

Study Inhibition of Armco Iron Corrosion by Some Polymers based on Poly (4-Vinyl Pyridine) (PVP) In 0.5M Sulfuric Acid Medium

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ABSTRACT

This paper focuses on the corrosion inhibition performance of Armco iron in sulfuric acid using [(poly N-vinylpyrrolidone (PNVP) -block- poly ϵ -caprolactone (PCL)- ω -hydroxyethylmethacrylate (HEMA) -graft-poly-4-Vinylpyridine (PVP)] (KFC) and KFC quaternized by octyl bromide (C_8Br) (KFCQ). The corrosion inhibition was investigated by both weight loss and potentiodynamic measurements at different concentrations. Experimental results showed that inhibition efficiency increases with increasing concentration of the inhibitor and reached a maximum efficiency of 84.50% and 73.23% at 100 mg / l for KFC and KFCQ respectively. Polarization curves indicate that the tested polymers functioned as cathodic inhibitors. The corrosion behavior of Armco iron in 0.5 M H_2SO_4 with and without inhibitor was studied in the temperature range 298–338 K, which negatively influences the effectiveness of the inhibition. The thermodynamic parameters (ΔH_a° , ΔS_a°) and the negative values of the free energy (ΔG_a°) show the spontaneity of the adsorption process corrosion inhibition by the new synthesized products.

Keywords: Corrosion Inhibitors, Armco Iron, Polymer, Weight Loss, Polarization.

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1. INTRODUCTION

Corrosion is the gradual destruction of metal by chemical attack or by aggressive environment (Prathibha, Kotteeswaran, and Bheema Raju, 2013). Corrosion never stops but its progress and severity can be lessened (Geethamani, Kasthuri and Aejitha, 2015; Chetouani et al., 2012). Recently, special attention was devoted to the use of polymers to control the corrosion on metal surfaces by adding even a small amount of acid as an aggressive medium (Umoren, Eduok and Solomon, 2014; Ali Saeed and Rahman, 2003), where their choice is based on their inherent stability and cost effectiveness. Sulfuric acid was widely used for pickling process as corrosive medium (Umoren and Ebenso, 2007; Quraishi and Rawat, 2000; Khan, Quraishi, 2010). The adsorption modes of organic inhibitors depend mainly on the chemical structure of the inhibitor, the chemical composition of the solution, the nature of the metal surface and the electrochemical potential of the metal-solution interface (El Attari et al., 2016). The polyvinyl pyridine compound is one of the most important N-heterocycles found in natural products, pharmaceuticals and functional materials. These N-heterocyclic compounds not only play an important role biological activity but also act as a potential corrosion inhibitor (Ansari, Quraishi and Singh, 2015). The power inhibitor of polymers is related structurally to various active adsorption centers which are a hinder to the corrosion such as oxygen, nitrogen or sulfur heteroatoms, particularly in the form of aromatic rings and π -conjugated systems, can exhibit

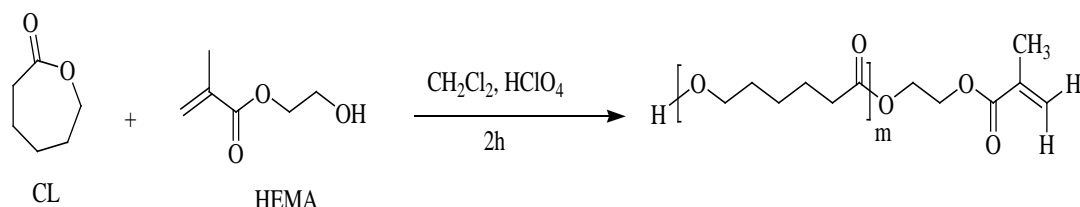
excellent inhibition efficiency (Meng et al., 2017; Prathibha et al., 2017). The thermodynamic model is an important tool for studying the mechanism of inhibition. In this context a thermodynamic model for the adsorption process was suggested (Zhao and Mu, 1999; Khamis, 1990).

Inhibitor polymers such as polyvinyl pyridine and their derivatives, were widely investigated, the Poly (4-vinylpyridine) was reported as a corrosion inhibitor for Armco iron in molar sulfuric acid solutions (Abed et al., 2001). Polarization measurements showed the cathodic nature of poly (4-vinyl pyridine). The influence of poly (4-vinyl pyridine-poly (3-oxide-ethylene) tosylate) on the corrosion of iron in sulfuric acid was tested by Chetouani et al (2004). Poly (vinyl caprolactone-co-vinyl pyridine) and poly (vinyl imidazol-co-vinyl pyridine) were reported as corrosion inhibitors for steel in phosphoric acid by Benabdellah et al (2007). Polarization curves indicated the cathodic nature of the polymeric inhibitors. The influence of newly synthesized poly (4-vinylpyridine-hexadecyl bromide) was investigated by Belkaid et al (2012) on the corrosion of mild steel in molar hydrochloric acid. A thorough study of Poly (methyl methacrylate-co-N-vinyl-2-pyrrolidone) was carried out for the corrosion of mild steel in 1M HCl solution using electrochemical and surface studies (Zhao et al., 2019). Lin Y et al (2015) also investigated the effect of poly (methyl methacrylate-co-N-vinyl-2-pyrrolidone) polymer on the corrosion of J55 steel in 3.5% NaCl solution saturated with CO_2 . In order to develop corrosion inhibitors with high effectiveness and efficiency, the polymers named [(PNVP-b-PCL- ω -HEMA)-g-PVP] KFC) and [(PNVP-b-PCL- ω -HEMA)-g-PVPC $_8$ Br]] (KFCQ) were used as novel corrosion inhibitors using weight loss and potentiodynamic polarization. The effect of temperature on the

corrosion and inhibition processes are thoroughly assessed and discussed. The main thermodynamic parameters governing the adsorption process are also investigated. NMR¹H spectroscopic technique is used to reveal the formation of polymer synthesized (El Korso et al., 2018).

2. MATERIALS AND METHODS

Hydroxyethylmethacrylate (HEMA), N-vinylpyrrolidone (NVP), 4-Vinylpyridine (VP) and ϵ -caprolactone (CL) were purchased from Sigma-Aldrich USA. Initiators Azobisisobutyronitrile (AIBN) and perchloric acid (HClO₄) were obtained from Sigma-Aldrich USA. Solvent tetrahydrofuran (THF), dichloromethane (DCM) and methanol (CH₃OH) were purchased from Shanghai Chemical Group, China). ¹H-RMN spectra were recorded in



Scheme.1. Synthesis of the (PCL- ω -HEMA)

2.2. Synthesis of the [(poly N-vinylpyrrolidone (PNVP)-block-poly ϵ -caprolactone (PCL)- ω -hydroxyethylmethacrylate (HEMA)].

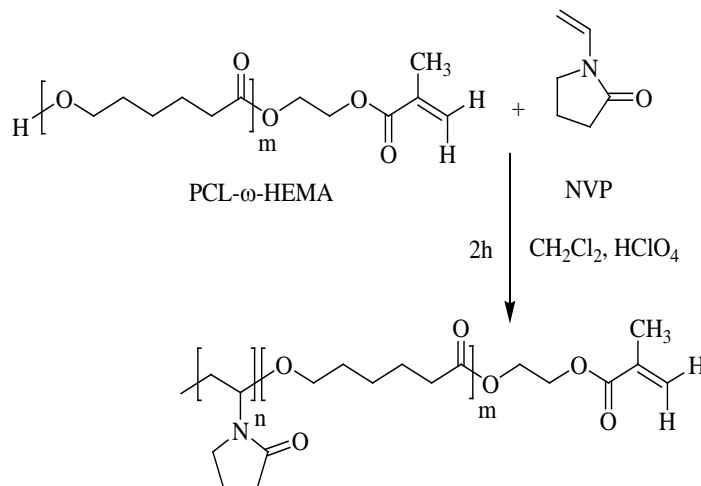
NVP was next polymerized in dichloromethane (DCM) under nitrogen atmosphere, using (PCL- ω -HEMA) macro-initiator in

CDCl₃ as a solvent on a Bruker AC spectrometer at (200, 400, 75.5) MHz using TMS as an internal standard.

2.1. Synthesis of the [Poly ϵ -caprolactone (PCL)- ω -hydroxyethylmethacrylate (HEMA)]

PCL- ω -HEMA macromonomer was prepared under nitrogen atmosphere, by cationic polymerization in the presence of monomer ϵ -CL and perchloric acid (HClO₄) as initiator in dichloromethane (CH₂Cl₂). After homogenization of the mixture reaction the hydroxyethylmethacrylate (HEMA) was added. The reaction system was kept at room temperature for 2h; the macromonomer was obtained then precipitated in methanol (CH₃OH), washed in dichloromethane (DCM) and dried (See scheme 1).

the presence of perchloric acid (HClO₄). The reaction was carried at room temperature for 2h. The copolymer (PNVP-b-PCL- ω -HEMA) (KFB) was obtained then precipitated in methanol (CH₃OH), washed in dichloromethane (DCM) and dried (See scheme 2).

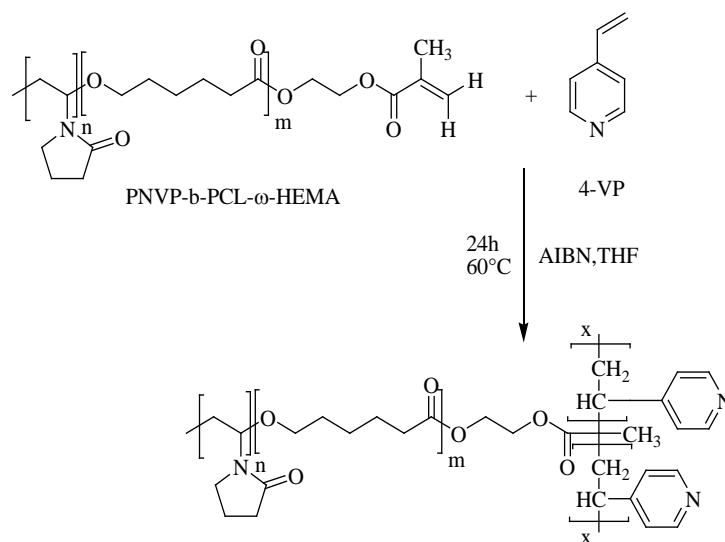


Scheme.2. Synthesis of the (PNVP-b-PCL- ω -HEMA)

2.3. Synthesis of the [(poly N-vinylpyrrolidone (PNVP)-block-poly ϵ -caprolactone (PCL)- ω -hydroxyethylmethacrylate(HEMA)-graft-poly-4-Vinylpyridine (PVP)]

Poly-4-Vinylpyridine (PVP) was prepared by radical polymerization of 4-vinyl pyridine (VP) in tetrahydrofuran

(THF), under vacuum, with 2, 2-azobisisobutyronitrile (AIBN) as initiator. The PNVP-b-PCL was added to the reaction mixture. The flask was thermostated at 60 °C for 24h of stirring. The product [(PNVP-b-PCL- ω -HEMA)-g-PVP] (KFC) was precipitated in methanol (CH₃OH) washed in chloroform (CHCl₃) and dried (See scheme 3).

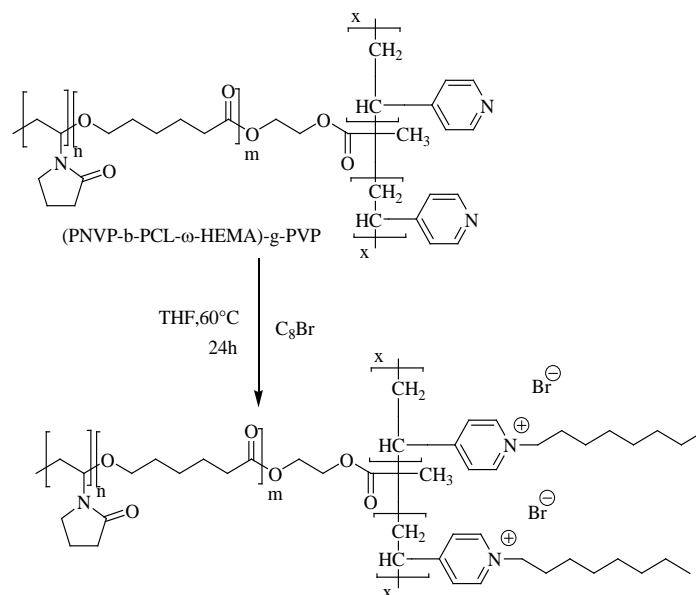


Scheme.3. Synthesis of the [(PNVP-b-PCL- ω -HEMA)-g-PVP] (KFC)

2.4. Synthesis of the [(poly N-vinylpyrrolidone (PNVP)-block-poly ϵ -caprolactone (PCL)- ω -hydroxyethylmethacrylate(HEMA)-graft poly-4-Vinylpyridine (PVP) octyl bromide (C₈Br)]

The [(PNVP-b-PCL- ω -HEMA)-g-PVPC₈Br] was obtained by mixing [(PNVP-b-PCL- ω -HEMA)-g-PVP]

in tetrahydrofuran (THF). The mixture was stirred at 60°C for 24h, the product named [(PNVP-b-PCL- ω -HEMA)-g-PVPC₈Br] (KFCQ) is obtained then precipitated in methanol (CH₃OH), washed in chloroform (CH₂Cl) and dried. (See scheme 4).



Scheme.4. the synthesis of [(PNVP-b-PCL- ω -HEMA)-g-PVPC₈Br] (KFCQ)

2.5. NMR¹H spectra

Figure 1 shows the molecular characteristic of the (PCL- ω -HEMA) macromonomer which is determined by ¹H-NMR spectroscopy, and whose structure was confirmed by characteristic methylene protons at 6.1 and 5.5 ppm respectively. **Figure 2** shows that peaks in the spectrum are attributed to both the (PNVP-b-PCL- ω -HEMA) units. The

chemical composition of (PNVP-b-PCL- ω -HEMA) was evaluated from relative intensities of the ¹H-NMR peaks at 3.2 and 4 ppm which are assigned to the PNVP ring methylene group in the α -position to the nitrogen atom and to the PCL methylene in the α -position to the ester oxygen, respectively (Veeran, Bhaw-Luximon and Jhurry, 2013).

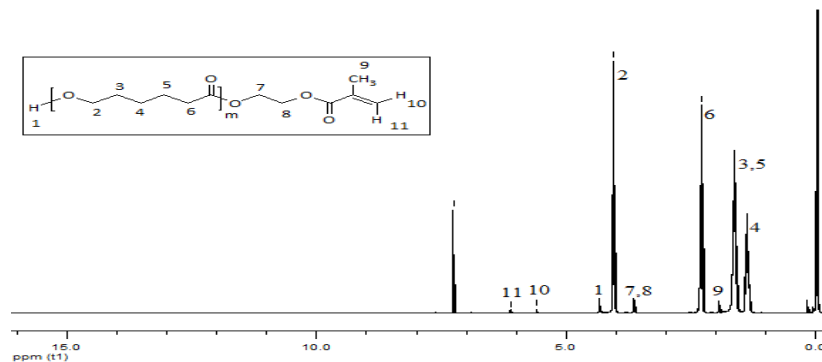


Figure 1: ¹H-NMR spectrum of the (PCL-ω-HEMA)

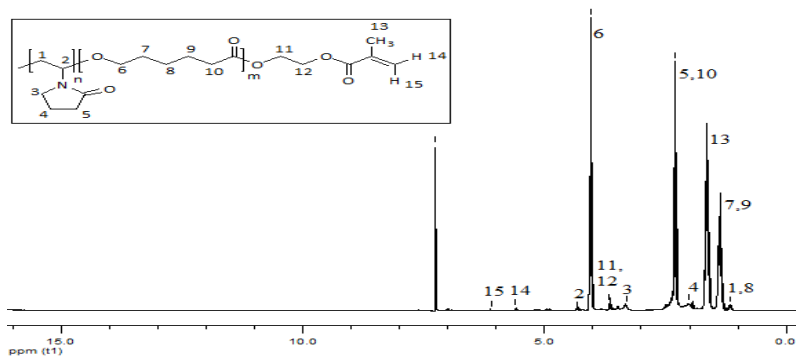


Figure 2: ¹H-NMR spectrum of the (PNVP-b-PCL-ω-HEMA)

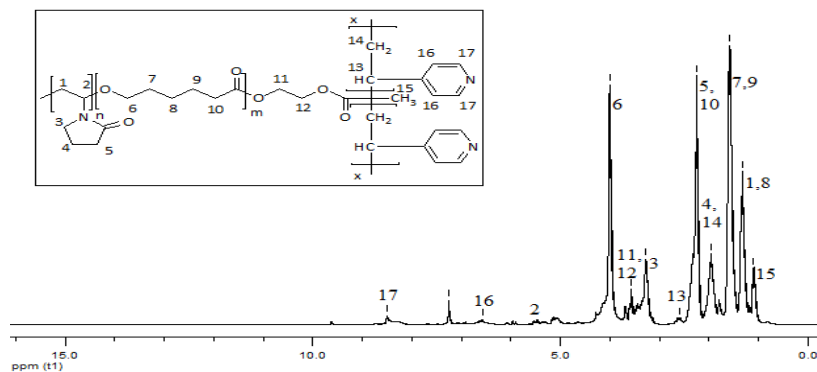


Figure 3: ¹H-NMR spectrum of the [(PNVP-b-PCL-ω-HEMA)-g-PVP]

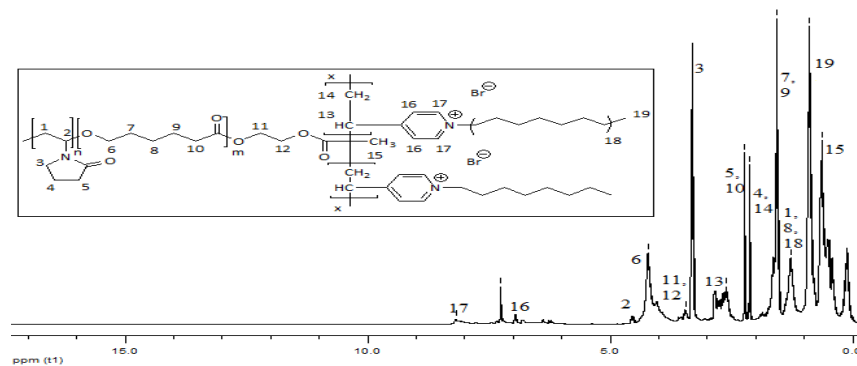


Figure 4: ¹H-NMR spectrum of the [(PNVP-b-PCL-ω-HEMA)-g-PVPC₈Br]

Figure 3 shows the aromatic protons of the pyridine ring at different position. The meta and ortho protons appear at around 6.57 and 8.49 ppm, respectively. The resonances signal around 2.59 ppm is assigned to CH region of pyridine unit. New peaks are shown in **figure 4** at 1.2 and 0.9 ppm respectively attributed to the methylene and methyl groups of alkyl chains of octyl groups.

2.6. Weight loss method

The solution of the corrosive medium 0.5M concentration of H_2SO_4 was prepared by dilution of analytical grad 98% H_2SO_4 with double distilled water. The Armco iron specimen of size (1 x 1 x 1cm) has the following chemical composition (Weight %) 0.14% C, 0.21% Si, 0.09% Mn, 0.012% S, 0.01% Al, 0.006% Cu, 99.532% Fe. The specimens were polished successively with a series of emery paper grades (600, 800 and 1200), washed thoroughly with double distilled water, degreased with acetone and properly dried at room temperature.

The pre-treated specimen's initial weights were noted accurately and were immersed in 30 ml of the corrosive medium of (0.5M H_2SO_4) with and without addition of different concentrations (100, 50, 10, 5, 1, 0.5 mg/l) of inhibitor. After the exposed period of 2h at 298K, the specimen was taken out, cleaned by double distilled water, followed by rinsing with acetone, dried and weighed by an electronic balance. The triplicate experiments were performed in each case. The inhibition efficiency (IE), surface coverage (θ) and corrosion rate (W) were calculated using the equation (Baba, Ould Kada and Bounaceur, 2016; Ahamad et al., 2011; Dasami, Parameswari and Chitra, 2014):

$$W = \left(\frac{a}{A \times t} \right) \quad (1)$$

Where a is the mean value of the weight loss of Armco iron specimen without and with inhibitor, A is the area of the Armco steel in cm^2 , and t is the immersion time hour. The inhibition efficiency (IE%) obtained from corrosion rate, can be evaluated using the following equation :

$$IE(\%) = \frac{W^o - W}{W^o} \times 100 \quad (2)$$

The surface coverage (θ) was calculated by:

$$\theta = \frac{W^o - W}{W^o} \quad (3)$$

2.7. Electrochemical measurement

2.7.1. Polarization studies

The experiments were performed using potentiostat-galvanostat PGP 201, in a classical three-electrode electrolysis cylindrical Pyrex glass cell. Armco iron specimen of $1cm^2$ area was used as the working electrode (WE) along with a platinum counter electrode as the auxiliary electrode (AE) and a saturated calomel electrode (SCE) as the reference electrode (RE). Prior to each experiment the working electrode surface was polished with emery paper degreased with acetone and rinsed with double-distilled water before use. The temperature was thermostatically controlled at 298 K. The polished WE was inserted and prepolarized at -800 mV for 15 min, the scan rate

was 20 mV/min. From the polarization curves Tafel slopes, corrosion potential and corrosion rate were calculated. The inhibitor efficiency was calculated using the equation [26].

$$IE(\%) = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \quad (4)$$

Where I_{corr} and I'_{corr} are corrosion current densities in the absence and presence of inhibitor.

3. RESULTS AND DISCUSSION

3.1. Weight loss method

3.1.1. Effect of concentration

The corrosion parameters obtained from weight loss measurements of Armco iron in various concentrations of inhibitor are listed in table 1. It is found that KFC, and KFCQ inhibits corrosion process of Armco iron in the acid in all case of concentration (from 100 to 0.5 mg/l). The corrosion rate decreases with increasing concentration of the inhibitor and the maximum efficiency was found at 100 mg/l of the inhibitors concentration. The KFC has marked inhibitive effect which attains 84.50%. The (PNVP-b-PCL- ω -HEMA)-g-PVP is therefore a most effective corrosion inhibitor. It corroborates that the inhibition efficiency increased with an increase in the concentration of the inhibitor.

Table 1: Weight loss parameters for the corrosion of Armco iron immersed in 0.5M H_2SO_4 in absence and presence of different concentration of inhibitor at 298 K after immersion of 2h.

Inhibitors	Concentration (mg/l)	W (mg cm^{-2} h $^{-1}$)	IE(%)	θ
Blank (0.5M)	//	35.5	//	//
KFC	100	5.5	84.50	0.84
	50	10	71.83	0.71
	10	12	66.19	0.66
	5	14.5	59.15	0.59
	1	16	54.92	0.54
	0.5	19.5	45.07	0.45
KFCQ	100	9.5	73.23	0.73
	50	11.5	67.60	0.67
	10	14	60.56	0.60
	5	15.5	56.33	0.56
	1	17.5	50.70	0.50
	0.5	20.5	42.25	0.42

3.1.2. The effect of temperature

The influence of the temperature ($298 \leq T \leq 338$ K) on the inhibitor at 100 mg/l in 0.5M H_2SO_4 was investigated for 2h of immersion and the results are summarized in **table 2**. From table 2 the corrosion rate increases with rise in temperature for all polymers in both inhibited and uninhibited solutions. The inhibitor was more effective at lower temperature suggesting that the protective film of these compounds formed

on the Armco iron surface is less stable at higher temperature which may be due to the desorption of some adsorbed molecules from the surface of the Armco iron in which greater area of the metal is exposed to the acidic medium, the dissolution of iron predominates over polymer adsorption. From **table 2** we clearly note that the inhibition efficiency of inhibitors of Armco iron corrosion decreases with increase the temperature, supporting the mechanism of physical adsorption.

Table 2: inhibition efficiency obtained from the corrosion rate in 0.5M H₂SO₄ at different temperature at 2h.

	Blank	KFC		KFCQ	
T (K)	W° (mg Cm ⁻² h ⁻¹)	W (mg Cm ⁻² h ⁻¹)	IE (%)	W (mg Cm ⁻² h ⁻¹)	IE (%)
298	35.5	5.5	84.50	9.5	73.23
308	37.5	8.5	77.33	13.5	64
318	44	14.5	67.04	19	56.81
328	47.5	18.5	61.05	23	51.57
338	49	24	51.02	28.5	41.83

3.2. Activation energy and thermodynamic parameters

The activation parameters of inhibition process for Armco iron were performed by weight loss measurements in the

temperature range 298-338 K in the absence and presence of inhibitor. The logarithm of the corrosion rate (W) can be expressed as a straight line function of the absolute temperature (1/T) according to the Arrhenius equation (Mansri, Bendraoua and Bouras, 2016):

$$W = Ae^{(-\frac{E_a}{RT})} \tag{5}$$

Where E_a is the activation energy; T absolute temperature; R universal gas constant and A Arrhenius pre-exponential factor. An alternative formulation of the Arrhenius equation is the transition state equation:

$$W = \frac{RT}{Nh} e^{(\frac{\Delta S^\circ}{R})} e^{(\frac{-\Delta H^\circ}{RT})} \tag{6}$$

Where ΔH_a[°] is the enthalpy of activation, ΔS_a[°] is the entropy of activation, h is Planck's constant, and N is Avogadro number.

Figure 1 shows linear plots of ln (W/T) against 1/T with a slope of (-ΔH_a[°]/R) and an intercept of (ln R/Nh + ΔS_a[°]/R). The values of activation energy, activation enthalpies, and activation entropies were calculated and given in **table 3**.

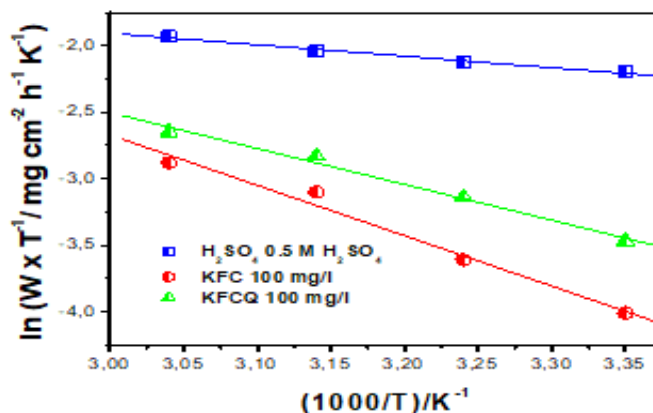


Figure 5: Plots of log (W/T) against of T⁻¹ of polymers inhibitors in 0.5M H₂SO₄

Table 3: Thermodynamic parameters for iron in 0.5M H₂SO₄ in the absence and presence of polymers inhibitors.

	Linear regression coefficient	E _a (KJ mol ⁻¹)	ΔH _a [°] (KJ mol ⁻¹)	ΔS _a [°] (J mol ⁻¹ K ⁻¹)
Blank	0.995	10	7.19	-277.62
KFC	0.990	34.3	31.49	-211.02
KFCQ	0.993	25.15	22.35	-236.93

Table 3 presents the calculated values of E_a in inhibited and uninhibited acid. It is clearly observed that the activation energy is higher in the presence of inhibitor. An increase in E_a in the presence of the inhibitor compared to the blank. The lower value of E_a in the presence of inhibitor as compared to its absence is attributed to the chemisorptions process. While the higher E_a is attributed to the physical adsorption behavior (El-Taib Heakal, Fouda and Radwan, 2011; Oguzie, 2008; Oguzie, Onuoha and Onuchukwu, 2005).

The positive sign of the enthalpy (ΔH_a[°]) highlights the endothermic nature of the iron dissolution process. E_a and ΔH_a[°] values vary in the same way with inhibitor concentration. This confirms the known thermodynamic relation between E_a and ΔH_a[°] (Gomma and Wahdan, 1995):

$$E_a - \Delta H^\circ = RT \tag{7}$$

The entropy of activation ΔS_a[°] of both process (in the absence and presence of polymers) is negative. This result indicated an increase in randomness at the interface after the adsorption (Khamis, Hosney and El-Khodary, 1995).

The values of free adsorption energy (ΔG_a[°]) are given in **table 4**. The negative values of ΔG_a[°] confirm that polymer inhibitors were strongly adsorbed on the surface of metal (Yadav et al., 2015). The adsorbed layer on the metal surface is stable when ΔG_a[°] is more negative (Majidi et al., 2010). The values of ΔG_a[°] of

all inhibitors confirm the spontaneity of the adsorption process, which takes place by physical adsorption (Elouali et al., 2010; Singh et al., 2017).

Table 4: The values of free energy of adsorption of polymers inhibitors

	Linear regression coefficient	K	ΔG_a° (KJ mol ⁻¹)
KFC	0.999	0.665	-56.07
KFCQ	0.999	0.492	-97.23

3.3. Electrochemical measurements

3.3.1. Potentiodynamic studies

The potentiodynamic polarization curves of Armco iron in 0.5M H₂SO₄ without and with addition of various concentrations (10, 5, 1, 0.5 mg/l) of polymer KFC and KFCQ at 298K are presented in **Figures 6-7**. The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slope (b_c) deduced from the polarization curves are given in **table 5**.

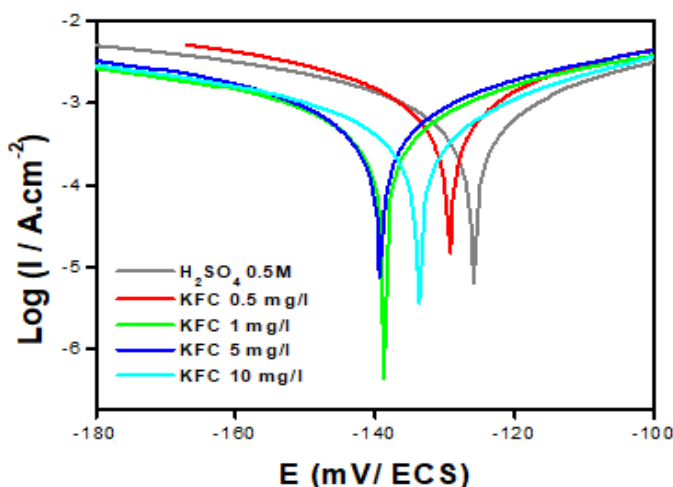


Figure 6: polarization curves of Armco iron in 0.5M H₂SO₄ at various concentration of KFC

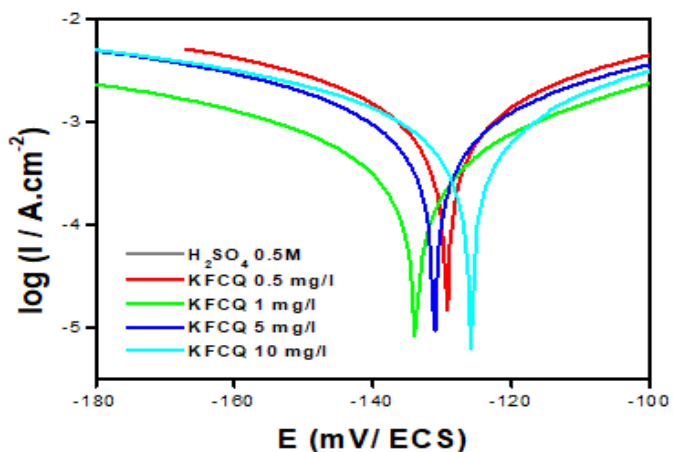


Figure 7: polarization curves of Armco iron in 0.5M H₂SO₄ at various concentration of KFCQ

Table 5: Electrochemical parameters of Armco iron at various concentrations of polymers KFC and KFCQ in 0.5M H₂SO₄ and corresponding inhibition efficiency.

	Concentration (mg.L ⁻¹)	$-E_{corr}$ / (mV/ECS)	b_c / (mV.dec ⁻¹)	I_{corr} / (mA.cm ⁻¹)	IE / (%)
Blank (0.5M)	-	128.1	-91.7	1.88	-
KFC	0.5	129.4	-28.4	0.64	65.95
	1	138.8	-38.3	0.43	77.12
	5	138.0	-42.6	0.21	88.82
	10	133.8	-41.7	0.13	93.08

KFCQ	0.5	129.8	-38.5	0.86	54.25
	1	135.2	-37.2	0.72	61.70
	5	133.8	-34.9	0.46	75.53
	10	128.5	-36.1	0.29	84.57

The curves show that the addition of the polymers at different concentrations leads to a decrease in the cathodic current densities. The cathodic current-potential curves give rise to Tafel lines indicating that the hydrogen evolution reaction is activation controlled.

The inhibition efficiency value was found to increase reaching a maximum value of 93.08% at (10 ppm) for KFC and 84.57% at (10 ppm) for KFCQ. The inhibition efficiency increases with increasing concentration of the inhibitor and the corrosion current also decreases. I_{corr} values of the inhibited acids are lower than those of the uninhibited acid, which indicates that the increase in corrosion inhibition property is due to an increase in blocked fraction by adsorption of inhibitor molecules on the electrode surface. The corrosion potential changes to the cathodic value when the concentrations of inhibitor increase. This confirms that KFC and KFCQ act as a cathodic inhibitor (Abed et al., 2001).

4. ACKNOWLEDGMENTS

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5. CONCLUSIONS

From these results, it concluded that KFC and KFCQ inhibit the corrosion of Armco iron in acidic medium with KFC being better than KFCQ. The inhibition efficiency rise with increasing the polymer concentration and decrease with rise of temperature for polymers tested. The data of polarization demonstrated that the polymers KFC and KFCQ act as cathodic inhibitors. Thermodynamic parameters obtained showed that the adsorption process was spontaneous.

REFERENCES

- Abed, Y., Arrar, Z., Hammouti, B., Taleb, S., Kertit, M., Mansri, A., (2001) Poly (4-vinylpyridine) and poly (4-vinylpyridine poly-3-oxide ethylene) as corrosion inhibitors for Cu60-Zn40 in 0.5M HNO₃. *Anti. Corr. Meth. Mater.*, 48, 304-308.
- Abed, Y., Hammouti, B., Touhami, F., Aouniti, A., Kertit, S., Mansri, A., Elkacemi, K., (2001). Poly (4-vinylpyridine) (P4VP) as corrosion inhibitors of Armco iron in molar sulfuric acid solution. *Bull. Electrochem*, 17(3), 105–110.
- Ahamad, I., Khan, S., Ansari, KR., Quraishi, MA., (2011) Primaquine: A pharmaceutically active compound as corrosion inhibitor for mild steel in hydrochloric acid solution . *J. Chem. Pharm. Res*, 3, 703-713
- Ali, SA., Saeed, MT., Rahman, SV., (2003) The isoxazolidines: a new class of corrosion inhibitors of mild steel in acidic medium. *Corr. Sci*, 45, 253.
- Ansari, KR., Quraishi, MA., Singh. A., (2015) Corrosion inhibition of mild steel in hydrochloric acid by some pyridine derivatives: an experimental and quantum chemical study. *J.Ind.Eng.Chem*, 25, 89-98.
- Baba, O., Ould Kada, S., Bounaceur, B., (2016) Cationic Copolymer of Poly (quaternary 4-vinylpyridine) Graft Poly (n-vinylpyrrolidone): Synthesis and Characterization. *Der. Pharma. Chem*, 8, 43-53.
- Belkaid, S., Tebbji, K., Mansri, A., Chetouani, A., Hammouti, B., (2012). Poly (4-vinylpyridine-hexadecyl bromide) as corrosion inhibitor for mild steel in acid chloride solution. *Res. Chem. Intermed*, 38(9), 2309–2325
- Benabdellah, M., Ousslim, A., Hammouti, B., Elidrissi, A., Aouniti, A., Dafali, A., Bekkouch, K., Benkaddour, M., (2007). The effect of poly(vinyl caprolactone-co-vinyl pyridine) and poly(vinyl imidazolco-vinyl pyridine) on the corrosion of steel in H₃PO₄ media. *J. Appl. Electrochem*, 37(7), 819–826.
- Chetouani, A., Medjahed, K., Al-Deyab, SS., Hammouti, B., Warad, I., Mansri, A., Aouniti, A., (2012) Inhibition of Corrosion of Pure Iron by Quaternized Poly(4-Vinylpyridine)-Graft-Bromodecanein Sulphuric Acid. *Int. J. Electrochem. Sci*, 7, 6025.
- Chetouani, A., Medjahed, K., Sid-Lakhdar, KE., Hammouti, B., Benkaddour, M., Mansri, A., (2004). Poly(4-vinylpyridinepoly(3-oxide-ethylene) tosyly) as an inhibitor for iron in sulphuric acid at 80C. *Corros. Sci*, 46(10), 2421–2430.
- Dasami, PM., Parameswari, K., Chitra, S., (2014) Inhibition of corrosion of mild steel in 1M sulphuric acid by a new Schiff base. *Int. J. Curr. Res. Rev*, 6(12), 1-11.
- E., Khamis, A., Hosney, S., El-Khodary, (1995) Thermodynamics of mild steel corrosion in inhibition in phosphoric acid by ethylene trithiocarbonate. *Afinidad*, 52, 95–106.
- El Attari, H., Lahmadi, K., Mengouch, S., Kameliche, E., Siniti, M., Investigation of synergistic inhibition effect of hydroxycoumarine and chloride ions on the corrosion of mild steel in sulphuric acid solution (2016) *Int. J. Adv. Sci. Res.* 1, 328.
- El Korso, N., Sebba, FZ., Ould Kada, S., Dib, N., (2018) Effect of Amphiphilic Copolymers on Armco Steel Corrosion. *Advances in Science, Technology & Innovation*, 199–200.
- Elouali, I., Hammouti, B., Aouniti, A., Ramli, Y., Azougagh, M., Essassi, EM., Bouachrine, M., (2010) Thermodynamic characterisation of steel corrosion in HCl in the presence of 2-phenylthieno (3, 2-b) quinoxaline . *J. Mater. Environ. Sci*, 1, 1-8.
- El-Taib Heakal, F., Fouda, AS., Radwan, M.S., (2011) Inhibitive effect of some thiadiazole derivatives on C-steel corrosion in neutral sodium chloride solution. *Mater. Chem. Phys*, 125, 26-36.
- Geethamani, P., Kasthuri, PK., Aejitha, S., (2015) Corosion inhibition of mild steel in sulfuric acid medium by ambroxol drug. *J. App. Chem. Sci. Int*, 3, 151.
- Gomma, MK., Wahdan, MH., (1995) Schiff bases as corrosion inhibitors for aluminium in hydrochloric acid solution. *Mater. Chem. Phys*, 39, 209-213.
- Khamis, E., (1990) The Effect of Temperature on the Acidic Dissolution of Steel in the Presence of Inhibitors. *E. Corr*, 46, 476-484.
- Khan, S., Quraishi, MA., (2010) Synergistic effect of potassium iodide on Inhibition performance of thiadiazoles during corrosion of mild steel in 20% sulfuric acid. *Arab. J. Sci. Engg*, 35, 71
- Lin, Y., Singh, A., Ebenso, EE., Wu, Y., Zhu, C., Zhu, H., (2015) Effect of poly(methyl methacrylate-co-N-vinyl-2-pyrrolidone) polymer on J55 steel corrosion in 3.5%

- NaCl solution saturated with CO². J. Taiw. Inst. Chem. Eng, 46, 214-222.
22. Majidi, L., Faska, Z., Znini, M., Kharchouf, S., Bouyanzer, A., Hammouti, B., (2010) Synthesis and anticorrosive effects of epoxy-allylpulegols on steel in molar hydrochloric acid. J. Mater. Environ. Sci, 1, 219.
 23. Mansri, A., Bendraoua, A., Bouras, B., (2016) Polyacrylamide-clay microcomposite as corrosion inhibitor for mild steel in 1M hydrochloric acid solution. J.Mater.Environ.Sci. 7, 808-819.
 24. Meng, Y., Ning, W., Xu, B., Yang, W., Zhang, K., Chen, Y., Li, L., Liu, X., Zheng, J., Zhang, Y., (2017) Inhibition of mild steel corrosion in hydrochloric acid using two novel pyridine Schiff base derivatives: A comparative study of experimental and theoretical results. RSC Adv, 7, 43014-43029.
 25. Oguzie, EE., (2008) Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel. Corr. Sci, 50, 2993-2998.
 26. Oguzie, EE., Onuoha, GN., Onuchukwu, AI., (2005) Inhibitory mechanism of mild steel corrosion in 2 M sulphuric acid solution by methylene blue dye. Mater. Chem. Phys, 89, 305-311.
 27. Prathibha, BS., Kotteeswaran, P., Bheema Raju, V., (2013) Study on the inhibition of mild steel corrosion by quaternary ammonium compound in H₂SO₄ medium. Res. J. recent. sci, 2 (4) 1-10.
 28. Prathibha, BS., Nagaswarupa, HP., Kotteeswaran, P., Bheema Raju, V., (2017) Inhibiting effect of quaternary ammonium compound on the corrosion of mild steel in 1M hydrochloric acid solution, its adsorption and kinetic characteristics. Materials Today: Proceedings, 4, 12245-12254.
 29. Quraishi, M.A., Rawat, J., (2000) Corrosion inhibition of mild steel in acid solutions by tetramethyl-dithia-octaazacyclotetradeca hexaene (MTAT). Anti. Corr. Meth. Mat, 47, 288.
 30. Singh, A., Talha, M., Xu, X., Sun, Z., Lin, Y., (2017) Heterocyclic Corrosion Inhibitors for J55 Steel in a Sweet Corrosive Medium. ACS Omega, 2(11), 8177-8186.
 31. Umoren, SA., Ebenso, EE., (2007) The synergistic effect of polyacrylamide and iodide ions on the corrosion inhibition of mild steel in H₂SO₄. Mat. Chem. Phy, 106, 387.
 32. Umoren, SA., Eduok, UM., Solomon, MM., (2014) Effect of polyvinylpyrrolidone – polyethylene glycol blends on the corrosion inhibition of aluminium in HCl solution. Pigm. Resin. Technol, 43, 299.
 33. Veeren, A., Bhaw-Luximon, A., Jhurry, D., (2013) Polyvinylpyrrolidone–polycaprolactone block copolymer micelles as nanocarriers of anti-TB drugs. Eur. Polym. J, 49, 3034.
 34. Yadav, M., Sinha, RR., Sarkar, TK., Tiwari, N., (2015) Corrosion inhibition effect of pyrazole derivatives on mild steel in hydrochloric acid solution. J. Adhes. Sci. Technol, 29, 1690–1713.
 35. Zhao, TP., Mu, GN., (1999) The adsorption and corrosion inhibition of anion surfactants on aluminium surface in hydrochloric acid. Corros. Sci, 41, 1937.
 36. Zhao, X., xiong, J., Zhu, S., Zhao, X., Singh, A., (2019) Poly (methyl methacrylate-co-N-vinyl-2-pyrrolidone) polymer as inhibitor for Mild Steel Corrosion in Acidic Media. Int. J. Electrochem. Sci, 14, 563 – 574.