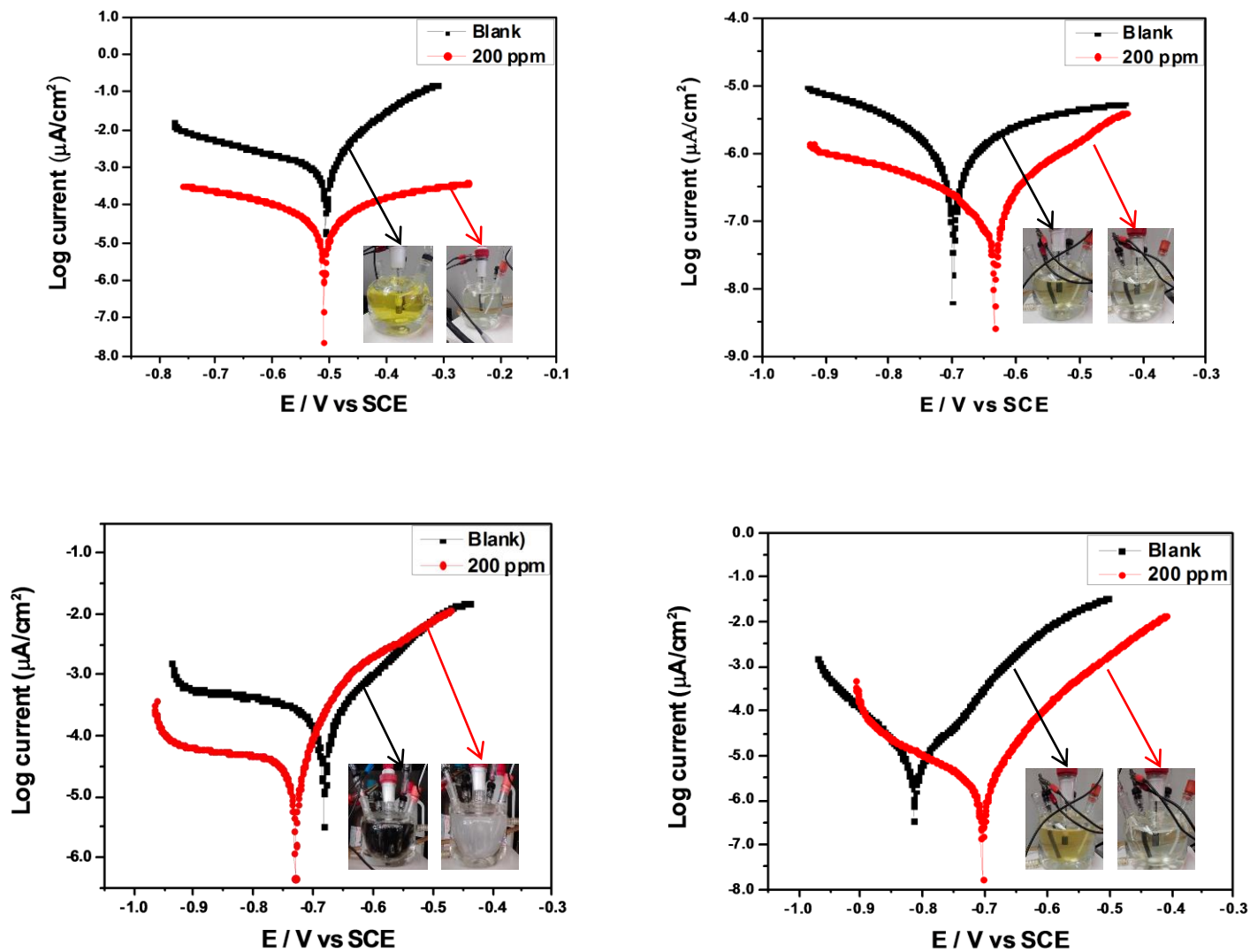


Figure 7.17 Tafel polarization curves of mild steel corrosion in (a) 5 M HCl, (b) 0.5 M NaCl, (c) 0.5 M NaCl, sat'd  $\text{H}_2\text{S}$  and (d) 0.5 M NaCl, sat'd  $\text{CO}_2$  in the absence (blank) and presence of 200 ppm PuCorr-1 at 25 °C

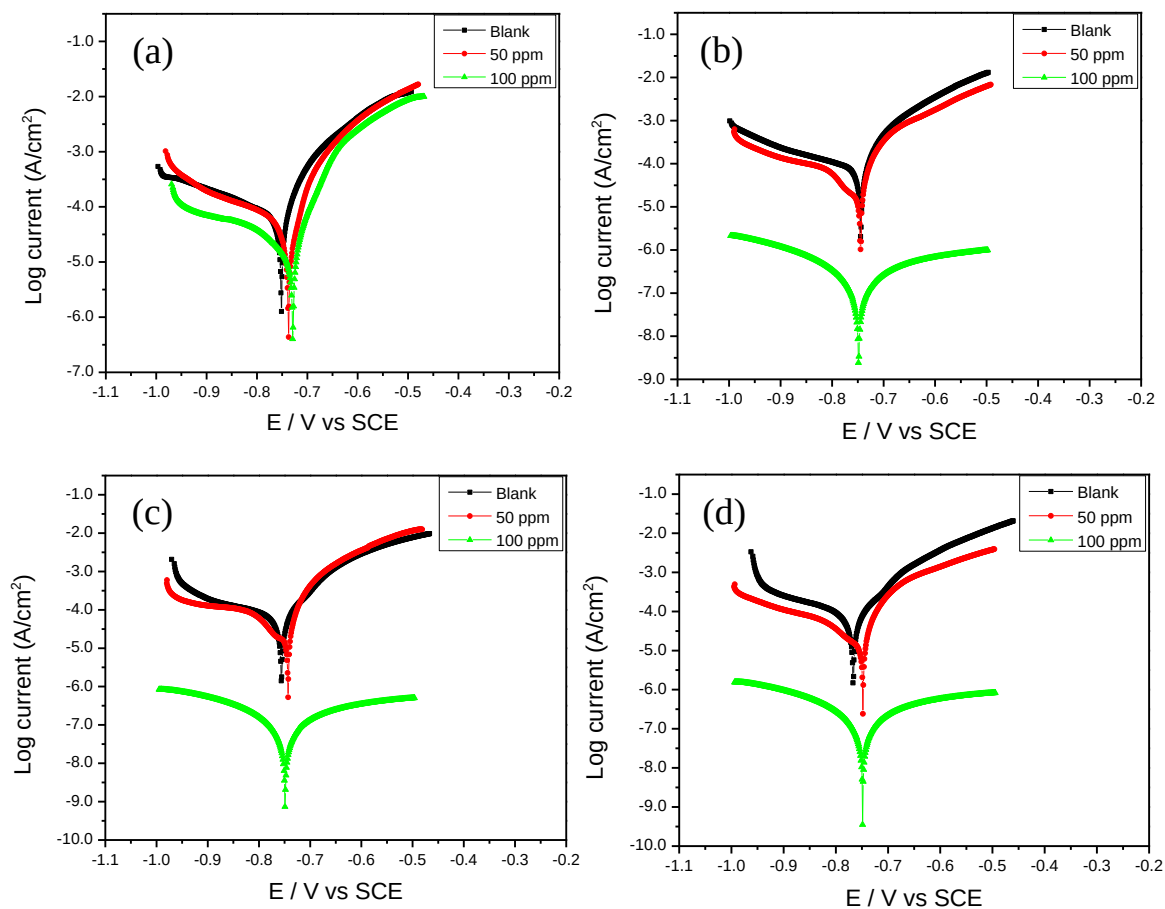


Figure 7.18 Tafel polarization curves of mild steel specimen in 0.5 M NaCl saturated with  $CO_2$  gas in the absence (blank) and presence of PUCorr-2 (50 – 100 ppm) at (a) 298 K, (b) 303 K, (c) 313 K and (d) 323 K

Table 7.6 Tafel polarization data of 200 ppm PuCorr-1 in 5.0 M HCl, and 0.5 M NaCl saturated with CO<sub>2</sub> and H<sub>2</sub>S at 25 °C

| <b>Medium</b>                                 | <b>E<sub>corr</sub> / V vs SCE</b> | <b>i<sub>corr</sub> (μA/cm<sup>2</sup>)</b> | <b>Corrosion rate (mmpy)</b> | <b>θ</b> | <b>η%</b> |
|-----------------------------------------------|------------------------------------|---------------------------------------------|------------------------------|----------|-----------|
| 5 M HCl                                       | -0.507                             | 1020.0                                      | 11.80                        | --       | --        |
| 5M HCl + PuCorr-1                             | -0.511                             | 2.90                                        | 0.03                         | 0.997    | 99.7      |
| 0.5 M NaCl                                    | -0.699                             | 5.02                                        | 0.06                         | --       | --        |
| 0.5 M NaCl + PuCorr-1                         | -0.634                             | 0.26                                        | 0.003                        | 0.948    | 94.8      |
| 0.5 M NaCl, sat'd CO <sub>2</sub>             | -0.682                             | 517.0                                       | 6.01                         | --       | --        |
| 0.5 M NaCl, sat'd CO <sub>2</sub> + PuCorr-1  | -0.731                             | 14.20                                       | 0.16                         | 0.972    | 97.2      |
| 0.5 M NaCl, sat'd H <sub>2</sub> S            | -0.815                             | 36.80                                       | 0.43                         | --       | --        |
| 0.5 M NaCl, sat'd H <sub>2</sub> S + PuCorr-1 | -0.705                             | 1.96                                        | 0.02                         | 0.947    | 94.7      |

Table 7.7 Tafel polarization data of mild steel in 0.5 M NaCl saturated with CO<sub>2</sub> in the absence and presence of PUCorr-2

| Temperature (K) | Medium   | Inhibitor Conc. (ppm) | E <sub>corr</sub> / V vs SCE | i <sub>corr</sub> (μA.cm <sup>-2</sup> ) | Corrosion rate (mmpy) | θ              | η%           |
|-----------------|----------|-----------------------|------------------------------|------------------------------------------|-----------------------|----------------|--------------|
| 298             | Blank    | 0                     | -0.752                       | 137.0                                    | 1.592                 | -              | -            |
|                 | PUCorr-2 | 50<br>100             | -0.737<br>-0.729             | 22.60<br>15.70                           | 0.262<br>0.183        | 0.835<br>0.885 | 83.5<br>88.5 |
| 303             | Blank    | 0                     | -0.744                       | 182.0                                    | 2.112                 | -              | -            |
|                 | PUCorr-2 | 50<br>100             | -0.745<br>-0.748             | 20.10<br>1.15                            | 0.233<br>0.013        | 0.889<br>0.994 | 88.9<br>99.4 |
| 313             | Blank    | 0                     | -0.756                       | 154.0                                    | 1.790                 | -              | -            |
|                 | PUCorr-2 | 50<br>100             | -0.743<br>-0.749             | 18.80<br>0.37                            | 0.218<br>0.004        | 0.877<br>0.997 | 87.7<br>99.7 |
| 323             | Blank    | 0                     | -0.767                       | 242.0                                    | 2.809                 | -              | -            |
|                 | PUCorr-2 | 50<br>100             | -0.748<br>-0.749             | 21.30<br>1.19                            | 0.247<br>1.19         | 0.912<br>0.995 | 91.2<br>99.5 |

### 7.3.3 Surface characterization studies

To further investigate the corrosion inhibitive action of the polymer materials, mild steel specimens were immersed in 1.0 M HCl in the absence and presence of 100 ppm PUCorr-1, and in 0.5 M NaCl in the absence and presence of 100 ppm PUCorr-2 at 25 °C for 24 h. The specimens were then rinsed with anhydrous ethanol, dried in a stream of nitrogen and SEM micrographs were recorded as shown in Figs. 7.19 and 7.20. Morphological features of the specimens immersed in 1.0 M HCl without the inhibitor

molecule shows an evidence of pitting corrosion. These pits were, however, absent on the specimens immersed in a solution containing both 1.0 M HCl and PUCorr-1 indicating the formation of protective films on the mild steel surface. The specimen immersed in 0.5 M NaCl (Fig. 7.20b) showed evidence of severe corrosion as compared to the bare specimen (Fig. 7.20a). With addition of CO<sub>2</sub> (Fig. 7.20c), there was further formation of corrosion products on the metal surface. However, on the specimen containing 100 ppm PUCorr-2 (Fig. 7.20d) these corrosion products were absent and the surface of the metal appeared covered by the adsorbed inhibitor molecules. This clearly demonstrates the corrosion inhibitive performance of PUCorr-2 in saline media.

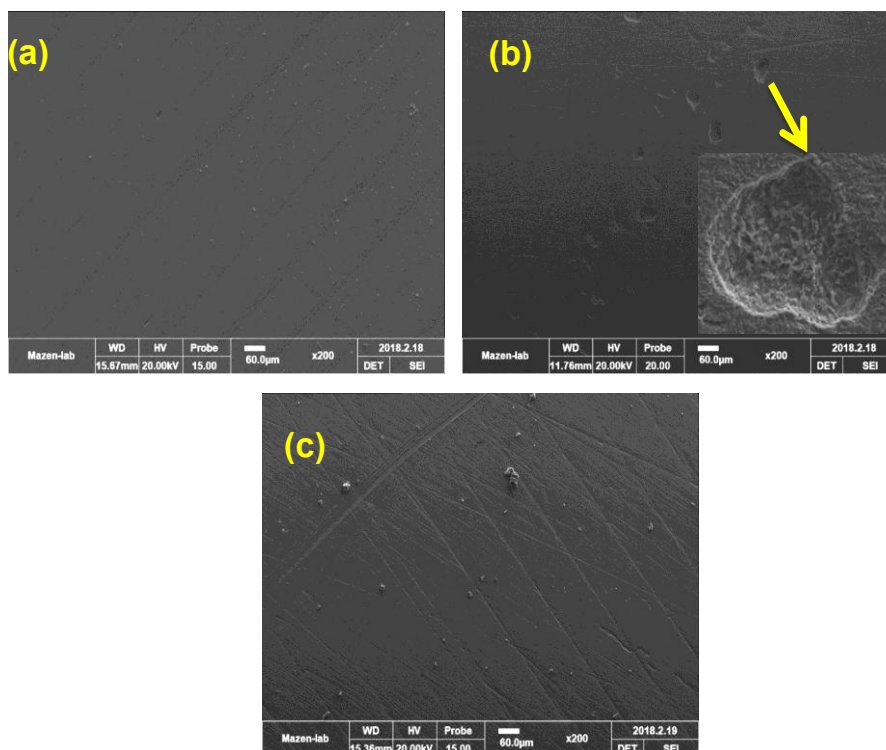


Figure 7.19 SEM micrographs of mild steel specimens (a) before immersion in 1.0 M HCl, (b) after immersion in 1.0 M HCl in the absence of PUCorr-1, and (c) after immersion in 1.0 M HCl in the presence of PUCorr-1 at 25 oC for 24 h

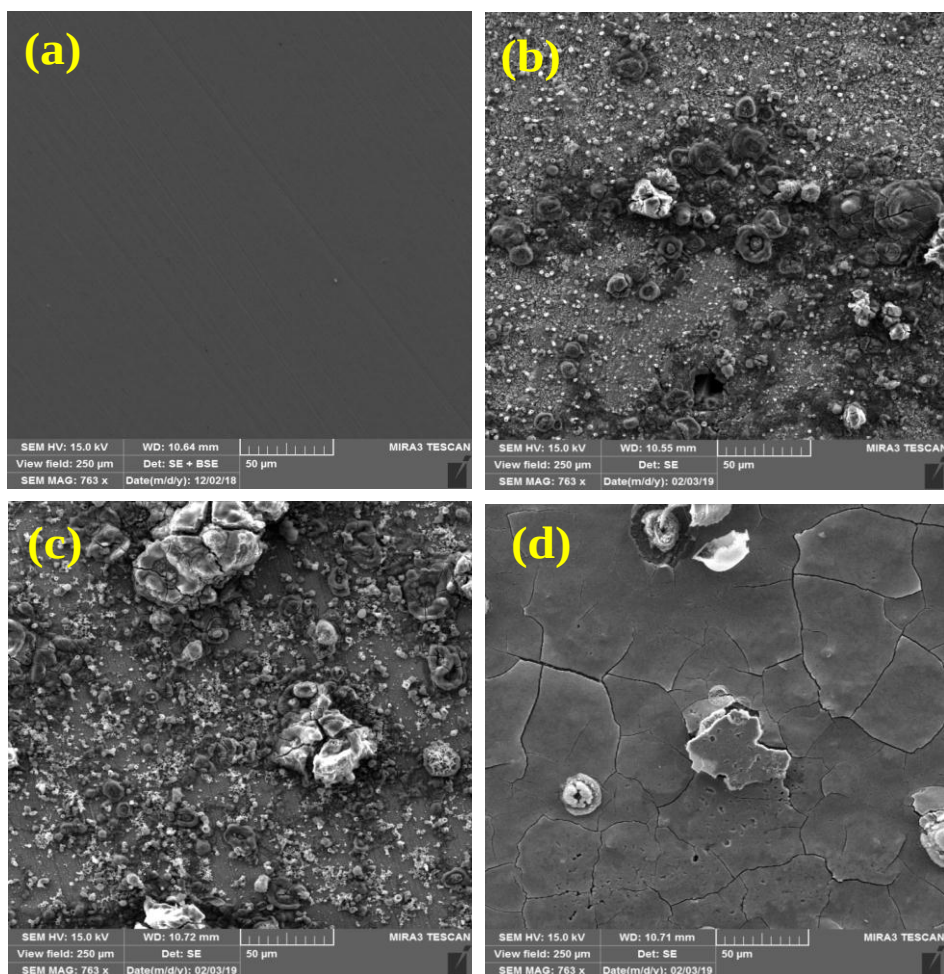


Figure 7.20 SEM micrographs of mild steel specimen (a) before immersion in 0.5 M NaCl, (b) after immersion in 0.5 M NaCl without inhibitor, (c) after immersion in 0.5 M NaCl saturated with CO<sub>2</sub> without inhibitor and (d) after immersion in 0.5 M NaCl in the presence of 100 ppm PUCorr-2 at 298 K for 24 h

Elemental composition of the adsorbed inhibitor molecules (PUCorr-1 and PUCorr-2) on mild steel specimen were further investigated by x-ray photoelectron spectroscopy (XPS) analysis. Data for PUCorr-2 are however presented in detail. High resolution XPS spectra of mild steel specimen immersed in 0.5 M NaCl saturated with CO<sub>2</sub> in the absence of

inhibitor molecules are presented in Fig. 8. The C1s spectrum after deconvolution (Fig. 7.21a) was fitted into three distinct peaks at 284.5 eV, 286.2 eV and 289.0 eV. The peak at 284.5 eV was assigned to  $sp^2$  carbon atoms, while the peaks at 286.2 eV and 289.0 eV were assigned to C-O and O-C=O, respectively [144]. The Cl2p spectrum (Fig. 7.21b) was fitted into a single peak at 198.5 eV corresponding to alkali chloride present on the surface of the metal. The O1s spectrum after deconvolution gave three distinct peaks at 529.0 eV, 531.0 eV and 534.0 eV (Fig. 7.21c). The peak at 529.0 eV was assigned to iron (II) in the form of FeO, while the peaks at 531.0 eV and 534.0 eV represents surface oxygens as a result of water chemisorption to form  $Fe(OH)_2$ , and carbonyl oxygen of the carbonate, respectively [117, 144]. Fe2p spectrum (Fig. 7.21d) consists of three peaks at 711.0 eV ( $Fe2p_{3/2}$ ), 725.0 eV ( $Fe2p_{1/2}$ ) and a satellite peak at 719.0 eV representing  $\alpha$ - $Fe_2O_3$  [121]. The fitted Fe2p spectrum reveals the presence of Fe in the ferric (712.5 eV) and ferrous (710.0 eV) forms almost at the same proportion. The presence of the ferric species is due to the oxidation of ferrous species of iron during the course of corrosion of the steel specimen. As for mild steel specimen immersed in 0.5 M NaCl saturated with  $CO_2$  in the presence of the inhibitor (Fig. 7.22), the C1s spectrum (Fig. 7.22a) in addition to the already assigned peaks in the blank solution gave two additional peaks at 285.0 eV and 288.0 eV corresponding to C-OH and C=O, respectively. The N1s spectrum (Fig. 7.22b) was fitted into three peaks at 398.0 eV, 400.0 eV and 402.0 eV which were assigned to pyridinic, pyrrolic and graphitic nitrogen atoms, respectively [145]. The O1s spectrum (Fig. 7.22c) also gave peaks similar to that of the blank specimen with an additional peak at 530.0 eV which represents characteristic peak of  $\alpha$ - $Fe_2O_3$  [117], while the Fe2p spectrum (Fig. 7.22d) gave characteristic peaks similar to that of the blank

specimen. The overall XPS data confirms the adsorption of PUCorr-2 onto mild steel specimen and is in agreement with other experimental results.

To investigate the change in surface characteristics of the mild steel as a result of adsorption of the inhibitor molecules, contact angle measurements were carried out on specimen immersed in 0.5 M NaCl with and without PUCorr-2 for 24 h (Fig. 7.23). The results showed the presence of adsorbed hydrophilic PUCorr-2 films on the mild steel surface as the wettability features changes significantly yielding contact angles of  $106^{\circ}$  (bare steel),  $67^{\circ}$  (steel immersed in 0.5 M NaCl), and  $43^{\circ}$ ,  $32^{\circ}$  and  $17^{\circ}$  for specimen immersed in 0.5 M NaCl containing 20 ppm, 50 ppm and 100 ppm PUCorr-2, respectively. Furthermore, the thin adsorbed film was scratched off and subjected to FT-IR analysis (Fig. 24). The results revealed the presence of adsorbed polymer species on the mild steel specimen as vibrational bands assigned to the functional groups in PUCorr-2 appeared in the adsorbed specie. In addition, the  $\text{-NH}$  bend and/or  $\text{C}=\text{C}$  stretch band at  $1550\text{ cm}^{-1}$  appeared broadened in the adsorbed specie due to bonding to Fe ions [146]. Furthermore, the  $\text{-NH}$  wag absorption band at  $650\text{ cm}^{-1}$  also appeared broadened and increased in intensity. Results from adsorption and spectroscopic studies, therefore, suggest that the polymers form chemically adsorbed thin films on mild steel, serving as a firm barrier which isolates the metal from the corrosive medium and leads to a decrease in corrosion attack.

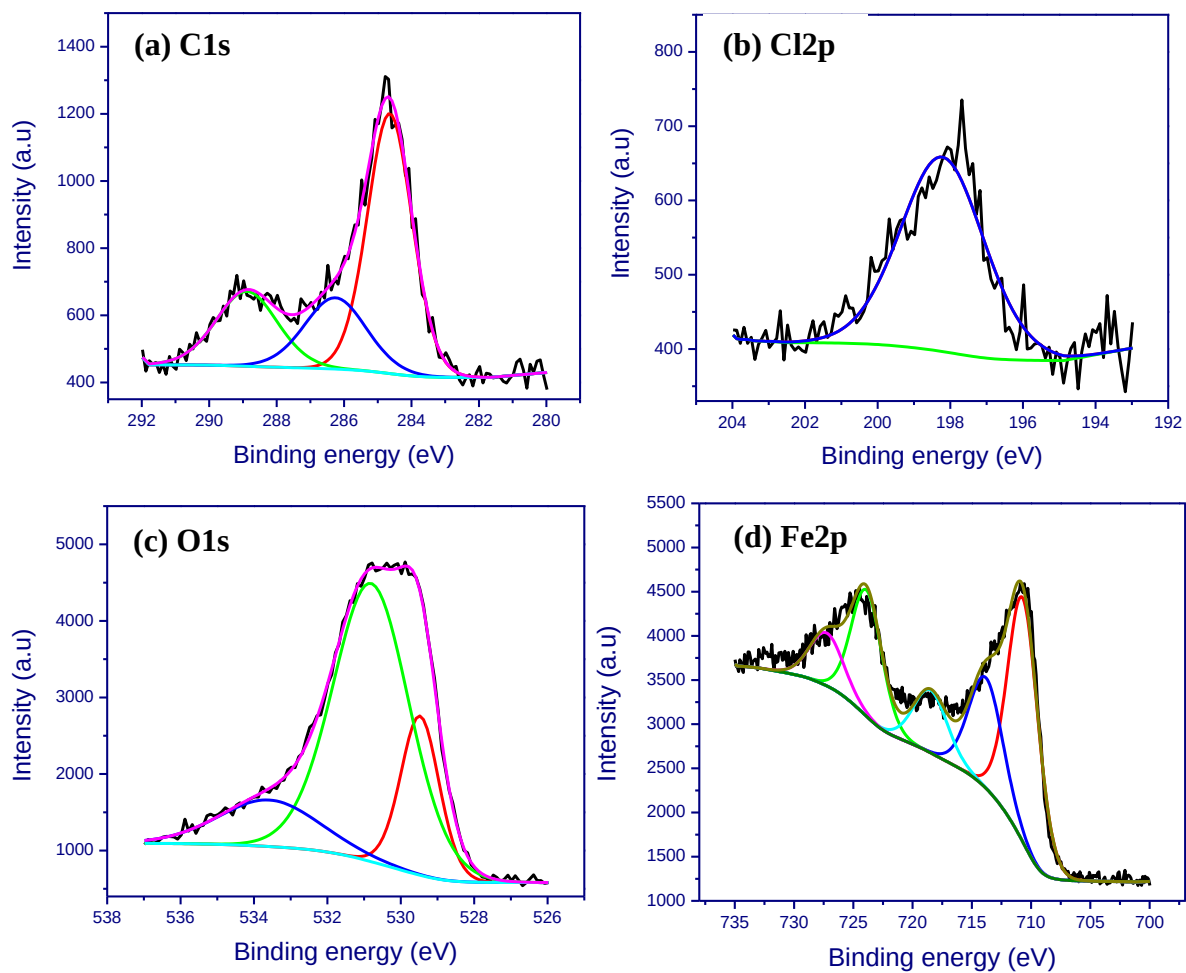


Figure 7.21 High resolution (a) C1s, (b) Cl2p, (c) O1s and (d) Fe2p spectra of mild steel specimen immersed in 0.5 M NaCl saturated with CO<sub>2</sub> in the absence of inhibitor molecule

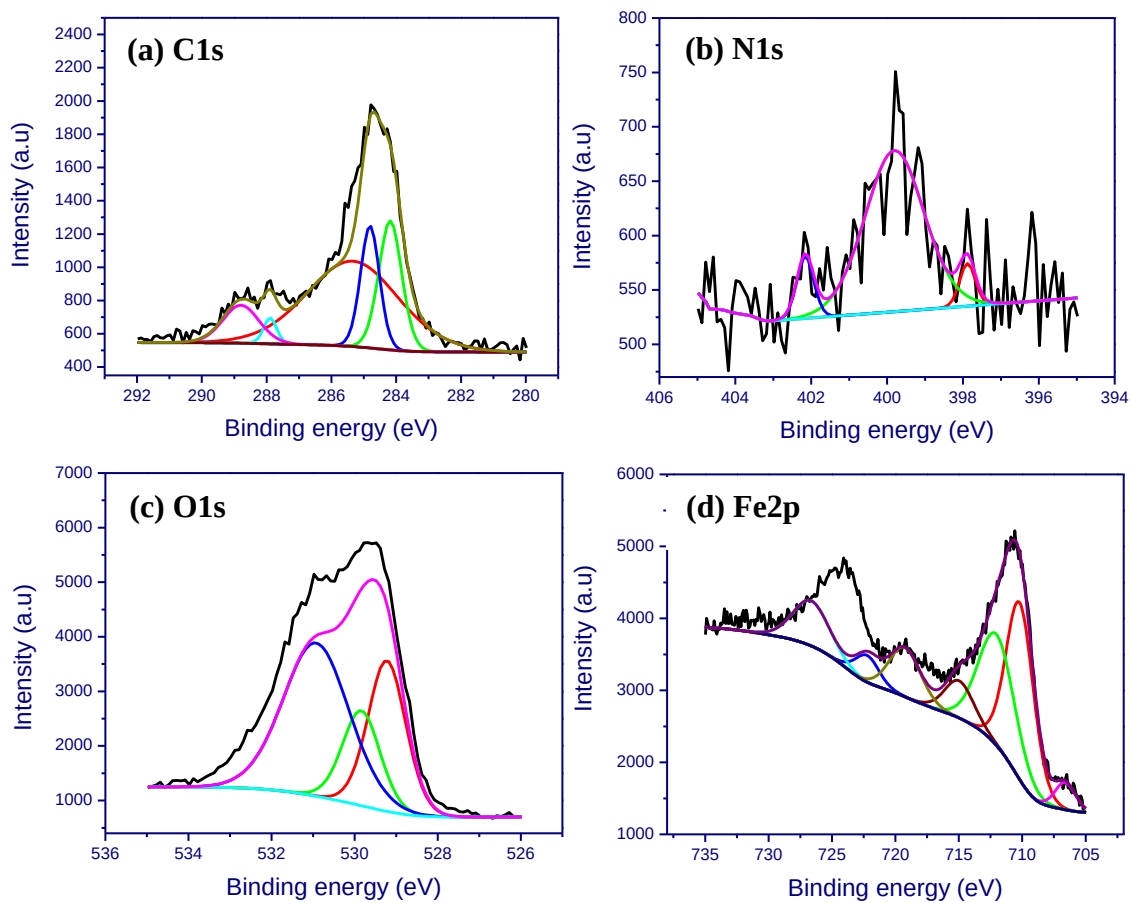


Figure 7.22 High resolution (a) C1s, (b) N1s, (c) O1s and (d) Fe2p spectra of mild steel specimen immersed in 0.5 M NaCl saturated with CO<sub>2</sub> in the absence of inhibitor molecule

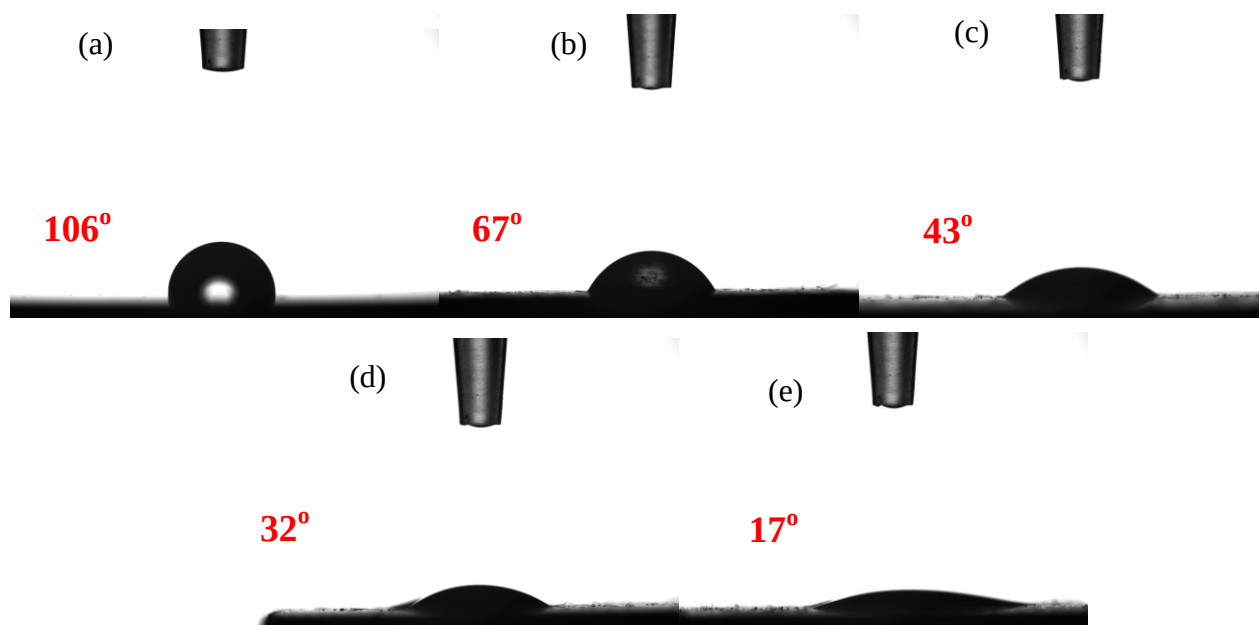


Figure 7.23 Water droplet contact angle of (a) bare mild steel, (b) mild steel specimen immersed in 0.5 M NaCl in the absence of PUCorr-2 and (c) – (e) mild steel specimen immersed in 0.5 M NaCl containing 20 ppm, 50 ppm and 100 ppm PUCorr-2, respectively

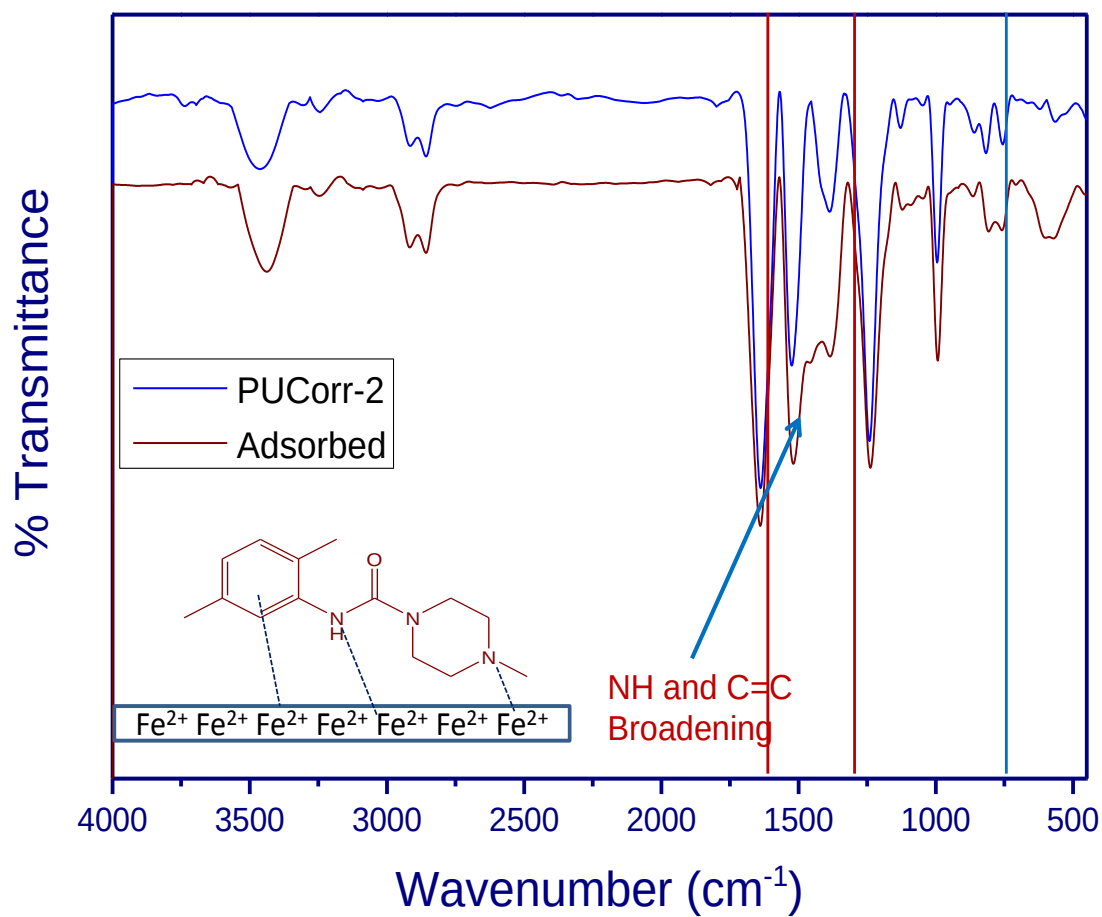


Figure 7.24 FT-IR spectra of PUCorr-2 and adsorbed species

### 7.3.4 DFT studies

Conformational properties and stabilities of the tautomeric forms of PUCorr-2 before and during interaction with atoms of the metal to form inhibitor-metal complex was further investigated using DFT calculations. Although the tautomeric forms of the inhibitor

displays comparable stabilities, the keto tautomer was predicted to be more stable by a factor of around 16 kcal/mol as shown in Fig. 7.25a. This implies that although the preferred geometry of PUCorr-2 in an un-complexed form is the keto-a form, it undergoes an intra-molecular proton transfer to form the enol-b tautomer prior to adsorption on the metal surface, as evidenced from XPS analysis results. Furthermore, molecular properties of the molecules were investigated to gain insight into the possible reactivities of the tautomers and to relate their donor-acceptor properties to PUCorr-2 corrosion potential. It is generally believed that charge transfer properties of any given molecule are a function of the spatial orientation of its frontier orbitals and the energy gap maintained therein. Frontier orbital analysis of the molecules (Fig. 25b) showed that the HOMO-LUMO orbitals were fairly distributed across the molecules, while the electron density around the phenyl and nitrogen fragments predicts more interactions with atoms of the metal within these sites [147, 148]. Other reactivity descriptors (Table 7.8) such as electronegativity ( $\chi$ ), global hardness ( $\eta$ ), electrophilicity ( $\omega$ ) and fraction of transferred electrons ( $\Delta N$ ) further indicated that whereas in a neutral medium, keto-a exhibit higher tendency towards corrosion inhibition, a greater fraction of the inhibitive properties of PUCorr-2 in acidic medium comes from enol-b tautomer [115, 149].

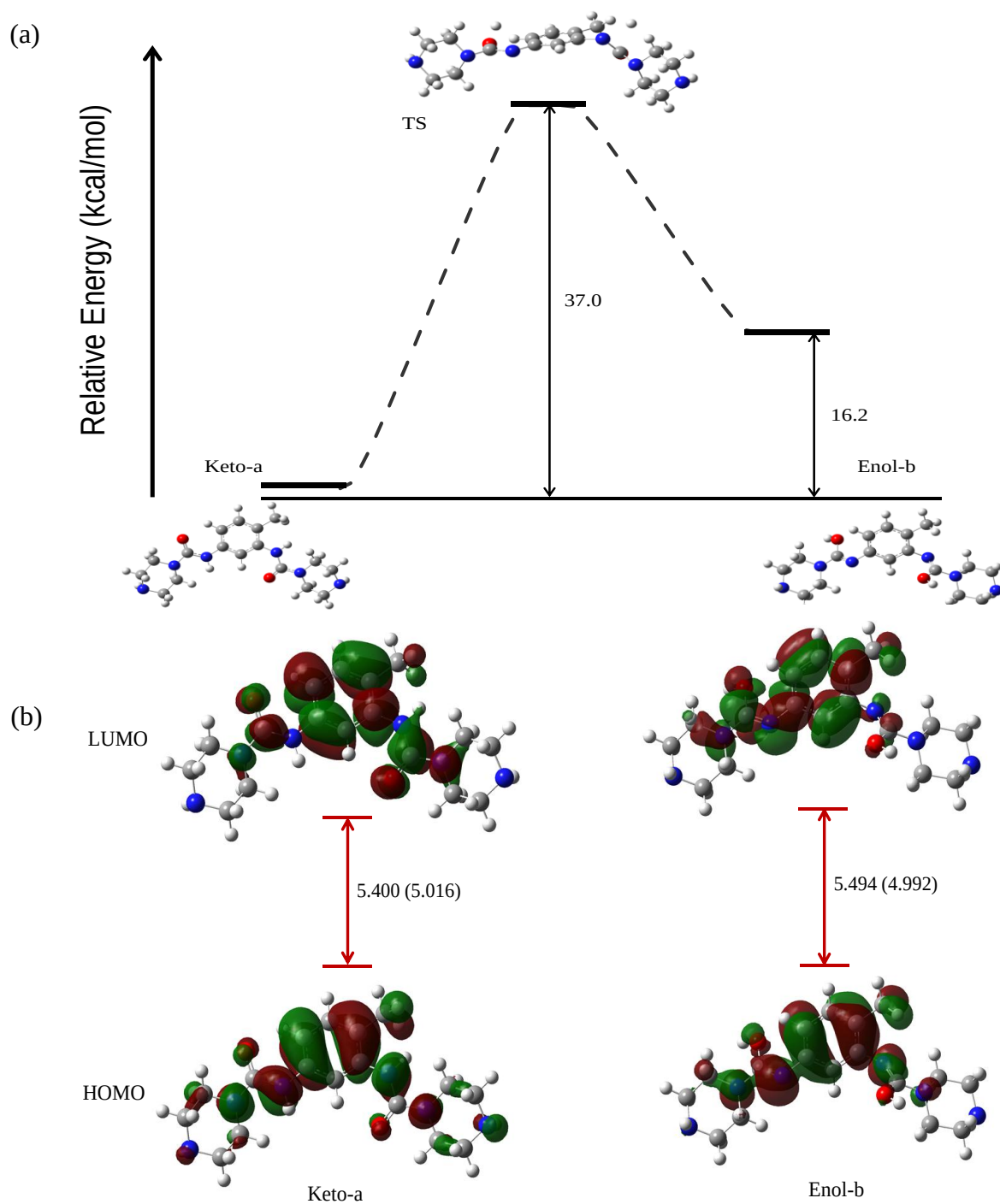


Figure 7.25 (a) Proposed step-wise keto-enol tautomerization of PUCorr-2 prior to adsorption onto metal surface, (b) frontier orbital distribution across the molecules; values in parenthesis represent protonated molecules

Table 7.8 Quantum chemical reactivity descriptors of inhibitor at B3LYP/6-31G(d)

| Parameter              | Non-protonated |        | Protonated |        |
|------------------------|----------------|--------|------------|--------|
|                        | Keto-a         | Enol-b | Keto-a     | Enol-b |
| $E_{\text{HOMO}}$ (eV) | -5.510         | -5.407 | -6.170     | -6.112 |
| $E_{\text{LUMO}}$ (eV) | -0.109         | 0.087  | -1.153     | -1.120 |
| $\Delta E$ (eV)        | 5.400          | 5.494  | 5.016      | 4.992  |
| $\eta$ (eV)            | 2.700          | 2.747  | 2.508      | 2.496  |
| $\chi$ (eV)            | 2.810          | 2.660  | 3.662      | 3.616  |
| $\omega$ (eV)          | 1.462          | 1.288  | 2.673      | 2.620  |
| $\Delta N$             | 0.776          | 0.790  | 0.665      | 0.678  |

## 7.4 Summary

Polyurea-based organic polymers (PUCorr-1 and PUCorr-2) were successfully synthesized and tested as inhibitors of mild steel corrosion in acidic and saline media. Quantum chemical DFT calculations revealed that the polymers maintain high electron density across their structural network and on the nitrogen, oxygen and the pi-system. Electrochemical corrosion tests, supported with surface characterization studies revealed that PUCorr-1 and PUCorr-2 adsorbs onto mild steel yielding stable films through chemisorption mechanism. Corrosion resistance of both polymers were noticed to increase with increase in the temperature and concentration of resulting with an excellent inhibition efficiency of 99.9% at 100 ppm and a temperature of 50 °C for PUCorr-1 and 99.9% and 99.2% for PUCorr-2 in acidic and saline media, respectively. In the presence of CO<sub>2</sub> and H<sub>2</sub>S gases, the polymers exhibited remarkable inhibition efficiencies making them potential corrosion inhibitors in aggressive industrial environments.

## CHAPTER 8

### SUMMARY, GENERAL CONCLUSION AND RECOMMENDATIONS

#### 8.1 Summary and conclusion

Mechanistic studies on the inhibition of mild steel corrosion by imidazole derivatives and the role played by various substituent groups has been carried out using periodic slab density functional theory (DFT) calculations, electrochemical corrosion measurements and surface characterization studies. From the results of the study conducted, the following can be summarized:

1. The presence of substituent groups on organic corrosion inhibitors plays a significant role on their corrosion inhibitive performance.
2. The role played by the substituents however varies. For simple molecules; the greater the ease of dissociation of the substituents, the higher the inhibitive performance. While for moderate to large molecules; the stronger the electron donation capability, the more effective the molecules as corrosion inhibitors.
3. The presence of aromaticity, pi system and donor heteroatoms such as O, N, S significantly enhances the corrosion inhibitive performance of organic molecules.
4. For high temperature and extremely harsh industrial environments in the presence of CO<sub>2</sub> and H<sub>2</sub>S gases, large polymeric inhibitors containing multiple heteroatoms and pi systems are preferable due to their tendency to adsorb and completely

isolate the metal from the aggressive environment. Whereas, for low temperature regions simple organic molecules are sufficient.

## **8.2 Recommendations for future studies**

Based on the outcomes of the present study, the following recommendations are provided:

1. A detailed quantitative structure-activity relationship (QSAR) model capable of predicting the inhibition efficiencies of both simple and polymeric organic molecules should be developed. This will further reduce the time and efforts spent in the design of effective corrosion inhibitors.
2. In-situ corrosion study systems should be developed capable of monitoring corrosion processes at a faster rate. This will provide more experimental details on the underlying mechanism of action of corrosion inhibitors.
3. A formulation comprising of simple organic molecules should be developed and investigated for harsh corrosion studies. This will reduce the efforts spent in the synthesis of polymeric corrosion inhibitors.
4. Lastly, as the present study mainly focused on mild steel corrosion inhibition studies, it is recommended that such studies be extended to other metals and alloys such as copper and aluminum to evaluate the inhibitive performance of organic molecules under various corrosive environments.

## References

- [1] Q. Sheng, K.C.d. Silveira, W. Tian, C. Fong, N. Maeda, R. Gubner, C.D. Wood, Simultaneous Hydrate and Corrosion Inhibition with Modified Poly(vinyl caprolactam) Polymers, *Energy & Fuels*, 31 (2017) 6724-6731.
- [2] J.J. Moloney, W.Y. Mok, C.G. Gamble, Compatible Corrosion And Kinetic Hydrate Inhibitors For Wet Sour Gas Transmission Lines, in: *CORROSION 2009*, NACE International, Atlanta, Georgia, 2009, pp. 23.
- [3] C.I. Ossai, B. Boswell, I.J. Davies, Pipeline failures in corrosive environments – A conceptual analysis of trends and effects, *Engineering Failure Analysis*, 53 (2015) 36-58.
- [4] D. Guzonas, R. Novotny, S. Penttilä, A. Toivonen, W. Zheng, 5 - Corrosion, in: D. Guzonas, R. Novotny, S. Penttilä, A. Toivonen, W. Zheng (Eds.) *Materials and Water Chemistry for Supercritical Water-cooled Reactors*, Woodhead Publishing, 2018, pp. 139-218.
- [5] L.A.C.J. Garcia, C.J.B.M. Joia, E.M. Cardoso, O.R. Mattos, Electrochemical methods in corrosion on petroleum industry: laboratory and field results, *Electrochimica Acta*, 46 (2001) 3879-3886.
- [6] I.B. Obot, E.E. Ebenso, M.M. Kabanda, Metronidazole as environmentally safe corrosion inhibitor for mild steel in 0.5M HCl: Experimental and theoretical investigation, *Journal of Environmental Chemical Engineering*, 1 (2013) 431-439.
- [7] F. Farelàs, M. Galicia, B. Brown, S. Nesic, H. Castaneda, Evolution of dissolution processes at the interface of carbon steel corroding in a CO<sub>2</sub> environment studied by EIS, *Corrosion Science*, 52 (2010) 509-517.
- [8] L.T. Popoola, A.S. Grema, G.K. Latinwo, B. Gutti, A.S. Balogun, Corrosion problems during oil and gas production and its mitigation, *International Journal of Industrial Chemistry*, 4 (2013) 35.

- [9] Q. Mahmood, A.F. Khan, A. Khan, Chapter 25 - Colloids in the Environmental Protection—Current and Future Trends A2 - Fanun, Monzer, in: *The Role of Colloidal Systems in Environmental Protection*, Elsevier, Amsterdam, 2014, pp. 635-677.
- [10] B.D.B. Tiu, R.C. Advincula, Polymeric corrosion inhibitors for the oil and gas industry: Design principles and mechanism, *Reactive and Functional Polymers*, 95 (2015) 25-45.
- [11] A. Zeino, I. Abdulazeez, M. Khaled, M.W. Jawich, I.B. Obot, Mechanistic study of polyaspartic acid (PASP) as eco-friendly corrosion inhibitor on mild steel in 3% NaCl aerated solution, *Journal of Molecular Liquids*, 250 (2018) 50-62.
- [12] S. Saker, N. Aliouane, H. Hammache, S. Chafaa, G. Bouet, Tetraphosphonic acid as eco-friendly corrosion inhibitor on carbon steel in 3 % NaCl aqueous solution, *Ionics*, 21 (2015) 2079-2090.
- [13] H. Ju, Z.-P. Kai, Y. Li, Aminic nitrogen-bearing polydentate Schiff base compounds as corrosion inhibitors for iron in acidic media: A quantum chemical calculation, *Corrosion Science*, 50 (2008) 865-871.
- [14] J. Aljourani, K. Raeissi, M.A. Golozar, Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1M HCl solution, *Corrosion Science*, 51 (2009) 1836-1843.
- [15] Y. Zhu, M.L. Free, R. Woollam, W. Durnie, A review of surfactants as corrosion inhibitors and associated modeling, *Progress in Materials Science*, 90 (2017) 159-223.
- [16] A. Igual Muñoz, J. García Antón, J.L. Guiñón, V. Pérez Herranz, Inhibition effect of chromate on the passivation and pitting corrosion of a duplex stainless steel in LiBr solutions using electrochemical techniques, *Corrosion Science*, 49 (2007) 3200-3225.
- [17] H.-S. Ryu, J.K. Singh, H.-S. Lee, M.A. Ismail, W.-J. Park, Effect of LiNO<sub>2</sub> inhibitor on corrosion characteristics of steel rebar in saturated Ca(OH)<sub>2</sub> solution containing NaCl: An electrochemical study, *Construction and Building Materials*, 133 (2017) 387-396.

- [18] A.A. Olajire, Corrosion inhibition of offshore oil and gas production facilities using organic compound inhibitors - A review, *Journal of Molecular Liquids*, 248 (2017) 775-808.
- [19] C. Andrade, C. Alonso, Corrosion rate monitoring in the laboratory and on-site, *Construction and Building Materials*, 10 (1996) 315-328.
- [20] F. Mansfeld, K.B. Oldham, A modification of the Stern—Geary linear polarization equation, *Corrosion Science*, 11 (1971) 787-796.
- [21] J. Vosta, J. Eliášek, Study on corrosion inhibition from aspect of quantum chemistry, *Corrosion Science*, 11 (1971) 223-229.
- [22] L. Feng, H. Yang, F. Wang, Experimental and theoretical studies for corrosion inhibition of carbon steel by imidazoline derivative in 5% NaCl saturated Ca(OH)<sub>2</sub> solution, *Electrochimica Acta*, 58 (2011) 427-436.
- [23] I. Lukovits, I. Bakó, A. Shaban, E. Kálmán, Polynomial model of the inhibition mechanism of thiourea derivatives, *Electrochimica Acta*, 43 (1998) 131-136.
- [24] J.M. Roque, T. Pandiyan, J. Cruz, E. García-Ochoa, DFT and electrochemical studies of tris(benzimidazole-2-ylmethyl)amine as an efficient corrosion inhibitor for carbon steel surface, *Corrosion Science*, 50 (2008) 614-624.
- [25] K.F. Khaled, Modeling corrosion inhibition of iron in acid medium by genetic function approximation method: A QSAR model, *Corrosion Science*, 53 (2011) 3457-3465.
- [26] A. Zeino, I. Abdulazeez, M. Khaled, M.W. Jawich, I.B. Obot, Mechanistic study of polyaspartic acid (PASP) as eco-friendly corrosion inhibitor on mild steel in 3% NaCl aerated solution, *Journal of Molecular Liquids*, (2017).
- [27] X. Zheng, M. Gong, Q. Li, L. Guo, Corrosion inhibition of mild steel in sulfuric acid solution by loquat (*Eriobotrya japonica* Lindl.) leaves extract, *Scientific Reports*, 8 (2018) 9140.

- [28] D. Gopi, E.-S.M. Sherif, M. Surendiran, M. Jothi, P. Kumaradhas, L. Kavitha, Experimental and theoretical investigations on the inhibition of mild steel corrosion in the ground water medium using newly synthesised bipodal and tripodal imidazole derivatives, *Materials Chemistry and Physics*, 147 (2014) 572-582.
- [29] A. Ismail, H.M. Irshad, A. Zeino, I.H. Toor, Electrochemical Corrosion Performance of Aromatic Functionalized Imidazole Inhibitor Under Hydrodynamic Conditions on API X65 Carbon Steel in 1 M HCl Solution, *Arabian Journal for Science and Engineering*, (2019).
- [30] M.B. Petrović Mihajlović, M.B. Radovanović, Ž.Z. Tasić, M.M. Antonijević, Imidazole based compounds as copper corrosion inhibitors in seawater, *Journal of Molecular Liquids*, 225 (2017) 127-136.
- [31] I. Abdulazeez, A. Zeino, C.W. Kee, A.A. Al-Saadi, M. Khaled, M.W. Wong, A.A. Al-Sunaidi, Mechanistic studies of the influence of halogen substituents on the corrosion inhibitive efficiency of selected imidazole molecules: A synergistic computational and experimental approach, *Applied Surface Science*, 471 (2019) 494-505.
- [32] K.R. Ansari, M.A. Quraishi, A. Singh, Pyridine derivatives as corrosion inhibitors for N80 steel in 15% HCl: Electrochemical, surface and quantum chemical studies, *Measurement*, 76 (2015) 136-147.
- [33] M. Bobina, A. Kellenberger, J.-P. Millet, C. Muntean, N. Vaszilcsin, Corrosion resistance of carbon steel in weak acid solutions in the presence of l-histidine as corrosion inhibitor, *Corrosion Science*, 69 (2013) 389-395.
- [34] B.D. Mert, M. Erman Mert, G. Kardaş, B. Yazıcı, Experimental and theoretical investigation of 3-amino-1,2,4-triazole-5-thiol as a corrosion inhibitor for carbon steel in HCl medium, *Corrosion Science*, 53 (2011) 4265-4272.
- [35] J. Aljourani, M.A. Golozar, K. Raeissi, The inhibition of carbon steel corrosion in hydrochloric and sulfuric acid media using some benzimidazole derivatives, *Materials Chemistry and Physics*, 121 (2010) 320-325.

- [36] V.V. Gite, P.D. Tatiya, R.J. Marathe, P.P. Mahulikar, D.G. Hundiware, Microencapsulation of quinoline as a corrosion inhibitor in polyurea microcapsules for application in anticorrosive PU coatings, *Progress in Organic Coatings*, 83 (2015) 11-18.
- [37] G. Bereket, E. Hür, C. Öğretir, Quantum chemical studies on some imidazole derivatives as corrosion inhibitors for iron in acidic medium, *Journal of Molecular Structure: THEOCHEM*, 578 (2002) 79-88.
- [38] K.F. Khaled, Experimental and theoretical study for corrosion inhibition of mild steel in hydrochloric acid solution by some new hydrazine carbodithioic acid derivatives, *Applied Surface Science*, 252 (2006) 4120-4128.
- [39] M. Yadav, S. Kumar, T. Purkait, L.O. Olasunkanmi, I. Bahadur, E.E. Ebenso, Electrochemical, thermodynamic and quantum chemical studies of synthesized benzimidazole derivatives as corrosion inhibitors for N80 steel in hydrochloric acid, *Journal of Molecular Liquids*, 213 (2016) 122-138.
- [40] K.F. Khaled, M.M. Al-Qahtani, The inhibitive effect of some tetrazole derivatives towards Al corrosion in acid solution: Chemical, electrochemical and theoretical studies, *Materials Chemistry and Physics*, 113 (2009) 150-158.
- [41] M.A. Hegazy, M. Abdallah, M.K. Awad, M. Rezk, Three novel di-quaternary ammonium salts as corrosion inhibitors for API X65 steel pipeline in acidic solution. Part I: Experimental results, *Corrosion Science*, 81 (2014) 54-64.
- [42] J. Haque, V. Srivastava, D.S. Chauhan, H. Lgaz, M.A. Quraishi, Microwave-Induced Synthesis of Chitosan Schiff Bases and Their Application as Novel and Green Corrosion Inhibitors: Experimental and Theoretical Approach, *ACS Omega*, 3 (2018) 5654-5668.
- [43] M.M. Antonijevic, M.B. Petrovic, Copper corrosion inhibitors. A review, *International Journal of Electrochemical Science*, 3 (2008) 1-28.

- [44] Z. Zhang, S. Chen, Y. Li, S. Li, L. Wang, A study of the inhibition of iron corrosion by imidazole and its derivatives self-assembled films, *Corrosion Science*, 51 (2009) 291-300.
- [45] H. Otmacic Curkovic, E. Stupnisek-Lisac, H. Takenouti, The influence of pH value on the efficiency of imidazole based corrosion inhibitors of copper, *Corrosion Science*, 52 (2010) 398-405.
- [46] M.N. El-Haddad, A.S. Fouda, Electroanalytical, quantum and surface characterization studies on imidazole derivatives as corrosion inhibitors for aluminum in acidic media, *Journal of Molecular Liquids*, 209 (2015) 480-486.
- [47] I.B. Obot, S.A. Umoren, Z.M. Gasem, R. Suleiman, B.E. Ali, Theoretical prediction and electrochemical evaluation of vinylimidazole and allylimidazole as corrosion inhibitors for mild steel in 1 M HCl, *Journal of Industrial and Engineering Chemistry*, 21 (2015) 1328-1339.
- [48] L. Zhang, Y. He, Y. Zhou, R. Yang, Q. Yang, D. Qing, Q. Niu, A novel imidazoline derivative as corrosion inhibitor for P110 carbon steel in hydrochloric acid environment, *Petroleum*, 1 (2015) 237-243.
- [49] H.R. Obayes, G.H. Alwan, A.H.M. Alobaidy, A.A. Al-Amiery, A.A.H. Kadhum, A.B. Mohamad, Quantum chemical assessment of benzimidazole derivatives as corrosion inhibitors, *Chemistry Central Journal*, 8 (2014) 21.
- [50] E. Garcia-Ochoa, S.J. Guzmán-Jiménez, J.G. Hernández, T. Pandiyan, J.M. Vásquez-Pérez, J. Cruz-Borbolla, Benzimidazole ligands in the corrosion inhibition for carbon steel in acid medium: DFT study of its interaction on Fe<sub>30</sub> surface, *Journal of Molecular Structure*, 1119 (2016) 314-324.
- [51] H.J. Guadalupe, E. García-Ochoa, P.J. Maldonado-Rivas, J. Cruz, T. Pandiyan, A combined electrochemical and theoretical study of N,N'-bis(benzimidazole-2-yl-ethyl)-1,2-diaminoethane as a new corrosion inhibitor for carbon steel surface, *Journal of Electroanalytical Chemistry*, 655 (2011) 164-172.

- [52] D. Zhang, Y. Tang, S. Qi, D. Dong, H. Cang, G. Lu, The inhibition performance of long-chain alkyl-substituted benzimidazole derivatives for corrosion of mild steel in HCl, *Corrosion Science*, 102 (2016) 517-522.
- [53] E. Gutiérrez, J.A. Rodríguez, J. Cruz-Borbolla, J.G. Alvarado-Rodríguez, P. Thangarasu, Development of a predictive model for corrosion inhibition of carbon steel by imidazole and benzimidazole derivatives, *Corrosion Science*, 108 (2016) 23-35.
- [54] Y. Tang, F. Zhang, S. Hu, Z. Cao, Z. Wu, W. Jing, Novel benzimidazole derivatives as corrosion inhibitors of mild steel in the acidic media. Part I: Gravimetric, electrochemical, SEM and XPS studies, *Corrosion Science*, 74 (2013) 271-282.
- [55] K.O. Sulaiman, A.T. Onawole, Quantum chemical evaluation of the corrosion inhibition of novel aromatic hydrazide derivatives on mild steel in hydrochloric acid, *Computational and Theoretical Chemistry*, 1093 (2016) 73-80.
- [56] I.B. Obot, D.D. Macdonald, Z.M. Gasem, Density functional theory (DFT) as a powerful tool for designing new organic corrosion inhibitors. Part 1: An overview, *Corrosion Science*, 99 (2015) 1-30.
- [57] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *The Journal of Chemical Physics*, 98 (1993) 5648-5652.
- [58] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Physical Review Letters*, 77 (1996) 3865-3868.
- [59] G.L. Gutsev, C.W. Bauschlicher, Electron Affinities, Ionization Energies, and Fragmentation Energies of Fen Clusters (n = 2–6): A Density Functional Theory Study, *The Journal of Physical Chemistry A*, 107 (2003) 7013-7023.
- [60] J. Tomasi, B. Mennucci, R. Cammi, Quantum Mechanical Continuum Solvation Models, *ChemInform*, 36 (2005) 2999-3093.
- [61] K.F. Khaled, Studies of iron corrosion inhibition using chemical, electrochemical and computer simulation techniques, *Electrochimica Acta*, 55 (2010) 6523-6532.

- [62] R.G. Pearson, Absolute electronegativity and hardness: application to inorganic chemistry, *Inorganic Chemistry*, 27 (1988) 734-740.
- [63] M. Mousavi, M. Mohammadalizadeh, A. Khosravan, Theoretical investigation of corrosion inhibition effect of imidazole and its derivatives on mild steel using cluster model, *Corrosion Science*, 53 (2011) 3086-3091.
- [64] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision B.01, in, Wallingford CT, 2009.
- [65] G. Gece, S. Bilgiç, Quantum chemical study of some cyclic nitrogen compounds as corrosion inhibitors of steel in NaCl media, *Corrosion Science*, 51 (2009) 1876-1878.
- [66] A. Popova, M. Christov, S. Raicheva, E. Sokolova, Adsorption and inhibitive properties of benzimidazole derivatives in acid mild steel corrosion, *Corrosion Science*, 46 (2004) 1333-1350.
- [67] R. Sanderson, *Chemical Bonds and Bond Energy* (Academic, New York, 1976), Google Scholar, (1983) 15.
- [68] A. Ghanbari, M.M. Attar, M. Mahdavian, Corrosion inhibition performance of three imidazole derivatives on mild steel in 1M phosphoric acid, *Materials Chemistry and Physics*, 124 (2010) 1205-1209.

- [69] H. Wang, X. Wang, H. Wang, L. Wang, A. Liu, DFT study of new bipyrazole derivatives and their potential activity as corrosion inhibitors, *Journal of Molecular Modeling*, 13 (2007) 147-153.
- [70] P.K. Chattaraj, H. Lee, R.G. Parr, HSAB principle, *Journal of the American Chemical Society*, 113 (1991) 1855-1856.
- [71] R.G. Parr, L.v. Szentpály, S. Liu, Electrophilicity Index, *Journal of the American Chemical Society*, 121 (1999) 1922-1924.
- [72] S.K. Saha, A. Dutta, P. Ghosh, D. Sukul, P. Banerjee, Adsorption and corrosion inhibition effect of Schiff base molecules on the mild steel surface in 1 M HCl medium: a combined experimental and theoretical approach, *Physical Chemistry Chemical Physics*, 17 (2015) 5679-5690.
- [73] I. Lukovits, E. Kálmán, F. Zucchi, Corrosion Inhibitors—Correlation between Electronic Structure and Efficiency, *CORROSION*, 57 (2001) 3-8.
- [74] D. Turcio-Ortega, T. Pandiyan, J. Cruz, E. Garcia-Ochoa, Interaction of Imidazoline Compounds with Fen ( $n = 1-4$  Atoms) as a Model for Corrosion Inhibition: DFT and Electrochemical Studies, *The Journal of Physical Chemistry C*, 111 (2007) 9853-9866.
- [75] P.J. Feibelman, B. Hammer, J.K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe, J. Dumesic, The CO/Pt(111) Puzzle, *The Journal of Physical Chemistry B*, 105 (2001) 4018-4025.
- [76] R.A. Olsen, P.H.T. Philipsen, E.J. Baerends, CO on Pt(111): A puzzle revisited, *The Journal of Chemical Physics*, 119 (2003) 4522-4528.
- [77] D.E. Jiang, E.A. Carter, Adsorption and dissociation of CO on Fe(110) from first principles, *Surface Science*, 570 (2004) 167-177.
- [78] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, *Physical Review B*, 47 (1993) 558-561.

- [79] K.M. Song, A.K. Ray, Ab initio study of cesium chemisorption on the GaAs(110) surface, *Physical Review B*, 50 (1994) 14255-14266.
- [80] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Computational Materials Science*, 6 (1996) 15-50.
- [81] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Physical Review B*, 54 (1996) 11169-11186.
- [82] P.E. Blöchl, Projector augmented-wave method, *Physical Review B*, 50 (1994) 17953-17979.
- [83] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Physical Review B*, 59 (1999) 1758-1775.
- [84] M. Methfessel, A.T. Paxton, High-precision sampling for Brillouin-zone integration in metals, *Physical Review B*, 40 (1989) 3616-3621.
- [85] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, *Physical Review B*, 13 (1976) 5188-5192.
- [86] G. Henkelman, B.P. Uberuaga, H. Jónsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, *The Journal of Chemical Physics*, 113 (2000) 9901-9904.
- [87] S. Choudhary, A. Garg, K. Mondal, Relation Between Open Circuit Potential and Polarization Resistance with Rust and Corrosion Monitoring of Mild Steel, *Journal of Materials Engineering and Performance*, 25 (2016) 2969-2976.
- [88] I. Felhősi, J. Telegdi, G. Pálincás, E. Kálmán, Kinetics of self-assembled layer formation on iron, *Electrochimica Acta*, 47 (2002) 2335-2340.
- [89] M. Talebian, K. Raeissi, M. Atapour, B.M. Fernández-Pérez, Z. Salarvand, S. Meghdadi, M. Amirnasr, R.M. Souto, Inhibitive effect of sodium (E)-4-(4-

nitrobenzylideneamino)benzoate on the corrosion of some metals in sodium chloride solution, *Applied Surface Science*, 447 (2018) 852-865.

[90] A. Yıldırım, M. Çetin, Synthesis and evaluation of new long alkyl side chain acetamide, isoxazolidine and isoxazoline derivatives as corrosion inhibitors, *Corrosion Science*, 50 (2008) 155-165.

[91] H. Hamani, T. Douadi, M. Al-Noaimi, S. Issaadi, D. Daoud, S. Chafaa, Electrochemical and quantum chemical studies of some azomethine compounds as corrosion inhibitors for mild steel in 1M hydrochloric acid, *Corrosion Science*, 88 (2014) 234-245.

[92] R. Solmaz, G. Kardaş, M. Çulha, B. Yazıcı, M. Erbil, Investigation of adsorption and inhibitive effect of 2-mercaptothiazoline on corrosion of mild steel in hydrochloric acid media, *Electrochimica Acta*, 53 (2008) 5941-5952.

[93] G.L.F. Mendonça, S.N. Costa, V.N. Freire, P.N.S. Casciano, A.N. Correia, P.d. Lima-Neto, Understanding the corrosion inhibition of carbon steel and copper in sulphuric acid medium by amino acids using electrochemical techniques allied to molecular modelling methods, *Corrosion Science*, 115 (2017) 41-55.

[94] N.A. Negm, N.G. Kandile, E.A. Badr, M.A. Mohammed, Gravimetric and electrochemical evaluation of environmentally friendly nonionic corrosion inhibitors for carbon steel in 1M HCl, *Corrosion Science*, 65 (2012) 94-103.

[95] N.A. Odewunmi, S.A. Umoren, Z.M. Gasem, Utilization of watermelon rind extract as a green corrosion inhibitor for mild steel in acidic media, *Journal of Industrial and Engineering Chemistry*, 21 (2015) 239-247.

[96] D. Daoud, T. Douadi, H. Hamani, S. Chafaa, M. Al-Noaimi, Corrosion inhibition of mild steel by two new S-heterocyclic compounds in 1 M HCl: Experimental and computational study, *Corrosion Science*, 94 (2015) 21-37.

- [97] M. Jeeva, G.V. Prabhu, M.s. Boobalan, C.M. Rajesh, Interactions and Inhibition Effect of Urea-Derived Mannich Bases on a Mild Steel Surface in HCl, *The Journal of Physical Chemistry C*, 119 (2015) 22025-22043.
- [98] S.M. Shaban, I. Aiad, M.M. El-Sukkary, E.A. Soliman, M.Y. El-Awady, Inhibition of mild steel corrosion in acidic medium by vanillin cationic surfactants, *Journal of Molecular Liquids*, 203 (2015) 20-28.
- [99] R.F.V. Villamil, P. Corio, S.M.L. Agostinho, J.C. Rubim, Effect of sodium dodecylsulfate on copper corrosion in sulfuric acid media in the absence and presence of benzotriazole, *Journal of Electroanalytical Chemistry*, 472 (1999) 112-119.
- [100] H.U. Nwankwo, L.O. Olasunkanmi, E.E. Ebenso, Experimental, quantum chemical and molecular dynamic simulations studies on the corrosion inhibition of mild steel by some carbazole derivatives, *Scientific Reports*, 7 (2017) 2436.
- [101] I.B. Obot, N.O. Obi-Egbedi, Adsorption properties and inhibition of mild steel corrosion in sulphuric acid solution by ketoconazole: Experimental and theoretical investigation, *Corrosion Science*, 52 (2010) 198-204.
- [102] E.E. Oguzie, V.O. Njoku, C.K. Enenebeaku, C.O. Akalezi, C. Obi, Effect of hexamethylpararosaniline chloride (crystal violet) on mild steel corrosion in acidic media, *Corrosion Science*, 50 (2008) 3480-3486.
- [103] I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, Antifungal drugs as corrosion inhibitors for aluminium in 0.1M HCl, *Corrosion Science*, 51 (2009) 1868-1875.
- [104] E.E. Oguzie, Y. Li, F.H. Wang, Corrosion inhibition and adsorption behavior of methionine on mild steel in sulfuric acid and synergistic effect of iodide ion, *Journal of Colloid and Interface Science*, 310 (2007) 90-98.
- [105] R. Karthikaiselvi, S. Subhashini, Study of adsorption properties and inhibition of mild steel corrosion in hydrochloric acid media by water soluble composite poly (vinyl alcohol-o-methoxy aniline), *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 16 (2014) 74-82.

- [106] A. Kokalj, Formation and structure of inhibitive molecular film of imidazole on iron surface, *Corrosion Science*, 68 (2013) 195-203.
- [107] K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T.A. Arias, R.G. Hennig, Implicit solvation model for density-functional study of nanocrystal surfaces and reaction pathways, *The Journal of Chemical Physics*, 140 (2014) 084106.
- [108] H. Lgaz, I.-M. Chung, R. Salghi, I.H. Ali, A. Chaouiki, Y. El Aoufir, M.I. Khan, On the understanding of the adsorption of Fenugreek gum on mild steel in an acidic medium: Insights from experimental and computational studies, *Applied Surface Science*, 463 (2019) 647-658.
- [109] C. Verma, I.B. Obot, I. Bahadur, E.-S.M. Sherif, E.E. Ebenso, Choline based ionic liquids as sustainable corrosion inhibitors on mild steel surface in acidic medium: Gravimetric, electrochemical, surface morphology, DFT and Monte Carlo simulation studies, *Applied Surface Science*, 457 (2018) 134-149.
- [110] R. Aslam, M. Mobin, J. Aslam, H. Lgaz, Sugar based N,N'-didodecyl-N,N'-digluconamideethylenediamine gemini surfactant as corrosion inhibitor for mild steel in 3.5% NaCl solution-effect of synergistic KI additive, *Scientific Reports*, 8 (2018) 3690.
- [111] D.B. Hmamou, R. Salghi, A. Zarrouk, M.R. Aouad, O. Benali, H. Zarrok, M. Messali, B. Hammouti, M.M. Kabanda, M. Bouachrine, E.E. Ebenso, Weight Loss, Electrochemical, Quantum Chemical Calculation, and Molecular Dynamics Simulation Studies on 2-(Benzylthio)-1,4,5-triphenyl-1H-imidazole as an Inhibitor for Carbon Steel Corrosion in Hydrochloric Acid, *Industrial & Engineering Chemistry Research*, 52 (2013) 14315-14327.
- [112] K. Azzaoui, E. Mejdoubi, S. Jodeh, A. Lamhamdi, E. Rodriguez-Castellón, M. Algarra, A. Zarrouk, A. Errich, R. Salghi, H. Lgaz, Eco friendly green inhibitor Gum Arabic (GA) for the corrosion control of mild steel in hydrochloric acid medium, *Corrosion Science*, 129 (2017) 70-81.

- [113] Q. Ma, S. Qi, X. He, Y. Tang, G. Lu, 1,2,3-Triazole derivatives as corrosion inhibitors for mild steel in acidic medium: Experimental and computational chemistry studies, *Corrosion Science*, 129 (2017) 91-101.
- [114] V. Rault, V. Vignal, H. Krawiec, F. Dufour, Quantitative assessment of local misorientations and pitting corrosion behaviour of pearlitic steel using electron backscattered diffraction and microcapillary techniques, *Corrosion Science*, 100 (2015) 667-671.
- [115] P. Singh, E.E. Ebenso, L.O. Olasunkanmi, I.B. Obot, M.A. Quraishi, Electrochemical, Theoretical, and Surface Morphological Studies of Corrosion Inhibition Effect of Green Naphthyridine Derivatives on Mild Steel in Hydrochloric Acid, *The Journal of Physical Chemistry C*, 120 (2016) 3408-3419.
- [116] G.P. Cicileo, B.M. Rosales, F.e. Varela, J.R. Vilche, Comparative study of organic inhibitors of coppercorrosion, *Corrosion Science*, 41 (1999) 1359-1375.
- [117] D.K. Bandgar, S.T. Navale, M. Naushad, R.S. Mane, F.J. Stadler, V.B. Patil, Ultra-sensitive polyaniline-iron oxide nanocomposite room temperature flexible ammonia sensor, *RSC Advances*, 5 (2015) 68964-68971.
- [118] S. Rahimnejad, J.H. He, W. Chen, K. Wu, G.Q. Xu, Tuning the electronic and structural properties of WO<sub>3</sub> nanocrystals by varying transition metal tungstate precursors, *RSC Advances*, 4 (2014) 62423-62429.
- [119] D. Bousa, J. Luxa, V. Mazanek, O. Jankovsky, D. Sedmidubsky, K. Klimova, M. Pumera, Z. Sofer, Toward graphene chloride: chlorination of graphene and graphene oxide, *RSC Advances*, 6 (2016) 66884-66892.
- [120] H. Zarrok, A. Zarrouk, B. Hammouti, R. Salghi, C. Jama, F. Bentiss, Corrosion control of carbon steel in phosphoric acid by purpald – Weight loss, electrochemical and XPS studies, *Corrosion Science*, 64 (2012) 243-252.

- [121] M.-H. Pham, C.-T. Dinh, G.-T. Vuong, N.-D. Ta, T.-O. Do, Visible light induced hydrogen generation using a hollow photocatalyst with two cocatalysts separated on two surface sides, *Physical Chemistry Chemical Physics*, 16 (2014) 5937-5941.
- [122] M.A. Quraishi, A. Singh, V.K. Singh, D.K. Yadav, A.K. Singh, Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of *Murraya koenigii* leaves, *Materials Chemistry and Physics*, 122 (2010) 114-122.
- [123] A.K. Singh, Inhibition of Mild Steel Corrosion in Hydrochloric Acid Solution by 3-(4-((Z)-Indolin-3-ylideneamino)phenylimino)indolin-2-one, *Industrial & Engineering Chemistry Research*, 51 (2012) 3215-3223.
- [124] F. Kandemirli, S. Sagdinc, Theoretical study of corrosion inhibition of amides and thiosemicarbazones, *Corrosion Science*, 49 (2007) 2118-2130.
- [125] A. Kokalj, Is the analysis of molecular electronic structure of corrosion inhibitors sufficient to predict the trend of their inhibition performance, *Electrochimica Acta*, 56 (2010) 745-755.
- [126] J. Fang, J. Li, Quantum chemistry study on the relationship between molecular structure and corrosion inhibition efficiency of amides, *Journal of Molecular Structure: THEOCHEM*, 593 (2002) 179-185.
- [127] F. Xu, J. Duan, S. Zhang, B. Hou, The inhibition of mild steel corrosion in 1 M hydrochloric acid solutions by triazole derivative, *Materials Letters*, 62 (2008) 4072-4074.
- [128] F. Zhang, X. Jiang, X. Zhu, Z. Chen, X.Z. Kong, Preparation of uniform and porous polyurea microspheres of large size through interfacial polymerization of toluene diisocyanate in water solution of ethylene diamine, *Chemical Engineering Journal*, 303 (2016) 48-55.
- [129] J. Sánchez-Márquez, D. Zorrilla, A. Sánchez-Coronilla, D.M. de los Santos, J. Navas, C. Fernández-Lorenzo, R. Alcántara, J. Martín-Calleja, Introducing “UCA-

FUKUI” software: reactivity-index calculations, *Journal of Molecular Modeling*, 20 (2014) 2492.

[130] H. Han, S. Li, X. Zhu, X. Jiang, X.Z. Kong, One step preparation of porous polyurea by reaction of toluene diisocyanate with water and its characterization, *RSC Advances*, 4 (2014) 33520-33529.

[131] Y. Yang, X. Jiang, X. Zhu, X.Z. Kong, A facile pathway to polyurea nanofiber fabrication and polymer morphology control in copolymerization of oxydianiline and toluene diisocyanate in acetone, *RSC Advances*, 5 (2015) 7426-7432.

[132] T.A. Saleh, S.A. Haladu, S.A. Ali, A novel cross-linked pH-responsive tetrapolymer: Synthesis, characterization and sorption evaluation towards Cr(III), *Chemical Engineering Journal*, 269 (2015) 9-19.

[133] Z. Ai, J. Jiang, W. Sun, X. Jiang, B. Yu, K. Wang, Z. Zhang, D. Song, H. Ma, J. Zhang, Enhanced passivation of alloy corrosion-resistant steel Cr10Mo1 under carbonation — Passive film formation, the kinetics and mechanism analysis, *Cement and Concrete Composites*, 92 (2018) 178-187.

[134] S. Kumar, H. Vashisht, L.O. Olasunkanmi, I. Bahadur, H. Verma, G. Singh, I.B. Obot, E.E. Ebenso, Experimental and theoretical studies on inhibition of mild steel corrosion by some synthesized polyurethane tri-block co-polymers, *Scientific Reports*, 6 (2016) 30937.

[135] M. Goyal, S. Kumar, I. Bahadur, C. Verma, E.E. Ebenso, Organic corrosion inhibitors for industrial cleaning of ferrous and non-ferrous metals in acidic solutions: A review, *Journal of Molecular Liquids*, 256 (2018) 565-573.

[136] C. Verma, L.O. Olasunkanmi, E.E. Ebenso, M.A. Quraishi, I.B. Obot, Adsorption Behavior of Glucosamine-Based, Pyrimidine-Fused Heterocycles as Green Corrosion Inhibitors for Mild Steel: Experimental and Theoretical Studies, *The Journal of Physical Chemistry C*, 120 (2016) 11598-11611.

- [137] R. Solmaz, Investigation of corrosion inhibition mechanism and stability of Vitamin B1 on mild steel in 0.5M HCl solution, *Corrosion Science*, 81 (2014) 75-84.
- [138] Z. Cao, Y. Tang, H. Cang, J. Xu, G. Lu, W. Jing, Novel benzimidazole derivatives as corrosion inhibitors of mild steel in the acidic media. Part II: Theoretical studies, *Corrosion Science*, 83 (2014) 292-298.
- [139] C. Verma, L.O. Olasunkanmi, T.W. Quadri, E.-S.M. Sherif, E.E. Ebenso, Gravimetric, Electrochemical, Surface Morphology, DFT, and Monte Carlo Simulation Studies on Three N-Substituted 2-Aminopyridine Derivatives as Corrosion Inhibitors of Mild Steel in Acidic Medium, *The Journal of Physical Chemistry C*, 122 (2018) 11870-11882.
- [140] L.R. Chauhan, G. Gunasekaran, Corrosion inhibition of mild steel by plant extract in dilute HCl medium, *Corrosion Science*, 49 (2007) 1143-1161.
- [141] R. Eustaquio-Rincón, M.E. Rebolledo-Libreros, A. Trejo, R. Molnar, Corrosion in Aqueous Solution of Two Alkanolamines with CO<sub>2</sub> and H<sub>2</sub>S: N-Methyldiethanolamine + Diethanolamine at 393 K, *Industrial & Engineering Chemistry Research*, 47 (2008) 4726-4735.
- [142] S. Nešić, Key issues related to modelling of internal corrosion of oil and gas pipelines – A review, *Corrosion Science*, 49 (2007) 4308-4338.
- [143] J. Zhao, H. Duan, R. Jiang, Synergistic corrosion inhibition effect of quinoline quaternary ammonium salt and Gemini surfactant in H<sub>2</sub>S and CO<sub>2</sub> saturated brine solution, *Corrosion Science*, 91 (2015) 108-119.
- [144] R. Sadri, M. Hosseini, S.N. Kazi, S. Bagheri, N. Zubir, K.H. Solangi, T. Zaharinie, A. Badarudin, A bio-based, facile approach for the preparation of covalently functionalized carbon nanotubes aqueous suspensions and their potential as heat transfer fluids, *Journal of Colloid and Interface Science*, 504 (2017) 115-123.

- [145] F. Pan, J. Jin, X. Fu, Q. Liu, J. Zhang, Advanced Oxygen Reduction Electrocatalyst Based on Nitrogen-Doped Graphene Derived from Edible Sugar and Urea, *ACS Applied Materials & Interfaces*, 5 (2013) 11108-11114.
- [146] S.A. Rounaghi, D.E.P. Vanpoucke, H. Eshghi, S. Scudino, E. Esmaeili, S. Oswald, J. Eckert, Mechanochemical synthesis of nanostructured metal nitrides, carbonitrides and carbon nitride: a combined theoretical and experimental study, *Physical Chemistry Chemical Physics*, 19 (2017) 12414-12424.
- [147] I. Abdulazeez, C. Basheer, A.A. Al-Saadi, Selective colorimetric sensing of nickel (II) ions using 2-hydroxy-5-nitrobenzaldehyde-4-hydroxybenzoylhydrazone ligand: Spectroscopic and DFT insights, *Journal of Molecular Liquids*, 264 (2018) 58-65.
- [148] I. Abdulazeez, C. Basheer, A.A. Al-Saadi, A selective detection approach for copper(ii) ions using a hydrazone-based colorimetric sensor: spectroscopic and DFT study, *RSC Advances*, 8 (2018) 39983-39991.
- [149] I. Obot, S. Umoren, Z. Gasem, R. Suleiman, B. El Ali, Theoretical prediction and electrochemical evaluation of vinylimidazole and allylimidazole as corrosion inhibitors for mild steel in 1M HCl, *Journal of Industrial and Engineering Chemistry*, 21 (2015) 1328-1339.

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## SELECTED PUBLICATIONS

1. **I. Abdulazeez**, A. Zeino, C.W. Kee, A.A. Al-Saadi, M. Khaled, M.W. Wong, A.A. Al-Sunaidi. Mechanistic Studies of the Influence of Halogen Substituents on the Corrosion Inhibitive Efficiency of Selected Imidazole Molecules: A Synergistic Computational and experimental approach. *Applied Surface Science* 31 (2019), 494-505
2. A. Zeino, **I. Abdulazeez**, M. Khaled, M.W. Jawich, I.B. Obot. Mechanistic study of polyaspartic acid (PASP) as eco-friendly corrosion inhibitor on mild steel in 3% NaCl aerated solution. *Journal of Molecular Liquids* 250 (2018), 50-62
3. **I. Abdulazeez**, C. Basheer, A.A. Al-Saadi. A selective detection approach for copper (II) ions using a hydrazone-based colorimetric sensor: spectroscopic and DFT study. *RSC Advances* 8 (2018), 39983-39991
4. **I. Abdulazeez**, C. Basheer, AA Al-Saadi. Selective colorimetric sensing of nickel (II) ions using 2-hydroxy-5-nitrobenzaldehyde-4-hydroxybenzoylhydrazone ligand: Spectroscopic and DFT insights. *Journal of Molecular Liquids* 264 (2018), 58-65
5. **A. Ismail**, A. Kawde, O. Muraza, M.A. Sanhoob, M.A. Aziz, A.R. Al-Betar. Modified Lanthanum–Zeolite for Sensitive Electrochemical Detection of Heavy Metal Ions. *Arabian Journal for Science and Engineering*, 2018, 1-10
6. A. Idris, U. Khalil, **I. Abdulazeez**, I. Makertihartha, M. Laniwati, A.R. Al-Betar, R. Mukti, O. Muraza. Fabrication zone of OSDA-free and seed-free mordenite crystals. *Powder Technology* 342 (2019), 992-997
7. **A. Ismail**, A. Kawde, O. Muraza, M.A. Sanhoob, A.R. Al-Betar. Lanthanum-impregnated zeolite modified carbon paste electrode for determination of Cadmium (II). *Microporous and Mesoporous Materials* 225 (2016), 164-173
8. A. Kawde, **A. Ismail**, A.R. Al-Betar, O. Muraza. Novel Ce-incorporated zeolite modified-carbon paste electrode for simultaneous trace electroanalysis of lead and cadmium. *Microporous and Mesoporous Materials* 243 (2017), 1-8

9. **I. Abdulazeez**, H.M. Irshad, A. Zeino, I.H. Toor. Electrochemical corrosion performance of aromatic functionalized imidazole inhibitor under hydrodynamic conditions on API 65 carbon steel in 1M HCl solution. *Arabian Journal for Science and Engineering*. (2019)

## CONFERENCE PRESENTATIONS

1. **I. Abdulazeez**, H.M. Irshad, I.H. Toor. Electrochemical corrosion performance evaluation of imidazole inhibitor under dynamic conditions for API 65 carbon steel in chloride solutions. 17<sup>th</sup> Middle East Corrosion Conference and Exhibition Bahrain, 2018. **NACE Paper no MECCOCT18-12607**
2. M.W. Wong, C.W. Kee, **I. Abdulazeez**, A.A. Al-Saadi, M. Khaled. Design of novel imidazole-based corrosion inhibitors – molecular dynamics and electrochemical studies. 4<sup>th</sup> International Conference on Physical and Theoretical Chemistry, Dublin, Ireland. **J. Phys Chem Biophys 2017, 7:4**
3. **I. Abdulazeez**, M. Khaled, A.A. Al-Saadi, M.W. Wong, C.W. Kee, A.A. Al-Sunaidi, A. Zeino. Molecular Dynamics Simulation and Electrochemical Studies of Imidazole Compounds as Corrosion Inhibitors of Mild Steel in Acidic Medium. 4<sup>th</sup> International Conference and Exhibition on Laboratory Technology (LABTECH) 2017, Bahrain.

## US PATENTS

1. **I. Abdulazeez** A.M. Kawde, O. Muraza, ALB. Abdul-Rahman. Rare earth metal incorporated zeolite modified electrodes for detection and quantification of heavy metal ions in aqueous solution  
**US Patent App. 15/446,035**
2. **I. Abdulazeez**, O. Al-Hamouz, A.A. Al-Saadi, M. Khaled Water Soluble Polyurea-Based Corrosion Inhibitor of Mild Steel: Synthesis and Electrochemical Studies  
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## **HOBBIES**

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