

INAUGURAL LECTURE OF PROF ENO EBENSO



**SO THAT METALS/ALLOYS MAY EXIST AND
SERVE HUMANITY FOR LONG: MY ODYSSEY IN
CORROSION CHEMISTRY RESEARCH**

Define tomorrow.

UNISA


college of
science, engineering
and technology

150
YEARS

METALS: OCCURRENCE & EXTRACTION

- **Metals occur as minerals in the earth's crust in the following chemical states: oxides, sulphides and to a lesser extent, in 'native' form. A mineral from which the metal of interest can be extracted at a profit is called an 'ore'. Chemically, an ore may contain three classes of minerals, namely: (a) Value minerals (b) Secondary Value minerals and (c) Gangue minerals.**
- **Ore preparation is a two-part process consisting of beneficiation and agglomeration. Beneficiation involves the separation of value mineral from the gangue while agglomeration is the process of reforming fine particles into larger lumps of appropriate size and strength. The main methods of agglomeration are sintering, nodulising, pelletizing and briquetting .**
- **One of the outstanding properties of a metal is its tendency to ionize. This tendency is measured by means of electrode potentials. If the metals are arranged in a decreasing order of their electropositivities (reactivities), we have an 'activity or electrochemical series'. In this arrangement the metals may be sub-divided into three categories namely most electropositive, moderately electropositive and least electropositive. Very reactive elements exist mainly in the form of chloride, trioxo-carbonate (IV) and oxide ores. Moderately electropositive metal ores exist in the form of oxides, tetraoxo-carbonate (IV) and sulphides while ores of least electropositive metals exist in the form of sulphides and native (free) elements. The method of extraction (reduction) of a particular metal depends on its electropositivity or its position in the electrochemical series. Most electropositive metals are extracted by electrolysis of molten ores (electrometallurgy) while moderately electropositive metals are obtained by reduction of oxides (pyrometallurgy). Ores of least electropositive metals are extracted by thermal or chemical methods (hydrometallurgy).**

- **Metals are opaque, lustrous elements that are good conductors, malleable and ductile. In Chemistry, metals may be defined as elements that readily form cations (positive ions) and form metallic bonds with other metal atoms and ionic bonds with non-metals. Metals may also be described as a lattice of positive ions surrounded by a cloud of localized electrons. The metallurgist considers metals as elements that have overlapping conduction bands and valence bands in their electronic structure. They react with oxygen in the air to form basic oxides. Metals constitute over 80% of the elements in the periodic table.**

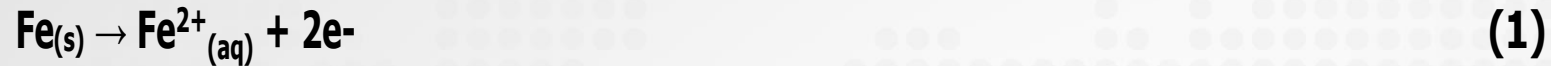
Metals are widely used in;

- **Construction – farming tools, bridges, household conveniences, building, communication etc.**
- **Transportation – cars, buses, trucks, ships, airplanes etc.**
- **Electric power generation and distribution.**
- **Biomedical applications.**
- **Ornaments and cooking utensils.**

DEFINITION OF CORROSION

- The process whereby a material breaks into its constituent atoms because of the chemical reactions with its surrounding is called **Corrosion**. Rusting of a metal is a commonly known type of electrochemical corrosion. In rusting, the metal actually undergoes electrochemical oxidation with oxygen as an oxidant. The metal oxide (rust) is then formed. This metal oxide (rust) is the damage that is of serious concern to most industries all over the world. Corrosion is not only limited to metals, it can also take place on other materials such as polymers and ceramics. Nevertheless, in polymers it is more often than not explained as degradation than corrosion although they are referring to a similar process. Amongst many metals, corrosion is experienced strongly in iron and steel. This is because the oxide that is formed during the process of oxidation does not hold firmly to the surface of the metal, as a result it moves off the metal easily. In the case of aluminum metal, an oxide coating that aluminum forms assist in bringing the oxide to strongly bond the surface of the metal thereby slowing down the corrosion (or stop further exposure to oxygen).
- Corrosion is usually described by its results, with terms like rust, scaling, discoloration, oxidation, pitting, etc. The actual electrochemical process however is much less noticeable. The word "rust", describes the corrosion of iron and steel, one of the most noticeable effects of corrosion.
- Corrosion acts upon engineered materials, usually metals. In essence, it changes a metal into a different substance that no longer has the same desired properties (e.g. strength, toughness, etc.).
- You can consider corrosion to be the opposite of producing a metal. Iron, for example, is made by first mining iron ore, and then introducing a large amount of energy to extract the iron. The resulting high-energy product is inherently unstable. Nature prefers low energy states. Iron transitions into a lower energy state by corroding.
- Corrosion is a natural process driven by energy considerations. The process of extraction of metals from their ores stores up vast quantity of energy in the metal. Corrosion is therefore a means of releasing this stored – up energy. The metal because of its high energy is in an excited state / state of high energy. The corrosion process is a means of going to the lower energy state (the combined state).

The process of rusting or corrosion takes place in multisteps. Firstly, iron is oxidized to ferrous (Fe^{2+}) ions, according to the reaction 1 given below;



Then the (Fe^{2+}) ions are oxidized to ferric ions (Fe^{3+}), as indicated by reaction 2;



The third step is the reduction of oxygen by the electrons from reactions (1) and (2). This reduction is summarized by reaction (3) below;

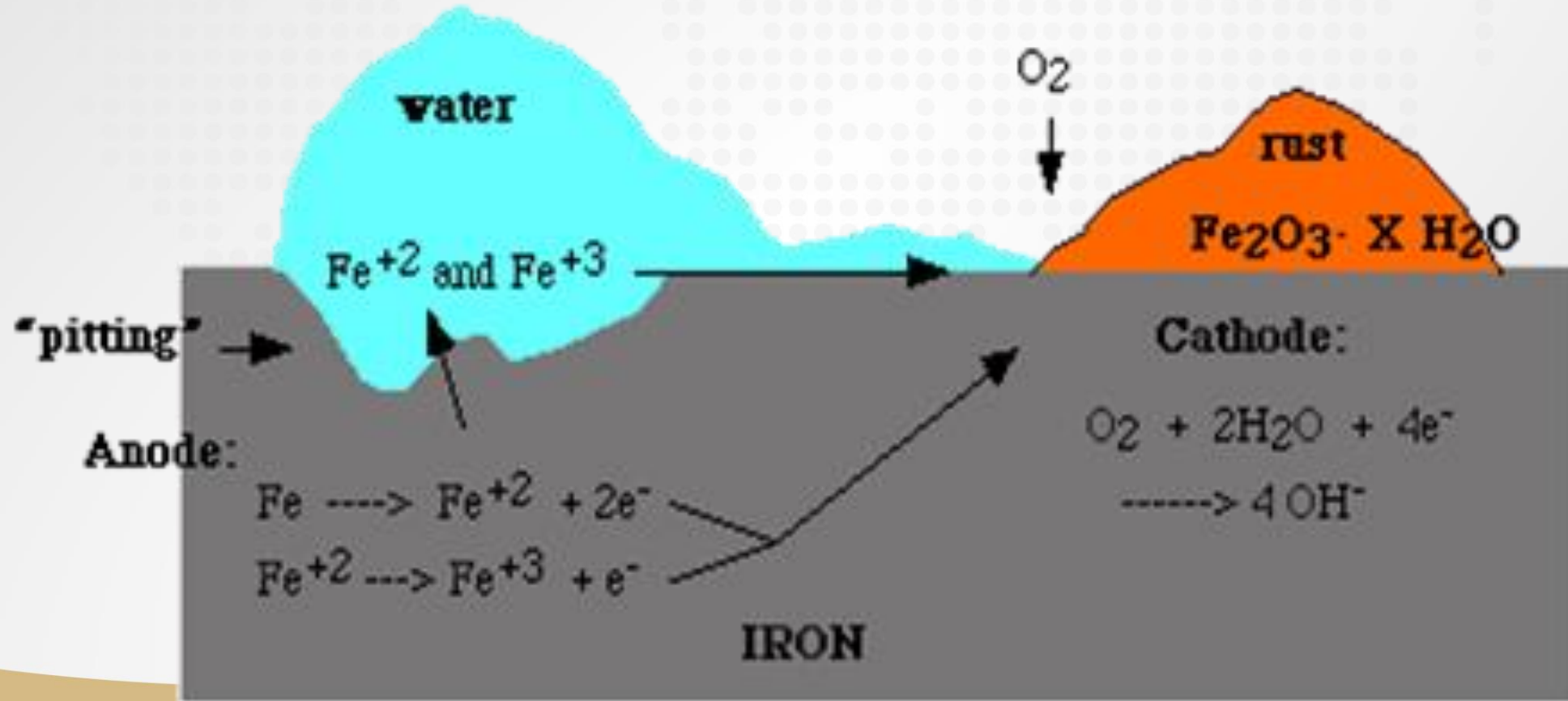


The last step involves the reaction between Fe^{2+} and O_2 to produce ferric oxide [iron (III) oxide]. Equation (4) illustrates this;



- In dry conditions (where there is no moist) such as in places like desert, corrosion is much less slower than in a moist area where there is moisture carrying oxygen (O_2). There are many other factors that influence the rate of corrosion of mild steel, including the presence of salt. This is true because the molten salt increases the conductivity of the aqueous solution that is formed at the surface of the metal. Because the conductivity is increased, the rate of electrochemical corrosion increases. The temperature of the system also affects the rate of corrosion of mild steel. The electrochemical reaction that causes corrosion consists of four factors namely; Anode, Cathode, Electrolyte and Electronic circuit.

Processes involved in the electrochemical cell to form Iron oxide (Rust)



TYPES OF CORROSION

There are many different types of corrosion that are known today namely;

- i. **Uniform corrosion:** which is also known as general corrosion since the corrosion is caused by direct chemical attacks on the substance.
- ii. **Galvanic corrosion:** when two different metals are placed in contact under electrochemical action.
- iii. **Concentration cell corrosion:** when two metals or more are allowed to come into contact with different concentration of the same solution.
- iv. **Pitting corrosion:** this type of corrosion takes place at microscopic defects on a metal surface.

- i. **Crevice corrosion:** also known as contact corrosion. It takes place right at the point of contact of the metal with the other metal or a metal with a non metal.
- ii. **Filiform corrosion:** this type of corrosion takes place on substances that are painted. When moisture finds its way in the coating of the surface that is painted, the result is likely to be a filiform corrosion.
- iii. **Intergranular corrosion:** the grain boundaries of a substance are attacked perhaps by a strong acid.
- iv. **Stress corrosion cracking:** this type of corrosion is also commonly abbreviated as SCC. The simultaneous effects of stress and the environment cause SCC.
- v. **Erosion corrosion:** the harsh chemical environment combined with high fluid surface speeds lead to a corrosion known as erosion corrosion.
- vi. **Dealloying:** although this type of corrosion is not commonly encountered, it remains problematic. This process occurs when the alloy loses its atomic component of the metal and retains its corrosion resistance component on the metal surface.
- vii. **Corrosion in concrete:** self explanatory type of corrosion. In the concrete material, there is a carbon steel among the components therein. While the steel is a very crucial component of the concrete for the strength purposes of the building, it is also important to note that steel is capable of undergoing corrosion.
- viii. **Refinery corrosion:** this is the type of corrosion that results from the equipment surface that has been attacked by the strong acid.
- ix. **Microbial corrosion:** also abbreviated as MIC, is caused by the activities of microbes.

Metals corrode because we use them in environments where they are chemically unstable. Only copper and the precious metals (gold, silver, platinum, etc.) are found in nature in their metallic state. All other metals, to include iron-the metal most commonly used-are processed from minerals or ores into metals which are inherently unstable in their environments.

This golden statue in Bangkok, Thailand, is made of the only metal which is thermodynamically stable in room temperature air. All other metals are unstable and have a tendency to revert to their more stable mineral forms. Some metals form protective ceramic films (passive films) on their surfaces and these prevent, or slow down, their corrosion process.

EFFECTS OF CORROSION

- The effects of corrosion are experienced by many human beings if not all. Lives, jobs and health of the human beings are amongst the other things that are affected by the effects of corrosion. Some of the effects of corrosion are briefly discussed:
- Health effects: Human beings continuously make use of metals or metal products. These include the metal piercing on their bodies. The other known example is the applications of metallic plates and cups by human beings. When the metallic plates and cups are affected by corrosion, the human health can be at a gross risk.
- Safety effects: In this world there are so many crucial means of transportation that are made of metals. These include cars, airplanes and ships. If any of the metals that is used in the construction of a car is attacked by any type of corrosion, the safety of the passengers may not be guaranteed. The use of metals in the construction industries such as construction of bridges and even buildings is one more crucial example. If these metals are attacked by corrosion the safety effects are likely to be experienced.
- Economic effects: The economy of each and every country has a share in the industries of that particular country. Petroleum industries continue to make use of metals for their fluid carrying pipes and tanks. These industries find themselves spending a great amount of money in their attempts to minimize corrosion. If a pipe or a tank breaks as result of corrosion, there will be a loss of production which in turn affects the economy.

- **Cultural effects:** Many nations pride themselves in their heroes. These heroes include political heroes, religious heroes and many more. In South Africa alone, there are a number of statues of many political heroes. These statues are mostly made up of metallic products which can be attacked by corrosion. Corrosion attacks these precious statues thereby affecting the cultural beliefs of a particular nation.
- **Technological effects:** Most of the technological gadgets are constructed from metallic products. These include electricity power stations and solar energy systems. When corrosion damages these metallic substances, the technological effect is experienced.
- **In the light of all the above mentioned effects of corrosion, control measures / procedures needs to be implemented in order to reduce or inhibit corrosion thereby prolong the life span of the metals or materials and prevent the return to the combined state (ore) from which they were initially obtained ("dust to dust" or "earth to earth").**

CORROSION INHIBITION

- An inhibitor is a substance that slows down or retards a chemical reaction.
- A corrosion inhibitor is a substance which when added to an environment, reduces the rate of attack by the environment.
- The use of corrosion inhibitors is one of the best methods of combating corrosion.
- In order that they can be used effectively, three factors must be considered, namely:
 - ✓ Identification of the corrosion problems,
 - ✓ The economics of the inhibition process.
 - ✓ The compatibility of the inhibitor with the process being used.
- Types of Inhibitors
There are six classes of inhibitors namely;
 - ✓ Passivating (anodic),
 - ✓ Cathodic,
 - ✓ Ohmic,
 - ✓ Vapour phase, and
 - ✓ Organic/Inorganic.

- **For the purpose of this lecture, I will concentrate only on the Organic/Inorganic type of inhibitors which happens to be the ones I have studied in the past 15 years. Organic and inorganic compounds constitute a large class of corrosion inhibitors, which as a general rule; affect the entire surface of a corroding metal when present in sufficient concentration. Most of the organic/inorganic compounds containing elements of Groups VB, VIB or functional groups of the type $-NH_2$, $=CO$ and $-CHO$ are known to be effective inhibitors. The principal mechanism suggested by several researchers in the field of corrosion inhibition studies is 'adsorption'. The inhibitor is adsorbed on the entire surface of the corroding metal and by so doing prevents attack from the corrodent. Organic inhibitors are adsorbed according to the ionic charge of the inhibitor on the metal's surface. Cationic inhibitors e.g. amines (positively charged) or anionic inhibitors e.g. sulphonates (negatively charged) will be adsorbed preferentially, depending on whether the metal is charged positively or negatively.**
- **The inhibitors may therefore be considered as two fundamental types namely;**
- **Type A: Those which form a protective barrier film on anodes or cathodes by reaction between the metal and the environment. The Type A inhibitors functions in neutral or in some cases, alkaline solution in which the main cathodic reaction is an oxygen reduction reaction in which the corroding metal surface is covered by a film oxide or hydroxide. Type A inhibitors tend to produce a protective film or stabilize an already existing ore.**
- **Type B: Those which are initially adsorbed directly onto the metal surface by interaction between surface charges and ionic and/ or molecular dipole charges. This division of inhibitor types results principally from the pH of the solution where they operate.**



**MY CONTRIBUTIONS TO CORROSION INHIBITION
STUDIES USING SYNTHETIC ORGANIC/INORGANIC
INHIBITORS.**

✓ The use of synthetic organic and inorganic compounds such as thiosemicarbazones and its derivatives, dyes (methyl red, methylene blue, methyl orange, thymol blue, solochrome black T etc), acetylphenothiazine, acetomidoaniline , and over 2000 compounds etc as corrosion inhibitors and the effect of halides in different media. A few of the publications resulting from these researches are below:

1. U. J. Ekpe, U. J. Ibok, B. I. Ita, O. E. Offiong and E. E. Ebenso, (1995). Inhibitory action of methyl and phenyl thiosemicarbazone derivatives on the corrosion of mild steel in HCl. Material Chemistry and Physics 40; 87 - 93.
2. E. E. Ebenso, (1998). Inhibition of aluminium (AA3105) Corrosion in HCl by acetamide and thiourea. Nigerian Corrosion Journal. 1(1); 29 - 44.
3. E. E. Ebenso, U. J. Ekpe, B. I. Ita, O.E.Offiong and U. J. Ibok, (1999). Effects of molecular structure on the efficiency of amides and TSC used for corrosion inhibition of mild steel in HCl. Materials Chemistry and Physics 60; 79 - 90.
4. E. E. Ebenso, (2001). Inhibition of corrosion of mild steel in HCl by some Azo dyes. Nigerian Journal of Chemical Research. 6; 8 – 12.
5. U. J. Ekpe, P. C. Okafor, E. E. Ebenso, O. E. Offiong and B. I. Ita (2001). Mutual effects of TSC derivatives on the acidic corrosion of aluminium. Bulletin of Electrochemistry 17(3); 131 - 135.
6. E. E. Ebenso, P. C. Okafor, O. E. Offiong, B. I. Ita, U. J. Ibok and U. J. Ekpe (2001). Comparative investigation into the kinetics of corrosion inhibition of aluminium alloy (AA 1060) in acidic medium. Bulletin of Electrochemistry 17(10); 459 - 464.
7. E. E. Ebenso, P. C. Okafor and U. J. Ekpe (2003) Studies on the inhibition of aluminium corrosion by 2-acetylphenothiazine in chloroacetic acids. Anti-Corrosion Methods & Materials 50(6); 414 - 421.

1. **E. E. Ebenso, (2003a). Effect of halide ions on the corrosion inhibition of mild steel in H₂SO₄ using methyl red. Part 1. Bulletin of Electrochemistry 19(5); 209 - 216.**
2. **E. E. Ebenso, (2003b). Synergistic effect of halide ions on the corrosion inhibition of aluminium in H₂SO₄ using 2-acetylphenothiazine. Materials Chemistry and Physics 79(1); 58 – 70.**
3. **P. C. Okafor, E. E. Ebenso, U. J. Ibok, U. J. Ekpe and M. I. Ikpi (2003) Inhibition of 4-acetamidoaniline on corrosion of mild steel in HCl solution. Transactions of SAEST 38 (3); 91 – 96.**
4. **E. E. Ebenso, P. C. Okafor, U. J. Ekpe, U. J. Ibok and A. I. Onuchukwu (2004). The joint effects of halide ions and methylene blue on the corrosion inhibition of aluminium and mild steel in acid corrodent. Journal of Chemical Society of Nigeria. 29(1); 15 – 25.**
5. **E. E. Oguzie, B.N. Okolue, E. E. Ebenso, G. N. Onuoha and A. I. Onuchukwu (2004) Evaluation of the inhibitory effect of methylene blue dye on the corrosion of aluminium in HCl solutions. Materials Chemistry and Physics 87(2-3); 394 – 401.**
6. **P. C. Okafor, E. E. Ebenso and U. J. Ekpe (2004). Inhibition of aluminium corrosion by some derivatives of thiosemicarbazone. Bulletin of Chemical Society of Ethiopia. 18(2): 181- 192.**
7. **E. E. Ebenso, (2004). Effect of methyl red and halide ions on the corrosion of aluminium in H₂SO₄ . Part 2. Bulletin of Electrochemistry. 20(12); 551 - 559.**
8. **E. E. Ebenso and E. E. Oguzie (2005) Corrosion inhibition of mild steel in acidic medium by some organic dyes. Material Letters 59 (17): 2163 – 2165.**

1. E. E. Oguzie and E. E. Ebenso (2006) Studies on the corrosion inhibitive effect of Congo red dye – halides mixture. Pigment and Resin Technology 35(1): 30 – 35.
2. Alfred I. Onen, B.T. Nwufu, Eno E. Ebenso and Mbuthi R. Hlophe (2010) Titanium (IV) oxide as corrosion inhibitor for aluminium and mild steel in acidic medium. International Journal of Electrochemical Science 5: 1563 – 1573.
3. Eno E. Ebenso, Ime B. Obot and L.C. Murulana (2010) Quinoline and its derivatives as effective corrosion inhibitors for mild steel in acidic medium. International Journal of Electrochemical Science 5: 1574 – 1586.
4. Eno E. Ebenso, Ime B. Obot (2010) Inhibitive Properties, Thermodynamic Characterization and Quantum Chemical Studies of Secnidazole on Mild Steel Corrosion in Acidic Medium. International Journal of Electrochemical Science 5; 2012 – 2035.
5. I.B. Obot, N.O. Obi- Egedi, S.A. Umoren and E. E. Ebenso (2011) Adsorption and kinetic studies of fluconazole for the corrosion of aluminium in HCl solution. Chemical Engineering Communications 198; 711 – 725.

✓ Synergistic, kinetics, adsorption and thermodynamic studies using synthetic polymers such as polyvinyl chloride (PVC), polyethylene glycol (PEG), polyvinyl alcohol (PVA), polyacrylamide (PAA) and polyvinyl pyrrolidone (PVP) as corrosion inhibitors and the effect of halides in different media. Most of the published papers in this category results from the PhD Thesis work I supervised of one of my good students (Dr. Saviour A. Umoren). A few of the publications resulting from these researches are listed below:

1. S.A. Umoren, O.Ogbobe, E.E.Ebenso and U.J.Ekpe (2006) Effect of halide ions on the corrosion inhibition of mild steel in acidic medium using polyvinyl alcohol. Pigment and Resin Technology 35 (5): 284– 292.
2. E. E. Ebenso, U.J. Ekpe, S. Umoren, Ekerete Jackson, O.K. Abiola and N. C. Oforka (2006) Synergistic effect of halide ions on the corrosion inhibition of aluminium in acidic medium by some polymers. Journal of Applied Polymer Science 100(4): 2889 – 2894.
3. S.A. Umoren, E.E.Ebenso, P.C.Okafor and O.Ogbobe (2006) Water soluble polymers as corrosion inhibitors of mild steel in acidic medium. Pigment and Resin Technology 35 (6): 346 - 352.
4. S.A. Umoren, O.Ogbobe and E.E.Ebenso (2006) The adsorption characteristics and synergistic inhibition between polyethylene glycol and halide ions on the corrosion of mild steel in acidic medium. Bulletin of Electrochemistry 22 (4): 155 – 167.
5. S.A. Umoren, E.E.Ebenso, P.C.Okafor, U.J.Ekpe and O.Ogbobe (2007) Effect of halide ions on the corrosion inhibition of aluminium in alkaline medium using polyvinyl alcohol. Journal of Applied Polymer Science 103(5): 2810-2816.

1. **S. A. Umoren, O.Ogbobe, P.C. Okafor and E. E.Ebenso (2007) Polyethylene glycol and polyvinyl alcohol as corrosion inhibitors of aluminium in acidic medium. Journal of Applied Polymer Science 105(6): 3363 - 3370.**
2. **S.A. Umoren and E.E.Ebenso (2007) The synergistic effect of polyacrylamide and iodide ions on the corrosion inhibition of mild steel in H₂SO₄. Materials Chemistry and Physics 106: 387- 393.**
3. **S.A. Umoren, O.Ogbobe , I.O. Igwe and E.E.Ebenso (2008) Inhibition of mild steel corrosion in acidic medium using synthetic and naturally occurring polymers and synergistic halide additives. Corrosion Science 50(7): 1998 – 2006.**
4. **S. A. Umoren and E. E. Ebenso (2008) Blends of polyvinyl pyrrolidone and polyacrylamide as corrosion inhibitors for aluminium in acidic medium. Indian Journal of Chemical Technology 15(4): 355 – 363.**
5. **S.A. Umoren, E.E.Ebenso and O.Ogbobe (2009) Synergistic effect of halide ions and polyethylene glycol on the corrosion inhibition of aluminium in alkaline medium. Journal of Applied Polymer Science 113: 3533 -3543.**

- ✓ The use of some quantum chemical ,molecular modeling , theoretical and Quantitative Structure Activity Relationship (QSAR) studies of compounds used as corrosion inhibitors [e.g. some sulphonamides (namely sulfaacetamide , sulfapyridine , sulfamerazine, sulfathiazole, sulfaguanidine, sulfamethazine, sulfamethoxazole and sulfadiazine); some antibiotics / antimicrobial drugs e.g rhodanine azo sulpha compounds (namely 5-sulphadiazineazo-3-phenyl-2-thioxo-4-thiazolidinone,5-sulphamethazineazo-3-phenyl-2-thioxo-4-thiazolidinone, 5-sulphadimethoxineazo-3-phenyl-2-thioxo-4-thiazolidinone, 5-sulphamethoxazoleazo-3-phenyl-2-thioxo-4-thiazolidinone)] using density functional theory (DFT) at the B3LYP/6-31G (d,p) and BP86/CEP-31G* basis set levels and other semi empirical methods and ab initio calculations using the RHF/6-31G (d,p). Most of the published papers in this category results from the PhD Thesis work I supervised of one of another of my good students (Dr. Nabuk O. Eddy). A few of the publications resulting from these researches are listed below:

1. **Taner Arslan, Fatma Kandemirli , Eno E. Ebenso, Ian Love and Hailemichael Alemu (2009) Quantum chemical studies on the corrosion inhibition of some sulphonamides on mild steel in acidic medium . Corrosion Science 51 (1): 35 – 47.**
2. **Nnabuk O. Eddy, Udo J. Ibok, Eno E. Ebenso, Ahmed El Nemr and ElSayed H.El Ashry (2009) Quantum chemical study of the inhibition of the corrosion of mild steel in H₂SO₄ by some antibiotics. Journal of Molecular Modelling 15: 1085 – 1092.**
3. **Eno E. Ebenso, Taner Arslan, Fatma Kandemirli , Necmettin Caner, Ian Love (2010) Quantum chemical studies of some rhodanine azosulpha drugs as corrosion inhibitors for mild steel in acidic medium. International Journal of Quantum Chemistry 110 (5): 1003 – 1018.**

1. **Eno E. Ebenso, Taner Arslan, Fatma Kandemirli, Ian Love, Cemil Ogretir, Murat Saracoglu and Saviour A. Umoren (2010) Theoretical studies on some sulphonamides as on corrosion inhibitors for mild steel in acidic medium. International Journal of Quantum Chemistry 110(5) : 2614 – 2636.**
2. **Nnabuk O. Eddy, Eno E. Ebenso and Udo J. Ibok (2010) Adsorption, synergistic effect and Quantum chemical studies on ampicillin and halides for the corrosion of mild steel in H₂SO₄. Journal of Applied Electrochemistry 40(2): 445 – 456.**
3. **Nnabuk O. Eddy and Eno E. Ebenso (2010) Quantum chemical studies on the inhibition potentials of some penicillin compounds for the corrosion of mild steel in 0.1M HCl. Journal of Molecular Modelling 16; 1291 – 1306.**
4. **Eno E. Ebenso , David A. Isabirye and Nabuk O. Eddy (2010) Adsorption and Quantum chemical studies on the inhibition potentials of some thiosemicarbazides for the corrosion of mild steel in acidic medium. International Journal of Molecular Sciences 11; 2473 – 2498.**
5. **Nnabuk O. Eddy and Eno E. Ebenso (2010) Adsorption and Quantum chemical studies on cloxacillin and halides for the corrosion of mild steel in acidic medium. International Journal of Electrochemical Science 5; 731 - 750.**
6. **Nnabuk O. Eddy, Stanislova R. Stoyanov and Eno E. Ebenso (2010) Fluoroquinolones as corrosion inhibitors for mild steel in acidic medium; experimental and theoretical studies. International Journal of Electrochemical Science 5; 1035 – 1058.**

1. **Eno E. Ebenso, Ime B. Obot (2010) Inhibitive Properties, Thermodynamic Characterization and Quantum Chemical Studies of Secnidazole on Mild Steel Corrosion in Acidic Medium. International Journal of Electrochemical Science 5; 2012 – 2035.**
2. **N.O. Eddy, B.I. Ita, N.E. Ibis and E.E. Ebenso (2011) Experimental and Quantum Chemical studies on the Corrosion Inhibition Potentials of 2 – (2- Oxindolin-3-Ylideneamino) Acetic acid and Indoline- 2,3-dione. International Journal of Electrochemical Science 6; 1027 – 1044.**
3. **V.F. Ekpo, P.C. Okafor, U.J. Ekpe and E. E. Ebenso (2011) Molecular Dynamics Simulation and Quantum Chemical Calculations for the Adsorption of some thiosemicarbazone (TSC) derivatives on mild steel. International Journal of Electrochemical Science 6; 1045 – 1057.**
4. **N.O. Obi-Egbedi, K.E. Essien, I.B. Obot and E. E. Ebenso (2011) 1, 2 – Diaminoanthraquinone as Corrosion Inhibitor for mild steel in hydrochloric acid: Weight loss and Quantum Chemical study. International Journal of Electrochemical Science 6; 913 – 930.**
5. **N.O. Eddy, F.E. Awe, C.E. Gimba, N.O. Ibis and E.E. Ebenso (2011) QSAR, Experimental and Computational Chemistry Simulation studies on the Inhibition potentials of some Amino Acids for the corrosion of mild steel in 0.1M HCl. International Journal of Electrochemical Science 6; 931 – 957.**

SCIENTIFIC REPORTS

OPEN

Experimental, quantum chemical and molecular dynamic simulations studies on the corrosion inhibition of mild steel by some carbazole derivatives

Received: 12 October 2016

Accepted: 11 April 2017

Published online: 26 May 2017

Henry U. Nwankwo^{1,2}, Lukman O. Olasunkanmi^{1,2,3} & Eno E. Ebenso^{1,2}

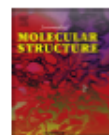
Five selected carbazole derivatives, namely carbazole, 3,6-dibromocarbazole, 2-hydroxycarbazole, 1,2,3,4-tetrahydrocarbazole and 9-(2-ethylhexyl)carbazole-3,6-dicarboxaldehyde were investigated for their inhibitive effects on *Desulfovibrio vulgaris* (*D. vulgaris*) induced corrosion of mild steel and in 1 M HCl medium using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The carbazole derivatives were found to be mixed type inhibitors with predominantly cathodic inhibitive effects for mild steel in 1 M HCl. Surface morphology results showed the compounds formed adsorbed film on mild steel surface in both aqueous acid and sulphate reducing bacteria (SRB) media. Quantum chemical calculations were used to provide molecular based explanations for the inhibitive effects of the compounds. The interactions of the molecules with mild steel surface was simulated based on molecular dynamic simulations approach using Fe(110) crystal surface as representative metallic surface.

Mild steel is a widely used alloy of iron with various industrial applications. The choice of mild steel as a preferred material for construction and other usages is attributed to its relatively low cost and high mechanical strength¹. However, mild steel readily undergoes corrosion in common environments of usage. Acid solutions especially hydrochloric acid used in many industrial practices such as acid cleaning, oil-well acidizing, acid descaling etc. are typical highly aggressive media for mild steel corrosion¹. Corrosion can also be induced by microorganisms. Such corrosion is called microbial influenced corrosion (MIC). It has been suggested that biocorrosion (MIC) follows the same mechanism as electrochemical corrosion in aqueous media^{2,3}.

Though both corrosion in aqueous environment and the MIC are destructive, the former is by far more investigated than the latter. Research in corrosion especially with respect to the use of corrosion inhibitors is often conducted in aqueous environment. A large number of these studies have been carried out on mild steel corrosion in aqueous acid solutions⁴⁻⁷. Meanwhile, a study conducted by Rajasekar *et al.*⁸ revealed that about 20% of corrosion damages are due to MIC. Miller *et al.*⁹ also reported that the cost of damages due to MIC stood at nearly 50% of all corrosion cost, which amounted to 140 billion USD in the US alone. In this regard, more studies that focus on MIC or more inclusive studies that encompass both acid corrosion and MIC should be promoted. Formation of biofilms, their characteristics, and influence on bacteria populations have been extensively discussed¹⁰⁻¹³. The effects of anaerobic bacteria on MIC and the contributions of sulphate reducing bacteria (SRB) to MIC can be found in literature¹⁴.

Various techniques used in the study of corrosion and corrosion inhibition in acid solution include electrochemical^{4,15-18}, quantum chemical¹⁹⁻²² and surface morphology^{4,21,22}. On the other hand, weight loss technique²³

¹Department of Chemistry, School of Mathematical & Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho, 2735, South Africa. ²Material Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho, 2735, South Africa. ³Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife, 220005, Nigeria. Correspondence and requests for materials should be addressed to E.E.E. (email: Eno.Ebenso@nwu.ac.za)



Experimental and theoretical investigation of the inhibitory effect of new pyridazine derivatives for the corrosion of mild steel in 1 M HCl



Motsie E. Mashuga^{a, b}, Lukman O. Olasunkanmi^{a, b, c}, Eno E. Ebenso^{a, b, *}

^a Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^b Material Science Innovation and Modelling (MaSiM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^c Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife 220005, Nigeria

ARTICLE INFO

Article history:

Received 1 November 2016

Received in revised form

30 January 2017

Accepted 1 February 2017

Available online 2 February 2017

Keywords:

Corrosion inhibition

Pyridazine derivatives

Mild steel

Electrochemical techniques

Quantum chemical calculation

Molecular dynamic simulation

ABSTRACT

The effects of four pyridazine derivatives namely, 2-(6-chloropyridazin-3-yl)-2-phenylacetonitrile (P1), 3-(6-chloro-3-pyridazinyl)-1H-indole (P2), 4-(6-chloropyridazin-3-yl)benzoic acid (P3) and 3-(6-chloropyridazin-3-yl)benzoic acid (P4) on electrochemical dissolution of mild steel in 1 M HCl were studied using electrochemical, spectroscopic, and theoretical computational chemistry techniques. The inhibition efficiency increases with increasing concentration of the inhibitors and the shift in corrosion potentials obtained revealed that the compounds are mixed-type inhibitors and steel dissolution was found to be a charge transfer process with the steel/electrolyte interface showed pseudo-capacitive behaviour. P1 and P2 showed the best protection performances for mild steel in the studied medium, attributable to the presence of more nitrogen atoms and unsaturated groups in their molecules compared to P3 and P4. The experimental adsorption data obeyed the Langmuir and Temkin isotherm models and was found to involve both physisorption and chemisorption. Spectroscopic studies revealed that the inhibitor molecules interact chemically with mild steel and the pyridazine ring is actively involved in these interactions. Quantum chemical calculations also showed that pyridazine ring has the tendency of interacting with metallic atoms via both forward and backward donations. Molecular dynamic simulation revealed that the molecules can adsorb strongly onto the surface of iron in a near flat orientation.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Corrosion is of serious concern to many industries all over the world. Industries, including oil and gas, construction, and chemical industries use metallic pipes and containers, which are susceptible to corrosion in common environments [1]. Iron and mild steel are popular metal and metal alloy respectively that are commonly used in many industries due to their low cost and favourable strengths [2]. They are however highly susceptible to corrosion in common environments of usage.

Application of corrosion inhibitors is a cost-effective and efficient method of repressing metal corrosion [3]. Organic compounds

that contain heteroatoms or heterocycles and/or π -electron functional groups are often considered for screening as potential corrosion inhibitors [4–6]. In this regard, pyridazine derivatives are promising corrosion inhibitors as they contain N-atoms, π -electron systems and other electronegative atoms from various substituent groups. Pyridazines are known for their pharmaceutical applications as inhibitors of aldose reductase and antioxidants [6,7]. Their uses as essential constituent of many pharmaceutical drugs portray them as potentially non-toxic substances.

Anticorrosion potentials of some pyridazine derivatives have also been reported. Chetouani et al. [8] had reported the inhibitive effects of 5-benzyl-6-methylpyridazine-3-ylthioethanoic acid its ester derivative for pure iron in 1 M HCl using gravimetric and electrochemical measurements. The compounds showed increasing inhibition efficiencies with increase in concentration and a value of 85% was reported at 10^{-4} M. Bouklah et al. [9] investigated the influence of some pyridazine-thiones steel

* Corresponding author. Material Science Innovation and Modelling (MaSiM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa. E-mail address: Eno.Ebenso@nwu.ac.za (E.E. Ebenso).



Influence of 6-phenyl-3(2H)-pyridazinone and 3-chloro-6-phenylpyrazine on mild steel corrosion in 0.5 M HCl medium: Experimental and theoretical studies

Lukman O. Olasunkanmi^{a, b, c, *}, Mabina Frans Sebona^{a, b}, Eno E. Ebenso^{a, b}^a Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa^b Material Science Innovation and Modelling (MaSiM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa^c Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife 220005, Nigeria

ARTICLE INFO

Article history:
Received 20 March 2017
Received in revised form
5 August 2017
Accepted 6 August 2017
Available online 9 August 2017

Keywords:
Corrosion accelerator
Pyridazine
Electrochemical
Spectroscopy
Quantum mechanical

ABSTRACT

Two pyridazine derivatives, namely, 6-phenyl-3(2H)-pyridazinone (P1) and 3-chloro-6-phenylpyrazine (P2) were investigated for their influence on mild steel corrosion in 0.5 M HCl, using Tafel polarization, electrochemical impedance spectroscopy (EIS), surface morphology, FTIR and UV–vis techniques. Quantum chemical calculations were also conducted to corroborate experimental findings. P1 was found to accelerate corrosion at low concentrations but exhibits inhibitive action at higher concentrations, attaining 61% inhibition efficiency at 1.25 mM. The inhibitive action of P2 increases with increasing concentration from 88% at 0.1 mM to 96% at 1.25 mM as deduced from EIS measurements. Both compounds are mixed type inhibitors. P2 seems to display chiefly anodic inhibitive effects. The adsorption of P2 on mild steel surface obeys the Langmuir adsorption isotherm and involved competitive physisorption and chemisorption mechanisms. Scanning electron microscopy analyses of steel surfaces in acid-inhibitor solutions showed that both compounds protect mild steel surface effectively at 1.25 mM. FTIR and UV–vis spectroscopic analyses revealed that N–H, C=O, and C–N functional groups of the pyridazine derivatives are actively involved in adsorption of the molecules onto steel surface. Quantum chemical parameters showed that the higher inhibition efficiency of P2 compared to P1 might be related to better electron acceptance ability of P2.

© 2017 Published by Elsevier B.V.

1. Introduction

Mild steel has applications in various industries, including petroleum, construction and transportation industries among others. It is a widely used material for diverse structural applications. The extensive use of this alloy of iron is related to its special features like high mechanical strength, moderate cost and ready availability [1–5].

Certain industrial processes like acid cleaning, acid descaling and oil well acidizing utilize acid solutions, which are notable aggressive solutions for metal corrosion. Mild steel being an alloy of

iron is therefore highly susceptible to corrosive attack by acidic ions [2–5].

One popular method of controlling metal corrosion is the use of corrosion inhibitors. Commonly used organic compounds in the formulation of corrosion inhibitors are those that contain O, S, N, P and/or Se heteroatoms [2–6]. Functional groups involving these heteroatoms and/or pi electron systems are also known to enhance inhibitive properties. The famous assumption on the mode of inhibitive actions of organic inhibitors is adsorption on metallic surface [2,4,5]. The popular belief is that inhibitors form protective film that shield the metal from direct exposure to aggressive ion and thereby decreases the dissolution of metal in the corrosive medium. In the process, the adsorbed film also reduces the exposed area of the metal and limits the active sites of the metal that interact directly with the environment. There are reports on corrosion inhibition potentials of various families of organic

* Corresponding author. Material Science Innovation and Modelling (MaSiM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa. E-mail address: wolololol@nwu.ac.za (L.O. Olasunkanmi).



Adsorption characteristics of Iota-carrageenan and Inulin biopolymers as potential corrosion inhibitors at mild steel/sulphuric acid interface



Nirmala Devi Gowaraju^a, Saranya Jagadeesan^b, Kiruthika Ayyasamy^a, Lukman O. Olanunkanmi^{c,d}, Eno E. Ebenso^{c,*}, Chitra Subramanian^{a,*}

^a Department of Chemistry, PSGR Nandha College for Women, Coimbatore, India

^b Department of H & S (Chemistry), OMR Institute of Technology, Hyderabad, India

^c Material Science: Innovation and Modelling (M&SIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University, Mafikeng Campus, Private Bag X2046, Mmabatho 2735, South Africa

^d Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ife-Ife 22005, Nigeria

ARTICLE INFO

Article history:

Received 20 November 2016

Accepted 14 February 2017

Available online 16 February 2017

Keywords:

Biopolymers

Weight loss

Electrochemical technique

Mild steel type inhibitors

Mild steel

Corrosion inhibition

ABSTRACT

The corrosion inhibition efficiency performance of biopolymers Iota-carrageenan (IC) and Inulin (INU) on mild steel in 0.5 M H₂SO₄ solution was evaluated using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The inhibition efficiency of the inhibitors increased with increase in concentration. Thermodynamic parameters (ΔG_{ads}) and activation parameters (E_a , ΔH^\ddagger , ΔS^\ddagger) were calculated to investigate the mechanism of inhibition. Polarization studies revealed that the studied inhibitors are mixed type. Scanning electron microscope (SEM), energy dispersive X-ray spectroscopic (EDX) and atomic force microscopy (AFM) studies were used to characterize the surface morphology of inhibited and uninhibited mild steel.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

A number of physical, chemical and mechanical properties favour the use of mild steel for construction and manufacturing purposes. Such properties include high carbon content of about 0.2 to 2.1% and ability to conduct electric current effectively without tarnishing the metal surface among others. Since it is prominently used as structural and instrumental material, the prevention of its corrosion is very essential [1–3]. Most organic compounds with presumed defending action against corrosion of metals and alloys do contain heteroatoms or electronegative atoms, especially N, O, S and P [4]. But the perils of these inhibitors are universally known and the restrictive ecological guidelines of many countries enforced researchers to emphasis on developing economical, non-toxic and naturally viable products [5].

Natural polymers have started to gain tremendous attention in corrosion inhibition studies in recent years. This is because they are effortlessly obtainable, biocompatible, non-toxic, economical, and safe to use without side effects [6]. Just like other organic corrosion inhibitors, naturally occurring polymers are capable of forming metal-polymer complexes that eventually protect metal surface from exposure to

corrosive medium. The compounds generally contain heterocyclic rings whose heteroatoms, mainly O and N serve as active centers of adsorption to metal surface [7,8]. Numerous works Literature search revealed that numerous works have been done on the use of synthetic and natural polymers as potential corrosion inhibitors in the last one decade [9–14]. Umoren and Ebenso have worked extensively with a number of other prolific authors on inhibitive effects of polymers on mild steel and aluminium corrosion in acidic environments [15–27]. A concise recap of the progress in application of carbohydrate polymers as corrosion inhibitors for metals is contained in a recent review paper by Umoren and Eduok [28].

Considerable efforts are still being channeled towards populating research database on environmental friendly polymeric corrosion inhibitors. Numerous naturally occurring polymers are yet to be duly appraised for their potential abilities to inhibit metal corrosion. Among them are water soluble polysaccharide based natural polymers, Iota-carrageenan (IC) and Inulin (INU). Iota-Carrageenan is a sulphated polysaccharide extract from the seaweed called carrageenan. The structural units of a carrageenan comprise 3,6-anhydro-galactose (3,6-AG) and β -D-galactose joined together by α -1,3 and β -1,4-glycosidic bonds (Fig. 1a). Carrageenan can have different structures depending on the extent of sulphonation and the nature of substitution of the hydroxyl groups on the polysaccharide chain. Some known forms of carrageenan include Iota (ι), Kappa (κ), Lambda (λ), and Nu (ν) carrageenan. The use

* Corresponding authors.

E-mail addresses: Eno.Ebenso@nwu.ac.za (E.E. Ebenso), rajibose1995@rediffmail.com (C. Subramanian).



Morpholine and piperazine based carboxamide derivatives as corrosion inhibitors of mild steel in HCl medium



Nnaemeka J.N. Nnaji^a, Oguejiofo T. Ujam^b, Nkechi E. Ibisi^c, Julius U. Ani^b, Thereasa O. Onuegbu^d, Lukman O. Olasunkanmi^{e,f,g}, Eno E. Ebenso^{e,h,*}

^a Department of Chemistry, Federal University Ndufu Afika, Ibesi, Ebonyi State, Nigeria

^b Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Enugu State, Nigeria

^c Department of Chemistry, Michael Okpara University of Agriculture, Umuahia, Abia State, Nigeria

^d Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka, Anambra State, Nigeria

^e Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^f Material Science Innovation and Modelling (MSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^g Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife 220005, Nigeria

ARTICLE INFO

Article history:

Received 6 November 2016

Received in revised form 9 January 2017

Accepted 22 January 2017

Available online 25 January 2017

Keywords:

Carboxamide

Gravimetric

Thermometric

Absorption

Quantum chemical calculations

ABSTRACT

N-(2-chloroethyl)morpholine-4-carboxamide (NCMC), *N*-(2-chloroethyl)piperazine-4-carboxamide (NCTC) and *N,N*-bis(2-chloroethyl)piperazine-1,4-dicarboxamide (NCPD) were studied as corrosion inhibitors for mild steel using atomic absorption spectroscopy (AAS) and gravimetry and thermometry. Results obtained from the three techniques are similar and reveal that the compounds inhibit mild steel corrosion. The inhibition efficiencies increased from 35.6% to 74.9% (NCMC), 44.5% to 82.4% (NCPD) and 52.6% to 90.1% (NCTC) at 30 °C when the inhibitor concentrations increased from 10 μM to 50 μM. The maximum inhibition efficiency values (at 50 μM) decreased to 46.6%, 58.1% and 61.2% for NCMC, NCPD and NCTC respectively, when the temperature was raised to 50 °C. The decrease in inhibition efficiency with increase in temperature suggested predominant physisorption mechanism in metal/inhibitor interactions. The formation of protective films of NCMC, NCPD and NCTC molecules on mild steel surface were confirmed by FTIR and XRD. The order of inhibitive strengths of the molecules is NCTC > NCPD > NCMC. Quantum chemical calculations revealed the prospective sites through which the molecules can interact with mild steel surface and some quantum chemically derived parameters were used to corroborate experimental.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Many facilities used at the oil and gas refinery plants are made of mild steel. Steel is a major construction material extensively used in chemical and allied industries for material constructions [1]. It has therefore become the most useful metal in human development. The utilization of mild steel in construction and fabrication of industrial facilities is not only due to its optimum strength to mass ratio that fits the strength requirement of many industrial equipment, but also as a result of its ready availability at moderately low cost. Unfortunately, mild steel being an active alloy of iron undergoes corrosion in nearly

all environments, most especially acidic environment. Corrosion of metals has both economic and environmental effects that are of great concern to corrosion and corrosion prevention experts. Corrosion products can be hazardous to man, animal and vegetation. El-Melgi [2] believes that corrosion products from various sources including car constructions, bridges and buildings, water pipeline system and petroleum industries are notable environmental pollutants.

Steel made materials are often used to hold acid, alkali and salt solutions in chemical and allied industries [2]. Acid induced steel corrosion is by far the most common in industries. Industrial processes that lead to steel corrosion by acids include acid pickling, acid cleaning and oil well acidizing [3]. Safety and cost-effective maintenance of steel materials used for these industrial activities are of paramount consideration [4]. Increased metal corrosion resistance can be achieved in various ways, but often at elevated cost. The use of corrosion inhibitors is therefore a more practical and economic alternative [5]. The use of corrosion inhibitors in industries is extensive and broad based [6].

* Corresponding author at: Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa.

E-mail address: Eno.Ebenso@nw.ac.za (E.E. Ebenso).



Anticorrosion performance of three newly synthesized isatin derivatives on carbon steel in hydrochloric acid pickling environment: Electrochemical, surface and theoretical studies



Y. Kharbach^a, F.Z. Qachchachi^a, A. Haoudi^a, M. Tourabi^b, A. Zarrouk^c, C. Jama^d, L.O. Olasunkanmi^{e,f}, E.E. Ebenso^f, F. Bentiss^{b,d,*}

^a Laboratoire de Chimie Appliquée, Faculté des Sciences et Techniques, Université El-Sidi Mohamed Ben Abdallah, PO Box 2202, Fez M-30050, Morocco

^b Laboratory of Catalysis and Corrosion of Materials, Faculty of Sciences, Chouaib Doukkali University, PO Box 20, M-24000 El Jadida, Morocco

^c LGAME-URAC 18, Faculty of Science, First Mohammed University, PO Box 717, 60 000 Oujda, Morocco

^d Univ. Lille, CNRS, INRA, ENSCL, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France

^e Department of Chemistry, Faculty of Science, Obafemi Awolowo University, 220005 Ik-ife, Nigeria

^f Material Science Innovation and Modelling (M&SIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University, (Mafikeng Campus) Private Bag X246, Mmabatho 2735, South Africa

ARTICLE INFO

Article history:

Received 17 July 2017

Received in revised form 11 September 2017

Accepted 16 September 2017

Available online 19 September 2017

Keywords:

Isatin

Carbon steel

HCl

Corrosion inhibition

Surface

Adsorption

Theoretical calculations

ABSTRACT

In this work, three new isatin derivatives (5-BEI, 5-HB and 5-FEI) were synthesized and their inhibition effect on carbon steel in hydrochloric acid medium has been evaluated. The detailed study of 5-BEI is given using gravimetric measurements and electrochemical methods (DC and AC techniques). The results showed that this new isatin is an efficient corrosion inhibitor for carbon steel in 1 M HCl and an inhibition efficiency of 95.2% was exhibited by 5-BEI at 1 mM concentration of 5-BEI after 6 h of immersion at 303 K. Polarization curves suggested that the 5-BEI acted as mixed type inhibitor. Electrochemical Impedance Spectroscopy showed that increase inhibitor (5-BEI, 5-HEI and 5-FEI) concentration leads to an increase in the values of the charge transfer resistance. Adsorption of 5-BEI, 5-HEI and 5-FEI molecules on the steel surface obeyed Langmuir adsorption isotherm model. X-Ray Photoelectron Spectroscopy (XPS) analyses revealed that the corrosion inhibition mechanism of 5-BEI is mainly controlled by a chemisorption process. The comparative study of inhibitive performance of the three isatin derivatives (5-BEI, 5-HEI and 5-FEI) using Density functional theory (DFT) calculations of orbital energies and reactivity indices suggested that the trend of inhibition potentials of the compounds depend on the effect of substituent atoms (–Br, –F, and –H) on the electron donating and/or accepting ability of the molecules. The trend of reactivity of the molecules was 5-BEI > 5-FEI > 5-HB. Theoretical Monte Carlo simulation studies also corroborated experimental findings.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The corrosion of iron and steel is a fundamental industrial and academic preoccupation that has received considerable amount of attention [1]. In past decades, slowing down or completely inhibiting corrosion has been an intensive field of interest. Hydrochloric acid solution is widely used for pickling, descaling, acid cleaning, acidification of oil wells and other applications; however, it is very corrosive and causes damage to metallic constituents [2]. To decrease the dissolution of the metal and the acid consumption, corrosion inhibitor molecules are also added to the pickling solution. The steel acid pickling inhibitors are almost

exclusively organic substances [3]. Their action is mainly due to adsorption phenomena (physisorption and/or chemisorption) resulting from the interaction of polar centres of the inhibitor's molecule with active sites on the metal surface [4]. In recent years, there is a significant amount of effort deployed to finding novel and efficient organic corrosion inhibitors and *N*-heterocyclic compounds have proven to be efficacious corrosion molecule inhibitors [5–10]. Some isatin derivatives and their Mannich bases have been reported as efficient corrosion inhibitors for aluminium, copper and steel [11–28] and the literature available according to our knowledge about the isatin derivatives functioning as corrosion inhibitors is limited.

In continuation of our work on development of *N*-heterocyclic molecules as corrosion inhibitors in acidic medium, this report resumes the results of our work on evaluation of some new isatin derivatives (5-BEI, 5-HEI and 5-FEI) as organic corrosion inhibitors for carbon steel in

* Corresponding author at: Laboratory of Catalysis and Corrosion of Materials, Faculty of Science, Chouaib Doukkali University, PO Box 20, M-24000 El Jadida, Morocco.
E-mail address: fbentiss@univ-lille.fr (F. Bentiss).

Polyurethane Based Triblock Copolymers as Corrosion Inhibitors for Mild Steel in 0.5 M H₂SO₄

Sudershan Kumar,[†] Hemlata Vashisht,[‡] Lukman O. Olasunkanmi,^{§,||} Indra Bahadur,[§] Hemant Verma,[†] Madhusudan Goyal,[‡] Gurmeet Singh,[‡] and Eno E. Ebenso^{*,§}

[†]Department of Chemistry, Hindu College, University of Delhi, Delhi 110007, India

[‡]Department of Chemistry, Kirori Mal, University of Delhi, Delhi 110007, India

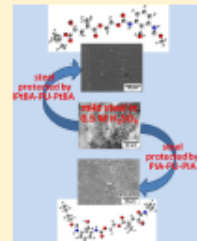
[§]Department of Chemistry, North-West University (Mafikeng Campus) and Material Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^{||}Department of Chemistry, Obafemi Awolowo University, Ile-Ife 220005, Nigeria

^{*}Department of Chemistry, University of Delhi, Delhi 110007, India

Supporting Information

ABSTRACT: Two polyurethane based triblock copolymers, namely, poly(*N*-isopropylacrylamide)-*b*-polyurethane-*b*-poly(*N*-isopropylacrylamide) (PIA-PU-PIA) and poly(*tert*-butylacrylate)-*b*-polyurethane-*b*-poly(*tert*-butylacrylate) (PtBA-PU-PtBA), were synthesized via atom transfer radical polymerization (ATRP) mechanism and characterized. The inhibition potentials of the polymers on mild steel corrosion in 0.5 M H₂SO₄ were studied using electrochemical, scanning electron microscopy (SEM), and atomic force microscopy (AFM) techniques. The results obtained from potentiodynamic polarization studies showed that the two polymers are mixed-type inhibitors and exhibit passivating activities. The adsorption of PIA-PU-PIA on mild steel surface obeys the Langmuir adsorption isotherm, while that of PtBA-PU-PtBA obeys the El-Awady isotherm. The two polymers adsorb on the mild steel surface via competitive physisorption and chemisorption mechanisms. Both SEM and AFM analyses confirmed the formation of protective layers of the inhibitor molecules on the steel surface. The results obtained showed that PIA-PU-PIA exhibited higher inhibition performance than PtBA-PU-PtBA, and the trend was corroborated by the results obtained from quantum chemical calculations.



1. INTRODUCTION

Corrosion is the destructive attack on a metal or metal alloy by chemical or electrochemical reaction with its environment.¹ Corrosion of metal is also considered as extractive metallurgy in reverse.² Mild steel is an alloy of iron (Fe) with various industrial and structural applications. It is relatively cheap and possesses high mechanical strength. Despite its quality properties and wide applications, mild steel is highly susceptible to corrosion in various aggressive environments, and as a result, the study of its corrosion/corrosion control in acidic medium is of great economic importance.³ Among several methods of corrosion control, such as cathodic protection, anodic protection, coating and alloying, etc., the use of corrosion inhibitors is often considered as one of the cheapest, most effective, and practical method of corrosion prevention. Inhibitors can also be added *in situ* during industrial processes. As a result, corrosion inhibitors are widely used in industries to prevent or reduce the corrosion rate of metallic materials in aggressive environment.^{4–6}

Organic compounds that contain heteroatoms such as nitrogen, oxygen, sulfur and/or electron rich aromatic systems are generally known to exhibit good anticorrosion properties.^{7–10} Organic compounds such as alkaloids,¹¹ thiourea,¹² benzene-thiol derivatives,¹³ imidazole/azo derivatives,¹⁴ quinoline

derivatives,¹⁵ quaternary ammonium salts,¹⁶ aldehydes,¹⁷ and Schiff bases¹⁸ are among the widely used corrosion inhibitors.

Research on the use of polymers as corrosion inhibitors has gained huge attention in recent years. This is because polymers are generally characterized with large surface area, intrinsic stability, and cost effectiveness.¹⁹ Many polymers possess atoms and/or functional groups that aid formation of complexes with metal ions or adsorption on metal surface. Metal complexes of polymers are capable of blocking the active sites on metal surface, thereby protecting the metal from making direct contact with corrosive environment. The inhibitive power of polymers is often structurally related to the presence of cyclic rings with π -electrons and heteroatoms, which are the major sites for adsorption.^{20–22} A review of literature has revealed that a number of studies have been conducted in the past decade to demonstrate the potential applications of both conducting and thermoplastic polymers as protective materials for metal corrosion, either as coating formulations or as corrosion inhibitors.^{23–26}

Received: October 13, 2016

Revised: December 2, 2016

Accepted: December 9, 2016

Published: December 9, 2016



Zinc Oxide Nanocomposites of Selected Polymers: Synthesis, Characterization, and Corrosion Inhibition Studies on Mild Steel in HCl Solution

Taiwo W. Quadri,^{†‡} Lukman O. Olasunkanmi,^{†‡,§} Omolola E. Fayemi,^{†‡} Moses M. Solomon,^{||} and Eno E. Ebenso^{*,†‡,||}

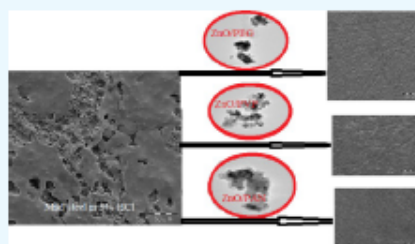
[†]Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology and

[‡]Material Science Innovation and Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

[§]Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife 220005, Nigeria

^{||}Department of Science Technology, Akwa-Ibom State Polytechnic, Ikot Osurua, P.M.B 2100, Ikot Ekpene, Nigeria

ABSTRACT: Nanocomposites of ZnO and some selected polymers, namely, poly(ethylene glycol), poly(vinylpyrrolidone), and polyacrylonitrile, were synthesized and characterized using Fourier transform infrared (FTIR) spectroscopy, ultraviolet–visible (UV–vis) spectroscopy, thermogravimetric analysis (TGA), and transmission electron microscopy (TEM) techniques. The FTIR and UV–vis spectra confirmed the successful formation of the polymer nanocomposites. TGA results revealed that the synthesized polymer nanocomposites are more thermally stable than the polymers alone. ZnO nanoparticles were about 50–75 nm in size, assumed a rod-like shape, and got embedded in the polymer matrices, as revealed by TEM images. Corrosion inhibition potentials of the synthesized ZnO/polymer nanocomposites were investigated for mild steel in 5% HCl solution using potentiodynamic polarization (PDP), linear polarization resistance, and electrochemical impedance spectroscopy measurements. The results showed that each ZnO/polymer nanocomposite inhibits mild steel corrosion in 5% HCl solution better than the respective polymer alone. The nanocomposites, according to PDP studies, behaved as a mixed-type inhibitor. The predominant mode of adsorption of the nanocomposites to a mild steel surface was found to be mixed type, and the adsorption process obeys the Langmuir adsorption isotherm model. Scanning electron microscopy images also revealed the protective attributes of the ZnO/polymer nanocomposites for mild steel in 5% HCl solution.



1. INTRODUCTION

Metals constitute a great part of materials in construction, medical, oil and gas, petrochemical, and allied industries. In these industries, the metallic material as a result of interaction with its surrounding environment loses its essential properties over a period of time. As a result, the material cannot perform the intended function effectively and reliably.^{1,2} Corrosion of metals has numerous adverse consequences and has been long known to be a matter of serious concern to experts in both academia and industries.³

The use of inhibitor as a cost-effective and easiest method of repressing metal corrosion is a common fact. Organic compounds top the chart of metal corrosion inhibitors at present.⁴ Nevertheless, some of these organic compounds are considered unfriendly to the ecosystem and expensive.⁵ Polymers have been identified as potential ecofriendly and affordable corrosion inhibitors.^{6,7} However, their limited solubility in common aqueous corrosive media and desorption at high temperatures have impeded their wide application as

corrosion inhibitors. Metal nanoparticles/polymer composites have proffered improvements over the earlier known limitations of polymers as corrosion inhibitors. Hefni et al.⁸ reported that chitosan-grafted-poly(ethylene glycol) (Ch-g-mPEG) self-assembled on silver nanoparticles exhibited superior corrosion inhibiting ability (ca. 93%) for carbon steel in 1 M HCl solution compared to that of Ch-g-mPEG without silver nanoparticles (ca. 77%). The incorporation of silver nanoparticles into the matrix of poly(propylene glycol),^{9,10} poly(methacrylic acid),^{11,12} chitosan,^{13,14} and carbonylmethyl cellulose¹⁵ had also been reported to enhance corrosion protection properties of the polymers.

Metal oxide nanoparticles are of special interest due to their diverse mechanical, structural, thermal, electronic, magnetic, and optical properties. Among the wide variety of metal oxide nanoparticles, ZnO is one of the most promising because of its

Received: September 16, 2017

Accepted: October 31, 2017

Published: November 29, 2017

SCIENTIFIC REPORTS

OPEN

Experimental and theoretical studies on inhibition of mild steel corrosion by some synthesized polyurethane tri-block co-polymers

Received: 23 March 2016

Accepted: 11 July 2016

Published: 12 August 2016

Sudershan Kumar¹, Hemlata Vashisht², Lukman O. Olasunkanmi³, Indra Bahadur⁴, Hemant Verma⁵, Gurmeet Singh⁶, Ime B. Obot⁷ & Eno E. Ebenso⁸

Polyurethane based tri-block copolymers namely poly(*N*-vinylpyrrolidone)-*b*-polyurethane-*b*-poly(*N*-vinylpyrrolidone) (PNVP-PU) and poly(dimethylaminoethylmethacrylate)-*b*-polyurethane-*b*-poly(dimethylaminoethylmethacrylate) (PDMAEMA-PU) were synthesized through atom transfer radical polymerization (ATRP) mechanism. The synthesized polymers were characterized using nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC) methods. The corrosion inhibition performances of the compounds were investigated on mild steel (MS) in 0.5 M H₂SO₄ medium using electrochemical measurements, surface analysis, quantum chemical calculations and molecular dynamic simulations (MDS). Potentiodynamic polarization (PDP) measurements revealed that the polymers are mixed-type corrosion inhibitors. Electrochemical impedance spectroscopy (EIS) measurements showed that the polymers inhibit MS corrosion by adsorbing on MS surface to form pseudo-capacitive interface. The inhibitive effects of the polymers increase with increasing concentration and decrease with increasing temperature. The adsorption of both the polymers on MS surface obey the Langmuir adsorption isotherm and involves both physisorption and chemisorption mechanisms. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses showed that the polymers formed protective film on MS surface and shield it from direct acid attack. Quantum chemical calculations and molecular dynamic simulations studies corroborate experimental results.

Acid solutions are routinely used in certain industrial activities such as acid pickling, cleaning, descaling etc. The aggressive acidic environment corrodes metallic structures and brings about deterioration of metal and its intrinsic properties^{1,2}. The use of organic inhibitors has been identified as one of the most efficient and cost effective methods of mitigating metal corrosion³⁻⁵. Organic compounds that contain N, S, and O heteroatoms as well as pi-electron systems have been documented to exhibit good anticorrosion properties⁶⁻⁸. The inhibition potential of an organic compound depends on its ability to adsorb on metallic surface. In other words, the inhibitive effect organic compound is usually premised on the displacement of water molecules from the surface of the metal and subsequent formation of protective film of the inhibitor molecules on the metal surface⁹.

Organic polymers have attracted considerable attentions in corrosion inhibition studies in recent years. This is due to the inherent stability, cost effectiveness, and relatively high inhibition efficiency at considerably low concentrations that have been identified with many of these polymers¹⁰⁻¹³. Polymers have a great tendency of forming complexes with metal ions and also adsorb on metallic surface effectively due to the presence of various functional groups in polymer molecules. Polymer molecules or their metal complexes occupy a large surface area on metallic surface and thereby block the active sites associated with corrosion and protect the metal from

¹Department of Chemistry, Hindu College, University of Delhi, Delhi, 110007, India. ²Department of Chemistry, Maharaja Agrasen College, University of Delhi, Delhi, 110007, India. ³Department of Chemistry and Material Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa. ⁴Department of Chemistry, University of Delhi, Delhi, 110007, India. ⁵Centre of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia. Correspondence and requests for materials should be addressed to E.E.E. (email: Eno.Ebenso@nwu.ac.za)


 Cite this: *RSC Adv.*, 2016, 6, 15639

5-Arylpyrimido-[4,5-*b*]quinoline-diones as new and sustainable corrosion inhibitors for mild steel in 1 M HCl: a combined experimental and theoretical approach†

 Chandrabhan Verma,^a L. O. Olasunkanmi,^{bc} I. B. Obot,^d Eno E. Ebenso^{bc} and M. A. Quraishi^{*,a}

The inhibition of mild steel corrosion in 1 M HCl by four 5-arylpyrimido-[4,5-*b*]quinoline-diones (APQDs), namely 5-(4-nitrophenyl)-5,10-dihydropyrimido[4,5-*b*]quinoline-2,4(1*H*,3*H*)-dione (APQD-1), 5-phenyl-5,10-dihydropyrimido[4,5-*b*]quinoline-2,4(1*H*,3*H*)-dione (APQD-2), 5-(4-hydroxyphenyl)-5,10-dihydropyrimido[4,5-*b*]quinoline-2,4(1*H*,3*H*)-dione (APQD-3) and 5-(2,4-dihydroxyphenyl)-5,10-dihydropyrimido[4,5-*b*]quinoline-2,4(1*H*,3*H*)-dione (APQD-4) has been investigated using weight loss, electrochemical, surface, and quantum chemical calculations and molecular dynamics simulation methods. The results showed that the inhibition efficiency (η_{in}) increased with increasing concentration of the inhibitors. Among the studied compounds, APQD-4 exhibited the highest inhibition efficiency of 98.30% at 20 mg l⁻¹ concentration. The studied compounds effectively retarded the corrosion of mild steel in 1 M HCl by adsorbing onto the steel surface, and the adsorption data conformed to the Langmuir adsorption isotherm. The results of potentiodynamic polarization measurements revealed that the studied compounds are cathodic-type inhibitors. Scanning electron microscopy (SEM) study confirmed the formation of adsorbed films of the inhibitor molecules on the steel surface. Quantum chemical calculations and molecular dynamics simulations were undertaken to corroborate experimental findings and provide adequate insight into the corrosion inhibition mechanisms and adsorption characteristics of the studied compounds.

 Received 22nd December 2015
 Accepted 28th January 2016

DOI: 10.1039/c5ra27417f

www.rsc.org/advances

1 Introduction

Metals and alloys undergo chemical and/or electrochemical reactions with the environment to form relatively more stable compounds and consequently there is a loss of metals due to the corrosion process. Among different available methods that have been identified for corrosion control, the use of synthetic corrosion inhibitors is one of the most appropriate, effective and economic ways of mitigating corrosion problem.^{1–4} However, most of the synthetic corrosion inhibitors are toxic and not environmentally friendly. In recent years, green

chemistry has attracted considerable attention from synthetic and medicinal chemists due to increasing ecological awareness and strict environmental regulation.^{5,6} Therefore, the current trend of research in corrosion inhibition is directed towards the development of green corrosion inhibitors that offer high inhibition efficiency at low environmental risk.^{7,8} In this regard, multicomponent reactions have emerged as a green and powerful technique in synthetic organic chemistry and drug discovery in the sense that several biologically active complexes/molecules can be synthesized in one step by using commercially available cheap starting materials.^{9,10} The multicomponent reactions have several advantages such as operational simplicity, facile automation and minimized waste generation, because of the reduction in the number of work-up, extraction and purification stages.^{11,12} Furthermore, the consumption of environmentally benign solvents and chemicals during the reactions provides the means of upholding the essential principles of green chemistry. Nowadays, the development of synthetically useful reactions using water as reaction medium has drawn considerable attention because of its non-flammable, non-hazardous, non-toxic, uniquely redox-stable, inexpensive and free availability.^{13–15} Moreover, in asymmetric organocatalysis, the use of proline, particularly in water and

^aDepartment of Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi 221 005, India. E-mail: masquraishi@iitbhu.ac.in; masquraishi@ndiffmail.com; Fax: +91-542-2369428; Tel: +91-9017025126

^bDepartment of Chemistry, School of Mathematical & Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^cMaterial Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^dCenter of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ra27417f



Cite this: RSC Adv., 2016, 6, 53933

2,4-Diamino-5-(phenylthio)-5H-chromeno [2,3-*b*]pyridine-3-carbonitriles as green and effective corrosion inhibitors: gravimetric, electrochemical, surface morphology and theoretical studies

Chandrabhan Verma,^a Lukman O. Olasunkanmi,^{b,c} I. B. Obot,^d Eno E. Ebenso^b and M. A. Quraishi^{*a}

The inhibition of mild steel corrosion in 1 M HCl by three newly synthesized 2,4-diamino-5-(phenylthio)-5H-chromeno[2,3-*b*]pyridine-3-carbonitriles (DHPCs) namely, 2,4-diamino-7-nitro-5-(phenylthio)-5H-chromeno[2,3-*b*]pyridine-3-carbonitrile (DHPC-1), 2,4-diamino-5-(phenylthio)-5H-chromeno[2,3-*b*]pyridine-3-carbonitrile (DHPC-2) and 2,4-diamino-7-hydroxy-5-(phenylthio)-5H-chromeno[2,3-*b*]pyridine-3-carbonitrile (DHPC-3) was studied using weight loss method, electrochemical techniques, surface morphology (SEM, AFM) studies and theoretical (quantum chemical calculations and molecular dynamic simulation) methods. The weight loss and electrochemical measurements showed that the inhibition efficiency increases with increasing inhibitor concentration and the relative trend of inhibition performance is DHPC-3 > DHPC-2 > DHPC-1. A potentiodynamic polarization study reveals that the investigated DHPCs act as mixed type inhibitors. The adsorption of the DHPCs on the mild steel surface obeys the Langmuir adsorption isotherm and involves both physisorption and chemisorption modes. The presence of the electron releasing -OH group at position seven on the chromenopyridine ring is considered to be responsible for the highest inhibition efficiency of DHPC-3 among the studied compounds. Whereas the presence of the electron withdrawing nitro (-NO₂) group at position seven on the chromenopyridine ring is responsible for the lowest inhibitive strength of DHPC-1. Quantum chemical calculations and molecular dynamic simulation studies were undertaken to provide mechanistic insight into the roles of the different substituents (-OH and -NO₂) on the corrosion inhibition behavior of the studied inhibitors.

Received 24th February 2016

Accepted 25th May 2016

DOI: 10.1039/c6ra04900a

www.rsc.org/advances

1. Introduction

Iron and its alloys are widely used as construction materials in the petroleum, food, power production, chemical and electrochemical industries. This is due to their high thermal and mechanical stability, ease of fabrication and joining, and low cost.¹⁻³ However, these materials become gradually destroyed by corrosion upon exposure to the environment due to chemical and/or electrochemical reactions with the environment. Therefore, several efforts are being channeled towards

preventing these undesirable reactions. Among the several available methods of corrosion protection, the utilization of synthetic corrosion inhibitors has become a popular method because of the ease and economic viability of the synthesis of these inhibitors, high inhibition efficiency, and practical-feasibility.⁴⁻⁶ Most of the efficient corrosion inhibitors are organic compounds containing polar functional groups and π -electrons in form of triple or conjugated double bonds. These synthetic compounds inhibit corrosion by adsorbing on metallic surface. Generally, the adsorption of these inhibitors on the metal surfaces depends on numerous physicochemical properties such as nature of functional groups, steric factors, aromaticity, electron density at the donor atoms and p-orbital character of donating electrons and the electronic structure of the inhibitors molecules.⁷ Previous literature had established that S-containing compounds show better inhibition efficiency in sulphuric acid solution, while N-containing compounds show better inhibition efficiency in hydrochloric acid solution.⁸ Whereas, compounds containing both N- and S-atoms generally give rise to even better inhibition efficiency.^{9,10}

^aDepartment of Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi 221 005, India. E-mail: maquraishi@iitbhu.ac.in; maquraishi@ndiffmail.com; Fax: +91-542-2368420; Tel: +91-9207025126

^bDepartment of Chemistry and Material Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^cDepartment of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife, 220008, Nigeria

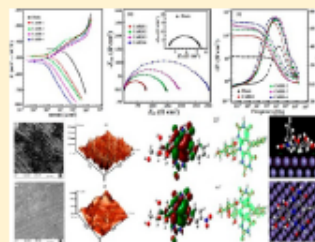
^dCentre of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Adsorption Behavior of Glucosamine-Based, Pyrimidine-Fused Heterocycles as Green Corrosion Inhibitors for Mild Steel: Experimental and Theoretical Studies

Chandrabhan Verma,[†] Lukman O. Olasunkanmi,^{‡,§} Eno E. Ebenso,^{‡,§} M. A. Quraishi,^{*,†} and I. B. Obot^{||}[†]Department of Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi 221005, India[‡]Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa[§]Material Science Innovation and Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa^{||}Center of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Supporting Information

ABSTRACT: Effects of electron donating ($-\text{CH}_3$ and $-\text{OH}$) and electron withdrawing ($-\text{NO}_2$) substituents on the corrosion inhibition efficiency of four glucosamine-based, substituted, pyrimidine-fused heterocycles (CARBs) on mild steel corrosion in 1 M HCl have been investigated using gravimetric, electrochemical, surface morphology (SEM, AFM, and EDX), and computational techniques. Gravimetric studies showed that protection performances of the compounds increase with increase in concentration. Both electron withdrawing ($-\text{NO}_2$) and electron donating ($-\text{CH}_3$ and $-\text{OH}$) groups were found to enhance the inhibition efficiency, but the effect is more pronounced with electron donating substituents. The compounds were found to be cathodic type inhibitors as inferred from the results of potentiodynamic polarization studies. EIS studies suggested that the studied compounds inhibit metallic corrosion by adsorbing on metallic surface. The adsorption of the inhibitor molecules on steel surface was further supported by SEM, AFM, and EDX analyses. Adsorption of CARBs on a mild steel surface obeyed the Langmuir adsorption isotherm. Theoretical studies using quantum chemical calculations and molecular dynamics simulations provided additional insights into the roles of the $-\text{OH}$, $-\text{CH}_3$, and $-\text{NO}_2$ substituents on the corrosion inhibition performances of the studied inhibitors.



1. INTRODUCTION

Mild steel has been widely used as a main construction material for piping works in various industries. It has found applications in downhole casing or tubing, flow lines, and transmission or distribution pipelines in oil and gas industries.^{1–3} Petroleum oil well acidization is an essential technique that is routinely used in oil and gas industries for the purpose of stimulating the oil well to ensure enhanced oil production.^{4,5} This process, however, endangers the life of steel gadgets as a result of acid-driven corrosion. In order to prevent this undesirable reaction, corrosion inhibitors are often added to the acid solution during the acidification process.^{6–8} These compounds inhibit corrosion by adsorbing on the metallic surface using heteroatoms (e.g., N, O, S), polar functional groups (e.g., $-\text{OH}$, $-\text{NH}_2$, $-\text{NO}_2$, $-\text{CN}$, etc.), π -electrons, and aromatic rings as adsorption centers.^{9–11} Inhibitors retard metal corrosion by adsorbing on metallic surface and the process is influenced by some factors, which include molecular size of inhibitor, nature of substituents, inhibitor concentration, solution temperature, and nature of test solution.^{9,11}

Multicomponent reactions (MCRs) have emerged as a powerful technique toward “green compliant” synthesis. MCRs have advantages of satisfying both economic and environmental provisos of the green chemistry approaches. In addition, it ensures high chemical selectivity, high yield, short reaction time, mild reaction condition, and operational simplicity.^{12,13} Being a one-step reaction in which three or more reactants are combined to yield product, MCRs are able to satisfy quite a number of other prerequisites of green chemistry synthesis including small number of steps, facile automation, minimum waste generation due to reduced workup steps, and a simple purification procedure, which enhances the synthetic efficiency.^{14–16} The increasing ecological awareness, strict environmental regulations, and the need to reduce environmental pollution together with its side effects on human health have necessitated the recent efforts in ensuring that corrosion inhibition studies are “green” chemistry compliant. In this

Received: May 2, 2016

Published: May 10, 2016

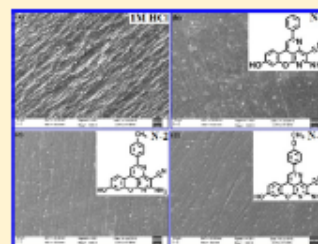
Electrochemical, Theoretical, and Surface Morphological Studies of Corrosion Inhibition Effect of Green Naphthyridine Derivatives on Mild Steel in Hydrochloric Acid

Priyanka Singh,[†] Eno E. Ebenso,^{‡,§} Lukman O. Olasunkanmi,^{‡,§} I. B. Obot,^{||} and M.A. Quraishi^{*,†}[†]Department of Chemistry, Indian Institute of Technology, Banaras Hindu University, Varanasi 221005, India[‡]Department of Chemistry and Material Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa[§]Department of Chemistry, Obafemi Awolowo University, Ile-Ife 220005, Nigeria^{||}Center of Research Excellence in Corrosion, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

Supporting Information

ABSTRACT: The corrosion inhibition efficiencies of three novel naphthyridines namely, 5-amino-9-hydroxy-2-phenylchromeno[4,3,2-de][1,6]-naphthyridine-4-carbonitrile (N-1), 5-amino-9-hydroxy-2-(p-tolyl)chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (N-2), and 5-amino-9-hydroxy-2-(4-methoxyphenyl)chromeno[4,3,2-de][1,6]naphthyridine-4-carbonitrile (N-3) have been investigated for mild steel in 1 M HCl solution by using weight loss, electrochemical impedance spectroscopy, and potentiodynamic polarization methods. All three compounds show high inhibition activities at 6.54×10^{-5} M: N-1, 94.28%; N-2, 96.66%; and N-3, 98.09%. Electrochemical impedance spectroscopy analysis reveals an increase in polarization resistance due to the adsorbed inhibitor molecules on metal surface. Potentiodynamic polarization analysis reveals that all three compounds act as mixed-type inhibitors but of predominantly cathodic type. The adsorption of the studied compounds on mild steel surface follows the Langmuir adsorption isotherm.

Surface morphology examined by using scanning electron microscopy and atomic force microscopy analysis shows a smoother surface for mild steel in the presence of naphthyridines in acidic solution. Quantum chemical parameters correlate well with the experimental results, which support higher inhibition efficiencies of N-3 and N-2 due to the electron-donating effects of $-\text{OCH}_3$ and $-\text{CH}_3$ substituents, respectively, than of N-1, which is devoid of substituents. The magnitudes of the adsorption energies obtained from Monte Carlo simulations also agree with the trend of the experimental inhibition efficiency.



1. INTRODUCTION

Mild steel (MS) is a widely used alloy in petroleum industries because of its low cost and high mechanical strength. Industrial processes such as oil well acidization, acid pickling, and acid descaling require the use of mineral acids, especially hydrochloric and sulfuric acids. These processes are important because they enhance oil recovery and remove unwanted scale and salt deposits or mill scales that are formed during manufacturing.^{1,2} Unfortunately, the acids used in the course of these processes promote corrosion of the oil well/pipe. The damage due to corrosion of metals engenders high cost for renovation and replacement of various equipment and causes public and environmental risks. The use of chemical corrosion inhibitors is a good option to protect metals from this type of corrosion.³ The adsorption of inhibitor molecules on metal surface prevents direct contact between the metal and the acid solution. Usually, N-heterocyclic compounds are considered to be good corrosion inhibitors because of the ease of electron donation to the metal from the nitrogen heteroatoms. Molecules with triple or conjugated double bonds and aromatic

rings are also promising corrosion inhibitors.^{4–7} However, most of these compounds are pricey and toxic to human beings and the environment. For this reason, current research activities are being garnered toward the development of cheap and “green” corrosion inhibitors with high inhibition efficiency. In view of this, naphthyridines are a suitable option because of their wide applicability in medicines, which portrays them as nontoxic compounds. The 1,6-naphthyridine derivatives are used for cancer chemotherapy as antitumor agents. In addition to that 1,6-naphthyridines possess well-documented biological activity, including antibacterial, antiviral, and antiproliferative activities, and also act as an inhibitor of human immunodeficiency virus (HIV) infection.^{8–11} These compounds are simply synthesized from “green” raw materials using silica gel (easily available, inexpensive, and nontoxic) as a green catalyst and water as a green solvent. More so, corrosion inhibition activities of various

Received: December 7, 2015

Revised: January 25, 2016

Published: January 25, 2016



Experimental and theoretical studies on some selected ionic liquids with different cations/anions as corrosion inhibitors for mild steel in acidic medium



Sasikumar Yesudass^a, Lukman O. Olasunkanmi^{a,b}, Indra Bahadur^a,
Mwadham M. Kabanda^a, I.B. Obot^c, Eno E. Ebenso^{a,*}

^a Department of Chemistry, School of Mathematical and Physical Sciences and Materials Science Innovation & Modelling Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^b Department of Chemistry, Obafemi Awolowo University, Ile-Ife 220005, Nigeria

^c Centre of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

ARTICLE INFO

Article history:

Received 6 November 2015

Revised 4 March 2016

Accepted 6 April 2016

Available online 12 May 2016

Keywords:

Ionic liquids

Mild steel

Corrosion inhibition

QSAR

Monte Carlo simulations

ABSTRACT

Inhibition of mild steel corrosion in 1 M HCl solution by some alkylimidazolium-based ionic liquids (ILs) namely 1-ethyl-3-methylimidazolium ethylsulfate [EMIM]⁺[EtSO₄]⁻, 1-ethyl-3-methylimidazolium acetate [EMIM]⁺[Ac]⁻, 1-butyl-3-methylimidazolium thiocyanate [BMIM]⁺[SCN]⁻, 1-butyl-3-methylimidazolium acetate [BMIM]⁺[Ac]⁻ and 1-butyl-3-methylimidazolium dicyanamide [BMIM]⁺[DCA]⁻ was investigated using electrochemical, spectroscopic, surface morphology, quantum chemical calculations, quantitative structure activity relationship (QSAR) and Monte Carlo simulation methods. The studied ILs showed appreciable inhibition efficiencies within the range of concentrations considered. Polarization measurements showed that the studied ILs are mixed-type inhibitors, that is, they inhibit both the anodic mild steel dissolution and cathodic hydrogen evolution reactions. The adsorption of the ILs on mild steel affords competitive physisorption and chemisorption processes and obeyed the Langmuir adsorption isotherm. Spectroscopic studies confirmed chemical interactions between the ILs and mild steel, while the scanning electron microscopy (SEM) images revealed the formation of protective film of the inhibitors on mild steel surface. Theoretical quantum chemical calculations, QSAR analyses and Monte Carlo simulations studies were used to correlate experimental results. The best fit QSAR equations are functions of molecular weight, fraction of electrons transferred from the inhibitor to the metal and dipole moment of the ILs.

© 2016 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

1. Introduction

The use of corrosion inhibitors to reduce the unwanted metal dissolution process associated with various industrial practices such as cooling water recirculation, acid pickling, acid descaling, oil-well acidizing etc. has been widely studied [1,2]. The use of corrosion inhibitors is one of the most practical and economical methods of protecting metals against corrosion and the initial mechanism involved in any corrosion inhibition process is the adsorption of the inhibitor on the surface of the metal [3–6]. Corrosion inhibitors are often synthesized from relatively cheap and readily available raw materials such as carbonyl compounds,

amines, alcohols etc. Most of these compounds contain π -electrons and functional groups such as $-C=C-$, $-OR$, $-OH$, $-NR_2$, $-NH_2$ and $-SR$, and heteroatoms such as S, O and N [7].

Ionic liquids (ILs) are among the compounds that have been gaining increasing popularity in corrosion inhibition studies in the recent times. Ionic liquids (ILs) are salts with low melting points, frequently below room temperature [8]. The most common ILs are based on imidazolium, pyridinium, quaternary ammonium and quaternary phosphonium cations, but there is growing interest in some other classes of salts. They usually exhibit diverse chemical and physical properties, as well as phase behavior with other compounds. ILs can be designed for a particular application by selectively choosing the cation, anion and functional groups. Most ILs exhibit extremely low volatility over normal operating temperatures. In addition, they show good thermal stability (473–673 K before noticeable decomposition) and thus, exists as liquids over a rather wide temperature range. This affords the possibility of

* Corresponding author at: Materials Science Innovation & Modelling Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa.
E-mail address: Eno.Ebenso@nwu.ac.za (Eno E. Ebenso).



Antioxidant properties, computational studies and corrosion inhibition potential of 3-hydroxy-1-(2-hydroxyphenyl)-5-(phenyl)-2,4-pentadien-1-one analogues



Mehbub I.K. Momin^a, Indra Bahadur^{b,c,*}, Eno E. Ebenso^{b,c}, Md. Shahidul Islam^d, Lukman O. Olasunkanmi^{b,f}, Deresh Ramjugernath^e, Neil A. Koorbanally^{a,g,*}

^a School of Chemistry, University of KwaZulu-Natal, Private Bag X54001, Durban 4001, South Africa

^b Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^c Material Science Innovation and Modelling (MSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^d Department of Biochemistry, School of Life Sciences, University of KwaZulu-Natal, Private Bag X54001, Durban 4001, South Africa

^e School of Chemical Engineering, University of KwaZulu-Natal, Durban 4001, South Africa

ARTICLE INFO

Article history:

Received 22 June 2016

Accepted 30 August 2016

Available online 31 August 2016

Keywords:

Corrosion inhibition

Antioxidant activity

DPPH

FRAP

Docking

Computational studies

ABSTRACT

Ten derivatives of (2Z,4E)-3-hydroxy-1-(2-hydroxyphenyl)-5-phenylpenta-2,4-dien-1-one were investigated for their antioxidant properties and corrosion inhibition potential. The compounds were screened for their antioxidant activity using the 2,2-diphenyl-1-picryl-hydrazyl (DPPH) radical scavenging assay and the ferric reducing antioxidant power (FRAP) assay. The methoxylated analogues generally showed better antioxidant activity than the fluorinated analogues. The compounds were screened for drug-likeness properties using *in silico* techniques. They were found to obey the Lipinski rule of five, which indicated promising absorption or permeability properties through biological membranes. The flexible-ligand docking studies were performed using Auto Dock 4.2 with protein tyrosinase (PDB code: 3NMB). Furthermore, the methoxy derivatives exhibited relatively high binding energies, indicating the possibility of greater interactions with proteins. The compounds were also tested for possible anticorrosion properties using the potentiodynamic polarization and electrochemical impedance spectroscopy techniques. All the compounds showed appreciable corrosion inhibition efficiency for mild steel in 1 M HCl. These compounds are mixed-type inhibitors. The adsorption of the compounds on a mild steel surface obeyed the Temkin adsorption isotherm and the derived adsorption thermodynamic parameters indicate a spontaneous and chemical adsorption process.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Oxidative stress is a common ailment that is associated with an imbalance in the production of oxidants and antioxidants in biological systems [1]. Antioxidants have attracted much attention for being used against life-style related diseases such as aging, cancer, diabetes, cardiovascular and other degenerative diseases, many of which have been linked with the harmful effects of pollution and exposure to harmful chemicals [2]. This in turn results in the accumulation of harmful free radicals in the system [3]. Free radicals are chemical species containing

an unpaired electron in the outermost orbital of the atom [4]. Free radicals generated from oxygen are called reactive oxygen species (ROS). These are typical free radicals and include all highly reactive oxygen-containing molecules, which are particularly harmful, causing damage to other molecules by extracting electrons from them in an attempt to attain stability [5,6]. Unfortunately, the human body does not synthesize an adequate amount of antioxidants when the human body is subject to stressful conditions, to compensate for the damaging effects of ROS [7].

Although synthetic antioxidants such as butylated hydroxytoluene, butylated hydroxyanisole, gallic acid esters and tertiary butylated hydroquinone have potential to neutralize free radicals, they have been criticized for their possible toxic effects, low solubility and moderate antioxidant activity [8]. Hence, there is a need for the discovery of new antioxidant compounds without the limitations identified with current synthetic antioxidants. Functional groups such as carbonyl and phenolic hydroxy and methoxy groups are known to enhance antioxidant

* Correspondence to: I. Bahadur, Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa.

[✉] Corresponding author.

E-mail addresses: bahadur.indra@nwu.ac.za (I. Bahadur), koorbanally@ukzn.ac.za (N.A. Koorbanally).

Cite this: *RSC Adv.*, 2015, 5, 76675

Synthesized photo-cross-linking chalcones as novel corrosion inhibitors for mild steel in acidic medium: experimental, quantum chemical and Monte Carlo simulation studies

Baskar Ramaganthan,^{ab} Mayakrishnan Gopiraman,^c Lukman O. Olasunkanmi,^{abd} Mwadham M. Kabanda,^{ab} Sasikumar Yesudass,^{ab} Indra Bahadur,^{ab} Abolanle S. Adekunle,^{abd} Ime B. Obot^a and Eno E. Ebenso^{a,ab}

New chalcone derivatives namely (E)-1-(5-(4-(3-(4-methylphenyl)-3-oxoprop-1-enyl)phenoxy)pentyl)-1H-1,2,3-triazol-4-yl)methyl acrylate (CH-5), (E)-1-(5-(4-(3-(4-methylphenyl)-3-oxoprop-1-enyl)phenoxy)hexyl)-1H-1,2,3-triazol-4-yl)methyl acrylate (CH-6) and (E)-1-(5-(4-(3-(4-methylphenyl)-3-oxoprop-1-enyl)phenoxy)decyl)-1H-1,2,3-triazol-4-yl)methyl acrylate (CH-10) were synthesized and characterized by Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopic techniques. Ultraviolet-visible (UV-vis) spectra of the synthesized compounds confirmed that the chalcones undergo photo-cross-linking upon irradiation with UV-light. Potentiodynamic polarization measurements showed that both the intact and photo-cross-linked chalcones are mixed-type corrosion inhibitors for mild steel in aqueous hydrochloric acid. The EIS results showed an increase in charge transfer resistance with increasing concentration of the inhibitors. The chalcone derivatives adsorb spontaneously on the mild steel surface and their adsorption obeyed the Langmuir adsorption isotherm. The adsorption mode revealed the possibility of competitive physisorption and chemisorption mechanisms. Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) analyses confirmed that the chalcones formed a protective film on the mild steel surface. The overall results showed that the photo-cross-linked chalcones are better corrosion inhibitors than the intact chalcones. The results of quantum chemical calculations and Monte Carlo simulation studies are in good agreement with experimental results.

Received 23rd June 2015
Accepted 4th September 2015

DOI: 10.1039/c5ra12097g

www.rsc.org/advances

1. Introduction

Mild steel (MS) is a popular alloy of iron with various applications in oil refineries, chemical and transportation industries among others. This is due to its excellent mechanical strength and relatively low cost compared to other metal alloys.^{1,2} Many industrial activities such as acid pickling, chemical etching, cleaning of oil refinery equipment, oil well acidizing and acid descaling involve the use of aqueous solutions of mineral acids which constitute strong corrosive media for mild steel.^{3,4} In

order to control metal dissolution associated with these industrial activities, various types of inhibitors are usually employed. It is well known that organic compounds containing heteroatoms such as sulphur, nitrogen, oxygen and aromatic rings display good inhibition properties for metal corrosion in aggressive media.⁵⁻⁹ However, many of the existing organic/inorganic corrosion inhibitors especially those that contain heavy metals and phosphates are highly toxic and not eco-friendly. As the quest for environmental friendly and/or non-toxic anticorrosion agents increases, studies on the development of new prospective efficient corrosion inhibitors that are free of heavy metals and organic phosphates are becoming sizeable.¹⁰⁻¹²

Chalcones are open-chain flavonoid compounds that exhibit interesting pharmacological activities.^{13,14} The inhibitive actions of some chalcone derivatives on the corrosion of MS in acidic environments have been reported by Li *et al.*^{15,16} However, information on the corrosion inhibition properties and the inhibition mechanism of many chalcone derivatives is still fragmentary. Chalcone derivatives are also known to exhibit excellent photo-cross-linking properties due to the presence of

^aDepartment of Chemistry, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2715, South Africa. E-mail: Eno.Ebenso@nwu.ac.za; Fax: +27 183892052; Tel: +27 183892050, +27 183892051

^bMaterial Science Innovation & Modelling (MSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2715, South Africa

^cNew Fusion Technology Research Lab, Interdisciplinary Graduate School of Science and Technology, Shizuoka University, Ueda, Nagano 416-8502, Japan

^dDepartment of Chemistry, Obafemi Awolowo University, Ile-Ife 220005, Nigeria
^eCentre of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia



Mitigating mild steel corrosion using environmentally benign Formamidine-based thiuram disulfides as inhibitors: Electrochemical, surface and theoretical studies

Objectives of the study

- Synthesis and characterization of new formamidine-based thiuram disulfides compounds.
- To evaluate corrosion inhibitory properties of these compounds using electrochemical methods (Electrochemical Impedance Spectroscopy, Linear Polarization, Tafel analysis), surface analyses and quantum chemical calculations.
- To propose the possible mechanism of the corrosion inhibition by applying thermodynamic, kinetics and adsorption principles.
- Establish correlation between experimental results and theoretical studies.

Overview of the study...

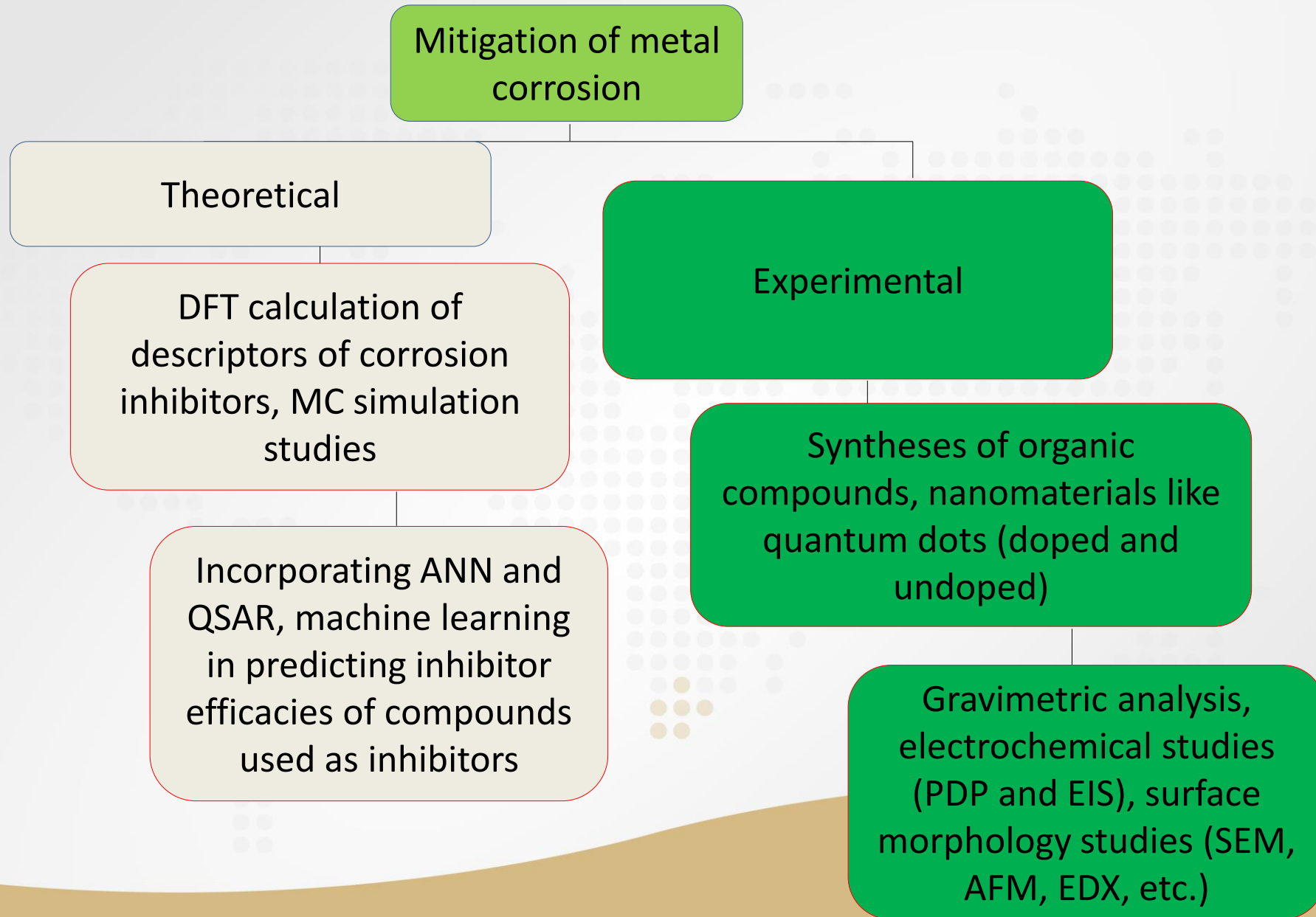
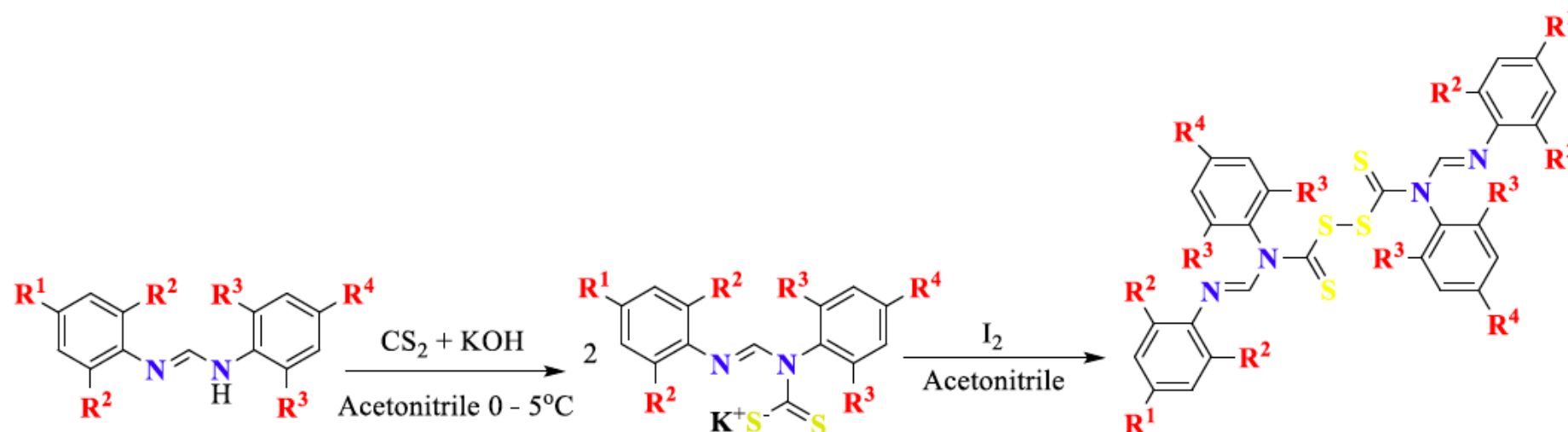


Fig. 1 Research project subdivisions.

Synthetic protocol for inhibitors



R¹ = R⁴ = H, R² = R³ = Me: **DS1**

R¹ = R⁴ = H, R² = R³ = iPr: **DS2**

R¹ = R² = R³ = R⁴ = Me: **DS3**

R¹ = R⁴ = H, R² = Cl, R³ = Me: **DS4**

Scheme 1. Synthesis routes for inhibitors **DS1**, **DS2**, **DS3** and **DS4**.

Inhibitor selection criteria

- They are easily synthesized, environmentally benign and non-toxic.
- They are readily soluble in acidic and minimal acetone mixture.
- Availability of multiple conjugated connections, more than two heteroatoms (N and S), imine functional group ($-C=N-$), multiple pi electron in the aromatic rings.
- Effect of methyl, isopropyl and Cl⁻ substitution on the phenyl ring.

Corrosion Studies

- Materials:
 - ✓ Test material: Mild steel with composition (wt%) C=0.076, Ni=0.039, P=0.015, Cr=0.050, S=0.030 and Fe=99.456 was used electrochemical measurements and surface studies
 - ✓ Cut mechanically to suitable dimensions
 - ✓ Abraded with different emery papers (600-1200 mesh)
 - ✓ Washed, cleaned and dried

Test solution: 1 M HCl

- ✓ Inhibitor conc. 1.00, 0.75, 0.50, 0.25 and 0.10 mM

Corrosion Studies: Methodology

Electrochemical measurements:

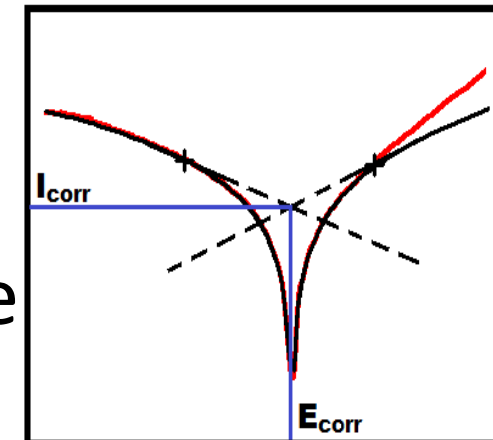
- Metrohm AutoLab Potentiostat/Galvanostat (PGSTAT302N).

Potentiodynamic Polarization

- Working electrode allowed to corrode until OCP
- Potential rate: -250 mV to +250 mV to nucleate
- Scan rate: 1 mV/s in relation to E_{corr}
- Electrochemical parameters obtained by extrapolation
- Protection abilities calculated



Three electrode cell



Extrapolation method

Corrosion Studies: Methodology

Electrochemical impedance spectroscopy:

- AC signal of 10 mV at a range of 10^{-1} to 10^5 Hz at OCP
- AutoLab Nova 2.1 and suitable Randle's equivalent circuit used in investigating the EIS spectra
- Inhibition efficiency $IE(\%)$:

$$IE(\%) = \frac{R_{ct(i)} - R_{ct}}{R_{ct(i)}} \times 100$$

R_{ct} and $R_{ct(i)}$ are the charge transfer resistances of uninhibited and inhibited systems

Corrosion Studies: Methodology

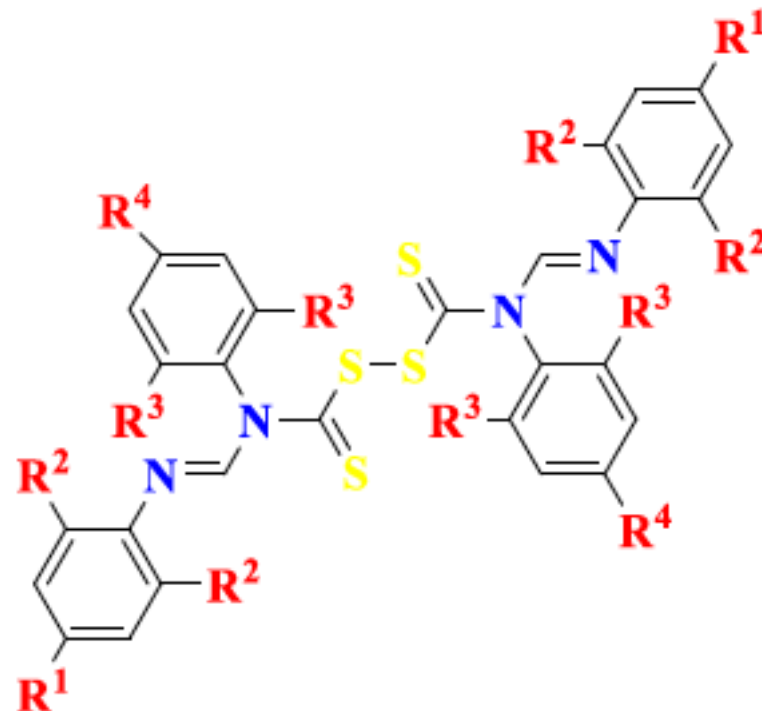
Surface morphology:

- Scanning electron microscopy (SEM) was carried out at high accelerating voltage by SEM model JEOL JSM-6610 LV. Atomic force microscopy (AFM) analyses were done using Icon Brock instrument, and data analyses, 3D images were obtained using Nanoscope analysis software.

Quantum chemical calculations:

- Using the density functional theory (DFT) with the B3LYP functional and 6-31G basis set with Gaussian 16
- Frontier molecular orbital energy parameters were derived

Results and discussion



- DS1; R¹ = R⁴ = H, R² = R³ = methyl
- DS2; R¹ = R⁴ = H, R² = R³ = isopropyl
- DS3; R¹ = R² = R³ = R⁴ = methyl
- DS4; R¹ = R⁴ = H, R² = Cl, R³ = methyl

Fig. 3 Molecular structure of the studied inhibitors

Results and discussion

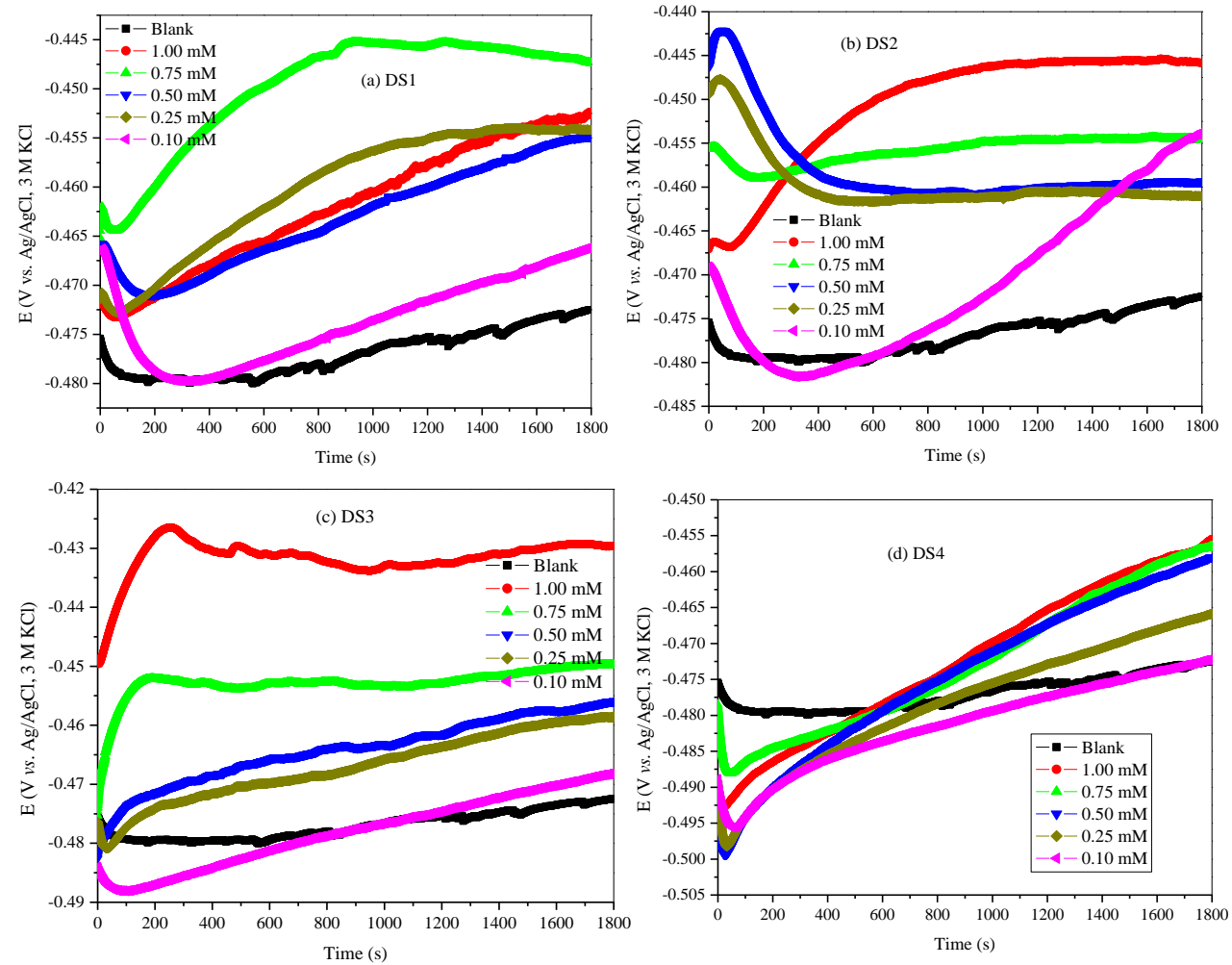


Fig. 4. OCP vs. time profile of mild steel in 1 M HCl without and with varying concentrations of (a) DS1, (b) DS2, (c) DS3 and (d) DS4 at 30 °C.

Results and discussion

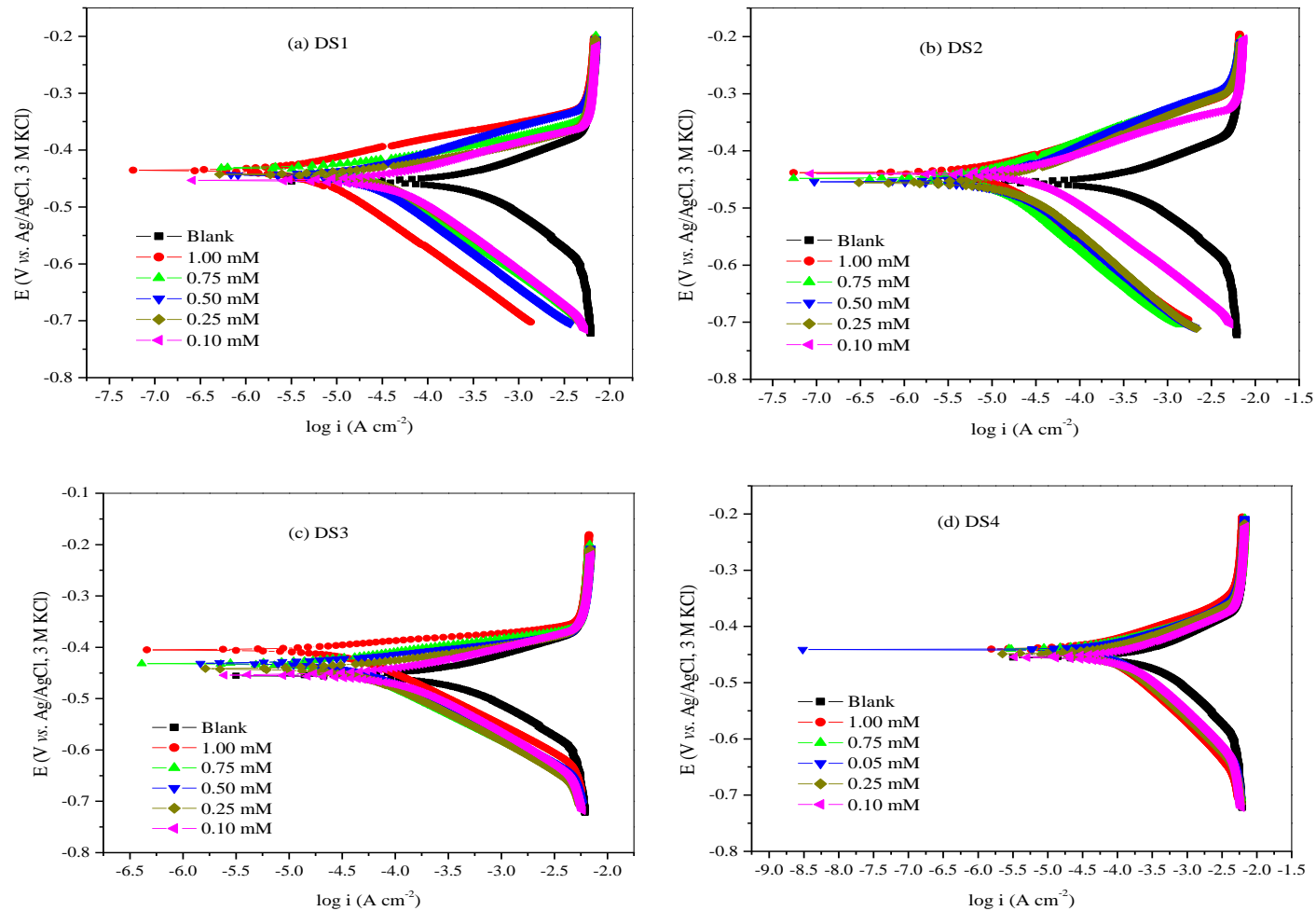


Fig. 5 (a-d) Tafel polarization plots for mild steel corrosion in the absence and presence of various concentrations of **DS1**, **DS2**, **DS3** and **DS4**.

Table 2. EC parameters and $\%IE_{PDP}$ obtained from Tafel polarization measurements

Inhibitors	Conc. (mM)	$-E_{corr}$ (mV, Ag/AgCl)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	$\%IE_{PDP}$
Blank	0	445.37	125.79 (± 1.24)	78.80 (± 1.24)	378.41 (± 1.88)	-
DS1	0.10	445.11	112.99 (± 1.02)	47.87 (± 0.65)	38.75 (± 1.36)	89.76
	0.25	435.85	105.74 (± 1.04)	36.45 (± 1.12)	27.58 (± 1.02)	92.71
	0.50	444.13	107.44 (± 1.15)	48.32 (± 0.88)	24.66 (± 0.96)	93.50
	0.75	427.92	101.45 (± 1.01)	29.67 (± 0.54)	15.59 (± 1.44)	95.88
	1.00	422.90	107.25 (± 1.12)	48.95 (± 1.21)	5.30 (± 0.98)	98.60
DS2	0.10	432.80	111.63 (± 1.42)	61.72 (± 0.88)	31.18 (± 0.45)	91.76
	0.25	449.15	129.19 (± 1.24)	68.81 (± 0.65)	19.70 (± 0.66)	94.79
	0.50	449.22	121.30 (± 1.05)	73.73 (± 0.96)	15.09 (± 1.86)	96.01
	0.75	441.43	127.40 (± 1.21)	65.09 (± 0.55)	10.59 (± 0.65)	97.20
	1.00	438.50	60.85 (± 1.52)	43.43 (± 1.42)	6.20 (± 0.48)	98.36
DS4	0.10	446.52	112.48 (± 1.26)	57.21 (± 0.84)	135.98 (± 1.32)	64.07
	0.25	442.24	111.60 (± 1.32)	52.13 (± 1.24)	93.37 (± 0.89)	75.33
	0.50	438.64	107.52 (± 0.98)	44.22 (± 0.97)	81.12 (± 1.42)	78.56
	0.75	434.49	103.44 (± 1.14)	41.44 (± 1.26)	73.32 (± 0.58)	80.62
	1.00	433.96	104.45 (± 1.18)	51.82 (± 1.28)	62.17 (± 1.06)	83.57

Results and discussion

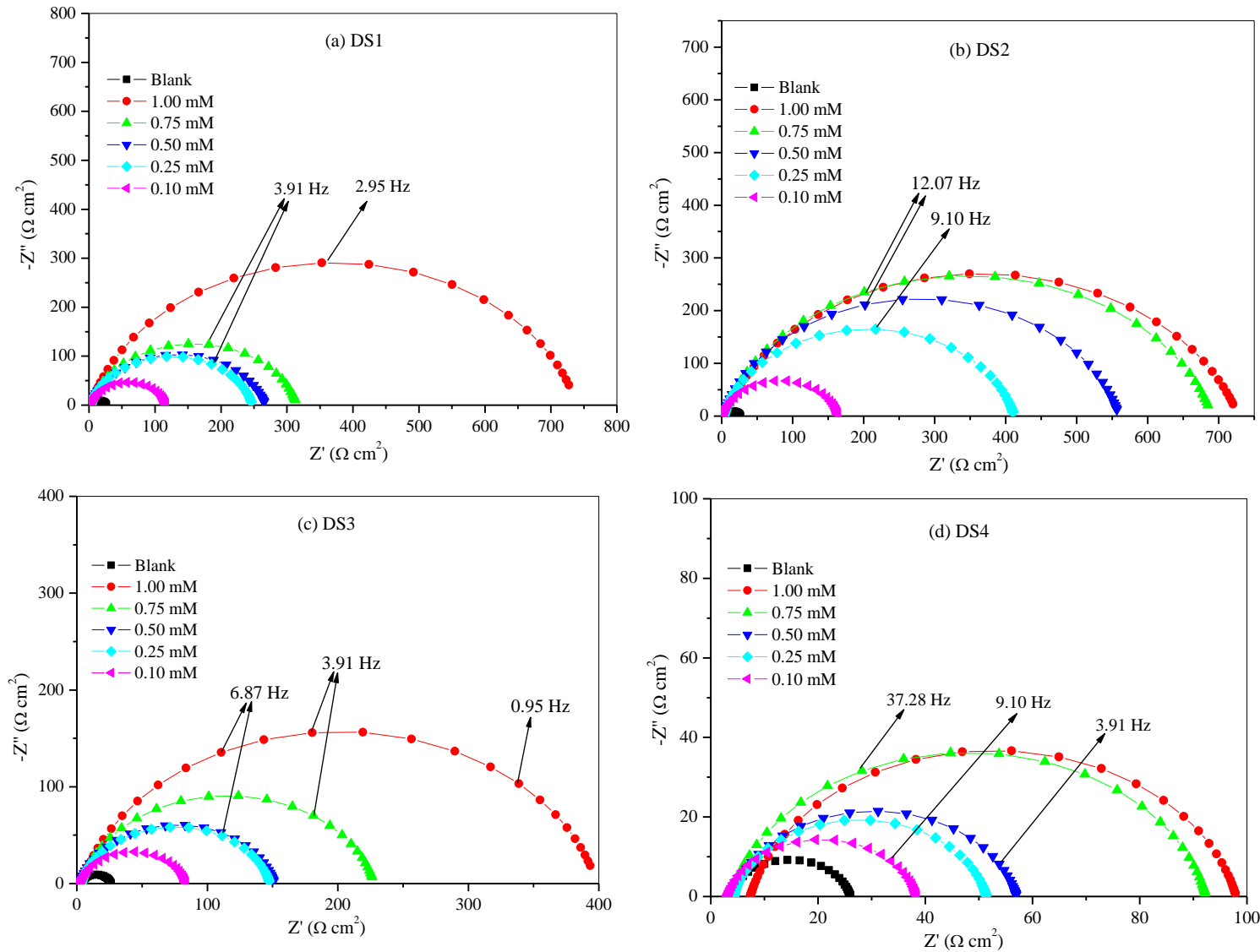


Fig. 6 (a-d) Nyquist plots for mild steel corrosion without the inhibitors and in the presence of various concentrations of (a) **DS1**, (b) **DS2**, (c) **DS3** and (d) **DS4** .

Results and discussion

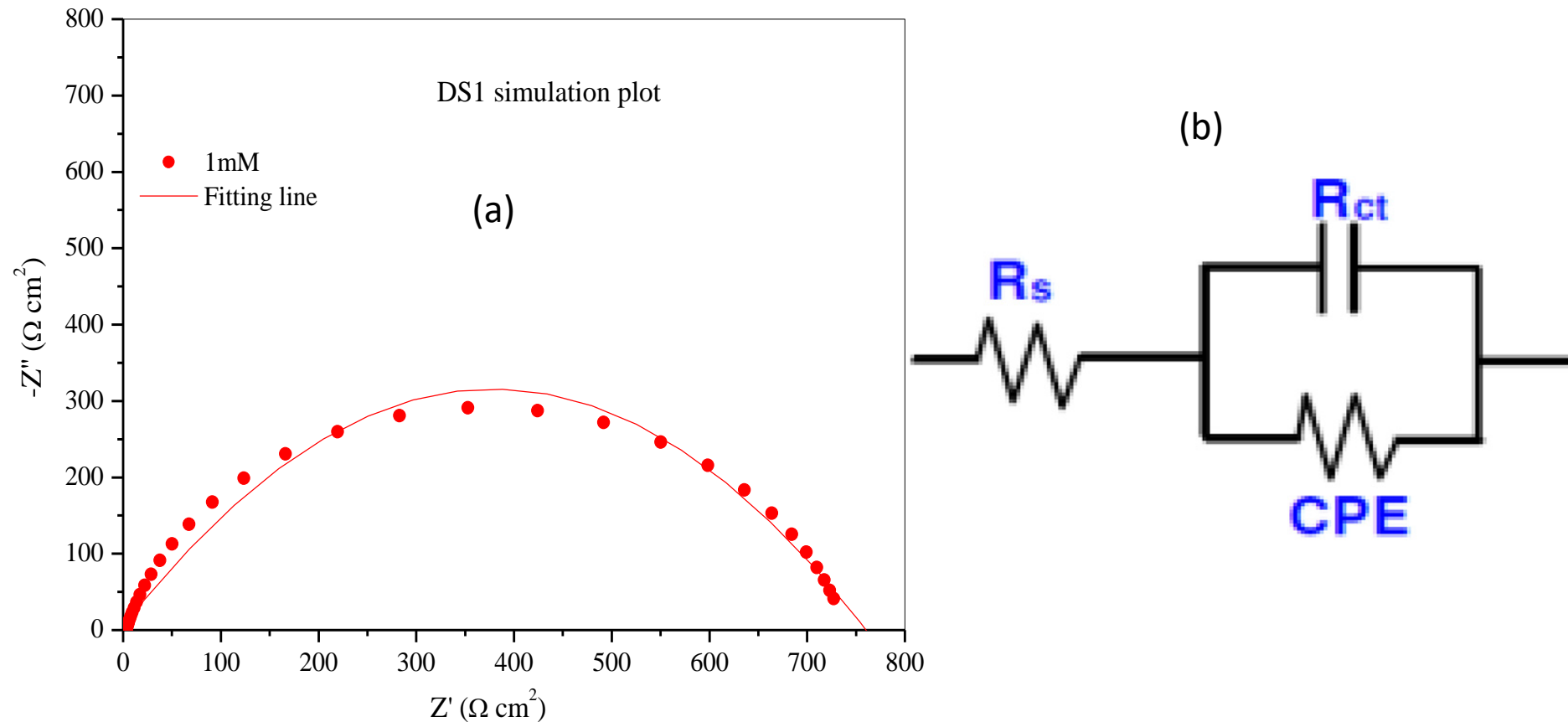


Fig. 7 (a) Simulated plot for **DS1** in 1 mM HCl at 30 °C **(b)** Equivalent Randle circuit used in the analyses of EIS data.

Table 3. EIS parameters for corrosion of mild steel varying conc. of Inhibitors

Inhibitors	Conc. (mM)	R_s (Ω cm ²)	R_{ct} (Ω cm ²)	n	Y_o ($\mu\Omega$ s ⁿ cm ⁻²)	-S	% I_{EIS}
Blank	0	3.50 (\pm 0.06)	22.5 (\pm 0.4)	0.873	243.0	0.64	-
DS1	0.10	2.18 (\pm 0.02)	114.0 (\pm 0.2)	0.869	213.0		80.26
	0.25	2.61 (\pm 0.01)	245.0 (\pm 0.2)	0.867	168.0		90.81
	0.50	2.15 (\pm 0.02)	265.0 (\pm 0.3)	0.844	148.0		91.51
	0.75	2.27 (\pm 0.02)	313.0 (\pm 0.1)	0.860	170.0		92.81
	1.00	3.18 (\pm 0.03)	736.0 (\pm 0.1)	0.852	120.0	0.77	96.94
DS2	0.10	1.65 (\pm 0.01)	163.0 (\pm 0.2)	0.877	200.0		86.20
	0.25	2.51 (\pm 0.03)	409.0 (\pm 0.1)	0.864	69.9		94.50
	0.50	2.10 (\pm 0.03)	558.0 (\pm 0.3)	0.858	62.4		95.97
	0.75	2.44 (\pm 0.02)	688.0 (\pm 0.3)	0.838	68.1		96.73
	1.00	3.08 (\pm 0.01)	725.0 (\pm 0.2)	0.816	67.7	0.69	96.90
DS4	0.10	3.16 (\pm 0.04)	35.3 (\pm 0.2)	0.869	269.0		36.26
	0.25	4.22 (\pm 0.04)	47.2 (\pm 0.3)	0.873	210.0		52.33
	0.50	4.18 (\pm 0.04)	52.8 (\pm 0.4)	0.869	205.0		57.39
	0.75	3.78 (\pm 0.02)	88.6 (\pm 0.3)	0.873	173.0		74.60
	1.00	7.38 (\pm 0.01)	90.6 (\pm 0.4)	0.868	144.0	0.58	75.17

Results and discussion

Adsorption Isotherm

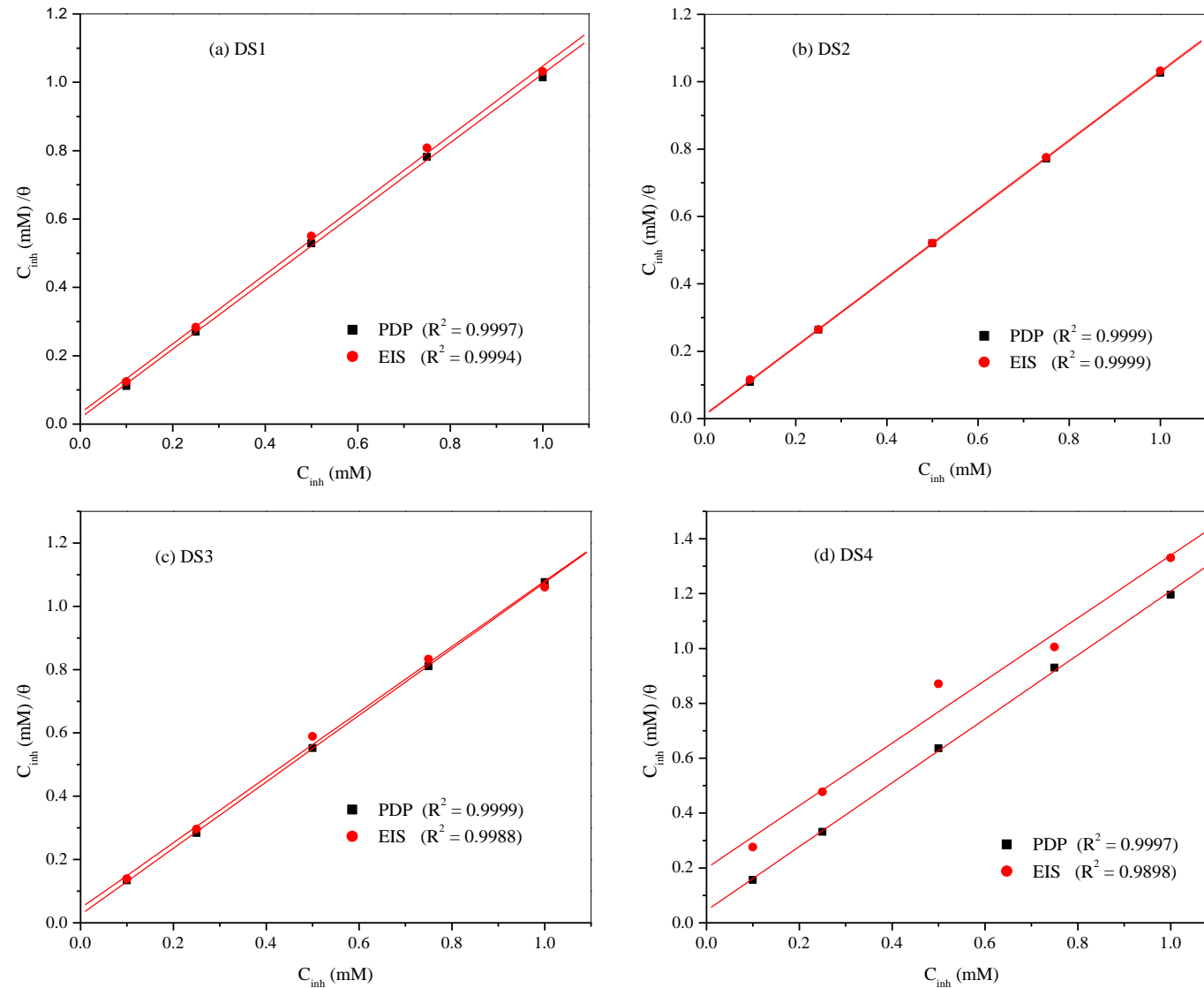


Fig. 8 Langmuir adsorption isotherm

Results and discussion

Table 4. Langmuir adsorption isotherm parameters of mild steel corrosion in 1.0 M HCl

Inhibitors	Method	R ²	Slope	Intercept	K_{ads} (M ⁻¹) × 10 ⁴	ΔG_{ads} (kJ mol ⁻¹)
DS1	PDP	0.9997	1.0067	0.0177	5.65	-37.69
	EIS	0.9994	1.0153	0.0317	3.15	-36.21
DS2	PDP	0.9999	1.0184	0.0088	11.36	-39.45
	EIS	0.9999	1.0191	0.0119	8.40	-38.69
DS3	PDP	0.9999	1.0495	0.0257	3.89	-36.75
	EIS	0.9988	1.0332	0.0462	2.16	-35.26
DS4	PDP	0.9997	1.1641	0.0450	2.22	-35.33
	EIS	0.9898	1.1399	0.1994	5.02	-37.39

Results and discussion

Surface analysis by SEM

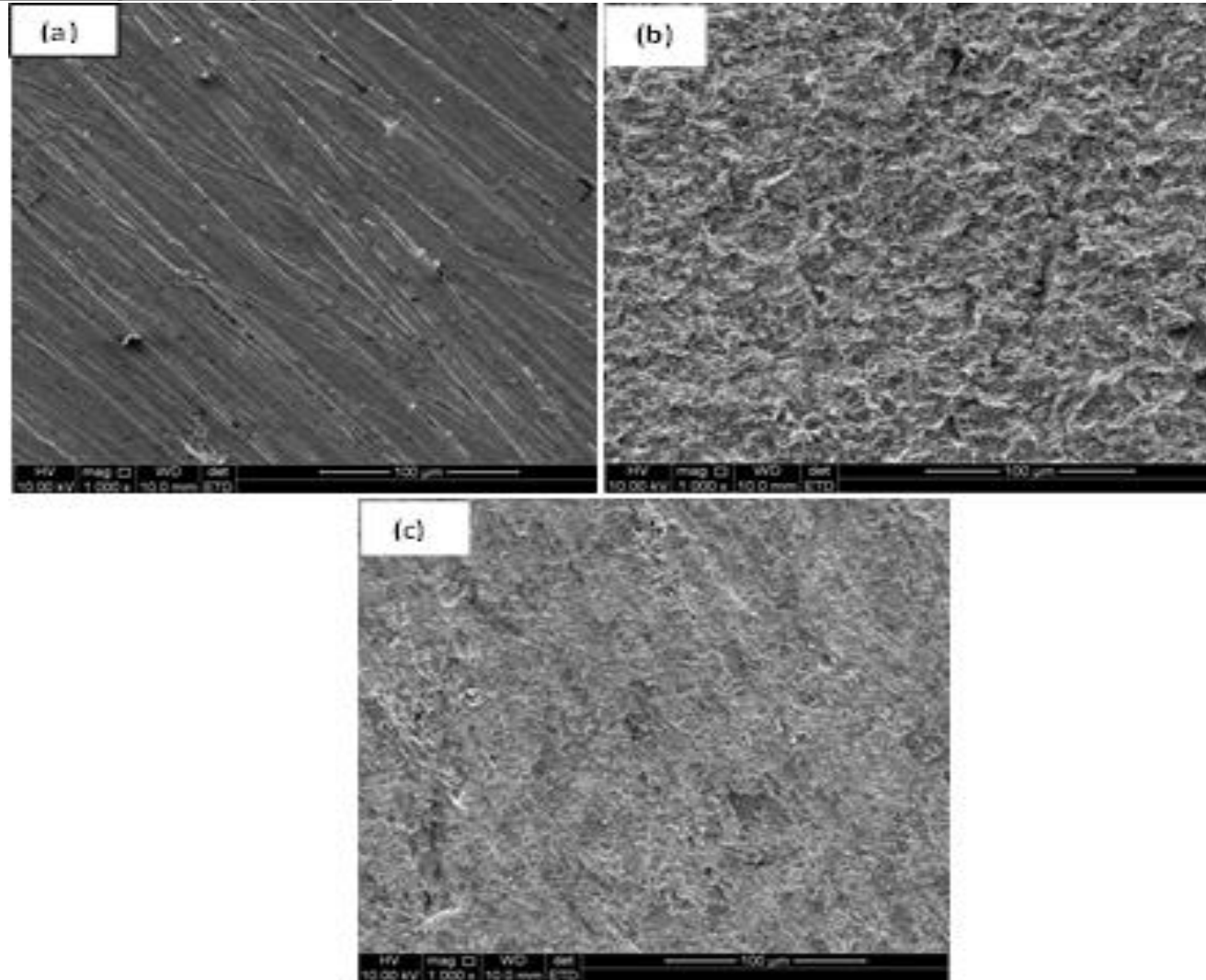


Fig. 9 (a-c) SEM micrographs of surfaces of mild steel: (a) abraded, (b) in 1.0 M HCl, (c) in the presence of 1.0 mM of **DS1**.

Results and discussion

Surface analysis by AFM

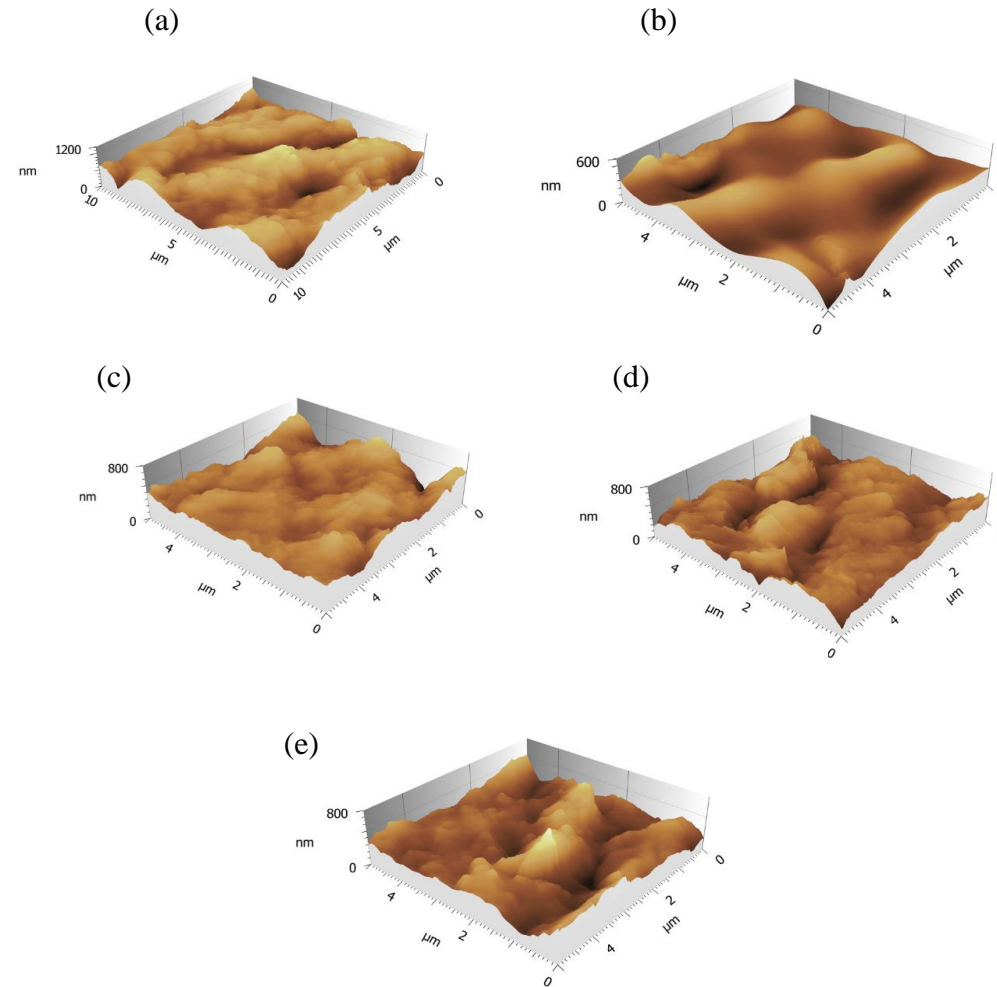


Fig. 10 (a) 3D AFM micrographs of mild steel in (a) 1 M HCl, and in the presence of 1.00 mM concentration of (b-e) inhibitors.

Results and discussion

DFT Study

Table 5 Aqueous phases quantum chemical reactivity indices of the molecule

Inhibitors	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	χ (eV)	ΔN	Dipole moment
DS1	-4.918	-2.918	1.999	3.918	0.451	0.000
DS2	-4.944	-2.875	2.069	3.910	0.440	0.272
DS4	-5.004	-2.981	2.023	3.992	0.409	0.001

Results and discussion

DFT Study

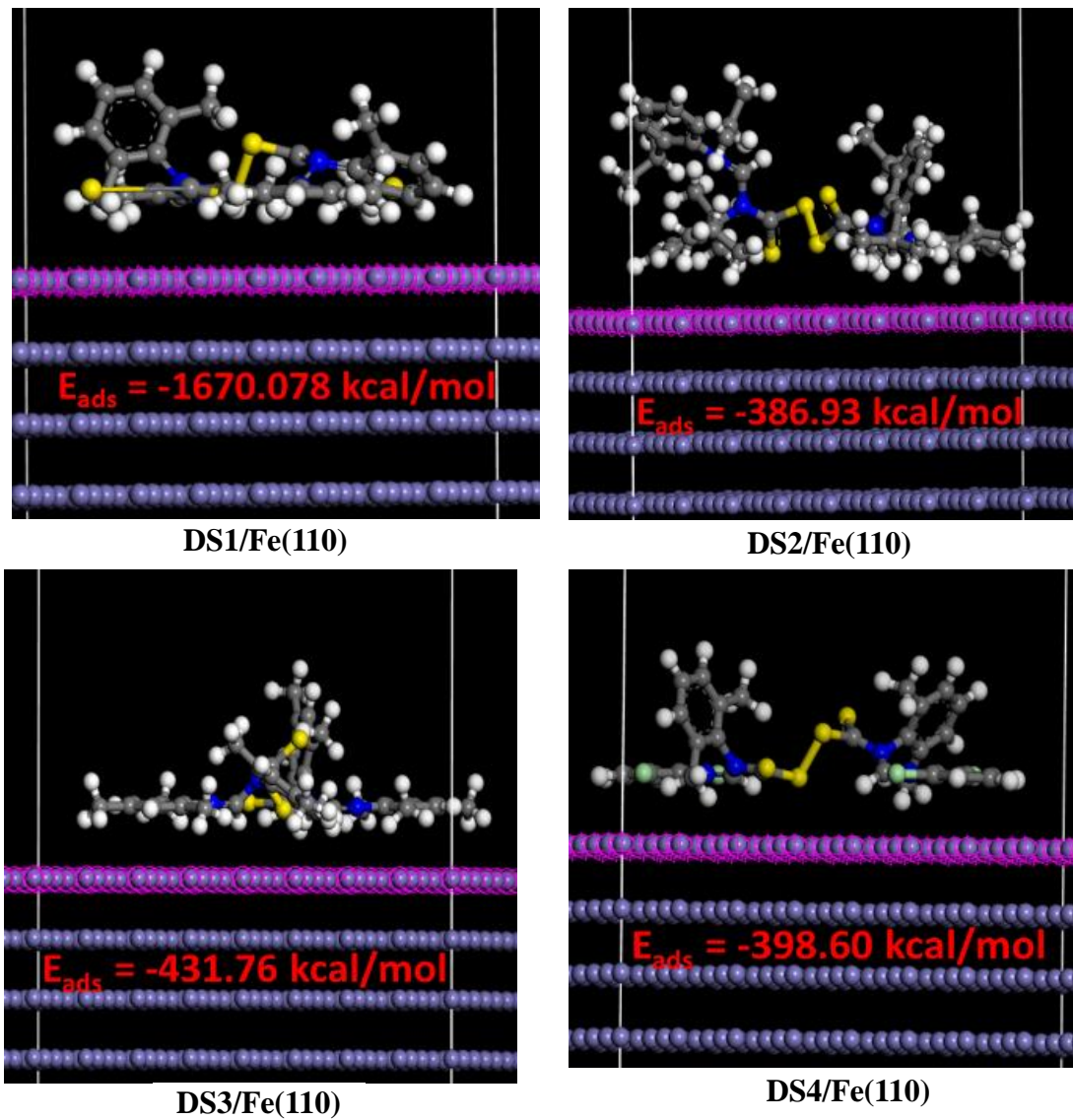


Fig. 11 Simulated adsorption of the studied inhibitor molecules on Fe(110) surface.

Results and discussion

Table 6. Comparison of the inhibition efficacies of studied thiuram disulfides

S/N	Disulfides	Metal/Electrolyte	Conc. (mM)	Max. %IE	Ref.
1.	Bis(1-benzylpiperazine)thiuram disulfide (P2)	Mild steel/ 3.9 M HCl	1	90.00	4
2.	Bis(4-benzyl piperidine)thiuram disulfide (P3)	Mild steel/ 5.5 M H ₃ PO ₄	1	93.00	5
3.	Diallyl disulfide (DAD)	Cu/ 0.5 M H ₂ SO ₄	5	91.50	6
4.	Bis(1-benzyl piperazine)thiuram disulfide (C5)	Mild steel/ 3.2 M H ₂ SO ₄	1	95.00	7
5.	2,2' benzothiazolyl disulfide	Mild steel/ 1 M HCl	0.15	98.34	8
6.	<i>N,N'</i> -(disulfanne-1,2-dicarbonothioyl)bis(<i>N,N'</i> -bis(2,6-dimethylphenyl)formimidamide) (DS1)	Mild steel/ 1 M HCl	1	98.60	PS

4. *J. App. Electrochem.* **2009**, 39 (7), 1075-1079. 5. *Res. Chem. Intermediates* **2014**, 40 (3), 1201-1221. 6. *J. colloid interf. Sci.* **2018**, 526, 268-280. 7. *Int. J. Electrochem. Sci* **2013**, 8, 5980-6004. 8. *Corros. Sci.* **2009**, 51 (11), 2752-2760

Conclusions

- Inhibition properties of formamidine disulfides increased with increasing concentration of the respective inhibitors, with DS1 having the best inhibition efficacy of 98.60% at 1.00 mM concentration
- Electrochemical studies established that all inhibitors investigated effectively minimized both the cathodic hydrogen evolution and the dissolution of the metal at the anode, with slight preference for the anodic protection, hence they are classified as mixed type inhibitors.
- The relationship established between the surface coverage and the concentrations of the respective inhibitors were consistent with Langmuir adsorption isotherm. Calculated Gibbs free energy (ΔG_{ads}) ranging between -35.26 and -39.45 kJ mol⁻¹ confirmed that the adsorption process was both chemical and physical, with preference towards chemisorption.
- SEM and AFM analyses show that the inhibitors protected the mild steel from electrolyte ions attacks by the formation of protective film at the metal surface.
- Molecular calculations and simulation on Fe(110) depicted a near zero dipole moment that favours adsorption of non-polar inhibitor molecules on the metal surface.
- Finally, a significant savings in terms of cost, and general mitigation of problems associated with corrosion of mild steel in acidic media will be achieved by the application of these new formamidine-based thiuram disulfides compounds as candidate inhibitors in commercial industries.

Formamidine-Based Thiuram Disulfides as Efficient Inhibitors of Acid Corrosion of Mild Steel: Electrochemical, Surface, and Density Functional Theory/Monte Carlo Simulation Studies

Ekemini D. Akpan, Segun D. Oladipo, Taiwo W. Quadri, Lukman O. Olasunkanmi, Esther E. Nwanna, Bernard Omondi,* and Eno E. Ebenso*

Cite This: *ACS Omega* 2022, 7, 26076–26091

Read Online

ACCESS |

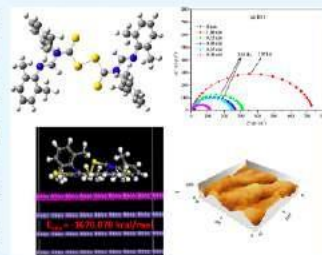
Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Electrochemical, surface, and density functional theory (DFT)/Monte Carlo (MC) simulation studies were used in investigating the characteristics of *N,N'*-(disulfanne-1,2-dicarbonothioyl)bis(*N,N'*-bis(2,6-dimethylphenyl)formimidamide) (DS1), *N,N'*-(disulfanne-1,2-dicarbonothioyl)bis(*N,N'*-bis(2,6-diisopropylphenyl)formimidamide) (DS2), *N,N'*-(disulfanne-1,2-dicarbonothioyl)bis(*N,N'*-dimesitylformimidamide) (DS3), and *N,N'*-(disulfanne-1,2-dicarbonothioyl)bis(*N,N'*-bis(2,6-dichlorophenyl)formimidamide) (DS4) as inhibitors of acid corrosion of mild steel. The inhibitors were found to effectively reduce the rates of steel dissolution at the anode as well as cathodic hydrogen evolution. The order of inhibition efficiencies of studied compounds is DS1 (PDP/LPR/EIS: 98.60/97.98/96.94%) > DS2 (PDP/LPR/EIS: 98.36/96.86/96.90%) > DS3 (PDP/LPR/EIS: 94.66/87.44/94.30%) > DS4 (PDP/LPR/EIS: 83.57/77.02/75.17%) at 1.00 mM, and the overall efficiencies appeared to depend on the molecular and electronic structures of the compounds.

The compounds offered high resistance to charge transfer across the electrode/electrolyte system by forming adsorbed film whose resistance increased with an increase in concentration. Findings suggested that the adsorption process involved combined chemisorption and physisorption. DFT calculations and MC simulations provided theoretical justifications for the experimental results.



1. INTRODUCTION

Over the years, carbon steel has been widely utilized in numerous domestic, industrial, and engineering processes, as well as in the construction of geothermal power plants. This attraction has been mainly attributed to the low cost, excellent mechanical properties, and weldability of carbon steel.¹ These low-alloyed materials could function well in a nonsaline environment with moderate pH, but undergo severe corrosion in a more aggressive environment. As of 2016, records available in NACE International's IMPACT report estimated the global cost of corrosion (excluding individual safety and environmental consequences) to be US\$ 2.3 trillion, which is approximately 3.4% of the global GDP.² Similar reports also stated that, using available corrosion control practices, an estimated savings of 15–35% of the cost of corrosion could be realized. As such, the development and use of corrosion protection strategies becomes invaluable, and the use of organic inhibitors has gained prominence in the mitigation of corrosion-related problems.^{3–5}

Organic compounds employed as corrosion inhibitors possess certain properties like the existence of heteroatoms (N, S, O, and P), aromatic rings, and rich electron clouds around the multiple bonds. Research studies have shown that the listed properties enhance the adsorption of these types of

chemicals on the surface of the metal by the formation of electrostatic interactions (physical adsorption) and/or coordinate covalent bond (chemical adsorption) between inhibitor molecules and the metal, ensuring the coverage of the active sites (on the metal), thereby, protecting it from aggressive ions.^{6–8}

Thiuram disulfide derivatives have been reported to possess antimicrobial activities,^{9–11} antioxidant activities,¹² and anticancer properties,^{13,14} respectively. These compounds are also used in vulcanizing synthetic rubber.¹⁵ As per corrosion studies, Ousslim et al.¹⁶ evaluated the mitigation of mild steel corrosion in 3.9 M HCl using bis(1-benzylpiperazine)thiuram disulfide and achieved an inhibition efficiency of 91.2% at 10⁻³ M. In a similar report, the team assessed the inhibitory performance of three piperidine compounds including bis(4-benzylpiperidine)thiuram disulfide (P2) for mild steel

Received: February 17, 2022

Accepted: July 8, 2022

Published: July 20, 2022



**ELECTROCHEMICAL, QUANTUM CHEMICAL CALCULATION AND
MOLECULAR DYNAMIC SIMULATION STUDIES ON SOME QUINOXALINE
DERIVATIVES AS CORROSION INHIBITORS FOR MILD STEEL IN ACIDIC
MEDIUM**

Aim and objectives of the study

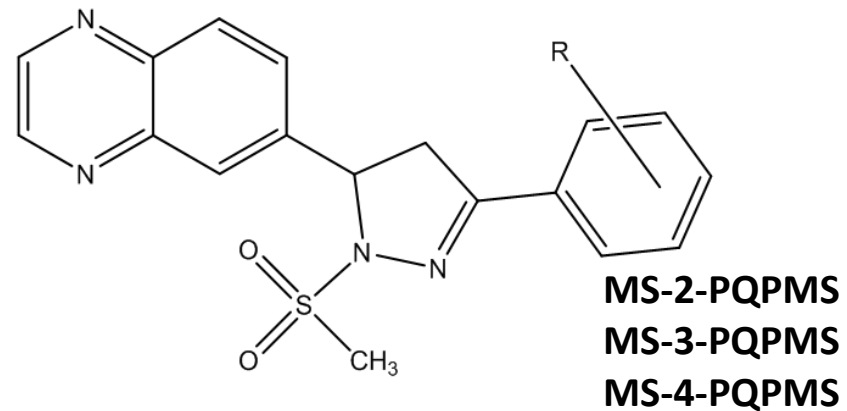
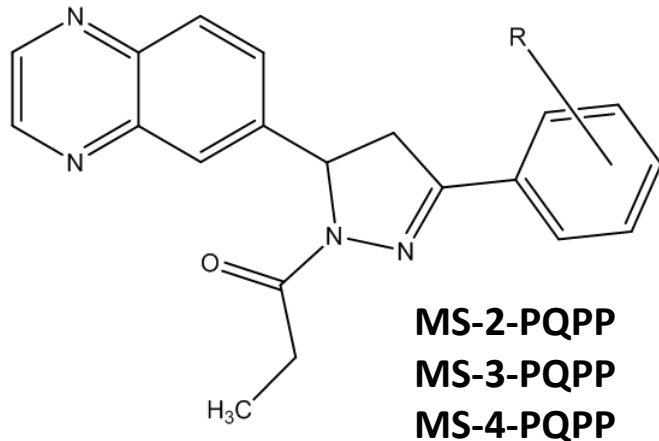
The main aim of this study is to investigate the corrosion inhibition properties of a set of quinoxaline derivatives that contain common nucleus of the quinoxaline ring with 3- phenyl-4,5-dihydropyrazolyl substituent at position 6 of the ring. The specific objectives of the work include:

- i. Investigation of corrosion inhibition efficiency of the studied compounds on MS corrosion in 1 M HCl solution using Tafel plots and electrochemical impedance spectroscopic (EIS) methods.
- ii. Investigation of the corrosion inhibition mechanisms and modes of adsorption of the quinoxaline derivatives on MS in 1 M HCl solution.
- iii. Quantum chemical study on the propensity of the studied compounds to get protonated in acid medium.
- iv. Correlations of quantum chemically derived molecular and electronic parameters with the experimental results.
- v. Theoretical investigation of the mode of adsorption of the studied compounds on iron surface using the Monte Carlo simulations approach.

Introduction

- **The present study:**

- **Methods of investigation: experimental and theoretical methods**
- **Corrosion inhibition potentials of some quinoxaliny-pyrazoly-methanesulfonamides for mild steel in 1 M HCl**



N-{*n*-[1-R-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-3-yl]phenyl}methanesulfonamides
n = 2, 3, 4

Materials and methods

Test Material

- Fe_{99.07} (C_{0.17}, Mn, Si, S, & P)
- Surface pretreated
- 1 cm² exposed surface area

Test Solutions

- 1 M HCl (blank solution)
- inhibitor concentrations: 5 – 100 ppm

Electrochemical measurements

- PGSTAT 302N (Metrohm)
- Ag/AgCl (RE), Pt-rod (CE) Mild steel (WE)
- Tafel polarization (+/- 100 mV vs OCP @ 1 mV/s scan rate)
- EIS (100 mHz – 100 kHz, 10 mV amplitude)

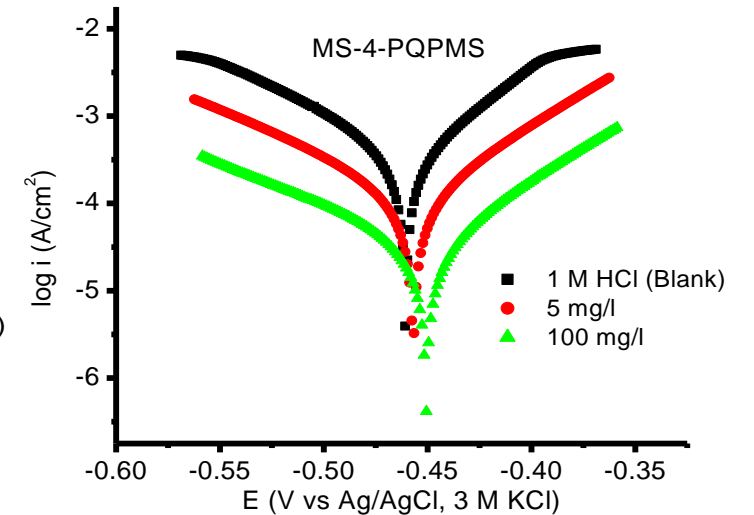
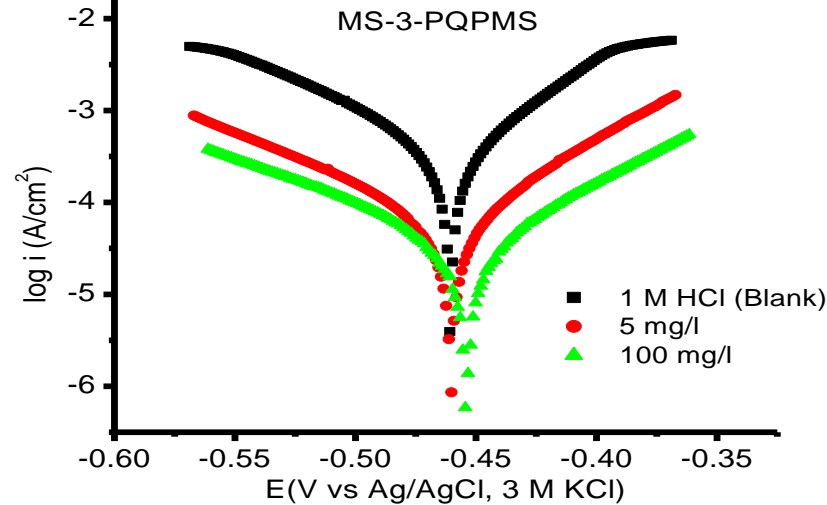
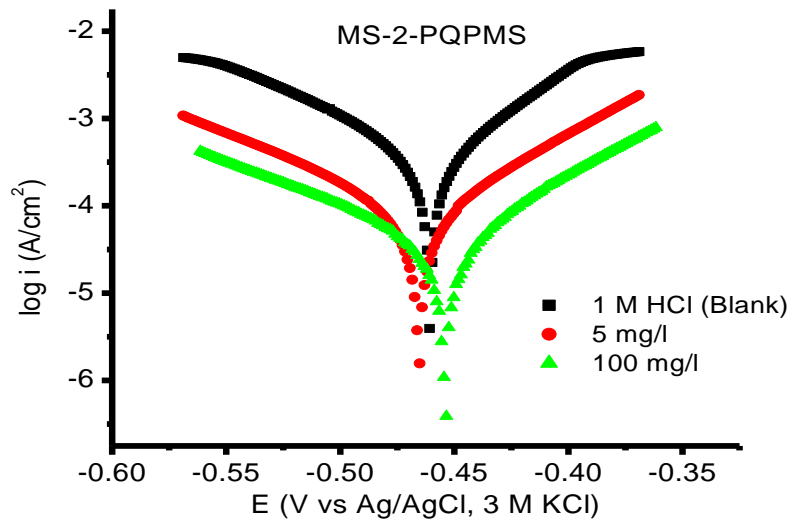
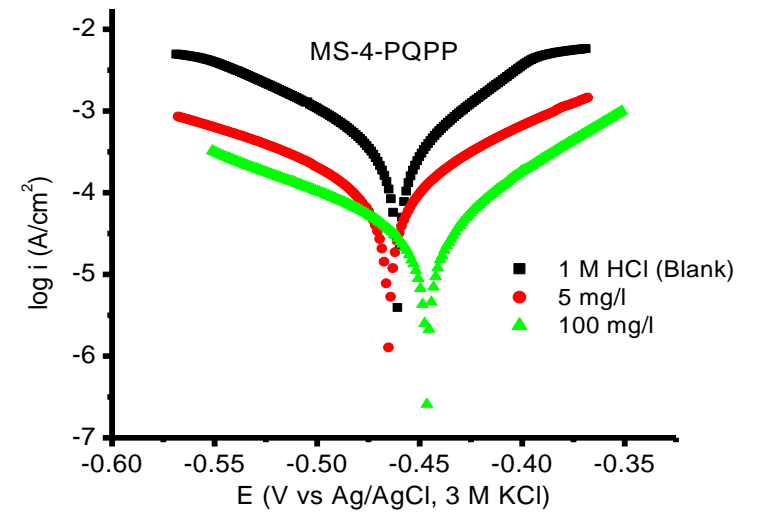
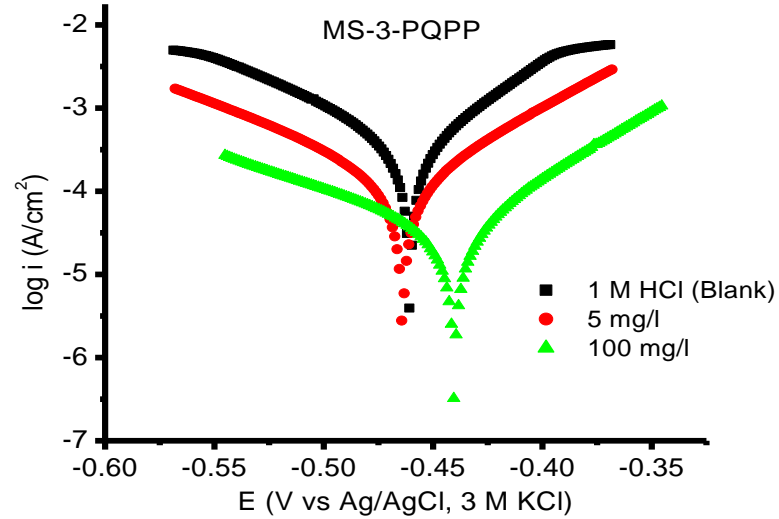
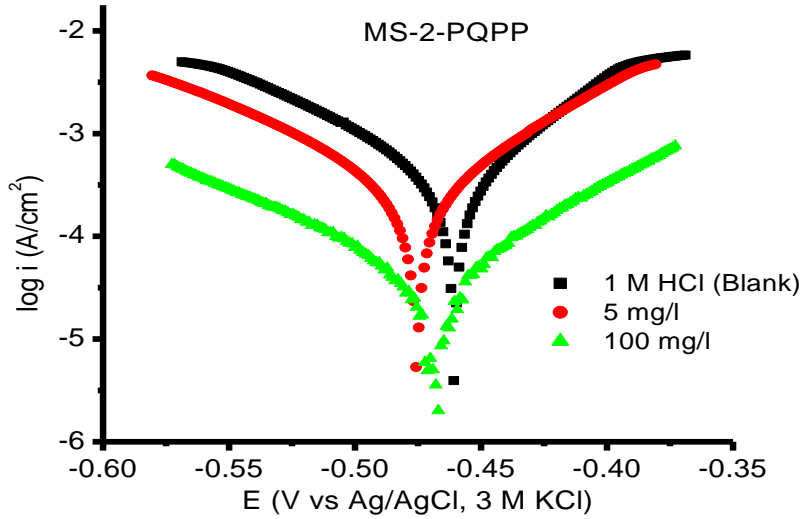
Quantum chemical study using Gaussian 09 software suite

- B3LYP/6-31G(d) model

QSAR analysis with the aid of XLSTAT

Molecular dynamic simulations using adsorption locator module in Materials studio

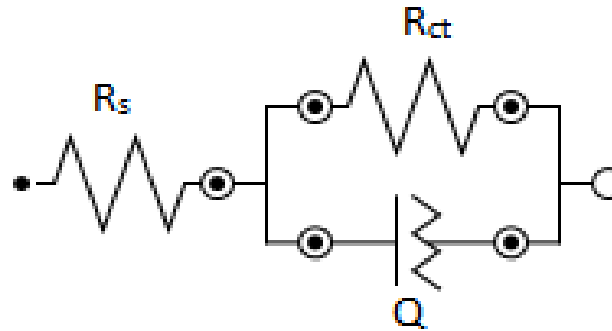
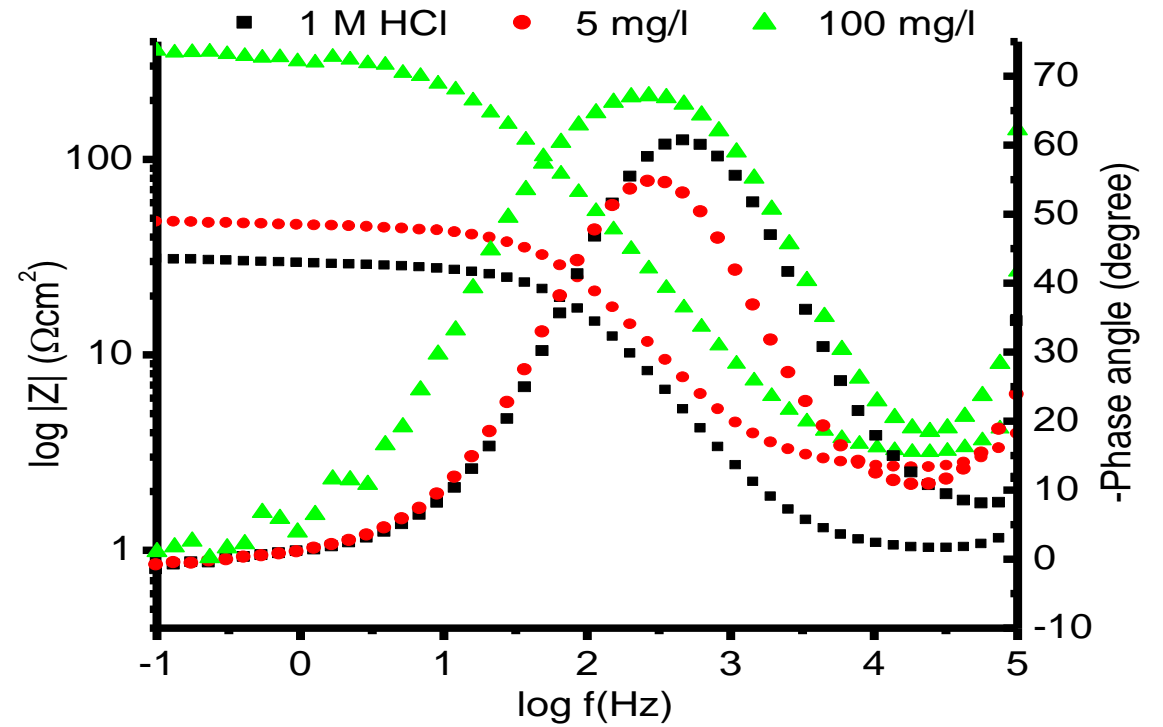
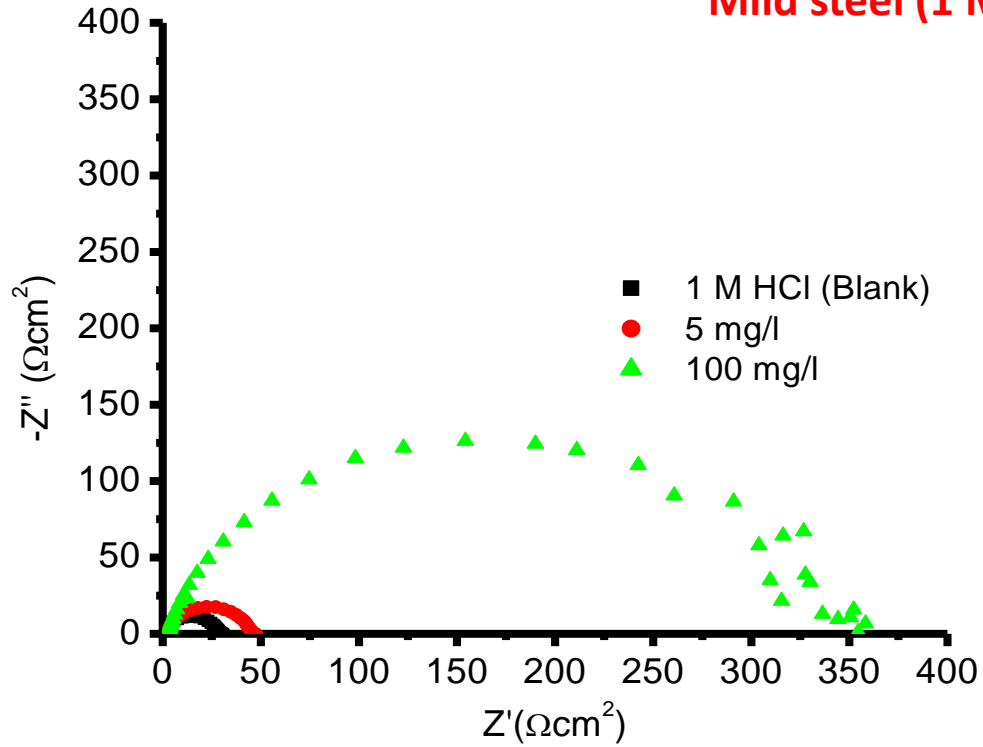
Tafel Polarization curves



Mild steel (1 M HCl, 303 K)

Impedance plots

Mild steel (1 M HCl/MS-2-PQPP, 303 K)



Tafel and EIS parameters

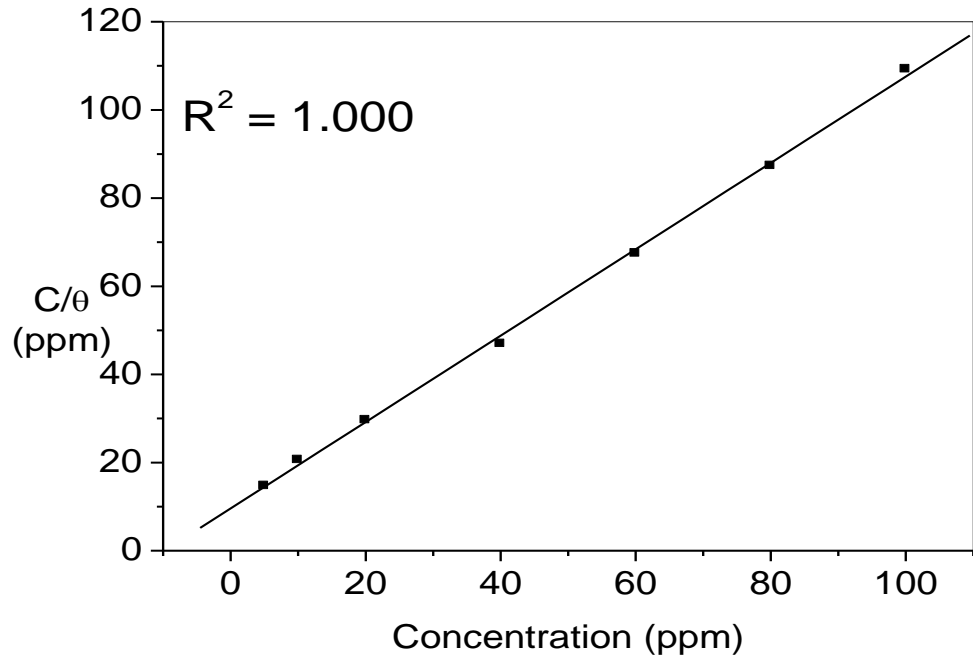
Compound	Conc.	$-E_{corr}$ (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	$\%IE_p$
Blank	1 M HCl	460.60	420.41	-
MS-2-PQPP	5 mg/l	475.46	318.55	24.19
	100 mg/l	455.35	51.34	87.78
MS-3-PQPP	5 mg/l	463.98	142.63	66.06
	100 mg/l	440.36	41.35	90.16
MS-4-PQPP	5 mg/l	465.03	148.12	64.75
	100 mg/l	446.57	41.50	90.12
MS-2-PQPMS	5 mg/l	465.56	89.66	78.66
	100 mg/l	453.77	45.36	89.20
MS-3-PQPMS	5 mg/l	460.43	69.86	83.38
	100 mg/l	454.09	41.20	90.20
MS-4-PQPMS	5 mg/l	456.99	131.53	68.70
	100 mg/l	450.79	38.47	90.84

Tafel

Compound	Conc.	R_s (Ωcm^2)	R_{ct} (Ωcm^2)	$ \theta $ (Degree)	$ S $	$\%IE_I$
Blank	-	1.01	28.20	60.59	0.64	-
MS-2-PQPP	5	2.65	42.6	54.68	0.66	34.04
	100	2.93	332	67.12	0.79	91.54
MS-3-PQPP	5	3.04	125	63.10	0.76	77.52
	100	2.17	459	71.74	0.84	93.88
MS-4-PQPP	5	1.60	134	42.60	0.53	79.03
	100	2.91	436	69.86	0.83	93.56
MS-2-PQPMS	5	3.17	178.00	65.00	0.77	84.21
	100	2.80	384.00	69.37	0.82	92.68
MS-3-PQPMS	5	2.26	229.00	66.96	0.79	87.73
	100	2.52	425.00	69.91	0.82	93.39
MS-4-PQPMS	5	2.96	91.39	61.79	0.75	69.25
	100	2.41	468.00	71.39	0.84	94.00

EIS

Adsorption isotherms

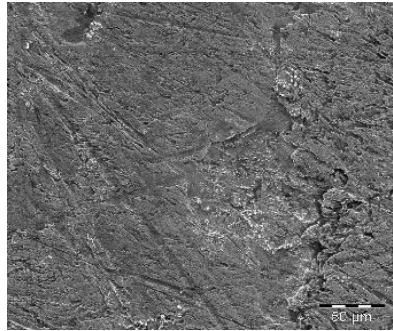
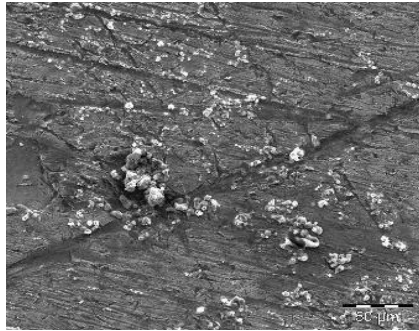
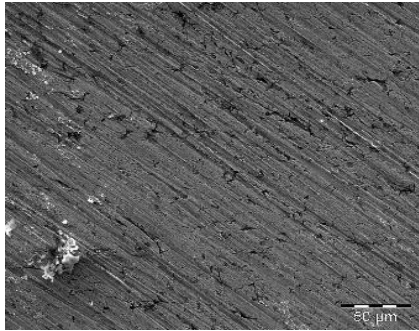
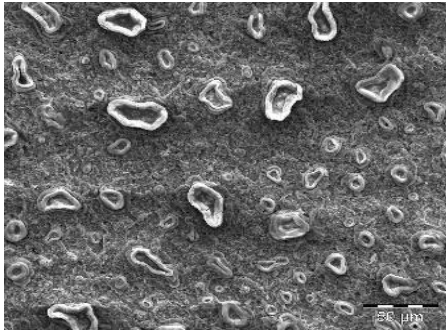


Inhibitor	K_{ads} ($\times 10^3$)	$-\Delta G_{ads}$ (kJ/mol)
MS-2-PQPP	44.15	37.08
MS-3-PQPP	397.80	42.62
MS-4-PQPP	226.20	41.20
MS-2-PQPMS	692.90	44.02
MS-3-PQPMS	791.10	44.35
MS-4-PQPMS	311.69	42.01

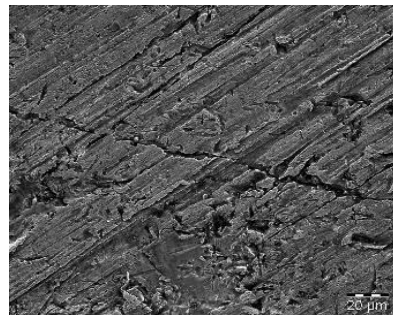
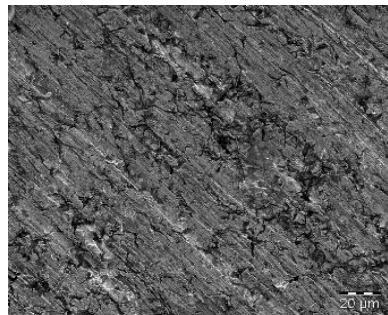
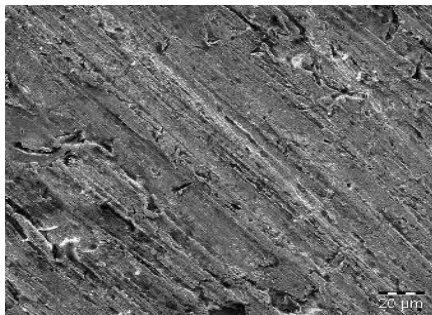
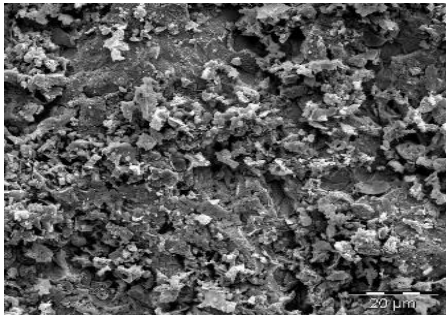


Physical and chemical adsorption

SEM plates: 3 h immersion time

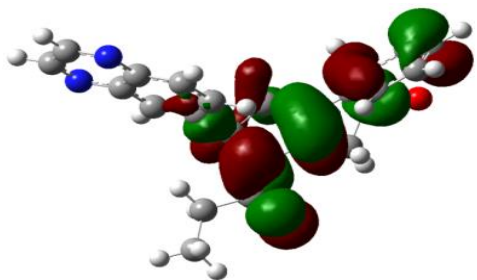


50 μm; Blank, MS-n-PQPP: n=2 -> 4

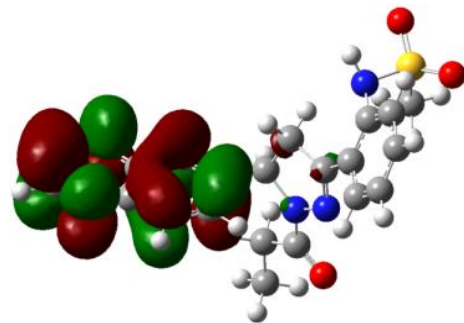


20 μm ; Blank, MS-n-PQPMS: n=2 -> 4

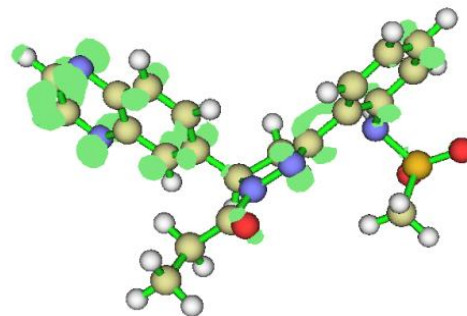
Quantum chemical calculations & QSAR



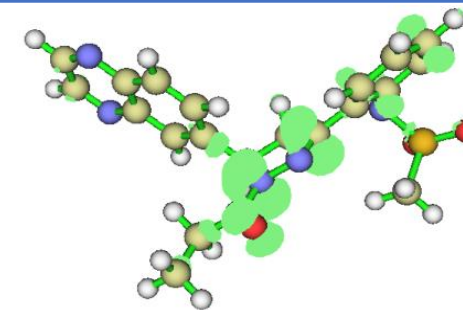
HOMO (MS-2-PQPP)



LUMO (MS-2-PQPP)



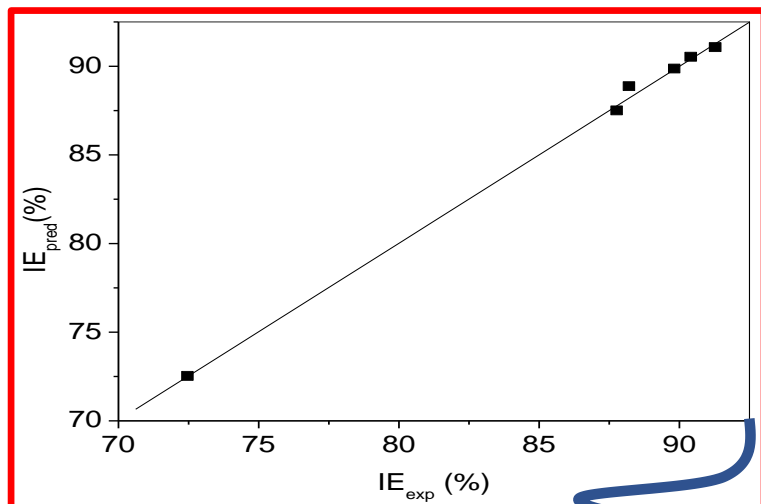
f⁺ (MS-2-PQPP)



f⁻ (MS-2-PQPP)

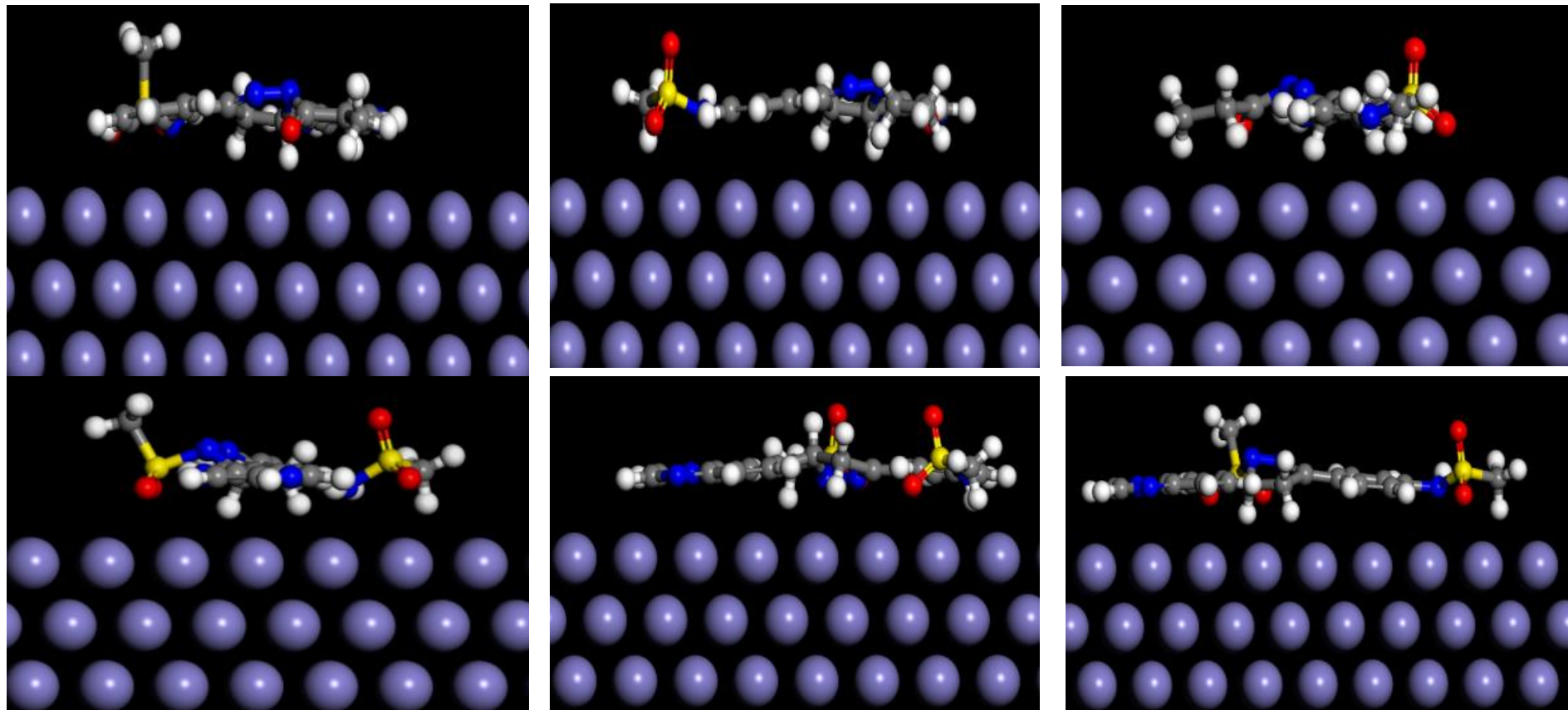
$$MSE = \sqrt{\sum_{i=1}^N (IE_{pred} - IE_{exp})^2}$$

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^N (IE_{pred} - IE_{exp})^2}$$



Parameters	QSAR Equations	R ²	MSE	RMSE
Neutral species				
E _{HOMO} , E _{LUMO} , ΔN, μ	IE = -553.872 - 97.162*E _{HOMO} + 76.955*E _{LUMO} + 283.672*ΔN - 0.476*μ	0.981	4.705	2.169
ΔE _{L-H} , χ, ΔN, μ	IE = -538.733 + 85.942*ΔE _{L-H} + 18.747*χ + 277.212*ΔN - 0.476*μ	0.981	4.719	2.172
ΔE _{L-H} , ΔN, μ, PA	IE = -98.640 + 58.233*ΔE _{L-H} + 158.817*ΔN - 0.415*μ - 0.174*PA	0.990	2.492	1.579
Protonated species				
ΔE _{L-H} , χ, μ, PA	IE = 708.421 + 5.056*ΔE _{L-H} + 23.748*χ + 0.910*μ - 0.866*PA	0.997	0.647	0.805
ΔE _{L-H} , χ, ΔN, PA	IE = 764.510 - 16.045*ΔE _{L-H} + 39.360*χ + 110.713*ΔN - 0.951*PA	0.998	0.546	0.739
E _{HOMO} , E _{LUMO} , μ, PA	IE = 707.979 - 6.798*E _{LUMO} - 17.033*E _{HOMO} + 0.920*μ - 0.867*PA	0.997	0.649	0.806

Molecular dynamics simulations



System	Adsorption energy (kJ/mol)
Fe (110) + MS-2-PQPP	-976.908
Fe (110) + MS-3-PQPP	-1113.337
Fe (110) + MS-4-PQPP	-1095.693
Fe (110) + MS-2-PQPMS	-868.230
Fe (110) + MS-3-PQPMS	-877.046
Fe (110) + MS-4-PQPMS	-846.833

Conclusions

- All the studied compounds showed substantial protection performances for mild steel in hydrochloric acid medium. Their inhibition efficiencies increased with increasing concentration
- All the studied compounds are mixed-type inhibitors
- The compounds adsorbed on mild steel surface via competitive physisorption and chemisorption mechanisms and their adsorption obeyed the Langmuir adsorption isotherm model
- Quantum chemical descriptors exhibit excellent correlations with inhibition performances and QSAR equations with high correlation coefficients and minimum statistical errors were derived. QSAR analyses suggested the participation of protonated species in the corrosion inhibition process
- Binding energies derived from molecular dynamics simulations are in agreement with the trend of experimental inhibition efficiencies
- Inhibitive strengths were affected by the position of sulfonamido group attached the phenyl ring, such that substitution at position 3 favours higher inhibition potential



Cite this: RSC Adv., 2016, 6, 86782

Adsorption and corrosion inhibition properties of *N*-(*n*-[1-*R*-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-3-yl]phenyl)methanesulfonamides on mild steel in 1 M HCl: experimental and theoretical studies†

Lukman O. Olasunkanmi,^{abc} Ime B. Obot^d and Eno E. Ebenso^{*de}

Six quinoxaliny-dihydropyrazoly-phenyl-methanesulfonamides were investigated for their adsorption characteristics and inhibition of mild steel corrosion in 1 M HCl medium. Tafel polarization measurements revealed that all the studied compounds are mixed-type inhibitors. Electrochemical impedance spectroscopy showed that the compounds form a pseudo-capacitive protective film on mild steel surface and protect the steel from direct acid attack. The inhibitors adsorb on mild steel in 1 M HCl via competitive physisorption and chemisorption mechanisms and their adsorption obeyed the Langmuir adsorption isotherm model. UV-vis spectra confirmed that the inhibitors interact with mild steel in solution to form Fe-inhibitor complexes. Scanning electron microscope (SEM) images also confirmed the protective efficacy of the studied compounds on mild steel in the acid. Quantum chemical calculations and quantitative structure activity relationship (QSAR) studies proposed good correlations between molecular quantum chemical descriptors and experimental inhibition efficiencies. Descriptors for protonated species correlate better than those of neutral species. Adsorption of the studied molecules was simulated on Fe(110) surface and the binding energies derived from molecular dynamics simulations corroborate experimental results. Compounds in which the sulfonamido group is attached to position 3 on the phenyl ring showed higher corrosion inhibition activities.

Received 2nd May 2016
Accepted 21st August 2016

DOI: 10.1039/c6ra11375g

www.rsc.org/advances

1 Introduction

Corrosion of metals is still considered a foremost source of economic and safety concerns to industries. This is in spite of copious research progress that has been documented in corrosion science and technology.¹ Corrosion tends to occur in almost all aqueous environments,² but the process is grievously shaped up in more aggressive media such as those encountered in oil and gas industries. Oil and gas processing and allied activities such as pipeline cleaning, pipeline/acid descaling and oil-well acidizing involve the use of mineral acids, most especially hydrochloric and sulfuric acids.³ Acid washing, matrix

acidizing and fracture acidizing involve pumping of acid (usually hydrochloric acid) into the well with the aim of improving well productivity or injectivity.^{4,5} These unavoidable production activities unfortunately expose the metal alloys that make up the oil well and pipelines to acid corrosion.

An ample number of studies in corrosion science researches focus on mild steel corrosion and prevention.^{6–13} The popularity of mild steel in this regards is connected with its wide usage, owing to its relatively high mechanical strength and low cost.^{6–10} As a type of carbon steel, mild steel also has advantages of ease of fabrication, availability and weldability over many other metal alloys.^{11,12} However, mild steel is highly susceptible to corrosion in common aqueous environments, especially acidic solutions.^{13,14} A comparative analysis of cost and efficiencies of known corrosion control and prevention methods puts the use of corrosion inhibitors at a rational edge.¹ Apart from the fact that many corrosion inhibitors can be synthesized from relatively cheap materials,¹ their utilization offers a convenient approach of repressing metal corrosion.¹⁵ Inhibitors can be injected into production channels *in situ* without necessarily disrupting the on-going production process.^{16,17} Many applications involve the use of corrosion inhibitors in conjunction with other methods such as coating and cathodic protection to achieve more enhanced protection efficiency.¹

^aDepartment of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, NorthWest University (Mafikeng Campus), Private Bag X2046, Mmabatho 2725, South Africa. Email: Eno.Ebenso@nwu.ac.za
Fax: +27 183892052; Tel: +27 183892050/2051

^bMaterial Science Innovation and Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, NorthWest University (Mafikeng Campus), Private Bag X2046, Mmabatho 2725, South Africa

^cDepartment of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife, 220005, Nigeria

^dCentre of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia

^eElectronic supplementary information (ESI) available. See DOI: 10.1039/c6ra11375g



Quinoxaline derivatives as corrosion inhibitors for mild steel in hydrochloric acid medium: Electrochemical and quantum chemical studies



Lukman O. Olasunkanmi^{a,b,c}, Mwacham M. Kabanda^{a,b}, Eno E. Ebenso^{a,b,*}

^a Department of Chemistry, School of Mathematics and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^b Material Science Innovation and ModelEng (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^c Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife, Nigeria

HIGHLIGHTS

- Quinoxaline derivatives used as corrosion inhibitors for mild steel.
- Polarization measurements show that the studied inhibitors are mixed type and obey Langmuir adsorption isotherm.
- SEM images reveal formation of protective film on the mild steel surface by the quinoxaline derivatives.
- Quantum chemical calculations are in good agreement with experimental results.

ARTICLE INFO

Article history:

Received 17 March 2015

Received in revised form

11 July 2015

Accepted 2 October 2015

Keywords:

A. Mild steel

B. Polarization

C. Mixed-type inhibition

D. Quantum Chemical Calculations

ABSTRACT

The corrosion inhibition potential of four quinoxaline derivatives namely 1-[3-(4-methylphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Me-4-PQPB), 1-[3-(4-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Mt-4-PQPB), 1-[3-(3-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Mt-3-PQPB) and 1-[3-(2H-1,3-benzodioxol-5-yl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Oxo-1,3-PQPB) was studied for mild steel corrosion in 1 M HCl solution using electrochemical, spectroscopic techniques and quantum chemical calculations. The results of both potentiodynamic polarization and electrochemical impedance spectroscopic studies revealed that the compounds are mixed-type inhibitors and the order of corrosion inhibition efficiency at 100 ppm is Me-4-PQPB > Mt-3-PQPB > Oxo-1,3-PQPB > Mt-4-PQPB. Fourier transform infrared (FTIR) and ultraviolet-visible (UV-vis) spectroscopic analyses confirmed the presence of chemical interactions between the inhibitors and mild steel surface. The adsorption of the inhibitor molecules on mild steel surface was found to be both physisorption and chemisorption but predominantly chemisorption. The experimental data obey Langmuir adsorption isotherm. Scanning electron microscopy studies revealed the formation of protective films of the inhibitors on mild steel surface. Quantum chemical parameters obtained from density functional theory (DFT) calculations support experimental results.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Mild steel is considered a material of choice in diverse industrial and structural applications, and used for a wide range of

equipment due to its relatively low cost and good mechanical strength [1,2]. But acid solutions used in many industrial processes such as acid cleaning, acid descaling, acid pickling and oil well acidizing are strong corrosive media that enhance the rate of mild steel corrosion [3]. As a result, corrosion of steel and other active metals has been identified as a common problem in today's industrial world. A popular method of protecting metals against corrosion is the use of corrosion inhibitors. Industrial solutions can be treated with corrosion inhibitors in order to reduce the corrosiveness of the aggressive medium. Inhibitors reduce corrosion

* Corresponding author at: Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus) Private Bag X2046, Mmabatho 2735, South Africa. Fax: +27 18882052.

E-mail address: Eno.Ebenso@nwu.ac.za (E.E. Ebenso).



Influence of 6-phenyl-3(2H)-pyridazinone and 3-chloro-6-phenylpyrazine on mild steel corrosion in 0.5 M HCl medium: Experimental and theoretical studies



Lukman O. Olasunkanmi^{a, b, c, *}, Mabina Frans Sebona^{a, b}, Eno E. Ebenso^{a, b}

^a Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^b Material Science Innovation and Modelling (MaSiM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

^c Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife 220005, Nigeria

ARTICLE INFO

Article history:
Received 20 March 2017
Received in revised form 5 August 2017
Accepted 6 August 2017
Available online 9 August 2017

Keywords:
Corrosion accelerator
Pyridazine
Electrochemical
Spectroscopy
Quantum mechanical

ABSTRACT

Two pyridazine derivatives, namely, 6-phenyl-3(2H)-pyridazinone (P1) and 3-chloro-6-phenylpyrazine (P2) were investigated for their influence on mild steel corrosion in 0.5 M HCl, using Tafel polarization, electrochemical impedance spectroscopy (EIS), surface morphology, FTIR and UV–vis techniques. Quantum chemical calculations were also conducted to corroborate experimental findings. P1 was found to accelerate corrosion at low concentrations but exhibits inhibitive action at higher concentrations, attaining 61% inhibition efficiency at 1.25 mM. The inhibitive action of P2 increases with increasing concentration from 88% at 0.1 mM to 96% at 1.25 mM as deduced from EIS measurements. Both compounds are mixed type inhibitors. P2 seems to display chiefly anodic inhibitive effects. The adsorption of P2 on mild steel surface obeys the Langmuir adsorption isotherm and involved competitive physisorption and chemisorption mechanisms. Scanning electron microscopy analyses of steel surfaces in acid-inhibitor solutions showed that both compounds protect mild steel surface effectively at 1.25 mM. FTIR and UV–vis spectroscopic analyses revealed that N–H, C=O, and C–N functional groups of the pyridazine derivatives are actively involved in adsorption of the molecules onto steel surface. Quantum chemical parameters showed that the higher inhibition efficiency of P2 compared to P1 might be related to better electron acceptance ability of P2.

© 2017 Published by Elsevier B.V.

1. Introduction

Mild steel has applications in various industries, including petroleum, construction and transportation industries among others. It is a widely used material for diverse structural applications. The extensive use of this alloy of iron is related to its special features like high mechanical strength, moderate cost and ready availability [1–5].

Certain industrial processes like acid cleaning, acid descaling and oil well acidizing utilize acid solutions, which are notable aggressive solutions for metal corrosion. Mild steel being an alloy of

iron is therefore highly susceptible to corrosive attack by acidic ions [2–5].

One popular method of controlling metal corrosion is the use of corrosion inhibitors. Commonly used organic compounds in the formulation of corrosion inhibitors are those that contain O, S, N, P and/or Se heteroatoms [2–6]. Functional groups involving these heteroatoms and/or pi electron systems are also known to enhance inhibitive properties. The famous assumption on the mode of inhibitive actions of organic inhibitors is adsorption on metallic surface [2,4,5]. The popular belief is that inhibitors form protective film that shield the metal from direct exposure to aggressive ion and thereby decreases the dissolution of metal in the corrosive medium. In the process, the adsorbed film also reduces the exposed area of the metal and limits the active sites of the metal that interact directly with the environment. There are reports on corrosion inhibition potentials of various families of organic

* Corresponding author. Material Science Innovation and Modelling (MaSiM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa. E-mail address: wolololol@nwu.ac.za (L.O. Olasunkanmi).



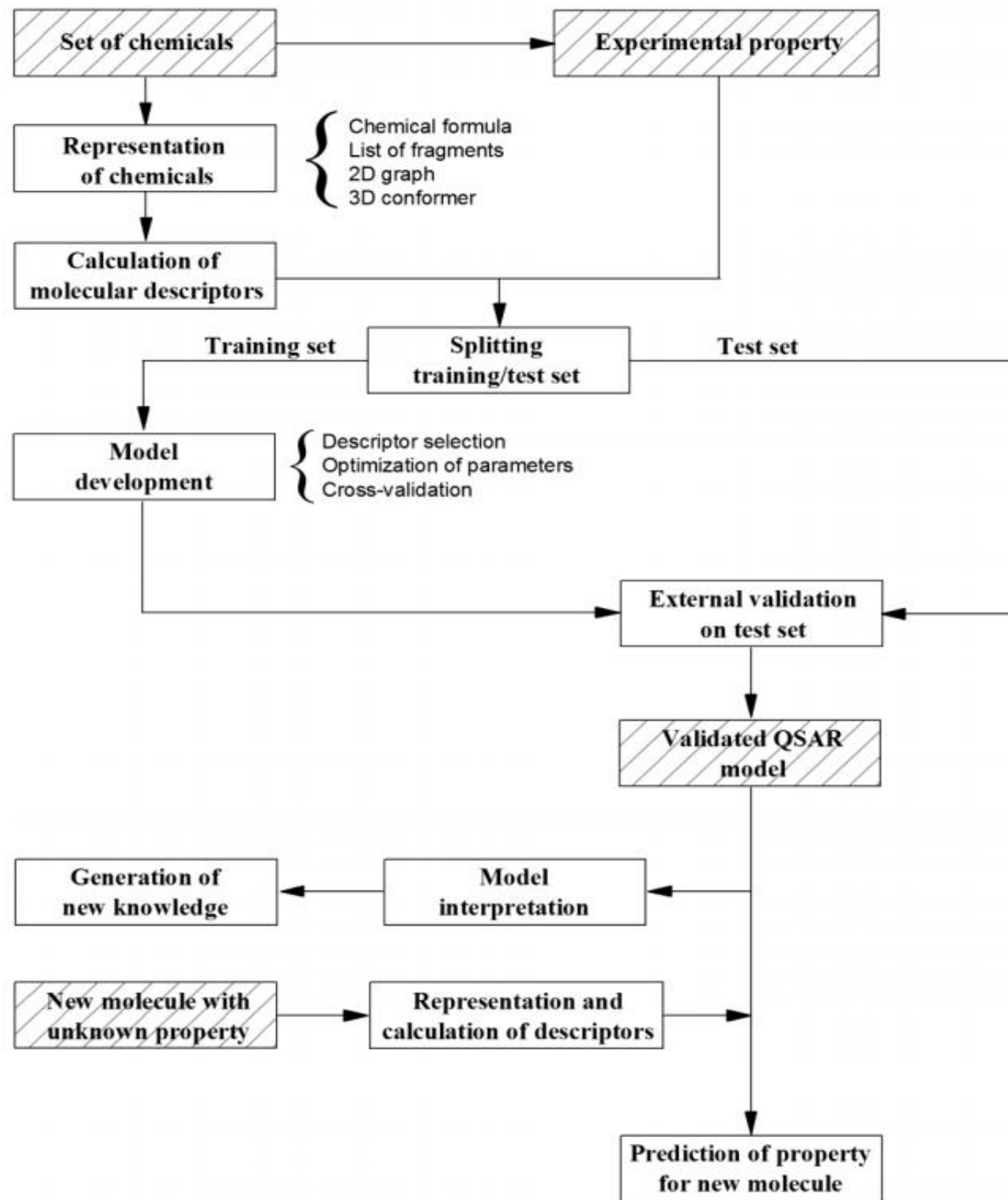
**Predictive model for the corrosion inhibition of
mild steel in HCl by pyrimidines: A QSAR-ANN
approach**

OBJECTIVES

The objectives of the study are to:

- calculate molecular descriptors using DFT and Dragon 7,
- select significant molecular descriptors,
- model the inhibition data using linear and nonlinear QSAR models,
- compare the prediction accuracy of the corrosion inhibition efficiencies obtained from both models,
- theoretically design novel pyrimidines and determine their effectiveness to inhibit mild steel corrosion in 1 M hydrochloric acid.

METHODOLOGY



DFT RESULTS — DFT Parameters for aqueous forms of pyrimidines

FORTY Pyrim	Conc (mM)	TE (eV)	HOMO (eV)	LUMO (eV)	ΔE (eV)	μ (D)	IE (%)
AMP-1	0.362	-27733.80	-6.819	-3.280	3.539	2.361	93.17
AMP-2	0.362	-22168.57	-6.461	-2.321	4.140	6.941	94.89
AMP-3	0.362	-24215.71	-6.124	-2.230	3.894	7.368	95.29
AMP-4	0.362	-26262.83	-6.014	-2.229	3.785	9.208	95.97

DFT RESULTS — Electron density distribution for pyrimidines

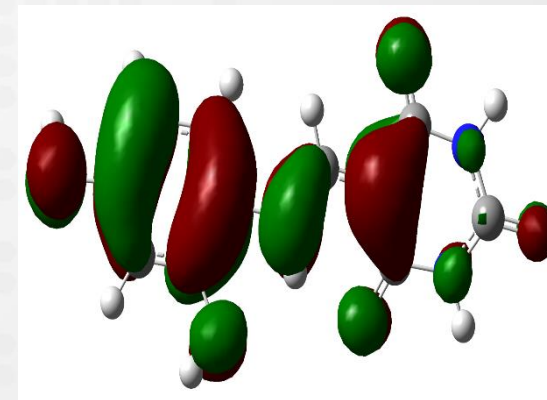
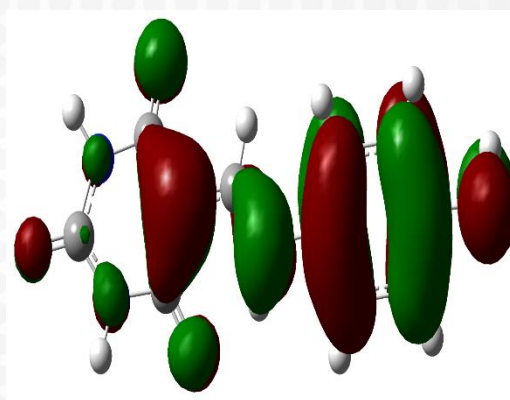
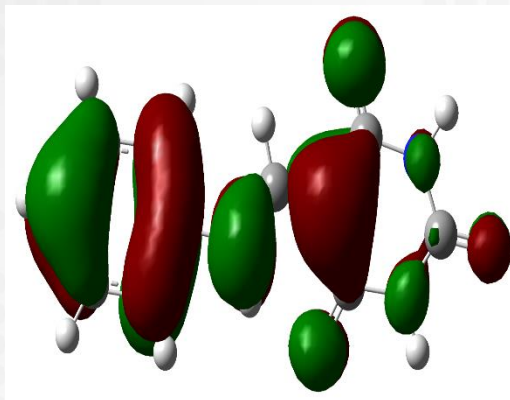
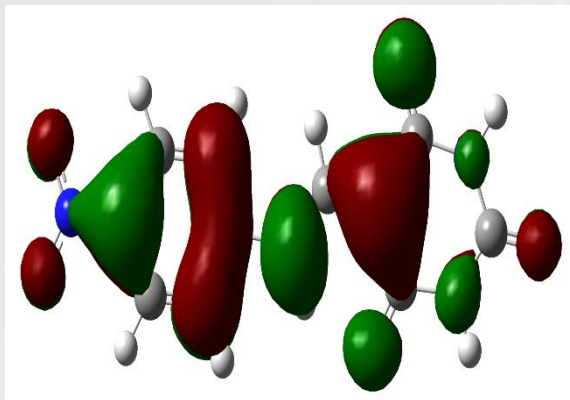
HOMO

AMP-1

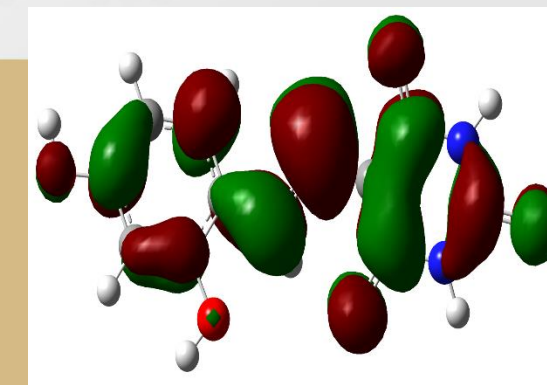
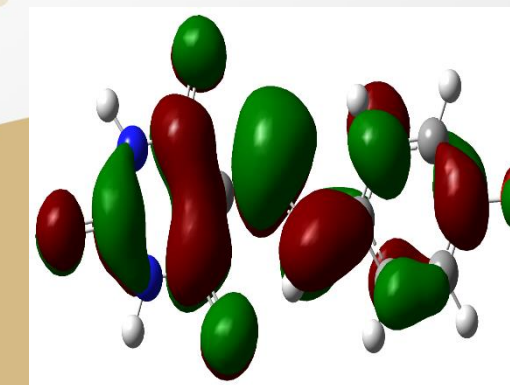
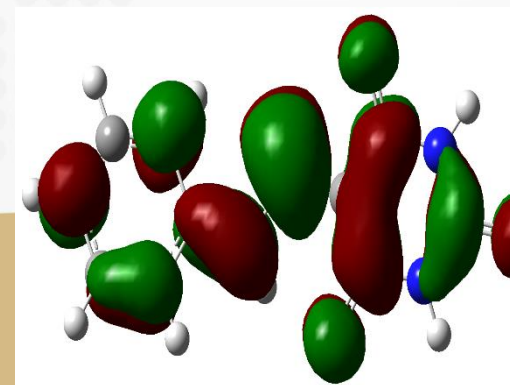
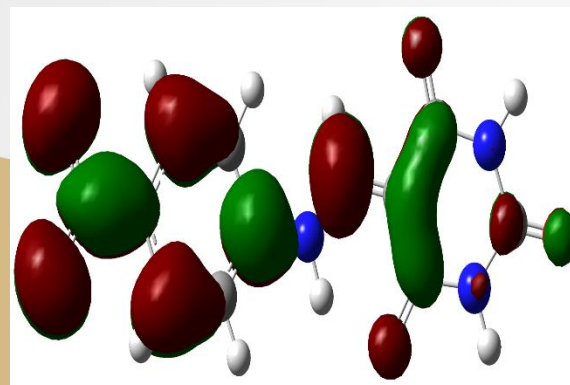
AMP-2

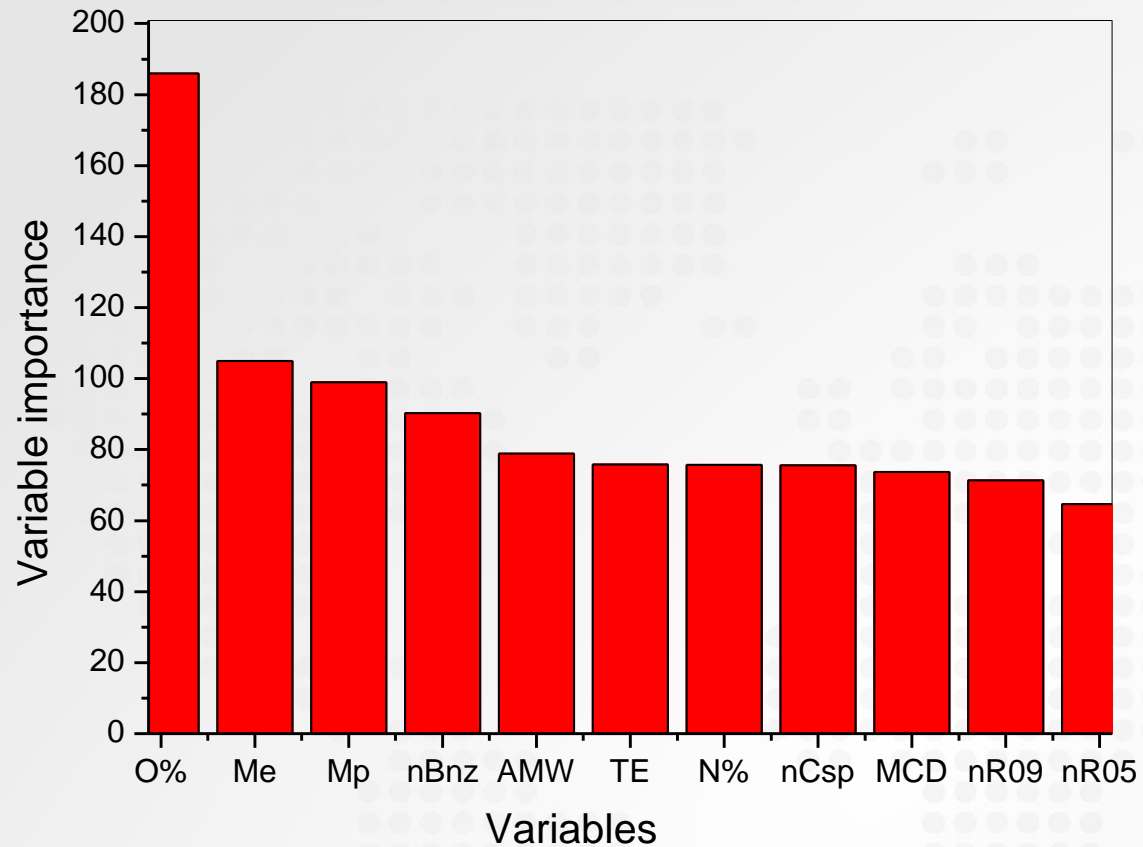
AMP-3

AMP-4



LUMO





Variable selection

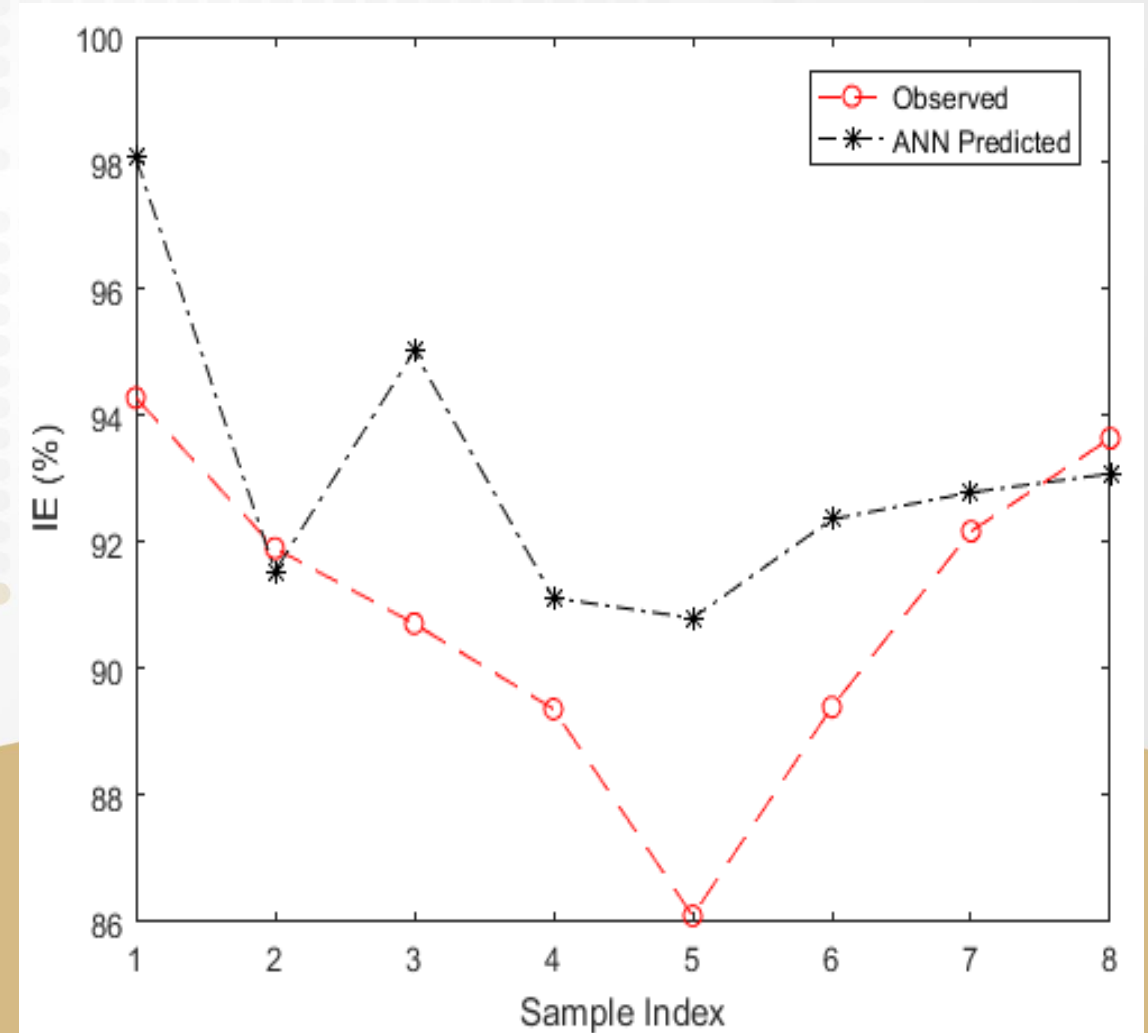
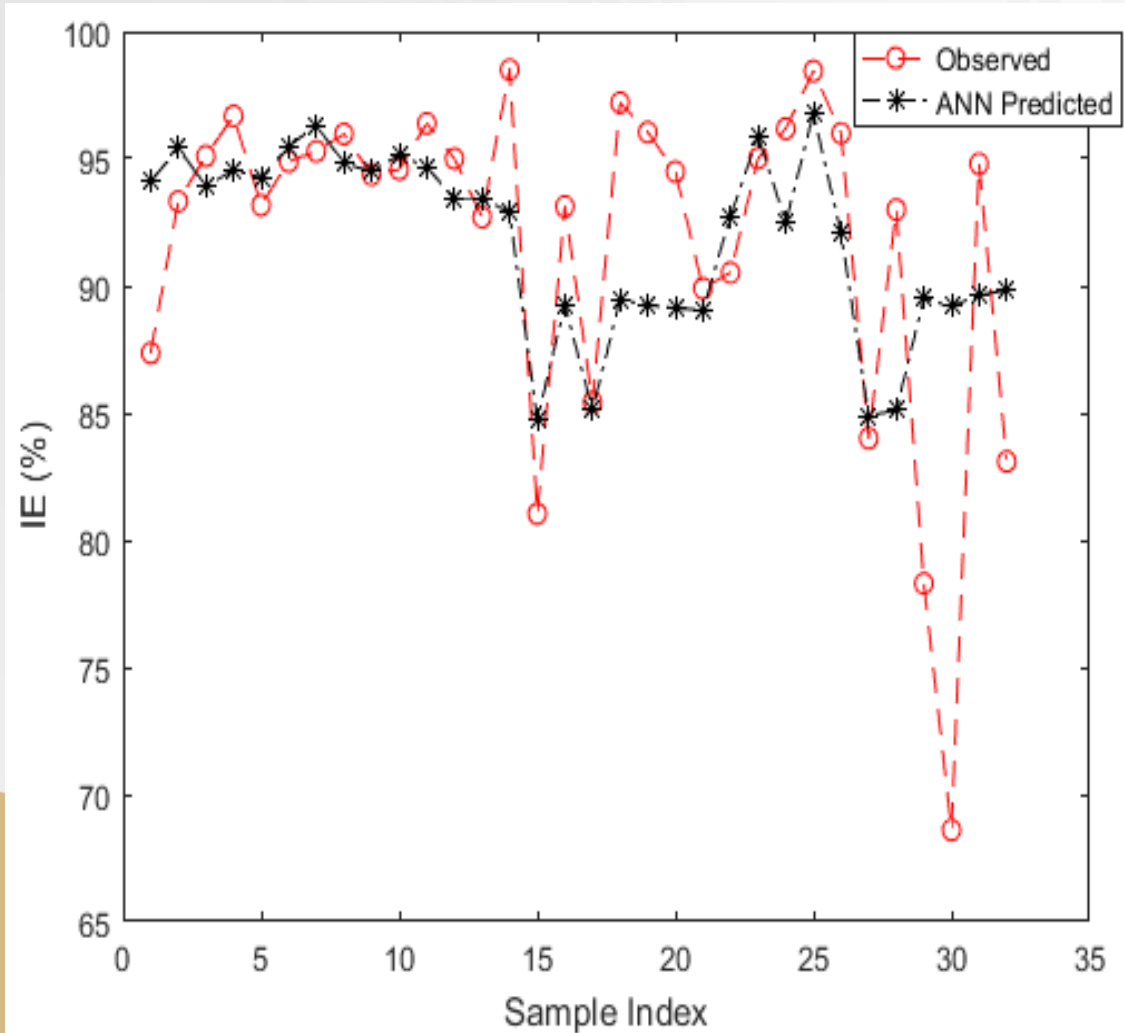
Descriptors	Group name	Description
AMW	Constitutional indices	Average molecular weight
Me	Constitutional indices	Mean atomic Sanderson electronegativity (scaled on carbon atom)
Mp	Constitutional indices	Mean atomic polarizability (scaled on carbon atom)
O%	Constitutional indices	Percentage of oxygen atoms
nBnz	Ring descriptors	Number of benzene-like rings

$$IE(\%) = 2949 + 403 \text{ Conc} + 49.3 \text{ AMW} - 2778 \text{ Me} - 682 \text{ Mp} + 4.28 \text{ O}\% - 7.60 \text{ nBnz}$$

$R^2 = 0.4162$, $SD = 5.01204$, $SSE = 828.98$

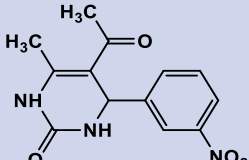
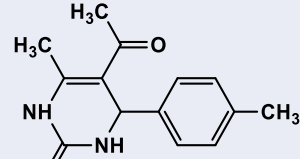
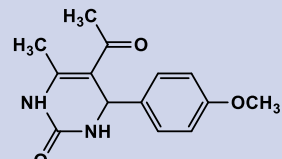
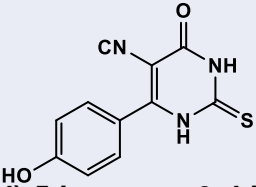
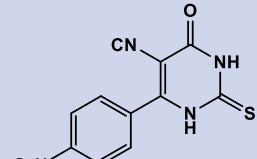
ANN Model 5 training and validation

Model 5: MSE = 8.479, RMSE = 2.912, MAD = 1.791, MAPE = 2.648

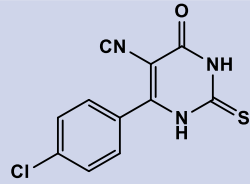
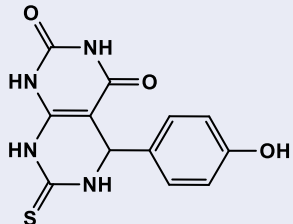
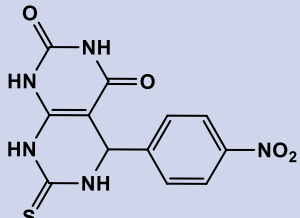
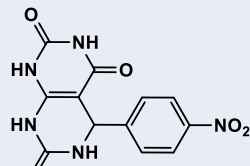


ANN predictive model performance at the training and validation phase

	Model 1		Model 2		Model 3		Model 4		Model 5	
Metric	Train	Valid	Train	Valid	Train	Valid	Train	Valid	Train	Valid
MSE	7.593	145.157	33.838	19.887	23.515	38.916	3.637	151.228	30.750	8.479
RMSE	2.756	12.048	5.817	4.460	4.849	6.238	1.907	12.298	5.545	2.912
MAD	1.300	9.207	4.281	2.848	2.162	3.998	1.054	8.433	3.743	1.791
MAPE	1.489	10.260	4.928	3.525	4.865	5.281	1.152	11.013	4.354	2.648
rMBE	0.086	-7.793	0.191	-0.667	-0.842	-1.899	0.010	7.035	-0.049	2.368
CoV	0.031	0.096	0.012	0.007	0.014	0.008	0.025	0.029	0.030	0.013
Iteration	435		501		462		1000		247	
Topology	7.5930	145.157	33.838	19.887	23.515	38.916	3.637	151.228	30.750	8.479

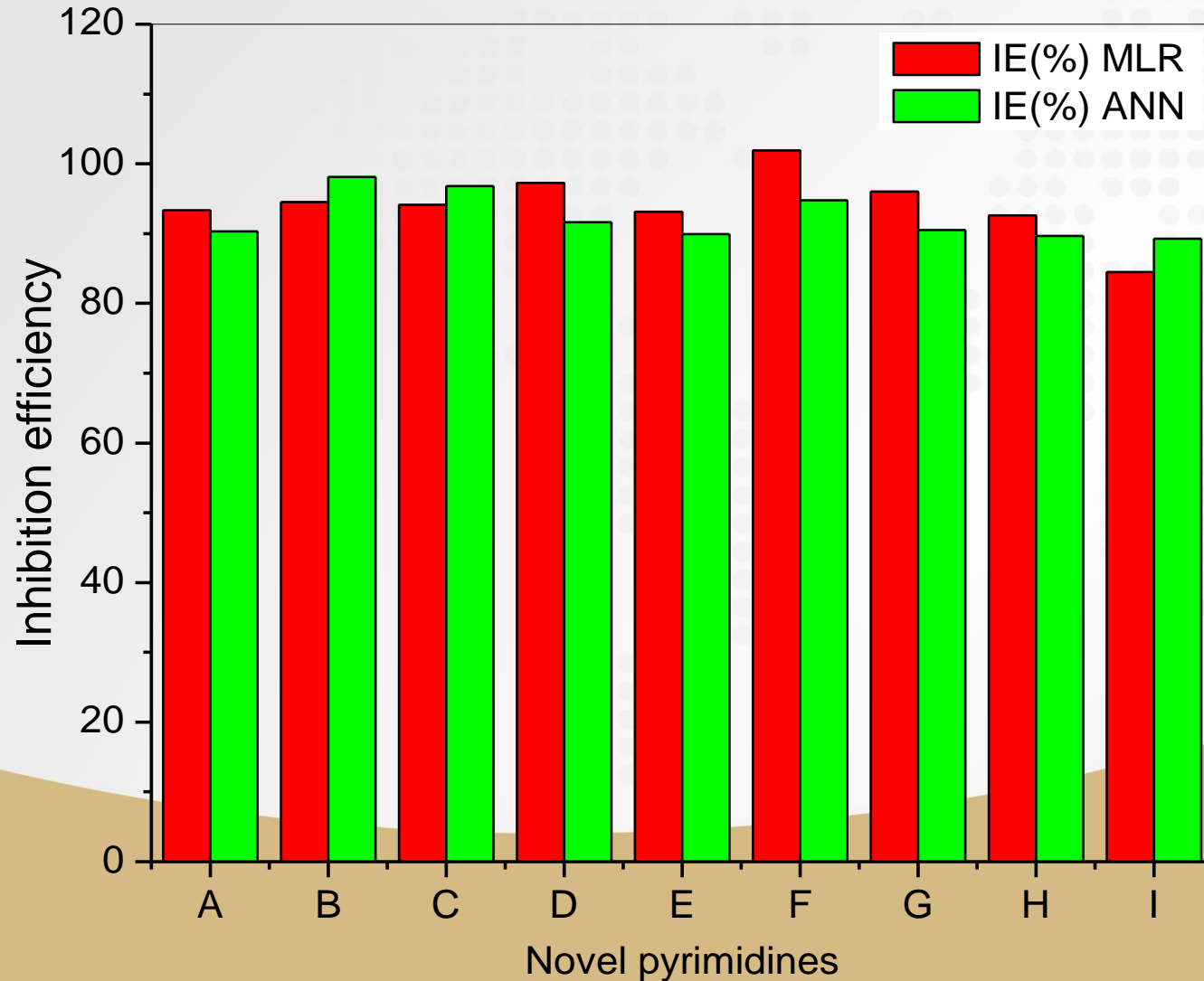
Pyrimidines	Molecular structure/ Name of compound	MLR Predicted IE(%)	ANN Predicted IE(%)
A.	 <p data-bbox="354 382 1281 415">5-acetyl-6-methyl-4-(3-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one</p>	93.34	90.28
B.	 <p data-bbox="354 606 1182 639">5-acetyl-6-methyl-4-(p-tolyl)-3,4-dihydropyrimidin-2(1H)-one</p>	94.52	98.10
C.	 <p data-bbox="354 858 1335 891">5-acetyl-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one</p>	94.13	96.80
D.	 <p data-bbox="354 1110 1314 1172">6-(4-hydroxyphenyl)-5-isocyano-2-thioxo-2,3-dihydropyrimidin-4(1H)-one</p>	97.27	91.63
E.	 <p data-bbox="354 1353 1319 1386">5-isocyano-6-(4-nitrophenyl)-2-thioxo-2,3-dihydropyrimidin-4(1H)-one</p>	93.16	89.94

MLR and ANN predicted results for novel pyrimidines

Pyrimidines	Molecular structure/ Name of compound	MLR Predicted IE(%)	ANN Predicted IE(%)
F.	 <p>6-(4-chlorophenyl)-5-isocyano-2-thioxo-2,3-dihydropyrimidin-4(1H)-one</p>	101.92	94.75
G.	 <p>5-(4-hydroxyphenyl)-7-thioxo-5,6,7,8-tetrahydropyrimido[4,5-d]pyrimidine-2,4(1H,3H)-dione</p>	96.04	90.50
H.	 <p>5-(4-nitrophenyl)-7-thioxo-5,6,7,8-tetrahydropyrimido[4,5-d]pyrimidine-2,4(1H,3H)-dione</p>	92.62	89.64
I.	 <p>5-(4-nitrophenyl)-5,8-dihydropyrimido[4,5-d]pyrimidine-2,4,7(1H,3H,6H)-trione</p>	84.47	89.24

MLR and ANN
predicted results for
novel pyrimidines

Comparison of predicted IE(%) of novel pyrimidines obtained with MLR and ANN models




- Novel pyrimidines acted as excellent corrosion inhibitors
- Compounds A, B and C with substituents $-\text{NO}_2$, $-\text{CH}_3$ and $-\text{OCH}_3$ respectively showed the IE(%) trend in the order $B > C > A$ in both prediction by MLR and ANN.
- This trend was also observed in compounds D, E, F and G, H and I and agrees with literature reports.

CONCLUSIONS

- QSAR models were developed for predicting the corrosion inhibition performances of pyrimidine derivatives.
- The models were developed by correlating previously reported experimental data of forty pyrimidine derivatives with systematically selected constitutional indices.
- MLR and ANN models were developed using the most significant descriptors, and the performances of the models were evaluated with different statistical metrics.
- The study revealed that the selected structural descriptors are critical in understanding the corrosion inhibition mechanism of pyrimidine molecules.
- Furthermore, the models developed can be used to design novel pyrimidine-based corrosion inhibitors with efficient inhibitive performances prior to experimental testing, as the search for new, safe and effective corrosion inhibitors continue.



Predicting protection capacities of pyrimidine-based corrosion inhibitors for mild steel/HCl interface using linear and nonlinear QSPR models

Taiwo W. Quadri¹ · Lukman O. Olasunkanmi^{2,3} · Omolola E. Fayemi¹ · Hassane Lgaz⁴  · Omar Dagdag⁵ · El-Sayed M. Sherif⁶ · Ekemini D. Akpan⁵ · Han-Seung Lee⁷ · Eno E. Ebenso⁵

Received: 1 June 2022 / Accepted: 25 July 2022

© The Author(s), under exclusive licence to Springer-Verlag GmbH Germany, part of Springer Nature 2022

Abstract

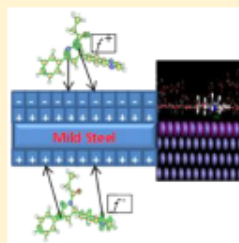
Pyrimidine compounds have proven to be effective and efficient additives capable of protecting mild steel in acidic media. This class of organic compounds often functions as adsorption-type inhibitors of corrosion by forming a protective layer on the metallic substrate. The present study reports a computational study of forty pyrimidine compounds that have been investigated as sustainable inhibitors of mild steel corrosion in molar HCl solution. Quantitative structure property relationship was conducted using linear (multiple linear regression) and nonlinear (artificial neural network) models. Standardization method was employed in variable selection yielding five top chemical descriptors utilized for model development along with the inhibitor concentration. Multiple linear regression model yielded a fair predictive model. Artificial neural network model developed using k-fold cross-validation method provided a comprehensive insight into the corrosion protection mechanism of studied pyrimidine-based corrosion inhibitors. Using a multilayer perceptron with Levenberg–Marquardt algorithm, the study obtained the optimal model having a MSE of 8.479, RMSE of 2.912, MAD of 1.791, and MAPE of 2.648. The optimal neural network model was further utilized to forecast the protection capacities of nine non-synthesized pyrimidine derivatives. The predicted inhibition efficiencies ranged from 89 to 98%, revealing the significance of the considered chemical descriptors, the predictive capacity of the developed model, and the potency of the theoretical inhibitors.

Keywords Corrosion inhibitors · Pyrimidines · Chemical descriptors · QSPR · MLR model · ANN model

Some Quinoxalin-6-yl Derivatives as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid: Experimental and Theoretical Studies

Lukman O. Olasunkanmi,^{†,‡,§} Ime B. Obot,^{||} Mwacham M. Kabanda,^{†,‡} and Eno E. Ebenso^{*,†,‡}[†]Department of Chemistry, School of Mathematical and Physical Sciences, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus) Private Bag X2.046, Mmabatho 2735, South Africa[‡]Material Science Innovation and Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus) Private Bag X2.046, Mmabatho 2735, South Africa[§]Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife 220005, Nigeria^{||}Centre of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia

ABSTRACT: The inhibition of mild steel corrosion in 1 M HCl by some quinoxalin-6-yl derivatives namely 1-[3-phenyl-5-quinoxalin-6-yl-4,5-dihydropyrazol-1-yl]butan-1-one (PQDPB), 1-(3-phenyl-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-1-yl)propan-1-one (PQDPP), and 2-phenyl-1-[3-phenyl-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]-ethanone (PQDPE) has been investigated using electrochemical studies and quantum chemical calculations. The results showed that PQDPP is the best corrosion inhibitor among the three compounds studied and the inhibition efficiency increases with increase in concentration for all the inhibitors. The adsorption of inhibitor molecules on mild steel surface was found to be spontaneous and obeyed the Frumkin adsorption isotherm. Scanning electron microscopy (SEM) images confirmed the formation of protective films of the inhibitors on mild steel surface. Quantum chemical calculations showed that the inhibitors have the tendency to be protonated in the acid and the results agree with experimental observations. Monte Carlo simulations were applied to search for the most stable configuration and adsorption energy for the interaction of inhibitors on Fe(110)/100 H₂O interface. The results of the Monte Carlo simulations accord with the experimentally determined inhibition efficiencies. Different carbonyl substituents on the common nucleus of the three compounds obviously contributed to the difference in inhibition efficiency.



1. INTRODUCTION

Corrosion of metals is of major economic and safety concern to many industries including construction and oil-refining industries.^{1,2} Mild steel is a widely used metal in most industries due to its relatively low cost and good mechanical strength.^{3,4} The use of corrosion inhibitors has been a popular method of protecting the surface of active metals against corrosion in various media.^{5–7} It is the simplest method of reducing corrosion rate until date, and it is relatively cheap.^{2,7,8} Nitrogen, oxygen, and sulfur-containing organic compounds, especially those with π -electron systems are commonly considered as corrosion inhibitors, and many of them have been reported to have appreciable inhibition efficiencies.^{8–10}

Quinoxaline derivatives are popular nitrogen-heterocyclic compounds that have attracted much attention in the past few years. These compounds are easy to synthesize, are environmentally friendly, and exhibit wide biological and photochemical activities.^{11–14} It is against this backdrop that different quinoxaline derivatives are continuously being synthesized and studied for diverse potential applications. Many quinoxaline derivatives have been reported as efficient inhibitors of metal corrosion in acidic medium in the past few years.^{15–26} The design of new corrosion inhibitors and the study of their

inhibition properties are gaining increasing attention from materials scientists and engineers.

Electrochemical techniques such as potentiodynamic polarization and electrochemical impedance spectroscopy have been successfully utilized to study electrochemical corrosion, and determine inhibition properties of corrosion inhibitors. But theoretical approaches are often used to make in-depth explanations of the experimental results. In this regard, quantum chemical calculations are usually employed to correlate molecular properties of inhibitor molecules with inhibition efficiencies.^{8,12,16,21,24} In addition, adequate description of the interactions between the inhibitor molecules and the metal surfaces is important in designing and investigating new corrosion inhibitors and molecular dynamic simulation has proven to be efficient tool in examining these interactions.^{2,427–32}

The objective of the present work is to examine the anticorrosive properties of three quinoxalin-6-yl derivatives namely 1-[3-phenyl-5-quinoxalin-6-yl-4,5-dihydropyrazol-1-yl]-

Received: April 5, 2015

Revised: June 25, 2015

Published: June 26, 2015



Full Length Article

Experimental, quantum chemical and Monte Carlo simulation studies on the corrosion inhibition of some alkyl imidazolium ionic liquids containing tetrafluoroborate anion on mild steel in acidic medium



Y. Sasikumar ^a, A.S. Adekunle ^{a,b}, L.O. Olasunkanmi ^{a,b}, I. Bahadur ^a, R. Baskar ^a, M.M. Kabanda ^a, I.B. Obot ^c, E.E. Ebenso ^{a,*}

^a Department of Chemistry, School of Mathematical and Physical Sciences and Material Science Innovation & Modelling Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University, Mafikeng Campus, Private Bag X2046, Mmabatho 2735, South Africa

^b Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria

^c Centre of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

ARTICLE INFO

Article history:
Received 28 March 2015
Accepted 17 June 2015
Available online xxx

Keywords:
Mild steel
Ionic liquids
Corrosion inhibition
DFT
Monte Carlo simulation

ABSTRACT

The inhibition of mild steel corrosion in 1 M HCl solution by some imidazolium-based ionic liquids (ILs), namely 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM]⁺[BF₄]⁻, 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [BDMIM]⁺[BF₄]⁻ and 1-decyl-3-methylimidazolium tetrafluoroborate [C₁₀MIM]⁺[BF₄]⁻ was investigated using experimental and theoretical techniques. All the studied ILs showed appreciable inhibition efficiencies. Polarization measurements showed that the studied compounds are mixed-type inhibitors and the results obeyed Langmuir adsorption isotherm. Spectroscopic studies confirmed chemical interactions between mild steel and the ILs. Scanning electron microscopy images revealed that the inhibitors formed protective film on mild steel surface. The results of quantum chemical calculations and Monte Carlo simulations agree with experimental observations.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Mild steel is widely used as construction material in many industries due to its exceptional mechanical properties and low cost. But, during some industrial processes such as acid cleaning, etching, etc. this metal corrodes easily, implying that the use of an inhibitor is necessary if the life of this valuable metal is to be protected [1–3]. The use of inhibitors is one of the most practical methods of protecting metals against corrosion [4–6]. It has been established that the initial mechanism involved in any corrosion inhibition process is adsorption of the inhibitor on the surface of the metal [7,8]. The inhibitors influence the kinetics of the electrochemical reactions which constitute the corrosion process and thereby modify the metal dissolution in acids. They change the structure of the electrical double layer by adsorption on the metal surface. The adsorption of the inhibitor on the metal surface is a complex mechanism involving a number of factors such as the nature of the metal, the environment, the electrochemical potential at the metal/solution interface and nature of the inhibitor [9]. Corrosion inhibitors are often synthesized from cheap raw materials and include compounds that have π-electrons and functional groups such as —C=C—, —OR, —OH, —NR₂, —NH₂ and —SR. These functional groups facilitate the

adsorption of the inhibitor on the metal surface [7,8,10]. However, many organic inhibitors are not environmentally benign. The increasing campaign towards the use of “green” compounds in industrial processes has shifted the attention of researchers to the study of ionic liquids (ILs) as environmental friendly corrosion inhibitors in the past few years [11–13].

Ionic liquids (ILs) are molten salts composed of organic cations and various anions. The organic cation usually has a π system and/or a heteroatom, such as nitrogen, sulfur or phosphorus as the central atoms for interaction with the metal surface. They possess a large number of physicochemical properties [14–17] such as good electrical conductivity, solvent transport and a relatively wide electrochemical window, making them highly efficient for both physisorption and chemisorption processes. ILs have been reported to have good corrosion inhibition properties for metals in acidic medium [12,18]. As a result, these compounds are reportedly used in oil field to minimize carbon dioxide induced corrosion [19,20]. Similarly, ILs have successfully mitigated the corrosion of carbon steel in hydrogen sulfide environment [21,22] and their inhibitive effects in aqueous HCl and H₂SO₄ media have also been reported [23,24]. ILs can be tailored to specific applications by fine-tuning the functional groups of the weakly coordinating organic cation and the inorganic/organic anion [25]. It is known that the alkyl chain length of the cation influences both the physical and chemical properties of room temperature ionic liquids (RTILs). A longer cation side chain is commonly accompanied by

* Corresponding author.
E-mail address: E.E.Ebenso@nwu.ac.za (E.E. Ebenso).



Electrochemical, thermodynamic and quantum chemical studies of synthesized benzimidazole derivatives as corrosion inhibitors for N80 steel in hydrochloric acid



M. Yadav^{a,*}, S. Kumar^a, T. Purkait^a, L.O. Olasunkanmi^b, I. Bahadur^{b,*}, E.E. Ebenso^b

^a Department of Applied Chemistry, Indian School of Mines, Dhanbad 826004, India

^b Department of Chemistry, School of Mathematical and Physical Sciences, Materials Science Innovation & Modelling (MSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

ARTICLE INFO

Article history:

Received 10 July 2015

Received in revised form 26 September 2015

Accepted 8 November 2015

Available online 6 December 2015

Keywords:

N80 steel

Hydrochloric acid

Corrosion inhibition

EIS

SEM

DFT

ABSTRACT

The inhibitive action of synthesized benzimidazole derivatives, namely: 2-(1-(morpholinomethyl)-1H-benzimidazol-2-yl)phenol (MBP), 2-(1-(piperazine-1-yl)methyl)-1H-benzimidazol-2-yl)phenol (PzMBP) and 2-(1-(piperidine-1-yl)methyl)-1H-benzimidazol-2-yl)phenol (PMBP) on corrosion of N80 steel in 15% HCl solution has been studied using weight loss measurement, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. It was found that the inhibition efficiency of all the three inhibitors increases with increase in concentration of inhibitors and decreases with increase in temperature. The inhibitors, PzMBP, MBP, and PMBP show corrosion inhibition efficiency of 96.3, 94.4 and 92.9% respectively, at 200 ppm and 303 K. Polarization studies showed that the studied inhibitors are mixed type in nature. The results of the Fourier transform infrared (FTIR) and UV-visible spectroscopy provided evidence of iron/inhibitors interactions. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were performed for surface analysis of N80 steel samples in acid solution without and with inhibitors. The Density Functional Theory (DFT) was employed for quantum chemical calculations to correlate the experimental findings.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Carbon steel is widely used as constructional material in a large number of industries. N80 steel is widely used as main constructional material for down-hole tubular, casings, flow lines and transmission pipelines in petroleum industry. Acid solutions widely used in various industrial processes such as oil-well acidizing, acid pickling, industrial acid cleaning and acid descaling lead to serious metallic corrosion. Acidification of petroleum oil-well for enhanced oil production is commonly carried out by forcing a solution of 15% to 28% hydrochloric acid solution [1–8] into the oil-well through N80 tubing. During this process tubing and casing materials (N80 steel) get adversely affected by corrosion. In order to reduce the aggressive attack of the acid on tubing and casing materials (N80 steel), inhibitors are added to the acid solution during the acidifying process. The use of inhibitors is one of the most economical and practical methods of reducing corrosive attack on metals. The selection of inhibitor is controlled by its economic availability, its efficiency to inhibit the substrate material and its environmental side effects. Most of the inhibitors for corrosion of steel in acidic medium are

organic compound containing nitrogen, oxygen and/or sulfur atoms [9–13]. The inhibiting action of these compounds is usually due to their adsorption onto the metal interface. The adsorption process depends upon the nature and surface charge of the metal, the type of aggressive media, the electronic and/or molecular structure of the inhibitor and the nature of its interaction with the metal surface [14].

Most of the reported organic corrosion inhibitors are effective only at high concentrations and are harmful to the environment due to their toxicity. Hence, it is important to search for new nontoxic and effective organic corrosion inhibitors for N80 steel in 15% hydrochloric acid. Some benzimidazole derivatives [15–19] have been reported as good inhibitors for the corrosion of metals and alloys in hydrochloric acid solution and their inhibition performance is influenced by the nature and position of substituent groups on the aromatic rings. In addition to their good corrosion inhibition potentials, benzimidazole derivatives exhibit good solubility, high stability, and lower toxicity [20], which are among the other desirable characteristics often considered in selecting corrosion inhibitors.

In continuation of our research for developing organic compounds with high corrosion inhibition efficiency [5–8], the present paper explores the synthesis of three benzimidazole derivatives, namely: 2-(1-(morpholinomethyl)-1H-benzimidazol-2-yl)phenol (MBP), 2-(1-(piperazine-1-yl)methyl)-1H-benzimidazol-2-yl)phenol (PzMBP)

* Corresponding authors.

E-mail addresses: yadav@mshendso@alumni.in (M. Yadav), bahadurindra@gmail.com (I. Bahadur).



Review

Progress on the coordination chemistry and application of hydantoins and its derivatives as anticorrosive materials for steel: A review



Ekemini D. Akpan^{a,b,*}, O. Dagdag^{a,b}, Eno E. Ebenso^{a,b,*}

^a Center for Materials Science, College of Science, Engineering and Technology, University of South Africa, 1710, Florida, South Africa

^b Institute of Nanotechnology and Water Sustainability, College of Science, Engineering and Technology, University of South Africa, 1710, Florida, South Africa

ARTICLE INFO

Keywords:

Hydantoins
Coordination chemistry
Corrosion inhibition
Synthesis
Metal complexes

ABSTRACT

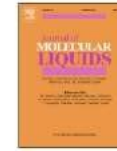
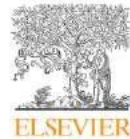
Hydantoin is a five-membered non-aromatic heterocycle, oxidized derivative of imidazolidine with five potential derivatizable sites, together with two hydrogen bond donors and acceptors existing mostly as a colourless solid. Synthesis of metal complexes that incorporates hydantoin ligand is regarded as a significant research area, given the vast applicability of hydantoin derivatives as compounds of biological interest with wide range of pharmacological activities, and corrosion inhibitory properties. Over the years, extensive literature reviews on synthesis of derivatives of hydantoins, biological properties and medicinal chemistry of hydantoins, and usage of multifunctional hydantoins in optoelectronics has been reported. This review deals strictly on the coordination abilities of hydantoin derivatives as ligands in organometallic chemistry, as well as report on the few applications of hydantoin derivatives as inhibitors of metal corrosion in diverse corrosion environments. It has been established, mainly by spectroscopic techniques, density functional theory analyses and few X-ray crystallography studies, that functionalized, deprotonated and reduced forms of hydantoins acts as mono-, bidentate and tridentate chelate ligands in metal complexes. Few corrosion inhibition capabilities of derivatives of hydantoins reported in scientific publications is also reviewed. Important research data gaps are noted, and future perspectives underlined.

1. Introduction

Hydantoin is a five-membered non-aromatic heterocycle with five potential derivatizable sites, together with two hydrogen bonding acceptors and donors, respectively (Fig. 1). The core hydantoin moiety is particularly of interest because it has double hydrogen bonds donors/acceptors, with potential to interact with various substituents physically and chemically [1]. Advantageous features of hydantoins includes their established synthetic routes *via* known cyclization reactions, and easiness of accepting varying substituents on its backbone [2]. Hence, various derivatives of hydantoin with varying substituents have been designed, synthesized and found applications in pharmacological [3-5], biological [6-11] and corrosion remediation fields. Hydantoin, an oxidized derivative of imidazolidine exists as a colourless solid with molecular

formula, $C_3H_4N_2O_2$. It's sometimes refers to as glycolylurea because a cyclic double condensation of glycolic acid and urea gives hydantoin as the reaction product [12].

Hydantoin possess high solubility in water (39.7 g/L at 100 °C) and a unique melting point temperature ranging 219–220 °C. In terms of spectral properties, hydantoin show two bands at approximately 1720 and 1780 cm^{-1} (that is carbonyl region). Hydantoin and its derivatives are applied in the manufacturing of adhesive compositions and also as raw materials for the production of high molecular compounds [13]. Aryl substituents and most electron withdrawing substituents could significantly increase hydantoin acidity. Hence, insertion of an aryl-methylene side chain at carbon-5 could increase the acidity of N-1 hydrogen because of distribution of the negative charge at N atom in position 1 into the carbon-5 substituent [14]. Hydantoins are known to



Recent progress on the anticorrosion activities of acridine and acridone derivatives: A review

Ekemini D. Akpan*, O. Dagdag, Eno E. Ebenso*

College of Science, Engineering and Technology, University of South Africa, Florida campus, Johannesburg, 1710, South Africa

ARTICLE INFO

Article history:

Received 8 April 2022

Revised 26 May 2022

Accepted 19 June 2022

Available online 23 June 2022

Keywords:

Acridine and acridone derivatives

Corrosion inhibition

Electrochemical analyses

Adsorption isotherms

Alloys

ABSTRACT

Acridine and acridone are heterocyclic organic compounds with nitrogen atoms in their molecular structure. Over the years, acridine and acridone derivatives have been investigated and known to possess antimicrobial, antibacterial, and antiprotozoal properties, but little is done to explore these compounds as efficient inhibitors for the corrosion of metallic alloys in acidic and neutral medium. This is despite their ease of synthesis, low toxicity and excellent coordination performance. The derivatives of acridine and acridone mostly contains polar substituents groups such as carbonyl ($-C=O$), amino ($-NH_2$), methoxy ($-OMe$), hydroxyl ($-OH$), and nitro ($-NO_2$) etc., which aids effective adsorption and formation of stable chelating complexes with metal surfaces via coordination bonding. This review summarizes important findings in using acridine and acridone derivatives as corrosion inhibitors for metals and alloys from 2001 to present. Synthesis of acridine and acridone derivatives, rationale for vital anticorrosion findings, mechanism of inhibition and prospects are discussed in this report.

© 2022 Elsevier B.V. All rights reserved.

Contents

1. Introduction	1
1.1. Synthesis of acridine and acridone derivatives	2
1.2. Cost analyses on the synthesis of acridine and acridone derivatives	4
2. Acridine and acridone derivatives as metal corrosion inhibitors (2001 – 2022)	5
3. Conclusions and outlook	19
Declaration of Competing Interest	19
Acknowledgement	19
References	19

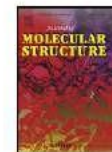
Abbreviations: NMR, Nuclear magnetic resonance; FTIR, Fourier Transform Infrared; MS-EIS, Mass spectrometry electrospray ionisation; DNA, Deoxyribonucleic acid; DMSO, Dimethyl sulfoxide; EDTA, Ethylenediamine tetra acetic acid; nM, Millimolar; M, Molar; DFT, Density functional theory; SCE, Saturated calomel electrode; WL, Weight loss; MDS, Molecular dynamic simulation; LPR, Linear polarization resistance; PDP, Potentiodynamic polarization; EIS, Electrochemical impedance spectroscopy; XPS, X-ray photoelectron spectroscopy; %IE, Percentage inhibition efficiency.

* Corresponding author.

E-mail addresses: akpaned@unisa.ac.za (E.D. Akpan), ebensee@unisa.ac.za (E.E. Ebenso).

1. Introduction

Attempts at improving the stability of crucial infrastructures (like oil pipeline, water pipes, rail tracks, storage tanks, bridges, buildings, industrial plants etc.) by reducing the rate of corrosion of their metallic parts has become very essential. Corrosion activities involves cathodic reactions in the presence of electron acceptor (like hydrogen or oxygen ions), and anodic dislodgment of metal ions into the corrosive electrolyte [1–3]. There is need to minimize the crisis of companies and industrial plants shutdown due to corroded equipment [4]. As at 2016, records available in



Synthesis, physicochemical properties, theoretical and electrochemical studies of tetraglycidyl methylenedianiline

O. Dagdag^{a,†,*}, R. Haldhar^{b,†}, Seong-Cheol Kim^{b,†,*}, Zaki. S Safi^{c,†}, Nuha Wazzan^{d,†}, Ahmed M Mkadmh^{e,†}, Avni Berisha^{f,g,†}, Elyor Berdimurodov^{h,†}, Shehdeh Jodeh^{i,†}, Esther E. Nwanna^{j,†}, Ekemini D. Akpan^{a,†}, Eno E. Ebenso^{a,†,*}

^a College of Science, Engineering and Technology, University of South Africa, Johannesburg, 1710, South Africa

^b School of Chemical Engineering, Yeungnam University, Gyeongsan, 712749, South Korea

^c Al Azhar University-Gaza, Chemistry Department, Faculty of Science, P.O. Box 1277, Gaza, Palestine

^d King Abdulaziz University, Chemistry Department, Faculty of Science, P.O. Box 42805, Jeddah, 21589, Saudi Arabia

^e Chemistry Department, Faculty of Applied Science, Alqasa University, Gaza, Palestine

^f Department of Chemistry, Faculty of Natural and Mathematics Science, University of Prishtina, 10000, Prishtina, Kosovo

^g Materials Science-Nanochemistry Research Group, NanoAlb-Unit of Albanian Nanoscience and Nanotechnology, 1000, Tirana, Albania

^h Faculty of Chemistry, National University of Uzbekistan, Tashkent, 100034, Uzbekistan

ⁱ Department of Chemistry, An-Najah National University, P. O. Box 7, Nablus, Palestine

^j Department of Biochemistry, Federal University of Technology, PMB 704, Akure, Nigeria

ARTICLE INFO

Article history:

Received 19 March 2022

Revised 30 May 2022

Accepted 10 June 2022

Available online 12 June 2022

Keywords:

Epoxy prepolymer

Viscosity

Thermochemistry

NLO

DFT

MC and MD simulations

ABSTRACT

In the current study, a tetra-functional aromatic epoxy pre-polymer namely, tetraglycidyl methylenedianiline (TGMDA) was synthesized and characterized using ¹H NMR (Nuclear Magnetic Resonance) and FT-IR (Fourier Transform Infrared Spectroscopy) spectral techniques. The rheological properties were tested using an advanced rheometer in isopropyl alcohol. The effect of temperature and solution concentration on the viscosity of the aromatic pre-polymer epoxy solution was evaluated. The study of shear rheology was performed at different temperatures of solutions of the epoxy pre-polymer in isopropyl alcohol on solutions of mass concentration (%; 0.5, 1.0, 1.5, 2.5, and 5%) and temperatures (298–328 K). The energies of the frontier molecular orbitals, as calculated by B3LYP method with 6-311++G(d, p) and 6-311++G(3d, 3p) basis sets permit the prediction of the chemical reactivity and stability of the TGMDA molecule. The thermochemical estimations of the studied compounds were also calculated and discussed. The heat of formation and Gibbs's free energy of the reactants and products were determined and analyzed. The study, likewise, showed that the reactions are endothermic and spontaneous in the reverse direction at 298.15 K. Non-linear optics (NLO) study concluded the existence of the opposite relationship between the β_{111} and the HOMO-LUMO energy gap values (E_{gap}). The anti-corrosive property of TGMDA for carbon steel (CS) corrosion in 1M HCl solution was evaluated using several electrochemical and theoretical methods. The TGMDA showed highest efficiency of 96.5% at 10^{-3} M concentration. Monte Carlo (MC) and Molecular Dynamics (MD) simulations showed that the response significantly affected the metal surface-inhibitor interaction, giving molecular proof to the geometry and the adsorption energy.

© 2022 Elsevier B.V. All rights reserved.

1. Introduction

Epoxy resins are one of the most significant pre-polymer materials utilized in a large number of industrial applications like paintings, coatings, composites, constructions, electrical and electronics, adhesives and wind turbines [1,2]. The unique physical and chemi-

cal properties of the epoxy materials are categorized by fast curing, unique mechanical properties, and superior adhesion to substrate, good thermal stability, excellent corrosion resistance and chemical resistance. In addition, it could be available at relatively low cost [3–5]. These alluring properties can incorporate high crosslinking and practical gatherings like amines (NH₂) and hydroxyl (OH) in epoxy prepolymers [6]. The synthesis of epoxy pre-polymers materials is well established and reported in the literature [7,8].

Metals are normally artificially stable minerals [9]. At the point when metals are taken out from the ore, they become temperamental and will in general return to their unique shape. The

* Corresponding authors.

E-mail addresses: dagdago@unisa.ac.za, omar.dagdag@uit.ac.ma (O. Dagdag), skkim07@ynu.ac.kr (S.-C. Kim), ebensee@unisa.ac.za (E.E. Ebenso).

[†] These authors contributed equally to this work.



Recent progress in epoxy resins as corrosion inhibitors: design and performance

Omar Dagdag^a, Rajesh Haldhar^b, Seong-Cheol Kim^b, Lei Guo^c, M. El Gouri^d, Elyor Berdimurodov^e, O. Hamed^f, S. Jodeh^f, Ekemini D. Akpan^a and Eno E. Ebenso^a

^aInstitute of Nanotechnology and Water Sustainability, College of Science, Engineering and Technology, University of South Africa, Johannesburg, South Africa; ^bSchool of Chemical Engineering, Yeungnam University, Gyeongsan, South Korea; ^cSchool of Materials and Chemical Engineering, Tongren University, Tongren, PR China; ^dDepartment of Process Engineering, Laboratory of Industrial Technologies and Services (LITS), Height School of Technology, Sidi Mohammed Ben Abdallah University, Fez, Morocco; ^eFaculty of Chemistry, National University of Uzbekistan, Tashkent, Uzbekistan; ^fDepartment of Chemistry, An-Najah National University, Nablus, Palestine

ABSTRACT

The utilization of organic compounds has been established to be perhaps the best, most proficient, and most powerful method for controlling corrosion. Organic compounds extend into benefits by complexing at the metal-environment interface applying their electron-dense centers, which are known as binding centers. Though, because they have small molecular size, they do not have satisfactory corrosion protection. Accordingly, there is an exceptional requirement for major atomic changes. Toward this path, unique accentuation is put on the utilization of epoxy resins (ERs)-based synthetic monomers as inhibitors for corrosion. The nature of the structure that includes polar functional groups makes the monomers adsorb strongly on the metal surface and give remarkable metal protection. This review report gives a concise outline of the most recent improvements in the utilization of ERs as corrosion inhibitors. This report gives a short outline of the consumption and general utilization of various sorts of ERs and corrosion inhibition processes.

ARTICLE HISTORY

Received 15 January 2022
Revised 16 February 2022
Accepted 13 March 2022

KEYWORDS

Organic compounds epoxy resins; corrosion inhibitors; molecular size; surface protection

1. Introduction

Steel is an effective open metallic compound that has distinctive mechanical properties [1–3]. In the research investigation, different steels were utilized to test specific properties of destructive projections [4]. Today, the current practice for some advancement, like cleaning, descaling, and pickling, is to take advantage of an acidic environment, and further disintegration of metals, for example, carbon steel (CS) is unavoidable [5–7]. To protect or secure the metal, several materials have been used to create a

CONTACT Omar Dagdag  omar.dagdag@uit.ac.ma; Seong-Cheol Kim  sckim07@ynu.ac.kr; Eno E. Ebenso  ebensee@unisa.ac.za

 Supplemental data for this article is available online at <https://doi.org/10.1080/01694243.2022.2055347>.

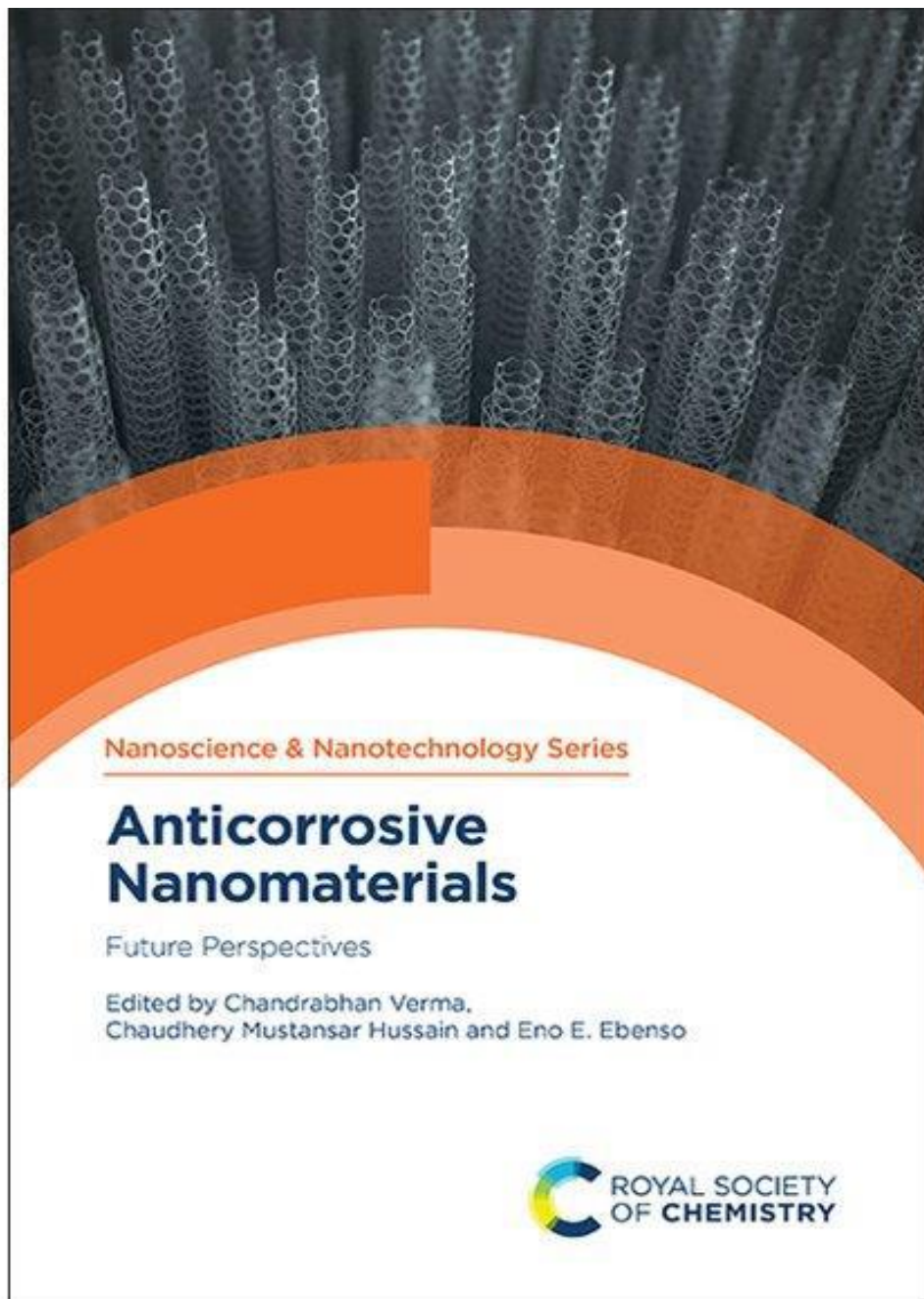
EDITED BY
CHANDRABHAN VERMA
CHAUDHERY MUSTANSAR HUSSAIN
ENO E. EBENSO

ORGANIC CORROSION INHIBITORS

SYNTHESIS, CHARACTERIZATION,
MECHANISM, AND APPLICATIONS

WILEY

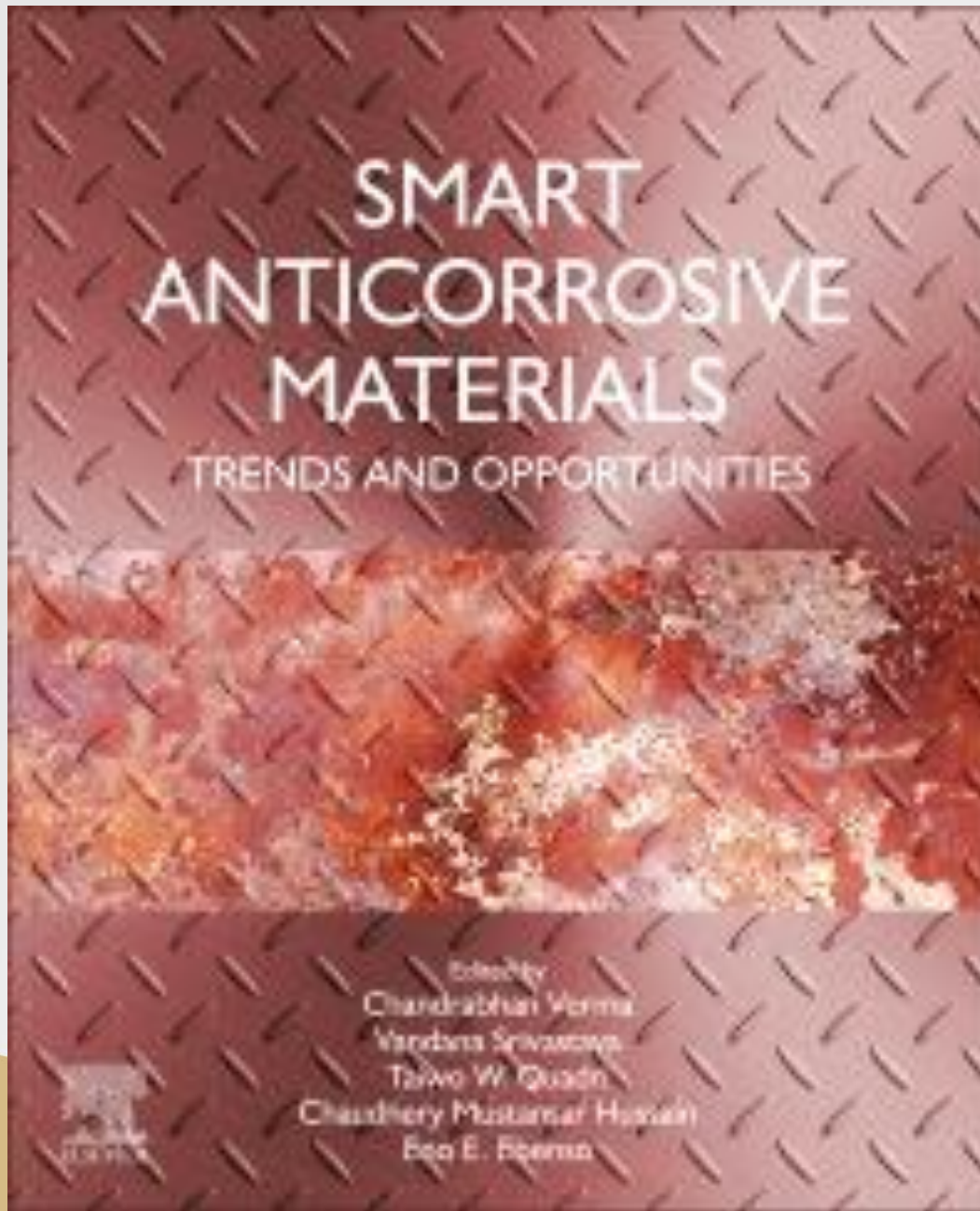
Organic Corrosion Inhibitors: Synthesis, Characterization, Mechanism, and Applications



Anticorrosive Nanomaterials: Future Perspectives: Volume 56 (Nanoscience & Nanotechnology Series) Hardcover – 9 May 2022

by [Chandrabhan Verma](#) (Editor),
[Chaudhery Mustansar Hussain](#) (Editor),
[Eno Ebenso](#) (Editor)

- Publisher : Royal Society of Chemistry (9 May 2022)
- Language : English
- Hardcover : 314 pages
- ISBN-10 : 1839164115
- ISBN-13 : 978-1839164118



Smart Anticorrosive Materials: Trends and Opportunities

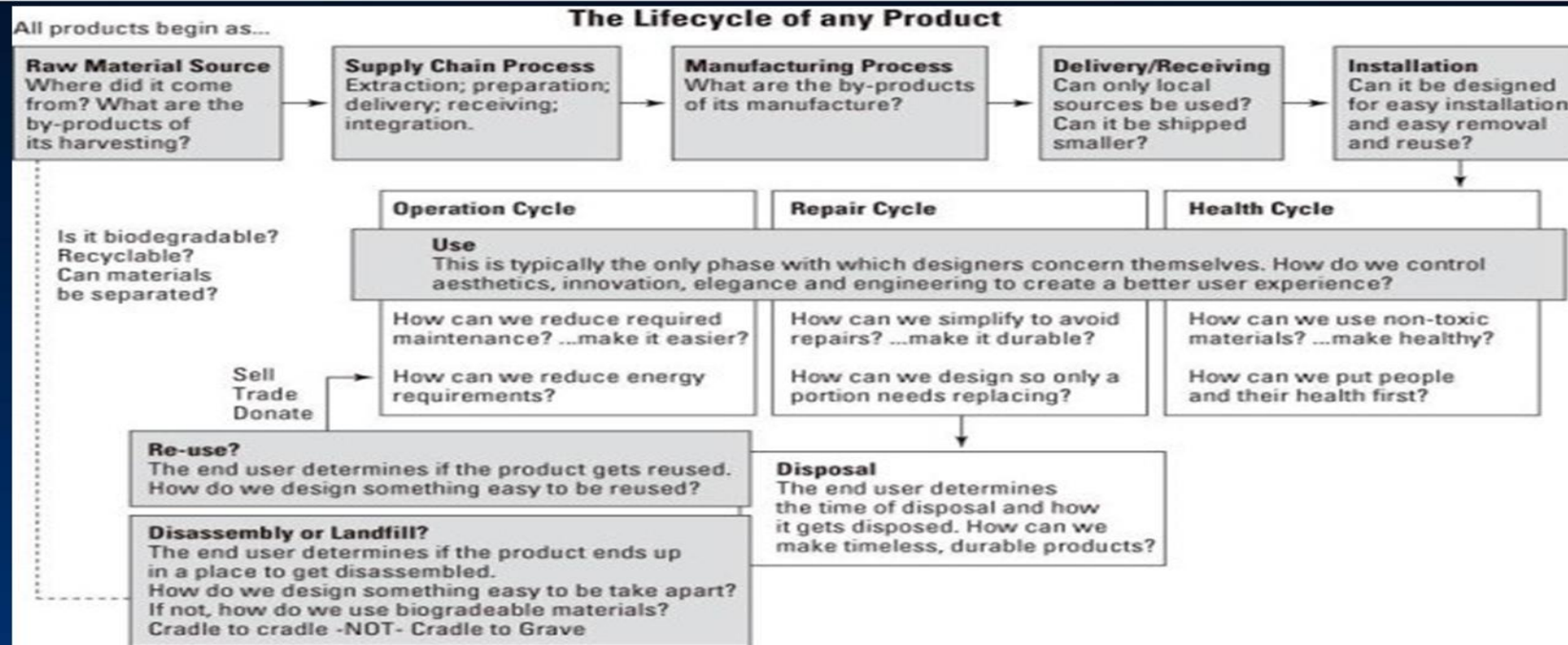
1st Edition - March 28, 2023

Editors: Chandrabhan Verma, Vandana Srivastava,
Taiwo W Quadri, Chaudhery Mustansar Hussain,
Eno Ebenso

- Paperback ISBN: 9780323951586
- eBook ISBN: 9780323951593

- ✓ **The use of plant extracts (green and environmentally friendly) - (*Carica papaya*, *Azadirachta indica*, *Phyllanthus amarus*, *Garcinia cola*, *Delonix regia*, *Ocimum basilicum*, *Piper guinensis*, *Musa sapientum*, *Allium cepa*, *Allium sativum*) and naturally occurring polymers (exudates gums namely *Raphia Hookeri*, *Pachylobus edulis*, *Gum Arabic*, *Dacryodes edulis* etc) as corrosion inhibitors.**

The publications generated from this category will be discussed under the subtheme ; Chemistry, Sustainable Development and Corrosion Inhibition.



If you were to map out the typical stages of the life cycle of any material – from its birth (production) to its death (disposal) – it would look something like this: Everything – every material, every product – has a life cycle. A life cycle is the journey a material goes through during its entire life. Every material starts in some raw form, is processed, and is made into a finished product. At some point – five, ten, or dozens of years later – the material reaches the end of its life and is disposed of. (In fact, most construction materials end up in a landfill.)

SUSTAINABLE DEVELOPMENT AND CORROSION INHIBITION

What is Sustainability?

- **“Sustainability is the ability to provide a healthy, satisfying and just life for all people on earth, now and for generations to come, while enhancing the health of ecosystems and the ability of other species to survive in their natural environments”.**
- **Sustainability is system-based.**
- **However, the concept of sustainability dates back to history. As the challenge of living in harmony with the earth becomes increasingly difficult, more than ever, society needs education and high quality cutting-edge research to meet these challenges.**

What is Sustainable Development?

- **“Sustainable development” is a process of change during which societies and their citizens learn to deal with the tension between ecological sustainability and economic development while doing justice to interests at both local and global level.**
- **This general definition can be interpreted differently depending on locality and geographical location.**
- **Sustainable development balances three principal requirements namely:-**
- **The needs of society (the social objective);**
- **The efficient management of scarce resources (the economic objective);**
- **The need to reduce the load on the eco-system in order to maintain the natural basis for life (the environmental objective).**

- **In 1987, a UN report defined "sustainable development as "development that meets the needs of the present without compromising the ability of future generations to meet their needs". Sustainability development can also be defined as "meeting the worlds demand for energy, food, water and medicine – in a sustainable way, while protecting the environment – requires development of new technologies and advanced materials."Sustainable development therefore is required to help meet the worlds need for:**
- **Energy - energy technologies**
- **Resources – use strategies**
- **Food**
- **Water**
- **Medicine**
- **Protection of the environment**

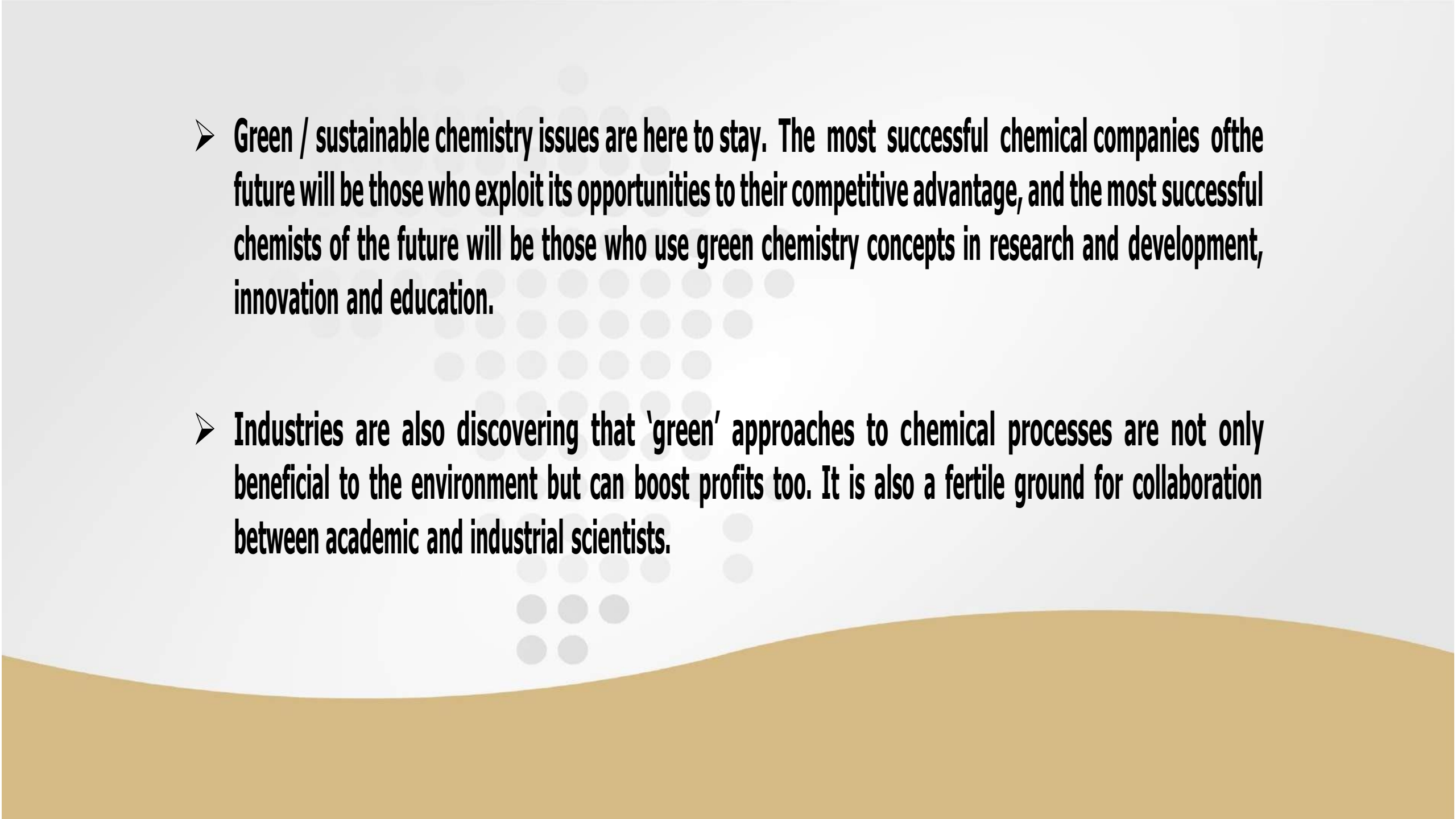
Therefore, given societal needs in the 21st century and beyond, the question now is what science and technology innovations do we need to achieve the goal of sustainable feature? SURE THE ANSWER IS CHEMISTRY!!!!

- **Sustainable chemistry is closely related to “green chemistry”; but with a slight difference in the definition: while green chemistry indicates that a not risky and polluting chemical production process may exist, the sustainable chemistry concepts links eco-efficiency, economic growth and quality of life in terms of the cost/benefit analysis. The sustainable chemistry approach emphasizes the concept of sustainable risk. The role of the chemist is to minimize this risk and reduce the impact on the environment to a level sustainable by the environment, assuring a good quality of life. Green chemistry is used to indicate technologies for which a careful cost/benefit or assessment study has not been made. “Sustainable chemistry” is thus the natural trend of chemistry, but not an independent factor from economic growth, quality of human life and health care. The evaluation of new “green” chemical processes and products follows a rigorous assessment in terms of eco-efficiency, risk minimization and socio-environmental impact which quantitatively evaluates the costs and benefits of the new process and alternative solutions. There is no doubt that our lives have been enhanced by chemistry. The importance of green chemistry as an alternative in the developing world and Africa is really a blessing and its gains should be exploited. Sustainability depends largely on the twelve principles of green chemistry namely:-**
 - ✓ **Prevention - It is better to prevent waste than to treat or clean up waste after it has been created.**
 - ✓ **Atom Economy - Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.**
 - ✓ **Less Hazardous Chemical Syntheses - Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.**

- ✓ **Designing Safer Chemicals** - Chemical products should be designed to effect their desired function while minimizing their toxicity.
- ✓ **Safer Solvents and Auxiliaries** - The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- ✓ **Design for Energy Efficiency** - Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
- ✓ **Use of Renewable Feed stocks** - A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- ✓ **Reduce Derivatives** - Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- ✓ **Catalysis** - Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- ✓ **Design for Degradation** - Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
- ✓ **Real-time analysis for Pollution Prevention** - Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- ✓ **Inherently Safer Chemistry for Accident Prevention** - Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

- **Inhibitors are often easy to apply and offer the advantage of *in-situ* application without causing any significant disruption to the process. However, there are several considerations when choosing an inhibitor namely:**
- **Cost of the inhibitor can be sometimes very high when the material involved is expensive or when the amount needed is huge.**
- **Toxicity of the inhibitor can cause jeopardizing effects on human beings, and other living species.**
- **Availability of the inhibitor will determine the selection of it and if the availability is low, the inhibitor becomes often expensive.**
- **Environmental friendliness.**
- **A number of heterocyclic compounds have been reported as corrosion inhibitors and the screening of synthetic heterocyclic compounds is still being continued. Though many synthetic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and environment. The safety and environmental issues of corrosion inhibitors arisen in industries has always been of global concern. These inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system *viz.*, kidneys or liver, or to disturb a biochemical process or to disturb an enzyme system at some site in the body. The toxicity may manifest either during the synthesis of the compound or during its applications. These toxic effects have led to the use of natural products/ plant extracts as anticorrosion agents or inhibitors which are eco-friendly and harmless. THIS HAS BEEN ONE OF THE FOCUSES OF MY RESEARCH IN CHEMISTRY OVER THE PAST 15 + YEARS.**

- **The use of natural products, which are renewable resources, can be seen as a long term contribution to sustainable development. The prudent exercise of advanced manufacturing technologies within Africa represents an opportunity for us to initiate sustainable, regional production and potentially create markets for export. Africa has an advantage over global industries in this regard by virtue of the ability to implement truly novel technologies without abandoning existing investments in outmoded or less than optimal manufacturing facilities, and by lowering fixed costs in human capital and construction. The elements of achieving sustainable regional production therefore include:**
 - **Coupling indigenous knowledge with good process and manufacturing practices.**
 - **Identifying technologies that are elegant by virtue of their simplicity.**
 - **Designing a "Green footprint" for advanced technology manufacturing and green / sustainable chemistry which includes such concepts as waste minimization, solvent selection, atom utilization, intensive processing and alternative synthetic routes from sustainable resources. The challenge for chemists is to develop products, processes and services in a sustainable manner, to improve quality of life, the natural environment and industry competitiveness.**

- 
- **Green / sustainable chemistry issues are here to stay. The most successful chemical companies of the future will be those who exploit its opportunities to their competitive advantage, and the most successful chemists of the future will be those who use green chemistry concepts in research and development, innovation and education.**
 - **Industries are also discovering that 'green' approaches to chemical processes are not only beneficial to the environment but can boost profits too. It is also a fertile ground for collaboration between academic and industrial scientists.**

ACKNOWLEDGEMENTS



*Thank
you!*

