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Anti-corrosive properties of *Polyvinyl-Alcohol* for carbon steel in Hydrochloric acid media : Electrochemical and Thermodynamic investigation

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Abstract

The corrosion and inhibitor adsorption processes in carbon steel / *Polyvinyl-Alcohol* / Hydrochloric acid systems was studied at different temperatures in the range from 298 to 328 K by a series of known techniques such as weight loss, polarization and electrochemical impedance spectroscopy (EIS). It was found that the studied compounds exhibit a very good performance as inhibitors for carbon steel corrosion in 1 M HCl. Results show that the inhibition efficiency increases with inhibitors concentration and depends on its temperature and immersion time. It has been determined that the adsorption for the studied inhibitors on carbon steel complies with the Langmuir adsorption isotherm at all studied temperatures. The kinetic and thermodynamic parameters for carbon steel corrosion and inhibitor adsorption, respectively, were determined and discussed. On the bases of thermodynamic adsorption parameters, comprehensive adsorption (physisorption and chemisorption) for the studied inhibitors on carbon steel surface was suggested.

Keywords: Corrosion and inhibition, *Polyvinyl-Alcohol*, Carbon steel, Hydrochloric acid, Adsorption isotherm, EIS.

1. Introduction

Acid solutions are commonly used for the removal of undesirable scale and rust in the metal working, cleaning of boilers and heat exchangers. Hydrochloric acids are most widely used for all these purposes. However, over-pickling of metal leads to a rough and blistered coating. Formation of protective film on the steel surface and characterization of metal surface is the major subject of interest. Carbon steel is among the most widely used engineering materials such as metal-processing equipment, marine applications, nuclear and fossil fuel power plants, transportation, chemical processing, pipelines, mining and construction. Iron and its alloys as construction materials in industrial sectors has become a great challenge for corrosion engineers or scientists nowadays [1]. In order to reduce the corrosion rate of metals, several techniques has been applied. The use of inhibitors is one of the most practical methods for protection against corrosion in acidic media. Inhibitors, which reduce corrosion on metallic materials, can be divided into three kinds: surfactant inhibitors [2], organic inhibitors [3] and inorganic inhibitors [4]. Heterocyclic inhibitors have many advantages such as high inhibition efficiency [5–8], low price, and easy production. The choice of effective inhibitors is based on their mechanism of action and their electron-donating capability. Moreover, inhibitory ability is reinforced by the presence of the molecular structure of adsorption active sites with the lone pair and or π orbitals, such as heterocyclic rings containing sulphur, oxygen, phosphorus and/or nitrogen atoms [9–11]. These compounds can form either a strong coordination bond with metal atom or a passive film on the surface [12]. The corrosion inhibition of a metal may involve either physisorption or chemisorption of the inhibitor on the metal surface. Electrostatic attraction between the charged hydrophilic groups and the charged active centers on the metal surface leads to physicosorption. Several authors showed that most inhibitors were adsorbed on the metal surface by displacing water molecules from the surface and forming a compact barrier film [13].

The choice of an optimal inhibitor should be based on three considerations: *(i)* it should have a convenient synthesis from inexpensive raw materials, *(ii)* the presence of phosphorus, nitrogen, oxygen, sulfur and multiple bonds in the inhibitor molecule are required for its efficiency and *(iii)* its toxicity toward the environment must be negligible [14].

Polyvinyl alcohol is a water-soluble synthetic polymer with excellent film forming, emulsifying, and adhesive properties. This versatile polymer offers outstanding resistance to oil, grease, and solvents, plus high tensile strength, flexibility and high oxygen barrier suitable applications for *Polyvinyl-Alcohol* are largely determined by its properties. *Polyvinyl-Alcohol* is used mainly in aqueous solution. Its solubility in water depends on its degree of polymerization and degree of hydrolysis, with the latter factor being especially significant [15-20].

The purpose of this paper is to study the effect of *Polyvinyl-Alcohol* addition as corrosion inhibitor on the carbon steel corrosion in 1 M HCl solution using weight loss and electrochemical measurements. The effect of temperature on the corrosion behavior was also studied in the range from 298 K to 328 K. The thermodynamic parameters such as adsorption heat ΔH_a^*, entropy of adsorption ΔS_a^* and adsorption free energy ΔG_a^* were calculated and discussed.

2. Experimental details

2.1. Material preparation

The chemical composition of steels sample is shown in *Table 1*. The specimen's surface was prepared by polishing with emery paper at different grit sizes (from 180 to 1200), rinsing with distilled water, degreasing in ethanol, and drying at hot air.

Corrosion tests were performed on carbon steel which had the following chemical composition *(wt%)* balanced with Fe.

Table 1: Chemical composition of low carbon steel used

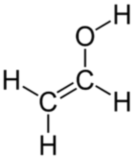
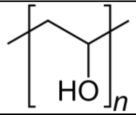
Material	*Composition, % by wt*											
	C	*Si*	*Mn*	*Cr*	*Mo*	*Ni*	*Al*	*Cu*	*Co*	*V*	*W*	*Fe*
Carbon steel	0.11	0.24	0.47	0.12	0.02	0.1	0.03	0.14	<0.0012	<0.003	0.06	Balance

The steels specimens used have a rectangular form 2.5 cm × 2.0 cm × 0.05 cm. The immersion time for weight loss was 6 h at 298 K. After immersion period, the specimens were cleaned according to ASTM G-81 and reweighed to 10^{-4} g for determining corrosion rate [21].

The aggressive solution of 1 M HCl was prepared by dilution of analytical grade 37 % HCl with distilled water.

The molecular formula of the examined inhibitor is shown in *Table 2*.

Table 2: Chemical structure of compounds

Names	*Chemical structure*	*Chemical formula*	*Abbreviation*
Vinyl alcohol		C_2H_4O	VA
Polyvinyl Alcohol		$(C_2H_4O)_n$	PVA

2.2. Measurements

2.2.1. Weight loss measurements

Weight loss experiments were done according to ASTM methods described previously [20, 21]. Tests were conducted in 1 M HCl for 6 h at 293 K. Gravimetric measurements were carried out in an electrolysis cell equipped with a thermostat-cooling condenser. The carbon steel specimens used have a rectangular form 2.5 cm × 2.0 cm × 0.05 cm. After immersion period, the specimens were cleaned according to ASTM G-81 and reweighed to 10^{-4} g for determining corrosion rate [21].Duplicate experiments are performed in each case, and the mean value of the weight loss is reported. Weight loss allows us to calculate the mean corrosion rate as expressed in ($mg.cm^{-2}.h^{-1}$). The resulting quantity, corrosion rate (ω_{corr}) is thereby the fundamental measurement in corrosion. W_{corr} can be determined either by chemical analysis of dissolved metal in solution or by gravimetric method measuring weight of specimen before and after exposure in the aggressive solution applying the following equation 1:

$$\omega_{corr} = \frac{m_i - m_f}{St} \qquad (1)$$

where m_i, m_f, S and t denote initial weight, final weight, surface of specimen and immersion time, respectively.

The inhibition efficiency, $\eta_w\%$, is determined as follows :

$$\eta_\omega\% = \frac{\omega^0_{corr} - \omega_{corr}}{\omega^0_{corr}} \times 100 \qquad (2)$$

where ω^0_{corr} and ω_{corr} are the corrosion rates in the absence and presence of inhibitors, respectively.

2.2.2. Electrochemical measurements

The carbon steel specimens used have a rectangular form 2.5 cm × 2.0 cm × 0.05 cm. The immersion time for weight loss was 6 h at 298 K. After immersion period, the specimens were cleaned according to ASTM G-81 and reweighed to 10^{-4} g for determining corrosion rate [21].

For electrochemical measurements, the electrolysis cell was a borrosilcate glass (Pyrex®) cylinder closed by a cap with five apertures. Three of them were used for the electrode insertions. The working electrode was pressure-fitted into a polytetrafluoroethylene holder (PTFE) exposing only $1 cm^2$ of area to the solution. Platinum and saturated calomel were used as counter and reference electrode (SCE), respectively. All potentials were measured against the last electrode.

The potentiodynamic polarization curves were recorded by changing the electrode potential automatically from negative values to positive values versus E_{corr} using a Potentiostat/Galvanostat type PGZ 100, at a scan rate of 1 mV/s after 1 h of immersion time until reaching steady state. The test solution was thermostatically controlled at 298 K in air atmosphere without bubbling. To evaluate corrosion kinetic parameters, a fitting by Stern-Geary equation was used. To do so, the overall current density values, i, were considered as the sum of two contributions, anodic and cathodic current i_a and i_c, respectively. For the potential domain not too far from the open circuit potential, it may be considered that both processes followed the Tafel law [22]. Thus, it can be derived from equation (3):

$$i = i_a + i_c = i_{corr}\left\{\exp\left[b_a \times \left(E - E_{corr}\right)\right] - \exp\left[b_c \times \left(E - E_{corr}\right)\right]\right\} \qquad (3)$$

where i_{corr} is the corrosion current density ($A\ cm^{-2}$), b_a and b_c are the Tafel constants of anodic and cathodic reactions (V^{-1}), respectively. These constants are linked to the Tafel slopes $\beta(V/dec)$ in usual logarithmic scale given by equation (4):

$$\beta = \frac{\ln 10}{b} = \frac{2.303}{b} \qquad (4)$$

The corrosion parameters were then evaluated by means of nonlinear least square method by applying equation (3) using Origin software. However, for this calculation, the potential range applied was limited to ±0.100V around E_{corr}, else a significant systematic divergence was sometimes observed for both anodic and cathodic branches.

The corrosion inhibition efficiency is evaluated from the corrosion current densities values using the relationship (5):

$$\eta_{\mathrm{PP}} = \frac{i^{0}_{\mathrm{corr}} - i_{\mathrm{corr}}}{i^{0}_{\mathrm{corr}}} \times 100 \qquad (5)$$

The surface coverage values (θ) have been obtained from polarization curves for various concentrations of inhibitor using the following equation [23]:

$$\theta = 1 - \frac{i_{corr}}{i^{0}_{corr}} \qquad (6)$$

where i^{0}_{corr} and i_{corr} are the corrosion current densities values without and with inhibitor, respectively.

The electrochemical impedance spectroscopy measurements were carried out using a transfer function analyzer (VoltaLab PGZ 100), with a small amplitude a.c. signal (10 mV rms), over a frequency domain from 100 kHz to 100 mHz with five points per decade. The EIS diagrams were done in the Nyquist representation. The results were then analyzed in terms of an equivalent electrical circuit using Bouckamp program [24].

The inhibiting efficiency derived from EIS, η_{EIS} is also added in Table 5 and calculated using the following equation (7):

$$\eta_{\mathrm{EIS}} = \frac{R_{\mathrm{ct}} - R^{0}_{\mathrm{ct}}}{R_{\mathrm{ct}}} \times 100 \qquad (7)$$

where R^{0}_{ct} and R_{ct} are the charge transfer resistance values in the absence and in the presence of inhibitor, respectively.

In order to ensure reproducibility, all experiments were repeated three times. The evaluated inaccuracy did not exceed 10 %.

3. Results and discussion

3.1. Weight loss measurements

The weight loss of carbon steel corrosion in 1 M HCl, with and without different concentrations of *Polyvinyl-Alcohol* compared with the Vinyl Alcohol compounds, was determined after 6 h of immersion at 298 K. The obtained results are presented in *Table 3*.

Table 3: Weight loss data of carbon steel in 1 M HCl without and with different concentrations of Vinyl-Alcohol and Polyvinyl-Alcohol at 298 K after 6 h of immersion.

PVA Concentration (ppm)	*VA*			*PVA*		
	ω_{corr_1} (mg cm^{-2} h^{-1})	η_{ω_1} (%)	θ	ω_{corr_2} (mg cm^{-2} h^{-1})	η_{ω_2} (%)	θ
0	36.01	-	-	36.01	-	-
100	23.99	33.4	0.33	12.8	64.5	0.65
150	15.64	56.6	0.57	8.01	77.8	0.78
200	16.72	53.6	0.54	3.07	91.5	0.92
300	19.29	46.4	0.46	3.82	89.4	0.89

It has been observed that 200 ppm of *Polyvinyl-Alcohol* serves as an optimum concentration that exhibit higher efficiency of corrosion inhibition. Since these provide the *Polyvinyl-Alcohol* in excellent corrosion inhibitor compared to Vinyl-Alcohol. The results indicated that *Polyvinyl-Alcohol* is concentration-independent as inhibition efficiency decrease at highest concentration (Fig. 1). The corrosion rate of carbon steel decreased on increasing the inhibitor concentration (until 200 ppm). This behavior could be attributed to the increase in adsorption of inhibitor at the metal/solution interface on increasing its concentration. An increase of inhibitor concentration beyond 200 ppm resulted in a diminished corrosion protection. This may be due to the withdrawal of adsorbate (inhibitor) back into the bulk solution when the concentration of inhibitor closed to or beyond the critical concentration. The above effect leads to the weakening of metal–inhibitor interactions, resulting in the replacement of inhibitor by water or chloride ions (Cl^-) with decrease in inhibition efficiency [21]. This may also be due to the inhibitor adsorption at the carbon steel surface through non-bonding electron pairs present on nitrogen and oxygen atoms as well as p-electrons [22]. However, the corrosion inhibition of *Polyvinyl-Alcohol* is essentially due to the presence of electron donor atoms of nitrogen in its molecular structure. So, the electron lone pair on the nitrogen will co-ordinate with the metal atoms of the active sites and will increase adsorption to hence higher inhibition efficiency [23].

3.2. Potentiodynamic polarization curves

Potentiodynamic polarisation curves of carbon steel in 1 M HCl without and with different concentrations of *Polyvinyl-Alcohol* at 298 K are given *Figure 1*. Their extrapolation parameters, inhibition efficiency and surface coverage values (θ) are plotted in *Table 4*. It can be seen that the *Polyvinyl-Alcohol* addition hinders the acid attack on carbon steel and an increase in their concentration gives a decrease in anodic and cathodic current densities indicating that the *Polyvinyl-Alcohol* acts as mixed-type inhibitors. However, the inhibitor addition does not change the hydrogen evolution reaction mechanism such as indicated by the slight changes in the cathodic slopes (β_c) values. This indicates that hydrogen evolution is activation controlled [29, 30]. It is also seen that the inhibition efficiency increases with concentration, reaches a maximum of 92,9 % at 200 ppm of *Polyvinyl-Alcohol* and exhibits both cathodic and anodic inhibition through adsorption on carbon steel surface blocking active sites [30]. So, no definite change observed in the corrosion potential (E_{corr}). According to Riggs [31] and others authors, if the displacement in E (i) is > 85 mV/ E_{corr}, the inhibitor can be seen as a cathodic or anodic type, *(ii)* if displacement in E is < 85 mV/ E_{corr}, the inhibitor can be seen as mixed type. In our study, the maximum displacement is less than 85 mV/ E_{corr}, which indicates that *Polyvinyl-Alcohol* is a mixed type inhibitor. The results obtained by the potentiodynamic polarization curves confirm those obtained by weight loss measurements.

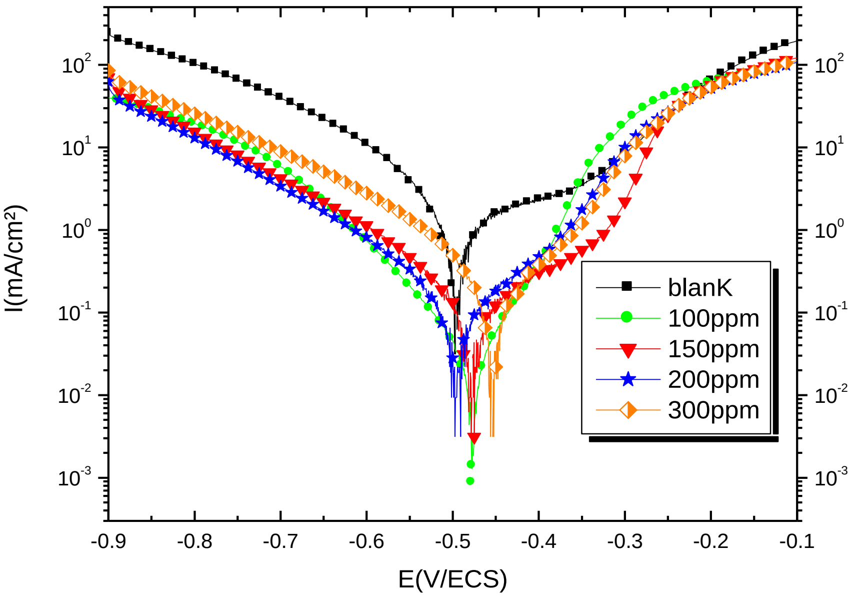


Figure 1 : *Potentiodynamic polarization curves for carbon steel in 1 M HCl in the absence and presence of various concentrations of Polyvinyl-Alcohol.*

Table 4: Electrochemical parameters for carbon steel in 1 M HCl at various concentrations of Polyvinyl-Alcohol at 298 K.

Compounds	*Concentration of PVA (ppm)*	$-E_{corr}$ (mV/SCE)	i_{corr} (μA cm^{-2})	$-\beta_c$ (mV dec^{-1})	η_{Tafel} (%)	θ
Blank	0	497	983	92	-	-
PVA	100	478	361	95	63.3	0.63
	150	479	204	102	79.3	0.79
	200	498	70	84	92.9	0.93
	300	454	121	110	87.7	0.88

3.3. Electrochemical Impedance Spectroscopy (EIS)

The aim of these investigations was to determine the influence of *Polyvinyl-alcohol* on the electrochemical behaviour of carbon steel in 1 M HCl. Polarisation curves of the carbon steel electrode in 1 M HCl without and with addition of various concentrations of *Polyvinyl-alcohol* are shown in Fig. 3. As it can be seen, the anodic and cathodic reactions are affected by the addition of *Polyvinyl-alcohol*. It is noted that this plot was composed for one capacitive loop in the absence and presence of *Polyvinyl-Alcohol*, indicating that almost no change in the corrosion mechanism with the presence of *Polyvinyl-Alcohol*. This behavior can be attributed to charge transfer of the corrosion process. It is also noted that the diameter of the semicircle increases with inhibitor concentration, indicating an increase in corrosion resistance of the material [32]. It allows employing *CPE* element in order to investigate the inhibitive film properties on metallic surface. Thus, the impedance of the *CPE* can be described by the following equation:

$$Z_{\text{CPE}} = \left[Q(j\omega)^n \right]^{-1} \qquad (8)$$

where j is the imaginary number, Q is the frequency independent real constant, $\omega = 2\pi f$ is the angular frequency (rad s^{-1}), f is the frequency of the applied signal, n is the *CPE* exponent for whole number of $n = 1, 0, -1$, *CPE* is reduced to the classical lump element-capacitor (C), resistance (R) and inductance (L) [33]. The use of these parameters, similar to the constant phase element (*CPE*), allowed the depressed feature of Nyquist plot to be reproduced readily.

However, the effective calculated double layer capacitance (C) derived from the *CPE* parameters according to the following equation [34]:

$$C = Q^{\frac{1}{\alpha}} \times R^{\frac{(1-\alpha)}{\alpha}} \qquad (9)$$

The most important data obtained from the equivalent circuit are presented in *Table 3*. It may be remarked that R_{ct} value increases and C_{ct} decreases with inhibitor concentration indicating that more inhibitor molecules are adsorbed on metallic surface and provided better surface coverage and/or enhanced the thickness of the protective layer at the metal/solution interface [35, 36]. In addition, these change in R_{ct} and C_{ct} can be attributed to the gradual displacement of water molecules and/or chloride ions on the carbon steel surface [37], leading to a protective solid film, then a decrease in the extent of dissolution reaction [38, 39]. In the other, the decrease of C_{ct} with concentration can be explained by the decrease in local dielectric constant and/or an increase in the protective layer thickness on the electrode surface. This trend is in accordance with Helmhotz model, given by the following equation [40]

$$C_{dc} = \frac{\varepsilon_0 \varepsilon}{e} S \qquad (10)$$

where ε is the dielectric constant of the protective layer, ε_0 is the permittivity of free space (8.854×10^{-14}Fcm^{-1}) and S is the effective surface area of the electrode.

However, the inhibition efficiencies obtained from electrochemical impedance measurements, increase with concentration and show the same trend as those obtained from potentiodynamic polarization and gravimetric measurements.

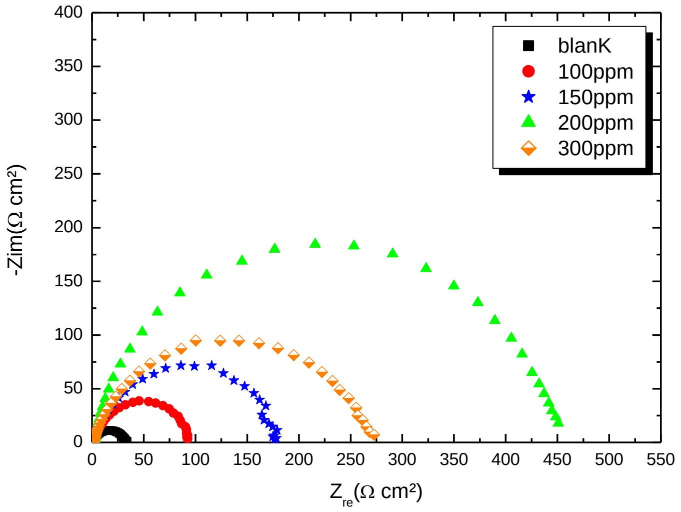


Figure 2:*Nyquist plots for carbon steel in 1 M HCl solution in the absence and presence of various concentrations of Polyvinyl-Alcohol at 298K.*

The results can be interpreted using equivalent circuit presented in *Fig. 4*, which has been used previously to model the iron/acid interface [41]. Various parameters such as charge-transfer resistance (R_{ct}) and double layer capacitance (C_{ct}) obtained from impedance measurements are shown in *Table 4*.

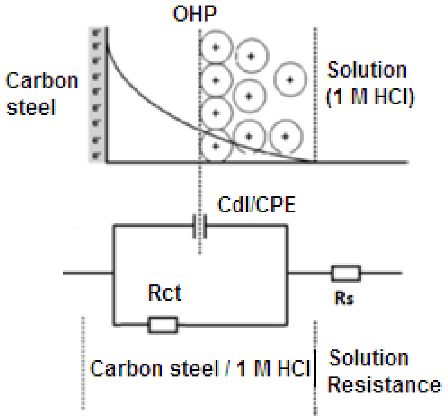


Figure 3 : Equivalent circuit used to model impedance data in 1M HCl solutions, OHP, outer Helmholtz plane; C_{dl}, double layer capacitance, R_s, solution resistance; R_{ct}, charge-transfer resistance.

Table 5: Electrochemical impedance parameters and inhibition efficiency for carbon steel in 1M HCl solution without and with different concentration Polyvinyl-Alcohol at 298K.

Compounds	*PVA Concentration (ppm)*	R_{ct} (Ω cm^2)	C_{ct} (μF cm^{-2})	η_{EIS} (%)
Blank	0	35	284	-
PVA	100	95	251	63.2
	150	179	181	80.5
	200	451	111	92.2
	300	272	155	87.1

It is obvious from the results that the *Polyvinyl-Alcohol* inhibits the corrosion of carbon steel in 1 M HCl solution at all concentrations used in this study and the η_{EIS}(%) was seen to increase continuously with increasingadditive concentration at 298 K*(Table 5)*. Indeed, the protection efficiency increases with increasing of inhibitor concentration, the maximum η_{EIS}*(%)*of 92.9 % was achieved at 200 ppm. The inhibition efficiencies, calculated from Tafel impedance results, show the same trend as those obtained from EIS polarisation and weight loss measurements. Comparison of the efficiencies values *(Table 6)*, obtained using these three methods, show acceptable agreement. The strong correlation (R^2= 0.989), reveal very good agreement between the obtained data from potentiodynamic polarization curves, electrochemical impedance spectroscopy techniques and weight loss measurement.

Table 6 : Inhibition efficiency values obtained from weight loss, Tafel polarisation and Ac impedance measurements of carbon steel in 1 M HCl containing various concentrations of Polyvinyl-Alcohol at 298K.

PVA Concentration (ppm)	*Inhibition efficiency η (%)*		
	Weight loss	*Tafel polarisation*	*Ac impedance*
100	64.5	63.3	63.2
150	77.8	79.3	80.5
200	91.5	92.9	92.2
300	89.4	87.7	87.1

3.4. Effect of temperature

Temperature can modify the interaction between the steel electrode and the acidic media without and with *Polyvinyl-alcohol* inhibitor. Polarisation curves for carbon steel in 1 M HCl in the absence and presence of 200 ppm of *Polyvinyl-alcohol* in the temperature range 298 to 328 K are shown in Figs. 4 and 5 respectively. The polarisation exhibits Tafel behaviour. The analysis of these figures reveals that raising the temperature decreases both anodic and cathodic polarisation and increases I_{corr}.

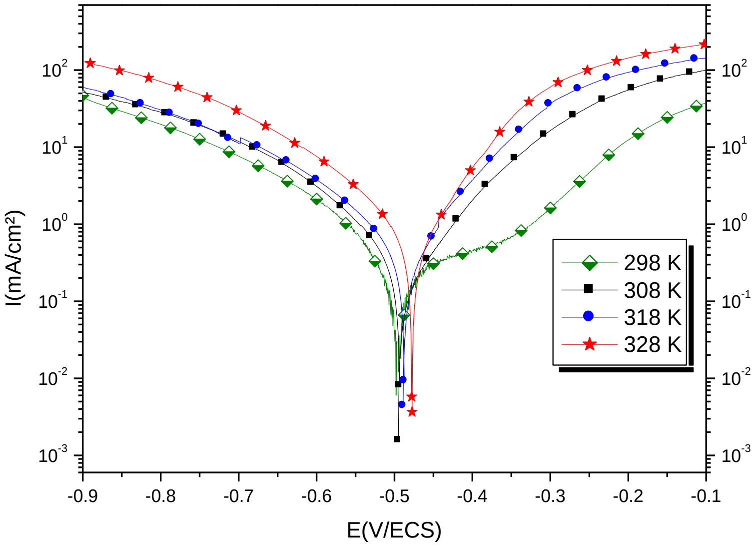


Figure 4 : Potentiodynamic polarization curves for carbon steel in 1 M HCl in the absence of Polyvinyl-Alcohol at different temperatures between 298 and 328 K.

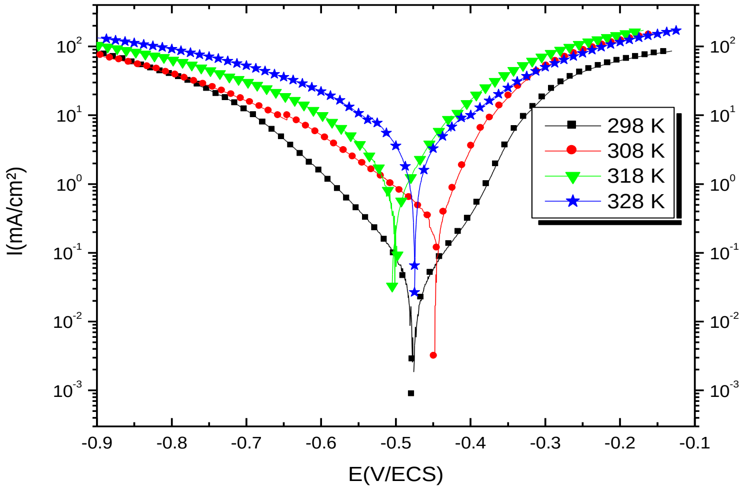


Figure 5 : Potentiodynamic polarization curves for carbon steel in 1 M HCl in the presence of 200 ppm of Polyvinyl-Alcohol at different temperatures between 298 and 328 K.

The various electrochemical parameters were calculated from Tafel plots and summarised in *Table6*.Percentage inhibition efficiencies and the surface coverage degree (θ) for steel are also shown in these tables. The surface coverage θ was calculated from the following equation [41, 44]:

$$I_{corr\,(inh)} = (1-\theta) \times I_{corr} + \theta \times I_{sat} \qquad (11)$$

Rearranging this equation gives:

$$\theta = (I_{corr} - I_{corr\,(inh)})/(I_{corr} - I_{sat}) \qquad (12)$$

where I_{corr}, $I_{corr(inh)}$ and I_{sat} are the corrosion current density values in the absence, presence of *Polyvinyl-Alcohol* and an entirely covered surface respectively ($I_{sat}= I_{corr}$ for the most elevated concentration of inhibitor).

$$\text{As } I_{sat} << I_{corr}, \quad \text{thus} \quad \theta = (I_{corr} - I_{corr\,(inh)})/I_{corr} \qquad (13)$$

As it can be seen from *Table 6*, I_{corr} increased with increasing temperature. The current corrosion density increased with increasing temperature both in uninhibited and inhibited solutions and the values of inhibition efficiency of *Polyvinyl-alcohol* decreased with increasing temperature range studied.

Table 6 : The influence of temperature on the electrochemical parameters for carbon steel in 1M HCl with 200 ppm of Polyvinyl-Alcohol

Temperature (°K)	*Blank*			*PVA*			
	-E_{corr} vs SCE (mV)	*i_{corr} (µA/cm²)*	*-β_c (mV)*	*-E_{corr} vs SCE (mV)*	*i_{corr} (µA/cm²)*	*-β_c (mV)*	*η_{ct} (%)*
298	498	983	92	498	70	80	93
308	491	1600	178	444	170	86	86
318	475	2420	165	512	341	984	83
328	465	3100	151	491	610	110	80

Thus, the *Polyvinyl-Alcohol* inhibitors efficiencies are temperature-dependent. The fact that $\eta_{ct}(\%)$ increases with temperature is explained by Ammar et al. as the likely specific interaction between the iron surface and the inhibitor [42]. Ivanov [43] considers the increase of η_{ct} *(%)* with temperature increase as the change in the nature of the adsorption mode, the inhibitor is being physically adsorbed at lower temperatures, while chemisorptions is favoured as temperature increases.

3.5. Adsorption isotherm and thermodynamic parameters

The values of surface coverage (θ) to different concentrations of the *Polyvinyl-Alcohol*, obtained from the polarisation measurements in the temperature range 298 to 328 K *(Table7)*, have been used to explain the best isotherm to determine the adsorption process. As it is known, the adsorption of an organic adsorbate onto metal/solution interface let's denote by a substitutional adsorption process between the organic molecules in the aqueous solution $PVA_{(sol)}$ and the water molecules on the metallic surface $H_2O_{(ads)}$ [31]:

$$PVA_{(sol)} + XH_2O_{(ads)} \leftrightarrow PVA_{(ads)} + XH_2O_{(sol)}$$

where $PVA_{(sol)}$and $PVA_{(ads)}$ are the organic molecules in the aqueous solution and adsorbed on the metallic surface, respectively, $H_2O_{(ads)}$ is the water molecules on the metallic surface, X is the size ratio representing the number of water molecules replaced by one molecule of organic adsorbate [44].

The adsorption isotherms models considered were as described in reference [45]:

Temkin isotherm $$\exp(f \times \theta) = K_{ads} \times C_{inh} \quad (14)$$

Langmuir isotherm $$\frac{\theta}{1-\theta} = K_{ads} \times C_{inh} \quad (15)$$

Frumkin isotherm $$\frac{\theta}{1-\theta}\exp(-2\times f \times \theta) = K_{ads} \times C_{inh} \quad (16)$$

Freundluich isotherm $$\theta = K_{ads} \times C_{inh} \quad (17)$$

Flory-Huggins isotherm $$\ln\left(\frac{\theta}{C_{\mathrm{inh}}}\right) = \ln(K_{\mathrm{ads}}) + a \times \ln(1-\theta) \quad (18)$$

where K_{ads} is the equilibrium constant of the adsorption process, C_{inh} is the inhibitor concentration, f is the factor of energetic inhomogeneity and the parameter '*a*' in Eq. (13) is the water molecules number replaced by inhibitor molecules on metallic surface.

In this study, the *Tempkin, Langmuir, Frumkin, Freundlich*and *Flory–Huggins* isotherm were fitted. The corresponding fitting curve results, where R^2 is the square of the correlation coefficient between the dependent variables and the estimated values, are shown in *Table 7*. It is noted that the inhibitor was adsorbed on metallic surface according to the Langmuir isotherm model *(Figure 7)*. So, the adsorption constant, K_{ads}, is related to the free energy of adsorption, ΔG^*_{ads}, by the following equation (14) [45]:

$$K_{ads} = \frac{1}{55{,}55}\exp\left(-\frac{\Delta G^*_{ads}}{RT}\right) \quad (19)$$

where 55.55 value represents the water concentration in solution by $mol\ L^{-1}$, R is the universal gas constant and T is the absolute temperature.

The value of standard free energy of adsorption $\Delta G°_{ads}$ is calculated from the adsorption isotherm. It is -17,3 kJ mol^{-1} at 298 K. It is well known that values of $\Delta G°_{ads}$ of the order of 20 kJ/mol or lower indicate a physisorption,

those of order of 40 kJ/mol or higher are associated with chemisorptions as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a co-ordinate [30, 35, 37].
The calculated values are tabulated in *Table 7*. The negative sign of free enthalpy of adsorption indicates that the adsorption of *Polyvinyl-Alcohol* substituted compounds at steel surface is a spontaneous process.

Table 7: Equilibrium constant and free energy of adsorption values for carbon steel 1 M HCl in the presence of Polyvinyl-Alcohol at different concentration.

Isotherms	*Linear forms*	*Curves*	*Parameters*	*Values*
Langmuir	$\frac{C_{\text{inh}}}{\theta}=\frac{1}{K_{\text{ads}}}+C_{\text{inh}}$	$\frac{C_{\text{inh}}}{\theta}=f\ (C_{\text{inh}})$	R^2	0.9770
			K_{ads}(L mol^{-1})	20
			Slope	0.94
Freundlich	$\ln\theta=\ln K_{\text{ads}}+\frac{1}{n}\ln C_{\text{inh}}$	$\ln(\theta)=f\ (\ln(C_{\text{inh}}))$	R^2	0.8343
			K_{ads}(L mol^{-1})	3.37
			Slope (1/n)	0.2334
			n	4.28
Temkin	$\theta=\frac{1}{f}\ln K_{\text{ads}}+\frac{1}{f}\ln C_{\text{inh}}$	$\theta=f\ (\ln(C_{\text{inh}}))$	R^2	0.8592
			K_{ads}(L mol^{-1})	154.93
			Slope (1/*f*)	0.24419
			f	4.1
Flory-Huggins	$\ln(\frac{\theta}{C_{\text{inh}}})=\ln(K_{\text{ads}})+a\times\ln(1-\theta)$	$\ln(\frac{\theta}{C_{\text{inh}}})=f\ (\ln(1-\theta))$	R^2	0.6275
			K_{ads}(L mol^{-1})	1248.87
			Slope (a)	1.2814

The best fitted straight line (strong correlation with R^2=0.9770) is obtained for the plot of C_{inh}/θ vs. C_{inh} with slopes around unity (*Figure 6*). This suggests that the adsorption of the studied inhibitor on metallic surface obeyed to the Langmuir's adsorption isotherm model, and exhibits single-layer adsorption characteristics. This kind of isotherm involves the assumption of no interaction between the adsorbed species on the electrode surface [47].

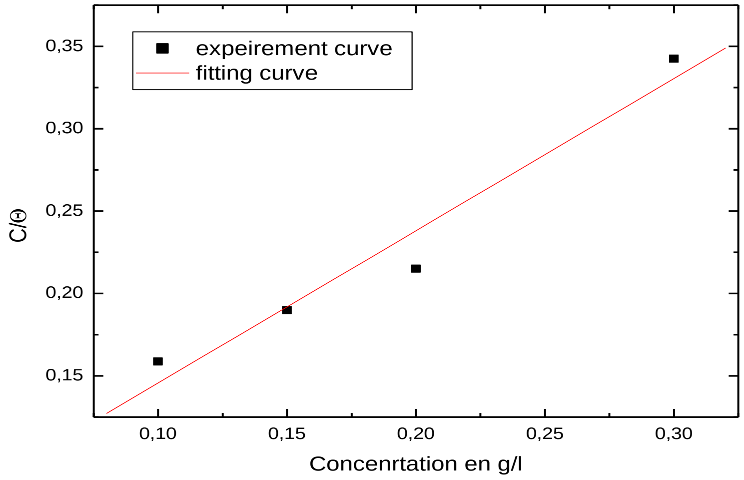


Figure 6: Plot of the Langmuir adsorption isotherm of Polyvinyl-Alcohol on the carbon steel surface at 298 K.

The values of K_{ads}, R^2, ΔG^*_{ads} and other parameters are calculated and are given in *Table 4*. The high value of K_{ads} reflects the high adsorption ability of this inhibitor on the carbon steel surface. In addition, the negative value of the free energy of adsorption, ΔG^*_{ads}, indicates spontaneous adsorption of organic molecules on the metallic surface and also the strong interaction between inhibitor molecules and the carbon steel surface [48, 49]. Generally, the standard free energy values of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface (physical adsorption); those of -40 kJ mol^{-1}or more negative involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [50, 51]. Based on the literature [52], the calculated ΔG°_{ads} values in this work indicate that the adsorption mechanism of *Polyvinyl-Alcohol* on carbon steel is both electrostatic-adsorption (ionic) and chemisorption (molecular) [53].

The constant *K* may be determined from the intercept in *Figure 10* according to the following assumptions:

(1) The inhibitor forms a mono (molecules) layer on the iron surface at the maximum corrosion inhibition using weight loss measurements.
(2) There is no interaction between the adsorbed species on the electrode surface [34].
(3) *Polyvinyl-Alcohol* is adsorbed via “O” on the iron surface.

3.6. Corrosion kinetic parameters

However, data in *Table 6* revealed that the *Polyvinyl-Alcohol* toke its inhibition efficiency at all temperature range. Consequently, the degree of surface coverage θ' $(\theta' = \eta_{pp} /100)$ slightly decrease with solution temperature. This behavior confirmed the higher adsorption equilibrium constant K_{ads} values indicating the physisorption of the *Polyvinyl-Alcohol* on the carbon steel surface. This result has been explained by some authors as likely specific interaction between the iron surface and the inhibitor. So, Ivanov [54] explained this increase with temperature by the change in the nature of the adsorption mode; the inhibitor is being physically adsorbed at lower temperatures, while Physisorption is favored by increasing of temperature. The same phenomenon was explained by other workers as an increase in the surface coverage by the inhibitor [55]. Thus, at a high surface coverage values, the diffusion through the surface layer containing the inhibitor and corrosion products became the rate-determining step of the metal dissolution process [56]. Thus, the inhibition properties of *Polyvinyl-Alcohol* can be explained by the kinetic model. The dependence of the corrosion value i_{corr} with the temperature can be regarded as Arrhenius-type process given by equation (15) [57]:

$$\ln i_{corr} = \ln A - \frac{E_a}{RT} \qquad (20)$$

where E_{a} is the apparent activation energy of corrosion process, *R* is the universal gas constant, *A* is the Arrhenius pre-exponential constant and *T* is the absolute temperature.

In order to assure that the achieved coverage degree is close to the maximal value; i.e. the concentration which gives the best inhibiting efficiency The Arrhenius plot according to equation (15) is presented in *Figure 7* for absence and presence of 200 ppm of *Polyvinyl-Alcohol*.

Plots of the logarithm of the corrosion rate *vs. 1000/T* are given in *Fig. 8*. The plots obtained are straight lines and the slope of each straight line gives its activation energy E_a. We note that the increase of corrosion rate is more pronounced with the rise of temperature for blank solution. In the presence of the inhibitor, the corrosion rate is highly reduced at explores temperatures. The E_a values were found to be equal to 31,5 KJ mol^{-1} in the absence of the inhibitors and equal to 60 KJ mol^{-1} in the presence of *Polyvinyl-Alcohol*.

The apparent activation energy values (E_a) for carbon steel in 1 M HCl in the absence and the presence of inhibitor were determined from the slope of $\ln(i_{corr}$ *vs.* $1/T)$ plots and shown in *Table 8* which include as well the pre-exponential term, *A*. All the linear regression coefficients between $\ln(i_{corr}$ *vs.* $1/T)$ are very close to one, indicating that the steel corrosion in 1 M HCl solution can be elucidated using the kinetic model.

The decrease in carbon steel corrosion rate is determined by the apparent activation energy, E_a value. It is well recognized that the temperature dependence of the inhibition effect and the comparison of the values of the apparent activation energy, E_a, of the corrosion process in absence and presence of inhibitors can provide further evidence [58, 59] concerning the mechanism of the inhibition action. The decrease of the inhibitor efficiency with increasing temperature, which refers to a higher value of E_a, when compared to free solution, is interpreted as an indication for an electrostatic character of the inhibitor’s adsorption. From the *Table5*, the addition of the studied inhibitor affects the values of E_a; this modification maybe attributed to the change in the corrosion process mechanism in the presence of adsorbed inhibitor molecules [60]. The higher value of E_a were obtained in the presence of *Polyvinyl-Alcohol* when compared to free solution is interpreted as an indication for electrostatic character of the inhibitor's adsorption. This increase in E_a indicates that a physical adsorption (electrostatic) occurred in the first stage. *Polyvinyl-Alcohol* is an organic nitrogen compound that easily protonate to give a cationic form in acid medium. The value of E_a was greater than 20 kJ mol^{-1}, which reveals that the entire process is controlled by the surface reaction [61].The investigated inhibitor block significantly some of the active sites on the metal surface inhomogeneous energetically. In general, the inhibitor adsorbs at the most active sites of the surface with lowest E_a and thus isolates them. Other active sites of higher E_a take part in the further corrosion process.

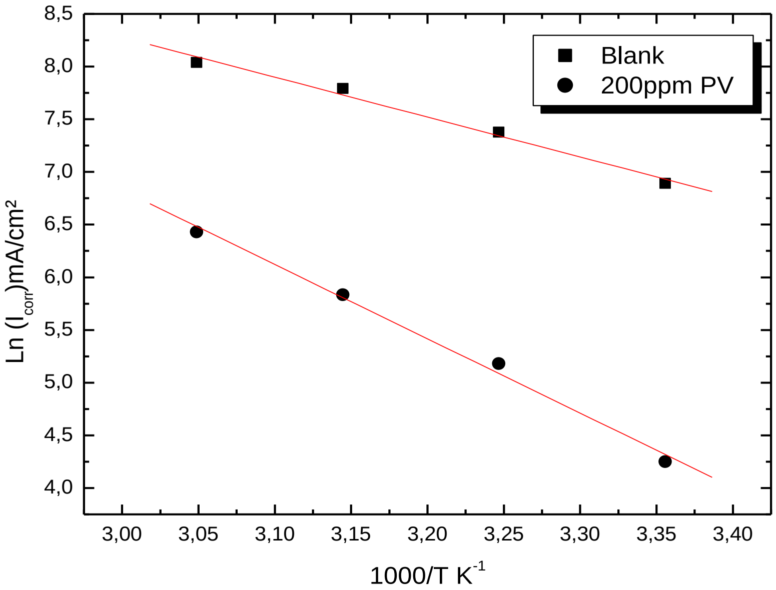


Figure 7 : Arrhenius plots of carbon steel in 1 M HCl without (a) and with (b) 200ppmof Polyvinyl-Alcohol.

Table 8 : The values of activation parameters E_a, ΔH_a* and ΔS_a* for carbon steel in 1 M HCl and added of 200ppm of the inhibitor.

Compounds	E_a ($KJ \times mol^{-1}$)	ΔH_a* ($KJ \times mol^{-1}$)	ΔS_a* ($J \times mol^{-1} \times K^{-1}$)
Blanc	31.5	28	-107
PVA	60	49	-150

Other kinetic data are accessible using the alternative formulation of the Arrhenius equation is (16) [62]:

$$\ln\frac{i_{corr}}{T} = (\ln(\frac{R}{Nh}) + \frac{\Delta S_a^*}{R}) - \frac{\Delta H_a^*}{RT} \qquad (21)$$

where h is Plank's constant, N is Avogadro's number, ΔS_a* is the entropy of activation and ΔH_a* is the enthalpy of activation.

Plot of $\ln(i_{corr}/T)$ versus the reciprocal of temperature $(1/T)$ are presented in *Fig.7* for the absence and the presence studied inhibitor at 200 ppm in 1 M HCl solution. Straight lines are obtained with a slope of $(-\Delta H_a^* /R)$ and an intercept of $(\ln R/Nh + \Delta S_a^*/R)$. The values of ΔH_a*and ΔS_a* are calculated and are listed in *Table 7*. The positive sign of the enthalpies ΔH_a* reflects the endothermic nature of the steel dissolution process whereas large negative values of entropies ΔS_a* imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [62, 60-64].

Conclusion

Concluding the experimental part, it was clearly demonstrated that all techniques used, are able to characterize and to follow the corrosion inhibition process promoted by *Polyvinyl-Alcohol*. The following conclusions can be drawn :

a) *Polyvinyl-Alcohol* exhibited good inhibiting properties for carbon steel corrosion in 1 M HCl solution and increased with increasing the concentration of inhibitor.
b) The obtained results show that *Polyvinyl-Alcohol* acts as mixed-type inhibitor of corrosion inhibition of carbon steel in 1 M HCl.
c) EIS measurement results indicate that the resistance of the carbon steel electrode increases greatly and its capacitance decreases by increasing the inhibitor concentration.
d) The inhibition efficiency of *polyvinyl-alcohol* can be stabilized by the participation of the tow adsorption mode, physisorption and chemisorptions control the adsorption phenomenon.
e) Thermodynamic adsorption parameters (ΔH^*_{ads}, ΔS^*_{ads}. and ΔG_{ads}) show that the studied inhibitors are adsorbed on carbon steel surface by an exothermic, spontaneous process.
f) Reasonably good agreement was observed between the obtained data from potentiodynamic polarization curves and electrochemical impedance spectroscopy techniques.

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