Journal of Basic and Environmental Sciences, 7 (2020) 34-44

ISSN
Online: 2356-6388
Print: 2536-9202

Research paper Open Access

Synthesis of Ionic Liquid based on Poly Vinyl Pyrrolidone as corrosion inhibitor of carbon steel in Aqueous Media

E. Habeb[1], Wagdy I. A. El-Dougdoug[2], M.A. Abbas[1], Mohamed Abo-Riya[2] and Z. Elbialy[3]

[1]Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, Egypt
[2]Chemistry Department, Faculty of science, Benha University, Benha, Egypt
[3]Egyptian Organization for Standards and Quality. Cairo, Egypt
Corresponding author email: eslam_habeb2012@yahoo.com

Abstract:

In this study, Poly vinyl Pyrrolidone was prepared then followed by quaternization reaction with different alkyl halides to obtain Ionic Liquids. The chemical structures of the prepared compounds were confirmed by IR, ^{1}HNMR and GPC. Poly Vinyl Pyrrolidone and Ionic Liquids have been investigated as corrosion inhibitor for carbon steel in 1 M HCl solution using different techniques such as electrochemical impedance spectroscopy (EIS) and potentiodynamic Polarization. The thermodynamic parameters (ΔG^o_{ads}, ΔH^* and ΔS^*) were evaluated. The film formation from corrosion product on the steel surface was confirmed by SEM and EDX techniques. The results show that these compounds act as efficient inhibitors for carbon steel in 1 M HCl solution.

Keyword: corrosion protection, polarization, impedance, SEM and EDX
Received; 20 Aug. 2019, Revised form; 17 Oct. 2019, Accepted; 17 Oct. 2019, Available online 1 Jan. 2020.

1. Introduction

Ionic liquids or molten salts are compounds that are composed entirely of ions and exist in a liquid state at Temperature under 100 °C [1,2]. Using Ionic Liquids due to their advantages include virtually non-measurable vapor pressure under moderate conditions, no volatility, in combination with moderately low flammability and the majority of ILs exhibit high thermal stability [3-6]. They represent a class of liquid materials with unique property profiles originating from a complex interplay of coulombic, hydrogen bonding, and van-der-Waals interactions of their ions [7]. Polyvinyl pyrrolidone was found to be a good corrosion inhibitor in alkaline solutions containing NaCl [8] and in neutral solutions [9]. Physical properties which can be tailored to the requirements of a process include the melting point, viscosity, density, solubility, and hydrophobicity of the IL[10]. Moreover, reaction products may be separated more easily from an IL than from conventional solvents [11]. Corrosion of metals and their alloys is of major economic and safety concern in several industries. Among several metals, mild steel is one of the widely used steel materials in various. Corrosion is the physicochemical interaction between a metal [12, 13] and its environment, which results in changes in the metal's properties and which may lead to significant functional impairment of the metal. Acidizing of petroleum in oil wells is an important technique for enhancing oil production. This process involves using a solution of 15–28% hydrochloric acid [14].

Corrosion inhibitors are compounds Inhibition Corrosion of metals by adsorption on surface of metal and prevent Corrosive Chemicals reaching metal surface [15]. A number of ionic liquids were reported to be efficient inhibitors for the corrosion of mild steel, aluminum and copper in acidic solutions [16, 17].

The aim of the present study is to investigate the inhibition of carbon steel (C-steel) corrosion by ionic liquid using different techniques.

2. Experimental

2.1. Materials

All the solvents and chemicals used for synthesis are of analytical grade N- vinyl pyrrolidone, BPO, Dodecyl Bromide and Dodecyl Chloride were purchased from Sigma-Aldrich and used without further purification. 37% HCl (GR grade) was purchased from Merck. Analytical grade Ethanol and Xylene were received from Fluka and used without any further purification.

2.2. Methods

2.2.1. Synthesis of Poly vinyl pyrrolidone:

Poly vinyl pyrrolidone was prepared by reaction of 60 gm of N-Vinyl-pyrrolidone, ethanol and (0.250 % from the weight of N vinyl pyrrolidone) BPO initiator for about 2 days at 70 °C under stirring then evaporate solvent to obtain pale yellow semisolid. Yield (97.17 %).

2.2.2. Synthesis of ionic liquid:

Poly vinyl pyrrolidone was refluxed with dodecyl bromide in molar ratio (1:1) in presence of ethanol as a solvent for 72 h at 70 °c, then left to be precipitated in petroleum ether to obtain final product as pale brown wax (scheme 1). The chemical structure of prepared compound was confirmed by IR, NMR and GPC.

2.3. Structural confirmation of the synthesized compound:

The chemical structures of the prepared surfactants were confirmed by:

1- FTIR spectra: The FT-IR spectra of the samples were characterized by an IR spectrometer (Thermo scientific Nicolet iS10) by using KBr as a dispersant, which ranged from 400-4000 cm^{-1}.
2- ^{1}HNMR: The NMR spectra of samples were characterized by Switzerland, Bruker Avance.
3- GPC: The GPC spectra of samples were characterized by Waters 515/2410 Gel Permeation Chromatograph (GPC, Waters, America) and an Ultrahydrogel column, Solvent is water.

2.4. Carbon steel

Carbon steel specimens with chemical composition (wt %) were used in the experiments: Carbon (C) 0.19%, Chromium (Cr) 0.009%, , Silicon (Si) 0.05%, Manganese (Mn) 0.94%, phosphorus (P) 0.009%, Sulphur (S) 0.004%, Nickel (Ni) 0.014%, Aluminum (Al) 0.034%, Vanadium (V) 0.016%, Titanium (Ti) 0.003%, Cupper (Cu) 0.022%, and the rest Iron (Fe). A pre-treatment procedure was carried out, prior to each experiment, in which the surface of Working Electrode was mechanically polished with different emery paper and cleaned with acetone and distilled water then dried at room temperature before use.

2.5. Electrochemical techniques.

Different techniques have been employed for studying the corrosion behavior of carbon steel in 1 M HCl in absence and presence of the synthesized compounds as follow:

2.5.1. Potentiodynamic polarization.

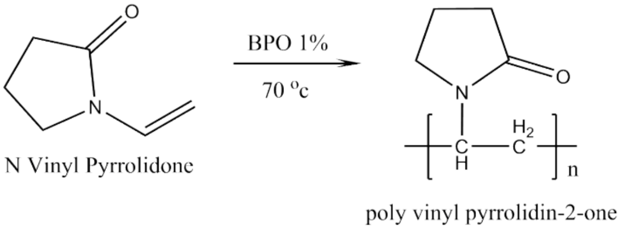
Potentiodynamic polarization method was used to determine the anodic and cathodic polarization curves of carbon steel in 1 M HCl in absence and presence of different concentrations of inhibitors at 40 °C. Potentiodynamic polarization was measured with a Radiometer Voltalab master (Model PGZ 301). E vs. log I curves recorded. The corrosion kinetic parameters such as corrosion current (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (β_c), and anodic Tafel slope (β_a) were derived from the Tafel curves.

2.5.2. Electrochemical impedance spectroscopy (EIS)

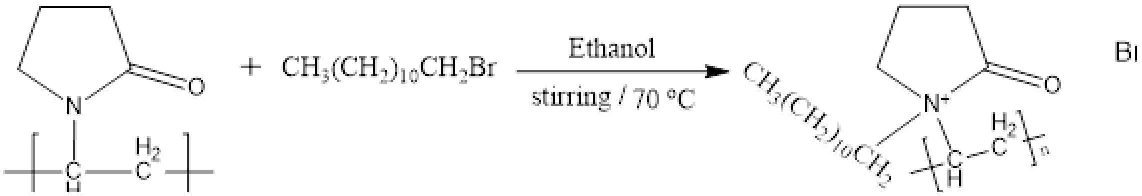
The same electrode of C-steel used in potentiodynamic polarization was also used. Each experiment was performed on new polished electrode using a new prepared electrolyte. Electrochemical impedance spectroscopy (EIS) was measured with a Radiometer Voltalab master (Model PGZ 301) at 40 °C.

2.6. Surface Examination:

1- SEM & EDX: The Scanning Electron Microscope spectra of samples were characterized by SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification14x up to 1000000 and resolution for Gun.1n.
2- XRD: X-ray spectra of the outer rust were taken using a Philips 2236/20 diffractometer.



Scheme 1



3. Results and discussion

3.1. Structural confirmation of N Dodecyl Polyvinyl Pyrrolidinium Bromide (PVP Br):

The FT-IR spectra confirm the expected functional groups in the synthesized N Dodecyl Polyvinyl Pyrrolidinium Bromide (Fig. 1) by showing bands at 2925 and 2855cm^{-1} cm^{-1} (νCH aliphatic chain), 1674 cm^{-1} (νC=O imide), 1462 $^{-1}$(νCH_2bending), 1374 cm^{-1}(νCH_3 bending) 1224 cm^{-1} (νC–N alkyl stretching) and 576 cm^{-1}(νC–Br stretching).

The data of ^{1}H-NMR spectra confirm the expected hydrogen proton distribution in the synthesized PVP Br δ (ppm) (Fig. 2): 0.8 (t, $(CH_2)_{12}\underline{\mathbf{CH_3}}$), 1.33 (m, $CH_2CH_2(\underline{\mathbf{CH_2}})_{12}CH_3$), 1.6 (d, $NCH\underline{\mathbf{CH_3}}$), 1.88 (m, $CH_2\underline{\mathbf{CH_2}}(CH_2)_{12}CH_3$), 1.99 (t, $NCH\underline{\mathbf{CH_2}}CHNCH_3$), 2.09 (t, $NCH\underline{\mathbf{CH_2}}CHN$), 2.18 (m, $NCH_2\underline{\mathbf{CH_2}}CH2CO$), 2.4 (t, $NCH_2CH_2\underline{\mathbf{CH_2}}CO$), 3.07 (t, $N\underline{\mathbf{CH_2}}CH_2CHN$), 3.21 (t, $\underline{\mathbf{CH_2}}N^+$), 3.30 (t, $N\underline{\mathbf{CH2}}CH_2CH_2CO$), 3.5 (m, $CH_2\underline{\mathbf{CHN}}CH_2$) and 3.77 (m, $\underline{\mathbf{CH}}NCH_3$).

The data extracted from GPC spectra of samples were listed in Table 1.

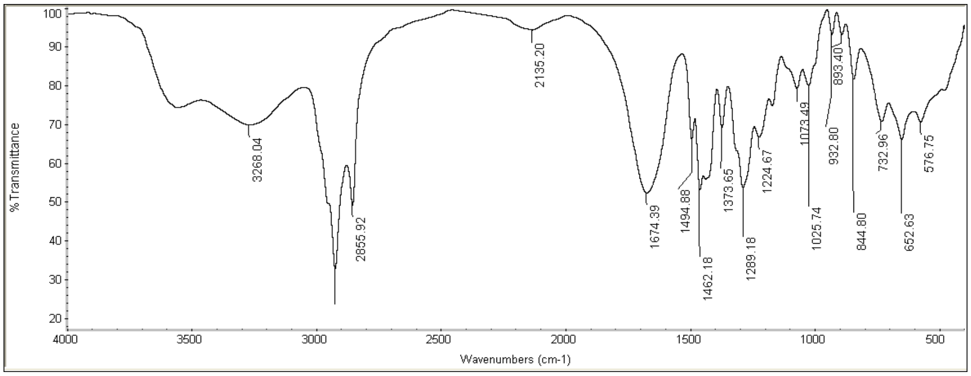


Fig (1): IR spectrum of N Dodecyl Polyvinyl Pyrrolidinium Bromide

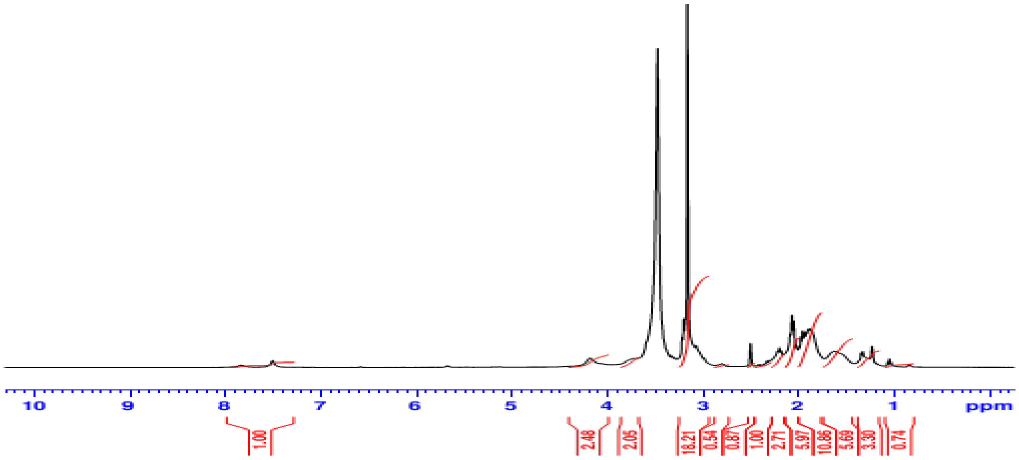


Fig (2): ^{1}HNMR spectrum of N Dodecyl Polyvinyl Pyrrolidinium Bromide

Table (1): Data of GPC of N Dodecyl Polyvinyl Pyrrolidinium Bromide

	Mn (Daltons)	Mw (Daltons)	MP	Poly-dispersity
PVP Br	27321	112319	89678	4.111

3.2. Potentiodynamic polarization technique

The representative potentiodynamic polarization curves of carbon steel in 1 M HCl solution in the absence and presence of various concentrations of the synthesized compound is shown in Fig. (3). Some corrosion kinetics parameters, such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c & β_a), corrosion current density (I_{corr}) achieved from the extrapolation of the anodic and cathodic polarization curves, corrosion rate (C_r) and inhibition efficiency (IE %) were computed and presented in Table. 2. The degree of surface coverage (θ) and the inhibition efficiency (IE %) were calculated as follow:

$$IE\ \% = (\theta) \times 100$$

$$(\theta) = (I_{corr"free"} - I_{corr"inh"}) / I_{corr"free"}$$

Where, $I_{corr"free}$ and $I_{corr"inh"}$ are the corrosion current densities for carbon steel electrode in absence and presence of the inhibitors.

Data in Table. 2. Reveals that, when the concentration of the synthesized inhibitor was increased, the inhibition efficiencies increased while the corrosion current densities decreased. This increase in inhibition efficiency with increasing inhibitor concentration indicated that these compounds were acting as an adsorption inhibitor. The inhibitive action of these compounds was discussed in terms of blocking the electrode surface by adsorption of the molecules through the active centers contained in its structure.

The adsorption of the inhibitor shifted the corrosion potential in the positive direction. The addition of PVP Br decreases both of the Tafel slopes ($ß_a$ and $ß_c$), the anodic and cathodic Tafel slopes. This indicates that PVP is a mixed-type inhibitor affecting the iron dissolution and hydrogen evolution. The reduction of the positive and negative currents in the presence of PVP Br can be explained by the blocking of active sites by the formation of a protective film on the surface of the electrode.

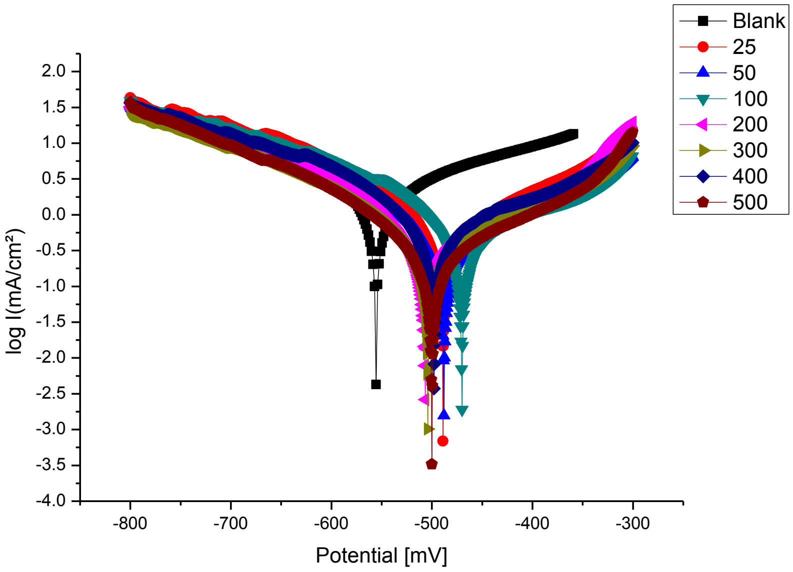


Fig (3): Potentiodynamic polarization curves of carbon steel in the presence and absence of different concentrations of PVP Br.

Table (2): Corrosion parameters of carbon steel in absence and presence of different concentrations of PVP Br.

Soln.	Ec mV	ic mA/cm²	Rp Ω.cm²	Ba mV/decade	Bc mV/decade	CR mm/Y	ɳ	Θ
free	-555.5	5.1562	14.78	495.6	-292.1	60.3	--	--
25	-488.9	0.9025	37.77	202.6	-140.6	10.55	82.50	0.8250
50	-487.9	0.8383	55.37	180.2	-169.7	9.805	83.74	0.8374
100	-470.3	0.799	46.09	332.1	-152.3	9.345	84.50	0.8450
200	-506.8	0.7609	57.87	135.5	-148.8	8.899	85.24	0.8524
300	-504.1	0.6809	68.26	283.3	-168.2	7.963	86.79	0.8679
400	-497.8	0.5209	42.37	192.3	-153.6	6.092	89.90	0.8990
500	-500	0.4218	84.08	211.9	-147.8	4.933	91.82	0.9182

3.3. Electrochemical impedance spectroscopy (EIS) technique

The corrosion behavior of carbon steel in 1M HCl solution in the absence and presence of different concentrations, ranging from 25-500 ppm of the synthesized compounds. The degree of surface coverage (Θ) and the inhibition efficiency (IE %) The- double layer capacitance (C_{dl}) were calculated as follow [18, 19]:

$$(\theta) = (\text{Rct"inh"} - \text{Rct"free"}) / \text{Rct"inh"}$$

$$\eta\% = (\theta) \times 100$$

$$C_{dl} = \frac{1}{2\prod R_{ct}\, f_{\max}}$$

Where, $R_{ct''free''}$ and $R_{ct''inh''}$ are the charge transfer resistance values in the absence and presence of inhibitors for carbon steel in 1M HCl. The degree of surface coverage (Ө), the inhibition efficiency (ɳ %) and charge transfer resistance values were listed in Table (3). C_{dl} represents the capacitance elements. The capacitor, in the equivalent circuit is a frequency dependent element related to the surface roughness [20]. The- double layer capacitance, C_{dl} was obtained at the frequency f_{max} (where the imaginary component of the impedance is a maximum) by the following equation.

The values of R_{ct}, C_{dl}, θ and % IE for C-steel in 1 M hydrochloric acid containing different concentrations for PVP Br inhibitor are shown in Table 3. The present data reveals that the R_{ct} values increase with increasing inhibitor concentration while the C_{dl} values decrease. The ɳ% and surface coverage values increase with increasing inhibitor concentration due to the adsorption of inhibitor on metal surface.

The Nyquist plots for HCl in the presence and absence of different inhibitor concentrations to different compounds, ranging from 25-500 ppm, are presented in Figure (4). The shapes of the impedance plots for the inhibited electrodes are not substantially different from those of the uninhibited electrodes. The presence of the inhibitor increases the Nyquist plots semicircle but does not change other aspects of the behavior. It is shown that the impedance response consisted of the characteristic semicircles, indicating that the dissolution of the C-steel process occurs under charge transfer control; hence, under activation control [21]. The charge transfer resistance values (R_{ct}) were obtained from the diameter of the semicircles of the Nyquist plots. The value of R_{ct} is a measure of the electron transfer across the C-steel surface and is inversely proportional to the corrosion rate. These semicircles are of capacitive type whose diameters increase with increasing the inhibitor concentrations and indicate an increase of the inhibition properties due to the adsorption of inhibitors [22, 23]. Similar Nyquist plots were obtained from previous studies for inhibitors containing nitrogen, such as pyrazolone [24], aliphatic amines [25], and poly (aniline-formaldehyde) [26].

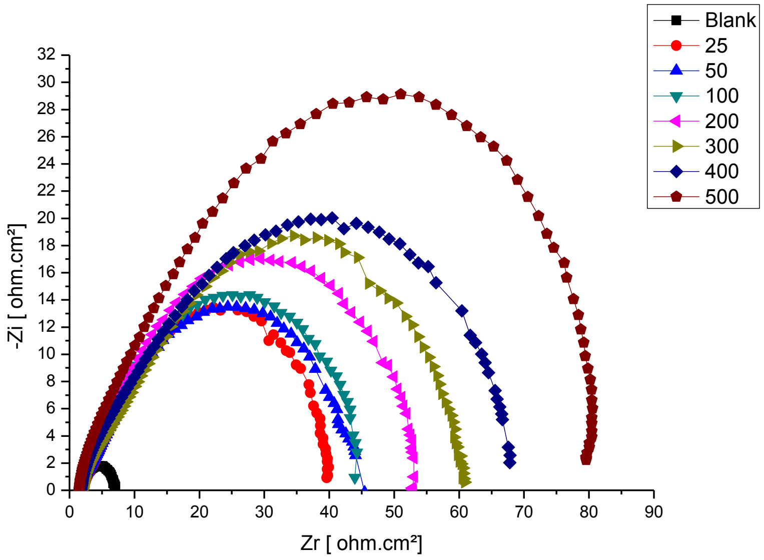


Fig (4): EIS plots for HCl in the presence and absence of different concentrations of PVP Br.

Table (1): EIS parameters for corrosion of C-steel in presence and absence of different concentrations of PVP Br

		R_s. (Ω)	R_{ct}. (Ω)	C µF/cm²	Ө	ɳ%
	blank	1.747	5.419	2631	--------	----------
PVP Br	25	2.54	38.78	183.8	0.8603	86.03
	50	2.126	43.65	204.1	0.8759	87.59
	100	2.057	44.84	141.9	0.8791	87.91

	200	2.289	52.4	108.1	0.8966	89.66
	300	2.601	59.67	149.3	0.9092	90.92
	400	2.01	69.38	102.7	0.9219	92.19
	500	2.426	81.51	78.09	0.9335	93.35

3.4. Kinetic parameter

The activation energy (E_a) for the corrosion of carbon steel in 1 M HCl solution in absence and presence of different concentration of the synthesized inhibitors at different temperatures were calculated from Arrhenius equation:

$$C_r = A\, e^{(-Ea/RT)}$$

And the logarithmic form:

$$\ln C_r = \ln A - (E_a /RT)$$

Where, C_r represents rate of corrosion reaction, A is the Arrhenius constant, R is the gas constant and T is the absolute temperature. Arrhenius plots of Ln Cr vs. 1/T gave straight line, as shown graphically in Fig. (5). with linear regression coefficients are very close to 1, indicating that the corrosion of steel in 1.0 M HCl without and with inhibitor follows the Arrhenius equation with slope of (- Ea / R). Activation energies were calculated and listed in Table 4. The data shows that the activation energy (Ea) of the corrosion of carbon steel in 1 M HCl solution in the presence of PVP Br was smaller than that in free acid solution, indicating that the PVP Br was adsorbed on the steel surface chemically. The change in enthalpy and entropy of activation values (ΔH^*, ΔS^*) were calculated from the transition state theory.

$$\text{Ln}\,(C_r/T) = [\text{Ln}(R / N_A h) + (\Delta S^*/ R)] - (\Delta H^* / RT)$$

Where, h is the Plank constant, N_A is the Avogadro's number, R is the ideal gas constant, ΔH^* is the enthalpy of activation and ΔS^* is the entropy of activation. Plotting of Ln (Cr / T) versus (1 / T), gave straight lines as shown in Fig. (6). with slope of – ($\Delta H^*/R$) and the intercept of Ln(R / N_Ah) + ($\Delta S^*/ R$). Values of ΔH^* and ΔS^* were calculated and listed Table 4.

The positive sign of the enthalpy of activation (ΔH^*), reflecting the endothermic nature of the corrosion process and means that the dissolution of carbon steel is difficult in the presence of inhibitors. The negative sign of entropy of activation (ΔS^*), indicates that the activated complex in the rate determining step represents an association rather than dissociation, reflecting that more order take place, going from reactant to activate complex.

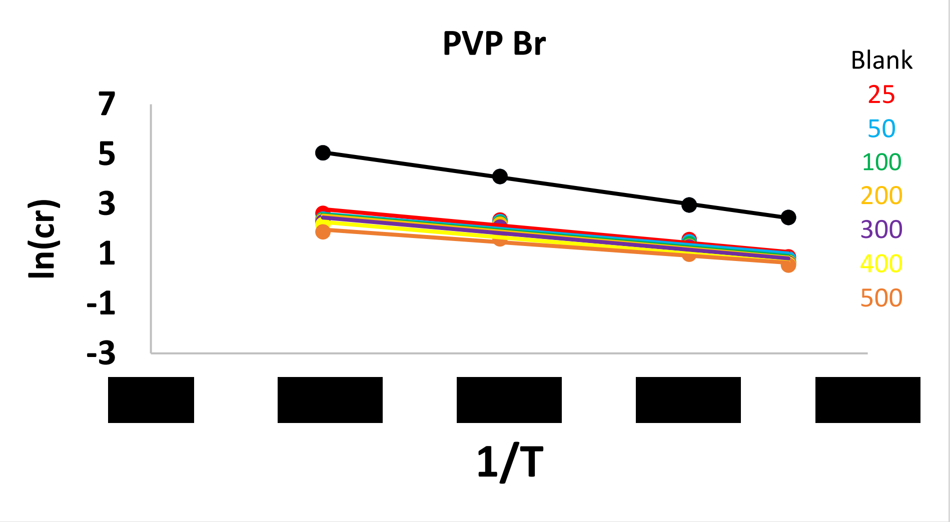


Fig (5): Arrhenius plots of carbon steel in 1 M HCl solution in absence and presence of different concentrations of PVP Br.

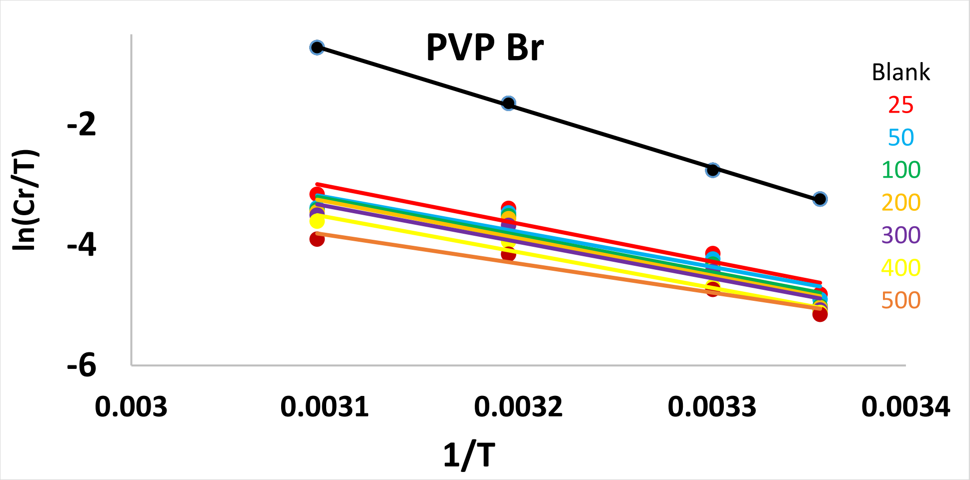


Fig (6): transition state of carbon steel in 1 M HCl solution in absence and presence of different concentrations of PVP Br.

Table (4): Activation thermodynamic parameters of carbon steel in 1 M HCl in absence and presence of different concentrations of PVP Br.

	Conc.	Ea	ΔH*	ΔS*
Blank		84214.49	81635.39	49.32514
PVP Br	25	55001.3	52422.2	- 60.0766
	50	51006.5	48427.4	-73.9881
	100	53560.84	50981.74	-66.2852
	200	53917.01	51337.91	-65.5687
	300	52595.12	50016.02	-70.3109
	400	51794.16	49215.06	-74.2832
	500	42606.56	40027.46	-105.257

3.5. Adsorption isotherm

The adsorption of the synthesized PVP Br was accompanied by desorption of water molecules from the surface. The degree of surface coverage (θ) for different concentrations of inhibitor were evaluated from the potentiodynamic polarization data. The values of surface coverage (θ) of different concentrations of the synthesized inhibitor have been used to explain the isotherm for adsorption of these inhibitors on the carbon steel surface.

Several adsorption isotherms were tested to describe the adsorption behavior of all inhibitors used in this study. The Langmuir isotherm is the best description of adsorption behavior of the inhibitor's molecules on carbon steel surface according to the following equation:

$$C / \theta = (1 / K_{ads}) + C$$

Where: C is the concentration of inhibitor, K_{ads} is the equilibrium constant of the adsorption process and (θ) is the surface coverage.

Fig. (7). Represents plots of C/θ versus C gave a straight line with intercept of (1/ K_{ads}), slope closed to 1 and the correlation coefficient (R^2) equal to 1. This indicates that, the adsorption of cationic surfactants on the carbon steel surface in 1M HCl solution follows Langmuir's adsorption isotherm.

$$\Delta G^o_{ads} = -RTLn(55.5\ K)$$

The value 55.5 in the above equation is the molar concentration of water in solution [27] in mol dm-3. In general, the values of ΔGoads around -20 kJ mol-1 or less negative are associated with an electrostatic interaction between charged inhibitor molecules and charged metal surface (physisorption), and the ΔGoads around -40 kJ mol-1 or more negative involve charge sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type bond (chemisorption) [28, 29]. The negative sign of ΔG^o_{ads} indicate that the adsorption of inhibitor is non spontaneous process. The values of ΔGoads for the inhibitor in 1 M HCl on carbon steel surface are listed in Table 5 were from -36.40 – 42.19 which means the adsorption of inhibitor's molecules on metal surface is mixed physical and chemical adsorption

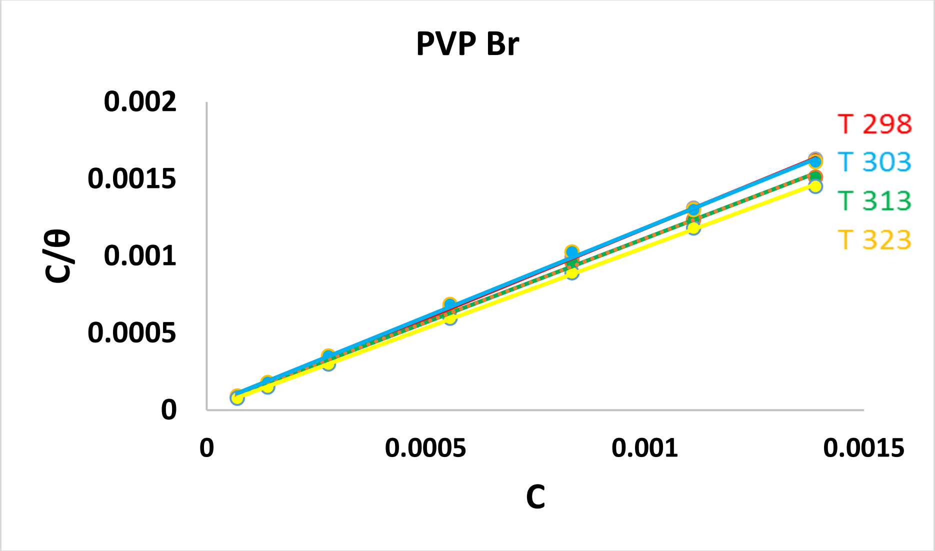


Fig (7): Langmuir isotherm adsorption on the carbon steel surface of different concentration of the synthesized of PVP Br.

Table (5): adsorption of thermodynamic parameters of the synthesized PVP Br on carbon steel surface.

	Temperature	K	ΔG_{ads} kJ mol^{-1}
PVP Br	298	122023	-38.96
	303	33998.79	-36.40
	313	39685.3	-38.01
	323	120128.1	-42.19

3.6. SEM & EDX

Fig. 8 shows SEM image of the surface of the steel specimen after immersion in acidic solutions for 24 h. The micrograph reveals that, the surface was strongly damaged in absence of inhibitors but shows SEM image of the surface of another steels specimen after immersion for the same time interval in all acidic solutions containing 500 ppm of corrosion inhibitor, relatively, The micrographs reveal that, the surface is free from pits and it is smooth , which indicates a good protective film present on the steel surface and also confirms the highest inhibition efficiency of the prepared ionic liquids at 500 ppm concentration.

Fig. 9 shows EDX spot scan of the specimens in absence and presence of corrosion inhibitors. From figure, it was possible to confirm that the crystal is only composed of iron, carbon, chloride and oxygen. The absence of nitrogen could be related to the low count rate of the EDX analysis for light elements and the overlapping of the strong oxygen peak with a possible weak nitrogen peak.

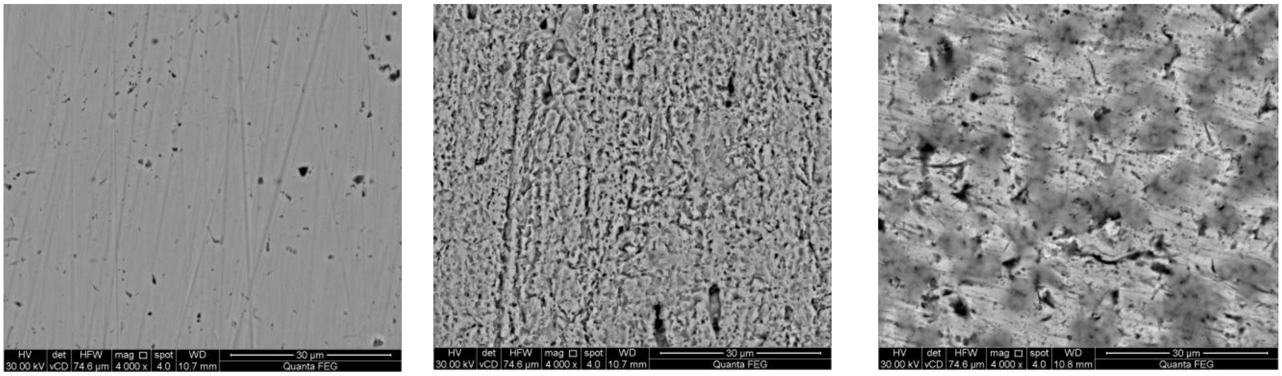


Figure (a) polished sheet *Figure* (b) Blank *Figure (c) PVP Br*

Fig (8): SEM image of the surface of the steel in absence and presence of free acid and inhibitor

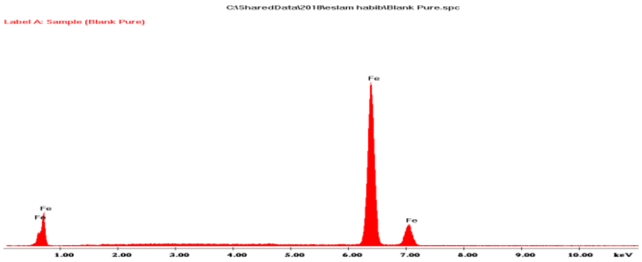


Figure 9 (a): polished sheet of carbon steel

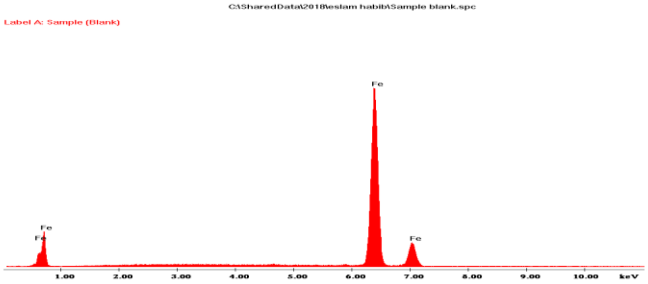


Figure 9 (b): Blank

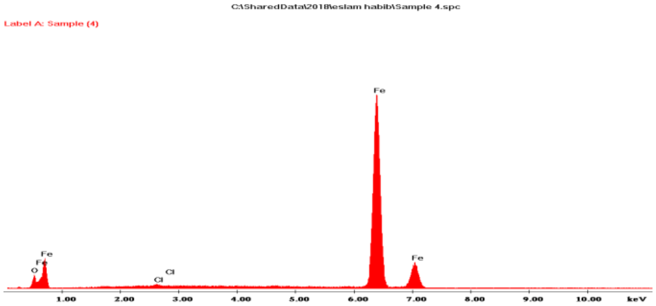


Figure 9 (c): PVP Br

Fig (9): EDX scan of the surface of the steel in absence and presence of free acid and inhibitor

3.7. XRD

XRD pattern of iron and JCPDS file 65-4899 are shown in Figure (10). The diffraction angles of JCPDS file 65-4899 [30] at 2θ = 45.2° and 65.6° are related to (110) and (200) planes of pure iron, respectively. According to intensity and sharp peaks was recorded as a function of Bragg's at 2θ angel in the angular range of 4°–70° and from figures (10) it was found that crystallinity decreased in Blank (1 M HCl) and increased in all solutions 500 ppm corrosion inhibitor in 1 M HCl. The data of XRD were listed in Table 6. The data of XRD intensity and sharp peaks in table 1 demonstrated that PVP Br best to keep crystallinity to iron due to inhibition of corrosion.

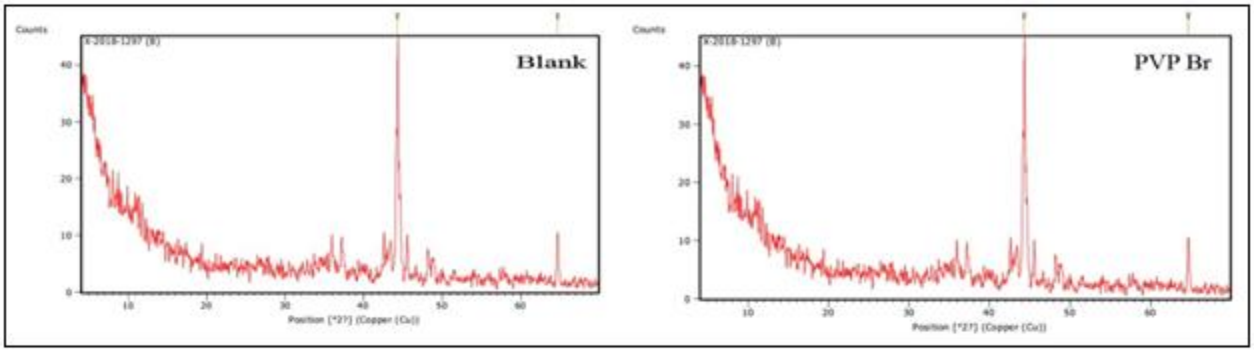


Fig (10): XRD in absence and presence of PVP Br

Table (6): The data of XRD of the steel in absence and presence of free acid and inhibitor

Solution	Pos. [°2θ]	Height [cts]	FWHM Left [°2θ]	d-spacing [Å]	Rel. Int. [%]	H	K	L
Blank (1 M HCl)	44.296	32.93	0.3149	2.04493	100	1	1	0
	64.6761	8.29	0.2362	1.44124	25.16	2	0	0
PVP Br 500 ppm	45.28	159.7	0.0984	2.00275	100	1	1	0
	65.5981	29.6	0.1968	1.42319	18.54	2	0	0

4. Conclusion:

1. From the present study, it was concluded that PVP Br is a good corrosion inhibitor and efficiency increasing at high temperatures.
2. From EIS, it was found PVP Br adsorbed on the surface of metal and formed a protective film on the metal.
3. From Tafel, it is observed that Compound is mixed-type inhibitor affecting the iron dissolution and hydrogen evolution.

References

[1] Wasserscheid, W. Schroer (eds), J. Mol. Liq. 192 (2014) 1.

[2] J. Hulsbosch, D.E.D. Vos, K. Binnemans, R. Ameloot, ACS Sustain. Chem. Eng. 4 (2016) 2917 –2931.

[3] L. Guo, Sh. Zhu, S. Zhang, J. Ind. Eng. Chem. 24 (2015) 174 –180.

[4] J. Hulsbosch, D.E.D. Vos, K. Binnemans, R. Ameloot, ACS Sustain. Chem. Eng. 4 (2016) 2917 –2931.

[5] V. Rajeswari, D. Kesavanb , M. Gopiramanc , P. Viswanathamurthi, K. Poonkuzhali, T. Palvannan, Appl. Surf. Sci. 314 (2014) 537 –545.

[6] E. Drioli, F. Macedonio, Ind. Eng. Chem. Res. 51 (30) (2012) 10051 –10056.

[7] P. Wasserscheid, W. Schroer (eds), J. Mol. Liq. 192(2014) 1.

[8] L. A. Al Juhaiman, A. A. Mustafa and W. K. Mekhamer, Int. J. Electrochem. Sci., 7 (2012)8578

[9] J. R. Macdonald and D. R. Franceschetti, in: J. R. Macdonald (Ed.), Impedance Spectroscopy, Wiley, New York, 1987.

[10] T. Makanyire, S. Sanchez-Segado, A. Jha, Adv. Manuf. 4 (2016) 33.

[11] M.V. Fedorov, A.A. Kornyshev, Chem. Rev. 114 (2014) 2978.

[12] R.W. Revie, H.H. Uhling, Corrosion and Corrosion Control, fourth ed. Wiley, 2007 1–3.

[13] S. Masadeh, J. Miner. Mater. Charact. Eng. 3 (2015) 271 –276

[14] Al Juhaiman, L. A. International Journal of Electrochemical Science 11(3): (2016) 2247-2262.

[15] Lai, C., et al. Results in Physics 7 (2017) 3434-3443.

[16] E. Kowsari, M. Payami, R. Amini, B. Ramezanzadeh, M. Javanbakht, Appl. Surf. Sci. 289 (2014) 478-486.

[17] T. Tiiken, F. Demir, N. Kicir, G. Sigircik, M. Erbil, Corros. Sci. 59 (2012) 110-118.

[18] El-Shamy, A., et al. Journal of Molecular Liquids 211 (2015) 363-369.

[19] Adawy, A. I., et al. Research on Chemical Intermediates 42(4) (2016) 3385-3411.

[20] Mohamed A. Abbas, Khaled Zakaria, A. Hamdy, O. M. Abo-Elenien, and Olfat E. El-Azabawy International Journal of Chemical, Environmental & Biological Sciences 3 (2) (2015) 2320–4087.

[21] H. Ashassi-Sorkhabi, N. Ghalebsaz-Jeddi, F. Hashemzadeh and H. Jahani, Electrochim. Acta, 51, (2006) 3848.

[22] R. Solmaz, G.Kardas, M.Culha, B.Yazici and M.Erbil, Electrochim. Acta, 53 (2008) 5941.

[23] A. S. Fouda, A. A. Al-Sarawy and E. E. El-Khatori, Desalin., 201 (2006) 1.

[24] A. S. Fouda, H. A. Mostafa, F. El-Taiband G. Y. Elewady, Corros. Sci., 47 (2005) 1988.

[25] M. A. Quraishi and S. K. Shukla, Mater. Chem. Phys., 85 (2004) 420.

[26] H. H. Uhlig, Corrosion and Corrosion Control, 2nd Ed., John Wiley and sons Inc. 1971.

[27] Wagdy, E.-D., et al. Journal of Basic and Environmental Sciences 3 (2016) 55-64.

[28] Yurt A, Bereket G, Kivrak A, Balaban A, Erk B. J Appl Electrochem, 35 (2005) 1025–32

[29] Saliyan VR, Adhikari AV. Corros Sci, 50 (2008) 55–61.

[30] Fekry AM, Mohamed RR. Electrochim Acta, 55 (2010) 1933–9.

[31] Lin, W.-S., et al. Journal of Nanomaterials 2013 (2013) 1-6.