

CORROSION INHIBITION OF CARBON STEEL IN HYDROCHLORIC ACID

Falah Kaify Matloub

falahkaify@gmail.com

University of Babylon - College of engineering - Department of chemical engineering

ABSTRACT

The corrosion of carbon steel in 0.3 and 3% mass hydrochloric acid containing the concentration range 50-800 ppm of Thiourea (Th), Quinoline (Q), Diethylamine (DEA) and Pyridine (P) were investigated using electrochemical methods. The investigation aims to mention the best organic inhibitor among several compounds to be used in synergic inhibitors. The inhibition efficiencies of thiourea and quinoline are better than pyridine and diethylamine in 0.3 mass% HCl. Thiourea is better than quinoline in 3 mass% HCl and its inhibition efficiency is 83.7%. Generally, the corrosion rate decreases with increasing inhibitors concentration. Diethylamine and pyridine are not effective. The polarization curves indicate that the used inhibitors influenced the cathodic reaction more than the anodic reaction and they are considered as a mixed type inhibitors.

Keywords: Corrosion, organic inhibitors, linear polarization technique.

تشبيط تاكل الفولاذ الكربوني في حامض الهيدروكلوريك

فلاح كافي مطلوب

الخلاصة

تم دراسة تاكل الفولاذ الكربون في حامض الهيدروكلوريك بتركيز 0.3 و 3% (نسبة كتلية) وتأثير اضافة مثبطات التاكل العضوية وهي الثايوريا، الكوينولين، الداى اثيل امين و البايردين و بتركيز من 50- 800 جزء بالمليون بالطرق الكهروكيميائية. ان الهدف من البحث هو تحديد افضل مثبط بين عدة مثبطات مختارة لاستعمالها ضمن خلطة من المثبطات المتنازرة. وجد ان كفاءة التشبيط للثايوريا والكوينولين افضل من الداى اثيل امين و البايردين في حامض الهيدروكلوريك 0.3% (نسبة كتلية). ووجد ان الثايوريا احسن من الكوينولين في 3% (نسبة كتلية) وكفاءة التشبيط لها 83.7%. عموما معدل التاكل يتناقص مع زيادة تركيز المثبط. ووجد ان الداى اثيل امين و البايردين غير كفوءة. تشير منحنيات الاستقطاب بان المثبطات المستعملة تؤثر على التفاعل الكاثودي اكثر من التفاعل الانودي وهي تعتبر كمثبطات مختلطة كاثودية وانودية.

INTRODUCTION

Hydrochloric acid is widely used in petroleum industry (drilling, production, separation, extraction, cracking and polymerization), acid cleaning, acid descaling and numerous manufacturing processes. Hydrochloric acid is harmful and aggressive to steel. Inhibition is commonly used to reduce the corrosive attack on carbon steel by the hydrochloric acid TrabANELLI (1991). The corrosion of carbon steel in acids can be inhibited by a wide range of substances, such halide ions and many organic compounds particularly those containing nitrogen, phosphorus and sulfur Abiola and Oforka (2002). Organic compounds containing multiple bonds, especially triple bonds are effective inhibitors. The organic inhibitors have been widely applied, since they are effective and their costs are attractive. Steel is a metal with numerous industrial applications and it is corroded in acids. The group of nitrogen-containing compounds is effective inhibitors in the corrosion prevention of steel and treatment with hydrochloric acid. The sulfur containing inhibitors compounds are also found in commercial inhibitors recommended for use in hydrochloric acid Sykes (1990), Elachouri (1995) and Mernari et al (1998). The choice of the right inhibitor often can be very difficult because the inhibitor performance is influenced by so many factors such as ions type and concentration, temperature, pH, stirring or velocity, conductivity of electrolyte and metal or alloy composition. Results obtained in one corrosion system can not be transferred to another corrosion system without further investigation Rozenfeld (1981). Most organic inhibitors act by absorption on the metal surface and influenced by the nature of surface change of metal, the type of aggressive solution and the inhibitors chemical structure Shrier (1976). Finally, the inhibitors must be effective at low concentrations, high temperatures, thermal, chemically stable and good surfactant and foaming characteristics [Rozenfeld (1981), Shrier (1976) and Schmitt (1984).

EXPERIMENTAL WORK

Cylindrical carbon specimens were used. The chemical composition of the carbon steel is: 0.16% C, 0.28% Si, 0.4% Mn, 0.02 %P, and 0.023 S (wt %). All specimens were annealed at 600°C for one hour in a vacuum furnace of 10^{-4} torr pressure and cooled to room temperature under vacuum. The specimens isolated by epoxy resin so that on a circle of 0.5 cm diameter was exposed to the acid solution. All tests were performed at (25 ± 0.5) °C. All experimental runs listed are duplicated and give satisfactory reproducibility. Analar hydrochloric acid and double distilled water were used for the preparation of 0.3 and 3 wt% hydrochloric acid solution. The inhibitors added in concentrations of 50 to 800 ppm. The polarization experiments were carried out in three electrode glass cell with capacity of 500 ml. The counter (auxiliary) electrode is platinum electrode. The calomel electrode used as a reference electrode with a fine lugging capillary bridge while the third electrode is working electrode which represents the studied specimen. The polarization curve was carried out using potentiostat type WINKING potentiostat, Germany. The sweep rate is 20mV/min. Before each experiment the specimen was wet polished on emery paper grades (200, 400 and 600) then rinsed in tap water, distilled water, ethanol and acetone and after each stage of rinsing dried by filter paper.

RESULTS AND DISCUSSION

The polarization curves for carbon steel in 0.3 and 3 wt% HCl in the presence of organic inhibitors (Th, Q, DEA, and P) and without addition of inhibitors were carried out as shown in figures (1) to (18). The calculated corrosion currents are shown in figures (19) and (20) and table (1). The corrosion currents (I_{corr}) were calculated by three points method and Jank and Junck method [9, 10] which are selected for potentials of $\pm \Delta E = \pm 10$, $\pm 2 \Delta E = \pm 20$ and

$\pm 3\Delta E = \pm 30$ mv. The anodic current symbols are I_1 , I_2 and I_3 and cathodic current symbols I_{-1} , I_{-2} , and I_{-3} .

The used methods for I_{corr} calculation are:

1. Barnartt method Barnartt (1977).

A. At Potentials of $2\Delta E$, ΔE and $-\Delta E$

$$R_1 = I_2/I_1, \quad R_2 = I_1/I_{-1}$$

$$I_{corr} = \frac{I_1}{(R_1 + 4R_2)^{0.5}} \quad (1)$$

B. At potentials of ΔE , $-\Delta E$ and $-2\Delta E$

$$R_1 = I_1/I_{-1}, \quad R_2 = I_{-2}/I_{-1}$$

$$I_{corr} = \frac{I_1}{((R_1 + 4R_2)^2 + 4R_1)^{0.5}} \quad (2)$$

C. At potentials of ΔE , $2\Delta E$ and $-2\Delta E$

$$R_1 = I_2/I_{-2}, \quad R_2 = I_2/I_1$$

$$I_{corr} = \frac{I_2}{R_2(R_2^2 - 4R_1^{0.5})^{0.5}} \quad (3)$$

2. Jank and Junck method Jankowski and Junkiewicz (1980).

At potentials of $\pm\Delta E$ and $\pm 2\Delta E$

$$I_{corr} = \frac{I_1 I_{-1}}{(I_2 I_{-2} - 4I_1 I_{-1})^{0.5}} \quad (4)$$

The corrosion currents values are the average values of the above four equations results. It was observed that the corrosion currents are decreased with increasing of inhibitors concentrations. These behaviors can be related to the increasing of the hydrogen overvoltage on the corroding metal and chemisorptions of the organic inhibitor at the alloy surface Gad et al. (1989), El-Egamy (2008), El-Egamy (2008), Abboud et al. (2007), Thomas and Nurse (1967), Bentis et al. (1999) and Popova(2007).The calculated inhibition efficiency percent (IE %) is shown in table (2) and figures (21) and (22). It can be obtained using

$$IE\% = \frac{I_{corr(uninhib)} - I_{corr(inhib)}}{I_{corr(uninhib)}} \times 100 \quad (5)$$

$$= \frac{(R_p)^{-1} - (R_p)_{inh}^{-1}}{(R_p)^{-1}} \times 100 = \theta \times 100 \quad (6)$$

R_p is the polarization resistance and θ is surface coverage.

At 0.3 wt% HCl, It was found that (IE%) of the inhibitor (Th, Q, DEA, and P) at concentrations 50-800 ppm increase from 47.2-83.25%, 6.4-71.62%, 41.25-56 and 46.5-54.1 respectively. It was deduced that the increasing of DEA and P concentration have no significant effect on (IE%) and they are about 50%. Th is the best inhibitor and its (IE%)

more than 80% at 800 ppm. Increasing Q concentrate from 800-960 ppm has no significant effect. In 3 wt% HCl, (IE %) have the same trend of 0.3wt% for Th and Q. In all concentrations, the inhibitors do not act as stimulator because they do not form soluble complexes which leading to the dissolution rate increase Brown and Hope (1995) and El-Egamy (2008). Th is a more efficient than the other tested inhibitors due to the nitrogen and sulfur atom in its groups, which confirm with Aksut and Onal results Aksut and Onal (1997) and Buyuksagis and Aksut (2008). Q is better than P and DEA because of the two rings in the structure which adsorbed on the steel Fu et al. (2012), Verma1 et al. (2014) and Mishra et al. (2018). (IE %) decreases with decreasing in the concentration of the acid which confirms with Rajappa (2003). The measured corrosion potential (E_c) referred to the standard calomel electrode (SCE) is shown in table (3). It was found that E_c have little shift in the positive direction almost in all inhibitors concentrations and this suggests that both anodic and cathodic processes are retarded. They are suggested as a mixed type inhibitor Shrier (1984), El-Egamy (2008) and Ergun (2008). Inhibited hydrochloric acid is the most efficient method to remove fouling Shrier (1984). The Tafel constants were calculated by extrapolation in the Tafel region (linear section) of the polarization curves are shown in tables (4) and (5) and Figures (23) to (26). It was observed that the Tafel constants increased with increasing of inhibitors concentrations. The cathodic Tafel constants (B_c) increased more than the anodic Tafel constants (B_a). Due to the above observations, the inhibitors could be suggested as a mixed type inhibitors and this confirms with Ergun (2008) and Rujappa (2003). From the Tafel constants, it was observed that the cathodic sites are blocked to greater extent than the anodic sites by the inhibitors molecules and the cathodic curves are much more polarized than anodic curves [Rozenfeld (1981), Shrier (1984). and Quraishi and Jamal (2003). It was deduced that adsorption of the inhibitors at low (eff) tend to occur preferentially at anodic sites, causing retardation of the anodic reaction, at higher surface coverage, adsorption occurs on both anodic and cathodic sites, and both reactions are inhibited Shrier (1984). The B_a increase may be ascribed to additional energy barrier due to the presence of adsorbed inhibitors Quraishi and Jamal (2003). The values of the polarization resistance (R_p) are shown in Table (6) and Figures (27) to (28). It was calculated by using four point methods of Bandy (1981) as follows:

$$R = \frac{I_1(I_{-1}/I_1)^{0.5}}{I_2(I_{-2}/I_2)^{0.5}} \quad (7)$$

$$m = \left[\frac{6(1-2R)}{\Delta E^2(8R-1)} \right]^{0.5} \quad (8)$$

$$R_p = \frac{\frac{m^2 \Delta E^3}{6} + \Delta E}{\sqrt{I_1 I_{-1}}} \quad (9)$$

It was found that R_p increased with increasing of the inhibitor concentration. It is clear that there is a good agreement between R_p and eff and it is inversely proportional to the corrosion current El-Egamy (2008).

CONCLUSIONS

The following conclusions can be drawn from the above research:

1. Thiourea is the best inhibitor among the used inhibitors.
2. All the inhibitors are considered as mixed type inhibitors.
3. The corrosion rate decreases with increasing of inhibitor concentration.
4. All inhibitors in all concentrations are not acting as stimulators.

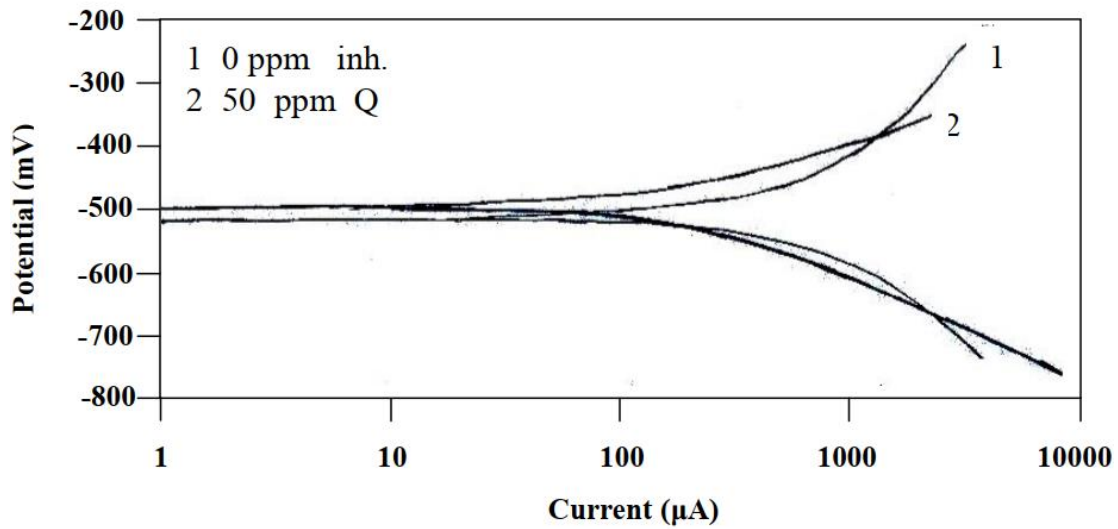


Fig. (1) Polarization curves of carbon steel in 3 wt% HCl

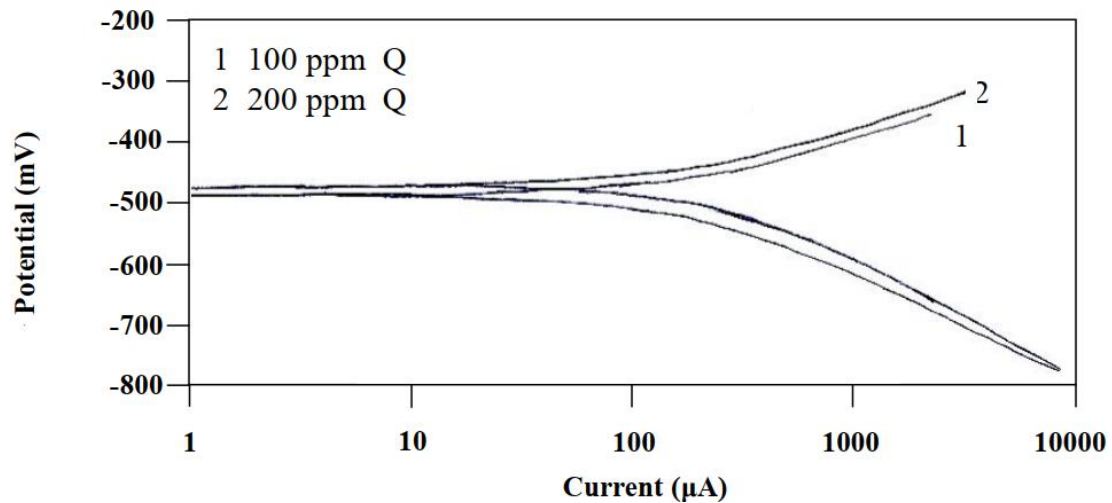


Fig. (2) Polarization curves of carbon steel in 3 wt% HCl

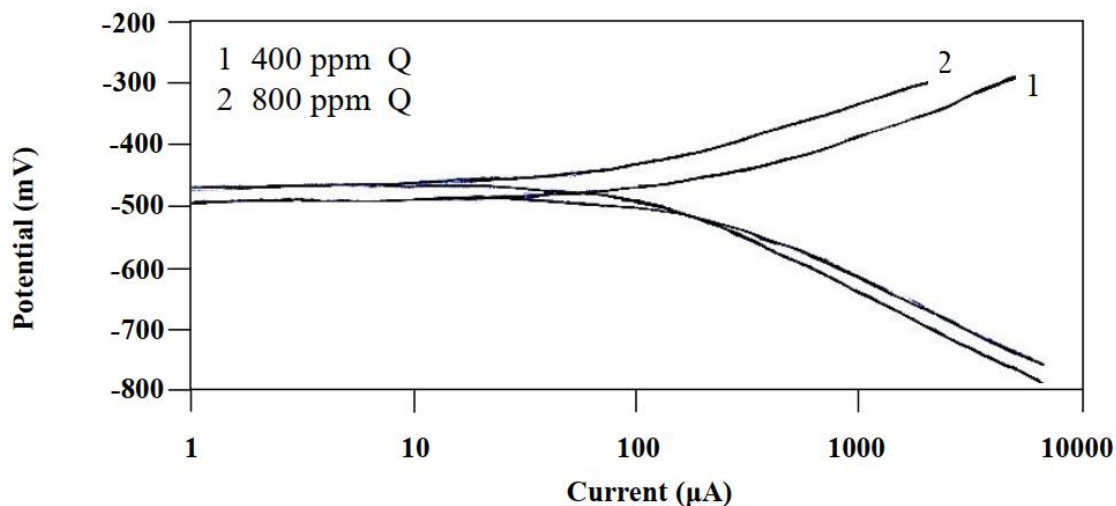


Fig. (3) Polarization curves of carbon steel in 3 wt% HCl

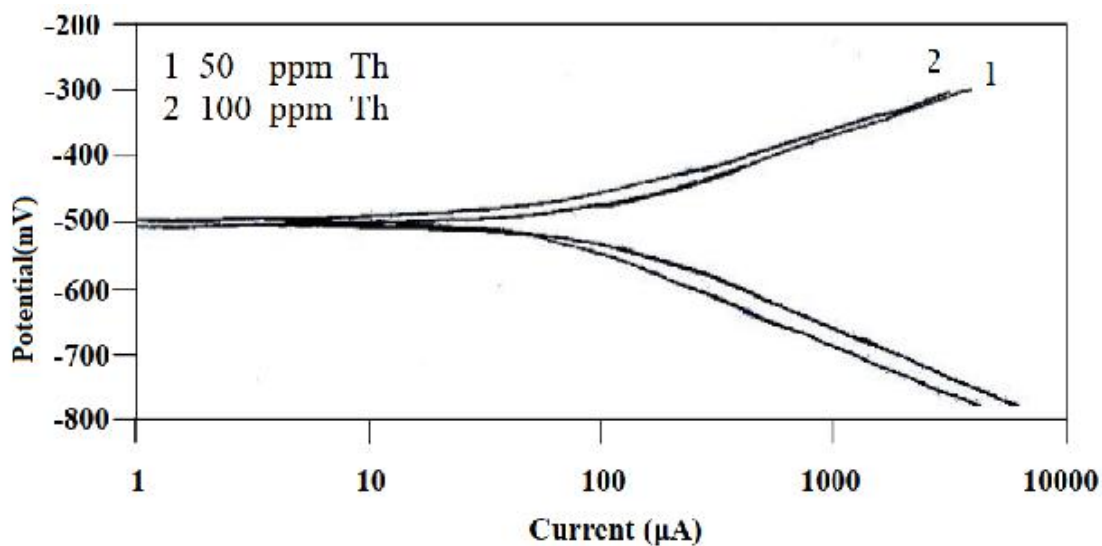


Fig. (4) Polarization curves of carbon steel in 3 wt% HCl

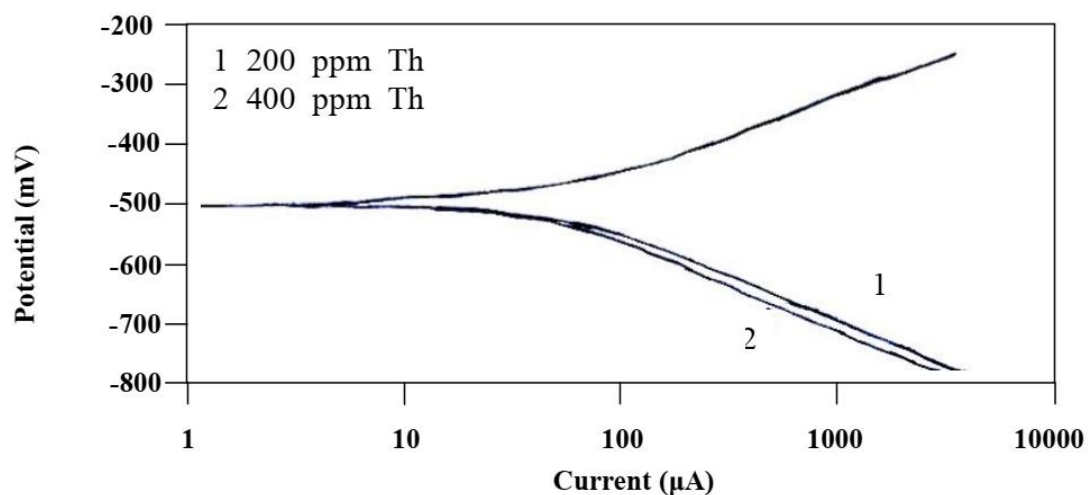


Fig. (5) Polarization curves of carbon steel in 3 wt% HCl

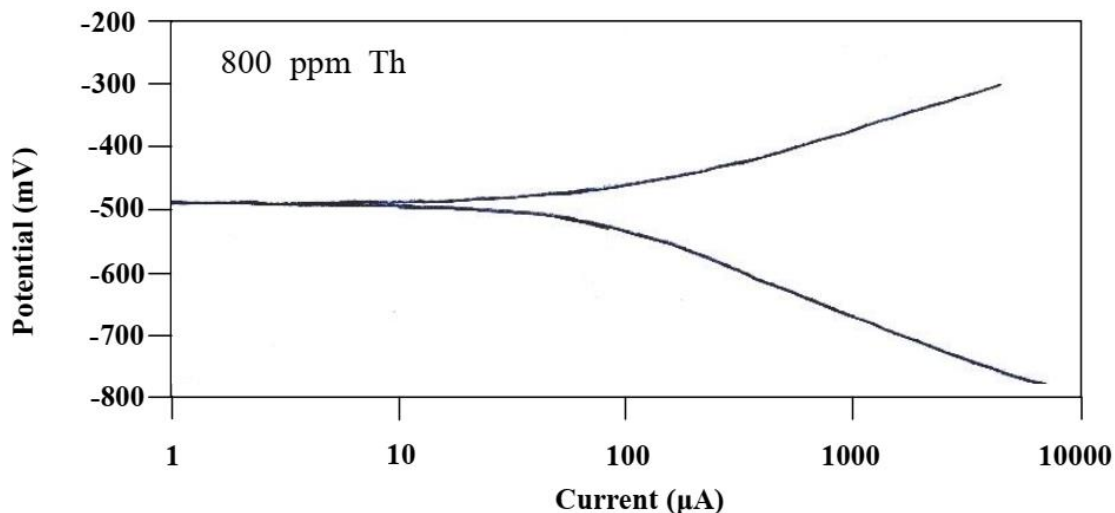


Fig. (6) Polarization curves of carbon steel in 3 wt% HCl

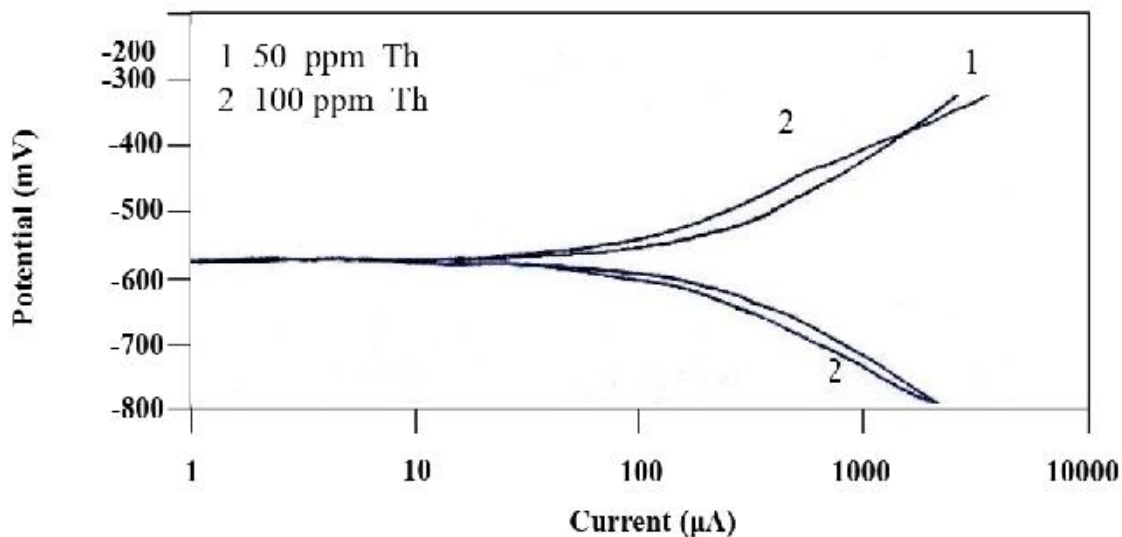


Fig. (7) Polarization curves of carbon steel in 0.3 wt% HCl

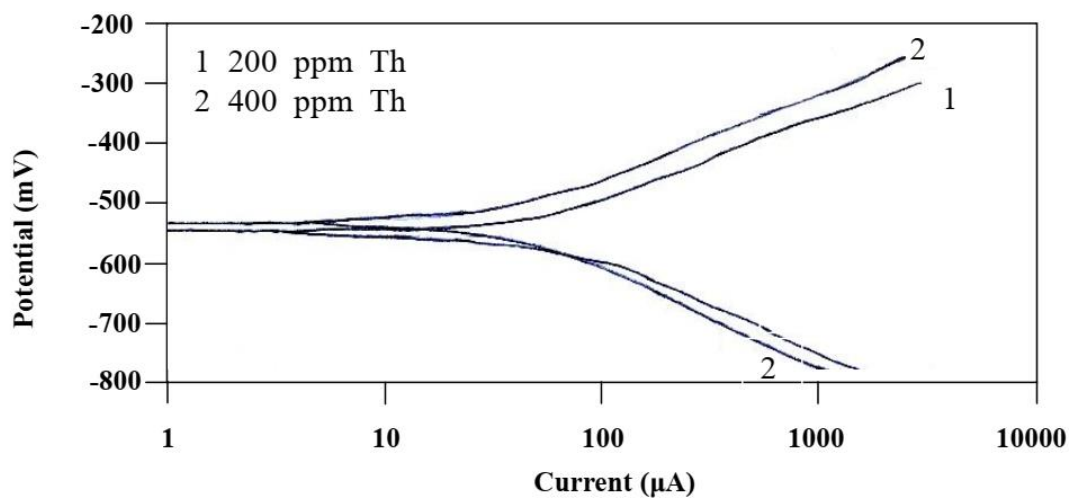


Fig. (8) Polarization curves of carbon steel in 0.3 wt% HCl

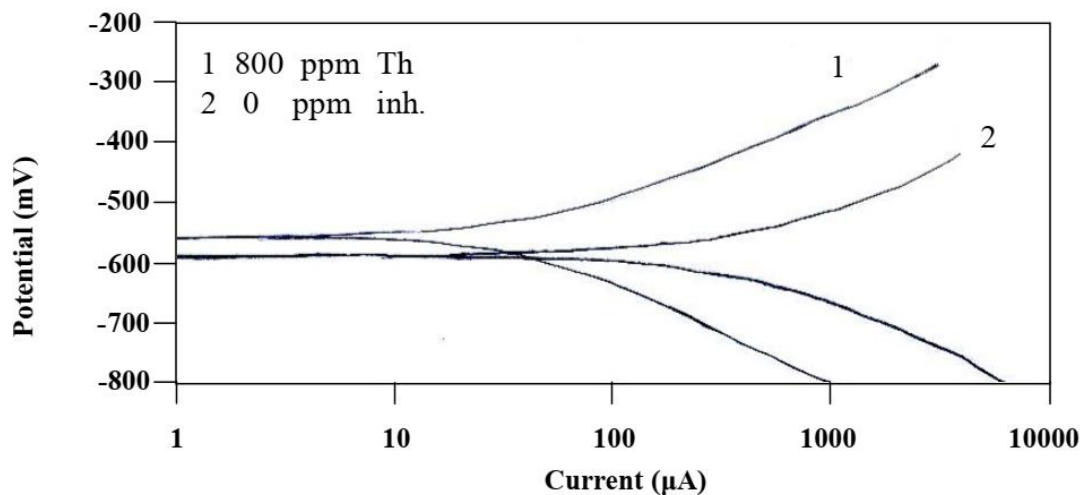


Fig. (9) Polarization curves of carbon steel in 0.3 wt% HCl

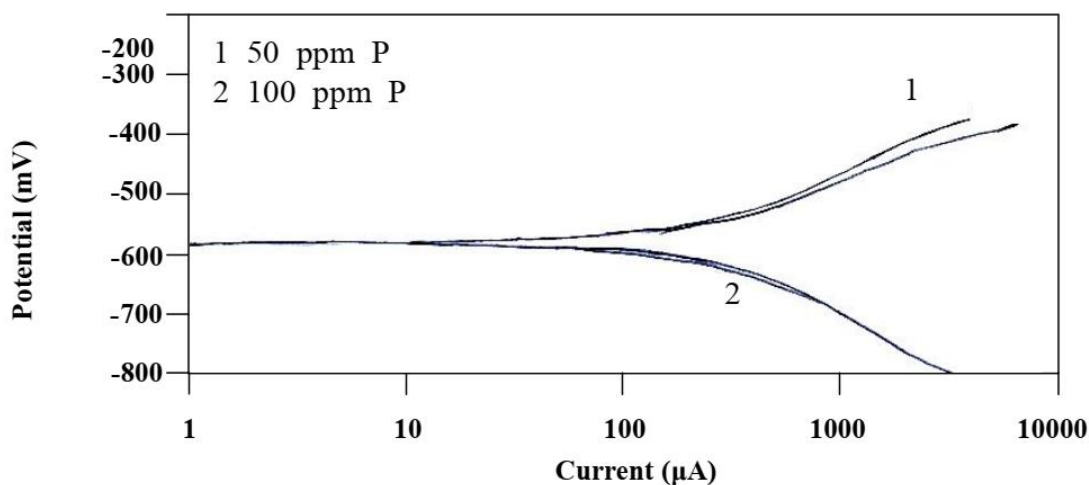


Fig. (10) Polarization curves of carbon steel in 0.3 wt% HCl

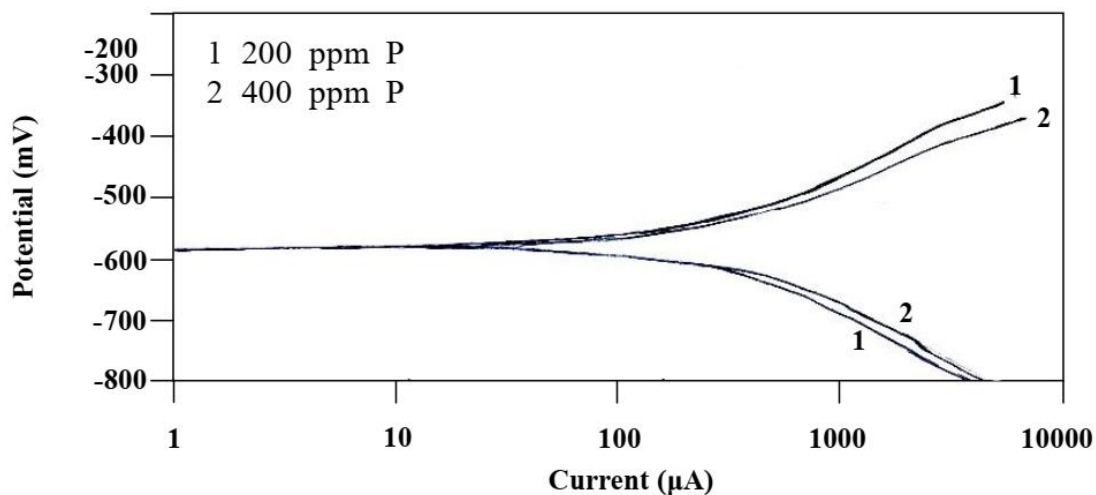


Fig. (11) Polarization curves of carbon steel in 0.3 wt% HCl

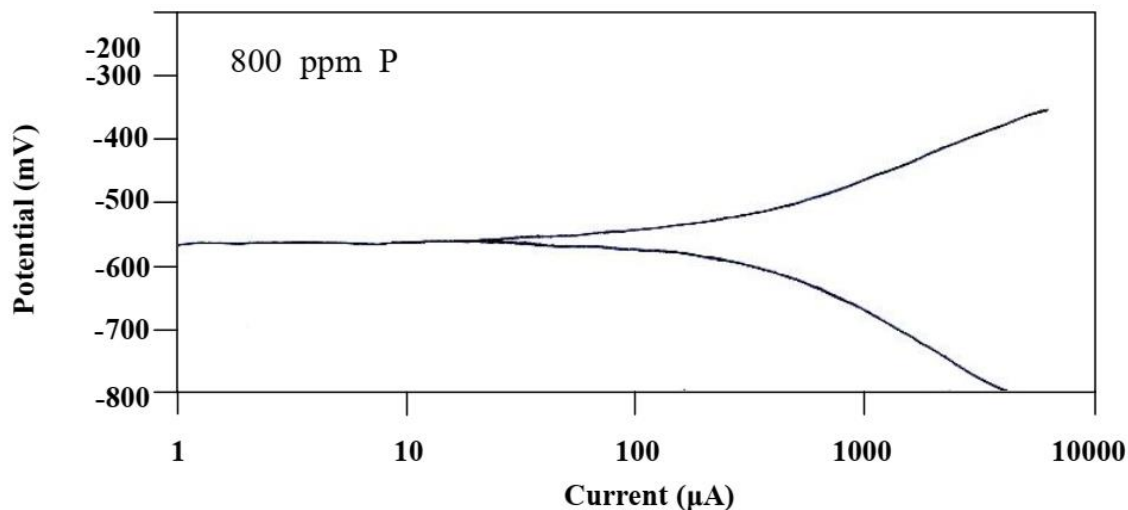


Fig. (12) Polarization curves of carbon steel in 0.3 wt% HCl

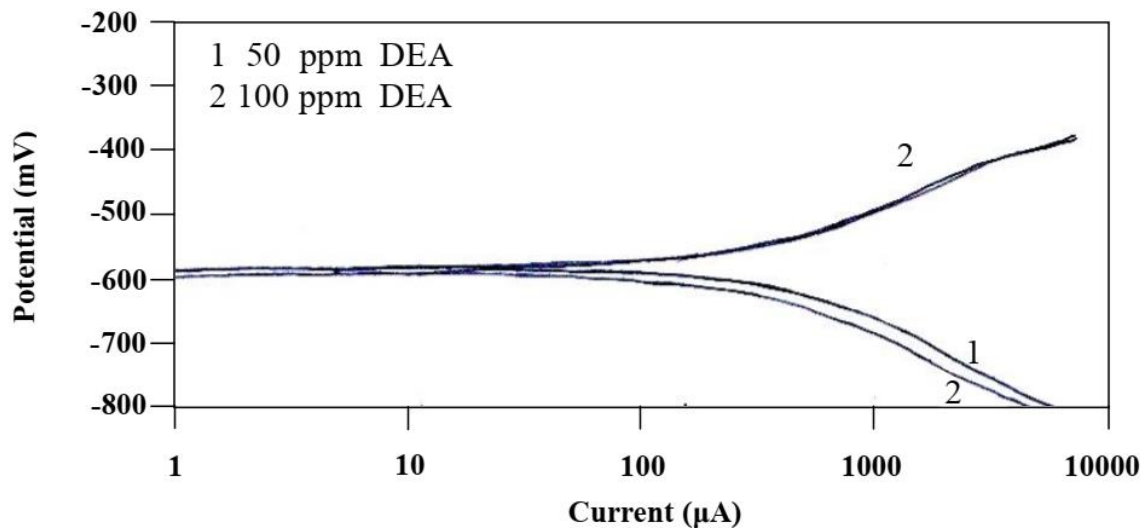


Fig. (13) Polarization curves of carbon steel in 0.3 wt% HCl

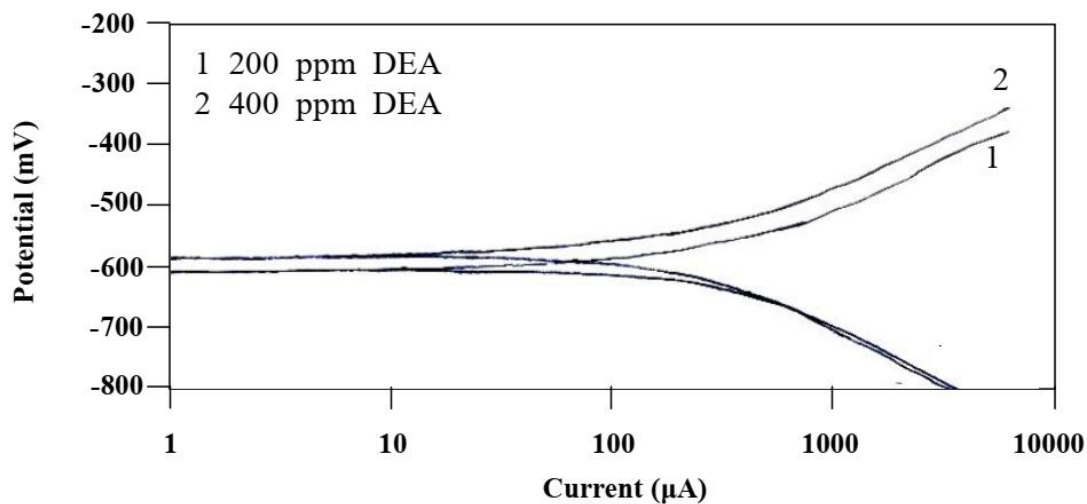


Fig. (14) Polarization curves of carbon steel in 0.3 wt% HCl

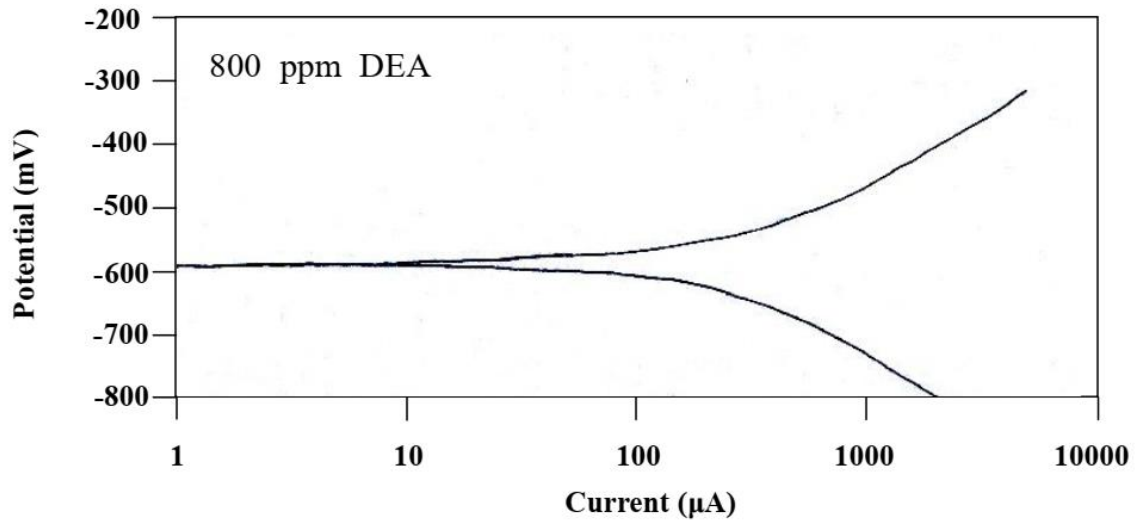


Fig. (15) Polarization curves of carbon steel in 0.3 wt% HCl

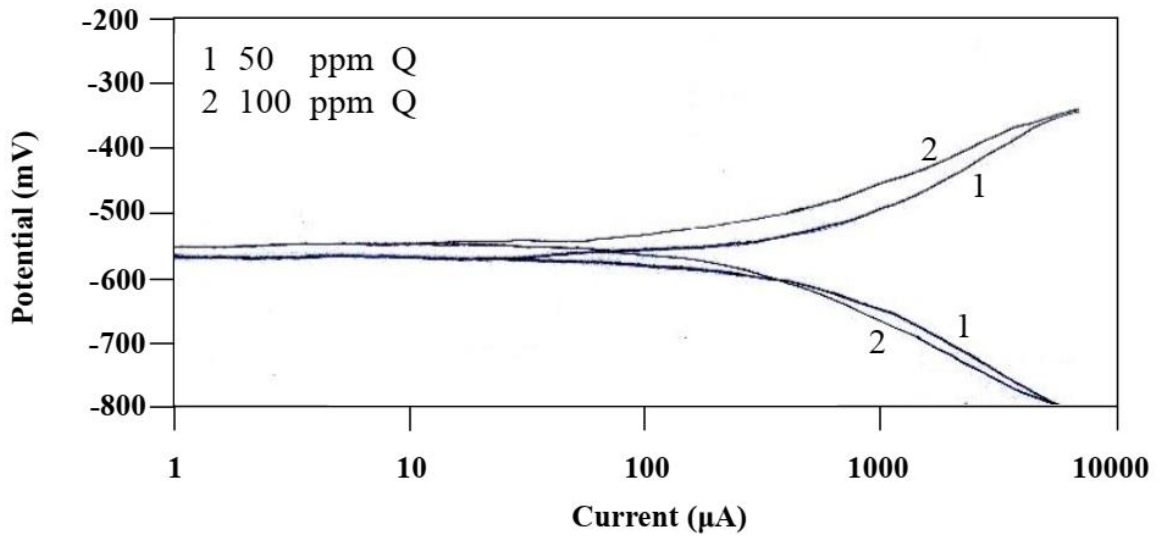


Fig. (16) Polarization curves of carbon steel in 0.3 wt% HCl

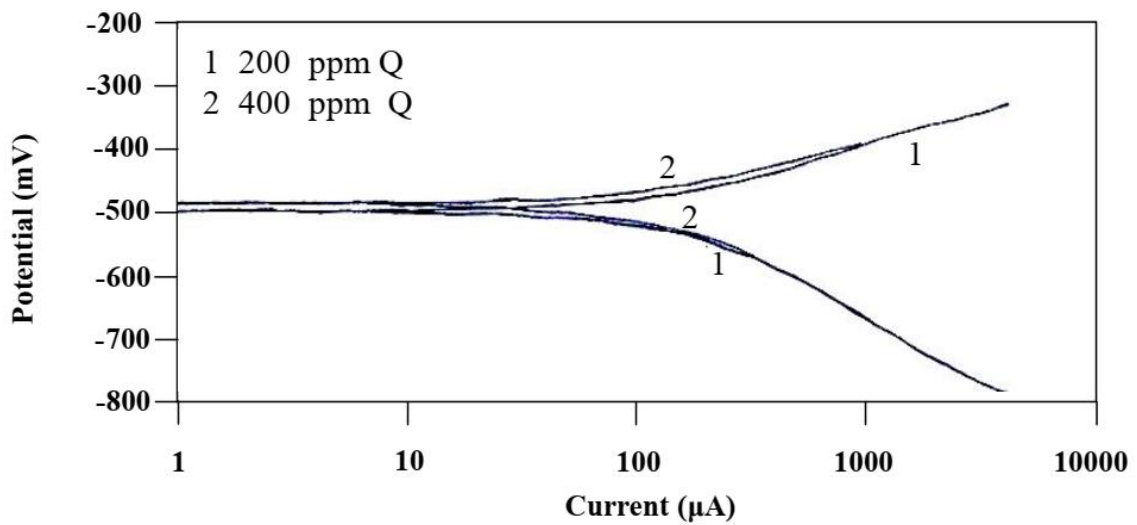


Fig. (17) Polarization curves of carbon steel in 0.3 wt% HCl

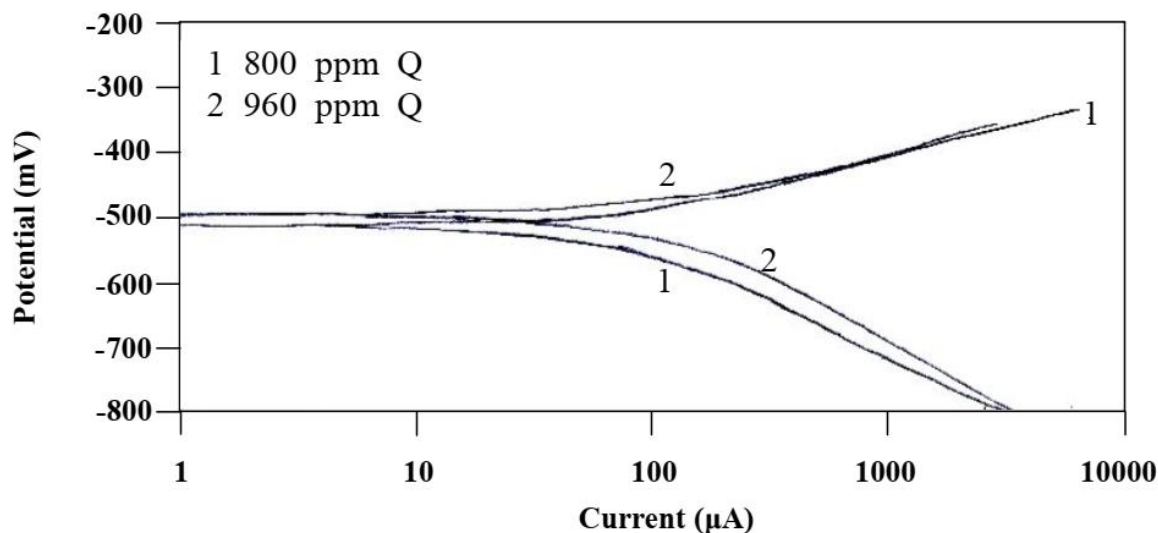


Fig. (18) Polarization curves of carbon steel in 0.3 wt% HCl

Table (1) Corrosion current (μA) of carbon steel in various inhibitors and HCl concentrations

	0 ppm	50ppm	100ppm	200ppm	400ppm	800ppm	960ppm
3 % HCl							
Thiourea	53.9184	15.96	14.1	8.77	10.73	11.93	
Quinoline		16.33	20.282	24.959	22.48	16.78	
0.3 % HCl							
Thiourea	44.412	23.451	13.254	14.231	9.187	7.43	
Quinoline		41.565	23.264	29.249	19.141	12.606	10.784
Pyridine		23.736	34.715	24.202	29.501	20.387	
Diethylamine		26.093	21.039	26.752	17.14	19.537	

Table (2) Inhibition efficiency percent of carbon steel in various inhibitors and HCl concentrations

	50ppm	100ppm	200ppm	400ppm	800ppm	960ppm
3 % HCl						
Thiourea	70.07	73.8	83.7	80.1	77.87	
Quinoline	69.7	62.4	53.7	58.3	68.87	
0.3 % HCl						
Thiourea	47.2	70.15	68	79.3	83.26	
Quinoline	6.41	47.61	45.98	56.9	71.62	75.72
Pyridine	46.5	21.83	45.5	33.6	54.1	
Diethylamine	41.25	52.62	39.76	61.9	56	

Table (3) Corrosion potential (mv) of carbon steel in various inhibitors and HCl concentrations

	0 ppm	50ppm	100ppm	200ppm	400ppm	800ppm	960ppm
3 % HCl							
Thiourea	-570	-575	-565	-560	-555	-550	
Quinoline		-560	-550	-535	-550	-535	
0.3 % HCl							
Thiourea	-620	-610	-610	-605	-595	-590	
Quinoline		-600	-590	-575	-565	-575	-560
Pyridine		-610	-610	-605	-600	-595	
Diethylamine		-605	-610	-610	-600	-600	

Table (4) Anodic Tafel constants of carbon steel in various inhibitors and HCl concentrations

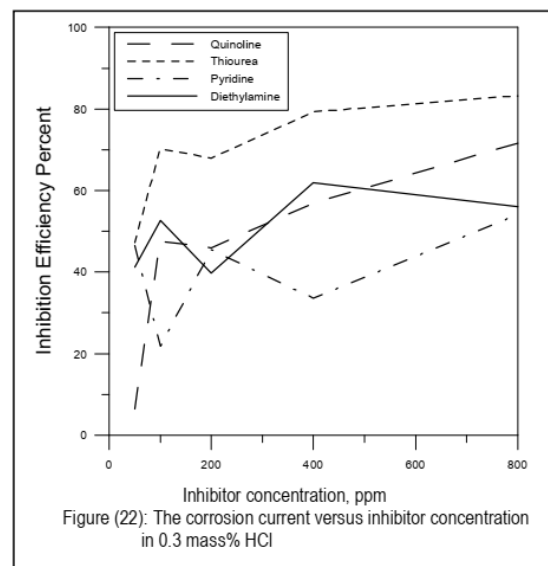
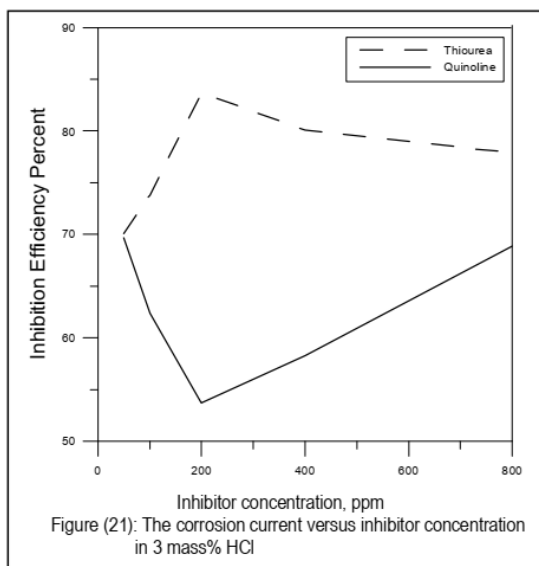
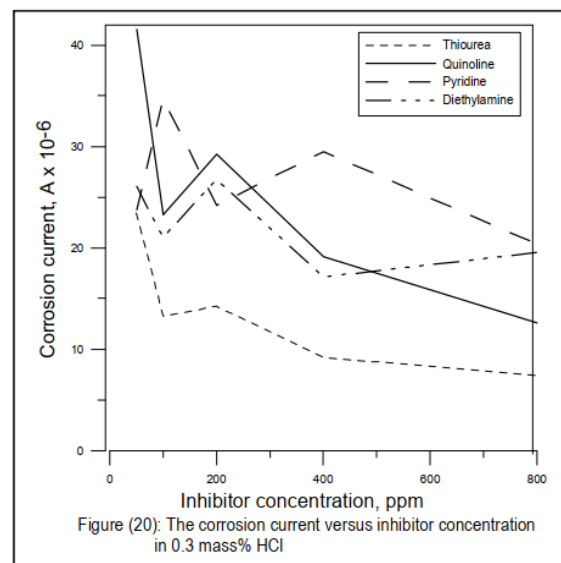
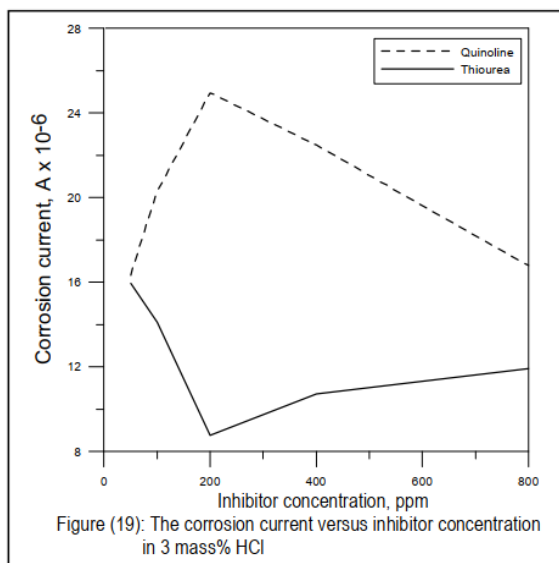
	0 ppm	50ppm	100ppm	200ppm	400ppm	800ppm	960ppm
3 % HCl							
Thiourea	0.05	0.183	0.19	0.25	0.25	0.21	
Quinoline		0.125	0.12	0.129	0.1	0.159	
0.3 % HCl							
Thiourea	0.1	0.196	0.296	0.43	0.53	0.456	
Quinoline		0.118	0.2	0.187	0.106	0.16	0.26
Pyridine		0.182	0.139	0.176	0.152	0.147	
Diethylamine		0.125	0.122	0.143	0.176	0.216	

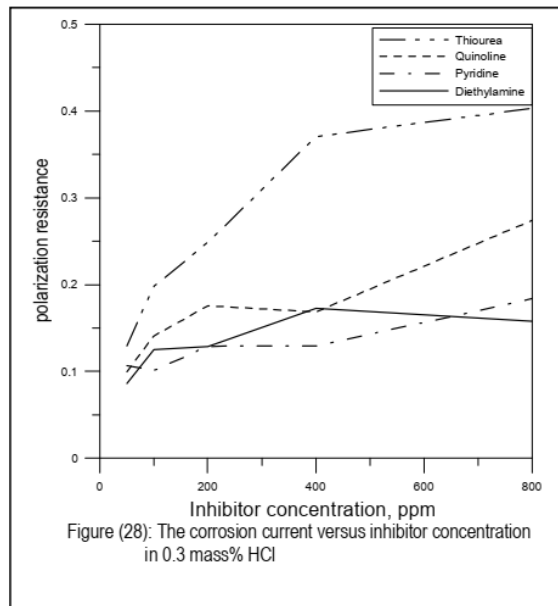
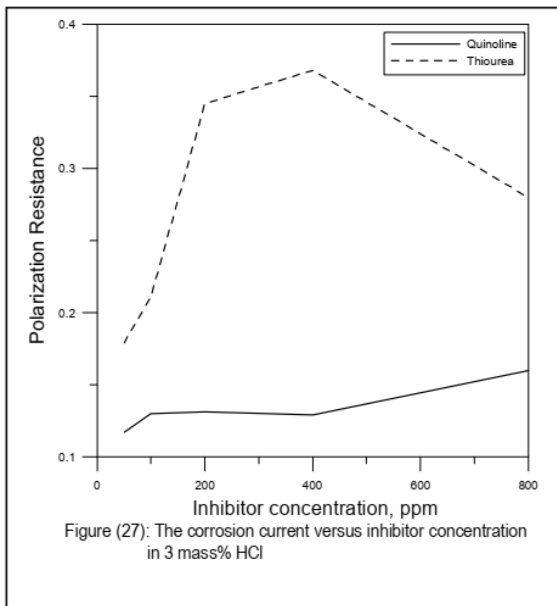
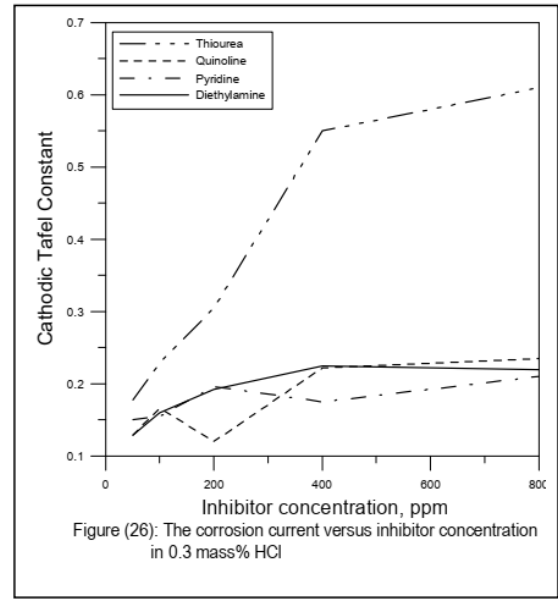
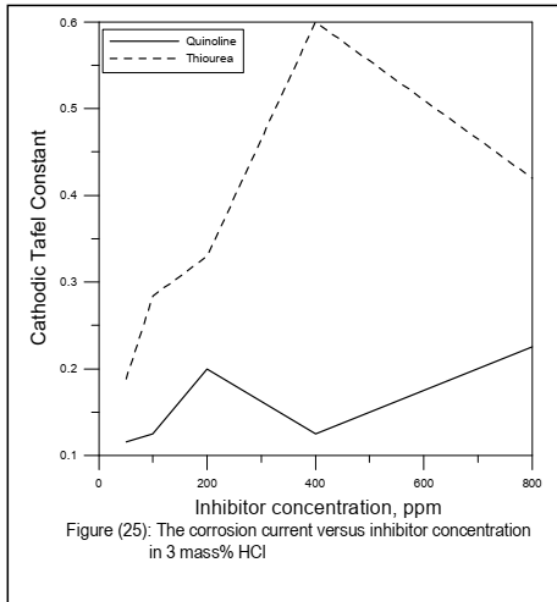
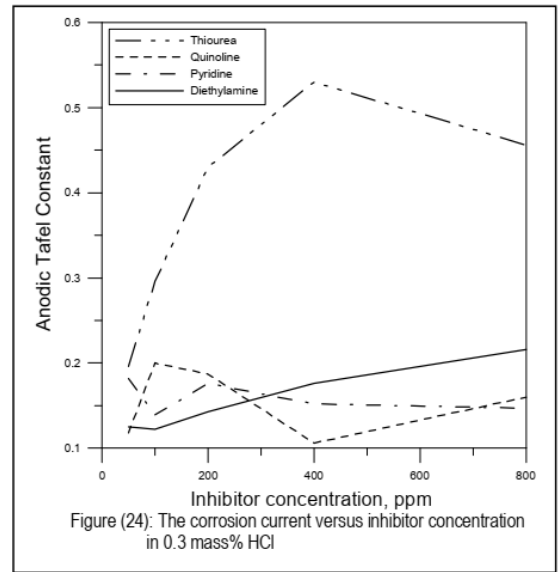
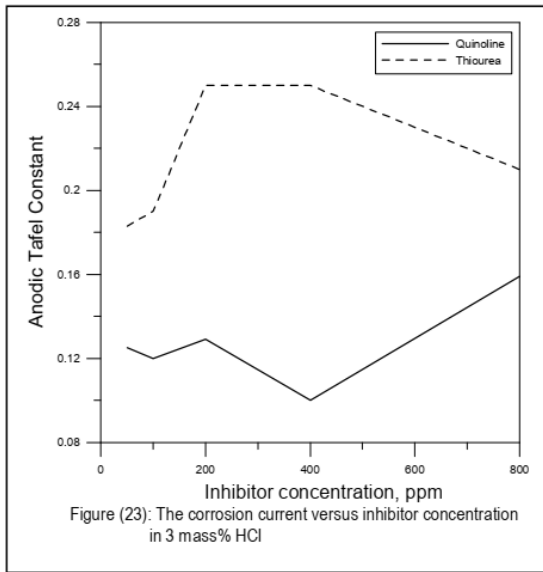
Table (5) Cathodic Tafel constants of carbon steel in various inhibitors and HCl concentrations

	0 ppm	50ppm	100ppm	200ppm	400ppm	800ppm	960ppm
3 % HCl							
Thiourea	0.068	0.188	0.284	0.33	0.6	0.42	
Quinoline		0.1154	0.125	0.2	0.125	0.225	
0.3 % HCl							
Thiourea	0.06	0.178	0.229	0.305	0.55	0.61	
Quinoline		0.129	0.166	0.12	0.222	0.235	0.2
Pyridine		0.15	0.155	0.196	0.175	0.21	
Diethylamine		0.129	0.16	0.192	0.225	0.22	

Table (6) Polarization resistance of carbon steel in various inhibitors and HCl concentrations

	0 ppm	50ppm	100ppm	200ppm	400ppm	800ppm	960ppm
3 % HCl							
Thiourea	0.55343	0.1792	0.2113	0.345	0.3679	0.28	
Quinoline		0.1170	0.13038	0.13083	0.12868	0.15948	
0.3 % HCl							
Thiourea	0.059624	0.1296	0.19796	0.2486	0.3706	0.403	
Quinoline		0.09959	0.1407	0.1757	0.1685	0.2739	0.3249
Pyridine		0.1073	0.1007	0.1288	0.1293	0.1837	
Diethylamine		0.08597	0.1248	0.1288	0.1725	0.15772	





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