Chapter 1

Introduction

Carbon steel is the most worldwide used material for industrial and domestic applications, because of its good mechanical properties, availability and relatively reasonable cost. However due to its susceptibility to corrosion attacks, one or more of the corrosion protection methods should be applied. Several methods have been investigated and implemented to reduce the corrosion process and extend the life time of the structures including design modification, coating, and cathodic protection. Corrosion inhibition by chemical additives is of great importance and become more common in protecting carbon steel particularly for internal corrosion. However because of more and more restrict environment regulations, development of a new non toxic, environmental friendly inhibitors are of high priority of corrosion research. In this thesis, organic compounds namely hydroxamic acids were investigated as a promise corrosion inhibitor for carbon steel. A hydroxamic acid is a class of chemical compounds sharing the functional group in which -NH is inserted into a carboxylic acid (RCONHOH). They are a class of weak acids and act as ligand, because of their strong affinity toward certain metal ions, the chelating sites being oxygen and nitrogen atoms of the head group. The non toxic nature of hydroxamic acid derivatives make the investigation of their inhibiting properties valuable in the context of the current priority to produce environmentally friendly inhibitors. Only a few studies were carried out testing and evaluating hydroxamic acids as corrosion inhibitor for copper as illustrated in the literature review chapter. This work is divided into three parts.

Firstly, selected dihydroxamic acid derivatives, namely oxalyl-dihydroxamic acid (C2), adipoyl-di-hydroxamic acid (C6) and pimeloyl-1,5-di-hydroxamic acid (C7) have been synthesized and evaluated as corrosion inhibitors for carbon steel in neutral and acidic aqueous solution.

Secondly, the influence of metal ions (Cu$^{2+}$, Mg$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$) on the adsorption process and corrosion inhibition of pimeloyl-1,5-di-hydroxamic acid (C7) on carbon steel surface have been investigated. The direct impact of the important process parameters was investigated by conducting electrochemical corrosion experiments using electrochemical polarization and impedance techniques under a wide range of
test conditions. These were molecular structure, molecular concentration, pH, presence of chloride and immersion time. Electrochemical techniques (potentiodynamic polarization and ac impedance measurements) have been used to understand the corrosion mechanism of carbon steel in the presence of different tested additives throughout measuring the kinetic values of corrosion parameters and interpretation of the polarization curves and impedance plots. Surface analysis techniques (X-ray Photoelectron Spectroscopy and Scanning Electron Microscopy) were used to identify the chemical composition, electronic state and to study the morphological of steel surface.

Thirdly, formation of self-assembled monolayers (SAMs) using mono hydroxamic acids \((\text{CH}_2)_n\text{CONHOH}\) with different alkyl lengths on the carbon steel electrode surface has been investigated. The corrosion protection properties of the monolayers were examined and characterized by electrochemical polarization curves, electrochemical impedance spectroscopy, X-ray photoelectron spectroscopy (XPS) and contact angle measurements. XPS results showed that the hydroxamic acid molecules adsorbed on the carbon steel surface, and the contact angle values on the modified surface supported the formation of hydrophobic hydroxamic acid SAMs.
Chapter 2

Literature Review

2.1 Corrosion Basic

Most people are familiar with corrosion in some form or another, and almost everyone has seen the rusting of iron fence, spots in car bodies, corroded iron nail, etc. The economic cost of corrosion is enormous, and has been estimated to be in the range of 2-4% of an industrialised country’s gross national product [1, 2]. In addition there are also indirect costs associated with plant shutdown, lower efficiency of equipment, contamination and overdesign. Much of this loss is due to the corrosion of iron and steel; although many other metals are susceptible to corrosion process as well. Corrosion is a natural process and defined as the deterioration of metal by electrochemical reactions with its environment. When metallic surface exposed to an aqueous electrolyte usually possesses sites for an oxidation (anodic reaction) that produces electrons in the metal at less stable sites (e.g., where there are dislocation, imperfections), and a reduction (cathodic reaction) that consumes the electrons produced by the anodic reaction. The anodic and cathodic "sites" together make up a corrosion cell. The anodic reaction is the dissolution of the metal atoms to the metal ions. These ions form either soluble ionic products or an insoluble compound of the metal, usually an oxide and can be explained by a simplified equation:

A typical anodic oxidation for metal is:

\[ M \rightarrow M^{2+} + 2e^- \]

The common corresponding cathodic reactions involved in corrosion process, at the cathodic sites at the metal/solution interface are:

1. (neutral and alkaline environments) \( O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \)
2. (acidic in the presence of oxygen environments) \( O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \)
3. (acidic environments) \( 2H^+ + 2e^- \rightarrow H_2 \)
2.2 Thermodynamics of Corrosion

Thermodynamics is concerned with energy states. The original metallic ores are said to be in a state of low energy. External energy is applied in the conversion of the ores to usable metals and alloys, transforming them to a higher energy state. The driving force that causes metal to corrode is the thermodynamic instability of metal in its surrounding environment, which is a natural consequence of their temporary existence in metallic form. Pourbaix [3] used thermodynamic data (Nernst equations) to identify regions of active corrosion, immunity when corrosion is thermodynamically not favoured, and regions of passivity, throughout construction of diagrams, which presents the relationship between potential and the solution pH. Pourbaix diagrams are useful as a reference for the selection of a corrosion protection method, e.g., by installing cathodic protection system where the potential is shifted to more negative value and the region is changed from active to immunity, or by applying a neutralizer to adjust the solution pH and reach the passivity region. While thermodynamics can predict whether a corrosion reaction will take place, it does not provide an indication of the rate of corrosion reactions. The rate of reactions is described by kinetic theory.

\[ \text{[reactant]} \rightarrow \text{[product]} + ne^- \]

(Nernst equation)

where
E is the measured potential in volts
E_0 is the standard potential volts
R is the gas constant, 8.31 JK^{-1}mol^{-1}
T is temperature in Kelvin
n is the number of electrons in electrochemical equation
F is Faraday’s constant, 96485 coulombs/mole
[reactant] is the concentration (in moles/litter) of reactant chemical species
[product] is the concentration (in moles/litter) of product chemical species.

The most simple type of these diagrams is based on a chemical system consisting of one element and water solution. Fig. 2.1 shows a typical Pourbaix diagram of iron-water system.
2.3 Corrosion Kinetics

The corrosion process is considered to be a heterogeneous phenomenon taking place in three sequential steps, i) transport of oxidizing agents from the electrolyte solution to the metal-solution interface, ii) electrochemical reaction at the interface and iii) transport of products away from the interface. The schematic representation of corrosion process is illustrated in Fig.2.2. The overall corrosion rate is controlled by the slowest of the three sequential steps. When the transport phenomena are capable of proceeding at rates higher than the interfacial electrochemical activities, corrosion is governed by electrode-kinetics and said to be under activation polarization. On the contrary when the capability of the electrochemical reaction is relatively high, the overall corrosion rate is controlled by mass transport (concentration polarization).
2.3.1 Activation Polarization

An activation controlled reaction is one for which the rate of reaction is controlled only by the rate of the electrochemical charge transfer process. The corrosion current density is not directly measurable because a corroding metal does not show any net current flow.

![Figure 2.2. Transport and kinetic of corrosion process [4]](image)

However, if the equilibrium potential of an electrode is changed to some other value (e.g. by connecting it to another electrode to form a galvanic cell or to a potentiostat) it is possible to determine the corrosion current density by using the Butler-Volmer equation (2.1).

\[
\text{(2.1)}
\]

where

- \( i \) is the net current density
- \( i_{\text{corr}} \) is the corrosion current density
- \( \alpha \) is the transfer coefficient
- \( \eta \) is the overvoltage in V
- \( R \) is the gas constant, 8.31 JK\(^{-1}\)mol\(^{-1}\)
\( T \) is temperature in Kelvin
\( n \) is the number of electrons in electrochemical equation
\( F \) is Faraday’s constant, 96485 coulombs per mole

The Butler-Volmer equation relates the net current density to the change in the electrode potential. The potential change is the potential by which the electrode is polarised away from the corrosion potential and its value depends on the reaction rate of electron transfer. The slower the reaction rate of electron transfer the greater is . The transfer coefficient is related to an energy barrier which the reacting species must overcome for electron transfer to occur. Depending on the ranges of potential the Butler-Volmer equation is used in following simplified forms.

a) In case of small over potentials, assuming that the transfer coefficients are equal for both anodic and cathodic, the equation (2.1) can be reduced to (2.2)

\[
\text{(2.2)}
\]

Hence

\[
\text{(2.3)}
\]

where

\( R_t \) is charge transfer resistance

b) In case of large over potentials, the Tafel equations are obtained

If \( \theta > -50 \text{ mV} \), equation (2.1) can be reduced to

\[
\text{(2.4)}
\]

If \( \theta > +50 \text{ mV} \) equation (2.1) can be reduced to

\[
\text{(2.5)}
\]
More generally, the Tafel equation is used as follows

\[ a + b \log i \] 

(2.6)

### 2.3.2 Concentration Polarization

When the interfacial concentration of reacting chemical species depleted and approach zero due to relatively high rate of electron transfer at interface, concentration polarization occurs and corrosion process is controlled by the transport of chemical species from the bulk to the surface. Generally corrosion rate in this case cannot exceed the limiting current density \( i_t \), which is restricted by the rate of diffusion of chemical species in the solution.

The limiting current density can be calculated from

\[ i_t = \frac{D n F C_B}{\delta} \]

\( D \) is the diffusion coefficient of the reacting species.

\( \delta \) is the thickness of concentration gradient.

\( C_B \) is the bulk concentration of chemical species.

The concentration polarization \( \delta \) can be defined as a function of current density as

For the corrosion process concentration polarization is significant only for cathodic reduction process namely reduction of dissolved oxygen, for anodic process usually ignored due to the availability of unlimited supply of metal atoms at the interface.
2.4 Iron Dissolution

The mechanism of iron dissolution in neutral solutions is similar to that encountered in alkaline media [5]. In acidic solutions the mechanisms are different from that in neutral and alkaline solutions, due to the absence of 3-dimension oxide and corrosion products on the metal surface [6-10]. These mechanisms are characterized by the formation of different oxide intermediates \([\text{Fe(OH)}_n]_{\text{ads}}\) depending on the pH and electrode potential [5].

Bessone [11] proposed a mechanism for iron dissolution in acidic media in which iron oxide is formed on the metal surface in acid solutions but whether, or not this oxide is protective and remain on the surface depends, among other factors, such as the solution pH. However there are some doubts on the pH value where the oxide layer provides protective properties and good adhesion to the metal surface. Geana et al. [6] have reported that at low pH (4 to 5.4) the metal surface remain uncovered and at pH ≥ 5.5 formation of \([\text{Fe(OH)}_2]_{\text{ads}}\) occurs at a higher rate and lead to reduces the iron dissolution. In contrasts to Geana et. al. [6], Lorbeer and Lorenz [5] reported that at pH > 4.2 oxide formation on iron surface is time-dependent and produces a porous film with sufficient thickness which could be identified visually. A proposed mechanism for the anodic dissolution of iron in alkaline solutions [12,13] said that the adsorption of OH\(^-\) on the iron surface is the first step to produce \([\text{Fe(OH)}]_{\text{ads}}\) and depending on the potential of the electrode, the adsorbed oxygen complex may return into solution or remain on the metal surface and at potential higher than open circuit potential the complex may transfer into an oxide with protection properties which remains on the metal surface. Lorbeer and Lorenz [5] stated that the coverage of iron surface with adsorbed oxide intermediates and oxide reaction products increases strongly with increasing pH. Guzman et. al. suggested that \(\text{FeOOH}\) and \(\text{Fe(OH)}_2\) at higher potentials transform into other more stable compounds either through a chemical reaction or via structural rearrangements [14]. Meaning the passivation of iron in alkaline solution is initially due to the formation of \(\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}\), which is eventually transforms to \(\text{Fe}_3\text{O}_4\) and hydrated \(\text{Fe}_2\text{O}_3\). While iron dissolution is the main anodic reaction at all pH values the cathodic reaction may be either charge-transfer controlled hydrogen evolution or diffusion controlled oxygen reduction depending on the solution pH [15,16]. Lorbeer and Lorenz reported that above pH values of 4.2 in aerated solution, oxygen reduction is the dominant cathodic reaction. It follows from oxygen reduction reactions that the pH increases at the electrode surface due to the consumption of
protons and production of hydroxyl ions. Turgoose [17] reported that the pH on a metal surface may be rise up to 10 in un-buffered solutions due to the oxygen reduction this alkaline condition favours formation of three dimensional oxides. Nagayama and Cohen [18] have demonstrated that a linear relationship between passivation potential and pH at constant Fe$^{2+}$ concentration in alkaline region. The presence of active compounds may affect the mechanism of iron dissolution, for example the iron corrosion inhibitors, the inhibitors used in acid solutions are different from those employed in neutral and alkaline solutions. In acid solutions the inhibitors is due to the adsorption of the inhibitor on to a bare metal surface [8,9]. Where, in neutral and alkaline solutions, the presence of oxide layers and corrosion products on the metal surface play an important role in the mechanism of inhibition. At pH > 4.2 the inhibition may affect the corrosion process via interaction with metal/oxide or the oxide film/solution interphase [19] and through interaction with the metal, as reported [20,21].

2.5 Corrosion Inhibitors

Referring to the electrochemical nature of corrosion process, corrosion inhibitor can be defined as a chemical compound, when added in a small amount to the corrosive environment alters the cathodic and/or anodic reactions, and consequently reduces corrosion rate. Because of this corrosion inhibitors are classified as anodic, cathodic or mixed type (inhibitors) depending on the inhibited part of the corrosion process [22]. Other proposed classifications have been used such as organic and inorganic [23] with regard to the chemical nature of the inhibitor compound, oxidising or non-oxidising [24] with regard to their redox characteristic, and interface (inhibitors forming two dimensional adsorption layer) and interphase (inhibitors forming three dimensional precipitated layer) [25,26] with regard to their retardation mechanism. Over the years many compounds have been tested and efficiently used as corrosion inhibitors for different materials and different environments. However the recently increasing concern toward environmental and health consideration is likely to restrict inhibitor choices. Many effective inhibitors such as chromate and nitrites will eventually abandoned due to the new regulations. Thus there is a need for testing and developing corrosion inhibitors that are effective and in addition being environmentally accepted. Because of the limited range of inorganic compounds, organic ones are most likely to meet those requirements. This review will focus on the organic corrosion inhibitors.
2.5.1 Organic Corrosion Inhibitors

Most organic inhibitors are facilitated by the presence of polar groups in the molecular structure which can strongly adsorb onto the metal surface or react with the corrosion product on the surface to form a protective layer. The most effective polar groups include sulphur, nitrogen, oxygen and phosphorous atoms. Many organic compounds were tested and exhibit inhibitive properties such as carboxylic acids, amines, and other nitrogen containing compounds. Carboxylic acid derivatives as corrosion inhibitor were reviewed and summarized as following. According to Sidgewick [27] monocarboxylic acids with n-alkyl chains of 6-9 carbon atoms are effective corrosion inhibitors and their efficiency increase with increasing molecular weight. The results obtained by Herschi et.al [28] supported Sidgewick’s results, indicating the octanoic and nonoic acid proved to be more effective than other monocarboxylic acids containing up to 14 carbon atoms under the same conditions. These authors also demonstrated qualitatively that some dicarboxylic acids such as suberic and sebacic acids are effective in the presence of chloride ions. The inhibition of iron corrosion by carboxylic acids has been studied in details by Smialowska et.al [29]. It was reported that the corrosion of iron can be inhibited in sulphuric acid, ammonium nitrate [30] and in sodium sulphate solution [31] in the presence of carboxylic acids containing more than four carbon atoms. The authors have demonstrated that in those solutions the efficiency of carboxylic acids increases with increasing number of carbon in the molecule. Horner [32] employed the concept of hard and soft acid and base (HSAB), proposed by Pearson [33] and explains that carboxylates are hard bases and therefore can be better adsorbed on oxide which is hard acid compared to a bare metal surface which is considered soft acid. In general, carboxylic acids are known as inhibitors which are effective in the presence of dissolved oxygen [34]. Mrowczynski and Smialowska [31,35] attribute the reduction of the corrosion rate of iron in aerated sodium sulphate solution to a synergistic action of these acids and dissolved oxygen. Reinhard et. al. [36] carried out a study on the role of some carboxylates, including straight chain monocarboxylate with one to eight carbons in their molecules on the inhibition of iron and mild steel. They reported that only carboxylate with $C \geq 6$ inhibit iron corrosion. Granata et. al. [37] investigated the inhibition of steel corrosion in mildly corrosive media in the presence of monocarboxalates. Their conclusion was somewhat different from that Reinhard et. al. [36] as they found that carboxylate with $C \geq 2$ inhibits iron corrosion. Granata et, al.
[38] proposed a mechanism of carboxylate inhibition. This mechanism is based on the formation of insoluble iron carboxylate at the metal oxide surface. The role of oxygen in this mechanism is to maintain iron in the ferric state. The presence of oxide layer is considered to be necessary for carboxylate adsorption. The hydrophobic part of the molecule which is oriented towards solution shields the metal surface from water molecules and aggressive ions.

2.5.2 Hydroxamic Acids as Corrosion Inhibitors

In this thesis, organic compounds namely hydroxamic acids were investigated as a promising corrosion inhibitor for carbon steel. A hydroxamic acid is a class of chemical compounds sharing the same functional group in which \(-NH\) is inserted into a carboxylic acid. Hydroxamic acids \((\text{RCONHOH})\) were first reported by Lossen in 1869 [39]. They are a class of weak acids and act as ligand, because of their strong affinity toward certain metal ions, the chelating sites being oxygen and nitrogen atoms of the head group [40] Farkas and co-workers conducted intensive research on mono- and di-hydroxamic acids as metal chelators [41-46]. Because of this property hydroxamic acids have been investigated and implemented in the field of medicinal chemistry [47-52], such as antibacterial agent and anti-inflammatory. However regarding hydroxamic acids as corrosion inhibitors, only a few studies were carried out testing and evaluating hydroxamic acids corrosion inhibition properties. Shaban et al [53] investigated the inhibition effect of benzo-hydroxamic acid on copper corrosion in sodium chloride solution. They related the protective effect to the formation of a low solubility complex layer between the inhibitor and copper corrosion product. They used quartz crystal microbalance technique in their work [54] and found that p-chloro-benzo-hydroxamic acid showed excellent protection to copper corrosion. Other data regarding application of hydroxamic acids as self-assembling molecules is presented in the section 2.6.3.

2.5.3 Effect of Cations on the Inhibition of Organic Inhibitors

Felhosi et.al [55] investigated the influence of calcium and zinc ions on the corrosion inhibition of 1-hydroxyethane-1,1-diphosphonic acid (HEDP) on carbon steel. They related the increasing in the inhibition efficiency of HEDP to the formation of different complexes species with the cation additives. They found that the molar ratio play an important role in the formation of protective complexes and reported that zinc ions have a better effect on the
inhibition efficiency of HEDP. Turgoose et.al [56] supported the results obtained by Felhozi et.al [55] they studied the effect of calcium and zinc ions on the effectiveness of 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) on the inhibition of mild steel corrosion. They reported that zinc-HEDP mixture give effective inhibition, at a molar ratio 2:1 of zinc-HEDP. Addition of calcium showed some inhibition for the corrosion of mild steel, but it is much lower than that for zinc. This is attributed by the authors to the low stability of calcium complexes compared with ferrous complexes, which facilitates the displacement of calcium ions from their complexes by ferrous ions forming soluble un-protective ferrous complexes. Gomma [57] suggested that addition of copper cations to the benzotriazole reduced the corrosion rate of steel in 0.1 M H$_2$SO$_4$, due to the co-adsorption process. Gaur et.al [58] investigated the effect of the cations (Cu$^{2+}$, As$^{3+}$, Sb$^{3+}$ and Sn$^{2+}$) on the inhibition of steel by hexamine in hydrochloric acid solution. They attributed the positive role of the cations on the inhibitive performance of hexamine to the formation of anion complexes with chloride ions of acid solution. These anions replace the adsorbed chloride ions from the metal-electrolyte interface owing to their higher affinity toward the interface and help the protonized molecules of hexamine to be adsorbed more strongly at the interface. Telegdi et. al. [59] demonstrated that bivalent cations (Ba$^{2+}$, Sr$^{2+}$, Ca$^{2+}$ and Zn$^{2+}$) synergically improved the inhibition efficiency of amino-phosphoric acid. They found that the addition of zinc ions influenced both anodic and cathodic process, while the rest of cations hindered the anodic iron dissolution. Pech-caul [60] reported that the N-phosphono-methyl-glycine/ Zn$^{2+}$ mixture inhibited steel corrosion in neutral chloride solutions by retardation of both the anodic dissolution and oxygen reduction reactions. Venkatachari [61] related the enhanced inhibition performance of polyaniline in the presence of cerium ions to the formation of metal-amine complexes, with more quinoid moiety which facilitate strong adsorption and higher coverage on iron surface. Gomma et.al [62] attributed the corrosion inhibition of oxalic to the adsorption of a stable Fe/oxalate complex having the formula FeL$_2$, where L is an acid ligand.

2.6 Self-assembled Monolayers

2.6.1 Concept and Application of Self-Assembled Monolayers

Self-assembled monolayers (SAMs), generally defined as well-ordered and oriented molecular films, which are formed spontaneously, upon immersion of a substrate (solid
surface) into a solution containing an active organic molecule. These molecules organize themselves in a two-dimensional (2-D) arrangement on the surface of the substrate. The structure of these respective molecules consists of three parts: a surface-active head group which binds strongly to the substrate, a long chain that connects the head and tail groups and specific tail group that constitutes the outer surface of the film and modifies bulk surface properties (Figure 2.3). Tail groups can also affect the self-assembled monolayers’ structure significantly, providing it has a strong polar characteristic or is sufficiently large. The process to prepare self-assembled monolayers is simple only minimum amounts of organic molecules are needed and can be obtained by chemical adsorption from aqueous or organic solutions. Studies on assembled monolayers process are back to the 1940s [64]. Organic self-assembled monolayers have attracted a considerable interest over the last 20 years. Owing to the flexibility to design and prepare SAM with different organic molecule for different substrates. Intensive research activities were carried out to obtain the desired surface properties. In addition to the SAM technique, other common methods were available and used for preparing organic thin films include 1. Langmuir films consist of amphiphilic molecules spread on a liquid surface like water. The hydrophilic head group has an affinity to the water while the hydrophobic end group sticks out on the other side [65,66]. 2. Langmuir-Blodgett (LB) films are prepared by transferring Langmuir films onto a solid substrate [67]. The head group is hydrophilic while the tail group is hydrophobic, so that the direction of the molecules is achieved prior to the transfer step. Multilayers are prepared by repeated (periodic) dipping of the substrate in appropriate solutions. Compared with the LB technique, the self-assembling method has more advantages [68]: (i) the layers are strongly attached to the substrate, throughout the chemisorptions process and electrostatic interactions; (ii) it does not need a specific experimental apparatus. Therefore, the self-assembling method seems to be simpler and more flexible, and for these reasons appears to be very attractive. Self-assembly technique has a number of applications such as chemical and biological sensors [69], efficient electronic and optical devices [71,71], nonlinear optical materials, artificial membrane [72], electron-transfer barriers [73] and high-density memory devices photo patterning methodology [74-79]. Also SAMs can be used either to provide model systems of organized functional molecules for studying the interfacial phenomena, such as electron transfer or redox behaviour [80].
2.6.2 Self-Assembled Monolayers as Corrosion Inhibitors

It is well known that organic coating is one of the important methods used for corrosion protection of different metals, these coating usually consist of a thick multilayer films with thickness ranging from 10 µm to 100 µm, and work as barrier between the substrate and environment. However, thin and ultrathin corrosion protecting films provided by SAM with thicknesses less than 10 nm are of considerable interest especially in modern areas of materials research such as microelectronic devices or micromechanics. Felhosi et al. [81] studied the corrosion protection of iron by 1-phosphonic-alkane SAM in aqueous solution. They reported that a significant corrosion protection was observed, due to the formation of SAM with a continuous and dense structure. The mechanism of inhibition is anodic type, hindering the active dissolution of iron. The formation process of SAM take place in two steps, firstly fast adsorption of molecules on bare iron surface, and secondly ordering in the layer structure is occur during long immersion time. Aramaki et al. [82-84] studied the effect of carboxylate and hexadecanoate self-assembled monolayers on the breakdown of iron passive film. They found that the formation of such SAM on the previously passivated iron electrode, prevent the breakdown of passive film, because of the ordered and densely packed SAM acted as a barrier layer to the diffusion of Cl⁻ through the layer, incorporation of Cl⁻ into
the passive film and accumulation of Cl\textsuperscript{−} at defects of the film suppressed by coverage of the film with the SAM. However many other SAM systems have been investigated from the corrosion protection point of view, for iron and other metals, but still the intensive thoroughly investigated system is the organic molecules containing sulphur compound on gold, silver and copper. Sulphur compounds have a strong affinity to transition metal surfaces and coordinate very strongly to the surface of the metal. For example alkanethiol SAM have proven to be excellent inhibitors of oxygen reduction throughout formation of a diffusion barrier to the oxygen transport [85-93].

2.6.3 Surface Modification by Hydroxamic Acids

To the best of our knowledge, only limited studies were carried out for hydroxamic acids as surface modification (SAM and LB). These studies were reviewed below. Using contact angle measurements and XPS analysis Folkers et al. [94] studied the properties of self-assembled monolayer of hydroxamic acids, carboxylic acid and phosphonic acid on the native oxides of copper, iron, silver, aluminium, zirconium and gold. They concluded that hydroxamic acids present an alternative and improvement to other organic acids for the formation of self-assembled monolayers. On the native oxides of aluminium, zirconium and iron, hydroxamic acid, appears to form more stable monolayer than either carboxylic acid or phosphonic acid. The smaller size of the hydroxamic acid compared to the phosphonic acid, may allow the formation of more coherent and more ordered monolayers. Telegdi et al. [95] studied the deposition of alkyl hydroxamic acid on copper surface as a Langmuir-Blodget (LB) and as a self-assembled molecular layer (SAM). They demonstrated that both LB and SAM were effective as corrosion inhibitors for copper, and the inhibition is influenced by the chain length of the amphiphiles, by increasing carbon atoms in the alkyl chain the corrosion inhibitive effect in acidic environment was enhanced. Rigo et al. [96] investigated the corrosion inhibition effect of hydroxamic acid and phosphonic acid Langmuir-Blodgett films on iron corrosion in sodium per chlorate solutions. They observed that both acids provide high inhibition efficiencies, due to the blocking effect of the applied LB layers. Moreover they found that hydroxamic acid LB is more compact and efficient than that of phosphonic acid.
3.1 Potentiodynamic Polarization

The potentiodynamic polarization scan, provide a considerable information on electrode processes such as, the corrosion rate, pitting susceptibility, passivity, as well as the cathodic behaviour of an electrochemical system. At the open circuit potential (potential at which the total anodic current is equivalent to the total cathodic current) the measured current will be zero. For determining electrochemical corrosion kinetics, a perturbation of the tested electrode is needed to shift the corrosion system from the open circuit potential. Electrochemical interface instruments (Potentiostat/Galvanostat) is used as external source for the polarization and to control the rate of reaction occurring at the electrode interface. This is done indirectly by controlling the potential, and hence the driving force, available for reactions which might occur. The rate of the available reactions will vary based on the size of the driving force and the nature of the reaction itself (i.e., mass or charge transfer controlled). The second function of the potentiostat is to measure the current applied by the potentiostat to achieve the desired degree of polarization. As such, it is important that the instrument be sufficiently sensitive to measure the currents which are anticipated. In addition a computer is used to control the experimentation and acquire the data. A personal computer equipped with a communication device, such as a GPIB board, to exchange information with the potentiostat, in combination with software capable of controlling the electrochemical interface and acquiring data. Example of such a software package is the combination of CorrWare (for hardware control and data acquisition) and CorrView (for data comparison and analysis). The interpretation of the collected data is carried out through the use of E-logi diagram (Evans diagram). In a potentiodynamic experiment, the current represents the rate with which the anodic or cathodic reactions are taking place on the working electrode. Typically, the current is expressed in terms of the current per unit area of the working electrode, or the current density. Many variables may influence the rate of a given electrochemical reaction, including the temperature, the surface condition of the tested electrode, as well as the chemical environment
in which the experiment is performed. In general, cathodic currents are considered to be negative and anodic currents to be positive. It should be noted that in an Evans diagram, the absolute value of the current density is plotted (i.e., both anodic and cathodic currents are plotted as positive values).

### 3.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a valuable tool for evaluating the performance of corrosion inhibitors and protective coatings, providing a non-destructive method to obtain specific information about corrosion kinetics and protection properties. [97] EIS has been defined as the method in which the impedance of an electrochemical system is studied as a function of the frequency of an applied AC wave. [98] Instead of applying a direct current or voltage, the technique utilise a continuous perturbation to a steady state system, using a low magnitude AC signal. Applying a sinusoidal AC potential centred on the open circuit potential ($E_{OCP}$) of the substrate causes the sample to cycle between anodic and cathodic polarisation, corresponding to a small AC current. The obtained impedance spectrum represent the components in the system with different frequency dependent properties (time constants), which can be used to evaluate corrosion properties. High frequency spectra correspond to kinetically controlled reactions and to charge transfer processes usually associated with the coating interface, while low frequencies correspond to slower processes generally occurring at the metal interface. A small (5–15 mV) amplitude ac signal is applied to the sample by the potentiostat and the current response is analyzed to extract the phase and amplitude relationship between the current and the voltage signals. The impedance is usually measured as a function of frequency over many decades, for example from 100 kHz to 1mHz. For this reason the measurement points are chosen logarithmically to get an even spread of points across. Choice of lower frequency is often a compromise between acquisition time and resolution, with 7-10 points per decade and a lower frequency limit of 10-1 mHz being a common compromise between accuracy and time needed for data collection [99]. Interpretation of impedance data can be carried out using different available graphs. The Nyquist, plots the real ($Z'$) and imaginary component ($Z''$) of impedance on x and y axis respectively and since almost all corrosion data have a negative imaginary component the y axis is inverted to show $-Z''$ above the x-axis. For a Nyquist plot, showing corrosion data it can be assumed that the frequency decrease from left to right but the graph doesn’t display the frequency for data collected. Bode plot displayed the same data, were
logarithm of the modulus of the impedance (log |Z|) and the phase angle (φ) is plotted on the y axis vs. logarithm of the frequency (log ω) in two separate graphs. Samples of these graphs will be demonstrated in the result chapters. From the Nyquist and Bode plot several parameters regarding the system can be obtained: the solution resistance (R_s) represents the uncompensated solution resistance between the working and reference electrode, the polarization resistance (R_p) relates to the electrochemical (corrosion) processes occurring in the system [101], the electrical double layer capacitance (C_dl). Electrical double layer exists on the interface between an electrode and its surrounding electrolyte. The value of the double layer capacitance depends on many variables (electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness, impurity adsorption, etc.). The analysis of impedance data is often performed by use of an equivalent circuit (EC). An EC is an electrical circuit displaying the same system impedance over all frequencies. Once an EC has been selected “fitting” can be performed using any of several existing modelling software. The values of the components are optimised by the program to produce a model with the minimum deviation possible from the measured data. The accuracy of the “fit” can be viewed graphically and by “weight sum of squares” (calc modulus weighting) (or chi-squared parameter (X^2)) [102]. However the translation from “electrochemical” to “electrical” does not always have a corresponding physical element and use of additional “components” is needed to describe the system. Examples of the most commonly used elements and their impedance expression include a standard resistor (R) is used for modelling resistance in the system. Charge and discharge behaviour corresponds to an electronic capacitor (C). An inductor (L) models behaviour that resists changes in the current. Other elements used to describe the impedance are; Warburg impedance (W), used to model impedance due to diffusion processes. The impedance increases with length of diffusion. At low frequencies the diffusion path is long resulting in high Warburg impedance. Constant Phase Element (CPE) is used in place of a capacitor to compensate the non-homogeneity (roughness and energetic in-homogeneity) of the surface.

3.3 X-ray Photoelectron Spectroscopy

XPS is one of the most powerful techniques for surface analysis, and is widely used for determination of chemical composition and chemical states of the surface elements. XPS is a sensitive technique that uses soft X-rays with small line widths < 1.0 eV and high line energy > 1000 eV to probe approximately the top 100 nanometres of the surface. In the 1950s Kai
Siegbahn, developed an electron spectrometer containing an X-ray emission source and with an electromagnetic energy analyser [86]. The first X-ray photoelectron spectrum was collected on sodium chloride in 1954 by Siegbahn’s group [86]. The physical basic of photoelectron spectroscopy is based on photon in/electron out process, (photo-ionization process) and can be considered as follows

\[ A + h\nu = A^+ + e^- \]

Where \( h\nu \) is the energy of a photon as given by Einstein relation \( (E = h\nu) \)

\( h = \) plank constant \((6.62 \times 10^{-34} \text{Js})\)

\( \nu = \) frequency \((\text{Hz})\) of radiation

Conservation of energy then requires that:

\[ E(A) + h\nu = E(A^+) + E(e^-) \]

Since the electron's energy is present solely as kinetic energy \((\text{KE})\) this can be rearranged to give the following expression for the KE of the photoelectron:

\[ \text{KE} = h\nu - (E(A^+) - E(A)) \]

The final term in brackets, representing the difference in energy between the ionized and neutral atoms, is generally called the binding energy \((\text{BE})\) of the electron, (the binding energy is the attraction energy between the electron and the atomic nucleus). Each atom in the surface has core electron with the characteristic binding energy that is conceptually, equal to the ionization energy of that electron - this then leads to the following commonly quoted equation:

\[ \text{BE} = h\nu - \text{KE} \]

XPS instruments consist of an X-ray source, an energy analyzer for the photoelectrons, and an electron detector. The analysis and detection of photoelectrons requires that the sample be placed in a high-vacuum chamber (Figure 3.1). The energy of the photoelectrons is analyzed
by an electrostatic analyzer, and the photoelectrons are detected by an electron multiplier tube or a multichannel detector such as a micro channel plate. When an X-ray beam directs to the sample surface, the energy of the X-ray photon is adsorbed completely by the core electron of an atom. The core electron, will then escape from the atom and emit out of the surface.

Now a days the most commonly employed X-ray sources are Mg K$\alpha$ radiation ($h\nu = 1253.6$ eV) and Al K$\alpha$ radiation ($h\nu = 1486.6$ eV). The emitted photoelectrons will therefore have kinetic energies in the range of ca. 0 - 1250 eV or 0 - 1480 eV. The incident radiation of 1486.6 eV for Al or 1253.6 eV for Mg has sufficient energy to overcome the binding energy of the electron residing in their respective shells and excite them. The core electron of an element has a unique binding energy, which seems like a "fingerprint". Thus almost all elements except for hydrogen and helium can be identified via measuring the binding energy of its core electron. Each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies. Furthermore the intensity of the peaks is related to the concentration of the element within the sampled region. Thus, the technique provides a quantitative analysis of the surface composition. The elements are identified by the correspondence of the peak position with those of the standards. The peak areas can be used to determine the composition of the materials surface. The shape of each peak and the binding energy can be slightly altered by the chemical state of the emitting atom. Hence XPS can provide chemical bonding information as well.

Figure 3.1. Simple block to the XPS instrument
3.4 Scanning Electron Microscopy (SEM)

SEM is one of the most widely used analytical tools, due to the extremely detailed images it can provide. Coupled to an auxiliary Energy Dispersive X-ray Spectroscopy (EDS) detector, this technique also offers elemental identification of nearly the entire periodic table. The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive to not charge and deflect the electron. The combination of higher magnification (higher than $10^5$), larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today.

3.5 Contact Angle

Contact angle is a measure of wettability (the degree to which a fluid spread on a surface), which is a measure of the hydrophobicity and hydrophilicity properties of the solid surface. Intermolecular bonds or cohesive forces between water molecules cause surface tension. When water contacts a solid substrate, there is usually attraction between the two materials. The adhesive forces between water and the substrate compete against the cohesive forces in the water, when the adhesive forces are stronger than the cohesive forces, water tends to spread over the substrate, when the adhesive forces are weaker than the cohesive forces, water tends to form a droplet on the substrate. Viewing from molecular scales, the type of chemical molecular groups at a surface determines the hydrophobicity or hydrophilicity. Water molecules are polar (positive and negative charge centres are separated); therefore they like to attract polar chemical groups. Polar groups such as -OH can form hydrogen bonds with water molecules, thus a surface having such groups shows hydrophilicity. A surface coated with polar groups such as -CH$_3$ shows hydrophobicity because interactions among water molecules are stronger than those between water molecules and the surface polar chemical groups. Hydrophilicity or hydrophobicity of a solid surface can be characterized by contact angle measurement. Generally water contact angles less than 90° are exhibit hydrophilic surfaces.
and greater than $90^\circ$ are hydrophobic surfaces. In this thesis, the contact angles of water on film surface were measured using the Nima dynamic surface tensiometer DST 9005. The measurement results revealed the chemical nature of the surface.
Chapter 4

Experimental Procedure

All the measurements were carried out with calibrated instruments and following the procedure steps mentioned below. The reliability and accuracy of the presented experimental results in this work were taken into the consideration. The experimental measurements repeated several times, all of these repeated measurements were close to each other in both graphical shape and the parameter values. In EIS measurements the fitting data Z view software show the error % for each measurement, all of the presented EIS measurements show less than 10 % error, in fact most of them were less than 2 %.

4.1 Protective Effect of Dihydroxamic Acids on Carbon Steel Corrosion

4.1.1 Chemical and Solutions

All test solutions were prepared with high purity water (Millipore Mill Q-system). The base electrolyte was 0.1 mol dm$^{-3}$ Na$_2$SO$_4$ naturally aerated at room temperature. Metal ions were used in the form of sulphate salts, unless otherwise stated. All other reagents were analytical grade and were used without further purification. Standard buffers for pH meter calibration were used. Where necessary the pH of each test Na$_2$SO$_4$ solution was adjusted to 7 ± 0.1 by addition of small quantities of 1M NaOH or 1M H$_2$SO$_4$ and 1M NaOH or 1M HCl of each test NaCl solution. The alkyl mono- and dihydroxamic acids (C$_n$H$_{2n+1}$CONHOH, n=9, 16; HOHNOCC$_n$H$_{2n}$CONHOH: n=0, 4, 5) were synthesized in our laboratory from hydroxylamine and the appropriate acyl chlorides/dichlorides in the presence of sodium carbonate dissolved in water. The hydroxamic acids were purified by re-crystallization from the appropriate organic solvents, identified by melting points, elemental analysis and thin layer chromatography. Their purity was ≥99.8% (see table 4.1).
4.1.2 Equipment

The pH meter of test solution were measured with (Laboratory Digital pH meter OP-211/2 radelkis) and combined glass electrode. Polarisation experiment were conducting by using an EG&G potentiostat /galvanostat model 283 with M352W software. Electrochemical impedance measurements were performed using Solartron 1286 Electrochemical Interface with 1250 Frequency Response Analyzer. Z view computer software was used to fit the experimental impedance data to the chosen electrical equivalent circuit model.

Table 4.1. The synthesized and tested hydroxamic acids

<table>
<thead>
<tr>
<th>chemicals</th>
<th>melting point [°C]</th>
<th>elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calc.</td>
<td>found</td>
</tr>
<tr>
<td>Oxalyl dihydroxamic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_4$N$_2$O$_4$ Mw:120</td>
<td>172</td>
<td>20.0</td>
</tr>
<tr>
<td>Succinyl dihydroxamic acid</td>
<td>157-158</td>
<td>32.43</td>
</tr>
<tr>
<td>C$_4$H$_8$N$_2$O$_4$ Mw:148</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adipoyl dihydroxamic acid</td>
<td>163-164</td>
<td>40.91</td>
</tr>
<tr>
<td>C$_6$H$_12$N$_2$O$_4$ Mw:176</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pimeloyl dihydroxamic acid</td>
<td>182-183</td>
<td>44.21</td>
</tr>
<tr>
<td>C$_7$H$_14$N$_2$O$_4$ Mw:190</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decanoyl hydroxamic acid</td>
<td>87-88</td>
<td>64.17</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{21}$NO$_2$ Mw:187</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearoyl hydroxamic acid</td>
<td>100-100.5</td>
<td>72.24</td>
</tr>
<tr>
<td>C$<em>{18}$H$</em>{37}$NO$_2$ Mw:299</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.1.3 Electrodes
Corrosion tests were performed on low carbon steel, cylindrical rod (0.17% C, 0.045% P, 0.045% S, 0.009% N, balance Fe) as working electrode (WE). The rod specimen was embedded in epoxy resin mould (Araldit Ay 103 and Hardener Hy 956) and only its cross-section (total surface area of 0.785 cm$^2$) was allowed to contact the electrolyte solutions. Saturated Calomel Electrode (SCE) was used throughout as the reference electrode (RE). All potential in these thesis are reported relative to this electrode, unless otherwise stated. Platinum sheet (0.5 × 1.0 cm) was used as the counter electrode.

### 4.1.4 Electrode Preparation

Before each experiment, the working electrodes were mechanically polished using emery paper of 200-1200 grit. After rinsing with deionised water the work electrodes were degreased with ethanol, washed again with distilled water, dried in a stream of nitrogen and then immersed immediately in the test solution. No attempt was made to remove the air-formed oxide film which may have formed on the metal surface prior to immersion.

### 4.1.5 Procedure

Electrochemical experiments were carried out in a glass cell with a capacity of 500 ml. The base electrolyte was 0.1 mol dm$^{-3}$ Na$_2$SO$_4$ solutions, and the pH was adjusted to 7. All electrochemical measurements were made after allowing the electrode to achieve the steady state potential under open-circuit condition (approximately 1 hour immersion time) unless otherwise stated. The solution temperature was room temperature ($25 \, ^\circ\text{C}$). The nature of inhibitor actions were obtained using wide range polarization curves with a potential sweep rate of 10 mV/min. (from $E_{ocp}$ to -1.4V in the cathodic direction and from $E_{ocp}$ to 1.2V in the anodic direction) on fresh electrodes. Inhibition efficiencies were evaluated from corrosion current densities calculated by the Tafel extrapolation method (the formula is presented in chapter 5.1). Impedance spectra were obtained in the frequency range of 30 kHz to 0.01Hz with perturbation amplitude of 10 mV. X-ray photoelectron spectra were recorded on a Kratos XSAM 800 spectrometer operated at fixed analyser transmission mode using Mg K$\alpha_{1,2}$ (1253.6 eV) excitation. The pressure of the analysis chamber was lower than $1 \times 10^{-7}$ Pa. Wide scan spectra were recorded for all samples in the 100-1300eV kinetic energy range using
80eV pass-energy, with 0.5 eV steps and 0.5 s dwell time. High-resolution spectra of photoelectron lines of the main constituent elements, and the C1s region for the carbon-containing layers and contaminations, were recorded at 40 eV pass energy by 0.1 eV steps and min.1 s dwell time. Spectra were referenced to the energy of the C1s line of the hydrocarbon type adventitious carbon, (present or build up at the surface of the samples during spectra acquisition), set at 284.6 eV B.E. (binding energy). Quantitative analysis, based on peak area intensities (after removal of the Shirley- or linear-type background), was performed by the Vision 2000 program using experimentally determined photo-ionisation cross-section data, provided by the manufacturer of the spectrometer. The morphology of the samples was investigated by scanning electron microscopy (SEM S570, HITACHI), equipped with an EDR288 energy dispersive X-ray spectrometer (RONTEC, EDR288) for chemical analysis. The SEM operated by commercial RONTEC software.

4.2 Inhibition of Carbon Steel Corrosion by SAMs of Mono-Hydroxamic Acids

4.2.1 Electrodes

The working electrode was in the form of a disc cut from carbon steel sheet and was embedded into epoxy resin mould with an exposed area of 1.65 cm². Reference and counter electrodes were the same as in paragraph 4.1.3.

4.2.2 Preparation of Hydroxamic Acid SAMs

Hydroxamic acids CH₃(CH₂)ₙCONHOH; n = 8 (C10), 16 (C18) were synthesized in our laboratory as reported previously. Solutions of 5mM concentration were prepared by dissolving the corresponding reagent in tetrahydrofuran (THF). The carbon steel electrode of 1.65mm diameter was polished using diamond paste of different grain size down to 0.03 μm particle diameter. The electrode was sonicated in water for 10 min, cleaned in absolute ethanol and rinsed with water. After drying in air, the clean carbon steel electrodes were immersed into the above mentioned solutions for different assembling times (15, 30 and 60 min), followed by rinsing off the residual and finally drying in air.
4.2.3 Procedure

Equipments were similar to that mentioned in paragraph 4.1.2. Electrochemical experiments were carried out in a glass cell with a capacity of 500 ml. The blank solution was 0.1 mol dm$^{-3}$ Na$_2$SO$_4$ solutions, and the pH was adjusted to 7. Electrochemical measurements on hydroxamic acid modified carbon steel electrodes were performed after 15 min of immersion time in sodium sulphate electrolyte. Potentiostatic polarization were conducted starting from $E_{ocp}$ to -900mV in the cathodic direction and from $E_{ocp}$ to 100mV in the anodic direction by a potential sweep rate of 10 mV/min. Inhibition efficiencies were evaluated from corrosion current densities calculated by the Tafel extrapolation method. Impedance spectra were obtained in the frequency range of 10 kHz to 0.01Hz with perturbation amplitude of 10 mV. X-ray photoelectron measurements were carried out using similar procedure as in the paragraph 4.1.5. The contact angle values were determined on the carbon steel surface, bare or covered with the hydroxamic acids monolayer by DST 9005 Nima Dynamic Surface Tensiometer. Calibration of the instrument and measurement of the surface tension of the tested liquid were carried out prior to the measurements. The samples were immersed 10 mm deep, into the Milli Q water (tested liquid) with immersion and withdraw speed of 5mm/min, using pre-programmable computer control. The measurements were performed under atmospheric condition and room temperature (25°C). Two subsequent cycles were recorded in each measurement both advancing and receding dynamic contact angles were measured. The average of advancing contact angles were reported in this thesis.
CHAPTER 5

Protective Effect of Oxalyl-Dihydroxamic Acid and Pimeloyl-Dihydroxamic Acid on Carbon Steel Corrosion

In this chapter the corrosion inhibition properties of oxalyl-dihydroxamic acid (C2) and pimeloyl-dihydroxamic acid (C7) were investigated. Electrochemical measurements were performed to evaluate the inhibition efficiency of the mentioned molecules at different concentrations, different immersion time and to study their adsorption process. It is worth to note that the following di-hydroxamic acids (succinyl dihydroxamic acid C₄H₈N₂O₄ (C4) and adipoyl dihydroxamic acid C₆H₁₂N₂O₄ (C6)) where tested as well, their results are not presented because we found that C4 and C6 behave almost similar to C7, hence only C7 data was selected. Furthermore C7 was chosen for further investigation in the presence of metal ions (chapter 6).

5.1 Polarization Measurements

Evaluation of the corrosion inhibition effect can be performed with different electrochemical techniques, and one very powerful technique is potentiodynamic polarization. From this measurement the current density at different potentials are obtained, which provide information of the electrochemical behaviour and corrosion resistance of carbon steel in the presence of oxalyl-dihydroxamic acid (C2) and pimeloyl-dihydroxamic acid (C7). The current density corresponds to the rate of electrochemical reactions associated with corrosion processes taking place on carbon steel surface in the electrolyte under polarization. The corrosion rate is proportional to the corrosion current density. It follows that a low corrosion current density indicates a high corrosion resistance. Fig.5.1 represent potentiodynamic polarization curves for carbon steel in 0.1 mol dm⁻³ Na₂SO₄ solution in the absence and presence of the C2 and C7 inhibitors. The corrosion kinetic parameters and inhibition efficiencies η % are given in the Table 5.1. The inhibition efficiency η % is defined as:
\[ \eta (\%) = \frac{i_{\text{corr}} - i_{\text{corr(inh)}}}{i_{\text{corr}}} \]

where \( i_{\text{corr}} \) and \( i_{\text{corr(inh)}} \) are the corrosion current density values without and with inhibitor, respectively, determined by Tafel extrapolation to the corrosion potential. It can be seen on Fig. 5.1 that the dominant cathodic reduction is oxygen reduction controlled by diffusion process, and the anodic reaction is iron dissolution controlled by charge transfer process. In the presence of C7 it can be observed that the corrosion potential shifts in the positive direction, the polarization curve Fig. 5.1(b) show that C7 act as anodic inhibitor. Polarization curve Fig. 5.1(c) clearly shows that the C2 decrease the current densities with respect to those for the blank for both anodic and cathodic reactions, without causing any appreciable change in values of corrosion potential, suggesting that the C2 is mixed type inhibitor, since affect both the metal dissociation and oxygen reduction reactions. The results show that C2 is more efficient than C7 which has only moderate inhibition effect (detailed explanation will be presented in the paragraph 5.3).

Table 5.1. Corrosion potential, corrosion current densities and inhibition efficiency of C2 and C7 at pH7 and different immersion time, (corrosion current density (i) calculated by Tafel extrapolation)

<table>
<thead>
<tr>
<th>Solution</th>
<th>Immersion time [h]</th>
<th>( E_{\text{corr}} ) [mV]</th>
<th>( i ) [( \mu \text{A/cm}^2 )]</th>
<th>( \eta ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(_2)SO(_4) (0.1M)</td>
<td>-644</td>
<td>8.71</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C2 (7.5×10(^{-4})M)</td>
<td>1</td>
<td>-610</td>
<td>0.83</td>
<td>90</td>
</tr>
<tr>
<td>C7 (10(^{-3})M)</td>
<td>1</td>
<td>-543</td>
<td>4.16</td>
<td>52</td>
</tr>
</tbody>
</table>
Figure 5.1. Polarization curve for carbon steel in (a) 0.1M Na$_2$SO$_4$ as a blank solution and in the presence of (b) C7 (10$^3$ M) and (c) C2 (7.5×10$^{-4}$M) after 1h immersion time. The pH of the solutions was adjusted to 7

5.2 EIS Measurements

The electrochemical behaviour of the material is crucial for the charge transfer processes occurring at electrode/solution interface, in this case EIS is very useful. In addition EIS measurements are particularly useful in long time tests because the applied small AC amplitude (14mV) do not perturb the system dramatically, and it is possible to monitor the gradual change of corrosion process in the inhibitor-metal system over time. In the experimental conditions used, the tests were carried out until 72 h, an immersion time that guarantees sufficient evaluation of the inhibition efficiency. Impedance diagrams obtained between the frequency range of 30 kHz - 0.01Hz at open circuit potential in the presence and absence of oxalyl-dihydroxamic acid and pimeloyl-dihydroxamic acid after different immersion time are shown in Figs. 5.2 and 5.3. The impedance data were fitted to the circuit model using Zview software and the fitted parameters are shown in Table 5.2.

Figure 5.2. EIS measurements for carbon steel in 0.1M Na$_2$SO$_4$ and C7 (7.5×10$^{-4}$M) at pH7 and different immersion time. The blank solution was measured after 1h of immersion time.
Figure 5.3. EIS measurements for carbon steel in 0.1M Na$_2$SO$_4$ and C2 (7.5×10$^{-4}$M) at pH7 and different immersion time. The blank solution was measured after 1h of immersion time.

For analysis of the impedance spectra containing one capacitive loop the equivalent circuit (EC) given in Fig. 5.4 (a) was used while the EC shown in Fig. 5.4(b) was used for the spectra exhibiting three capacitive time constants. Constant phase element (CPE) is used in place of a capacitor to compensate the non-homogeneity of the surface [104,105]. In the used Zview software the CPE consists of two components CPE-T reflect the capacitance of the CPE impedance and CPE-P reflect the uniformity of the interfaces. In the presence of C2 molecules a complicated interfacial structure was observed where each spectrum consists of three capacitive time constants, this most likely because the inhibitor film is a multi-layered film and so shows more than one time constant. The inhibitor film is supposed to be a combination of an inner layer which would be an inhibitor-metal complex and outer layer would be inhibitor molecule layer. However the satisfactory simulation of the impedance characteristic of the inhibitor-filmed electrode surface by EC model, as shown in Fig. 5.4 (b), indicate that the inhibitor film has a multi-layered structure. The inhibition efficiency ($\eta$) was calculated using the equation below.

$$\eta \% = \frac{R_{ct} - R_t}{R_{ct}} \times 100$$

where $R_{ct}$ is the transfer resistance of electrons through the inhibitor film and $R_t$ is the charge-transfer resistance for the inhibitor free carbon steel electrode in the corrosive solution. $\eta$
values of C2 and C7 were calculated and are also given in table 5.2.

![Electric circuit models](image)

(a) (b)

Figure 5.4. Electric circuit models used in fitting the experiments data (Rs = solution resistance, CPE_{dl} = double layer constant phase element, R_{ct} = charge transfer resistance, R_{l1} = first layer resistance, R_{l2} = second layer resistance, CPE_{l1} = first layer constant phase element and CPE_{l2} = second layer constant phase element.

5.3 Protective Effect of Di-hydroxamic Acids

The results obtained in this work reveal that C7 provided moderate corrosion protection to the carbon steel with inhibition efficiencies 65% compared to 91% for C2, after 1h of immersion, as can be seen in Figs. 5.1, 5.2, 5.3 and Tables 5.1, 5.2. Generally it is known that good inhibition can be obtained by using organic corrosion inhibitor molecules containing reasonably large hydrocarbon chain, so as to form a better barrier to the water molecules and active species between the electrode surface and corrosive solutions. However the results of C2 and C7 behave differently from this fact, where C7 with \((\text{CH}_2)_5\) hydrocarbon chain provide less inhibition efficiency. This has been attributed to the fact that the C7 with long single hydrocarbon chain probably tend to be adsorbed with only one hydrophilic group (HONHOH) on the metal surface, Fig. 5.5 (a), moreover the single bond of this chain could be make the orientation of C7 molecule susceptible to free movement and rotation about C-C bond which is negatively affect the adsorption process. However as can be seen in the next chapter, the addition of metal ions to C7 significantly improved the inhibition efficiency of C7. This can be explained as the metal ions form a dense compact layer of complexes with C7, making the adsorbed C7 molecule immobilized on the surface. In contrary C2 molecules are considered to have a rigid and planar structure which is conductive to surface adsorption and hence most likely tend to be adsorbed with the two hydrophilic groups onto the metal surface Fig. 5.5 (b). The results showed that in the presence of C2 the values of capacitance \(\text{CPE}_{l-T}\) decreased (Table 5.2) which indicates a good adsorption of C2 molecule on the electrode surface. As the
formation of multiple bonds with metal ions in a solution leads to an increased stability constant, multiple attachments to the metal (oxide) surface by an inhibitor containing several function groups can lead to stronger adsorption and better inhibition. C2 is a very effective corrosion inhibitor, it is well adsorbed and forms protective film on the surface, this film seems to be a combination of an inner-layer which is likely to be C2/metal complexes, some authors proposed that the ability of the inhibitor to form complexes with ferrous or ferric ions play a key role in the inhibition mechanism [106]. And outer-layer which is likely to be inhibitor layer with possible inhibitor molecular cross-linked.

![Figure 5.5. Models of C7 (a) and C2 (b) adsorption on carbon steel surface](image)

Table 5.2. The electrochemical parameters and inhibition efficiency of carbon steel in 0.1M Na₂SO₄ solution obtained from EIS data for C2 and C7 at (7.5×10⁻⁴M), pH7 and different immersion time
<table>
<thead>
<tr>
<th>solution</th>
<th>time [h]</th>
<th>CPE(_{l2})-T [(\mu\text{Fcm}^{-2})]</th>
<th>CPE(_{l2})-P [(\Omega\text{cm}^2)]</th>
<th>R(_{c}) [(\Omega\text{cm}^2)]</th>
<th>CPE(_{l1})-T [(\mu\text{Fcm}^{-2})]</th>
<th>CPE(_{l1})-P [(\Omega\text{cm}^2)]</th>
<th>R(_{\text{ct}}) [(\Omega\text{cm}^2)]</th>
<th>CPE(_{\text{ct}})-T [(\mu\text{Fcm}^{-2})]</th>
<th>CPE(_{\text{ct}})-P [(\Omega\text{cm}^2)]</th>
<th>(\eta) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>1</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>24</td>
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</table>
5.4 Effect of Concentration

One of the variables that might control the adsorption rate of inhibitors on the metal surface and the inhibition coverage is the concentration. Fig. 5.6 presents inhibition efficiency values as a function of C2 and C7 concentration. At lower concentration (C ≤ 10^{-4} M) insufficient adsorption and low surface coverage hence low inhibition efficiency was observed. By increasing the concentration the inhibition efficiency increased up to an optimal concentration (C=7.5.10^{-4} M) where a maximum in the inhibitive efficiencies of the tested molecules are observed. Increasing further the concentration (C >10^{-3} M), results in a decrease in the inhibition efficiency. This phenomenon must likely due to the formation of water soluble non-protective ferrous complexes at higher concentration of the inhibitors, facilitate the replacement of adsorbate by water and aggressive ions lead to withdrawal back into the solution bulk, and result in corrosion rate increase. Similar behaviour was often observed using organic compound, such as phosphonic acid and sodium-dodecylbenzenesulphonate [107-108].

![Figure 5.6. Variation of inhibitor efficiency vs. C2 and C7 concentration (C)](image)

5.5 Effect of Immersion Time

Fig. 5.7 shows that inhibition efficiency of C7 decreased over the time and lost the inhibitive efficiency gradually with time. C2 acts as a better corrosion inhibitor, the efficiencies reaches
91%, after one hour of immersion time, and almost remain unchanged over the time, which is due to a good adsorption and the stability of the protective films.

Figure 5.7. Effect of immersion time (h) on the inhibition efficiency in the presence of C7 (7.5×10^-4M), and C2 (7.5×10^-4M)

5.6 Discussion and Conclusion

Oxalyl-dihydroxamic acid (C2) is a very effective corrosion inhibitor for carbon steel, it well adsorb and form a protective film on the surface, this film consist of two layers, an inner-layer which is most likely to be C2/metal complexes, and outer-layer which is likely to be inhibitor layer with possible inhibitor molecular cross-linked. The high efficiency of C2 is attributed to the adsorption process, where the molecules tend to be adsorbed with the two hydrophilic groups onto the metal surface creating a strong bond and good adhesion between C2 and the substrate.

Pimeloyl-dihydroxamic acid (C7) provided a moderate corrosion protection to the carbon steel with inhibition efficiencies 65% compared to 91% for C2. This has been attributed to the fact that the C7 with long single hydrocarbon chain probably tend to be adsorbed with only one hydrophilic group (HONHOH) on the metal surface, this single bond could be make the orientation of C7 molecule susceptible to free movement and rotation about C-C bond which is negatively affect the adsorption process and as a consequence the inhibition properties. Both C2 and C7 molecules perform at optimum concentration. Higher concentrations beyond the optimum value results in reducing the corrosion protection rate. This phenomenon most likely due to the formation of water soluble non-protective ferrous complexes at higher
concentration of the inhibitors, facilitate the replacement of adsorbate by water and aggressive ions lead to withdrawal back into the solution bulk, and result in corrosion rate increase. This phenomena is common with organic corrosion inhibitors
Chapter 6

Effect of Metal Ions on Corrosion Inhibition of Pimeloyl-Dihydroxamic Acid

Synergistic inhibition effect between organic corrosion inhibitors and some metal ions are common phenomena and have been tested and implemented in different systems. Here we study the inhibition performance of pimeloyl-dihydroxamic acid in the presence of some divalent cations. The protection efficiency was determined by electrochemical impedance spectroscopy and polarization measurements. XPS was applied to characterise and identify the chemical composition of the electrode surface and SEM to study the morphological of steel surface.

6.1 Protective Effect of Pimeloyl-Dihydroxamic Acid in the Presence of Metal Ions

The influence of metal ions namely (Zn$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, and Mg$^{2+}$) on the adsorption process and corrosion inhibition of C7 on carbon steel surface has been investigated by EIS. In the presence of C7/Ni$^{2+}$ or C7/Mg$^{2+}$ inhibitor mixtures only one capacitive loop appears in the spectrum. The presence of a single semicircle depicts the presence of a single charge-transfer process during dissolution. The impedance data in this case were analyzed using the equivalent circuit (EC) given in Fig. 6.1 (a). In the presence of C7/ Zn$^{2+}$ the diagrams could be characterized by two semi-circle one (not clearly resolved) at high frequency range due to the inhibitor film, and the other at lower frequencies due to the corrosion processes. The impedance spectra exhibiting two capacitive time constants, was analyzed with the EC given in Fig. 6.1(b).
Figure 6.1. EC models used in fitting the experimental impedance data. In which $R_s$ represent the solution resistance, $R_{ct}$ charge transfer resistance, $R_f$ film resistance, CPE$_f$ and CPE$_{dl}$ are constant phase elements for the film and double layer, respectively.

One of the features of hydroxamic acid derivatives is their complexing capacity towards a series of metal ions [109-111]. After deprotonation, C7 form stable complexes with metal ions via co-ordination through the two oxygen atoms of the –CONHO$^-$ group [112]. As illustrated in the Figs. 6.2, 6.3 and showed in the Tables 6.1, the presence of Zn$^{2+}$ or Ni$^{2+}$ remarkably increase the inhibition efficiency of C7. The decrease in the capacitance CPE-T values, indicate the adsorption and the formation of stable complexes on the carbon steel surface, which is protect the carbon steel from further corrosion [113,114]. On the other hand we can notice, that the addition of Mg$^{2+}$ has no effect on the inhibition performance of C7 (see Fig. 6.4), this is because of their low stability constants with hydroxamic acid derivatives as observed by Farkas et al. [115,116]. However the molar ratio of C7/metal ions plays an important role in the inhibition performance of carbon steel corrosion (Fig. 6.5). Further details will be presented in the XPS results about this phenomenon.
Figure 6.2. EIS measurements for carbon steel in 0.1M Na$_2$SO$_4$ and 0.001M C7 in the presence of Zn$^{2+}$ at different molar ratio, measured after 1h immersion time at pH7

Figure 6.3. EIS measurements for carbon steel in 0.1M Na$_2$SO$_4$ and 0.001M C7 in the presence of Ni$^{2+}$ at different molar ratio, measured after 1h immersion time at pH7

Figure 6.4. EIS measurements for carbon steel in 0.1M Na$_2$SO$_4$ and 0.001M C7 in the presence of Mg$^{2+}$ at different molar ratio, measured after 1h immersion time at pH7
Figures 6.6 and 6.7 represent potentiodynamic polarization curves for carbon steel in 0.1 mol dm$^{-3}$ Na$_2$SO$_4$ solutions in the absence and presence of the C7/Ni$^{2+}$ and C7/Zn$^{2+}$. The corrosion kinetic parameters and inhibition efficiencies ($\eta$ %) are given in the Table 6.2. The corrosion current density values without and with inhibitor was determined by Tafel extrapolation to the corrosion potential. In the presence of the optimum molar ratio of C7/metal ions, which is 1/0.5 for Ni ions and 1/2 for Zn ions, the corrosion potential ($E_{corr}$) has shifted to more positive values (-539mV in the presence of Ni$^{2+}$ and -504mV in the presence of Zn$^{2+}$ compared to the measured in blank solution -644mV), and anodic currents of the iron dissolution decreases. At longer immersion time 72h for Ni$^{2+}$ (Fig. 6.6) and 24h for Zn$^{2+}$ (Fig. 6.7), both anodic and cathodic reactions of carbon steel are inhibited, and further decrease in the current densities were recorded. Thus C7/metal ions reduce the iron dissolution and decrease the oxygen reduction reaction as well. This is most likely due to the formation of insoluble stable complexes of C7/metal ions on the carbon steel surface. However the results obtained from the polarization curves are in good agreements with EIS results see tables 6.1 and 6.2.
Figure 6.6. Polarization curve for carbon steel in (a) 0.1M Na$_2$SO$_4$ as a blank solution; and in the presence of C7 ($10^{-3}$M) + Ni$^{2+}$ ($5\times10^{-4}$M) after (b) 1h and (c) 72h immersion time

Figure 6.7. Polarization curve for carbon steel in (a) 0.1M Na$_2$SO$_4$ as a blank solution and in the presence of C7 ($10^{-3}$M) + Zn$^{2+}$ ($2\times10^{-3}$M) after (b) 1h and (c) 24h immersion time
Table 6.1. The electrochemical parameters and inhibition efficiency of carbon steel in 0.1M Na$_2$SO$_4$ solution obtained from EIS data for C7 (10$^{-3}$M) and different molar ratio of metal ions at pH7 and different immersion time

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<th>CPE$_{f}$-P [µF cm$^{-2}$]</th>
<th>$R_f$ [Ω.cm$^2$]</th>
<th>CPE$_{dl}$-T [µF cm$^{-2}$]</th>
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Table 6.2. Corrosion potential, corrosion current densities and inhibition efficiencies of C7 (10^{-3}M) and metal ions, at pH7 and different immersion time, (corrosion current density (i) was calculated by Tafel extrapolation)

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<th>E\textsubscript{corr} [mV] vs. SCE</th>
<th>i [µA/cm\textsuperscript{2}]</th>
<th>η [%]</th>
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</tr>
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<td>1/2</td>
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6.2 Effect of pH

In the presence of metal ions, pH has a significant influence on the C7 corrosion inhibition, as the complexes formation of C7 + metal ions are directly function of pH. In addition to pH7 the effect of C7/Ni\textsuperscript{2+} and C7/ Cu\textsuperscript{2+} has been also tested at pH5. The impedance spectra of these measurements are presented on Figs. 6.8 and 6.9. It can be seen that C7/Ni\textsuperscript{2+} provide better protection at pH7 than at pH5 (see Tables 6.1 and 6.3). This is due to the formation of different types of complexes at each pH with different compositions, structure and properties.

The natural form of the C7 ligand has two dissociable protons, H\textsubscript{2}L, (Fig. 6.10) and the dissociation constant (pK) refers to the following equilibria.

\begin{align*}
pK1: \quad [H\textsubscript{2}L] & = [HL^-] + [H^+] \\
pK2: \quad [HL^-] & = [L\textsuperscript{2-}] + [H^+] 
\end{align*}

The general abbreviation of the C7 ligands are L\textsuperscript{2-} relating to the completely deprotonated form of C7 and HL\textsuperscript{-} referring to the partially deprotonated form. Hence the overall reactions between the metal ions (M\textsuperscript{n+}) and C7 ligand, as well as the overall stability constant (β) of the complexes formed in the system can be defined as.

\begin{align*}
M\textsuperscript{n+} + HL\textsuperscript{-} & = MLH \\
\beta & = \frac{[MLH]}{[M\textsuperscript{n+}][HL\textsuperscript{-}]} \\
M\textsuperscript{n+} + L\textsuperscript{2-} & = ML
\end{align*}
Distributions curve for C7/Ni in Fig. 6.11 show that only a very small fraction of MLH is formed at pH5 and the rest of fraction is in un-dissociated form, H$_2$L. At pH7 we can notice the formation of both MLH and ML complexes, as a result of increasing the dissociation in the acidic functional groups, the negative charge on the functional groups increased to produce an electric field attracting the nickel ions leading to form a more stable complex. This explanation is in agreement with observation recorded, for other hydroxamic acid derivative [117,118]. In the case of C7/Cu$^{2+}$ different behaviour was observed, at pH7 heavy green precipitation of insoluble material was formed, on the bottom of the electrochemical cell, this is because Cu$^{2+}$ has high stability constant and tendency to form ML complex at this pH. Fig. 6.12 shows that at this pH the fraction of ML complex is 100%. Similar observation was reported in the literature [118,119]. However Fig.6.12 shows the formation of both MLH and ML complexes at pH5. The results showed that the addition of Cu$^{2+}$ to C7 at pH5 significantly improved the inhibition performance with 96% efficiency after 72 h immersion time (Table 6.3). Moreover Fig. 6.13 shows the distribution species of C7/Mg$^{2+}$ complexes, it can be seen that the dominant species at pH7 and lower is the un-dissociated form (H$_2$L) and formation of C7/Mg$^{2+}$ complexes occurs only at higher pH values. This is further support the electrochemical results that show no effect of Mg$^{2+}$ on the inhibition performance of C7 at pH7. It is worth to note that similar results were presented in the literature for other complex forming inhibitors, namely Turgoose et. al. [120] attributed the corrosion inhibition efficiency of phosphonate/Zn$^{2+}$ system to the presence of MHL complexes.

Table 6.3. The electrochemical parameters and inhibition efficiency of carbon steel in 0.1M Na$_2$SO$_4$ solution obtained from EIS data for C7+ Cu$^{2+}$ or Ni$^{2+}$ at pH5 and different immersion time. (C7 10$^{-3}$M and metal ions 5×10$^{-4}$M)
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<th>CPE$_{t}$-P</th>
<th>$R_t$ [Ω cm$^2$]</th>
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<th>CPE$_{a}$-P</th>
<th>$R_{ct}$ [Ω cm$^2$]</th>
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Figure 6.8. EIS measurements for carbon steel in 0.1M Na$_2$SO$_4$ and C7 ($10^{-3}$ M) + Cu$^{2+}$ ($5\times10^{-4}$M) at pH5 and different immersion time
Figure 6.9. EIS measurements for carbon steel in 0.1M Na$_2$SO$_4$ and C7 ($10^{-3}$ M) + Ni$^{2+}$ ($5\times10^{-4}$M) at pH5 and different immersion time

Figure 6.10. Species distribution diagram for the C7 system (data obtained from ref. 121)

Figure 6.11. Species distribution diagram for the Ni$^{2+}$-C7 system (data obtained from ref. 121)
Figure 6.12. Species distribution diagram for the Cu$^{2+}$-C7 system (data obtained from ref. 121)

Figure 6.13. Species distribution diagram for the Mg$^{2+}$-C7 system
(data obtained from ref. 121)
6.3 Effect of Immersion Time

Figure 5.7 shows that inhibition efficiency decreased over the time for C7. In contrary it was observed that the addition of Cu$^{2+}$ or Ni$^{2+}$ or Zn$^{2+}$ to C7 act as a better corrosion inhibitor and the efficiency increased over the time as presented in Fig. 6.14. It is worth to note that increasing the immersion time result in increasing the inhibition efficiency for both C7/Zn$^{2+}$ and C7/Ni$^{2+}$ at all the molar ratios, particularly for C7/Ni$^{2+}$ at the optimal molar ratio, where the inhibition is greatly but gradually increased with time (Table 6.1). These observations suggest that a continuous build up of inhibitor film is taking place due to the increase in the thickness and the persistency with time resulting in formation of a protective layer at the carbon steel surface.

![Figure 6.14](image)

<table>
<thead>
<tr>
<th>time [h]</th>
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<th>Zn</th>
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<td>72</td>
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<td>96</td>
<td>45</td>
<td>97</td>
</tr>
</tbody>
</table>

Figure 6.14. The effect of immersion time (h) on the inhibition efficiency of $10^{-3}$ M C7 + $5\times10^{-4}$ M Cu$^{2+}$ at pH5, $10^{-3}$ M C7 + $5\times10^{-4}$ M Ni$^{2+}$, $10^{-3}$ M C7 + $5\times10^{-4}$ M Mg$^{2+}$ and $10^{-3}$ M C7 + $2\times10^{-3}$ M Zn$^{2+}$ at pH7.

6.4 Inhibition Effect in NaCl Solution

The inhibition performance of C7 in the presence of zinc ions on carbon steel surface has been investigated by electrochemical techniques in 0.1 mol dm$^{-3}$ NaCl solution, too. Impedance spectra measured at open-circuit potential are recorded after 1 and 24h of immersion time. Impedance parameters were obtained using the identical equivalent circuit model shown in
In NaCl solution and as can be seen in Bode plots in Fig. 6.15, only one time constant is detected for C7/Zn$^{2+}$ after 24h immersion time, and the corresponding phase angle-frequency plots shows that the maximal phase angle values were kept high in a wide frequency range, even at low frequency region. This demonstrates that a uniform and protective layer of C7/Zn$^{2+}$ with insulating characteristics is formed on the steel surface. On contrary in Na$_2$SO$_4$ solution two time constants were obviously observed (see Fig. 6.16) due to two different contributions; the first one related to the film and located at high frequency, (growth and build up of the film reach a sufficient thickness to characterize its contribution in the impedance measurements [122]), and the second one to the charge transfer at the interface. It is worth to note that only one time constant was recorded for 1h immersion time in Na$_2$SO$_4$ system. The addition of Zn ions significantly improve the inhibition performance of C7 in NaCl solution as can be seen in Table 6.4, this is attributed to the enhanced adsorption and formation of a protective layer of the C7/Zn$^{2+}$ complexes on the metal surface, furthermore increasing the immersion time result in increasing the inhibition efficiency. In addition, Fig. 6.17 represent the polarization curves for carbon steel in 0.1 mol dm$^{-3}$ NaCl solutions, in the absence and presence of the inhibitor. The corrosion kinetic parameters and inhibition efficiencies $\eta$ (%) are given in the Table 6.5. In the presence of C7/Zn$^{2+}$, it can be observed that the corrosion potential shifts in the positive direction, and anodic currents decreases. At longer immersion time, after 24h, both anodic and cathodic reactions of carbon steel are inhibited (Fig. 6.17(c)), but the anodic effect is more pronounced, further decrease in the current densities were recorded. Thus C7/Zn$^{2+}$ ions reduce the iron dissolution and decrease the oxygen reduction reaction as well in NaCl solution. This is most likely due to the formation of insoluble stable complexes of C7/Zn$^{2+}$ ions on the carbon steel surface. In NaCl solution the inhibition efficiency of C7/Zn$^{2+}$ after one hour immersion time was noticeably less than that of Na$_2$SO$_4$ solution. The reason is could be due to the adsorption of chloride ions and formation of iron chloride and zinc chloride, which are easily dissolve and goes into solution. This process alters the formation of the protective film of C7/Zn. Some studies suggest that chloride ions have a stronger tendency to adsorb than sulphate ions [123]. However as the immersion period increases a continuous build up and coverage of the protective film of C7/Zn$^{2+}$ on the electrode surface were take place, this was observed throughout the decrease in the capacitance CPE-T values and the increase in the charge transfer resistance $R_{ct}$ (Table 6.4). The efficiency became closer to that recorded for Na$_2$SO$_4$ after 24h of immersion time. From this we can conclude that once the protective film is established, chloride ions have less effect on the inhibition performance. It is seen, that there
is a good agreement between potentiodynamic polarization and impedance techniques, where
the two different techniques gave the same trend of the inhibition of C7/ Zn$^{2+}$ in both
solutions. It is worth to note that the anodic curve of the electrode in the blank solution in Fig.
6.17(a) shows an indication of pitting formation due to the influence of NaCl at potential
-552mV (113mV more positive than corrosion potential). Similar behaviour was observed for
iron corrosion in NaCl solution [124]. It was found that the deviation of current density from
Tafel behaviour is significant at potentials 100 mV more positive than corrosion potential.

Table 6.4. The electrochemical parameters and inhibition efficiency of carbon steel in 0.1M
Na$_2$SO$_4$ solution obtained from EIS data for 1mM C7 + 2mM Zn$^{2+}$ at pH7 and different
immersion time

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<th>solution</th>
<th>time [h]</th>
<th>$E_{corr}$ [mV]</th>
<th>CPE$_T$ [µFcm$^{-2}$]</th>
<th>CPE$_P$ [µFcm$^{-2}$]</th>
<th>$R_f$ [Ω.cm$^2$]</th>
<th>CPE$_{dl}$-T [µFcm$^{-2}$]</th>
<th>CPE$_{dl}$-P [µFcm$^{-2}$]</th>
<th>$R_{ct}$ [Ω.cm$^2$]</th>
<th>$\eta$ [%]</th>
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Figure 6.15. Impedance spectra of carbon steel in aerated 0.1 mol dm$^{-3}$ NaCl solution pH7.

(a) blank (b) in the presence of $10^{-3}$M C7 + $2 \times 10^{-3}$M Zn$^{2+}$ after 24h immersion time.
Figure 6.16. Impedance spectra of carbon steel in aerated 0.1 mol dm$^{-3}$ Na$_2$SO$_4$ solution at pH7. (a) Blank (b) in the presence of 10$^{-3}$M C7 + 2×10$^{-3}$M Zn$^{2+}$ after 24 h immersion time

Table 6.5 Corrosion potential, corrosion current densities and inhibition efficiencies of 1mM C7 + 2mM Zn$^{2+}$ at pH7 and different immersion time, (corrosion current density (i) were calculated by Tafel extrapolation)

<table>
<thead>
<tr>
<th>solution</th>
<th>immersion time [h]</th>
<th>$E_{corr}$ [mV]</th>
<th>$i$ [$\mu$A/cm$^2$]</th>
<th>$\eta$ [%]</th>
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<tbody>
<tr>
<td>Na$_2$SO$_4$ (0.1M)</td>
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<td>-644</td>
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<tr>
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<td>52</td>
</tr>
<tr>
<td>C7/Zn$^{2+}$</td>
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<td>93</td>
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<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>24</td>
<td>-514</td>
<td>0.31</td>
<td>95</td>
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Figure 6.17. Polarization curve for carbon steel in (a) 0.1M NaCl as a blank solution and in the presence of C7 \((10^{-3}\text{M}) + Zn^{2+} (2 \times 10^{-3}\text{M})\) after (b) 1h and (c) 24h immersion time

6.5 Morphological Studies of Steel Surface

The SEM micrograph in Fig. 6.18 shows a badly corroded carbon steel specimen surface after immersion in 0.1M Na\(_2\)SO\(_4\) without inhibitor. Figs. 6.19 and 6.20 shows the micrograph of carbon steel surface in the presence of C7/Ni at 1/0.5 molar ratio. Fig. 6.19 after 1h of immersion time shows the presence of a thin layer of the inhibitor and no sign of damage in the surface. This explains the effect of only the anodic inhibition at this stage. After 24h of immersion time Fig. 6.20 shows the formation of a thick adsorbed film on the carbon steel surface, which is responsible for the inhibition of corrosion; this is in a good accordance with the results obtained from potentiodynamic measurements, where the inhibition efficiency increases gradually with increasing immersion time, because the build-up of this thick precipitated inhibitor film with time work as a barrier to the oxygen diffusion and hence in addition to anodic inhibition the cathodic reactions were inhibited as well. Figs. 6.21 and 6.22 show the micrographs of the carbon steel in the presence of C7/Ni at 1/2 molar ratio. At this molar ratio only moderate inhibition were observed. After 1h immersion time Fig. 6.21 shows a corroded surface including localised corrosion identified, by a black points. After 24h of immersion time Fig. 6.22 micrograph shows the formation of a protective layer, meanwhile it can be seen the presence of white particles distributed in a random way on the whole surface of specimen, most likely NiO and/or Ni(OH) on the top of the layer. However Fig. 6.22 gives explanation to the increase in the inhibition efficiency from 13% to 60%, (see Table 6.1).
Fig. 6.23 shows the micrograph of the carbon steel in the presence of C7/Zn at 1/0.5 molar ratio and 1h immersion time. It can be seen that the presence of a small white particles distributed in a random way on the whole surface of specimen, most likely ZnO and/or Zn(OH). Fig. 6.24 presents the optimal molar ratio of C7/Zn at 1/2 and 1h immersion time, the micrograph of the carbon steel surface shows a smooth morphology with some polished nicks still can be observed and no sign of corrosion, which is in a good accordance with the results obtained from potentiodynamic and impedance measurements, where the inhibition efficiency reach 93% (Table 6.1).

Figure 6.18. SEM micrographs of the carbon steel surface, in blank solution

Figure 6.19. SEM micrographs of the carbon steel surface, treated by $10^{-3}$ M C7 in the presence of $5.10^{-4}$ M Ni$^{2+}$ after 1h
Figure 6.20. SEM micrographs of the carbon steel surface, treated by $10^{-3}$ M C7 in the presence of $5 \times 10^{-4}$ M Ni$^{2+}$ after 24h

Figure 6.21. SEM micrographs of the carbon steel surface, treated by $10^{-3}$ M C7 in the presence of $2 \times 10^{-3}$ M Ni$^{2+}$ after 1h

Figure 6.22. SEM micrographs of the carbon steel surface, treated by $10^{-3}$ M C7 in the presence of $2 \times 10^{-3}$ M Ni$^{2+}$ after 24h
Figure 6.23. SEM micrographs of the carbon steel surface, treated by $10^{-3}$ M C7 in the presence of $5 \times 10^{-4}$ M Zn$^{2+}$ after 1h

Figure 6.24. SEM micrographs of the carbon steel surface, treated by $10^{-3}$ M C7 in the presence of $2 \times 10^{-3}$ M Zn$^{2+}$ after 1h
6.6 XPS Analysis

XPS analysis was used to identify the chemical composition of the surface. XPS was performed for the following samples: sample A (0.001M C7 without metal ions), sample B (C7/Zn at 1/0.5 molar ratio), sample C (C7/Zn at 1/2 molar ratio) and sample D (C7/Ni at 1/0.5 molar ratio) after 1 h immersion time, sample E (C7/Ni at 1/0.5 molar ratio) after 72 h immersion time.

N 1s region has been scanned in order to detect the presence and intensity of inhibitor (C7 molecule) in the surface film. The XPS spectra of N 1s measured on the surface of carbon steel for the mentioned samples are shown in Figs. 6.25, 6.28, 6.31, 6.34 and 6.37. Three kinds of N 1s peak components are present in XPS spectra measured on the surface of carbon steel for all the tested samples, which indicate the presence of C7 molecule on the carbon steel surface. The binding energy at 398 eV is assigned to the N-H group in the organic molecule, while the peaks at 400 eV ascribed to the protonated nitrogen N-H2 and at 401 eV may be attributed to the interacted N-H group with metal ions (N-Hx) [125].

The corresponding C 1s spectrum on Figs. 6.26, 6.29, 6.32, 6.35 and 6.38 indicate the presence of C7 molecule, where the largest peak at around 284.5-284.9 eV, assigned to the C-C aliphatic bonds, which related to the carbon rich structure of C7. The remaining C 1s peak components have a very low intensity signal and properly associated to the adventitious carbon due to the exposed of the samples to air. O 1s spectra are shown in Figs. 6.27, 6.30, 6.33, 6.36, and 6.39. The intensities of N, O and C in atomic concentration percent for the tested samples are shown in Tables 6.6-6.8. The XPS results are in a good agreement with the electrochemical measurements, where the recorded inhibition efficiencies are in proportional to the amount of N and C. (The higher the amount of N and C in the surface film the higher the inhibition efficiency, and the lower the amount of O the lower the formation of iron oxides.)

<table>
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<tr>
<th>sample</th>
<th>N 1s</th>
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<th>C 1s</th>
<th>Fe 2p</th>
<th>Zn 2p</th>
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Table 6.7. Binding energies (eV) and relative intensities of N1s signals

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Table 6.8. Binding energies (eV) and relative intensities of C1s signals

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<td>6.21</td>
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Figure 6.25. N 1s spectra of carbon steel exposed to 0.1M Na₂SO₄ solution containing sample A (10⁻³M C7)
Figure 6.26. C 1s spectra of carbon steel exposed to 0.1M Na$_2$SO$_4$ solution containing sample A (10$^{-3}$M C7)

Figure 6.27. O 1s spectra of carbon steel exposed to 0.1M Na$_2$SO$_4$ solution containing sample A (10$^{-3}$M C7)

Figure 6.28. N 1s spectra of carbon steel exposed to 0.1M Na$_2$SO$_4$ solution containing sample B. (C7/Zn$^{2+}$ mixture at 1/0.5 molar ratio)
Figure 6.29. C1s spectra of carbon steel exposed to 0.1M Na$_2$SO$_4$ solution containing sample B. (C7/Zn$^{2+}$ mixture at 1/0.5 molar ratio)

Figure 6.30. O 1s spectra of carbon steel exposed to 0.1M Na$_2$SO$_4$ solution containing sample B. (C7/Zn$^{2+}$ mixture at 1/0.5 molar ratio)

Figure 6.31. N 1s spectra of carbon steel exposed to 0.1M Na$_2$SO$_4$ solution containing sample C. (C7/Zn$^{2+}$ mixture at 1/2 molar ratio)
Figure 6.32. C 1s spectra of carbon steel exposed to 0.1M Na$_2$SO$_4$ solution containing sample C. (C7/Zn$^{2+}$ mixture at 1/2 molar ratio)

Figure 6.33. O 1s spectra of carbon steel exposed to 0.1M Na$_2$SO$_4$ solution containing sample C. (C7/Zn$^{2+}$ mixture at 1/2 molar ratio)

Figure 6.34. N 1s spectra of carbon steel exposed to 0.1M Na$_2$SO$_4$ solution containing sample D. (C7/Ni$^{2+}$ mixture at 1/0.5 molar ratio)
Figure 6.35. C 1s spectra of carbon steel exposed to 0.1M Na₂SO₄ solution containing sample D. (C7/Ni²⁺ mixture at 1/0.5 molar ratio)

Figure 6.36. O 1s spectra of carbon steel exposed to 0.1M Na₂SO₄ solution containing sample D. (C7/Ni²⁺ mixture at 1/0.5 molar ratio)

Figure 6.37. N 1s spectra of carbon steel exposed to 0.1M Na₂SO₄ solution containing sample E. (C7/Ni²⁺ mixture at 1/0.5 molar ratio) 72 h
6.7 Comparative Study between Hydroxamic Acid and Carboxylic Acid

A hydroxamic acid is a class of chemical compounds sharing the same functional groups in which an -NH is inserted into a carboxylic acid as shown in the scheme 1

Scheme 1. General structure of hydroxamic and carboxylic acids
Different carboxylic acid derivatives were tested as corrosion inhibitor for different metals and environments as mentioned previously (chapter 2, paragraph 2.4.1). However a selected hydroxamic and carboxylic acids that is match in their molecular structure except the presence of -NH group in the hydroxamic acid as presented in the scheme 2, were tested by EIS and their corrosion inhibition for carbon steel was evaluated for the sake of comparing and to see the influence of the hydroxamic acid nitrogen atoms on the corrosion inhibition performance.

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<th>structure</th>
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<td>C₂H₂O₄N₂</td>
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<td>Ox</td>
<td>C₂H₂O₄</td>
</tr>
<tr>
<td>Adipoyl-dihydroxamic acid</td>
<td>C6</td>
<td>C₆H₁₂O₄N₂</td>
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<tr>
<td>Adipic acid</td>
<td>Ad</td>
<td>C₆H₁₀O₄</td>
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</table>

Scheme 2. Name and structure of the tested hydroxamic and carboxylic acids

Table 6.9 obviously show that oxalyl-dihydroxamic acid has higher protection efficiency 91% than oxalic acid 36% and the same with adipoyl-dihydroxamic acid has higher protection efficiency 56% than adipic acid 13%. Simply we can notice that the dihydroxamic acids provided a better corrosion protection to the carbon steel in the tested conditions and conveniently we attributed the higher inhibition efficiencies of dihydroxamic acids to the presence of nitrogen atoms, which participate in the adsorption process and enhancing the inhibition efficiency. The high inhibition efficiency of Ad + Zn (87%) is most likely related to the Zn ions, which work as cathodic inhibitor this can be seen as the corrosion potential (E_{corr}) has shifted to more negative values (-706 mV) compared to the measured in blank solution similar observation on the effect of Zn ions on the cathodic reactions was reported [55].
Table 6.9. Corrosion potential, polarization resistance and inhibition efficiency of C2, Ox, C6 and Ad. At pH7 (determined by EIS measurements)

<table>
<thead>
<tr>
<th>Solution</th>
<th>Immersion time [h]</th>
<th>E&lt;sub&gt;corr&lt;/sub&gt; [mV]</th>
<th>R&lt;sub&gt;ct&lt;/sub&gt; [Ω.cm&lt;sup&gt;2&lt;/sup&gt;]</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; (0.1M)</td>
<td>1</td>
<td>-650</td>
<td>1300</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>1</td>
<td>-584</td>
<td>14396</td>
<td>91</td>
</tr>
<tr>
<td>Ox</td>
<td>1</td>
<td>-659</td>
<td>2050</td>
<td>36</td>
</tr>
<tr>
<td>C6</td>
<td>1</td>
<td>-530</td>
<td>2990</td>
<td>56</td>
</tr>
<tr>
<td>Ad</td>
<td>1</td>
<td>-622</td>
<td>1500</td>
<td>13</td>
</tr>
<tr>
<td>C6/Zn</td>
<td>24</td>
<td>-518</td>
<td>19800</td>
<td>93</td>
</tr>
<tr>
<td>Ad/Zn</td>
<td>24</td>
<td>-706</td>
<td>10600</td>
<td>87</td>
</tr>
</tbody>
</table>

6.8 Discussion and Conclusion

Stability constant and molar ratio of C7/metal ions mixture, play an important role in the inhibition performance of carbon steel corrosion. It can be seen from the impedance results (table 6.1), that the addition of Mg ions to C7 have no inhibition effect, the reason is related to the lower stability of the Mg complexes compared with the ferrous complexes [117,126], this result in ferrous ions (Fe ions released during the corrosion reaction of the tested electrodes) displace Mg ions from Mg complexes, and form a soluble non-protective complexes. However the high inhibition efficiency recorded in the presence of Zn and Ni ions compared to the Mg ions is related to the relatively high stability of Zn and Ni complexes compared to the ferrous complexes [120], and hence the formation of ferrous complexes is unlikely to take place. Although Zn and Ni ions have almost similar relatively high stability constants [121], the molar ratio of C7/Zn and C7/Ni play an important role in the C7 inhibition efficiencies. It was found that they behave totally different as can be seen in Fig.6.5 where the order of inhibition efficiency to the molar ratio of C7/Zn is 1/2 > 1/1 > 1/0.5 and of C7/Ni is 1/0.5 > 1/1 > 1/2. The reason of this is most likely due to the formation of different types of complexes with different concentration at different C7/metal ions molar ratio. At low Zn ion concentration (1/0.5), it seems to be the formed C7/Zn complexes have no effect on the inhibition efficiency of C7. This explanation is based on the XPS results (see Table 6.6), where the intensities of C7 molecule elements (N and C) sample B, are almost similar to that
of C7 without metal ions sample A, and both have close inhibition values (see Table 6.1). The addition of Zn ions at higher concentration (1/2 molar ratio) have a remarkable influence on the inhibition process of C7, where the electrochemical measurements show high efficiency 93% after 1 hour of immersion time, moreover the SEM micrograph Fig. 6.24 shows no sign of corrosion, and XPS analysis (sample C) show relatively high intensity of the C7 molecule elements (N and C), and very low intensity of Fe (0.9%), (Table 6.6). These indicate the adsorption of C7/Zn complexes and formation of a protective film on the carbon steel surface. High efficiency of C7/Ni was obtained at the molar ratio 1/0.5, supported by XPS results which show the presence of molecule elements (N and C) at relatively high percent. From these it can be observed that the formation of protective C7/Ni complexes is favour at this low concentration. Increasing the immersion time result in increasing the inhibition efficiency for C7/metal ions, particularly for C7/Ni\(^{2+}\) at the optimal molar ratio, where the inhibition is greatly but gradually increased with time, this proved by electrochemical and supported by the XPS results of sample E which show higher percent of the molecule elements (N and C), than that of sample D. Further increase of Ni ions, result in decreasing the inhibition efficiency probably due to the formation, of soluble complexes.
Chapter 7

Hydroxamic Acid Self-Assembled Monolayers

As reviewed in the Chapter 2, the formation of densely packed and crystalline organic molecules self-assembled monolayers provides a convenient system to protect the underlying metal surface from corrosion [127-151]. However after studying the properties of different hydroxamic acid molecules as corrosion inhibitor for carbon steel, in this chapter, we investigated the corrosion protection properties of two monohydroxamic acids with different alkyl chain length, namely decanoyl hydroxamic acid (C\textsubscript{10}H\textsubscript{21}NO\textsubscript{2}) and stearoyl hydroxamic acid (C\textsubscript{18}H\textsubscript{37}NO\textsubscript{2}) as self-assembled monolayer (SAMs), for carbon steel surfaces. The protection efficiency of SAMs, the effect of chain length and assembling time were investigated, and the interface properties of carbon steel substrates modified with mono hydroxamic acids C\textsubscript{10} and C\textsubscript{18} as SAMs were characterized, in the place of corrosive solutions using electrochemical methods and XPS technique. The protection efficiency was determined by electrochemical impedance spectroscopy and polarization measurements. XPS was applied to characterise and identify the chemical composition of the electrode surface and contact angle to study the wettability of the hydroxamic acid monolayers.

7.1 Protective Effect of Decanoyl Hydroxamic acid SAMs

Impedance spectra of carbon steel electrodes modified with hydroxamic acid C\textsubscript{10} was measured in sodium sulphate electrolyte at open-circuit potential after 15 min immersion time. Figure 7.1 shows the Nyquist impedance plot of the unmodified carbon steel electrode and a C\textsubscript{10} SAMs modified carbon steel electrode in 0.1 M Na\textsubscript{2}SO\textsubscript{4} solutions. C\textsubscript{10} SAMs were formed by immersing the carbon steel electrode in 1 mM C\textsubscript{10}/ THF solution. The value of $R_{ct}$ retrieved from fitting parameters was $2.17 \times 10^4 \Omega$. The easier the carbon steel is corroded in a corrosive solution, the smaller the charge transfer resistance, $R_{ct}$ is. The values of capacitance CPE-T decreased, which was caused by the adsorption of C\textsubscript{10} on the electrode surface. In the Na\textsubscript{2}SO\textsubscript{4} solution, the corrosion at the carbon steel surface was due to the anodic dissolution of carbon steel and the cathodic reduction of the dissolved oxygen. Impedance spectra of C\textsubscript{10} SAMs-modified carbon steel changed significantly from that of unmodified one. Semi-circles with much bigger diameters were observed in the case of C\textsubscript{10}
SAMs-covered carbon steel. Many types of equivalent circuit models have been proposed and used in the literature to interpret impedance behaviour of the SAMs covered electrodes [152-155]. The equivalent circuit in figure 5.4 (a) best models our EIS data. It consists of $R_s$ solution resistance, $R_{ct}$ charge transfer resistance and CPE$_{dl}$ constant phase elements for the double layer. The charge transfer resistance is corresponding to the corrosion reaction at metal substrate/solution interface, which value is a measure of electron transfer across the surface and is proportional to corrosion rate. The parameters values of the equivalent circuit elements obtained by fitting of the Nyquist plot and the inhibition efficiency values are given in Table 7.1.

### 7.2 Influence of Alkyl-Chain Length on the Protection Properties of SAMs

To address the effect of molecular structure on the SAMs protection properties, impedance spectra were also obtained for stearoyl hydroxamic acid (C18) SAMs prepared by immersing carbon steel electrode in 1mM C18/THF solution and compared with the data obtained with C10 SAMs prepared using the same conditions, see Fig.7.2. Values of $R_{ct}$ and $\eta$ for C18 SAMs are given in Table 7.2. The values of capacitance CPE-T significantly decreased which indicate the adsorption of C18 on the electrode surface. The coating resistance of C18 SAMs was 4.6 times higher than that of C10 SAMs; therefore, C18 SAMs have higher protection efficiency and provide better protection against carbon steel corrosion in Na$_2$SO$_4$ solutions. The better corrosion protection of C18 SAMs is attributed to the formation of more densely packed monolayer of C18 molecules than C10 molecules. As can be seen in Bode plots in Fig.7.3, only one time constant is detected for all the measurements. In the presence of C10 or C18 layers the corresponding phase angle-frequency plots shows that the phase angle values were kept high in a wide frequency range, even at low frequency region. This demonstrates the formation of a uniform and protective layer of C10 or C18 on the steel surface with insulating characteristics.

### 7.3 Influence of Self-assembling Time

The growth of SAMs on carbon steel substrate was reported to have two processes. A fast process in which a disordered monolayer is deposited in a few seconds for millimolar to higher concentrations is followed by a much slower process in which a highly oriented and
densely packed monolayer is formed over a period of time. Here the change in the SAMs properties of a C10/carbon steel and C18/carbon steel were monitored after various self-assembling time of a freshly prepared carbon steel electrodes in the C10 and C18/THF solution. As can be seen in Figs. 7.4, 7.5 and Tables 7.1, 7.2 the values of capacitance CPE-T decreases while the values of \( R_{ct} \) increases with increasing the assembling time, results in increasing the inhibition efficiency, for both molecules, thus a better oriented and densely packed hydroxamic acid monolayer on the carbon steel surface is formed by increasing the assembling time. Better constructed SAMs may be achieved by increasing the assembling time beyond 60 min. However we could not study the effect of longer assembling time because the epoxy resin material used for insulating the working electrodes dissolved out by THF solvent, at assembling time ('2h) resulting in the formation of crevice at the edge of electrodes, which as a consequence affect the reliability of electrochemical measurements.

Figure 7.1. EIS spectra of unmodified and C10 modified carbon steel in 0.1M Na$_2$SO$_4$ solution at pH7. Surface modification was made in hydroxamic acid solutions for 1h assembling time

![EIS spectra](image)
Figure 7.2. EIS spectra of unmodified and C18 modified carbon steel in 0.1M Na$_2$SO$_4$ solution at pH7. Surface modification was made in hydroxamic acid solutions for 1h assembling time.

Figure 7.3. Bode plots of unmodified, C10 and C18 modified carbon steel electrode in 0.1M Na$_2$SO$_4$ after 1h assembling time and 15 min exposure to the electrolyte.
7.4 Potentiodynamic Polarization

Fig. 7.6 shows the cathodic and anodic polarization curves of unmodified and modified carbon steel electrodes in 0.1 M Na$_2$SO$_4$ solution. In the presence of the SAMs, the electrodes had a more noble behaviour where the corrosion potential ($E_{corr}$) has shifted significantly to more positive values (-314mV in the presence of C10 and -290mV in the presence C18 compared to that measured for unmodified electrode -665mV). The anodic currents of the iron
dissolution significantly decrease, indicating that hydroxamic acids work as an anodic inhibitor throughout the adsorption and blocking the corrosion process. Table 7.3 gives the values of kinetic corrosion parameters as the corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), and inhibition efficiency ($\eta \%$). The corrosion current densities were estimated by extrapolation of the anodic and cathodic Tafel lines. It is seen, that there is a good agreement between potentiodynamic polarization and impedance techniques, where the two different techniques gave the same trend of the corrosion inhibition values for both C10 and C18.

![Polarization curve for unmodified and C10 or C18 modified carbon steel in 0.1M Na₂SO₄ solution at pH7. Surface modification was made in hydroxamic acid solutions for 1h assembling time.](image)

Table 7.1. The electrochemical parameters and inhibition efficiency of unmodified and C10 modified carbon steel in 0.1M Na₂SO₄ solution obtained from EIS data at pH7

<table>
<thead>
<tr>
<th>solution</th>
<th>assembling time [min]</th>
<th>$E_{corr}$ [mV]</th>
<th>CPE$_{ar}$-T ($\mu$Fcm$^{-2}$)</th>
<th>CPE$_{ar}$-P</th>
<th>$R_o$[Ω.cm$^2$]</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td></td>
<td>-665</td>
<td>1970</td>
<td>0.77</td>
<td>880</td>
<td></td>
</tr>
<tr>
<td>C10</td>
<td>15</td>
<td>-631</td>
<td>188</td>
<td>0.80</td>
<td>974</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-359</td>
<td>71</td>
<td>0.79</td>
<td>10913</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>-346</td>
<td>51</td>
<td>0.67</td>
<td>21756</td>
<td>96</td>
</tr>
</tbody>
</table>
Table 7.2. Electrochemical parameters and inhibition efficiency of unmodified and C18 modified carbon steel in 0.1M Na$_2$SO$_4$ solution obtained from EIS data at pH7

<table>
<thead>
<tr>
<th>solution</th>
<th>assembling time [min]</th>
<th>$E_{\text{corr}}$ [mV]</th>
<th>CPE$_{\text{dl-T}}$ [$\mu$Fcm$^{-2}$]</th>
<th>CPE$_{\text{dl-P}}$</th>
<th>$R_{\text{ct}}$ [\Omega.cm$^{-2}$]</th>
<th>$H$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td></td>
<td>-665</td>
<td>1970</td>
<td>0.77</td>
<td>880</td>
<td></td>
</tr>
<tr>
<td>C18</td>
<td>15</td>
<td>-336</td>
<td>85</td>
<td>0.66</td>
<td>13505</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-385</td>
<td>24</td>
<td>0.69</td>
<td>27813</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>-299</td>
<td>26</td>
<td>0.78</td>
<td>101080</td>
<td>99</td>
</tr>
</tbody>
</table>

Table 7.3. Corrosion potential, corrosion current densities and inhibition efficiencies of unmodified and C10 or C18 modified carbon steel in 0.1M Na$_2$SO$_4$ solution at pH7 (corrosion current density ($i$) calculated by Tafel extrapolation).

<table>
<thead>
<tr>
<th>solution</th>
<th>assembling time [min]</th>
<th>$E_{\text{corr}}$ [mV]</th>
<th>$i$ [$\mu$A/cm$^2$]</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td></td>
<td>-663</td>
<td>10.7</td>
<td>-</td>
</tr>
<tr>
<td>C10</td>
<td>60</td>
<td>-314</td>
<td>0.75</td>
<td>93</td>
</tr>
<tr>
<td>C18</td>
<td>60</td>
<td>-292</td>
<td>0.23</td>
<td>98</td>
</tr>
</tbody>
</table>

7.5 Wettability of SAMs Modified Steel Surface

The measured advancing contact angle on the non-modified carbon steel was about 60°, while on the samples modified with C10 and C18 were about 100° and 105°, respectively. After the adsorption of hydroxamic acids through the hydrophilic polar functional groups, their hydrophobic alkyl chains were arranged toward the solution, creating hydrophobic interface, which result in increasing the contact angle values. The contact angle value in the presence of C18 monolayer was slightly higher than that of C10. This is due to the densely packed large alkyl tails in C18, have higher hydrophobicity degree. Study by Telegdi et. al. [156] showed that the advancing contact angle of C18 SAMs on copper substrate using tetrahydrofuran as deposition solution was 108°. Whitesides et. al. [157] reported the advancing contact angles of C18 SAMs on the iron native oxides, which was 135.95° using isooctane as deposition solution and 131.9° using ethanol as deposition solution. The current results evidently support that the hydroxamic acid self-assembled monolayers were formed on carbon steel surface.
7.6 Chemical Composition of Surface Layers

Presence of hydroxamic acid SAMs on the carbon steel were detected using the characteristic of the molecule elements, N 1s and C 1s signals. The XPS spectra of N 1s measured on the surface of carbon steel modified with C10 or C18 are shown in Figs. 7.7 and 7.8. The N 1s spectra showed two components, one at 400.9-401.2 eV assigned to the N-H group in the organic hydroxamic acid molecule and a second peak at slightly lower binding energy 399.4-399.8 eV due to the de-protonated head groups. The intensity of these two components are almost the same in Figs. 7.7 and 7.8, hence the layer consists of both deprotonated hydroxamate and hydroxamic acid species bounded to the substrate surfaces [158].

The corresponding C 1s spectra in Figs. 7.9 and 7.10 indicate also the presence of hydroxamic acid on the carbon steel surface, where the largest peak at 284.8-284.9 eV are assigned to the C-C aliphatic bonds of the hydroxamic acid, which carbon rich structure. The remaining C 1s peak components have a very low intensity signal. The component at 286.5-286.7 eV is attributed to C-O bonds partly related to the molecule head group and partly to the other C-O groups in the contamination. The third component at 288.2-288.4 eV is properly associated to the carbonyl groups due to the contamination.

Fe 2p peak is consisted of two close peaks as illustrated in Figs. 7.11 and 7.12. At 710.7-710.8 eV Fe doublet with Fe 2p\textsubscript{3/2} component indicating the presence of Fe\textsuperscript{3+} and Fe\textsuperscript{2+} on the surface and a certain degree of oxidation of Fe occurred most likely during the preparation process [159].

The O 1s spectra in Figs. 7.13 and 7.14 display three peaks. The peak at 532.7 eV is assigned to O=C the oxygen atom of hydroxamic acid molecule, the two other peaks at 530 eV and 531.6 eV are attributed to O-Fe and HO-Fe in the iron oxides and hydroxides, respectively [160-163]. The presence of these oxides prior to assembling process may enhance the adsorption process of hydroxamic acid. Fe\textsuperscript{3+} and Fe\textsuperscript{2+} are classified as hard and intermediate acids, hydroxamic acid as a hard base, hence and according to hard and soft acids and bases (HSAB) principle hydroxamic acid forms more stable adsorption bonds with Fe\textsuperscript{3+} and Fe\textsuperscript{2+} than Fe\textsuperscript{0} a soft acid [164-167]. The thickness of the formed hydroxamic acid layers on the carbon steel surface was determined using the model assuming ordered hydroxamic acid monolayer with the head group facing toward the steel surface. The calculated thickness of the organic tail layer ((CH\textsubscript{2})\textsubscript{n}) was 1.18 nm for C10 and 2.23 nm for C18 and the head group layer.
(CONHOH) was estimated to be 0.4 nm for both molecules. The determined total layer thickness of C18 was 2.63 nm corresponding approximately to the length of C18 molecule (2.5nm) [156], which indicates the formation of hydroxamic acid monolayer. Evaluation of XPS data show that the structure of the C10 and C18 self-assembled monolayers are very similar with identical spectral characteristic intensities of nitrogen. The atomic concentration percent are almost similar, 2.2% for C10 and 2.8% for C18 and are proportional to the amount of carbon for each molecule. These indicate that the adsorption mechanism and self-assembly process are similar for both molecules. Hence the higher corrosion inhibition efficiency of C18 compared to C10 obtained by electrochemical measurements is attributed to the longer alkyl chain length of C18 which form a thicker and more densely packed barrier layers to corrosion process. In contrast the shorter chain monolayer of C10 could have a less dense structure with lower packing and coverage [168-169].

Figure 7.7. N 1s spectra of carbon steel modified with C10 after 1h assembling time

Figure 7.8. N 1s spectra of carbon steel modified with C18 after 1h assembling time
Figure 7.9. C 1s spectra of carbon steel modified with C10 after 1h assembling time

Figure 7.10. C 1s spectra of carbon steel modified with C18 after 1h assembling time

Figure 7.11. Fe 2p spectra of carbon steel modified with C10 after 1h assembling time
Figure 7.12. Fe 2p spectra of carbon steel modified with C18 after 1h assembling time

Figure 7.13. O 1s spectra of carbon steel modified with C10 after 1h assembling time.

Figure 7.14. O 1s spectra of carbon steel modified with C18 after 1h assembling time

7.7 Discussion and Conclusion
Decanoyl hydroxamic acid (C10) and stearoyl hydroxamic acid (C18) are successfully deposited and formed protective self-assembled monolayers on carbon steel surfaces. Electrochemical measurements showed that the adsorption of these molecules on carbon steel surfaces reduce the corrosion process with inhibition efficiencies reached 96% for C10 and 99% for C18.

In the presence of the SAMs, the electrodes had a more noble behaviour where the corrosion potential ($E_{corr}$) has shifted significantly to more positive values in the presence of C10 or C18 compared to that measured for unmodified electrode. In the polarization curve the anodic currents of the iron dissolution significantly decreases, indicating that the mono-hydroxamic acids work as an anodic inhibitor, throughout the adsorption and blocking the corrosion process. The higher corrosion inhibition efficiency of C18 is attributed to the long chain length of the molecule, which forms a thicker and more densely packed barrier layers. A better oriented and densely packed hydroxamic acid monolayer on the carbon steel surface is formed by increasing the assembling time. Evaluation of XPS data confirm the presence of the hydroxamic acid on the modified electrode surfaces, and show that the structure of the C10 and C18 self-assembled monolayers are very similar with identical spectral characteristic, indicating that the adsorption mechanism and self-assembly process are similar for both molecules. The XPS data confirm the presence of the hydroxamic acid SAMs on the modified electrode surfaces, as a single layer. Contact angle measurements show the formation of hydrophobic interface which indicate the change in the physical properties of the surface in the presence of hydroxamic acid SAMs.
References


Thesis

1. Oxalyl-dihydroxamic acid (C2) was proven to be a very effective corrosion inhibitor for carbon steel. The high efficiency of C2 is attributed to the adsorption process, where the molecules tend to be adsorbed with the two hydrophilic groups onto the metal surface creating a strong bond and good adhesion between C2 and the substrate.

2. Pimeloyl-dihydroxamic acid (C7) provided moderate corrosion protection on carbon steel with inhibition efficiency of 65% compared to 91% of C2. This has been attributed to the fact that the C7 with long hydrocarbon chain probably tends to be adsorbed with only one hydrophilic group (-CONHOH) on the metal surface. Single C-C bonds allow C7 molecules move and rotate freely, which has negatively affect the adsorption process and, as a consequence, on the inhibition properties. The adsorption process proved to be a key factor in the inhibitor performance.

3. It was confirmed that the addition of Ni$^{2+}$, Zn$^{2+}$ and Cu$^{2+}$ at the optimum molar ratio significantly enhances the inhibition performance of C7 with inhibition efficiency reaching 95%. This is due to the co-adsorption and the formation of stable complexes on the carbon steel surface, which protects the carbon steel from further corrosion.

4. It was established that the molar ratio of C7/metal ions mixture plays an important role in the inhibition performance on carbon steel corrosion at pH 7. The best inhibition effect was obtained at molar ratios of C7/Zn$^{2+}$ = 1/2, and C7/Ni$^{2+}$ = 1/0.5. Correlation was found between the stability constant of C7/metal ion complexes and their inhibition efficiencies. C7/Ni$^{2+}$, C7/Zn$^{2+}$ and C7/Cu$^{2+}$ have considerably high stability constants and high inhibition effects. C7/Mg$^{2+}$ has low stability constant and has no effect on the inhibition property of C7.

5. It was confirmed that the immersion time and pH play also an important role in the inhibition efficiency of C7/metal ions. A continuous build up of inhibitor film takes place which result in increase in the thickness and the persistency with time resulting in formation of a protective layer at the carbon steel surface. The pH-dependent inhibition efficiency of C7/metal ions is related to the formation of different C7/metal ion complexes.

6. Comparative study between a selected hydroxamic and carboxylic acids show that the corrosion inhibition efficiencies of hydroxamic acids are much far better than that of
carboxylic acids. The presence of nitrogen atom plays an important role in enhancing inhibition efficiency of dihydroxamic acids, which is due to the electron releasing of -NH-group participating in the adsorption process.

7. Decanoyl hydroxamic acid (C10) and stearoyl hydroxamic acid (C18) successfully deposited in a form of protective self-assembled layers on carbon steel surfaces, reduce the corrosion rate with inhibition efficiencies reaching 96% for C10 and 99% for C18. The increasing assembling time results in increased inhibition efficiency for both molecules, indicating that the formation of hydroxamic acid monolayers on carbon steel surface is a time dependent process.

8. Quantitative evaluation of the XPS data confirms the presence of the hydroxamic acid SAMs on the modified electrode surfaces, with total layer thickness of 1.58 nm for C10 and 2.63 nm for C18 that proves the formation of a monolayer.

**Possible applications**

The tested di-hydroxamic acid molecules can be used for corrosion protection of water cooling systems equipment. Particularly for malty systems where the equipment consists of different materials such as steel, copper, zinc. In these systems usually different metal ions exist in the flow as a result of corrosion process. It is well known that the presence and accumulation of copper ions on the carbon steel surface work as extra cathodic reaction leading to increase the carbon steel corrosion, furthermore the precipitation of copper ions in certain places in the system reduced to copper metal and create a galvanic corrosion with carbon steel which increase corrosion rate as well. This is a common problem in many industrial plants. However we assume that the tested hydroxamic acids can work as efficient corrosion inhibitors and in addition prevent the negative effect of such ions (if present in the system) throughout the formation of stable complexes between hydroxamic acids and metal ions which improve the inhibition efficiency instead of causing problems.

Hydroxamic acid self-assembled monolayer provide an excellent model system to study the interfacial properties of organic layers and in practical point of view, it can be applied as a temporary corrosion protection for material under storage or transportation.
Publications and Conferences

List of Publication


Abdulmajed Alagta, Ilona Felhösi, Judit Telegdi,Imre Bertoti, Erika Ka´lmá’n (Effect of metal ions on corrosion inhibition of pimeloyl-1,5-di-hydroxamic acid for steel in neutral solution), *Corrosion Science 49* (2007) 2754–2766


List of Conference


Abdulmajed Alagta, Ilona Felhösi, Erika Kálmán (Characterization of Carbon Steel Surface Modified by Hydroxamic Acid Self-Assembled Monolayer) International