Poly Acryl Amide as Acid Corrosion Inhibitor of C-steel in 15% HCl

Dr. Ghassan Burhan Yaqoob
North Oil Company
E-mail: ghassan7jul@yahoo.com

Abstract:

The effect of poly acryl amide in the 15% HCl solution of carbon steel (class L-80) was studied using weight loss method , the efficiency of inhibitor increased by increasing inhibitor concentration and decreasing temperatures. Inhibition attributed to insoluble complex adsorbed on the coupon (L-80) carbon steel surface. The iron complex was identified by FTIR. And the mechanism of inhibition was explained as Langmuir adsorption isotherm. The thermodynamic parameters of adsorption operation was calculated and explained.

Introduction:

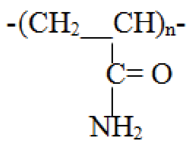
Corrosion phenomenon occurs in the nature chemically or electrochemically decays the metallic properties of alloys making them ineffective; Corrosion of alloys is big problem in industries that need much researches and investigations, oil well acidising is widely used in oil companies for cleaning and de scaling to reduce the corrosive attack on pipe lines and well pipes inhibitors are generally used to control the metal degradation. Most of organic inhibitors contain nitrogen, sulphur and/or oxygen atoms for that the most of the organic inhibitors work by adsorption on the metal surface [1].

Physical and chemical properties of corrosion inhibitor (molecular size, and weight, steric effect , electron density at the donor atoms, aromaticity, orbital character of donating electrons [2-6], the electronic structure of molecules [7-11] is an important factors in inhibitors adsorption. Most of the corrosion inhibitors are expensive and an acceptable environmentally because of its hazardous and environmentally safe corrosion inhibitors it is very desirable [12-17].

The goal of the present work is to study the inhibitive activity of Poly acryl amide to prevent the corrosion of C-steel in 15% HCl solution by weight loss , and the effect of temperature on carbon steel (L-80) was studied in exist of poly acryl amide and some thermodynamic parameters were founds.

Method:

Used (60) gr of carbon steel (L-80) has ingredients (wt%) 0.019 Cr, 1.41Mn , 0.353 Si, 0.263 C, 0.159 Ni, 0.03 P, 0.001 S and the remained Fe. with dimension of (2.5 x 4.5 x 0.7) cm. C-steel coupons surface was polished with smoothing paper, degreased with acetone, and rinsed with distilled water. the cleaned C-steel coupons were weighed before and after immersion in (50) ml of (%15) HCl solution at the times (3,4,5,6) hr. The weight loss of coupon in experiments was taken in grams. The temperature (40, 60, 80, and 90)^{o}C was adjusted using air thermostat. poly acryl amide $(C_3H_5NO)_n$ used as inhibitor was prepared by Fluka company and has the following structure:



Results and Discussion

Figures (1, 2, 3, 4) illustrates clearly that corrosion and weight loss of carbon steel (L-80) became very low in the exists of poly acryl amide by adsorbing and making a thin film on the surface of the coupon objected the corrosion process [18], the linearity follows Langmuir equation .Table (1) has inhibition efficiency (%E) and surface coverage (Ө) surface covered by the inhibitor molecules as in equation (1, 2).

$$\%E = (1- W_{inh.} / W_{free}) X 100 \quad \text{............} (1)$$

$$\Theta = (1- W_{inh.} / W_{free}) \quad \text{..............} (2)$$

Where W_{free} and $W_{inh.}$ Are the weight losses of C-steel in the absence and exists of inhibitors the weight loss decreases as the concentration of poly acryl amide was increased.

Effect of Temperature:

Corrosion rates increases with increasing temperature in this study corrosion rate measured by the following equation [19]:

$$R_{corr} = \Delta W/St \qquad \text{.................. (3)}$$

Where Δw is the loss of weight S is the surface area (cm^2) and t is the displayed time (hr). The data listed in Table (1) illustrate that the highest inhibition efficiency is happened at 40°C by using poly acryl amide as inhibitor in (%15) HCl . The activation energy Ea* of the corrosion operation calculated using Arrhenius equation [20].

$$\log R_{corr} = \log A - Ea^* / 2.303\ RT \qquad \text{............. (4)}$$

Where R_{corr} is the rate of corrosion from weight loss, A is Arrhenius constant, R is the gas constant ($8.31 J.K^{-1}.mol^{-1}$) and T is absolute temperature. Figures (5, 6, 7, 8) shows Arrhenius curves between (log R_{corr}) and (1/T) in the exist or absence of different concentrations of poly acryl amide and from the slope of the straight lines activation energy Ea* can be calculated from the slope of curve and in the increasing of activation energy at exists of inhibitor means decrease in the adsorption operation on coupon surface, the data listed in Tables (2, 3, 4, 5) illustrates by increasing in temperature the corrosion rate increase and surface area of coupon that is displayed to acid became greater [21]. in our study Ea^* increases with increasing the poly acryl amide concentration

Effect of adsorption:

Poly acryl amide adsorbed on coupon and covered (Θ) part of its surface in different concentration, temperature and time and the data are listed in Table (1) and it was found the value of (Θ) increase with increasing the concentration of poly acryl amide and decrease with rise in temperature from 40 to 90°C.

Depending on Langmuir adsorption isotherm [22], we will get equation (5)

$$\Theta / 1- \Theta = AC \exp(- \Delta H /RT) \qquad \text{..................... (5)}$$

Where A is constant C is concentration of poly acryl amide and ΔH is the heat of adsorption getting logarithmic scale of equation (5) convert to equation (6).

$$\log \Theta / 1- \Theta = \log A + \log C - \Delta H / 2.303\ RT \ ....(6)$$

Figures (9, 10, 11, 12) shows the relations between log Ө / 1- Ө and 1/T at different concentrations and different time of poly acryl amide the adsorption of poly acryl amide on the (L-80) carbon steel follows Langmuir adsorption isotherm, ΔH of the adsorption can be calculated form the slope of the straight line and are given in Tables (2, 3, 4, 5). The positivity of ΔH means the endothermic adsorption behavior of poly acryl amide on (L-80) carbon steel surface.

Thermodynamic parameter:

The adsorption equation formulated on Langmuir as:

$$C/ \Theta = 1/K + C \qquad .... (7)$$

Where K is the equilibrium constant for adsorption operation. Figures (13, 14, 15, 16) shows the curve of log C/ Ө agonist log C for poly acryl amide the striate line indicates that the adsorption on surface of (L-80) carbon steel obey Langmuir absorption isotherm. The result states clearly there is no reaction between the adsorbed species. The equilibrium constant (K) for adsorption operation can be calculated from the equation (7). The thermodynamic parameters for adsorption operation. $(\Delta G)_{inh.}$ and entropy $(\Delta S)_{inh}$ of the investigated poly acryl amide can be obtained from the thermodynamic relations (8,9) .

$$K = \exp - \Delta G_{inh} / RT \qquad .... (8)$$

$$\Delta G = \Delta H - T\,\Delta S \qquad ....(9)$$

The ΔG_{inh} and $(\Delta S)_{inh}$ values at temperature range from 40 to 90°C are given in Tables (2, 3, 4, 5). The negative values of ΔG_{inh} for poly acryl amid indicates the spontaneous adsorption on the surface of coupon (L-80) carbon steel the positive value of $(\Delta S)_{inh}$ means the molecular of inhibitor is at the continues movement to obtain high absorbability of poly acryl amide on surface of coupon (L-80) carbon steel by making the activated complex with metal.

Mechanism of inhibition:

The action of poly acryl amide as a corrosion inhibitor on carbon steel in acid media can be attributed to some factors such as structure, nature of molecule, types of adsorption sites and the ability to form complexes [23]. The inhibition mechanism of poly acryl amide is happened as a result of complex formation between Fe^{2+} ion, and poly acryl amide. The iron complexes adsorbed on coupon of (L-80) carbon steel and isolated the surface metal from more corrosion happens and these complexes forming by an electron donating groups NH_2 and electron withdrawing group C=O that order the inhibition efficiency of the poly acryl amide .

Spectra (FTIR):

The FTIR spectrum of poly acryl amide complex that adsorbed on (L-80) carbon steel coupon shows an intense peak at ~3100 cm^{-1} which is a characteristic feature of N-H stretching frequency and peak at ~ 1600 cm^{-1} for C=O stretching [23-25]. M-O and M-N stretching vibration in low frequency provide direct evidence for the complexation. In the vibration of M-O bond there are many dipole moment changes in comparison with M-N bond [26]. M-N vibrations occur in the region 500–600 cm^{-1} and M-O occur in the region 400-500 cm^{-1} and Figures (17, 18) shows FTIR peaks for poyl acryl amide and adsorbed complex [27].

Conclusions:

1- Poly acryl amid can be used as acid corrosion inhibitor.
2- The efficiency of poly acryl amide depends on concentration of poly acryl amide and temperature of the medium.
3- Poly acryl amide makes stable and insoluble complexes on carbon steel surface.
4- The chemical adsorption of poly acryl amide on coupon of (L-80) carbon steel follows Langmuir equation (absorption isotherm).

Table (1) Inhibition efficiency of poly acryl amide on coupon of (L 80) in (%15) HCl at different temperature different time and Temp.

time 6hr				time 5hr				time 4hr				time 3hr				Tem. C^O	Concentration %
R_{corr} $mg/cm^2 h$	Θ	E %	Weight loss (gr)	R_{corr} $mg/cm^2 h$	Θ	E %	Weight loss(gr)	R_{corr} $mg/cm^2 h$	Θ	E %	Weight loss(gr)	R_{corr} $mg/cm^2 h$	Θ	E %	Weight loss (gr)		
5.64	----	----	1.18	6.35	-----	------	1.15	7.83	-----	------	1.12	9.68	----	----	1.09		Blank
1.98	.6440	64.40	0.42	2.21	.6434	64.34	0.41	2.77	.6428	64.28	0.40	3.34	.6422	64.22	0.39		1
1.51	.7203	72.03	0.33	1.83	.7130	71.30	0.33	2.23	.7142	71.42	0.32	2.18	.8165	81.65	0.30		2
1.01	.8135	81.35	0.22	1.19	.8173	81.73	0.21	1.42	.8214	82.14	0.20	1.71	.8348	83.48	0.18	40	3
0.39	.9237	92.37	0.09	0.45	.9304	93.04	0.08	0.48	.9375	93.75	0.07	0.43	.9541	95.41	0.05		4
0.35	.9322	93.22	0.08	0.37	.9391	93.91	0.07	0.29	.9642	96.42	0.04	0.28	.9724	97.24	0.03		5
5.96	----	----	1.26	7.12	-----	-----	1.24	8.83	------	----	1.21	10.92	----	----	1.18		Blank
2.08	.6507	65.07	0.44	2.49	.6551	65.51	0.44	2.85	.6528	65.28	0.42	3.98	.6525	65.25	0.40		1
1.75	.6984	69.84	0.38	2.09	.6935	69.35	0.38	2.40	.7024	70.24	0.36	3.05	.7033	70.33	0.35		2
1.16	.7936	79.36	0.26	1.44	.7903	79.03	0.26	1.70	.8016	80.16	0.24	2.19	.8050	80.50	0.23	60	3
046	.9206	92.06	0.10	0.47	.9274	92.74	0.09	0.56	.9338	93.38	0.08	0.55	.9491	94.91	0.06		4
0.41	.9285	92.85	0.09	0.33	.9516	95.16	0.08	0.34	.9586	95.86	0.05	0.38	.9661	96.61	0.04		5
10.58	----	----	2.30	11.59	-----	-----	2.1	12.97	------	-----	1.88	16.43	----	----	1.85		Blank
2.43	.7826	78.26	0.50	2.76	.7666	76.66	0.49	3.32	.7500	75.00	0.47	3.92	.7567	75.67	0.45		1
2.12	.8086	80.86	0.44	2.30	.7952	79.52	0.43	2.89	.7765	77.65	0.42	3.40	.7891	78.91	0.39		2
1.52	.8608	86.08	0.32	1.90	.8523	85.23	0.31	2.01	.8404	84.04	0.30	2.57	.8540	85.40	0.27	80	3
0.57	.9478	94.78	0.12	0.52	.9523	95.23	0.10	0.63	.9521	95.21	0.09	0.74	.9567	95.67	0.08		4
0.55	.9521	95.21	0.11	0.49	.9571	95.71	0.09	0.57	.9574	95.74	0.08	0.54	.9675	96.75	0.06		5
11.18	----	----	2.50	13.03	-----	-----	2.3	13.65	------	-----	1.95	17.48	----	----	1.91		Blank
2.57	.7640	76.40	0.59	3.12	.7608	76.08	0.55	3.59	.7333	73.33	0.52	4.27	.7434	74.34	0.49		1
2.28	.8120	81.20	0.47	2.59	.7956	79.56	0.47	3.19	.7641	76.41	0.46	3.75	.7748	77.48	0.43		2
1.62	.8520	85.20	0.37	1.90	.8434	84.34	0.36	2.48	.8205	82.05	0.35	3.15	.8272	82.72	0.33	90	3
0.64	.9440	94.40	0.14	0.62	.9478	94.78	0.12	0.77	.9435	94.35	0.11	0.90	.9528	95.28	0.09		4
0.59	.9480	94.80	0.13	0.52	.9565	95.65	0.10	0.60	.9538	95.38	0.09	0.61	.9633	96.33	0.07		5

Table (2) Thermodynamic parameters of poly acryl amide in time (3) hours.

SΔ ($J.mol^{-1}.k^{-1}$)	GΔ ($k.J.mol^{-1}$)	HΔ ($K.J.mol^{-1}$)	Ea* ($K.J.mol^{-1}$)	K ($K.J.mol^{-1}$)	Temp. K	Conc. %
41.91	-13.00^3			$1.81x10^2$	313	
43.60	-14.40			$1.88x10^2$	333	
47.90	-16.80	120	44	$3.12x10^2$	353	1
47.40	-17.10			$2.94x10^2$	363	
45.10	-14.00			$2.22X10^2$	313	
39.97	-13.20			$1.19X10^2$	333	
43.65	-15.30	111	55	$1.88X10^2$	353	2
43.00	-15.50			$1.72X10^2$	363	
42.72	-13.30			$1.69X10^2$	313	
41.10	-13.60			$1.38X10^2$	333	
43.83	-15.40	72	109	$1.96X10^2$	353	3
42.34	-15.30			$1.61X10^2$	363	
52.25	-16.30			$5.26X10^2$	313	
51.22	-17.00			$4.76X10^2$	333	
52.56	-18.50	57	135	$5.50X10^2$	353	4
51.67	-18.70			$5.00X10^2$	363	
54.36	-17.00			$7.14X10^2$	313	
52.90	-17.60			$5.88X10^2$	333	
53.02	-18.70	17	158	$5.88X10^2$	353	5
52.11	-18.90			$5.26X10^2$	363	

Table (3) Thermodynamic parameters of poly acryl amide in time (4) hours.

SΔ $(J.mol^{-1}.k^{-1})$	GΔ K.$(J.mol^{-1})$	HΔ $(K.J.mol^{-1})$	Ea* $(K.J.mol^{-1})$	K $(K.J.mol^{-1})$	Temp. K	Conc. %
41.87	-13.00			$1.81x10^2$	313	
43.56	-14.40			$1.88x10^2$	333	
47.61	-16.70	107	51	$3.03x10^2$	353	1
46.85	-16.90			$2.77x10^2$	363	
40.17	-12.50			$1.25x10^2$	313	
39.86	-13.20			$1.19x10^2$	333	
42.99	-15.10	76	70	$1.75x10^2$	353	2
42.35	-15.30			$1.63x10^2$	363	
41.71	-13.00			$1.53x10^2$	313	
40.71	-13.50			$1.35x10^2$	333	
42.93	-15.10	57	109	$1.75x10^2$	353	3
35.96	-13.00			$1.53x10^2$	363	
49.34	-15.40			$3.84x10^2$	313	
48.78	-16.20			$3.57x10^2$	333	
51.96	-18.30	44	126	$5.00x10^2$	353	4
50.25	-18.20			$4.16x10^2$	363	
52.47	-16.40			$5.55x10^2$	313	
51.12	-17.00			$4.76x10^2$	333	
50.77	-17.90	24	172	$4.54x10^2$	353	5
50.20	-18.20			$4.16x10^2$	363	

Table (4) Thermodynamic parameters of poly acryl amide in time (5) hours.

SΔ ($J.mol^{-1}.k^{-1}$)	GΔ ($K.J.mol^{-1}$)	HΔ ($K.J.mol^{-1}$)	Ea* ($K.J.mol^{-1}$)	K ($K.J.mol^{-1}$)	Temp. K	Conc. %
41.99	-13.00			$1.81x10^2$	313	
39.46	-13.00			$1.81x10^2$	333	
43.18	-15.10	143	57	$3.33x10^2$	353	1
44.19	-15.90			$3.22x10^2$	363	
40.30	-12.50			$1.25X10^2$	313	
39.38	-13.00			$1.13X10^2$	333	
43.95	-15.40	116	67	$1.96X10^2$	353	2
44.12	-15.90			$1.96X10^2$	363	
41.86	-13.00			$1.49X10^2$	313	
40.25	-13.30			$1.26X10^2$	333	
43.92	-15.40	105	101	$1.92X10^2$	353	3
43.26	-15.60			$1.81X10^2$	363	
48.51	-15.10			$3.33X10^2$	313	
48.00	-15.90			$3.22X10^2$	333	
51.80	-18.20	86	130	$5.00X10^2$	353	4
50.90	-18.40			$4.54X10^2$	363	
47.82	-14.90			$3.12X10^2$	313	
49.75	-16.50			$4.00X10^2$	333	
50.90	-17.90	68	134	$4.54X10^2$	353	5
50.60	-18.30			$4.34X10^2$	363	

Table (5) Thermodynamic parameters of poly acryl amide in time (6) hours.

SΔ ($J.mol^{-1}.k^{-1}$)	GΔ ($K.J.mol^{-1}$)	HΔ ($K.J.mol^{-1}$)	Ea* ($K.J.mol^{-1}$)	K ($K.J.mol^{-1}$)	Temp. K	Conc. %
42.02	-13.00			$1.81x10^2$	313	
43.70	-14.40			$1.88x10^2$	333	
49.44	-17.30	155	63	$3.70x10^2$	353	1
48.63	-17.50			$3.33x10^2$	363	
40.68	-12.60			$1.29x10^2$	313	
39.74	-13.10			$1.16x10^2$	333	
44.85	-15.70	134	68	$2.12x10^2$	353	2
44.99	-16.20			$2.17x10^2$	363	
41.51	-12.90			$1.44x10^2$	313	
40.31	-13.40			$1.28x10^2$	333	
44.45	-15.60	93	78	$2.08x10^2$	353	3
43.78	-15.80			$1.92x10^2$	363	
47.56	-14.80			$3.03x10^2$	313	
47.41	-15.70			$2.94x10^2$	333	
50.95	-17.90	88	88	$4.54x10^2$	353	4
50.65	-18.30			$4.34x10^2$	363	
46.91	-14.60			$2.77x10^2$	313	
46.49	-15.40			$2.63x10^2$	333	
49.81	-17.50	84	91	$4.00x10^2$	353	5
49.26	-17.80			$3.70x10^2$	363	

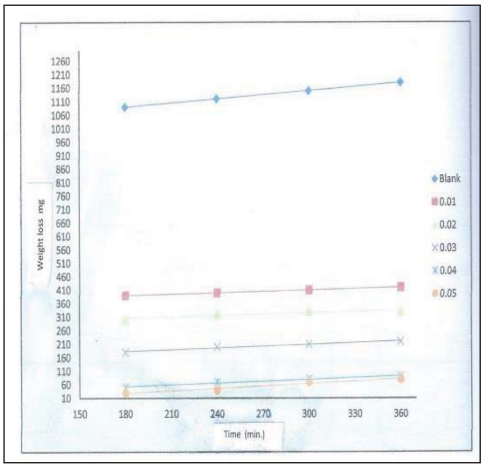


Fig. (1) The weight loss–time plot for (L-80) C-steel in the presence and absence different concentrations of poly acryl amide at (40) °C and %15HCl.

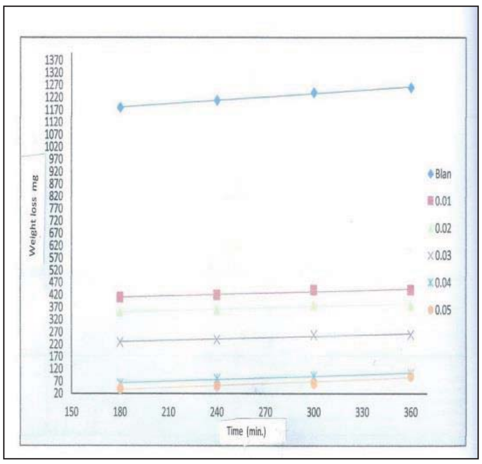


Fig. (2) The weight loss-time plot for (L-80) C-steel in the presence and absence different concentrations of poly acryl amide at (60) °C and %15HCl.

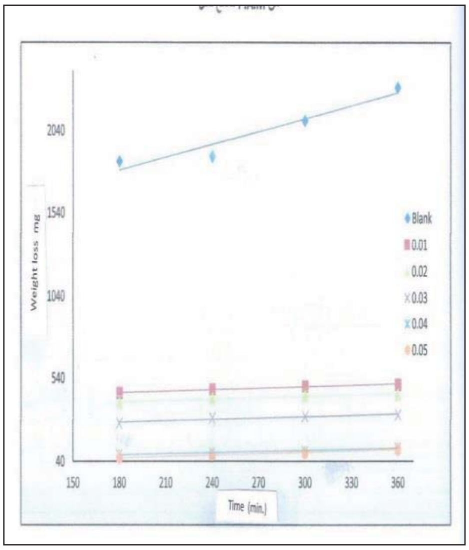


Fig. (3) The weight loss–time plot for (L-80) C-steel in the presence and absence different concentrations of poly acryl amide at(80) oC and %15HCl.

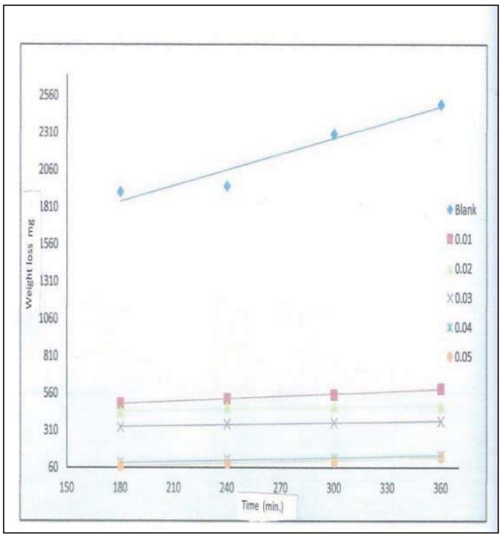


Fig. (4) The weight loss-time plot for (L-80) C-steel in the presence and absence different concentrations of poly acryl amide at (90) oC and%15HCl.

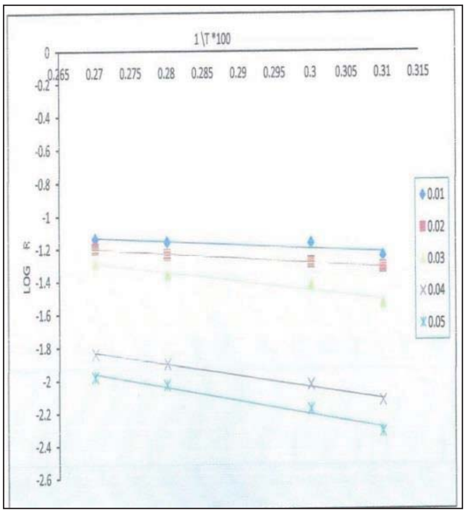


Fig. (5) The (log R_{corr} - 1/T) plot of (L-80) C steel in the presence and absence different concentrations of poly acryl amid at time of (3) hr and %15HCl.

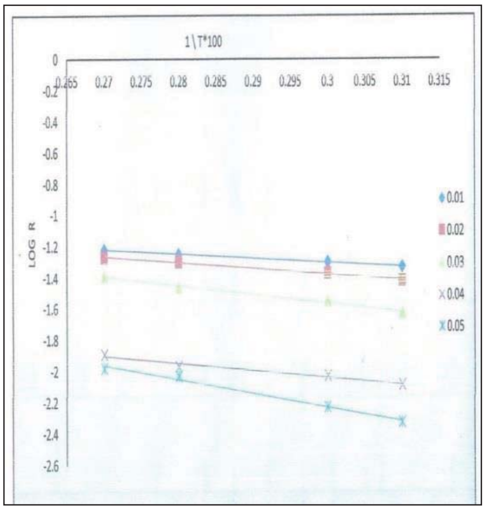


Fig. (6) The (log R_{corr} - 1/T) plot for (L-80) C steel in the presence and absence different concentration of poly acryl amide at time of (4)hr and %15HCl.

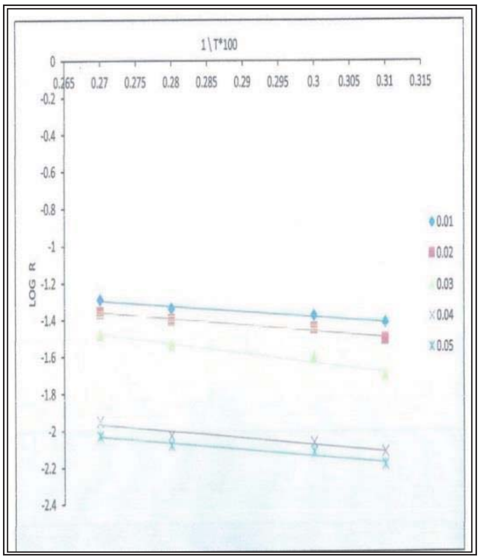


Fig. (7) The (log R_{corr} - 1/T) plot for (L-80) C steel in the presence and absence of different concentrations of poly acryl amide at time of (5) hr and%15HCl.

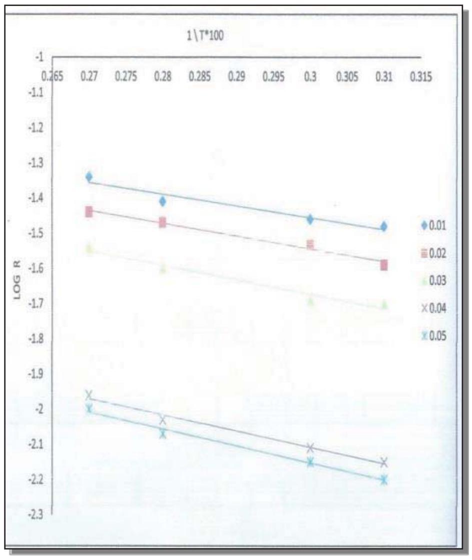


Fig. (8) The (log R_{corr} - 1/T) plot for (L-80) C steel in the presence and absence of different concentration of poly acryl amide at time of (6)hr and %15HCl.

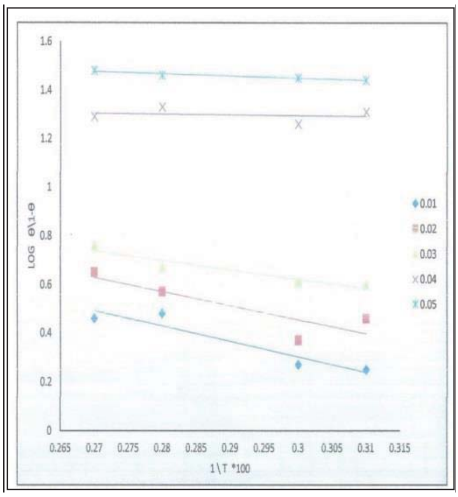


Fig. (9) The (log ϴ/(1- ϴ) - 1/T) plot for (L-80) C steel in the presence and absence of different concentrations of poly acryl amide at time of (3) hr and %15HCl

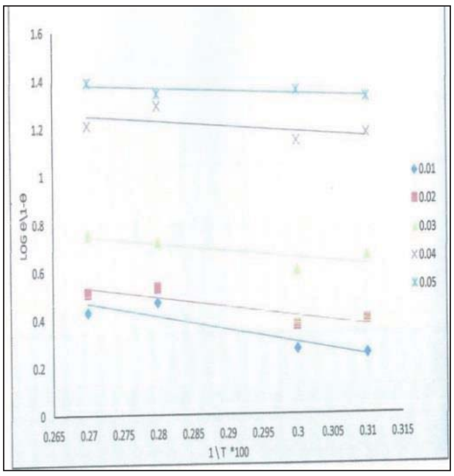


Fig. (10) The (log ϴ/(1- ϴ) - 1/T) plot for (L-80) C steel in the presence and absence of different concentration of poly acryl amide at time of (4) hr and %15HCl

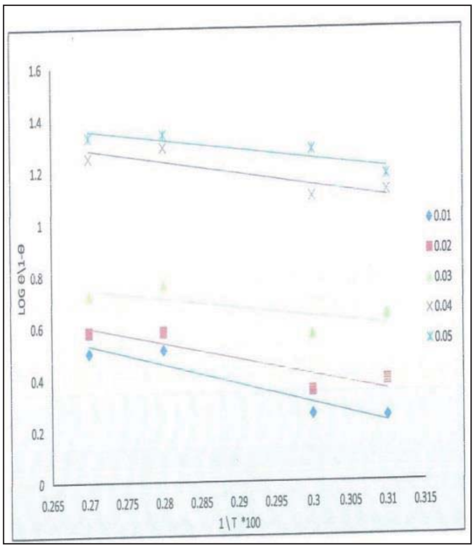


Fig. (11) The (log Θ/(1- Θ) - 1/T) plot for (L-80) C steel in the presence and absence of different concentrations of poly acryl amide at time of (5) hr and %15HCl.

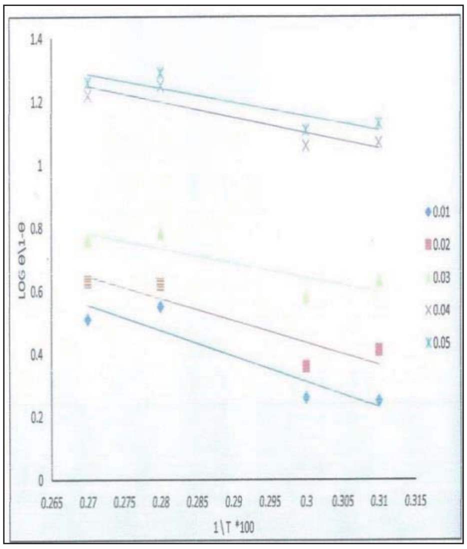


Fig. (12) The (log Θ/(1- Θ) - 1/T) plot for (L-80) C steel in the presence and absence of different concentration of poly acryl amide at time of (6) hr and %15HCl.

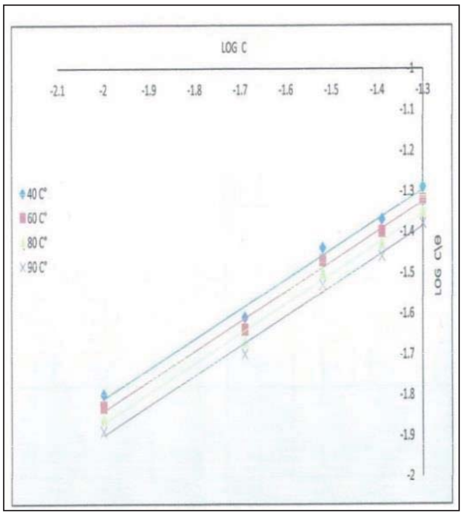


Fig. (13) The (log C/Θ - log C) plot for (L-80) in the absence and presence of different concentration of poly acryl amide at time of (3) hr and %15HCl

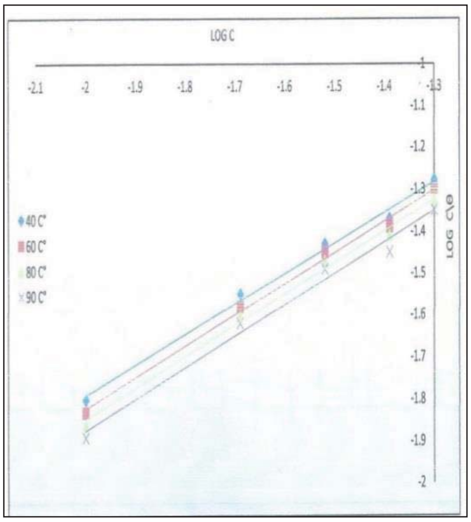


Fig. (14) The (log C/Θ - log C) plot for (L-80) in the absence and presence of different concentration of poly acryl amide at time of (4) hr and %15HCl.

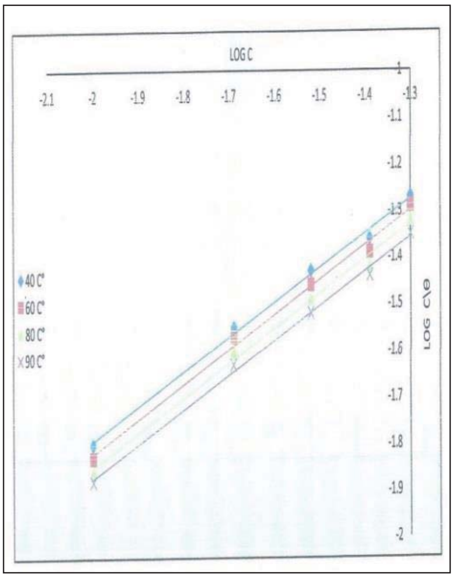


Fig. (15) The (log C/Ө - log C) plot for (L-80) in the presence and absence of different concentration of poly acryl amide at time of (5) hr and %15HCl.

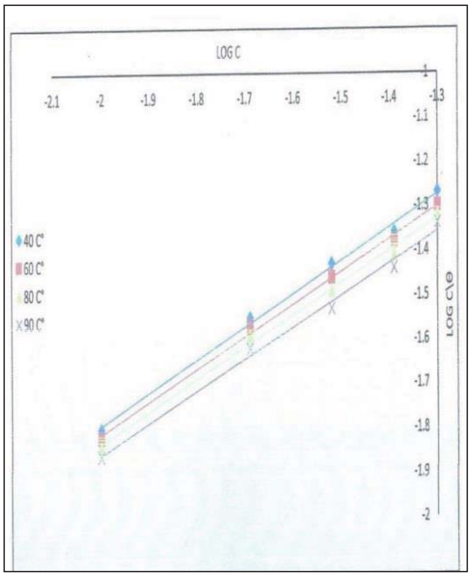


Fig. (16) The (log C/Ө - log C) plot for (L-80) in the presence and absence of different concentration of poly acryl amide at time of (6) hr and %15HCl.

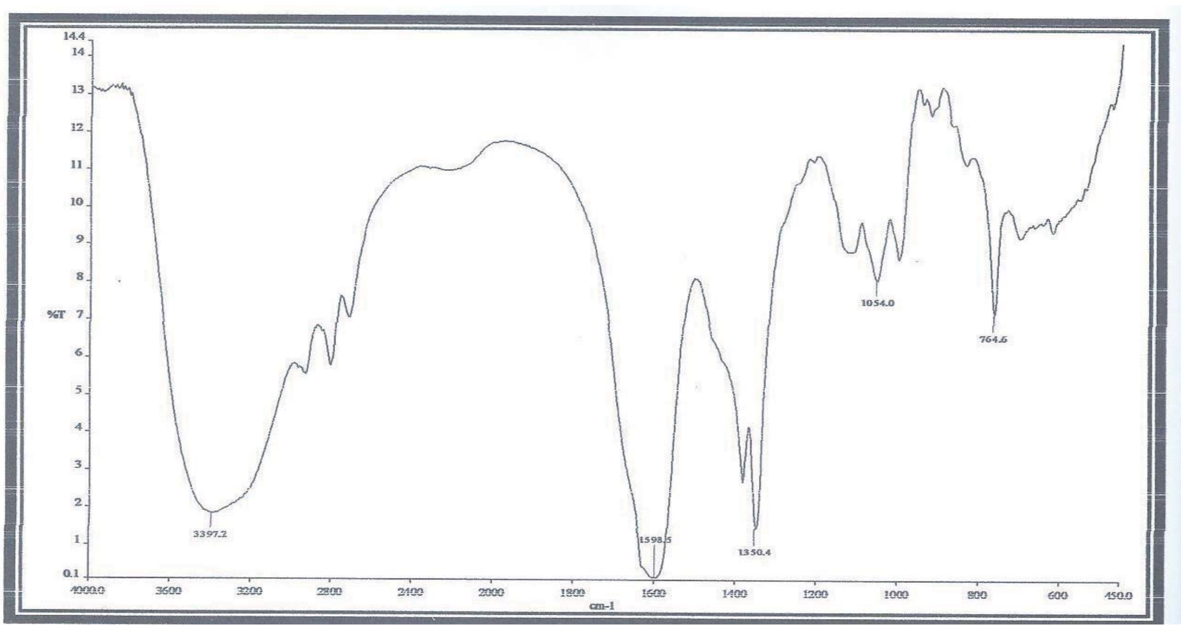


Fig. (17) The FTIR spectrum for poly acryl amide

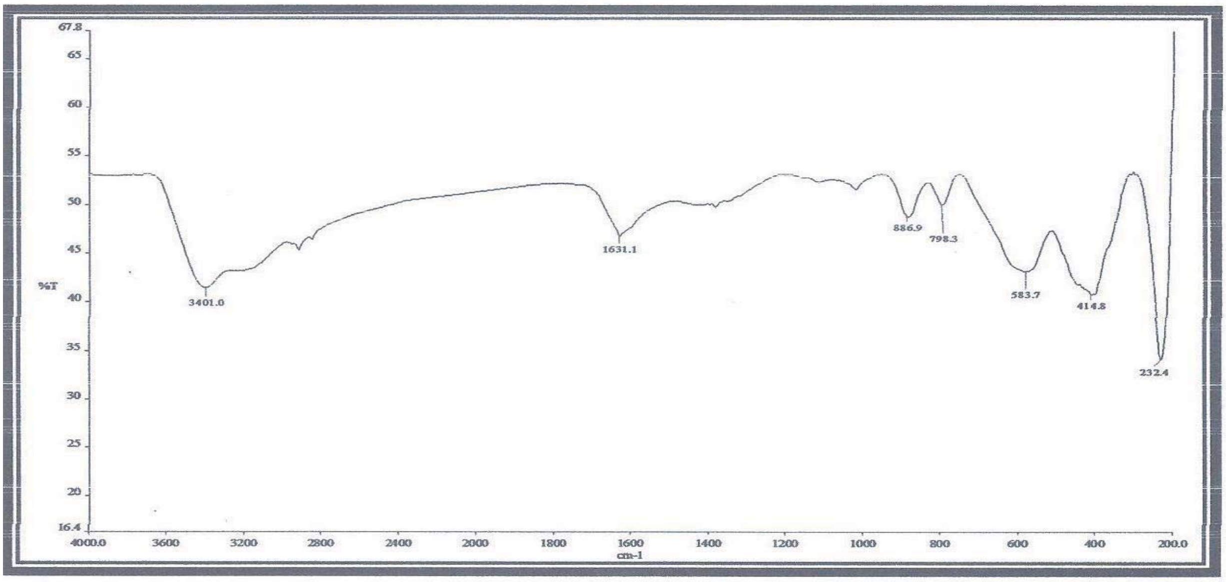


Fig. (18) The FTIR spectrum of poly acryl amide complex on C-steel

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