Int. J. Electrochem. Sci., 7 **(2012)** 8578 - 8596

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Polyvinyl Pyrrolidone as a Green Corrosion Inhibitor of Carbon Steel in Neutral Solutions Containing NaCl: Electrochemical and Thermodynamic Study

Layla A. Al Juhaiman[*], *Amal Abu Mustafa, Waffa K. Mekhamer*

Chemistry Department, Faculty of Science, King Saud University; PO Box 22452, code 11495,
Riyadh, Saudi Arabia
[*]E-mail: ljuhiman@ksu.edu.sa

Received: 20 July 2012 / *Accepted:* 14 August 2012 / *Published:* 1 September 2012

The corrosion inhibition of carbon steel (CS) using the “green” inhibitor, polyvinyl pyrrolidone (PVP) was investigated. This study was conducted at pH 7 and pH 8 in an aerated medium containing 0.1 M NaCl. The effects caused by some additives (KI and untreated clay) were investigated. The study was done over a range of concentrations, temperatures and times. Gravimetric method and electrochemical methods (electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation) were applied. The adsorption of PVP led to the formation of a protective film on the metal/solution interface and an increase in the thickness of the electronic double layer as revealed by EIS results. Tafel results indicated that PVP is a mixed-type inhibitor, affecting the iron dissolution and the cathodic reaction as well. The addition of KI to PVP and NaCl-containing solutions significantly increased the inhibition efficiency, while the addition of UC reduced the inhibition efficiency. The adsorption mechanism was fitted with a Langmuir isotherm. The kinetic and thermodynamic parameters (E^*_{app} , K, ΔG^o_{ads}, ΔH^o and ΔS^o) were evaluated. The thermodynamic parameters support the % IE results of WL, EIS, and Tafel indicating that PVP is a good corrosion inhibitor for CS in solutions containing NaCl at pH7 and pH8. The addition of KI additives improves the % IE of PVP especially at pH8.

Keywords: Carbon steel; PVP inhibitor; neutral medium; Surface coverage; Adsorption mechanism; Thermodynamic parameters.

1. INTRODUCTION

Metallic surface corrosion can be reduced or controlled by the addition of an inhibitor, which decreases the rate of anodic oxidation, cathodic reduction or both [1]. The inhibitors form a protective film on the surface of the metal by physical (electrostatic) adsorption or chemisorption [2]. Green inhibitors receive attention for the replacement of synthesised inorganic inhibitors which are often toxic, expensive and environmentally unfriendly [3]. Polymers, such as polyvinyl alcohol, polyethylene glycol and polyvinyl pyrrolidone (PVP), have been reported [4-6].

The chelating properties of PVP make it useful in a multitude of applications in aqueous or polar organic solutions. The wide variety of usable solvents is due to the presence of imide, methylene and carbonyl groups in PVP [5]. There are numerous studies that investigated the corrosion inhibition of iron and iron alloys in acidic media [5-7], neutral media [8], and basic media [9, 10].

Carbon steel (CS) is used in alkaline and neutral media in the petroleum industry, such as its use for oil drilling in the presence of drilling fluids. There are a few studies in this field, thus the aim of this work was to investigate the corrosion inhibition characteristics of PVP to CS in neutral media containing chloride ions at pH 7and pH 8. The weight loss method and electrochemical techniques (cyclic polarisation, and electrochemical impedance spectroscopy) were applied for corrosion measurements of CS. The effects of some additives used in petroleum drilling fluids, such as polymers and clay, were examined.

2. EXPERIMENTAL CONDITIONS

2.1 Materials

The CS specimens were commercial rods (grade 1046) from the ODS company in Germany. The chemical composition of CS is: C=0.460%, Si=0.180%, P=0.013%, S=0.006%, Cr=0.180%, Cu=0.030%, Al=0.023% and the rest is iron)

CS rods were cut mechanically into circular disks with a thickness of approximately 0.55 cm, a diameter of 2.5–2.9 cm, and an area of 13–17 cm^2. Before use, the CS disks were polished with a polishing machine (Metaserve 2000) using a series of emery papers with different grades (60–1200), starting with the coarsest to the finest grade, until a mirror image was obtained. The CS disks were washed thoroughly with distilled water then immersed in acetone under sonication for 3 min in an ultrasonic cleaner (from Cole Palmer). The disks were used immediately after drying. CS disks were used for the weight loss method whereas CS rods were used as working electrodes for electrochemical techniques. A CS rod was coated with an epoxy resin to insure that a constant cross-sectional area (1.33 cm^2) would be exposed to the solution then mounted in a glass tube of the appropriate diameter. The surface of the working electrode was polished and prepared using the same method as the CS disks described in the weight loss method.

Polyvinyl pyrrolidone (PVP) was purchased from Sigma Aldrich. The molecular weight of PVP was 8000 g/mol. The chemical structure of PVP is shown in Figure 1. Sodium chloride (AR, Win lab Company) was used to prepare a 0.1 M NaCl solution. Calcium hydroxide was purchased from BDH Limited Poole England, and potassium iodide from VWR International Ltd. The untreated clay sample (UC) was collected from the bentonite deposits of Kholais in north Jeddah, Kingdom of Saudi Arabia. The UC was used in a powdered form.

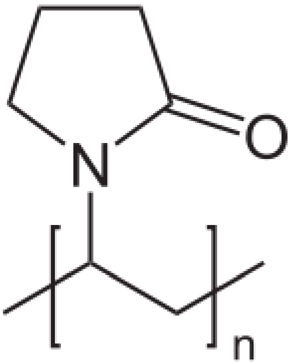


Figure 1. The molecular formula of polyvinyl pyrrolidone (PVP).

2.2 Solution and Sample Preparation

All solutions were prepared from analytical grade chemicals and distilled water. The blank solution was 0.1 M NaCl aqueous solution. A concentrated solution of $Ca(OH)_2$ was used to adjust the pH of the blank solution to pH 7 and pH 8. The solution pH was monitored using a pH meter from Cole Palmer Company. PVP was dissolved in a 0.1 M NaCl solution to a final concentration of 500-3000 ppm. Solid potassium iodide was added to the blank solution to adjust the molarity of KI to the desired range of 0.02-0.18M. UC was added to the blank solution until a concentration in the range of 2-6 g/L was reached.

2.3 Test procedures

2.3.1 Weight loss method (WL)

Weight loss is a chemical method employed in this work to investigate the actual effects caused by the concentration of inhibitor (PVP), pH of the solution, temperature, time and effect of additives (KI, UC) in 0.1 M NaCl solutions. Before the disks were immersed into the test solutions, the dimensions were measured. Clean CS disks were weighed before and after immersion in 50 ml of the test solution (with the absence and presence of different concentrations of PVP for one hour at a constant temperature that was maintained using a thermo stated water bath. At the end of each run, the disks were washed with distilled water, cleaned with acetone in the ultrasonic cleaner, dried and immediately weighed. The mass was measured on a sensitive analytical balance ± 0.00001(Metler), which was used to determine the weight loss. The average weight loss for two identical experiments was recorded and expressed in mg. The corrosion rate (CR) obtained from the WL, the inhibition efficiency (% IE) of PVP and the surface coverage (θ) were calculated using the following equations:

$$CR = \frac{\Delta w}{A * t} \qquad (1)$$

$$\%\,\mathrm{IE} = \left(1 - \frac{CR}{CR_{o}}\right) \times 100 \qquad (2)$$

$$\Theta = \frac{\%\ \mathrm{IE}}{100} \qquad (3)$$

where CR_o and CR are the corrosion rates (mg/cm^2.hr) in the absence and presence of PVP respectively; Δw is the weight loss of CS (mg); A is the surface area (cm^2) and t is the immersion time (hours).

2.3.2 Electrochemical measurements

Two electrochemical techniques were used in this study: cyclic polarisation (Tafel plots), and electrochemical impedance spectroscopy (EIS). Electrochemical measurements were performed using a potentiostat/galvanostat (ACM) connected to a computer. These measurements were performed in a corrosion cell using a three neck, 250 ml round bottom flask. The three-electrode cell assembly consisted of a CS rod embedded in an epoxy resin holder as the working electrode (WE), a platinum sheet of negligible impedance as the counter electrode (CE), and a saturated calomel electrode as the reference electrode (RE). All electrochemical measurements were performed in aerated solutions. The temperature of the electrolyte was maintained at the required temperature using a water bath. The CS electrode was prepared directly before use then immersed in the test solution. The variations of corrosion potentials (E_{corr}) with time were recorded with respect to a saturated calomel reference electrode at 30°C for approximately 60-90 minutes. EIS was performed using AC signals (15 mV) peak-to-peak at open circuit potential. The Nyquist diagrams show the relationship between Z'-real impedance and Z"-imaginary impedance over a wide range of frequency values (10^3 to 0.05 Hz).

For polarisation measurements, the potential was scanned at a scan rate of 25 mV/min from the cathodic to the anodic direction. From the polarisation data, the corrosion current densities (I_{corr}) were deduced manually, and the degree of surface coverage (θ) and the % IE were calculated.

3. RESULTS AND DISCUSSION

3.1 Weight loss method (WL)

3.1.1 Effect of pH

Weight loss is a non-electrochemical technique for the determination of corrosion rates and inhibitor efficiency which provides more reliable results than electrochemical techniques because the experimental conditions are approached in a more realistic manner. However, immersions tests are time-consuming. In this study the corrosion rates at pH 7 and pH 8 were recorded, as shown in Table 1. The addition of 1000 ppm of PVP to the blank solution caused the corrosion rates of CS to decrease. The inhibition efficiency and the surface coverage (Θ) increased with increasing pH values. The addition of PVP increased the surface coverage from 19% at pH 7 to 41% at pH 8.

Table 1. Corrosion rates, inhibition efficiencies and surface coverage from WL at 30 °C for CS in 0.1M NaCl in absence and presence of 1000ppm PVP.

Solution	pH	CR(mg/cm^2.hr)x10^2	% IE	ϴ
blank	7	3.18	--	**--**
blank	8	4.02	--	**--**
blank +PVP	7	2.51	18.55	0.21
blank +PVP	8	2.35	41.40	0.41

The inhibition of CS corrosion in the presence of a polymeric material could be attributed to the adsorption of the polymer onto the CS surface, which would block the metal surface and do not permit the corrosion process to occur [11-13]. It is structurally related to the various active centres of adsorption as cyclic rings with hetero atoms (e.g., oxygen and nitrogen). PVP contains oxygen atoms in its molecular structure, which have lone pairs of electrons. PVP could be adsorbed due to the interaction between the lone pair of electrons of the oxygen atoms and the CS's surface, which may be facilitated by the presence of the vacant d-orbitals of iron [5, 6, 14]. The adsorption of PVP on the surface of CS creates a barrier for mass and charge transfers. Consequently, the metal is protected from aggressive anions [11].

3.1.2 Effect of PVP concentrations on inhibition efficiency

The corrosion rates for blank solutions at pH 7 with various concentrations of PVP ranging from 500 ppm (6.25×10^{-5} M) to 3000 ppm (3.75×10^{-4} M) are shown in Table 2. As observed the CR decreased with increasing inhibitor concentration, while the inhibition efficiency increased till a maximum value of 34% at 2000 ppm.

The degree of protection increased with increasing PVP concentration due to the higher degree of surface coverage, which resulted from enhanced inhibitor adsorption. Steric hindrance begins to dominate in the solution upon reaching the highest concentration of 3000 ppm PVP due to an increase in the viscosity of the polymer with increasing concentration of PVP. The transfer of polymer chains from the solution to the metal surface became more difficult, and the surface coverage (ϴ) decreased [5]. Other studies reported the presence of a threshold concentration for the steel inhibition in alkaline medium [12, 13].

Table 2. The effect of PVP concentration on CR for blank at pH 7 from WL method.

Solution	CR x 10^2 (mg/cm^2.hr)	IE %	ϴ
Blank , pH7	3.18	--------	--------
500 ppm of PVP (6.25×10^{-5} M)	2.71	14.78	0.15
1000 ppm of PVP (1.25×10^{-4}M)	2.51	18.55	0.21
1500 ppm pf PVP (1.875×10^{-4}M)	2.30	27.67	0.28
2000 ppm of PVP (2.50×10^{-4}M)	2.10	33.96	0.34
3000 ppm of PVP (3.75×10^{-4}M)	2.16	32.07	0.32

3.1.3 Effect of temperature

The effect of temperature on the corrosion parameters of CS was studied in the absence and presence of 1000 ppm of PVP at pH 7 and pH 8 at 30, 40, 50, and 60°C. Table 3 shows that the corrosion rate increased with rising temperature in the absence and presence of 1000 ppm of PVP. As the temperatures increased the inhibition efficiencies increased from19% to 37% at pH 7 and from 41% to 47% at pH 8.The values of the apparent activation energy (E_{app}^*) of the corrosion process in 0.1 M NaCl in the presence and absence of PVP was calculated using the Arrhenius equation:

$$\ln \mathrm{CR} = \ln \mathrm{A} - \frac{E_{app}^*}{\mathrm{RT}} \qquad (4)$$

Where CR is the rate of corrosion from the weight loss, A is Arrhenius constant, E_{app}^* is the apparent activation energy, R is the gas constant and T is the absolute temperature.

Arrhenius-type dependence was observed by plotting ln CR versus the inverse of T. From the Arrhenius plots, the E_{app}^* of the corrosion process was calculated as shown in Table 4. The E_{app}^* values obtained for the blank solution and the blank + PVP decreased as the pH increased from pH 7 to pH 8. The decrease observed for E_{app}^* in the presence of 1000 ppm PVP compared to the blank is consistent with the role of the inhibitor where it provides an easier route for the reaction to occur. These observations are not consistent with other studies of steel in acidic solutions in which the addition of inhibitor increased the E_{app}^* [15-18].

3.1.4 The effect of the change of pH with time

The ratio of chloride to hydroxyl ions was shown to have an effect on the steel's tendency to be passivated in alkaline medium [15]. In the present study, the concentrations were $[Cl^-] = 0.1$ M and $[OH^-] = 1\times10^{-7}$M at pH7 and $[OH^-] = 1\times10^{-6}$ M at pH8. The change in pH values over time was studied in the absence and presence of PVP and CS in blank solutions at pH7.

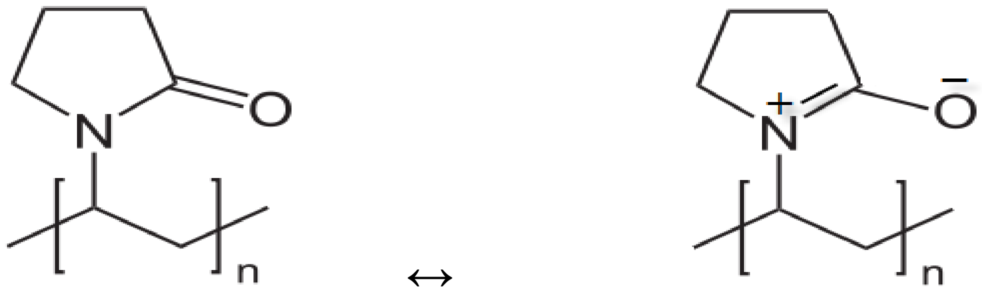
Table 3. The effect of temperature on the corrosion parameters of CS at pH 7 and pH 8 in absence and presence of 1000 ppm of PVP from WL method.

T(°C)	pH	CR x 10^2 (mg/cm^2.hr) Blank	CR x10^2 (mg/cm^2.hr) Blank+PVP	% IE	ϴ
30	7	3.17	2.59	18.56	0.19
40	7	3.70	2.84	23.21	0.23
50	7	4.95	3.22	34.95	0.35
60	7	5.48	3.46	37.00	0.37
30	8	4.02	2.35	41.40	0.41
40	8	4.66	2.62	43.84	0.44
50	8	5.04	2.73	45.90	0.46
60	8	5.67	2.99	47.15	0.47

Table 4. The apparent activation energy E_{app}^* of the corrosion process at pH 7 and pH8 in 0.1M NaCl in presence and absence of 1000 ppm PVP.

solution	CR(mg/cm^2.hr)x10^2 Blank	E^*_{app} (kJ) blank	CR(mg/cm^2.hr)x10^2 Blank +PVP	E^*_{app} (kJ) Blank +PVP
pH 7	3.18	16.17	2.59	8.35
pH 8	4.02	9.30	2.35	6.39

A small reduction in the pH of the blank solution occurred after two hours ($\Delta pH_7 = 0.13$), which indicated that there was no reaction. The addition of CS to the blank solution did not cause a significant change in pH ($\Delta pH_7 = 0.16$). The addition of PVP to the blank solution only resulted in a remarkable reduction in the pH value ($\Delta pH_7 = 1.83$). Thus we believe that PVP hydrolysed in the neutral solution, which produced a positive charge on the nitrogen atom and a negative charge on the oxygen atom. The OH^- groups from $Ca(OH)_2$ will attach to the positively charged nitrogen atom of PVP, resulting in the removal of OH^- from the solution and a reduction in pH values. The protons may be attached to the water molecules as H_3O^+. There is precedence for competition between chloride and hydroxide ions for adsorption on N^+ sites in acidic media to occur [5, 6, 19]. In the present study we believe that the same competition will prevail in neutral media as shown in the following scheme:



The addition of PVP + CS together to the blank solution had a small reduction in the pH of the solution after two hours ($\Delta pH_7 = 0.03$). Thus the action of PVP as a corrosion inhibitor for CS may be attributed to a strong adsorption bond which is of a chemiosorptive nature from the oxygen double bond in PVP molecule to the positively charged CS surface to form a coordinate-type bond and an electrostatic attraction between the cationic NH_2 species and Cl^-.

3.1.5 Effect of additives

Clay and polymers are used in drilling fluids for oil drilling. The effects of using untreated clay (UC) were investigated, and the data are shown in Table 5. The CR of CS increased in the presence of UC. Increasing the concentration of UC from 2-6 g/L at pH7 and pH8 increased the CR of CS in the blank. Adding 1000 ppm PVP to UC and blank decreased the CR slightly as revealed in Table 5.

KI is another additive used to enhance the inhibition efficiency of the polymer. The effects on the corrosion parameters of steel caused by adding different concentrations of iodide ions and UC in the absence and presence of 1000 ppm PVP were studied. The results presented in Table 6 show that the corrosion rate of steel in the blank solution decreased as iodide ions were added. Moreover, when 0.02 M KI was added to the blank solution in the presence of 1000 ppm PVP, a significant increase in the % IE was observed which indicates that the effect of adding KI+PVP is a synergistic effect. A remarkable corrosion-rate reduction was obtained upon the addition of 0.06 M of KI compared to 0.02 M of KI in the absence and presence of 1000 ppm of PVP for pH 7 and pH 8, as shown in Table 6. The % IE for blank +0.06M KI+1000ppm PVP increased from 58% at pH7 to 72% at pH8. Other researchers reported similar results for KI additives in increasing the inhibition efficiencies of the inhibitors [4, 20].

The inhibition of CS corrosion by halide ions has been reported to be caused by the adsorption of the halide ions on the metal surface and by the formation of surface compounds that are insoluble in the corrosive media [4, 20]. Generally, the adsorption of anions is related to the degree of hydration, and the less hydrated ion is preferentially adsorbed on the metal surface. The adsorption ability on the metal surface, which leads to inhibition potential of the halides, has been estimated to be in the order of $I^- > Br^- > Cl^-$ [4]. The iodide ion is more predisposed to adsorption than the bromide and chloride ion. Authors have reported synergistic inhibition of iodide ions and some compounds, including polymers, in acidic medium. Reports on the influence of halide ions and polymers as corrosion inhibitors in alkaline medium are rare. Stabilisation of the adsorbed halide ions by means of interaction with the inhibitor leads to greater surface coverage (ϴ) and thereby greater inhibition efficiency [20, 21].

Table 5. The effect of adding UC at pH7 and pH8 on the corrosion parameters of CS at pH7 and pH8 in absence and presence of 1000 ppm of PVP.

solution	pH	PVP (ppm)	$CR*10^2$ $(mg/cm^2.hr)$	% IE	ϴ
Blank	7	--------	3.18	--------	--------
Blank	7	1000	2.59	18.56	0.19
Blank +2g/L UC	7	-------	3.78	----------	--------
Blank +2g/L UC	7	1000	2.33	26.69	0.27
Blank +6g/L UC	7	-------	4.12	-----------	--------
Blank +6g/L UC	7	1000	2.44	23.15	0.23
Blank	8	-------	4.02	----------	--------
Blank	8	1000	2.36	41.4	0.41
Blank +2g/L UC	8	-------	4.42	-----------	--------
Blank +2g/L UC	8	1000	1.83	54.47	0.54
Blank +6g/L UC	8	-------	5.03	----------	--------
Blank +6g/L UC	8	1000	2.1	47.76	0.48

3.1.6 Effect of time

Immersion times of 1-3 hours were studied by weight loss method in 0.1 M NaCl at pH 7 and pH 8 in the presence of PVP and the results are shown in Table 7. The % IE after 3 hours increased slightly from 19% to 25% at pH 7 but decreased from 41% to 20% at pH 8.

3.3 Electrochemical measurements

3.3.1 Electrochemical Impedance Spectroscopy (EIS)

The AC impedance measurements for metal dissolution in aggressive media in the presence of inhibitors can be interpreted in terms of the charge transfer resistance (R_{ct}). R_{ct} is defined as the limiting zero frequency value of the real part of the complex impedance. Moreover, it was reported that R_{ct} is more intimately correlated to the corrosion rate more than the polarisation resistance (R_p) [22]. Electrochemical theory states that ($1/R_{ct}$) is proportional to the corrosion rate and is analogous to the use of polarisation resistance in the Stern-Geary equation [11]. The %IE of any particular compound was calculated from the impedance data by applying the following relationship [11]:

$$\% \mathrm{IE} = \left(\frac{R_{ct} - R_{ct}^{\circ}}{R_{ct}}\right) \times 100 \qquad (5)$$

where R_{ct}^{o} and R_{ct} are the charge transfer resistance of CS in the absence and presence of certain concentrations of the inhibitor, respectively.

Table 6. The effect of adding KI on the corrosion parameters of CS at pH 7 and pH 8 in absence and presence of 1000 ppm of PVP from WL method.

Solution	pH	PVP (ppm)	$CR*10^2$ ($mg/cm^2.hr$)	%IE	ϴ
Blank	7	--------	3.18	--------	--------
Blank	7	1000	2.59	18.56	0.19
Blank +0.02M KI	7	-------	2.44	23.15	0.23
Blank +0.02M KI	7	1000	1.91	39.78	0.40
Blank +0.06M KI	7	-------	1.85	40.73	0.42
Blank +0.06M KI	7	1000	1.35	57.54	0.57
Blank	8	-------	4.02	----------	--------
Blank	8	1000	2.36	41.4	0.41
Blank +0.02M KI	8	-------	2.69	33.1	0.33
Blank +0.02M KI	8	1000	2.03	49.41	0.49
Blank +0.06M KI	8	-------	1.44	64.18	0.64
Blank +0.06M KI	8	1000	0.93	76.81	0.77
Blank +0.06M KI + 2g/L UC	8	1000	1.11	72.39	0.72

All impedance measurements were performed under potentiostatic conditions after one hour immersion. The Nyquist diagrams for CS were obtained in the absence and presence of various concentrations of PVP ranging from 1000-3000 ppm at steady-state potentials are presented in Table 8 for pH 7 and pH 8. The impedance data at pH 7 is shown in Figure 2. Depressed charge transfer semicircle is observed at low frequency, which is attributed to the time constant of the charge transfer and double- layer capacitance [22]. The intersection of this semicircle with the real axis at high frequencies furnished a value for the ohmic resistance (R_s) of the solution enclosed between the working electrode and the tip of the tube containing the reference electrode. At low frequencies, a charge transfer resistance (R_{ct}) was found from the difference in impedances at lower and higher frequencies. As can be seen in Table 3, slightly higher R_s values were obtained in the presence of the high concentration of PVP. This was to be expected because organic compounds, in general, reduce the dielectric constant of aqueous solutions, increasing their resistance. However, more important, are the observations related to C_{dl} and R_{ct}. The EIS results clearly indicate that PVP decreases the double-layer capacitance and increases the charge transfer resistance; as consequence a larger diameter of the semicircle is observed in Nyquist plots in presence of PVP as shown in Figure 2. The decrease in C_{dl} can be explained as due to the adsorption of PVP on the electrode surface. The double layer formed at the CS–solution interface may be considered as an electric capacitor, whose capacitance decreases due to the displacement of water molecules and other ions originally adsorbed on the electrode by PVP molecules to form a protective film. The thickness of the film increases with increasing concentrations of the inhibitor resulting in lower Cdl values. Such behaviors are in good agreement with previous reports on the inhibition of steel corrosion [6, 10].

Table 7. Effect of time on the corrosion parameters of C-steel at pH 7 and pH8 in absence and presence of 1000 ppm of PVP

t(hr)	pH	CR*10^2 (mg/cm^2.hr) blank	CR*10^2 (mg/cm^2.hr) blank+ PVP	% IE	ϴ
1	7	3.18	2.59	18.56	0.18
2	7	4.20	3.45	17.84	0.18
3	7	5.85	4.40	24.81	0.25
1	8	4.02	2.35	41.40	0.41
2	8	5.07	3.25	33.13	0.33
3	8	6.91	5.56	19.53	0.20

The impedance plots for inhibited electrodes were not substantially different from those of uninhibited electrodes indicating that a charge transfer process controls the corrosion of CS and the presence of the inhibitor increases the impedance but does not change other aspects of the behaviour. Approximately all the plots have a distorted semicircular shape with a capacitive loop at high frequency (HF) followed by a capacitive loop at low frequency (LF) and an incomplete inductive loop in the low-frequency (LF) regions. The LF inductive loop may be attributed to the relaxation process

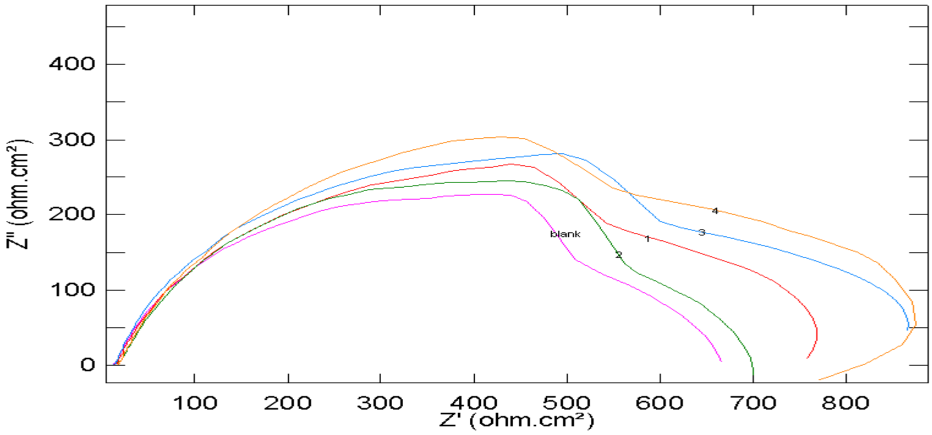


Figure 2. EIS Plots at pH 7 in absence and presence of different concentrations of PVP [1] 1000ppm of PVP, [2] 1500ppm of PVP, [3] 2000ppm of PVP, [4] 3000ppm of PVP.

obtained by adsorption of species such as Cl^- on the CS surface. The LF loop may also be attributed to the re-dissolution of the passivated surface at low frequencies [7]. The equivalent circuit used to analyse the electrical behaviour of CS in the presence of PVP was the well-known Randell cell as shown in Figure 3. This model is represented by a capacitor (ǁ) and a resistor in parallel, which represents the oxide layer. The capacitor represents the electric properties of the oxide layer (C_{dl}), whereas the resistor represents the charge-transfer process through the oxide layer (R_{ct}), and R_{sol} represents the solutions resistance between the reference and working electrode. These results are calculated and presented in Table 8. The adsorption of PVP led to the formation of a protective film on the metal/solution interface and an increase in the thickness of the electronic double layer.

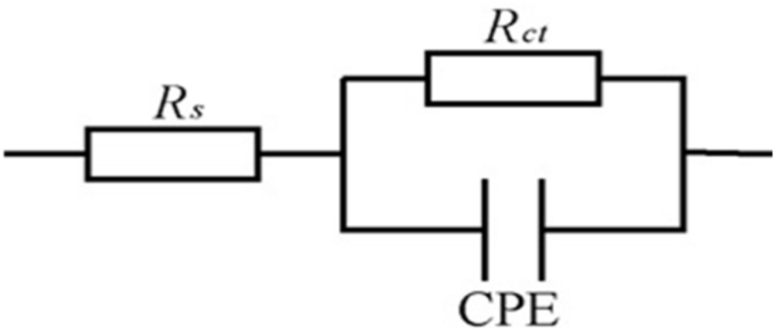


Figure 3. The equivalent circuit model used to fit the experimental EIS data.

3.3.2 Tafel plots

The variations of corrosion potentials (E_{corr}) with time were recorded with respect to a saturated calomel reference electrode. Regular Tafel plots were obtained as shown in Figure 4. for pH7 in absence and presence of different concentrations of the inhibitor. Table 9 shows the Tafel parameters determined using the extrapolation method for CS at 30°C in 0.1 M NaCl in the absence and presence of different concentrations of PVP. The addition of PVP caused a decrease in the anodic and cathodic Tafel slopes, which indicated that PVP is a mixed-type inhibitor affecting the iron dissolution and the cathodic reaction. Table 8 shows that for E_{corr} the trend was not clear in the presence of blank + PVP or in presence of blank + PVP + KI. The addition of PVP to blank solutions at pH7 decreased I_{corr} value. The %EI values and the threshold concentration for the CS inhibition was 44% with 2000 ppm PVP. The same trend was observed by weight loss results in Table 2 whereas the threshold concentration was 2000 ppm of PVP.

Table 8. EIS parameters for CS corrosion at 30°C in 0.1M NaCl at at pH7 and pH8 in absence and presence of different concentrations of PVP.

Solution	pH	R_{sol} (Ω.cm^2)	R_{ct} (Ω.cm^2)	C_{dl} (μF)	%IE
Blank	7	1.675×10	6.91×10^2	9.27	---------
Blank+1000PVP	7	2.18×10	7.74×10^2	1.137	10.78
Blank+1500PVP	7	2.295×10	7.32×10^2	1.121	5.67
Blank+2000PVP	7	2.664×10	10.88×10^2	1.45	36.51
Blank+3000PVP	7	2.647×10	7.13×10^2	1.34	3.11
Blank	8	1.04×10	6.07×10^2	8.91	---------
Blank+1000PVP	8	1.11×10	6.25×10^2	1.066	2.88
Blank+1500PVP	8	1.44×10	7.50×10^2	1.586	19.06
Blank+2000PVP	8	1.634×10	7.31×10^2	1.093	16.96
Blank+3000PVP	8	1.92×10	7.02×10^2	1.24	13.53

At pH 8, the same trend was noticed but the threshold concentration for the CS inhibition was 30% with 1500 ppm PVP. As can be observed in Table 9, adding 0.06 M KI to the blank solution in the presence of 1000 ppm of PVP decreased E_{corr}, I_{corr} and CR at pH 7 and 8. The present results are consistent with other studies that the use of natural and synthetic polymers increases the inhibition of mild steel corrosion in neutral medium [23, 24]. Similar synergistic influences caused by iodide ions in the presence of some aliphatic amines as inhibitors of corrosion of CS in 1 M H_2SO_4 were observed [20].

The present results calculated from the Tafel plots are in complete agreement with those obtained from EIS and weight loss experiments. The slight discrepancy in the IE% values obtained from different methods can be interpreted as the result of different techniques times and that the weight loss were done without removing the system from equilibrium. Some researchers in the past 10 years tried to correlate molecular electronic structure parameters with inhibition efficiency. The difficulty in obtaining a direct relation between quantum chemical parameters and corrosion inhibition efficiency

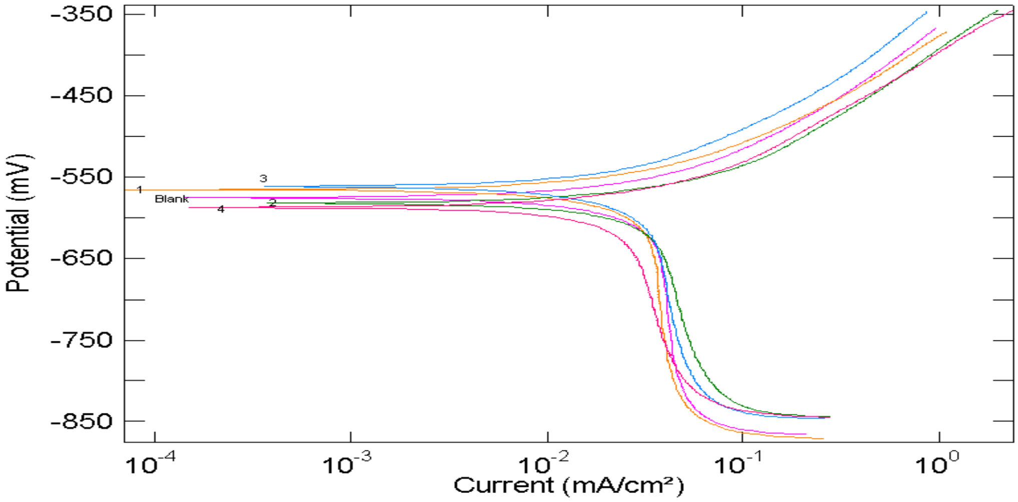


Figure 4. Tafel Plots for pH7 in absence and presence of different concentrations of the inhibitor (PVP) [1] 1000ppm of PVP, [2] 1500ppm of PVP, [3] 2000ppm of PVP, [4] 3000ppm of PVP.

provides a confirmation of the complex nature of interactions that are involved in the corrosion inhibition process [19]. The quantum chemical calculation approach was critically examined by Kokalj in a very powerful study which "supports the proposition that inhibition effectiveness cannot be directly related to molecular electronic properties"[25]. Instead he emphasized the need of more modeling studies of the inhibitor–surface interaction. Although in this study the old weight loss method is applied, using it with adsorption models can give the real picture of the extent of corrosion in real life.

Table 9. Tafel parameters for CS corrosion at 30^{o}C in 0.1M NaCl at neutral and near neutral medium in absence and presence of different concentrations of PVP.

Solution	pH	-E$_{corr}$ (mV)	I$_{corr}$ (mA/cm^{2})	B$_{a}$ (mV/dec)	-B$_{c}$ (mV/dec)	CR (mm/year)	%IE
Blank	7	575	0.0210	88.3	276	0.236	------
Blank+1000PVP	7	566	0.0187	81	263	0.211	10.59
Blank+1500PVP	7	583	0.018	71.5	216.5	0.203	13.98
Blank+2000PVP	7	600	0.01176	74	236	0.132	44.07
Blank+3000PVP	7	588	0.0152	68	222	0.171	27.54
Blank+1000 PVP+0.06M KI	7	624	0.0108	57.17	159.8	0.112	58.82
Blank	8	597	0.0242	87.5	335.4	0.272	------
Blank+1000PVP	8	581	0.0203	79	213	0.228	16.18
Blank+1500PVP	8	592.7	0.01674	70.6	221	0.190	30.13
Blank+2000PVP	8	573	0.0187	63	227	0.211	22.70
Blank+3000PVP	8	582.2	0.0196	88.9	311.7	0.221	18.75
Blank+1000 PVP+0.06M KI	8	617	0.0132	61.88	194.6	0.148	45.59

3.3. Adsorption mechanism

In general, corrosion inhibition mechanisms in neutral and alkaline media can be explained as the adsorption of the inhibitor molecules onto the metal surface. Adsorption of inhibitors may affect the corrosion rate in two ways [11] (i) by decreasing the available reaction area (geometric blocking effect); and (ii) by modifying the activation energy of the cathodic and/or anodic reactions occurring during the inhibited corrosion process. It is difficult to determine which aspects of the inhibiting effect are connected to the geometric blocking action and which are connected to the energy effect. Theoretically, no shifts in the corrosion potential should be observed after adding the corrosion inhibitor if the geometric blocking effect is stronger than the energy effect [11]. The slight change observed in the OCP and E_{corr} values upon addition of PVP (Table 9) indicates that the energy effect is stronger, although the blocking effect cannot be ignored.

In order to evaluate the adsorption process of PVP on CS surface, Langmuir, Temkin and Freundlich adsorption isotherms were tested to determine which adsorption isotherm best fit the present results.The adsorption of PVP on the CS surface is frequently modelled by the Freundlich or Langmuir equation. The surface coverage values for pH 7 at different concentrations of PVP and temperatures are listed in Table 2 and Table 3, respectively. The results of this study did not fit with the Freundlich equation ($R^2 = 0.93$) or Temkin ($R^2 = 0.77$). However our data was best presented using the Langmuir adsorption isotherm equation:

$$\frac{C}{\Theta} = \frac{1}{K} + C \qquad (6)$$

Where C is the concentration of the inhibitor, θ is the surface coverage and K is the equilibrium constant of the adsorption process [26]. A linear relationship with a linear regression coefficient close to 1 was obtained ($R^2 = 0.99$), as shown in Figure. 5. The present results confirm that the polymer is adsorbed as a monolayer on the metal surface. Adherence to Langmuir adsorption isotherm is generally regarded to indicate chemisorptions with monolayer adsorption.

The adsorption–desorption equilibrium constant K was determined from the intercept of the Langmuir isotherm, and the free energy of adsorption (ΔG^{o}_{ads}) was calculated according to equation (7):

$$\Delta G^{o}_{ads} = -RT \ln(55.5K) \qquad (7)$$

Where 55.5 is the water concentration in mol/L, R is the universal gas constant, and T is the absolute temperature.

The adsorption–desorption equilibrium constant K was determined from the intercept of Figure .2 to be 3.333×10^3 L/mol, leading to a $\Delta G^{o}_{ads} = -30.05$ kJ /mol. The negative value of ΔG^{o}_{ads} indicates that the adsorption process of the inhibitor is spontaneous. Generally values of ΔG^{o}_{ads} around −20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between charged molecules and charged metal surface (physisorption) [26]; those values around −40 kJ mol^{-1} or higher involve charge sharing or charge transfer from organic molecules to the metal surface to form a coordinate type of metal bond (chemisorption).

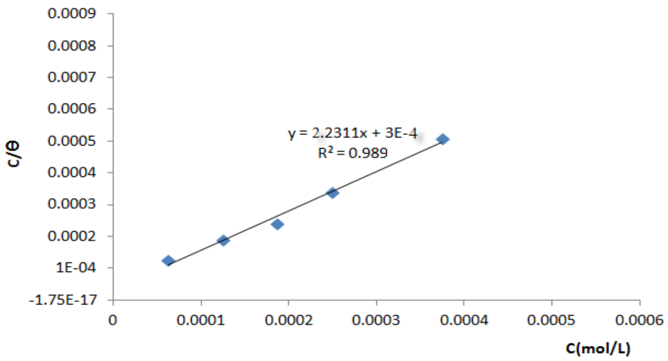


Figure 5. Langmuir adsorption isotherm of PVP on CS in 0.1M NaCl at 30° at pH 7.

In the present work, the calculated $\Delta G_{ads.}$ values are more than −20 kJ mol^{-1} but less than −40 kJ mol^{-1} indicating that the adsorption of PVP molecules reveals physical and chemical adsorption. Similar thermodynamic data were obtained for the adsorption of PVP on CS in an HCl solution [6] and the adsorption of some triazoles in mild steel in HCl [19].

According to Thangavel and Rengaswamy, the role of chloride is unique. It can be reused, and even a small amount of chloride can sustain the corrosion process [27].

$$Fe^{+2} + 2Cl^{-} \rightarrow FeCl_2 \qquad (8)$$

$$FeCl_2 + 2H_2O \rightarrow Fe\,(OH)_2 + 2H^{+} + 2Cl^{-} \qquad (9)$$

$$6FeCl_2 + O_2 + 6H_2O \rightarrow 2Fe_3O_4 + 12H^{+} + 12Cl^{-} \qquad (10)$$

From the present results, a tentative mechanism is proposed for the observed corrosion-inhibition phenomena. However, based on the results from Table 5 and the Pourbaix diagram for iron, the following mechanism can be postulated:

$$Fe \rightarrow Fe^{+2} + 2e^{-} \qquad (11)$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \qquad (12)$$

$$Fe^{+2} + 2Cl^{-} \rightarrow FeCl_2 \qquad (13)$$

$$FeCl_2 + 2H_2O \rightarrow Fe\,(OH)_2 + 2H^{+} + 2Cl^{-} \qquad (14)$$

$$Fe^{+2} + 2H_2O \rightarrow Fe\,(OH)_2 + 2H^{+} \qquad (15)$$

Equation (10) is excluded because a large decrease in the pH over time would occur due to the large number of protons produced in this reaction, which is not consistent with the present results where the change of pH for CS +blank at pH7 was small. If these findings (ΔG^{o}_{ads} value, E_{app} value calculated from Arrhenius plots) are taken into consideration, the action of PVP as a corrosion inhibitor for CS in alkaline medium may be attributed to a strong adsorption bond of a chemiosorptive nature. The bond involves the charge sharing or charge transfer from the oxygen double bond in the PVP molecules to the positively charged CS surface to form a coordinate-type bond and an electrostatic attraction between the cationic NH_2 species and Cl^{-}_{ads}. Iron is a transition metal with a vacant, low-energy electron orbital, and the loosely bound electrons of oxygen in a PVP molecule support this proposition for the adsorption mechanism. The hydrophobic part of a PVP polymer is believed to face the solution, which provides the added advantage of strongly locking the chains on the metallic surface.

3.4 .Thermodynamic Parameters

Using the well known transition state equation [26]:

$$\ln\left(\frac{CR}{T}\right) = \left[\frac{\ln RT}{Nh} + \frac{\Delta S}{RT}\right] - \frac{\Delta H}{RT} \qquad (16)$$

where N is the Avogadro's number and h is the Plank constant, a plot of lnCR/T against T^{-1} yields a straight line(not shown). The slope equals ΔH^{o}_{ads} /R and the intercept equals the parameters between the brackets. The standard enthalpy (ΔH^{o}_{ads}) change and the standard entropy change (ΔS^{o}_{ads})for the adsorption process were evaluated and listed in Table.10.

Table 10. Thermodynamic Parameters of blank solutions and Blank+1000PVP at pH 7 and pH8

Solution	ΔS^{*}_{ads} (J/K)	ΔH^{*}_{ads} (kJ/mol)	E^{*}_{app} (kJ/mol)
Blank (pH 7)	116.2-	18.98	16.17
Blank(pH 8)	-136.99	12.03	9.30
Blank+1000PVP(pH 7)	-144.0	11.06	8.35
Blank+1000PVP(pH 8)	-151.13	9.11	6.39

All values of ΔS^{*}_{ads} are negative for the blank and inhibited solution. The negative values for ΔS^{*} implies that the activation complex in the rate determining step represents association rather than dissociation step which means that a decrease in disorder takes place on going from reactant to the activated complex as found by others[28, 29]. For the blank solution there is more order at pH 8 which is consistent with the higher CR value at pH 8 (Table 1). For the blank+ PVP solution there is more order at pH 8 which is consistent with the lower CR value at pH 8(Table 1). Before the adsorption process, the inhibitor molecules may freely move in the bulk solution (PVP were chaotic), but with the progress of adsorption, the inhibitor molecules became adsorbed orderly onto the steel surface, thus a decrease in disorder (entropy) is observed.

All values of ΔH^*_{ads} are positive for the blank and inhibited solution. For the blank solution, the ΔH^*_{ads} value are less at pH 8 which implies that the energy needed for the corrosive action of Cl^- at pH 8 is less than pH7 which is consistent with the higher CR value at pH 8(Table 1). The same logic applies for the blank+ PVP solution, however the action of the PVP inhibitor on adsorption process makes CR less at pH8 (Table 1).

It is noticed that the difference $|E^*_{app.} - \Delta H^*|$ is approximately equal to RT. From the thermodynamic and kinetic point of view, the unimolecular reactions are characterized by following equation [26]:

$$\Delta E^*_{app.} - \Delta H^* = RT \qquad (17)$$

This is consistent with the fitting of the present data on Langmuir adsorption isotherm which implies unimolecular adsorption.

4. CONCLUSION

1. From the present study, it was found that PVP is a good corrosion inhibitor in neutral medium containing NaCl, even at high temperatures. The inhibition efficiency of PVP increased with increased inhibitor concentration until a threshold concentration was reached. A remarkable reduction in the corrosion rate was observed in the presence of KI. The addition of UC reduced the % IE of blank + PVP whereas the addition of KI to the blank + PVP + clay mixture increased the surface coverage.
2. According to the EIS results, the adsorption of PVP led to the formation of a protective film on the metal/solution interface and an increase in the thickness of the electronic double layer. From the Tafel results, PVP was a mixed-type inhibitor, which affected iron dissolution and the cathodic reaction.
3. Langmuir adsorption isotherm was obeyed which indicate unimolecular adsortion. From the changes of pH values for NaCl + PVP and NaCl +PVP + CS solutions, the ΔG^o_{ads}, E_{app} values, and the positive nature of the CS surface in the present study, we may assume that PVP molecules were physically adsorbed on the CS by the protonated NH_2 species and Cl^-_{ads} and adsorbed chemically through the negatively polarised oxygen atom.
4. All values of ΔS^*_{ads} are negative for the blank and inhibited solution which implies that the activation complex in the rate determining step represents association rather than dissociation step. The thermodynamic parameters support the % IE results of WL, EIS and Tafel which indicate that

PVP is a good corrosion inhibitor for CS in solutions containing NaCl which makes PVP a promising polymer in the drilling industry especially at pH 8 rather than pH 7 as the % IE reached the surface coverage of 0.72 for [Blank +1000 ppm PVP +0.06M KI + 2g/L UC].

ACKNOWLEDGEMENTS
The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding the work through the research group project No. RGP-VPP-102.

References

1. L. L. Shreir, R. A. Jarman, G. T. Burstein, *Corrosion volume1,Metal/ Environment Reactions,* 3rd edition, Butter worth – Heinemann, London,(1994).
2. P. A. Scheweitzer, *Encyclopedia of Corrosion Technology*, Marcel Dekker, London(1998).
3. M. A. Deyab, S. S. Abd El-Rehim, *Electrochim. Acta*, 53 (2007) 1754.
4. S. A.Umoren, O. Ogbobe, I. O. Igwe, E. E. Ebenso, *Corr. Sci.*,50(2008)1998.
5. Y. Jianguo, W. Lin, V. Otteno-Alegoi, D. P. Schweinsberg, *Corros. Sci.*, 37 (1995)975.
6. L. A. Al Juhaiman, "PVP Polymer as a Corrosion Inhibitor for CS in HCl Solutions" presented in 13th Middle East Corrosion Conference &Exhibition, Bahrain, 2010.
7. M. A. Amin and K. F. Khaled, *Corros. Sci.*, 52 (2010) 1762.
8. H. H. Hassan, *Electrochim. Acta,* 51 (2005) 526.
9. S. M. Abd El Haleem, S. Abd El Wanees, E. E. Abd El Aal, A. Diab, *Corros. Sci.*, 51 (2009) 1611.
10. S. A. M. Refaey, F. Taha, A. M. Abd El-Malak, *Appl. Surf. Sci.,* 242 (2005) 114.
11. D.A. Jones, "*Principles and Prevention of Corrosion*", 2 nd ed. Prentice Hall Engineering (1995).
12. A. M. Shams El Din, L. Wang, *Desalin.,* 107 (1996) 29.
13. P. Galicia, and I. Gonzalez, *Electrochim. Acta.,* 50 (2005) 4451.
14. A. Chetouani, K. Medjahed, K. E. Benabadji, B. Hammouti, S. Kertit, A. Mansri, *Org. Coat. Prog.,* 46 (2003) 312.
15. M. B. Valcarce, M. V´azquez , *Electrochim. Acta*, 53 (2008) 5007.
16. E. E. Abd El Aal, S. Abd El Wanees, A. Diab, S. M. Abd El Haleem, *Corros. Sci.*, 51 (2009) 1611.
17. M. Sanchez-Moreno, H. Takenouti, J. J. Garcia-Jare˜no, F. Vicente, C. Alonso, *Electrochim. Acta*, 54 (2009)7222.
18. A. Popova, E. Sokolova, S. Raicheva, M. Christov,*Corros. Sci.*,45 (2003) 33.
19. S. Zhang, Z. Tao a, W. Li b, B. Hou, *Appl. Surf. Sci.*, 255 (2009) 6757.
20. A. S. Fouda, H. A. Mostafa, F. El-Taib, G. Y. Elewady,*Corros. Sci.*, 47 (2005) 1988.
21. G. Blustein, and C. F. Zinola, *J. Colloid Interf. Sci.*, 278 (2004) 393.
22. W.J. Lorenz, F. Mansfeld, *Corr. Sci.*, 21 (1981) 647.
23. S. A. M. Refaey, *Appl. Surf. Sci.*, 157 (2000) 199.
24. M. Finšgar, S. Fassbender, F. Nicolini, I. Milošev, *Corros. Sci.*, 51(2009) 525.
25. A. Kokalj, *Electrochim. Acta.*, 56 (2010) 745.
26. K. Laidler, J. Meiser, B. Sanctuary, *Physical Chemistry* , 4th ed., Houghton Mifflin,(2003).
27. K. Thangavel, N. S. Rengaswamy, *Cement Concrete Comp.*, 20 (1998) 283.
28. S.S. Abd El-Rehim, H.H. Hassan, M.A. Amin, *Mater. Chem. Phys.*, 70 (2001) 64.
29. E. A. Noor, A. H. Al-Moubaraki, *Mater. Chem. Phys.* ,110 (2008) 145.