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Corrosion Inhibition of Iron in 1M HCl by Three Quaternized Copolymers Poly(4-Vinylpyridine-g-Polyethylene-Oxide)

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The inhibitive action of some poly(4-vinylpyridine-g-polyethylene-oxide) in three degree of quaternisation 5%, 15% and 45%, (P4VPPgOE) (g=136), against the corrosion of iron in 1M hydrochloric acid (HCl) has been studied at 298 K using weight loss measurements, potentiodynamic polarisation, and impedance spectroscopy (EIS) methods. Results obtained shows that (P4VPPgOE) (g=136) in degree of quaternisation 5%, is the best inhibitor and its inhibition efficiency increases with the increase of concentration of inhibitor to attain 100% since $5*10^{-7}$M. Polarisation measurements show also that the compound acts as a mixed-type inhibitor and were adsorbed on the iron surface according to the Langmuir adsorption isotherm model. E (%) values obtained from various methods used are reasonably good agreement. The temperature effect on the corrosion behaviour of iron in 1M HCl without and with the inhibitor at 10^{-6}M was studied in the temperature range from 298 to 338 K, the associated activation energy have been determined and proved that the adsorption is a spontaneous process.

Keywords: iron, poly(4-vinylpyridine-g-polyethylene-oxide), inhibition, corrosion, hydrochloric acid, P4VP

1. INTRODUCTION

The importance of inhibitive protection in acidic solutions is increased by the fact that iron materials which are more susceptible to be attacked in aggressive media, are the commonly exposed metals in industrial environments. The effect of organic nitrogen compounds on the corrosion behaviour of iron and steel in acidic solutions has been well documented in our laboratories [1-10]. It's shown that the protective properties of such compounds depended upon their ability to reduce corrosion rate and enhanced at higher electron densities around the nitrogen atoms. Numerous works have been devoted to the corrosion inhibiting effect of aqueous soluble polymers on metallic materials. Many studies on the addition of inhibitors have been done in the field of iron corrosion inhibition in acid solutions. The inhibitive power of polymers [11-24] is related structurally to the various active centres of adsorption as cyclic rings. Among these inhibitors, polymers as polyvinylpyridine, polyvinylbipyridine, polyvinylpyrrolidine, polyvinylpyrolidone (PVP), polyethylenimine and polyvinylimidazoles has been widely examined [16-25]. Their choice is based on their low-cost and stability as corrosion inhibitors for metallic materials in acidic media. The inhibitive power of the polymers is related structurally to the various active centres of adsorption such as cyclic rings and heteroatom's (oxygen and nitrogen). PVP has received particular attention and has been applied to the inhibition of Fe, Cu, Al, Zn and their alloys in various acidic media [21-28]. Good results were obtained with poly(4-vinylpyridine) (P4VP) and its derivative, the poly(4-vinylpyridine-g-tri-ethylene-oxide) (P4VPPOE) [16,29] on the corrosion of iron in 1M H_2SO_4.

Recently, the effect of addition of poly(4-vinylpyridine-g-tri-ethylene-oxide) [30-31] on the corrosion of iron in acid solutions has incited us to modify the molecular structure by introducing the g=136.

In this work, the study was made using pure iron immersed in molar hydrochloric acid without and with addition of poly(4-vinylpyridine-g-polyethylene-oxide) in three degree of quaternisation 5%, 15% and 45%, P4VPPgOE, (Figure 1) newly synthesised, with the respective average molecular weights, $10,1.10^5$, $22,5.10^5$ and $67,5.10^5$, respectively as inhibitor for the iron corrosion in 1M HCl.

2. EXPERIMENTAL

2.1. Chemicals

Prior to all measurements, the iron samples were polished with different emery paper up to 1200 grade and washed thoroughly with bi-distilled water and dried with acetone. Pure iron (99.5%, thickness = 0.05 cm from Good Fellow, Cambridge, England) was used.

The aggressive solution (1M HCl) was prepared by dilution of Analytical Grade 37% HCl with double distilled water. All tests are conducted at different temperatures in magnetically stirred solutions.

2.2. Inhibitors

P4VP was prepared by radical polymerisation of 4-vinylpyridine in methanol, under vacuum, with azobisisobutynitrile as inhibitor, as described elsewhere [29-30]. The polymer was fractionated by partial precipitation from methanol solution with ethylacetate. P4VPPgOE was obtained by mixing P4VP and tri-3,6,9-oxaethylene bromide (Br-POE) in DMF in a thermostatted bath (333K).

After this, it was precipitated in ether, washed in methanol, then precipitated again in ether and dried. The structure was checked by ^{1}H NMR and IR spectra. The molecular weight was estimated by the viscosity technique using ethanol as solvent [32,33].

The average molecular weight of poly(4-vinylpyridine-g-polyethylene-oxide) in three degree of quaternisation 5%, 15% and 45% was 2.5210^5, 6.410^5, and 18.0310^5 respectively.

The polymer of 5% as a degree of quaternisation is obtained after 6 hours. After that, it was precipitated in ether, washed in methanol, then precipitated again in ether and dried. The molecular structure of P4VPPgOE is shown in Figure 1.

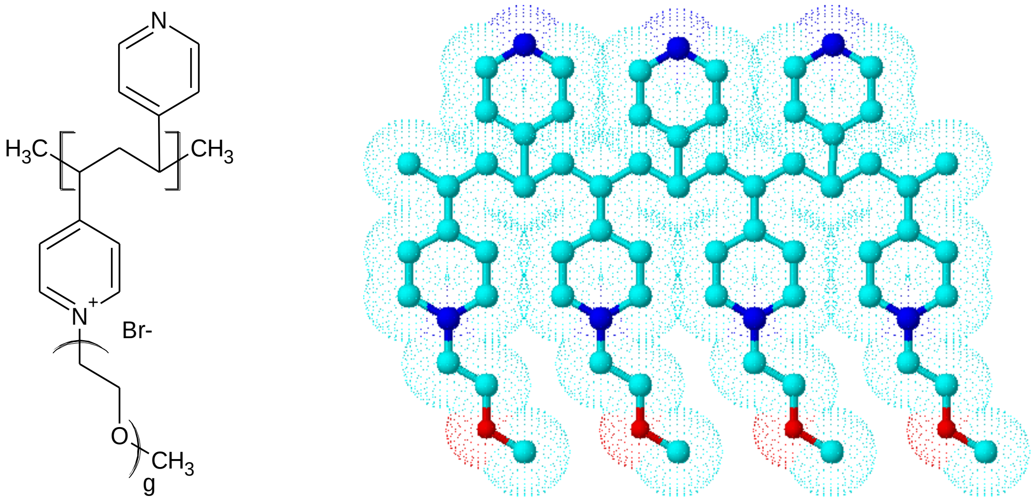

Figure 1. Molecular Structure of poly(4-vinylpyridine-g-polyethylene-oxide)) P4VPPgOE g=136

2.3. Gravimetric, polarisation and impedance spectroscopy measurements

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 50 cm^3. The used had a rectangular form. The active surface pure iron specimens of the foil was not fixed and varied from 4cm^2 to 6cm ^{2}. The immersion time for the weight loss is 1h at 298 K and 1h at the others temperatures.

The electrochemical experiments were carried out in a three-electrode electrochemical electrolysis cylindrical Pyrex glass cell with a platinum counter electrode and saturated calomel electrode (SCE) as reference. The working electrode (W.E) had the form of a disc cut form pure iron sheet. The cylindrical iron-working electrode was used for all the electrochemical studies. For this purpose, an iron embedded in Araldite and having an exposed area of 1cm^2 was used. It was provided with a screw type stem for the electrical contact. The temperature was thermostatically controlled at 298 ± 1K.

The polarization curves were recorded with a potentiostat (Amel 549) using a linear sweep generator (Amel 567) at a scan rate of 20 mV/min. Before recording the polarization curves the pure iron electrode, kept at its open circuit value after 30min free corrosion, and was polarized at - 800mV for 10 min. The potential of the electrode was then swept to the potential corrosion value. The test solution was de-aerated in magnetically stirred for 30 min in the cell with pure nitrogen. Gas bubbling was maintained throughout the experiments.

The electrochemical impedance spectroscopy (EIS) measurements were carried out at the open circuit potential with the electrochemical system (Tacussel) which included a digital potentiostat model Voltalab PGZ 100 computer at Ecorr after immersion in solution without pebbling, the circular surface of iron exposing of 1cm^2 to the solution were used as working electrode. After the determination of steady-state current at a given potential, sine wave voltage (10mV) peak to peak, at frequencies analysers from between 100 kHz to 10-2Hz, were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure. The Nyquist plots were made from these experiments. Values of R t and C dl were obtained from Nyquist plots.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

Table 1. collects the values of corrosion rates of iron and inhibition efficiency of P4VPPgOE.

Inhibitor	Concentrations (M)	W (mg.cm^2.h-1)	Ew (%)
Blank	1	0.405	-
P1 P4VPPgOE (degree of quaternisation 5%)	10^{-6}	0.000	100
	5 10^{-7}	0.000	100
	10^{-7}	0.046	94
	5 10^{-8}	0.068	90
	10^{-8}	0141	80
	510^{-9}	0.470	36
	10^{-9}	0549	26
	510^{-10}	0606	18
	10^{-10}	0670	09
P2 P4VPPgOE (degree of quaternisation 15%)	10^{-6}	0.026	96
	5 10^{-7}	0.057	92
	10^{-7}	0.084	88
	5 10^{-8}	0.123	83
	10^{-8}	0.284	61
	510^{-9}	0.0.454	38
	10^{-9}	0.740	0
P3 P4VPPgOE (degree of quaternisation 45%)	10^{-6}	0.129	82
	5 10^{-7}	0.162	78
	10-^{7}	0.192	74
	5 10^{-8}	0236	68
	10^{-8}	0399	46
	510^{-9}	0.569	23
	10^{-9}	0652	12

The corrosion rate in 1M HCl (W$_0$corr) and at various concentration of each tested compound (Wcorr) was determined after 1h of immersion. Values of corrosion rate and inhibition efficiencies are given in table (1). In the case of the weight loss method, determines the inhibition efficiency Ew bay the relation:

$$E_w = 100 \times \left(1 - \frac{W_{corr}}{W^{\circ}_{CORR}}\right) \qquad (1)$$

Table (1) collects the values of corrosion rates of iron and inhibition efficiency of Poly (4-vinylpyridine-poly-g-oxide ethylene) in tree degree of quaternisation 5%, 15% and 45%, P4VPPgOE (g=136), compound tested at various concentrations. According to this table, it is clear that for this P4VPPgOE, the iron corrosion rate values decrease when the concentration increases. The inhibiting action is more pronounced with 5.10^{-7} M (100%) which is the maximal concentration of poly(4-vinylpyridine-g-polyethylene-oxide) in degree of quaternisation 5% (polymer P1). We conclude finally that P1, P2, P3 is a best inhibitor.

3.2 Effect of temperature

We have studied the temperature influence on the efficiency of Poly (4-vinylpyridine-poly-g-oxide ethylene) in tree degree of quaternisation 5 %, 15 % and 45 %, P4VPPgOE (g=136). For this purpose, we made weight-loss measurements in the range of temperature 298-338 K, in the absence and presence of P1, P2, P3, at 10^{-6}M. The corresponding data are shown in table (2).

Table 2. Effect of temperature on the corrosion of pure iron in 1M HCl and in presence of 10^{-6}M of P4VPPgOE

inhibitors	T(K)	W^0_{corr} (mg/cm^2.h)	W_{corr} (mg/cm^2.h)	E_W%
P1	298	0.740	0.000	100
	308	1.493	0.000	100
	318	2.526	0.059	97
	328	5.159	0.242	95
	338	7.522	0.461	93
P2	298	0.740	0.026	96
	308	1.493	0.063	95
	318	2.526	0.130	94
	328	5.159	0.369	93
	338	7.522	0.603	92
P3	298	0.740	0.129	82
	308	1.493	0.313	79
	318	2.526	0.606	76
	328	5.159	1.341	74
	338	7.522	2.030	73

From the table (2) we can deduce that the inhibition efficiency of the P4VPPgOE polymer is seen to be almost constant with the rise of temperature

3.3. Polarisation measurements

Current-potential characteristics resulting from cathodic and anodic polarization curves of iron in normal HCl at various concentrations of P4VPPgOE (P1, P2, P3), inhibitors are evaluated. Figure (2) and figure (2) shows the typical cathodic Tafel plots of P_1 at different concentrations. Table (3) collects electrochemical parameters at various concentrations of *P1*, *P2*, *P3*, and inhibition efficiencies E_I.

$$E_I = 100 \times \left(1 - \frac{I_{corr}}{I^{\circ}_{corr}}\right) \tag{2}$$

I°_{corr} and I_{corr} are the corrosion current density values without and with the inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to corrosion potential.

Table 3. Electrochemical parameters for iron in 1M HCl at various concentrations of P4VPPgOE, *at* 298K.

Concentration (M)		**Ecorr (mV/SCE)**	**β (mV/dec)**	**I_{corr} (µA/cm^2)**	**E_I%**
Blank		475	176	115	-
P_1	10^{-6}	440	188	4	96
	5.10^{-7}	438	190	5.2	95
	10^{-7}	445	194	8.7	92
	5.10^{-8}	439	186	16	86
	10^{-8}	440	189	18	84
	5.10^{-9}	445	190	63	45
	10^{-9}	448	190	79	31
	5.10^{-10}	445	192	85	26
P2	10^{-6}	442	208	15	86
	5.10^{-7}	440	200	18	84
	10^{-7}	440	204	21.8	81
	5.10^{-8}	436	205	28	75
	10^{-8}	433	208	50	56
	5.10^{-9}	426	208	64	44
P3	10^{-6}	450	211	211	73
	5.10^{-8}	450	208	208	52
	10^{-8}	458	209	209	39
	5.10^{-9}	450	198	198	17

The cathodic and anodic curves of iron in 1 M HCl without and with the Poly (4-vinylpyridine-poly-g-oxide ethylene) in degree of quaternisation 5%, at various concentrations are presented in Figure (2).

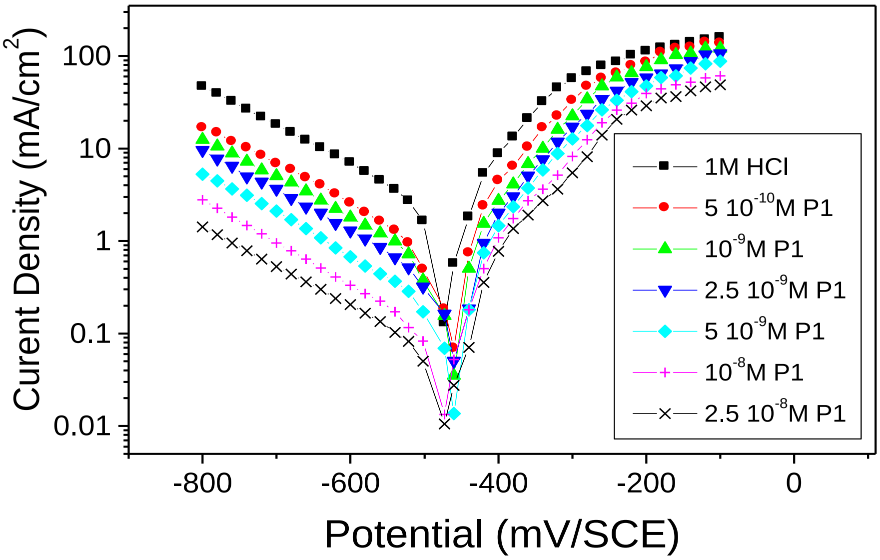

Figure 2. Some of polarisation curves of iron with P4VPPgOE at various concentrations

From the anodic curves we deduce that P4VPPgOE acts as a mixed-type inhibitor. The inhibition efficiencies of P4VPPgOE obtained by electrochemical and weight loss methods are in good agreement

3.4. Impedance spectroscopy measurements

The corrosion behaviour of iron, in acidic solution in the presence and absence of P4VPPgOE (g=136) polymer compounds, is investigated by the electrochemical impedance spectroscopy (EIS) at 298 K after 30 min of immersion.

The charge-transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al [34]. To obtain the double layer capacitance (C_{dl}) the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) is found as represented in equation.

$$C_{dl} = \left(\frac{1}{\omega}\right) R_t \qquad \text{Where} \quad \omega = 2\pi f_{\max} \qquad (3)$$

The inhibition efficiency obtained from the charge transfer resistance is calculated by:

$$E(\%) = \frac{\left[R_{t/inh} - R_t\right]}{R_{t/inh}}.100 \qquad (4)$$

R_t and $R_{t/inh}$ are the charge transfer-resistance values with and without inhibitor, respectively.

Electrochemical impedance techniques are widely used to understand the interaction mechanism between inhibitor molecules and metal in 1M HCl and to examine electrochemical processes

Figure (3) shows Nyquist plots obtained at the interface of an iron electrode in 1M HCl in the absence and presence of the polymer at 10^{-9}, $10^{-7}$and 10^{-6}M. The diagrams obtained show a semicircle in the complex impedance plane (one capacitive loop).

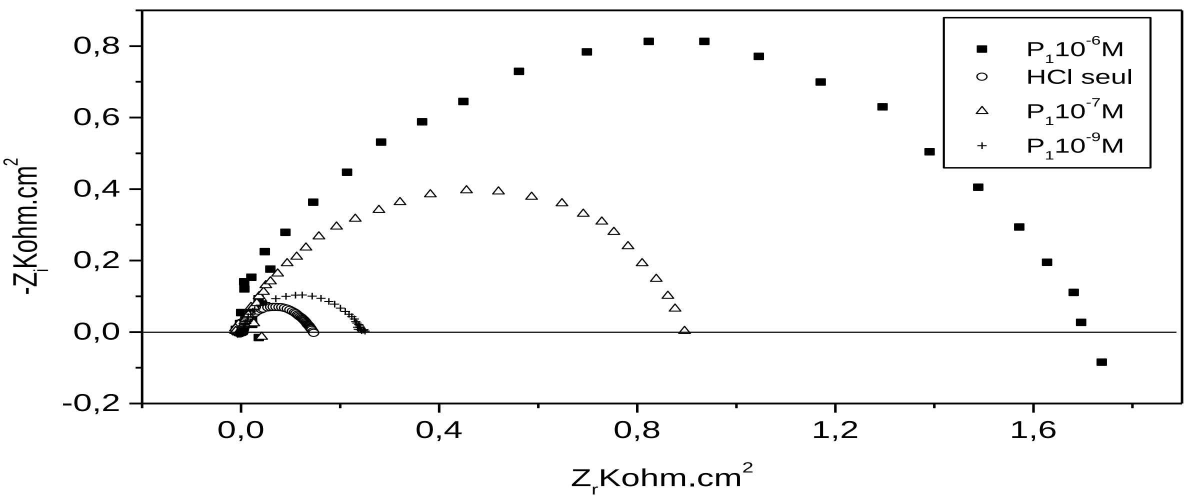

Figure 3. Electrochemical galvanostatic impedance diagrams of iron electrode in 1M HCl at Ecorr in presence and absence of P1 inhibitors at different concentrations.

The characteristic parameters associated with this impedance diagram (charge transfer resistance R_t, the capacity of the double layer and inhibition efficiency) are given in table (4).

Table 4. Characteristic parameters evaluated from the impedance diagrams in presence and absence of P1, P2, P3 inhibitors at different concentrations.

Concentration of inhibitors		R_t ($\Omega.cm^2$)	Fo (Hz)	C_{dl} ($\mu F/cm^2$)	E%
Blank		0.126	15.904	79.420	-
P1	10^{-6}	1.712	0.992	93.640	93
	10^{-7}	0.939	1.957	86.590	87
	10^{-9}	0.245	12.314	52.750	48
P2	10^{-6}	1.661	1.042	91.930	92.4
	10^{-7}	0.693	11.563	19.860	81
P3	10^{-6}	1.099	1.575	91.9	89
	10^{-8}	0.415	6.276	61.1	69

We observe from this table that the value of R_t increases in the concentrations of the inhibitor. As impedance diagrams for solutions examined have almost a semicircular appearance, it indicates that the corrosion of iron is mainly controlled by a charge transfer process. In fact, the R_t value is highly increased in the presence of this polymer.

3.5. Duscussions

The results of weight loss of pure iron in 1M HCl with and without the addition of various concentrations of the Poly (4-vinylpyridine-poly-g-oxide ethylene) in tree degree of quaternisation 5%, 15% and 45% are given in Table (1). These results show for each compounds tested, the pure iron corrosion rate values decrease when the concentration of poly(4-vinylpyridine-g-polyethylene-oxide) in tree degree of quaternisation 5%, 15% and 45% increases. Pure iron was found to dissolve at an appreciable rate (0.740 $mg.cm^{-2}.h^{-1}$) in 1M HCl. Both of the polymers reduce the corrosion rate of the pure iron but P4VPPgOE derives has a marked inhibitive effect, which attains 100% since 5.10^{-7}M of P1 (in degree of quaternisation 5%). These results are in good agreement with the study of the action of a poly (4-vinylpyridine-g-tri-ethylene-oxide)) in corrosion of iron in 1M H_2SO_4 acid [30]

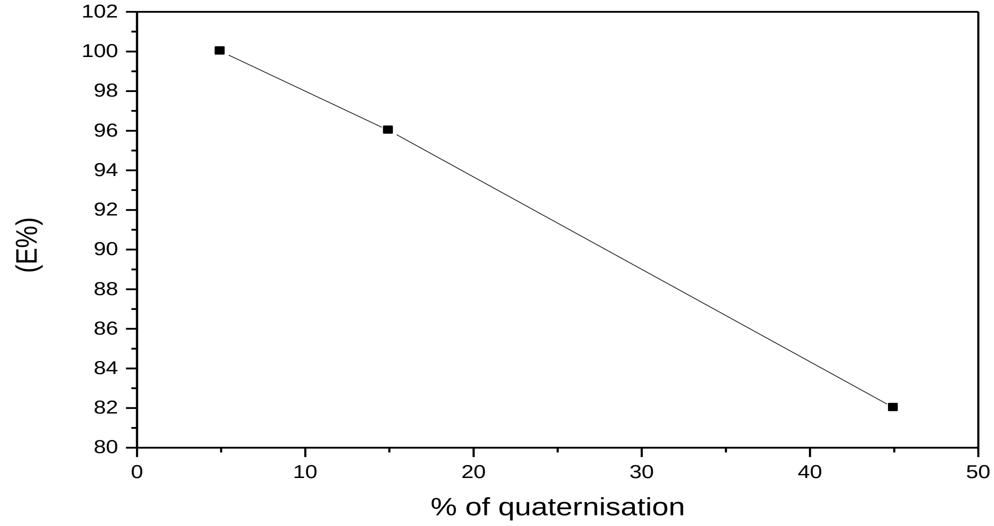

Figure 4. shows degrees of quaternisation with inhibition efficiency E%, of P4VPPgOE at 10^{-6}M

We note again, the inhibitory efficiency is dependent of quaternisation degree of poly(4-vinylpyridine-g-polyethylene-oxide). Results obtained with the P1, P2, P3, in three degrees of quaternisation 5%, 15% and 45 % respectively are the same as those obtained. This indicates that P1 is excellent inhibitor with degrees of quaternisation 5%, than P2 with degrees of quaternisation 15%, than P3 with degrees of quaternisation 45% , figure (4).

(%E) of P1 > (%E) of P2 > (%E) of P3

It is evident from the results (table 3) that the addition of Poly (4-vinylpyridine-poly-g-oxide ethylene) in tree degree of quaternisation 5%, 15% and 45%; caused a decrease of the current density. The values of the corrosion current (I_{corr}) of iron in the inhibited solution were smaller than those for those for the inhibitor free solution. Cathodic current potential curves figure (2) gave rise to parallel Tafel lines indicating that the hydrogen evolution is activation controlled and the reduction mechanism is not affected by the presence of inhibitors. The addition of new poly(4-vinylpyridine-g-polyethylene-oxide) in tree degree of quaternisation 5%, 15% and 45%; did not change the values of corrosion potential (E_{corr}) when the concentration increases. These results demonstrated that the hydrogen evolution reaction was inhibited and that the inhibition efficiency increased with inhibitor concentration and attains a maximum value of 96% at 10^{-6} M. the poly(4-vinylpyridine-g-polyethylene-oxide) in degree of quaternisation 5%; P1 is then an excellent inhibitor.

From results presented in table (3), the inhibition efficiency of the poly(4-vinylpyridine-g-polyethylene-oxide) in tree degree of quaternisation 5%, 15% and 45%; reaches maximum values of 96 % at 10^{-6} M, 86% at 10^{-6}M and 73% at 10^{-6}M respectively. This method shows that the efficiency actually depends on the degree of quaternisation.

The inhibition efficiency of the compounds depends on many major factors such as the number of adsorption active centres in the molecule and their charge density, molecule size, mode of adsorption and formation of metallic complex [13, 35]. Abed and Hammouti demonstrated that the Poly (4-vinylpyridine-poly-3-oxide ethylene) possesses three nitrogen donor sites. The inhibiting process is explained by the formation of a protective film of copper complexes on the surface copper [30-31].

Effectively, the presence of an atoms of nitrogen, π-electrons of phenyl rings and oxygen atom in alkyl in the molecule of the Poly (4-vinylpyridine-poly-g-oxide ethylene) (n'=136) has a major effect on the inhibition efficiencies and consequently on the phenomenon of adsorption on the steel. In addition, offers a widespread covering of the surface [37-38]. In another large study, show t also that the nitrogen atoms are essentially the major an active adsorption centres for their interaction with the metal surface [39].

The anodic range figure (2), the polarisation curves of iron in 1 M HCl with the Poly (4-vinylpyridine-poly-g-oxide ethylene) compounds show that the addition of these molecules decreases the current densities in large domain of potential. This result indicates that these Poly (4-vinylpyridine-poly-g-oxide ethylene) in tree degree of quaternisation 5%, 15% and 45%; tested act as mixed-type inhibitors.

The inhibition efficiencies of (P4VPPgOE) (g=136) obtained by electrochemical and weight loss measurements are in good agreement.

As mentioned above, the Poly (4-vinylpyridine-poly-g-oxide ethylene) compounds tested adsorbs on the iron surface and leads to form stable complexes with Iron. We suggest that the presence of the Poly (4-vinylpyridine-poly-g-oxide ethylene) tested will act on the iron surface by adsorption succeeded by a formation of a complex as shown in Figure (5). Immediately afterwards, as the corrosion reaction starts, ferrous ion is surrounded by two (P4VPPgOE) nitrogen and oxygen atoms at Fe-N and Fe-O [2-30] . Bonding may also as explained as follows figure (5).

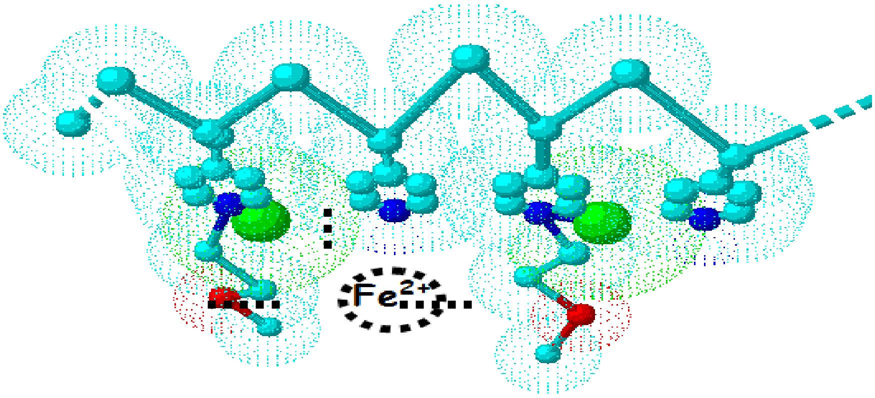

Figure 5. Complexes suggested to be formed on the iron surface.

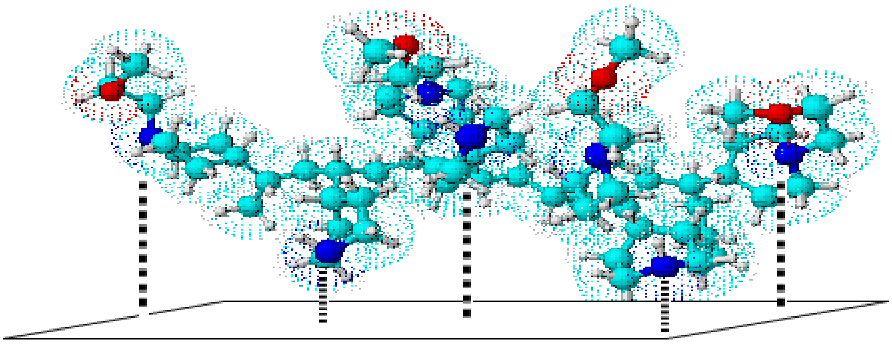

Figure 6. Adsorption suggested to be formed on the iron surface.

The adsorption of poly(4-vinylpyridine-g-polyethylene-oxide) on the metal surface can occur either directly on the basis of donor-acceptor interactions between the π-electrons of the ring and the vacant d-orbital of iron surface atoms, Figure (6), or an interaction of poly(4-vinylpyridine-g-polyethylene-oxide) with already adsorbed ions as proposed by Hackerman. Murakawa et al [40-41]. Brand et al [42] reported that the nitrogen atom is the active centre of the aliphatic in their interaction with the metal surface. The presence of the N atom causes a drastic change in its adsorption mechanism [1-5].

Gravimetric measurements were taken at various temperatures 298-353 K for pure iron in 1M HCl without and with 10^{-6}M of inhibitor poly(4-vinylpyridine-g-polyethylene-oxide) in tree degree of quaternisation 5%, 15% and 45%, during a period of one hour, the corresponding results are given in Table (2). We remark that the corrosion rate increases in the blank with the rise of temperature, but in the presence of the polymer, the dissolution of the pure iron does not occur. The inhibitive efficiency of the polymer doesgt change with the rise of temperature indicating the physical nature of adsorption mechanism.

The model is stable and preferred since the covered fraction of the surface is high and thus explains the cathodic effect of P4VPPgOE. This adsorption is favoured by establishing « donor-acceptor » links between the empty d orbitals of iron and the pairs of free electrons on nitrogen atoms by electrostatic interaction. As mentioned above, the P4VPPgOE compounds tested lead to form stable complexes with ferrous ion. The non-modification of the reduction mechanism is explained by the presence of a free part of the surface permitting a free access of H^+. The increase in the surface coverage (θ) with increase in concentration may be illustrated by the following schematic, Figure (6).

The poly(4-vinylpyridine-g-polyethylene-oxide) derives may be adsorbed on the metal surface in the form of neutral molecules involving the deplacement of water molecules from the metal surface and sharing of electrons between the nitrogen atoms and the metal surface [46]. This heterocyclic nitrogen may also be adsorbed through electrostatic interactions between the positively charged nitrogen atom and the negatively charged metal surface [47]. It has been observed that the adsorption of the inhibitor can be influenced by the nature of anions in acidic solution [48-49]. The specific adsorption of anions having a smaller degree of hydration, such as chloride ions, is expected to be more pronounced. Being specifically adsorbed, they create a layer of excess negative charge directed towards the solution and favour more adsorption of the captions [50]. Strong adsorption of organic molecules is not always a direct binding of the molecule with the metal surface. In some cases, the adsorption can occur through the already adsorbed chloride ions which interact with the subsequently adsorbed organic molecules. The inhibition is to be expected for an anion–cation pair in which both ions have appreciable tendencies toward covalent binding [34].

From these results, we can deduce that the inhibition efficiency of the polymer is seen to be almost constant with the rise of temperature.

The logarithm of the corrosion rate of iron Wcorr can be represented as a straight-line function of 1000/T (Arrhenius equation) in the figure (7), where T is the temperature in Kelvin. The relation can determine the apparent activation energies:

$$W = K\exp\left(\frac{-E_a}{RT}\right) \quad \text{And} \quad W' = K\exp\left(\frac{-E'_a}{RT}\right) \qquad (5)$$

Ea and Ea' are the apparent activation energy in the absence and presence of the inhibitor, respectively.

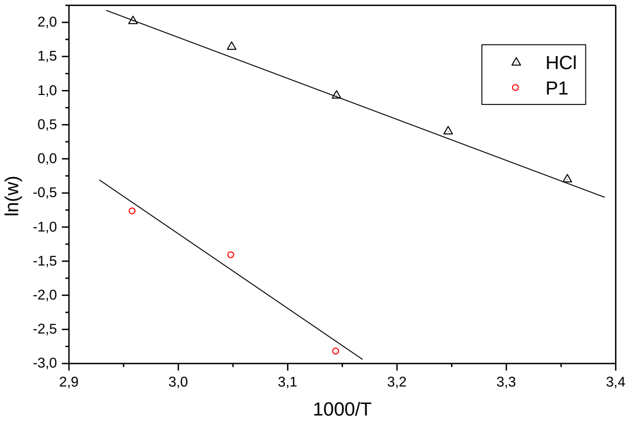

Figure 7. shows Arrhenius plots of the corrosion rate for both the blank and the solution of P1 inhibitor.

Table (5) shows the Characteristic parameters evaluated from Arrhenius straight lines for P1, P2, and P3. The calculated value of E_a is 49.86kJ/mol, and the calculated value of E_a' for the inhibited HCl solution is 91.41kJ/mol this result indicates that the presence of inhibitor P1 in the acid solution apparently has affected the value of the activation energy of the corrosion reaction table (5). Since the presence of inhibitor causes a slight change in the values of apparent activation energy. It is obvious that the effective activation energy of the inhibited solution in this study is greater that in the free acid solution and E% independent of temperature. This may indicate the physical nature of adsorption mechanism [43].

Table 5. Characteristic parameters evaluated from Arrhenius straight lines for P4VPPgOE

Inhibitors	E_a (kJ/mol)	E_a' (kJ/mol)
P1	49.86	91.41
P2		66.48
P3		58.17

The corrosion behaviour of iron, in acidic solution in the presence of P1, P2, and P3 was investigated by the electrochemical impedance spectroscopy (EIS) at 298 K after 30min of immersion. Impedance diagrams are obtained for frequency range 100 KHz – 10 mHz at the open circuit potential for iron in 1M HCl in the presence and absence of (P4VPPgOE) (n'=136). The locus of the Nyquist plots was regarded as one part of a semicircle. Nyquist plots of iron in inhibited and uninhibited acidic solution containing various concentrations of P1 are shown in Figure (4). The impedance diagrams obtained are not perfect semicircles and this difference has been attributed to frequency dispersion [44]. The charge transfer resistance, R_t values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru and Haruyama [45]. To obtain the double capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum ($-Z_{max}$) is found and C_{dl} values are obtained from the equation:

$$f(-Zmax) = \frac{1}{2\pi C_{dl} R_t} \qquad (6)$$

The impedance parameters derived from these investigations are given in Table (4). It is found that, as the P2, P3 concentration increases, the R_t values increase, but the C_{dl} values tend to decrease. The decrease in the C_{dl} values is due to the adsorption of inhibitor on the metal surface. The better performance of P1 in 1M HCl can be explained in the following way. In aqueous acidic solutions, the poly(4-vinylpyridine-g-polyethylene-oxide) in degree of quaternisation 5% exists either as neutral molecules or in the form of cations.

A good correlation was obtained between the percentage inhibition efficiencies calculated from the polarisation (EIS) and weight loss data.

Several adsorption isotherms were assessed and the Langmuir adsorption isotherm was found to be the best description of the adsorption behaviour of the studied inhibitor:

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{7}$$

$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G^\circ_{ads}}{RT}\right) \tag{8}$$

C is the P1 concentration; θ the fraction of the surface covered determined by E /100, K the equilibrium constant and ΔG°_{ads} the standard free energy of adsorption. Figure 5 shows the dependence of the ratio C/θ as function of C. Where K is the equilibrium constant of the adsorption reaction.

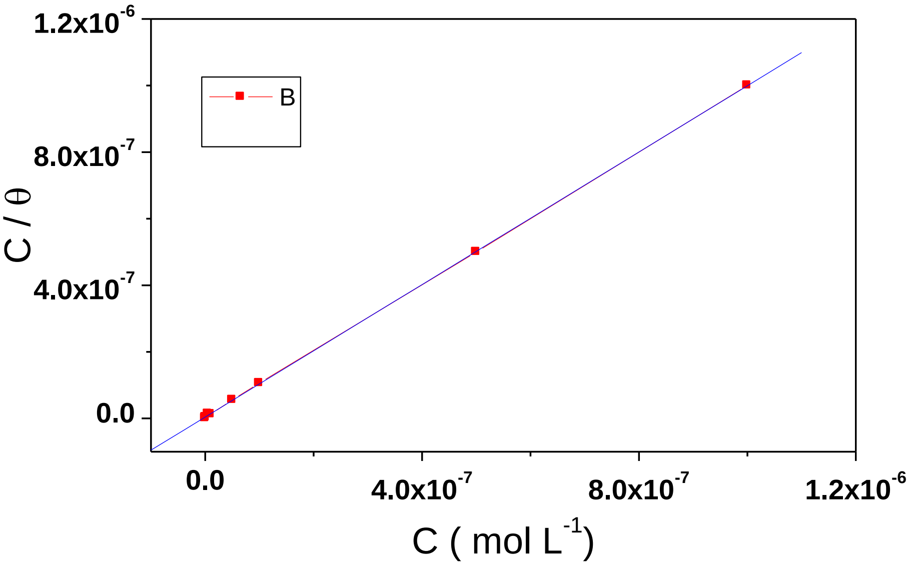

Figure 8. Langmuir isotherm adsorption model of P1 $_{\text{on}}$ iron in 1MHCl

Figure (8) shows the dependence of the ratio C/θ as function of C. The obtained plot is linear with a slope 1.09 to close to unity. The regression coefficient is R=0.999. The intercept permit the calculation of the equilibrium constant K which is 2.41x10^8 L/mol which leads to evaluate ΔG° = -57.77 kJ/mol.

Generally, values of ΔG°_{ads} around - 20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption). Those more negative than - 40 kJ mol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [52]. The calculated value of ΔG°_{ads} is too lower than - 40 kJ mol^{-1}, indicating that the adsorption of mechanism of the polymer tested on steel in HCl solution at the studied temperatures may be a combination of chemisorptions. This findings may be consolidated by the effect of temperature indicating that the efficiency decreased slightly with temperature (100 % from 298 to 93 % at 338K) and by the mixed nature of inhibitor by double action on anodic and cathodic reactions. Also, this kind of polymer was used satisfactory as a sensor for halides in aqueous solutions [53].

4. CONCLUSIONS

The principal finding of present work can be summarised as follows:

- A good correlation was obtained between the percentage inhibition efficiencies calculated from the polarisation (electrochemical, impedance methods) and weight loss data
- Steady state electrochemical measurements have shown that the polymer acts mixte inhibitor for the corrosion of iron in 1M HCL without modifying the mechanism of hydrogen evolution reaction.
- The adsorption of the polymer on the iron surface in molar in hydrochloric acid obeys to the Langmuir adsorption isotherm model.
- The inhibitory efficiency is dependent of the quaternisation degree of the polymer. The efficiency reaches 100% at 5.10^{-7} M of poly(4-vinylpyridine-g-polyethylene-oxide) in three degree of quaternisation 5%, (P4VPPgOE) (g=136) inhibitor.

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