IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.17 No.1 (March 2016) 21- 36
ISSN: 1997-4884

University of Baghdad
College of Engineering

Corrosion Inhibition of Low Carbon Steel in Sulfuric Acid Using Polyvinyl Alcohol

Majid I. Abdulwahab*, Ayad B. Ahmed and Aprael S. Yaro***
**Chemical Eng. Department University of Baghdad*
***Medical Tech. Inst. /Al-Mansour Middle Technical University*

Abstract

The inhibitive power of Polyvinyl Alcohol (PVA) was investigated toward the corrosion of carbon steel in 0.2N H_2SO_4 solution in the temperature range of 30-60˚C and PVA concentration range of 150-2000 ppm.

The corrosion rate was measured using both the weight loss and the electrochemical techniques. The weight loss results showed that PVA could serve as a corrosion inhibitor but its inhibition power was found to be low for the corrosion of carbon steel in the acidic media. Electrochemical analysis of the corrosion process of carbon steel in an electrochemical corrosion cell was investigated using 3-Electrode corrosion cell. Polarization technique was used for carbon steel corrosion in 0.2N H_2SO_4 solutions in presence and absence of the inhibitor investigated. Electrochemical runs were done in the PVA concentrations of 150, 1000, and 2000 ppm and temperatures of 30, 40, 50, and 60˚C.

It was shown that the inhibition efficiency for PVA decreased with increasing temperature at a given PVA concentration. On the other hand it was shown that at given temperature the inhibition efficiency of PVA was increased with increasing of PVA concentration in the corrosive acid until a PVA concentration of 2000 ppm was reached.

The Maximum inhibition efficiency reached was about 71 % at 30ºC and 2000 ppm concentration, calculated by the weight loss technique. It was indicated also that the corrosion of carbon steel in 0.2N H_2SO_4 is highly activation controlled and inhibition action is occurring at both anodic and cathodic sites on the metal surface.

Key Words: Carbon Steel, Corrosion Inhibition, Sulfuric Acid, PVA, Weight Loss, Polarization.

Introduction

Carbon steel alloys are widely used in most industries for its low cost and availability in case for fabrication of various reaction vessels such as heat exchangers, cooling towers, and pipes [1]. Corrosion of metals in contact with acids as in acid cleaning of metal surfaces indicates that the use of inhibitors is necessary [2]. Many reports on using organic compounds as potential corrosion inhibitors for metals in acidic media are available [3, 4]. Inhibitors especially the organic ones work by an adsorption mechanism. The resultant film of inhibitor protects metal by blocking the metal surface from the environment so retarding the electrochemical processes. A number of reviews on the organic inhibitors for metals in different media are available [5, 6].

Polymers are used as corrosion inhibitors because; through their functional groups can form complexes with metal ions and on the metal surface, these complexes occupy a large surface area, protecting the metal from corrosive attack.

The applications of water-soluble polymers are related to their outstanding properties. The film forming and adhesive qualities enable nearly all water-soluble polymers to find uses as binders, thickeners and adhesives. The use of water-soluble polymers as corrosion inhibitors has attracted considerable attention in recent times due to the fact that they have been shown to be low cost and stable for metallic materials in acidic environment [7,8,9].The application of polyacrylic acid and polyacryl amide as corrosion inhibitors for iron and steel in H_2SO_4 and HCl has been reported [10,11]. Other polymers studied to date include poly vinyl imidazoles [9], poly vinyl pyrrolidone, poly ethyl enimine, aliphatic polyamines, and poly vinyl pyridines, poly anilines [12, 13, and 14].

Water soluble polymers as promising corrosion inhibitors are low cost and essentially stable for metallic materials in acidic environment [15, 16, and 17]. Most organic inhibitors act by adsorption on the metal surface [18]. The inhibitive power of these polymers is related structurally to the cyclic rings and heteroatoms (oxygen and nitrogen) that are the active centers of adsorption. The polymers form complexes with metal ions on the metal surface which occupy a large surface area and protect the metal from corrosive attack by agents present in the solution [17].

Attempts were made to study polyvinyl alcohol (PVA) as corrosion inhibitor for carbon steel in acidic media. [19, 20].

The present study is aimed at investigating inhibitive and adsorption properties of a water soluble polymer (PVA) for the corrosion of mild steel in 0.2N H_2SO_4. An aim also was to find the effects of inhibitor concentration and temperature on the inhibition efficiency. The concentration range of polyvinyl alcohol was 0.15 – 2.0 g/l, while the temperature range was 30- 60^oC.

Experimental Work

1- Materials and Equipment

Throughout this study carbon steel with the following composition was employed in all tests. The analysis of the carbon steel specimens in wt. % was Mn 1.4, P 0.045, C 0.15, S 0.04 and the rest is Fe analyzed at the State Company of Geological Survey and Mining. Rectangular shaped coupons with dimensions 1cmx3cmx0.1cm were used in the weight loss experiments.

Thermodynamically controlled water baths was used to maintain the metal coupons in experimental designed temperatures. The temperature variations was no more than ± one degree Celsius all the time and this was done by carefully monitoring the temperature in corrosion cells through thermometers immersed in the corrosive media.

Analar sulfuric acid was used in preparing solutions to simulate the corrosive media. Double distilled water was used in all acid dilution preparation steps to ensure the desired solution concentrations. The desired acid- inhibitor concentration was obtained for each run.

Water soluble polymer polyvinyl alcohol (PVA) was used as inhibitor in this study. Different grades are available in practical use depending mostly on the polymer molecular weight. The molecular mass and of PVA used in the present investigation is 15000 g/mole and the molecular formula is shown in Fig. 1:

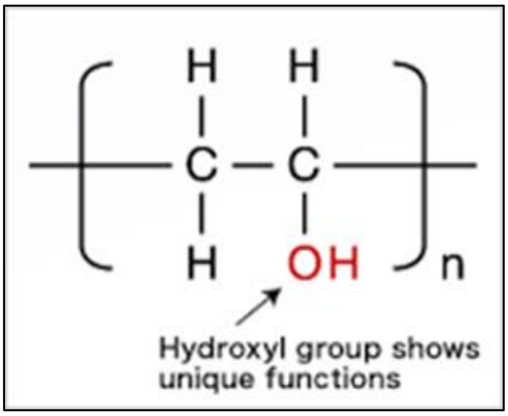

Fig. 1, Chemical formula of Polyvinyl Alcohol

2- Specimen Preparation

The rectangular test specimens with dimensions (1x3x0.1) cm were cut and a hole for suspension of 0.1 cm in diameter were made in the upper suspension area so that it can be hanged by an inert Teflon thread used to hold the coupons in position during experiments. Thermal stresses are released by annealing the coupons in a vacuum furnace at 600°C for 1 hour; the coupons were left in furnace to cool gradually to room temperature.

The coupons then are kept in a desiccator over silica gel bed until future use. Prior to weight loss experiments each coupon was abraded under running tap water using silicon carbide emery papers of different grades beginning with number 200,300,400 and 600 then washed by distilled water ,dried with clean tissue, then immersed in absolute ethanol, dried, immersed in annular acetone then dried again. The cleaned coupons were then kept in a desiccator over silica gel bed ready for use.

3- Experimental Procedure

Experiments were conducted under total immersion conditions of the pre cleaned carbon steel coupons in aerated and unstirred 400 ml of the respective inhibitor/blank solutions maintained at the desired temperatures of 30^{o}C, 40^{o}C, 50^{o}C, and 60^{o}C in a thermostatic water bath (± 1 °C). The immersion period was 3 hours for each experiment at the desired temperature, acid concentration and inhibitor concentration. At the end of the exposure time the metal coupons were withdrawn, cleaned, washed with running tap water followed by distilled water, then dried with clean tissue, followed by immersion in absolute ethanol, dried, immersed in analar acetone, dried then saved in a moisture free desiccator ready to be weighed. The dimensions of each coupon were measured with a vernier to the second decimal of millimeter and the analytical balance weigh accuracy was to the 0.0001 gram.

4- Polarization Experiments

The potentiostat type used in this study was Weking M-lab 200 supplied from the Bank Electronic company originated in Germany. This potentiostat has two data channels and two corrosion cells could be connected at the same time.

A one liter spherical shaped glass vessel, with five necks to insert three electrodes, a thermometer, and a gas inlet opening. The vessel has a heat exchanging jacket with openings for inlet and outlet heat regulating water imported from a nearby thermostatic water thermostatic bath. Figure 2 shows a schematic diagram for the electrodes arrangement in the corrosion cell.

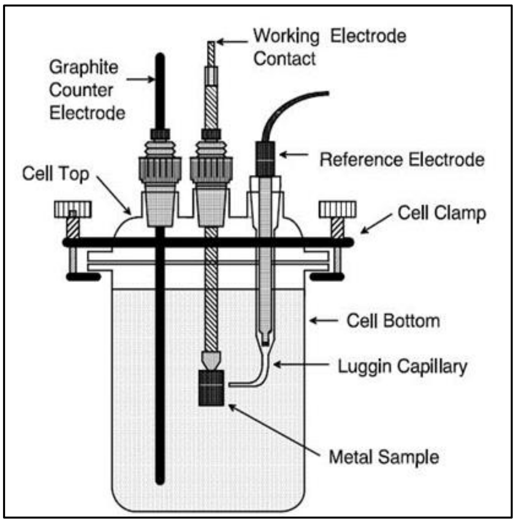

Fig. 2, Schematic Diagram of the Corrosion Cell

The cell holds three electrodes; the working electrode was mild steel cut in circular shape, 1cm^2 surface area fitted in the electrode holder. The reference electrode (saturated calomel electrode) was used throughout this work which is calibrated with standard calomel electrode. This electrode consists from a paste of mercury and mercury chloride (Hg_2Cl_2) which are in contact and equilibrium with chloride ions in potassium chloride solution (KCl). The reference electrode was hosted in the Luggin capillary which is made of glass or plastic and is generally filled with the test solution.

The third electrode was the counter electrode or auxiliary electrode. This was made from platinum metal and it is fixed in the electrode holder in a similar way to working electrode. It was saved in de-ionized water to be ready for use.

The auxiliary electrode is distinct from the reference electrode, which establishes the electrical potential against which other potentials may be measured, and the working electrode, at which the cell reaction takes place.

The corrosion cell heat jacket is connected to efficient water thermostatic bath equipped with circulating water pump (Fig. 3). The observed efficiency of temperature control was± 1℃.

Fig. 3, Picture of the Thermostatic Water Circulating Bath

The potentiostat was interfaced with a PC for intercepting results obtained. The PC has a software named M-Lab installed in advance .The potentiostat input and output menus is digitized by the PC and readings were available to be read on a monitor. Both potentiostat modes, i.e. the open circle mode, and the polarization mode, were controlled by commands designed through the software. Steady state duration times, operation modes, scan rates, types and potential sweep magnitude in addition to many functions and commands were controlled through software commands and adjustments. Figure 4 shows a picture of Tafel plot of the M-Lab Software.

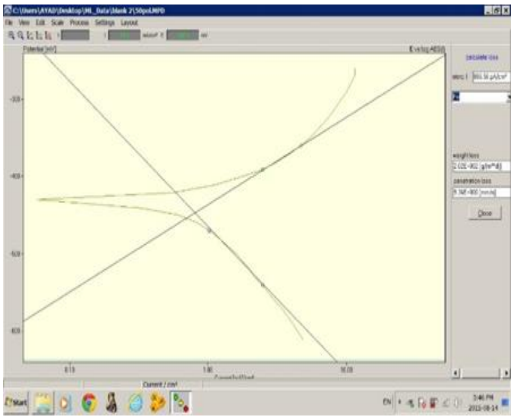

Fig. 4, Picture of Tafel Plot of the M-Lab Software

5- Polarization Procedure

Polarization methods involve changing the potential of the working electrode and monitoring the current which is produced as a function of time or potential. Polarization mode is used to perturb the equilibrium corrosion process.

The response is used to develop a model of the sample's corrosion behaviour.

The potentiostat has two tasks: To measure the potential difference between working electrode and reference electrode without polarizing the reference electrode, and to compare the potential difference to a preset voltage and force a current through the counter electrode towards the working electrode in order to counter act the difference between preset voltage and existing working electrode potential.

Prior to each test the working electrode was cleaned and abraded with emery paper in the recommended sequence and the reference electrode, counter electrode held in position in the cell with taking care that the Capillary Login tip is located near the working electrode.

Figure 5 shows a picture of combined of the experimental arrangement including corrosion cell, potentiostat, circulating thermostatic water bath, and PC assembly.

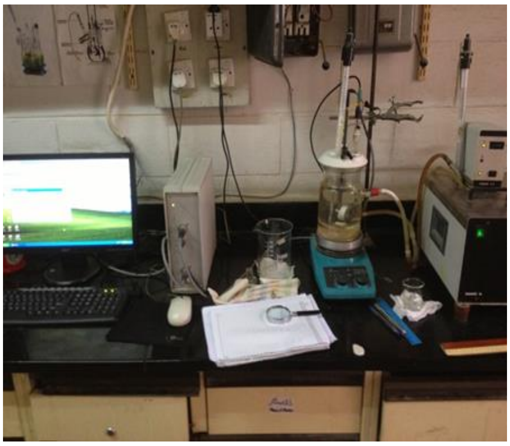

Fig. 5 Combined Corrosion Tests Assembly

Before starting the polarization, the rest potential (OCP) should be allowed to achieve a stable value. Then the working electrode is polarized 200 mV from the rest potential in the anodic and cathodic directions. Tafel plots were established and corrosion currents were calculated.

Results and Discussion

1- Weight Loss Data

The corrosion rates of carbon steel in 0.2 N H_2SO_4 solutions as function of temperature in absence and presence of different concentrations of Polyvinyl Alcohol (PVA) are summarized in Table 1 the following two equations were used to calculate weight loss corrosion rate and inhibition efficiency respectively.

$$CR\ (gmd) = weight\ loss\ (g)/area\ (m^2) \times time\ (day) \quad \ldots (1)$$

$$IE\% = (CRun_{.}-CR_{in.}) / CR_{un.} \quad \ldots (2)$$

Where;

$CR_{un.}$ And CR_{in} represents the corrosion rates (gmd) in absence and presence of inhibitor, respectively.

In Table 1, the values of the corrosion rate are calculated as grams per square meter per day which is denoted (gmd) here after.

Table 1, Corrosion Rate Data ($gm^{-2}d^{-1}$) as a Function of Temperature and Inhibitor Concentrations for Carbon Steel

C(g/l)	Corrosion rate (gmd)				IE %			
Temp.	30	40	50	60°C	30	40	50	60°C
0	97.6	135.2	242.2	392.7	-	-	-	-
0.15	35.2	59.97	114.0	232.8	63.8	55.6	52.9	40.7
0.5	30.5	56.45	105.8	225.7	68.7	58.3	56.3	42.5
1.0	28.2	52.92	99.96	214.0	71.1	60.9	58.7	45.5
1.5	25.8	44.69	94.08	201.0	73.5	66.9	61.2	48.8
2.0	22.3	41.16	87.79	168.1	77.1	69.6	67.4	57.2

2- Corrosion Rate Evaluation

a. Uninhibited Acid

It was found that the corrosion rate of carbon steel in 0.2N H_2SO_4 acid increased from 97.6 g/m^2 .day to 392.78(gmd) as the temperature increased from 30 to 60 ºC. Figure 6 shows the variation in corrosion rate with temperature.

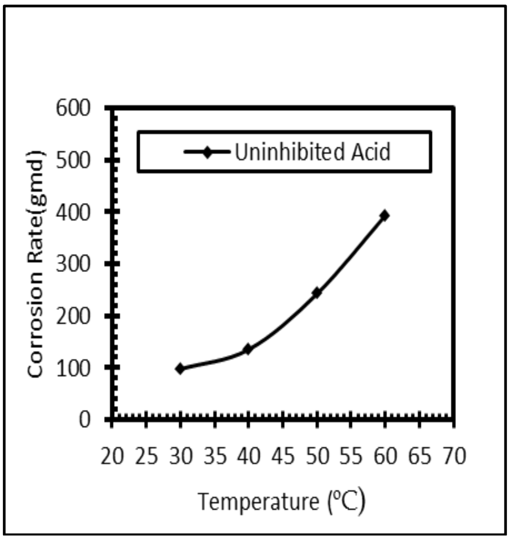

Fig. 6, Variation of Corrosion Rate of Carbon Steel in Uninhibited 0.2 N H_2SO_4 at Different Temperatures at Exposure Time 3h

It is obvious that the corrosion rate is highly dependent on the temperature of the uninhibited acid; this dependence is more sharp at higher temperatures, it was found that the corrosion rate nearly increased four folds in the temperature range 30-60 ºC with big jumps happening in the temperature range 40-60 ºC while less effect was noticed at lower temperatures, i.e. from 30-40 ºC. This behavior might be attributed primary to higher acid dissociation and hence more hydrogen ions available for the cathodic reaction to proceed.

b. Inhibited Acid

Generally the addition of (PVA) reduces the corrosion rate; the reduction depends on the amount of inhibitor added. Table 1 and Fig. 7 show the variation of corrosion rate with (PVA) concentration at various temperature levels

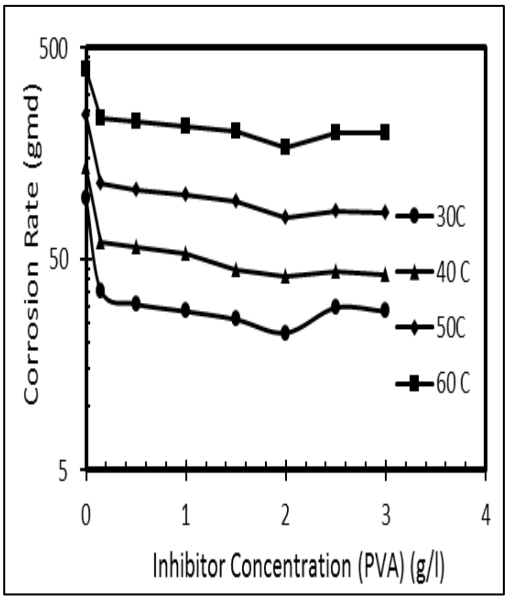

Fig. 7, Effect of PVA Concentration on the Corrosion Rate of Carbon Steel exposed to 0.2 N H_2SO_4 at Different Temperatures, Immersion Period 3 hr.

As the concentration of PVA increases from 0.15 to 2.0 g/l, the corrosion rate decreases from 35.28 to 22.34 gmd at 30ºC, from 59.97 to 41.16 gmd at 40ºC, from 114.07 to 78.79 gmd at 50ºC, and from 232.84 to 168.17gmd at 60ºC, as shown in Fig. 8. It is clear that the inhibitor efficiency decreases with increasing the temperature. The maximum value of inhibitor efficiency was 77.1% at 2 g/l PVA concentration and 30 ºC.

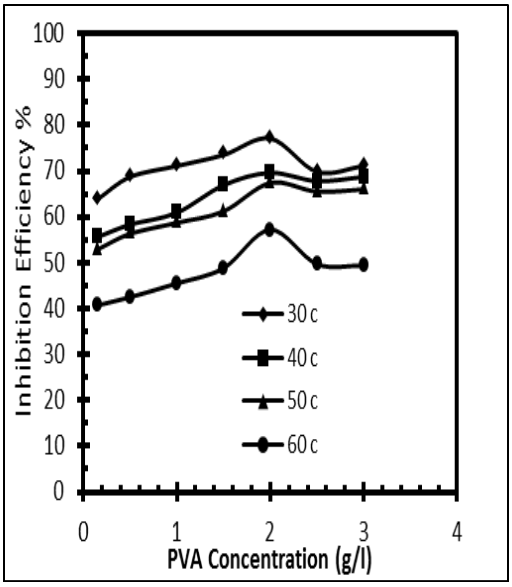

Fig. 8, Variation of PVA Inhibiting Efficiency with PVA Concentration for Low Carbon Steel in 0.2N H_2SO_4 at Various Temperatures, Immersion Time 3 hr.

3- Effect of Temperature

As observed from Table 1 and the preceding discussions the corrosion rate increases with increasing temperature for all concentrations of inhibitors used. To get more information on the role of temperature on the inhibitor performance some thermodynamic properties were calculated. Applying Arrhenius equations to the experimental data in Table 1, plotting the logarithm of corrosion rates versus the reciprocal of absolute temperatures should give straight lines with slopes equal to –2.303 E/R. From best line fitting to the experimental points the activation energy for corrosion at each temperature was calculated. Figure 9 shows Arrhenius plots used to calculate the activation energy for PVA inhibitor.

The results of this plot are listed in Table 2.

Table 2, Activation Energies for the Corrosion Reaction of Carbon Steel in Presence and Absence of PVA for Temperature Range 30-60°C

PVA Inhibitor Concentration(g/l)	Activation Energy (kJ/mol)
0.00	39.88
0.15	52.82
0.50	55.58
1.00	54.45
1.50	57.73
2.00	56.22

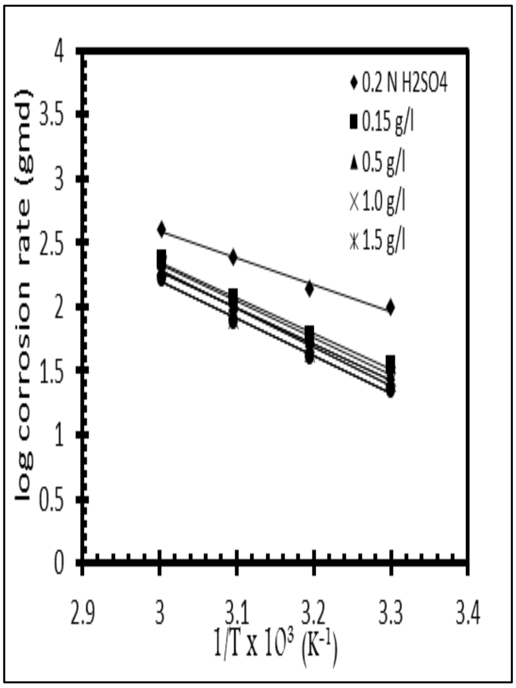

Fig. 9, Arrhenius Plots for Log Corrosion Rates versus Reciprocals of Temperature in Presence and Absence of Different concentrations of PVA

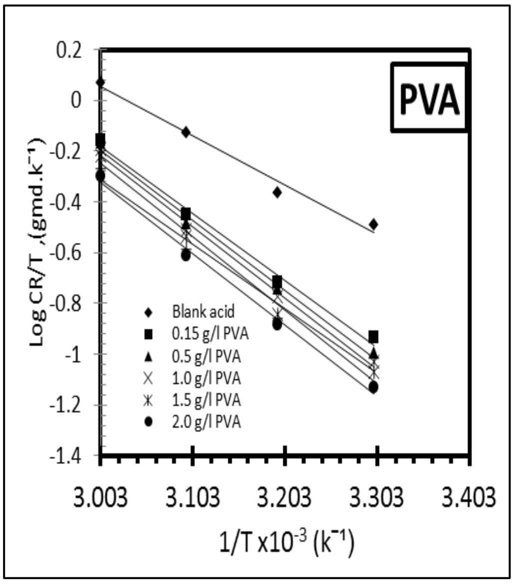

Fig. 10, Transition State Plot for Carbon Steel in 0.2 N H_2SO_4 in Absence and Presence of Different Concentrations of PVA

4- Thermodynamic Parameters of the Corrosion Process

Experimental corrosion rates from weight loss technique for carbon steel in 0.2 N H_2SO_4 in absence and presence of PVA was used to determine the enthalpy of activation and (ΔH*) and apparent energy of activation (ΔS*) for the formation of the activation complex in the transition state equation. An alternative formula for the Arrhenius equation is the transition state equation [21].

$$C_R = (RT/N.h)\ \exp\ (\Delta S^*/R).\exp\ (-\Delta H^*/RT) \quad \ldots (3)$$

Where:
h is the Planck's constant, N is the Avogadro's number, ΔS* the apparent entropy of activation and ΔH* the enthalpy of activation. A Plot of log C_R/T versus 1/T is shown in Fig.10.

Straight lines are obtained with slopes -2.303(ΔH*/R) and intercepts of {log(R/Nh) + 2.303(ΔS*/R)}, from which ΔH* and ΔS* were calculated and listed in Table 3.

Table 3 Activation Parameters of PVA in 0.2 N H_2SO_4

Inh. Conc. (g/l) PVA	ΔH* (kJ/mol)	ΔS* (J/mol.K)	ΔG* (kJ/mol)			
T, K			303	313	323	333
Blank acid	37.22	-84.78	62.91	63.75	64.93	65.45
0.15	50.18	-50.38	65.44	65.95	66.45	66.95
0.50	52.86	-42.58	65.76	66.19	66.61	67.04
1.0	53.65	-40.63	65.96	66.37	66.77	67.18
1.5	55.08	-36.93	66.27	66.64	67.01	67.38
2.0	53.55	-42.93	66.56	66.99	67.42	67.84

The positive sign of ΔH^* indicates that the adsorption of the inhibitor molecules is an endothermic process. In exothermic process, physic-sorption is distinguished from chemi-sorption by considering the absolute value of ΔH^*. For physic-sorption process, the enthalpy of adsorption is lower than 40 kJ / mol while that for chemisorption approaches 100 kJ/ mol [22].

5- Adsorption Isotherms

Adsorption isotherms: Inspection of Table 1 suggests that PVA is a moderate corrosion inhibitor for carbon steel corrosion in H_2SO_4 media. The adsorption of the inhibitor is an essential step of the inhibition mechanism and it can provide information about the nature of metal-inhibitor interaction.

The surface coverage (θ) is an important parameter in discussing the adsorption characteristics and it is calculated by,

θ = [CR (blank acid) – CR (inhibited acid)]/CR (blank acid) … (4)

Where:
CR denotes to the corrosion rates as calculated in Table 1

By using surface coverage θ values at different inhibitor concentrations, several adsorption isotherms like Langmuir, Temkin and Freundlich etc., were assessed. Langmuir equation can be written as

$$log \frac{\theta}{1-\theta} = log\, A + log\, C - \frac{Q}{RT} \quad \ldots (5)$$

The plot of log θ/(1- θ) vs. log C according to Langmuir gave Straight lines with slope values close to unity suggesting that The adsorption of PVA on mild steel correlates well with Langmuir isotherm, Fig. 11.

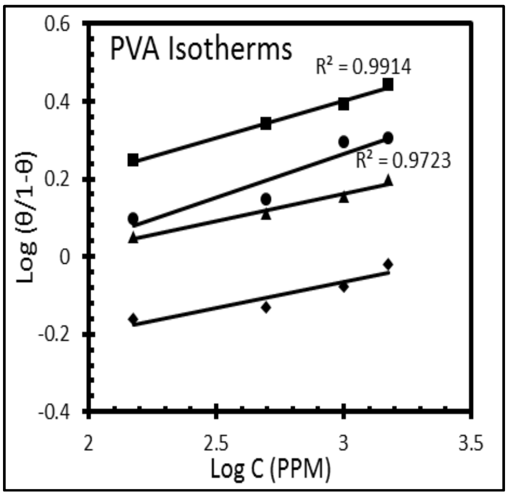

Fig. 11, Adsorption Isotherms for PVA on Carbon Steel According to Langmuir Isotherm at Various Temperatures

6- Linear Polarization Results

The inhibition power of a water soluble polymer (PVA) was examined in the corrosion cell employing Tafel extrapolation as a corrosion current measuring criteria.

Corrosion rates were estimated from corrosion currents and converted to weight loss in (gmd) and penetration depth in (mm/y). Tables 4 through 7 lists the results of runs carried out in the corrosion cell in three inhibitor concentrations ranging from 150 ppm , 1000 ppm, 2000 ppm and in the temperature range 30-60°C.

Table 4, Polarization Results for Carbon Steel in Blank Acid (0.2N H_2SO_4)

T °C	E_{corr} (mv)	$I_{corr.}$ (µA/cm^2)	b_c	b_a	Wt. loss (gmd)	Pen. loss (mm/y)
30	-434.4	404.54	-173.5	67.0	101.0	4.7
|40	-435.0	575.08	-186.5	92.2	144.0	6.67
50	-436.0	809.18	-215.9	97.2	202.0	9.39
60	-441.0	1190	-239.4	129.5	297.0	10.38

Table 5 Polarization Results for Carbon Steel in 150 ppm PVA

T°C	E_{corr} (mv)	$I_{corr.}$ (µA/cm^2)	b_c	b_a	Wt. loss (gmd)	Pen. loss (mm/y)
30	-437.0	220.26	-110.5	37.0	55.0	3.11
40	-438.8	327.1	-160.5	87.6	81.8	3.8
50	-443.8	500.2	-133.6	84.6	125.0	5.81
60	-452.2	897.5	-134.5	148	224.0	9.4

Table 6 Polarization Results for Carbon Steel in 1000 ppm PVA

T°C	E_{corr} (mv)	$I_{corr.}$ (µA/cm^2)	b_c	b_a	Wt. loss (gmd)	Pen. loss (mm/y)
30	-438.0	170.83	-132.9	51.4	42.7	1.98
|40	-440.0	261.74	-138.2	52.1	65.4	3.04
50	-440.0	394.2	-133.6	60.8	98.5	4.58
60	-455.0	733.2	-116.6	97.5	183.0	8.51

Table 7 Polarization Results for Carbon Steel in 2000 ppm PVA

T°C	E_{corr} (mv)	$I_{corr.}$ (µA/cm^2)	b_c	b_a	Wt. loss (gmd)	Pen. loss (mm/y)
30	-445.0	130.81	-116.0	53.9	32.7	1.52
|40	-451.3	238.8	-128.9	62.8	59.7	2.77
50	-452.0	381.0	-124.5	77.4	95.4	4.43
60	-450.0	600.87	-118.0	76.0	150.0	6.97

Figures 11 through 14 show plots of the polarization data obtained from the corrosion cell using the potentiostat. These plots represent scattered data type drawings of the logarithm of current density in (µA/cm^2) against the working electrode potential in mv.

a. Blank Acid

Figure 11 represents data obtained for the working electrode polarization in a solution of 0.2N H_2SO_4 in the absence of any added inhibitor (blank acid). Four curves were observed each one represent polarization at certain temperature. The temperature range considered was 30, 40, 50 and 60˚C.

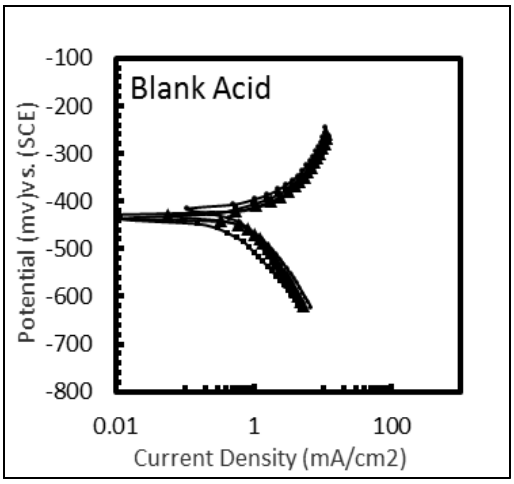

Fig. 11, Experimental Polarization curves for Carbon Steel in Blank 0.2N H_2SO_4 at Various Temperatures in Absence of any Additive.

Figure 11, together with Table 8, show that the polarization of the mild steel coupon in the acid under consideration is influenced by the temperature variation of the corrosive media. In the temperature range 30-40 ˚C the influence on the corrosion potential was only moderate although the corrosion current calculated was influenced more pronouncedly, which may be attributed the adsorption behavior at the adsorption film. As the temperature was raised from 50˚C to 6o˚C the corrosion potential showed a pronounced jump, it is largely known that high temperatures promote metals polarization and the corrosion current obtained was clearly much higher at 60˚C. Comparison of these results with the results obtained in the weight loss technique indicates that they are in the same trend.

b. Effects of 150 PPM PVA Polymer

Figure 12, along with Table 5 gives the results of polarization of carbon steel coupon in 0.2N H_2SO_4 in which 150 ppm of the polymer poly vinyl alcohol (PVA) was dissolved. Experiments were carried out in the temperature range 30-60˚C.

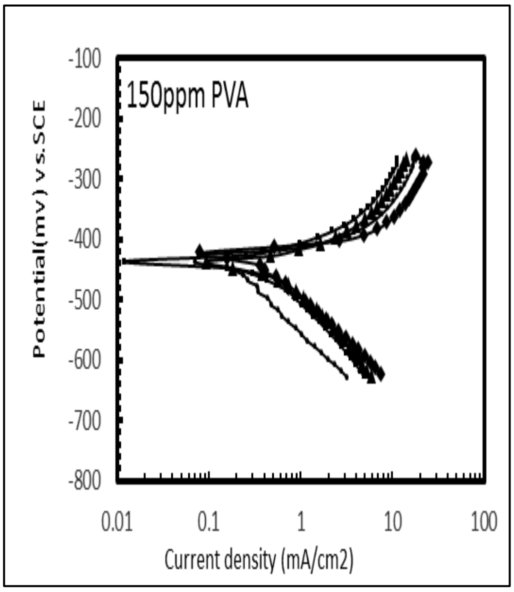

Fig. 12, Polarization curves for Carbon Steel in 0.2N H_2SO_4 in presence of 150 ppm of PVA at various Temperatures.

The inhibition power of the polymer (PVA) could be deduced from Tables 4 and 5, at 40˚C the corrosion rate dropped from 144 gmd for the blank acid to 81.8 gmd for the 150 ppm PVA inhibited acid giving an inhibition efficiency of about 43.2%.

c. Effects of 1000 ppm PVA Polymer

Figure 13 shows results of a series of experiments carried out in electrochemical corrosion cell for carbon steel corrosion in 0.2N H_2SO_4 in the presence of 1000 ppm of the water soluble polymer (PVA) dissolved in temperature range (30-60˚C).

Table 6 and Fig. 13 shows the effect of inhibitor concentration on the corrosion current and corrosion rate. The increase in PVA concentration from 150 ppm to 1000 ppm caused the corrosion current to decrease in all temperature range studied.

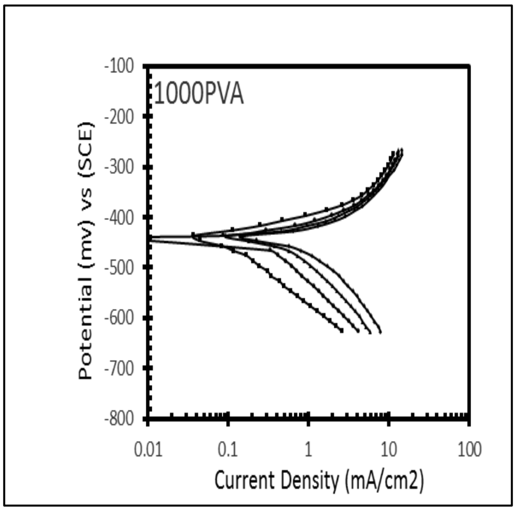

Fig. 13, Polarization Curves for Carbon Steel in 0.2N H_2SO_4 in Presence of 1000 ppm of PVA at Various Temperatures.

The corrosion rate at 40˚C dropped from 81.8 gmd for 150 ppm PVA to 58.3 gmd in the case of 1000 ppm PVA added (a 22.7 % increase in inhibition power). Same result was observed at other temperatures but in different proportions which demonstrate that increasing the polymer concentration in this range increases the inhibition power of the polymer in the acid for mild steel corrosion inhibition. The effect of temperature is also shown. Increasing the temperature led to a decrease in the inhibition power of the polymer. An increase in temperature from 30˚C to 60˚C led to corrosion rate increase from 55.2 gmd and 183.0 gmd with corresponding corrosion current increase.

d. Effects of 2000 PPM of PVA polymer

Figure 14 represent a series of curves obtained for the polarization results of the mild steel in acid environment consisting from 0.2N H_2SO_4 with 2000 ppm of the water soluble polymer (PVA) dissolved in at a temperature ranging from 30- 60˚C.

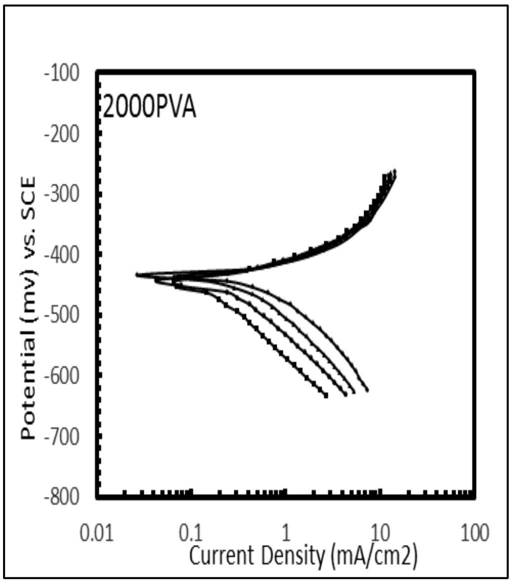

Fig. 14, Polarization curves for Carbon Steel in 0.2N H_2SO_4 in presence of 2000 ppm of PVA at various Temperatures.

Examining Table 7 and Fig. 14 again shows the improved inhibition power gained by increasing the inhibitor concentration. The corrosion rate decreased in all temperature range studied, with increasing the polymer concentration, for instance, at 40˚, the corrosion current dropped from 327.11 to 289.70 and 238.81 µA using 150 ppm, 1000 ppm, and 2000 ppm of PVA respectively. The same observation is true for the other series of tests conducted in this study. The effect of corrosive media temperature variation in this series was similar to the proceeding series. Temperature increase increased the corrosion rate significantly, the corrosion current calculated increased from 150 µA to 530.6 µA as the temperature increased from 30 to 60˚C at the same PVA concentration of 2000 ppm. Table 8 shows the corrosion rates in gmd and inhibition efficiencies as calculated from polarization data.

Table 8 (a) Corrosion Rates and (b) Corrosion Efficiencies

(a)

Inhibitor	Conc. ppm	Corrosion Rate (gmd)			
		30˚C	40˚C	50˚C	60˚C
Nil	NIL	101	144	202	297
PVA	150	55.0	81.8	125	224
	1000	42.7	65.4	98.5	183
	2000	32.7	59.7	95.4	150

(b)

Inhibitor	Conc. ppm	Inhibition Efficiency (IE %)			
		30˚C	40˚C	50˚C	60˚C
Nil	NIL	0	0	0	0
PVA	150	45.5	43.1	38.1	24.5
	1000	57.7	54.5	51.2	38.4
	2000	67.6	58.5	52.8	49.5

7- Discussion of the polarization Data

a. Effect of PVA Concentration on Polarization curves

Polarization measurements were carried out in order to gain knowledge concerning the kinetics of the cathodic and anodic reactions. Figure 15 shows the effect of addition of PVA on the cathodic and anodic polarization curves of mild steel in 0.2N H_2SO_4 at 60˚C. Both the cathodic and anodic reactions were affected with the addition of the polymer PVA, which suggests that PVA reduced anodic metal dissolution and also retarded the hydrogen evolution reaction Electrochemical corrosion kinetics parameters, such as corrosion current density, Tafel slopes obtained from the extrapolation of the polarization curves for Fig. 15 were given in Tables 4, 5, 6, and 7, respectively.

It followed that the values of b_c is changed with increasing inhibitor concentration, indicating the influence of the polymer compounds on the kinetics of hydrogen evolution. The PVA molecule is believed to be adsorbed at the active metal sites of the mild steel which are amenable for corrosion reaction and block these sites most probably by its negatively charged hetro- atoms thus blocking these anodic and cathodic corrosion reactions, similar results were found by Oz can et al. [23, 24]. Being adsorbed on the metal surface PVA controlled the anodic and cathodic reactions occurring in the corrosion reaction, and then its inhibition efficiency is directly proportional to its amount adsorbed with increasing concentration. As it was seen the above tables the corrosion current is reduced corrosion potential shifting not exceeding 85mv which suggests that PVA is a mixed type inhibitor in agreement with other findings in previous studies [25, 26].

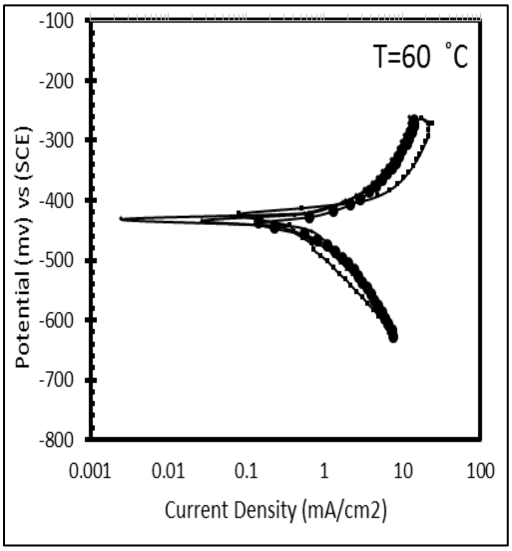

Fig. 15, Polarization Curves for Carbon Steel in 0.2N H_2SO_4 in Absence and presence of different concentrations of PVA at 60˚C.

Similar conclusions could be withdrawn from the polarization kinetic data at the other temperatures, i.e., 30, 40, and 50˚C. The Kinetic parameters obtained from polarization, Such as corrosion current, Tafel slopes were showing to follow the same trend with respect to the concentration of the PVA inhibitor.

b. Inhibition Efficiency Discussions

Tables 8 tabulate the results obtained from Polarization runs analysis. Corrosion currents calculated from Tafel slopes interceptions in the vicinity of the corrosion potentials was calculated and converted to the corresponding weight losses which was used to estimate the corrosion rates in presence and absence of inhibitors.

Figure 16 represents these data graphically. The corrosion retarding effect of PVA is obvious. Corrosion rates are increasing with temperature and decreasing with increasing PVA concentration. This is in agreement with former results recorded in weight loss method.

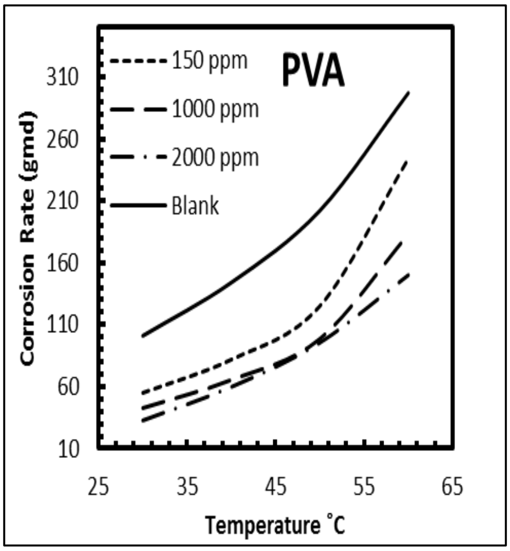

Fig. 16, Effect of Inhibitor Concentration on Corrosion Rate of Carbon Steel in 0.2N H_2SO_4 in Presence and absence of Inhibitor (PVA)

To further understand the corrosion behavior of mild steel in such circumstances the effect of temperature and inhibitor concentration and type on the penetration depth for carbon steel in 0.2N H_2SO_4 in presence and absence of inhibitor is represented in bar diagrams, Fig. 17 utilizing data from Table 8.

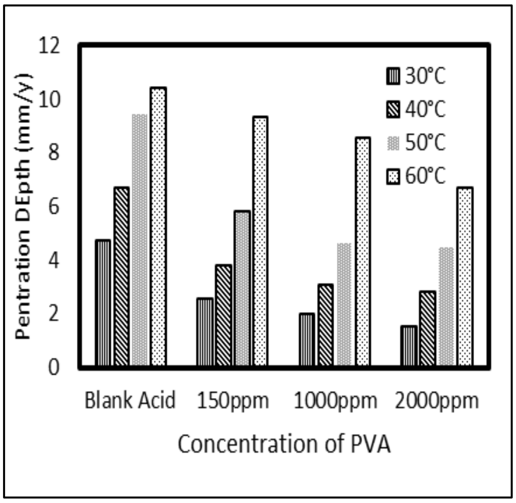

Fig. 17 Effect of Inhibitor Concentration and Temperature on Penetration Depth for Carbon Steel inhibited by PVA only

Conclusions

The findings of this research suggest the following conclusions:

1- The corrosion rate of mild steel in 0.2 N H_2SO_4 solution is highly temperature dependent especially at higher temperatures.

2- Polyvinyl alcohol is one of those polymers which are water soluble and eco -friendly, however its inhibition power in acidic media is only moderate especially at higher temperatures and low PVA concentrations.

3- Corrosion inhibition power of PVA increases with increasing PVA concentration in the acid solution and reaches a maximum at about 2000 ppm at all temperatures investigated.

4- Corrosion inhibition power of PVA decreases with increasing temperature showing maximum dissolution rates at 60°C.

5- Kinetic study shows that the temperature dependence of the corrosion rate correlates well with the Arrhenius equation in presence and absence of all inhibitor modes investigated.

6- Thermodynamic parameters showed that following the addition of inhibitor the activation energy values are larger confirming that these inhibitor combinations retards the corrosion of mild steel in H_2SO_4 by adding an extra energy barrier to the corrosion reaction.

7- Linear polarization method findings show that the corrosion reaction in the acid media is activation controlled and oxygen diffusion plays only a minor role.

8- Tafel extrapolation method to estimate corrosion currents and corrosion rates shows results with similar trends with corrosion rates calculated by the weight loss techniques.

9- The overall corrosion process is a function of the metal, corrodent, inhibitor structure, temperature as well as concentration.

References

1- Ramesh, BS. Rajeswari, S., Maruthamuthu, S., (2003), “Effect of inhibitors and biocide on corrosion control of mild steel in natural aqueous environment”, Materials letters, 57, 4547.

2- Abdallah, M., (2004), “Guar gum as corrosion inhibitor for carbon steel in sulfuric acid solutions”, Portug. Electrochica Acta, 22, 16.

3- Yaldirim, A., Cetin, A.M., (2008), “Synthesis and evaluation of new long alkyl side chain acetamide, isoxazolidine and isoxazoline derivatives as corrosion inhibitors”, Corrosion Sci., 50, 155-165.

4- Anees A. Khadom, Aprael, S. Yaro, Abdul Amir H. Kadum, (2010), “Corrosion inhibition by naphthylamine and phenylenediamine for the corrosion of copper–nickel alloy in hydrochloric acid”, J. of Tiwan institute of Chem. Engineers, 41, 122-125.

5- Sanyal B., (1981), “Organic compounds as corrosion inhibitors in different environments-a review”, Prog. Org. Coating, 9, 165-236.

6- Abd-El-Maksoud S. A., (2008), ” Effect of organic compounds on the electrochemical behavior of steel in acidic media- A review”. Int. J. Electrochem. Sci. 3, 528.

7- Ayman M. A., Gamal A. E., Husein S. I., Hamad A. A., (2012), “Effects of Water Soluble Rosin on the Corrosion Inhibition of Carbon Steel’, Int. J. Electrochem. Sci., 7, 11834 – 11846.

8- Grchev, T., Cvetkovska, M. and Schutze, J. W. (1991), “The electrochemical testing of polyacrylic acid and its derivatives as inhibitors of corrosion”, Corr. Sci., 32,103-9.

9- Karthikaiselvi R., Subhashini S., Rajalakshmi R., (2012), “Poly (vinyl alcohol – aniline) water soluble composite as corrosion inhibitor for mild steel in 1 M HCl”, Arabian Journal of Chemistry, 5, 4, 517–522.

10- Schweinsberg, D. P., Hope, G. A., Trueman, A., Otieno- Alego, V., (1996), “An electrochemical and SERS study of the action of polyvinylpyrrolidone and polyethylenimine as inhibitor for copper in aerated H_2SO_4”, Corr. Sci., 38, 587-99.

11- Rajendran, S., Apparao, B. V., Palaniswamy, N., (1998), “Synergistic effect of ethyl phosphate and Zn2+ in low chloride media”, Anti-Corr. Methods and Mater. 45, 5, 338-43.

12- Kralijie, M., Mandie, Z. and Duie, L. J., (2003), “Inhibition of steel corrosion by polyaniline coating”, Corr. Sci., 45, 181-98.

13- Desai, M. N., Talati, J. D., Shah, N. K., (2003), “Orthosubstituted aniline-N-salicylidenes as corrosion inhibitors for zinc in H2SO4”, Indian J. of Chem., 42A, 12, 101-6.

14- Shoeib, M. A., Mokhtar, S. M. and Abd El-Ghaffar, M. A., (1998), “Mechanical and corrosion protection properties of electroless nickel-polymer composite coatings”, J. Metal Finishing, 96, 11, 58-9.

15- David Ebuka Arthur, Achika Jonathan, Paul Ocheje Ameh and Crystal Anya, (2013), “A review on the assessment of polymeric materials used as corrosion inhibitor of metals and alloys”, International Journal of Industrial Chemistry, 4, 2, 2-9.

16- Grchev, T., Cverkovska, M. and Schutze, J.W., (1991), “The electrochemical testing of polyacrylic acid and its derivatives as inhibitors of corrosion”, Corr.Sci, 32,103-112.

17- Rajendran, S., Sridevi, S., Anthony, N., John Amalraj. A., (2005), “Corrosion behaviour of carbon steel in polyvinyl alcohol”, Anti-Corr. Methods and Mater. 52, 2,102-107.

18- Bentiss, F., Traisnel, M., Lagrenee, M., (2000), “The inhibition action of 3, 6-bis(2-methoxyphenyl)-1, 2-dihydro-1, 2, 4, 5-tetrazine on the corrosion of mild steel in acidic media”, Corr. Sci., 42,127-146.

19- Umoren, S.A., and Solomon M.M., (2014), “Recent Developments on the Use of Polymers as Corrosion Inhibitors - A Review, The Open Materials Science Journal, 8, 39-54.

20- Srimathi, M., Rajalakshmi, R., Subhashini, S., (2014), “Polyvinyl alcohol–sulphanilic acid water soluble composite as corrosion inhibitor for mild steel in hydrochloric acid medium", Arabian J. of Chem., 7, 5, 647-656.

21- Bank Electronic Intelegent Controls-GmBh 'An introduction to the principle of potentiostatic control, including basic potentiostatic circuits', Freiberger Strasse 1, D-38678-Zeller feld.

22- Zarrok, H., Zarrouk, A., Salghi, R., Assouag, M., Hammouti, B., Oudda, H., Boukhris, S., Al Deyab, S. S., Warad, I., (2013), "Inhibitive properties and thermodynamic characterization of quinoxaline derivative on carbon steel corrosion in acidic medium", Der Pharmacia Lettre, 5 (2)), 43-53.

23- Badiea, A. M., Mohana, K. N., (2009), "Effect of temperature and fluid velocity on corrosion mechanism of low carbon steel in presence of 2 – hydrazine–4,7–dimethyl benzothiazole in industrial water", Corrosion Science 51, 2231 – 2241.

24- Ozcan, M., Dehri, I., Erbil, M., (2004), "Organic sulphur containing compounds as corrosion inhibitors for mild steel in acidic media: correlation between inhibition efficiency and chemical structure", Appl. Surf. Sci., 236,155-164.

25- Fouda, A., Moussa, M., Taha, F. I., ElNeanaa, A. I., (1986), "The role of some thiosemicarbazide derivatives in the corrosion inhibition of aluminum in hydrochloric acid", Corr. Sci., 26, 719-726.

26- McCafferty, E., Hackerman, N., (1972), "Double layer capacitance of iron and corrosion inhibition with polymethylene diamines," J. Electrochem. Soc. 119, 146-154.