Relative Performance of Isopropylamine, Pyrrole and Pyridine as Corrosion Inhibitors for Carbon Steels in Saline Water at Mildly Elevated Temperatures

I.M Ibrahim, S Yunus and M.A Hashim

Abstract— Pyrrole, pyridine and isoropylamine are organic chemicals known to possess corrosion inhibition behaviour for carbon steels, and were tested for relative inhibition property in still, moving environment and at mildly elevated temperatures. Saline water was chosen as the working aqueous media, and under these conditions all of these organics exhibited inhibition property. However, it is still unknown which of these organics performed better than another. It is also a known facts that these organics have electron lone pairs in their molecular structures which accounts for surface adsorption on to steel surfaces. Surface adsorption is a phenomenon in which the steel surfaces is being protected from ingression of oxygen molecules to steel surface to initate micro-anodic sites. Inhibition tests showed that pyrrole and isopropylamine out-performed pyridine when present in small quantity in the saline water at various stirring speeds and elevated temperatures. The inhibitive effects was attributed to the surface adsorption phenomenon of the organic molecules on steel surfaces which formed the protective or barrier layers.

Keywords— corrosion inhibitors, , ingresion of oxygen molecules, micro-anodic sites, saline water, surface adsorption phenomenon .

——————————————— ◆ ———————————————

1 INTRODUCTION

Carbon steels are widely employed as the material of conctruction in the processing industries and in other civil structures. In relation to down stream and up-stream processing of crude oil and gas, carbon steels are used as the material for pipelines and storage containers This steel is used due to its advantages such as easiness in fabrication and joining, acccetable tensile strength, availability in the market and relatively low cost. Generally, however, carbon steels are prone to oxidation if it is left unprotected in the aqueous environment, especially in the marine environment. This situation leads to the corrosion processes. Corrosion occurs in the forms of general, galvanic, crevice, pitting, intergranular, selective leaching, erosion and stress corrosion cracking.

Corrosion process also known as an electrochemical process in which a metal will reacts with its environment to form an oxide or other compound. In this electrochemical reaction iron (Fe) will oxidize to form corrosion while, water will cause metals to corrode. The first reaction of corrosion process is an oxidation reaction that converts metal to metal ions and electrons while, a second reaction consumes those electrons by converting oxygen and water to hydroxide ions. In order to these reactions to occur, the electrons must be transported from the place where the metal dissolves to the place where the oxygen is consumed and an ionic current must also flow between the sites to complete the circuit.

This ionic current flows more easily through water containing electrolytes for example sodium chloride, NaCl. This explains the rapid corrosion of unprotected steel in a salty environment. In sea water, water with Cl^- or contaminated aggregates are introduced onto the steel surface, the corrosion protection is damaged. In the general corrosion process of steel, the carbon steel loses its ions at the anode by the oxidation reaction as shown in reaction (1) below:

$$Fe \longrightarrow Fe^{2+} + 2e \qquad \text{(Reaction 1)}$$
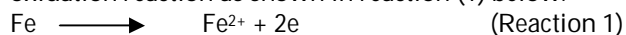
Electrons are released and transported to the cathode for the reduction of oxygen as shown in reaction (2) below:

$$O_2 + 4e + 2H_2O \longrightarrow 4\,OH^- \qquad \text{(Reaction 2)}$$
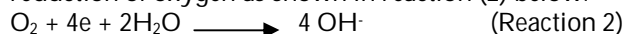
Corrosion inibitor is known as the chemical compund that added into the liquid or gas to decrease or prevent the corrosion rate. In this research, three types of corrosion inibitor are used which are isopropylamine, pyrrole and pyridine. They are choose as the corrosion inhibitor because the presence of nitrogen atom with electron lone pair which participate in the adsorption process.Generally, chemical compound with more than one electron pair binds more strongly to metal surfaces and makes it become more effective as the corrosion inhibitor. Normally, chemical compound that leaves the nitrogen lone pair more exposed for donation. in addition, the three type of chemical compound have sp2-hybridized nitrogen and C-N-C bond angles often perform best as corrosion inhibitor [1]. The presence of an adsorbed chemical layer on the metal surfaces creates a zone of high reactance between the metal surfaces and the electrolyte. This resistance slows down or stops galvanic reactions and the electron loss from the metal surfaces that leads to corrosion.

- I.M Ibrahim & S. Yunus are currently pursuing masters degree program in Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia. Email: zenny_conan@yahoo.com
- M.A Hashim is a member of Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia. Email: aminhashim@salam.uitm.edu.my

The aim of this study is to investigate thhe effectiveness of isopropylamine, pyrrole and pyridine as corrosion inhibitor for carbon steel in saline water at mildly elevated temperature. At the same time, the surface morphology of cleaned and corrosion inibited steel surfaces were examined using Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM).

2 EXPERIMENTAL METHOD

2.1 Specimen Preparation

The specimens are prepared by cutting carbon steel into pieces measuring 10mmx10mm and soldered to nichrome wire where the length of nichrome wire should was about 7 inch. After soldering the nichrone wire was inserted into the PTFE tubing to form the external most casing of about 1 to 1 and half inch from one end, the PTFE tubes was heated and bend to about 90o bend from the horizontal. Next step is prepare the cold mounting polymer by mixing the hardener and the main polymer in a recommended proportion and when the hardened mounting polymer is formed, the specimen was removed from the mould. After that, grinding and polishing processes were done in order to remove scratches brought from the previous grinding stages. The prepared specimens were then stored in a desiccator for the next process.

2.2 Preparation of Test Solution

The test solution used is a 3.5 wt% sodium chloride (NaCl). On a basis of 1000 mL of NaCl solution; a 3.5 wt% NaCl solution requires35 gram of NaCl. This quantity of NaClis carefully placed in a 1000 ml conical flask and was half-filled with distilled water. The flask and its content was carefully swirl to dissolve the salt and later it was top-up to the 1000 mL mark. The flask was then labeled and ready for testing.

2.3 Testing of corrosion inhibitor

The corrosion inhibitor in this research are isopropylamine, pyrrole and pyridine is injected into 800 ml of the prepared NaCl solution in a 1 liter beaker. Then, three electrodes system which comprise of reference electrode, counter electrode and working electrode is then immersed in the beaker. After connecting all the electrodes and the wires are connected, the linear polarization resistance method was selected as the mode of testing. This equipment was worked with help of computer software program.

The inhibitor was injected into the beaker and for every 10 minutes, reading of required parameter was taken until a time of 1 hour. This experiment proceeded from 20 ppm until an addition of 200 ppm of the organic. The values of the polarization resistance were recorded. This research was done at mildly elevated temperatures of 28 oC, 46 oC and 61 oC.

2.4 Surface morphology examination using SEM and AFM

The surface morphology of carbon steel was analyzed by using a Carl Zeiss SMT (SUPRA 40 VP), Scanning Electron Microscope (SEM) and Atomic Force Microscopic (AFM) - Park System (XE-100). The analysis was performed on carbon steel surface under ambient air condition.

Three samples of each different concentration of the organics were selected to be analyzed using SEM and AFM. They are:

- Sample No.1 : A 3.5 wt% NaCl solution without organic addition
- Sample No. 2: A 3.5 wt% NaCl solution with 20 ppm inhibitor addition
- Sample No. 3: A 3.5 wt% NaCl solution with 200 ppm of inhibitor added.

In SEM examination, it was suggested that the magnification of specimen to vary between 1000 to 10,000 times. While surface morphology observation by Atomic Force Microscope (AFM) is to be performed on suggested area measuring 2.5 µm x 2.5 µm and 10 µm x 10 µm.
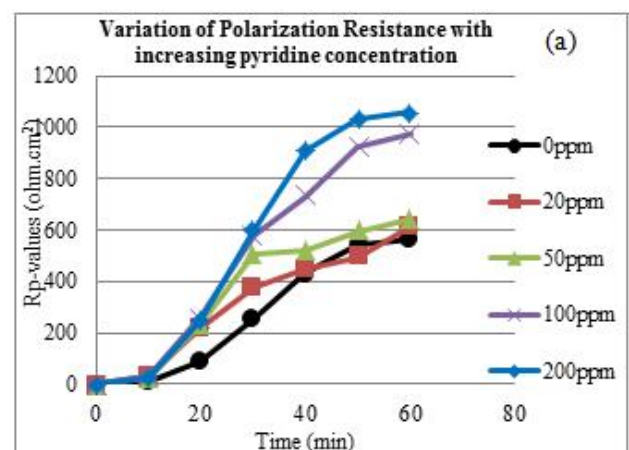
2.5 FTIR analysis

The inhibitors was analyzed using Fourier Transform Infrared (FTIR) Spectroscopy. FTIR is an analysis technique that provides information regarding the molecular structure and also chemical bonding of inhibitors molecules.

3 RESULT AND DISCUSSION

3.1 Polarisation Resistance in still saline water with addition of inhibitors at room temperature

The performance of pyridine, pyrrole and isopropylamine as a corrosion inhibitor for carbon steel when immersed in still saline water at room temperature was studied. Plot of Rp-values against immersion time with increasing addition of inhibitors were shown in Figure 1.
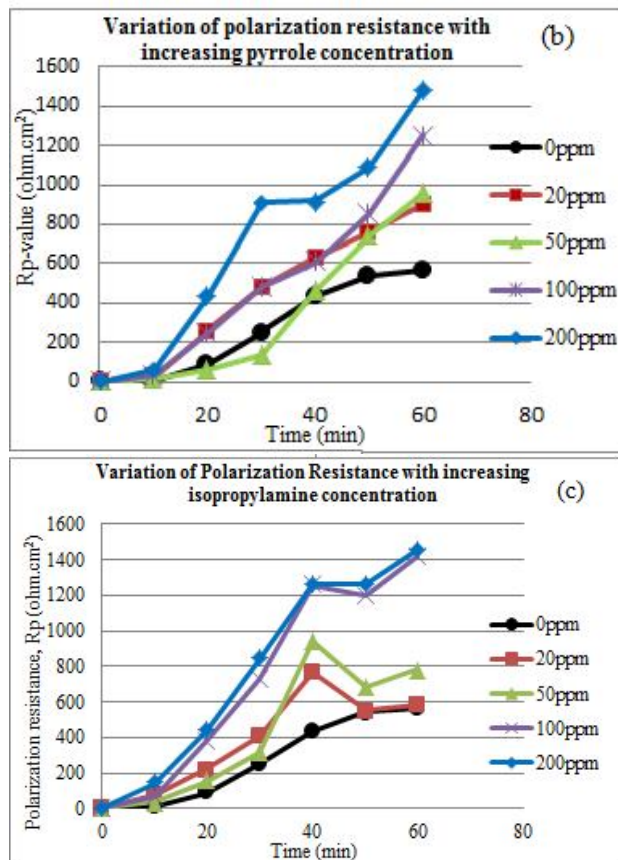
lution (3.5 wt% NaCl) is lowest than those obtained in solutions containing concentration of inhibitors. It means that the corrosion rate of steel that immersed in blank solution is highest than those obtained in solutions containing various concentrations of the inhibitors. It also indicates that the corrosion of carbon steel in saline solution can be inhibited by various concentrations of pyridine, pyrrole and isopropylamine. It was found that the polarization resistance of steel increased with an increased in the concentration of each inhibitor. This is because the increase in concentration of inhibitors in 3.5% sodium chloride solution causes increase in number of protective ions [2]. Therefore, the inhibitory potential of pyridine, pyrrole and isopropylamine for carbon steel increase with increasing concentration of inhibitors [3].

The most important aspect in corrosion inhibition is the relationship between molecular structure and efficiency of corrosion inhibition. Two of investigated inhibitors which are pyrrole and pyridine, both compounds are containing π bonds, nitrogen as well as the aromatic rings in their structure in which these features are the major adsorption centers. While, isopropylamine is a compound that containing heteroatom of nitrogen but not containing π bonds in the structure. The structures of inhibitors are shown in Figure 2.

Figure 1: Variation of polarization resistance with immersion time for (a)pyridine (b)pyrrole, and (c)Isopropylamine concentration in still saline water

Figure 1 shows Rp-values of carbon steel was immersed in saline water without inhibitor and with increasing concentration of pyridine at 20ppm, 50ppm, 100ppm and 200ppm. The carbon steel polarization resistance increases with time. In Figure 1(a) in overall, it is clearly showed that the polarization resistance of steel was sharply increased in the first 30 minute and it decayed at about 50 minute after initial immersion. It is mostly likely after an immersion of 50 to 60 minute the Rp-values may formed a plateau. However, it was not demonstrated in this experiment. Figure 1(b) shows the value of polarization resistance of steel was also found to increase with increasing immersion time. The results show that the corrosion behaviour of carbon steel is significantly different under the different concentration of pyrrole added in the saline solution. Overall, it clearly shows that the polarization resistance of the steel increased sharply in the initial time and then this resistance is keeping higher and higher value until it at 60 minute of immersion time. Figure 1(c) shows that isopropylamine exhibits the instability performance as inhibitor due to the fluctuation of polarization resistance values as immersion time increases.

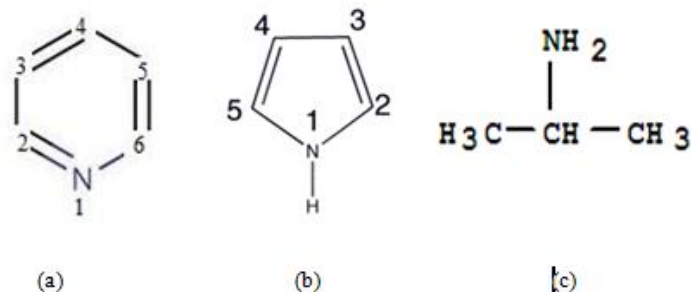The polarization resistance of carbon steel for the blank so-

Figure 2: The structures of (a) pyridine (b) pyrrole, and (c) isopropylamine [4]

Therefore, the efficiency of these compounds as corrosion inhibitors is attributed to the number of electron pair present, the π orbital character of free electrons and the electron density around nitrogen atom. The effectiveness of the functional atom in the adsorption processes varies. There is why the results of polarization resistance obtained from the three investigated inhibitor are different from each other. The performances of those three inhibitors are then discussed according to the concentration (20, 50, 100 and 200 ppm) of inhibitors added to the saline water.

for carbon steel when immersed in moving saline water at mildly elevated temperature was investigated. The effect of different moving environment (300, 600 and 900 rpm) in different temperatures of saline water (28 °C , 46 °C and 61 °C) with different addition concentration of isopropylamine (20,
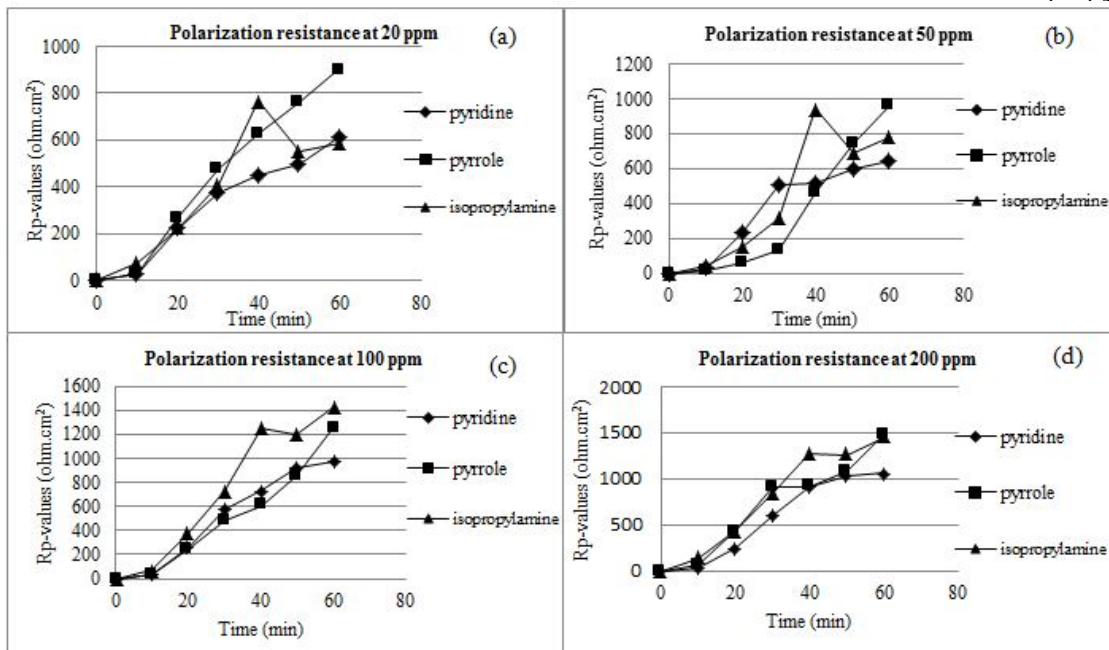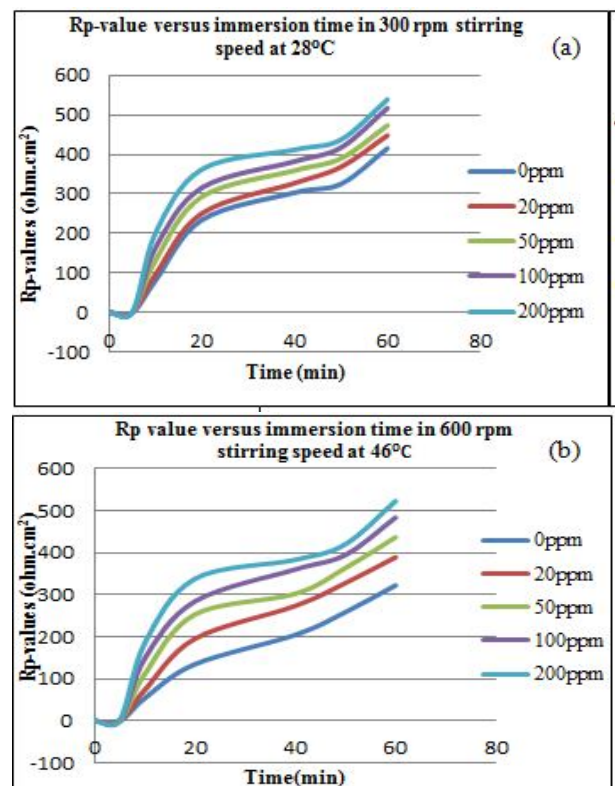

Figure 3: The effect of concentration (a) 20 ppm, (b) 50 ppm (c) 100 ppm and   (d) 200 ppm of three inhibitors in still saline water at room temperature

Referring to the Figure 3 (a), (b), (c) and (d), in general it could be said that, in the range time of 10 minutes to 60 minutes, the polarization resistance, Rp of carbon steel is increased with immersion time. Under small concentration of inhibitors (20 ppm and 50 ppm), it shows that pyrrole inhibitors exhibit excellent performance in inhibiting the corrosion rate by providing the highest resistance to the carbon steel. Under 20 ppm and 50 ppm inhibitor concentrations, the inhibition efficiencies decrease in the following trend, pyrrole > isopropylamine > pyridine. Under concentration of inhibitors 100 ppm, it shows that isopropylamine inhibitors exhibit excellent performance in inhibiting the corrosion rate by providing the highest resistance to the carbon steel. Under 200 ppm concentrations of inhibitors, it shows that isopropylamine as well as pyrrole inhibitors exhibit excellent performance in inhibiting the corrosion rate by providing the highest resistance to the carbon steel. In overall, it shows that pyrrole and isopropylamine exhibit the excellent performance due to both compound containing N-H bonds that are capable in forming surface adsorption of nitrogen molecules and the metal surface and thus acting as strong adsorption type inhibitors [5].

3.2 Polarisation Resistance in moving saline water with addition of isopropylamine at mildly elevated temperatures

The performance of isopropylamine as a corrosion inhibitor

50, 100 and 200 ppm) were conducted. These values were arbituary chosen. Plots of Rp-values against immersion time with different stirring speed and temperature were shown in Figure 4.
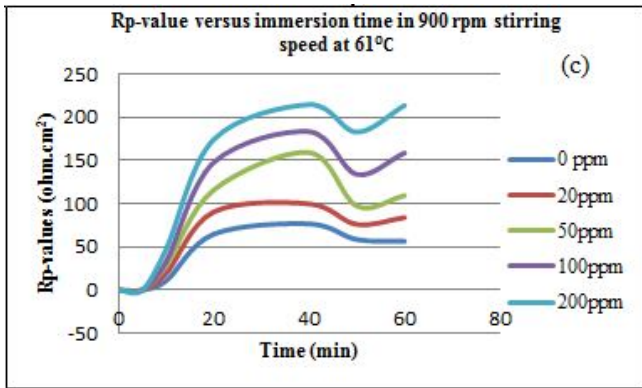
Figure 4: Variation of Rp-value with immersion time at different stirring speeds and temperatures.

The plotted graphs show the effects of elevated temperature of saline water decreased the Rp-values of the carbon steel therefore it indicates that the corrosion rate of carbon steel increased at elevated temperature of saline water. This is because, increasing temperature of saline water results in greater anodic dissolution therefore more irons (Fe) ions are available in the saline water. Besides that, there is a net increase in dissolved oxygen in the saline water as the results of temperature rise and increased in stirring speeds. Dissolved oxygen in saline water has an influence on corrosivity of steel specimen since the oxygen is the principal reactant involved in the cathodic reaction and it is involved in the passivation reactions that occur for most metals in aqeous media. Stirring speed is the one of factor that affects the corrosion inhibitor performance. The Rp-value of carbon steels decreased when the stirring speed increased (300, 600 and 900 rpm). It indicated that the corrosion rate of carbon steel is increased because at sufficiently high stirring speed, there is enough oxygen molecules to reach the steel surface and causes an increased in rate of corrosion.

The addition of isopropylamine increases the values of polarization resistance of carbon steel. When immersion time increased, the Rp-values of carbon steel also increased. In fact, with increasing concentration of isopropylamine (20, 50, 100 and 200 ppm) added to saline water, it increased the Rp-value of carbon steel. This is because an increase in the concentration of isopropylamine water causes an increase in number of adsorption molecules on the metal surface. Indirectly, it shows that the presence of nitrogen atom with electron lone pair in the molecular structure of isopropylamine is effective in inhibiting the corrosion rate by creating adsorption (protection) layer on the steel surface. However, when the stirring speed was increased to 900 rpm at 61ºC, the Rp-value was observed decreased. It may need more concentrated dosing of isoprop-

ylamine in order to maintain the Rp-value as was obtained at lower temperatures and lower stirring speeds.

3.3 Surface Morphology Studies by SEM technique

Surface morphology of carbon steel specimen that immersed in 3.5wt% sodium chloride solution without and with inhibitors in still, moving environment and at mildly elevated temperatures was investigated and were shown in Figure 5.
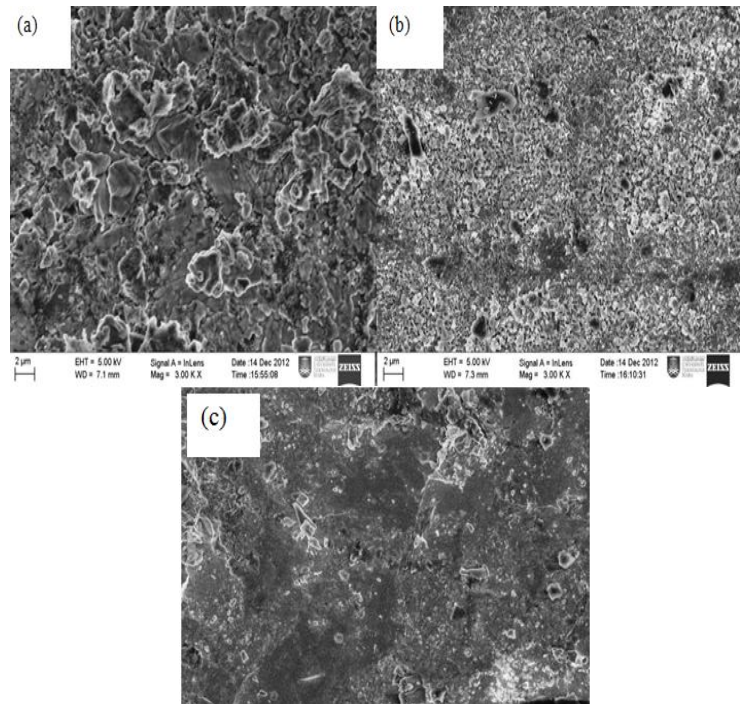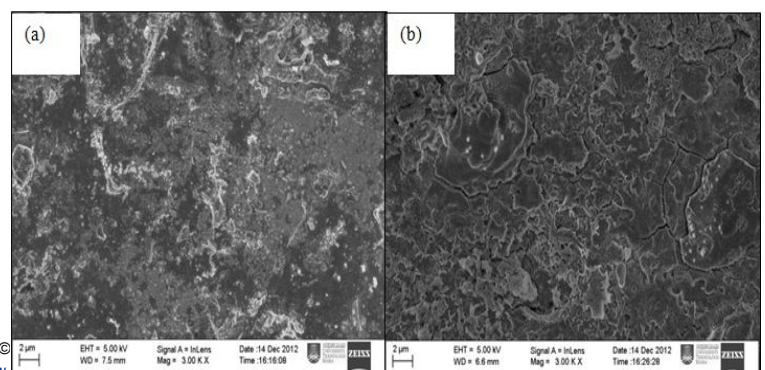

Figure 5: Specimen surface morphology (a) in absence of isopropylamine (b) addition of 20 ppm pyrrole, and (c) addition of 200 ppm isopropylamine

Figure 5(a) shows the corrosion products deposit on the surface of carbon steel in absence of inhibitor and it appears as irregular globular structures known as cotton balls [6]. Figure 5(b) shows an irregular porosity structure of corrosion layer on the specimen's surface is due to penetration of easy access corrosive species to the metallic substrate [6]. Figure 5(c) shows good condition of carbon steel due to the effective protection of carbon steel specimen with addition of 200 ppm of isopropylamine inhibitor.
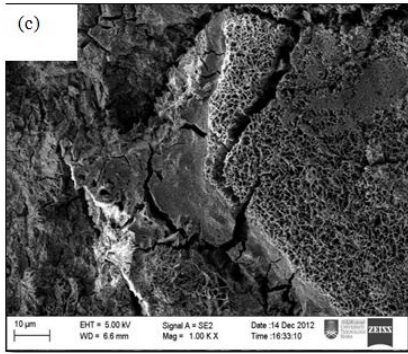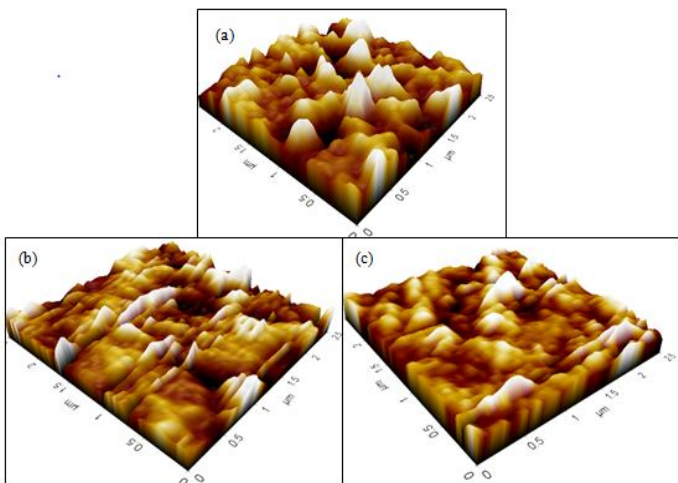
Figure 7: Comparative three dimensional AFM images of carbon steel immersed in still saline water (a) with absence of inhibitor (b) with presence of 20 ppm pyrrole (c) with presence of 200 ppm isopropylamine.

Figure 7(a) is a surface morphology obtained using AFM in the absence of isopropylamine showing a lot of bulges. These bulges are thought to be corrosion product which was formed on bare metal surfaces. Figure 7(b) shows lower surface roughness than in Figure 7(a) which indicated it has smoother surface morphology compared to the unprotected steel surface. Figure 7(c) displays the surface morphology of thel surface with the smoothest structure compared to the other two images displayed, indicating that this metallic surface is protected from oxidation.
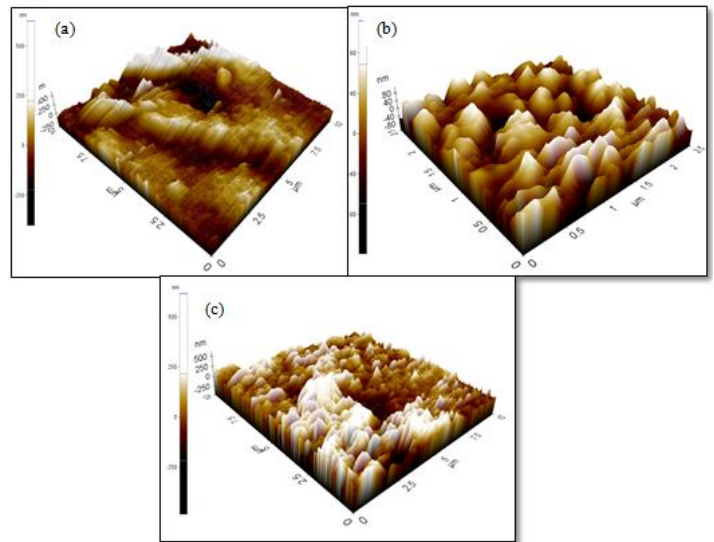

Figure 8: Comparative three dimensional AFM images of carbon steel immersed in saline water added 20 ppm with (a) 300 rpm at 28 $^\circ$C (b) 600 rpm at 46 $^\circ$C (c) 900 rpm at 61 $^\circ$C

Figure 8(a) shows it is not much bulges appear at the surface of sample and surface roughness is also low which indicate the corrosion rate occurred during this condition is low. Figure 8(b) shows there is more bulges arise on the metal surface compared to the previous image. Then, Figure 8(c) shows a lot of bulged appeared on the carbon steel surface. It means a lot of corrosion product deposited resulting from high state oxide during the experiment.

3.5 FTIR Analysis

FTIR analysis was conducted on the selected organic chemicals to confirm their purity and also to confirm the presence of various radicals in the organic molecules.

3.5.1 Pyridine

FTIR analysis on pyridine reveals the information as shown in Table 1.

Figure 6: Surface morphology on addition of 20 ppm isopropylamine and at (a) 300 rpm at 28 $^\circ$C, (b) 600 rpm at 46 $^\circ$C, and (c) 900 rpm at 61 $^\circ$C

The Figure 6 (a) shows there is no corrosion products deposited on the steel's surface. Figure 6 (b) shows structures of cracking on the metal surface indicating there is corrosion occurring on the specimen's surface. However, surface cracking on the steel surface was observed to be immense, when immersed in the higher stirring speed and water temperature, as shown in Figure 6 (c).

3.4 Surface Morphology Studies by AFM technique

AFM is a powerful technique to investigate the surface morphology at nano to micro-scale and currently has become a preferable choice to study the influence of inhibitor on the generation and progress of the corrosion at the metallic interfaces. The three dimensional (3D) AFM images for the steel surfaces immersed in still, moving saline water and at room temperature and elevated temperatures are as shown in Figure 7.

bonding and C=C bonding in the molecule. This helps very much the adsorption phenomenon of pyrrole on the surface of carbon steel. The FTIR spectrum for pyrole is shown in Figure 10.

3.5.3 Isopropylamine

Table 3 shows the FTIR spectrum obtained for isopropyl-mine.

Table 1: FTIR spectrum for Pyridine

| Radical | Wavelength (cm^{-1}) | | Inferences |
	Literature [7]	FTIR reading	
C = C	1700 – 1500	1579.82 1597.22	C=C bonds in molecule.
C = N	1660 – 1480	1632.89	C = N bond in molecule.
C – H	860 – 680	699.52 746.51	Presence of C – H bond in molecule.
C – N	1200 – 1025	1029.92 1068.0 1146.33	C-N bonds in the molecule is exist in the structure

The FTIR spectrum reveals the presence of C=C bonds and C-N bond which help in the surface adsorption phenomenon. It also shows the purity of pyridine used in the test conducted. The FTIR spectrum for pyridine is shown in Figure 9.

3.5.2 Pyrrole

FTIR analysis on pyrrole reveals the information as collected in Table 2.

Table 2: The FTIR spectrum for Pyrrole

| Radical | Wavelength (cm^{-1}) | | Inferences |
	Literature [7]	FTIR reading	
C = C	1700 – 1500	1529.20 1568.88	C=C bonds in the molecule.
C – H	860 – 680	721.72 838.51	Bonding of C – H in the molecule
C – N	1200 – 1025	1046.85 1074.24 1141.94	C-N bonds in the molecule
N – H	3500 – 3300	3392.98	N – H bonding in the molecule

FTIR spectrum examination reveals the presence of N – H

| Radical | Wavelength (cm^{-1}) | | Inferences |
	Literature [7]	FTIR reading	
C – H	2960 – 2850 1350 – 1470	2872.92 2958.28 1379.15	Presence of C – H bonding in the molecule.
N – H	3180 – 3500	3281.06 3359.06	Presence of N – H bonding in the molecule.
C – N	1200 – 1025	1035.88 1132.25 1171.05	Presence of C – N bonding in the molecule.
C(CH$_3$)$_2$	1150–1130 1175–1165	1132.25 1171.05	Alkane residues attached to carbon

Table 3: FTIR spectrum for Isopropylamine

FTIR spectrum of isopropylamine is shown in Figure 11. The FTIR spectrum analysis shows the presence of N – H bonding in the molecule. This is the source of adsorption which takes place on the surface of carbon steels.

4 CONCLUSION

The research work demonstrated that pyridine, pyrrole and isopropylamine are corrosion inhibitors for carbon steels exposed to the conditions described. The effective amount to be added depends very much on the surface adsorption capability of these organics on the steel surfaces, and they are easily upset by environmental conditions such as changes in fluid flow velocity and temperatures.
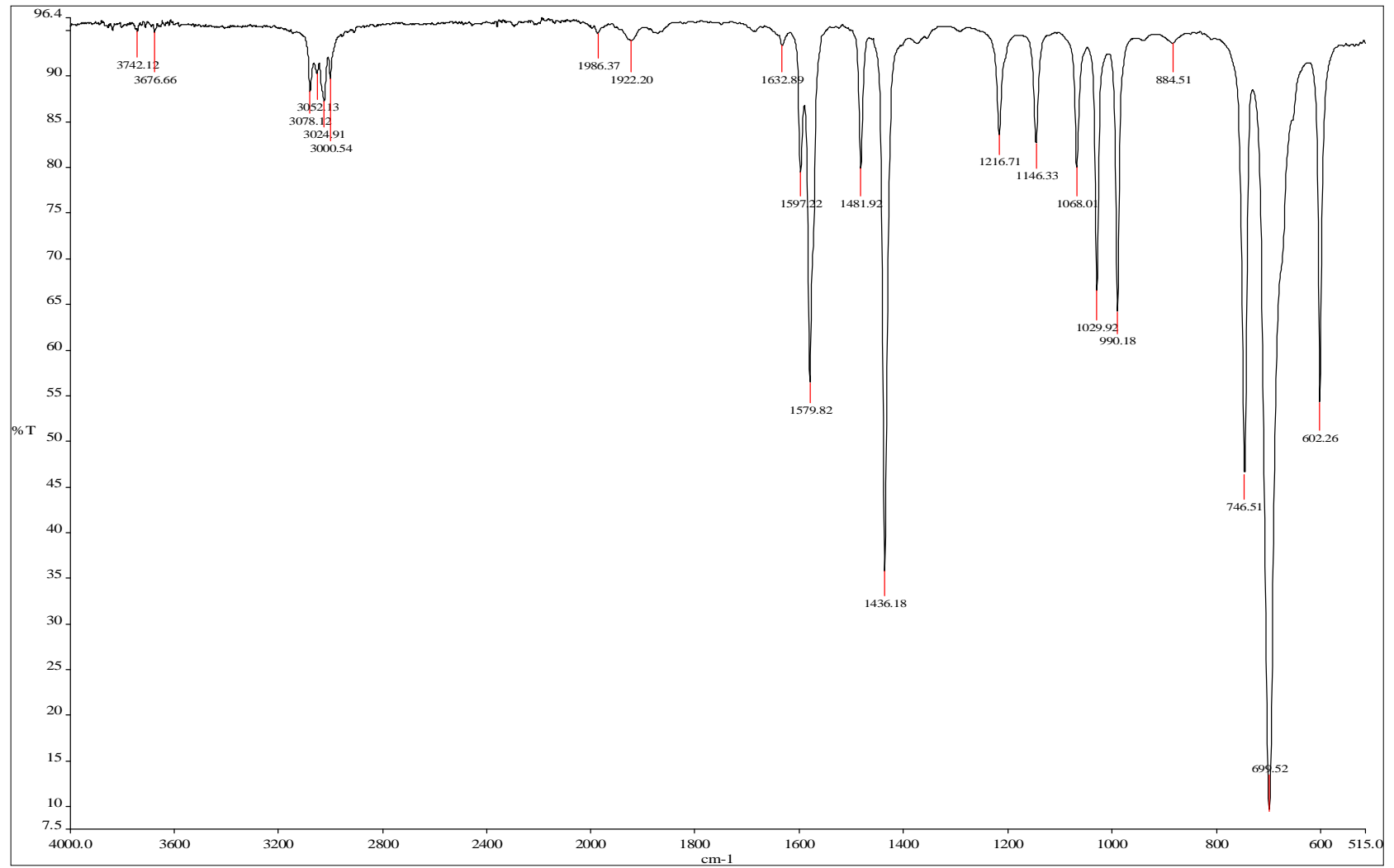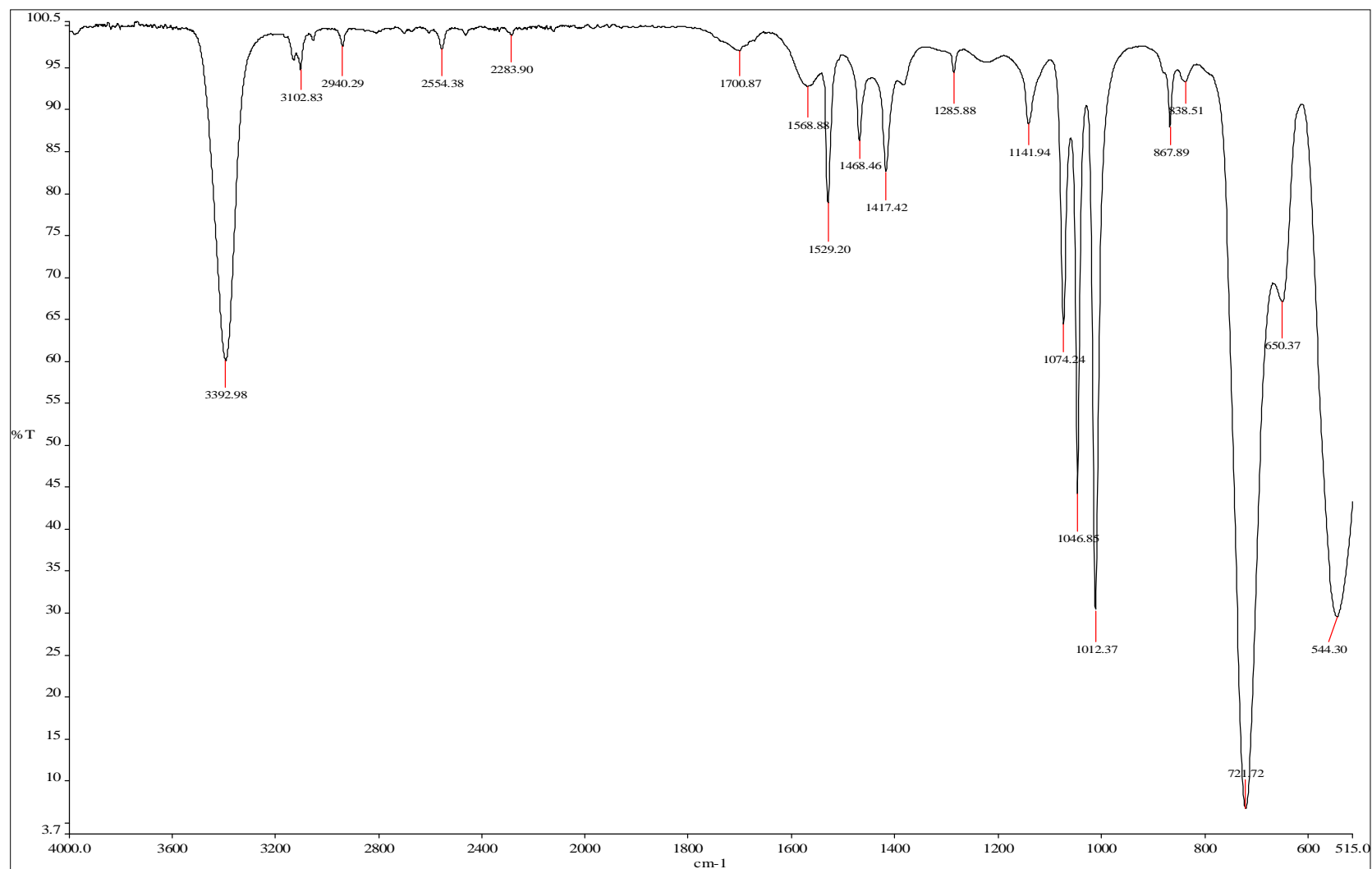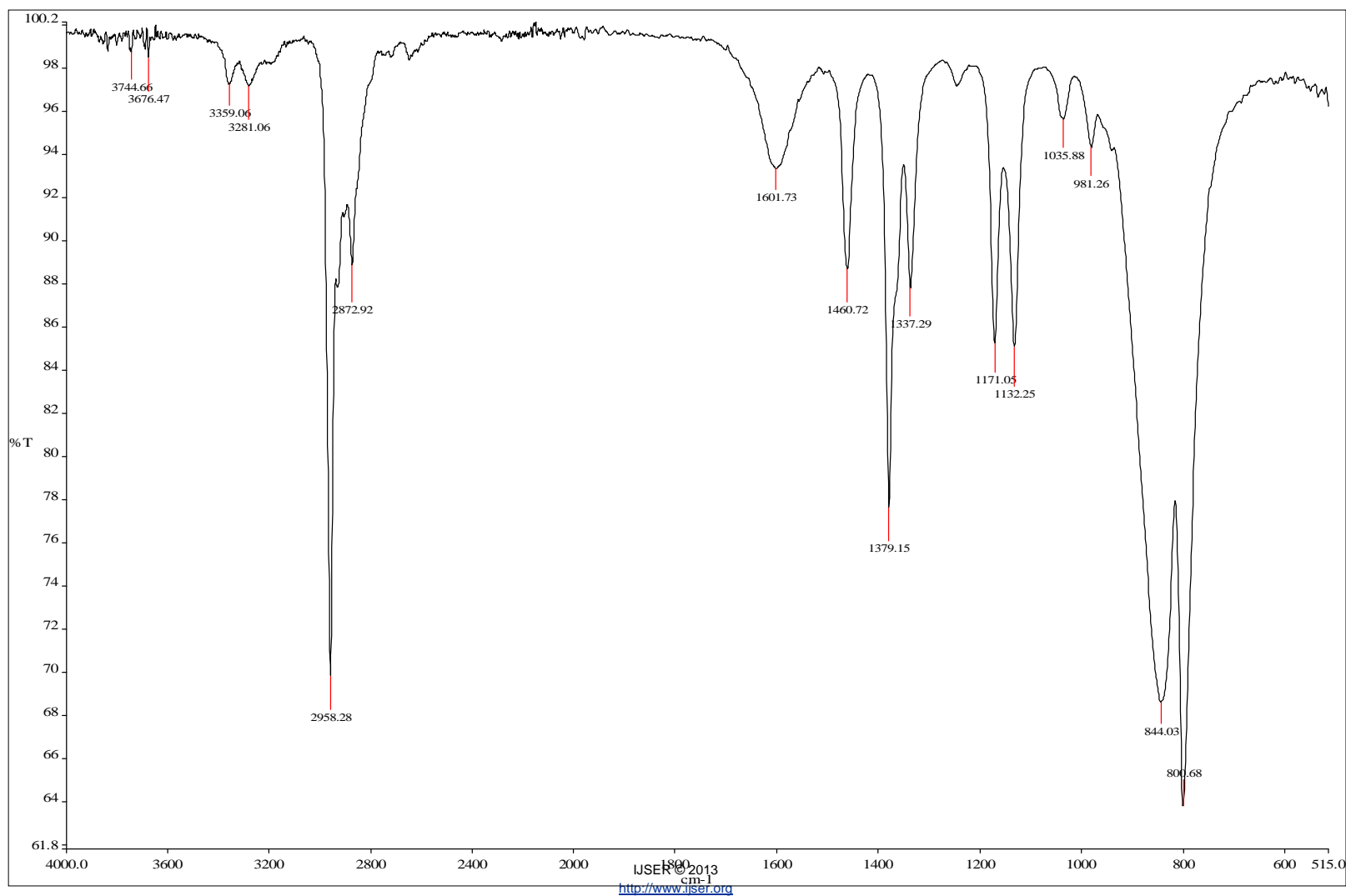
Figure 9: FTIR spectrum of Pyridine

Figure 10: FTIR spectrum of Pyrrole

Figure 11: FTIR spectrum of I

ACKNOWLEDGMENT

REFERENCES

[1]   Lawrence, S.A. (2004) *Amines: Synthesis, Properties and Applications*. New York: The Press Syndicate of The University of Cambridge.

[2]   Acharya, S. and Upadhyay (2004) Inhibition of Corrosion of Mild Steel by some Fluoroquinolones in Sodium Chloride Solution. *Trans. Indian Inst. Met.* Vol.57, No. 3, pp. 297-306.

[3]   Ebenso, E.E., Isabirye, D.A. and Eddy, N.O. (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, pg: 2473-2498.

[4]   Gensler, W.J. (2008) Pyrrole in Access Science, ©Mcgraw-Hill Companies, 2008,

[5]   Loto, R.T., Loto, C.A., Popoola, A.P.I., and Ranyaoa, M. (2012) Pyrimidine derivatives as environmentally-friendly corrosion inhibitors: A review. *International Journal of Physical Sciences.* Vol. 7(14), pg: 2136 – 2144.

[6]   Tiwari, A and Hihara, L.H. (2007) High Silicone Content Barrier Coatings for Corrosion Protection of Metals. *Tri-Service Corrosion Conference.*

[7]   Gokel, G.W. (2004) Dean's Handbook of Organic Chemistry. Mcgraw-Hill