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AQUEOUS EXTRACT OF LEAVES OF ZIZIPHUS AS AN ECO-FRIENDLY INHIBITOR FOR THE CORROSION OF MILD STEEL IN POTABLE WATER

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ABSTRACT

The inhibitive effect of the aqueous extract of Ziziphus leaves on the corrosion of mild steel in drinking water have been investigated by using an electrochemical polarization and weight loss method. The results obtained shows, that, the extract of leaves of Ziziphus could work as an effective inhibitors against the corrosion of steel in drinking water network. The inhibition percentage increases with the increasing of the leaves of Ziziphus concentration at 30°C. The inhibitor percentage efficiency above (98 %) was attained at extract of Ziziphus leaves concentration (1% v/v). The inhibition efficiencies of the extract of leaves of Ziziphus obtained from weight loss method and polarization measurements were in good agreement. electrochemical polarization studies clearly reveal that the extract of leaves of Ziziphus behaves predominantly as an anodic inhibitor. The study also shows that the inhibition efficiency was insignificantly affected by the temperature rise of the medium.

Key words: corrosion; inhibition; organic inhibitor; extract of leaves of Ziziphus.

المستخلص المائي لورق السدر كمثبط ودي للبيئة لتآكل الفولاذ في الماء الصالح للشرب

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الخلاصة

تم دراسة التأثير التثبيطي للمستخلص المائي لورق نبات السدر على تآكل الفولاذ في المياه الصالحة للشرب باستخدام قياسات الاستقطاب الكهروكيميائي وطريقة فقدان الوزن . بينت النتائج ان المستخلص يمكن ان يعمل بشكل فاعل كمثبط لتآكل الفولاذ في شبكات مياه الشرب . كما وجد ان نسبة التثبيط تزداد مع زيادة تركيز المثبط المستخدم عند درجة حرارة (30°م) حيث ان نسبة التثبيط بلغت اكثر من (98%) عند تركيز من المستخلص مقداره (1%) كنسبة حجمية .ان كفاءة التثبيط المحسوبة من كلا الطريقتين المستخدمتين في البحث كانتا متوافقتين ،كما ان دراسة سلوك الاستقطاب لمستخلص ورق السدر بين انه يمتلك سلوك المثبط الانودي بالدرجة الاولى ، كذلك بينت الدراسة ان كفاءة التثبيط تأثرت بشكل لايذكر بارتفاع درجة حرارة الوسط .

1- INTRODUCTION

Corrosion of metals in wet environments is a serious problem in many industries and civil services such as water distribution systems. Potable water distribution systems are usually durable in average water compositions but their integrity can be compromised when exposed to water compositions containing aggressive chemicals such as chloride, sulfate and the like. Corrosion reduces the service life of the system and changes the quality of water conveyed through these distribution systems [Guidelines 1994,Tebbut 1993and Lohrengal 2004].

A number of options exist for mitigating corrosion of potable water distribution systems and use of corrosion inhibitors is among the best options. However, the choice of a proper corrosion inhibitor to be applied in these systems is limited due to the potable criteria of water. Inhibitors to be used in potable water systems ought to be safe to human and friendly to the environment. Currently, there is public criticism of synthesized chemicals that are used in water systems and hence, the search for inhibitors derived from natural products seems to be an interesting option [Farooqi *et al.* 1997, Mukherjee *et al.* 1997].

Nowadays, natural products are viewed as incredibly rich sources of naturally synthesized chemicals for use in most applications. Some of the advantages that natural chemicals have over other types of chemicals include being environmentally acceptable and is a readily available resource. Some investigations have been reported using such economic natural resources [Abdel-Gaber *et al.* 2006].

Most organic inhibitors contain at least one polar group with an atom of nitrogen, oxygen or sulphur through which they can be adsorbed usually by chemisorption, into the metal surface and suppress metal dissolution and reduction reactions. In most cases, it appears that adsorption inhibitors affect both the anodic and cathodic processes, although in many cases the effect is unequal. The classical examples of adsorption inhibitors are the aliphatic and aromatic amines, thiourea and substituted thiourea and various aldehydes. Chemisorption usually occurs through donation of electrons from a nitrogen, sulphur or oxygen functional atom to the metal surface. Aliphatic organic amines adsorb via the $-NH_2$ group which contains a pair of unshared electrons which are available for donation to the metal surface. In organic compounds differing in the functional donor atom, the order of corrosion inhibition is usually $S > N > O$ which is reverse order of electronegativity.[Al-Malki 2007, Jamil *et al.* 2004]

The inhibition efficiency of surface active compounds appeared both from chemical and electrochemical factors. The chemical factors influenced the formation of the protective surface layer in the interface metal – corrosive medium. The electrochemical factors influenced the equilibrium potential on the metal surface and consequently, directed the charge transfer processes. Physical adsorption may be due to electrostatic attractive forces between ionic charges or dipoles on the adsorbed species and the electric charge on the metal at the metal-solution interface.[Hazzazi 2007]

The use of natural products as corrosion inhibitors for metallic protection can be traced to the last half of the nineteenth century, recently started to study the application of extracts of some common plant as corrosion inhibitors as Lawsonia extract, natural honey, opuntia extract, Ficus extract and Jojoba oil for steel in aqueous and acidic media. These extracts contain different hydroxy organic compounds, e.g. tannins, pectin, flavoniods, anthraquinones, steroids, saponins and coumarins in addition to other nitrogen containing compounds.[Buchweishaija and Mhinzi 2008]

In this work of natural corrosion inhibitor materials, aqueous extract of leaves of Ziziphus are introduced as a safe and cheap corrosion inhibitor for commercial grade metals used in potable water systems . Structurally, these leaves of Ziziphus consist of surface- active units such as amino ($-NH_2$), hydroxyl (-OH) and carboxyl (-COOH) [Sudhersan and Hessian 2003 , Sudhersan *et al.* 2001], which suggest them to be electrochemically active and they can therefore interact with metallic surfaces through these units and inhibit corrosion .

This work presents a study of the aqueous extract of leaves of Ziziphus as an inhibitor for mild steel corrosion in drinking water systems and discusses the effect of temperature on its inhibition mechanism.

2- EXPERIMENTAL

The working electrode employed in this work were made from the parent metallic pipe material , this steel had the chemical composition shown in **Table 1** .

For weight loss measurements, corrosion inhibition tests were performed using cylindrical specimens (d=1cm , h=0.2cm) ,the specimens were polished with an emery papers(400,800 and1000), then degreased with an acetone and washed with distilled water , then dried and kept in a desiccator . The weight loss ($g.cm^{-2}$) was determined at different immersion times at (30°C) by weighing the cleaned samples before and after immersion in (100 ml) of the corrosive solution in the absence and presence of various concentrations of the inhibitor . After the time elapsed the cleaning procedure consisted of wiping the samples with a paper tissue, polishing lightly with emery paper(400,800 and1000), washing with distilled water and acetone .

For electrochemical measurements, the investigated materials were cut as cylindrical rods, welded with Cu-wire for electrical connection and mounted into polyester hold of appropriate diameter to offer an active flat disc shaped surface of (0.78 cm^2) geometric area, to contact the test solution . Prior to each experiment, the surface pretreatment of the working electrode was performed by mechanical polishing of the electrode surface with successive grades of emery papers down to 1200 grit up to a mirror finish. The electrode was then, rinsed with acetone, distilled water, and finally dipped in the electrolytic cell. A conventional electrochemical cell was used containing three electrodes (working, platinum and reference electrode). The reference electrode was a normal calomel one used directly in contact with the working solution. The current–potential curves were recorded by changing the electrode potential automatically by (10 mV/min) .

The corrosive medium is tap water , the corrosion inhibitor was monitored in the concentration range from(0.25 to 1 v/v) at 30° C. For each experiment fresh water solutions as well as freshly polished metallic samples were used . The effect of temperature on the performance of the optimal concentration of a extract of leaves of Ziziphus was also studied at 30, 50 and 80°C.

3- RESULT AND DISCUSSION

3-1- Polarization Measurements:

It is well established that polarization curves can help to understand how a certain corrosion inhibitor works. Inhibitors can modify the anodic process, the cathodic process or both leading to a decreased rate of the global corrosion process. **Figs. 1,2,3,4 and 5** shows polarization curves for mild steel carried in potable water in the absence and presence of varied concentrations of the extract of leaves of Ziziphus respectively .

The polarization curves consist of two regions , the first the cathodic region where the reduction can occur accordance with :

$$O_2 + 2H_2O + 4e = 4OH^- \quad (1)$$

The second the anodic region where the dissolution of mild steel can occur according to the following reaction :

$$Fe = Fe^{2+} + 2e \quad (2)$$

In these figures, two important trends are evident. Firstly, that the extract of leaves of Ziziphus is found to block the electrochemical processes taking place on the steel undergoing corrosion in water. It reduces both the rate of cathodic and anodic reactions by reducing the current densities on both sides of the polarization curves in the potential region studied and hence reduces the corrosion rate. Secondly, it shifts the open corrosion potentials towards less negative values with reference to the blank. These factors suggest that inhibitor acts as anodic type corrosion inhibitor [Eddy *et al.*2008 , Riggs 1983].

The data obtained from polarization curves by Tafel extrapolations are presented in **Table 2**. These include corrosion potential ($E_{corr.}$) and corrosion current density ($i_{corr.}$) at varied extract of leaves of Ziziphus concentrations. It can be seen from (table 2) that the corrosion inhibition increase tremendously as the inhibitor concentrations increases. The corrosion potential becomes less negative as the concentration increases. However, there is a slight variation in both anodic and cathodic Tafel slopes indicating that the inhibiting action takes place by simple blocking of the available cathodic and anodic sites on the metal surface [Hazzazi 2007].

The table also gives the percentage Inhibitor Efficiency for the extract of leaves of Ziziphus applied. The (% IE) was calculated using the relation [Eddy *et al.*2008]:

$$\%IE = (1 - \frac{i_{corr,i}}{i_{corr,w}}) \times 100 \quad (3)$$

where ($i_{corr.,i}$) and ($i_{corr.,w}$) are the corrosion current with and without inhibitor respectively, and we note that the efficiency of inhibition about (99 %) with (1% v/v) of the inhibitor.

3-2- Weight Loss Measurements :

The variation of the weight loss ($g.cm^{-2}$) of mild steel in potable water with and without the addition of different concentrations of inhibitor with the immersion time has been studied at (30° C) . The results is shown in **Fig. 6** , and we can seen from the figure the weight loss decrease with increasing the concentration of inhibitor. Thus, the corrosion rate of mild steel decreased with the increase of the inhibitor concentration. This trend may result from the fact that adsorption amount and the coverage of the inhibitor on the electrode surface increases with increasing concentration. Thus, the electrode surface is efficiently separated from the medium.

The inhibition efficiencies (IE%) of the additives **(Table 3)** are calculated from the total weight loss by the equation [Hazzazi 2007]:

$$IE\% = (1 - \frac{R_{corr,i}}{R_{corr,w}}) \times 100 \quad (4)$$

where ($R_{corr.,i}$) and ($R_{corr.,w}$) are the corrosion rate with and without inhibitor respectively , it follows from the data of (table 3) that the corrosion rate depending on concentration of inhibitor and the increasing the additives concentration is accompanied by an increase in the inhibition efficiency. The inhibition efficiencies obtained by weight loss studies are in agreement with those obtained employing electrochemical polarization technique.

3-3- Effect Of Temperature :

In order to further understand on the extract of leaves of Ziziphus corrosion inhibition properties, the influence of temperatures on its performance was also investigated. Temperatures up to (80° C) were studied, using an optimal concentration of the extract of leaves of Ziziphus (1% v/v). **Fig. 7 and 8** show electrochemical polarization plots for steel in drinking water with and without inhibitor at (30, 50 and 80° C) respectively. The measurements were performed after (8 hours) of immersion in the media. The inhibitor efficiencies calculated from these results are shown in **Table 4** together with the extrapolated corrosion current densities and corrosion potentials. The table shows that the percentage inhibitor efficiencies are nearly constant in the temperature range studied and hence change in temperature was found to have insignificant influence on the performance of the extract of leaves of Ziziphus. This shows that the extract of leaves of Ziziphus is temperature insensitive.

It has been reported by a number of researchers that the logarithm of corrosion rate is a linear function with the reciprocal of the absolute temperature (Arrhenius equation): [Behrsing 2003]

$$i_{corr} = K \exp\left(\frac{-E_a}{RT}\right) \qquad (5)$$

where *Ea* is the apparent activation energy and *K* is a constant. The activation energies for the mild steel dissolution process in the absence and presence of (1% v/v) inhibitor were evaluated from the linear square fit of (ln i_{corr}) vs (1000/T) as shown in **Fig. 9** .The plots have slopes of (-4.1155) and (-2.4516) for without and with inhibitor, respectively. Similarly, the intercepts (ln i_{corr}) are (15.362) and (5.450) for without and with inhibitor, respectively. Because of the reduced parameters when inhibitor is used, corrosion current which reflects the rate of corrosion, increases less rapidly with increasing temperature for situations with inhibitor than without in the temperature range used in these experiments. This indicates that the temperature does not affect the adsorption of the extract of leaves of Ziziphus.

From the Arrhenius plots above, the apparent activation energies were (34.2 kJ/mol) and (20.4 kJ/mol) for the blank and inhibited, respectively. From these results, it is evident that addition of inhibitor reduces the value of the apparent activation energy. This reduction of the activation energy in the presence of extract of leaves of Ziziphus may be attributed to the chemisorption [Clarke *et al.*2002 , Behrsing *et al.* 2003].

4- CONCULUSION

In conclusion, the extract of leaves of Ziziphus, a natural product from Ziziphus, was found to inhibit efficiently the corrosion of mild steel exposed in potable water. The study also shows that the inhibition efficiency was insignificantly affected by the temperature rise. Electrochemical polarization studies clearly reveal that the aqueous extract of leaves of Ziziphus behaves predominantly as an anodic inhibitor.

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Table 1. chemical composition for the steel specimens used in the study .

Fe%	Mo%	Ni%	Si%	Mn%	Cr%	C%
Balance	0.1	0.01	0.25	1.3	0.02	0.07

Table 2. Electrochemical parameters for the corrosion of mild steel exposed in potable water with different concentrations inhibitor and the corresponding corrosion inhibition efficiency at T = 30° C .

C_{inh} (v/v %)	$-E_{corr}$ (mV)	i_{corr} ($\mu A/cm^2$)	b_c (mV/dec)	b_a (mV/dec)	IE (%)
blank	415	6.40	-49	50	—
0.25	405	1.59	-36	36	75.2
0.50	320	0.28	-39	49	95.6
0.75	240	0.09	-33	44	98.5
1.00	230	0.07	-34	37	98.9

Table 3. Corrosion rate for the mild steel exposed in potable water with different concentrations inhibitor and the corresponding corrosion inhibition efficiency at T = 30° C .

C_{inh} (v/v %)	C.R ($mg/cm^2.hr$)	IE (%)
0	0.0275	—
0.25	0.0077	72
0.50	0.0014	94.9
0.75	0.0004	98.5
1.00	0.00033	98.8

Table 4. Electrochemical parameters for the corrosion of mild steel exposed in potable water with different concentrations inhibitor and the corresponding corrosion inhibition efficiency at T = 30° C .

Temp. (°C)	Blank		(1 % v/v) Inhibitor		
	$-E_{corr}$ (mV)	i_{corr} ($\mu A/cm^2$)	E_{corr} (mV)	i_{corr} ($\mu A/cm^2$)	IE (%)
30	415	6.40	-230	0.07	98.9
50	615	19.98	-180	0.12	98.3
80	605	44.65	-190	0.24	98.4

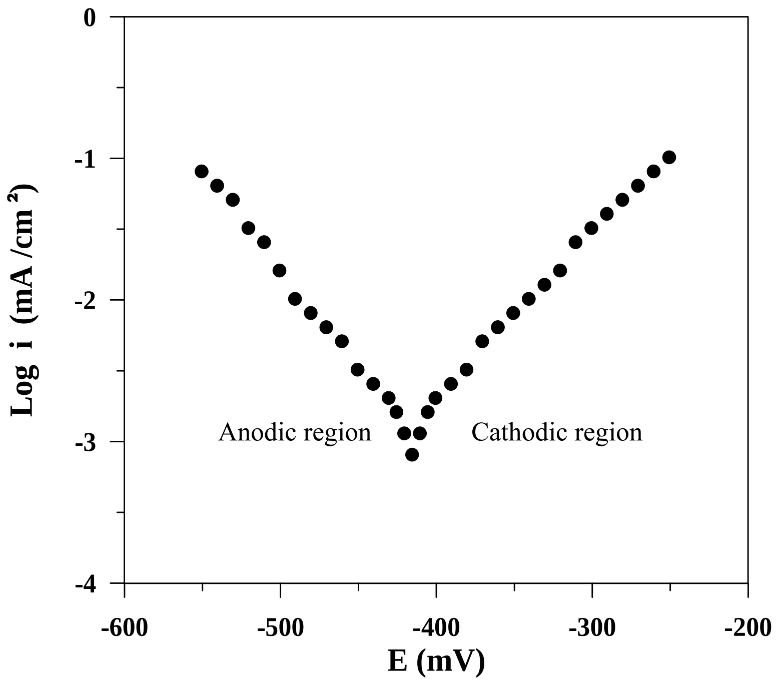

Fig.(1): Polarization curves for mild steel in potable water at T = 30°C.

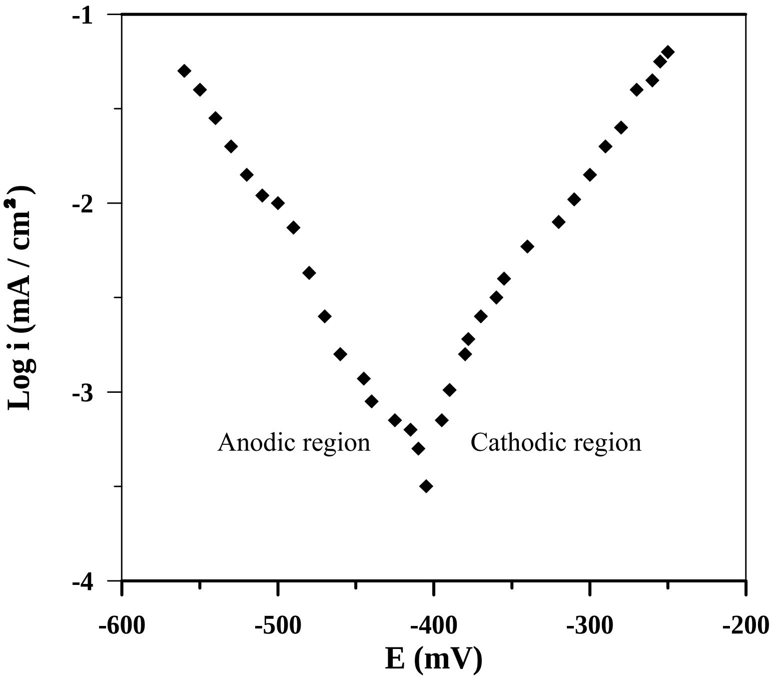

Fig.(2): Polarization curves for mild steel in potable water containing concentration (0.25 % v/v) of the inhibitor at T = 30°C.

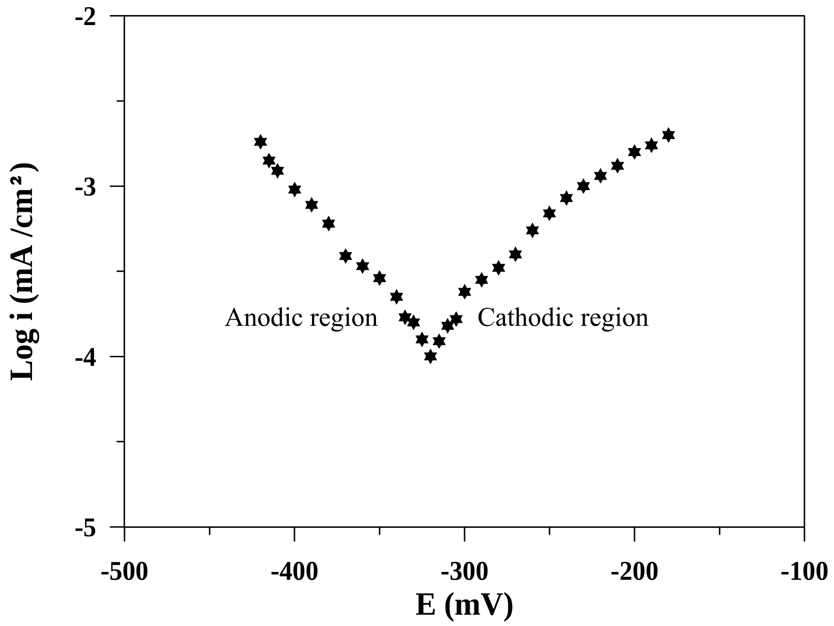

Fig.(3): Polarization curves for mild steel in potable water containing concentration (0.50 % v/v) of the inhibitor at T = 30°C.

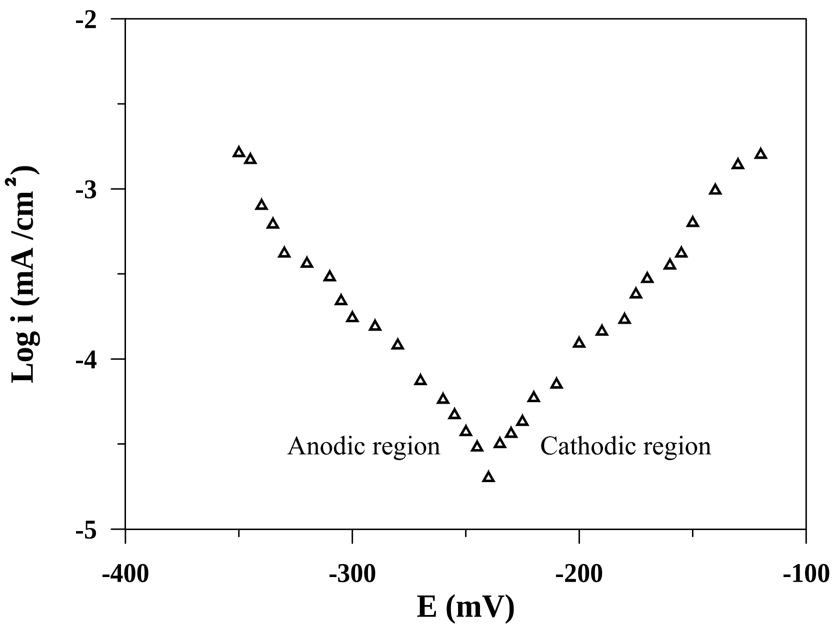

Fig.(4): Polarization curves for mild steel in potable water containing concentration (0.75 % v/v) of the inhibitor at T = 30°C.

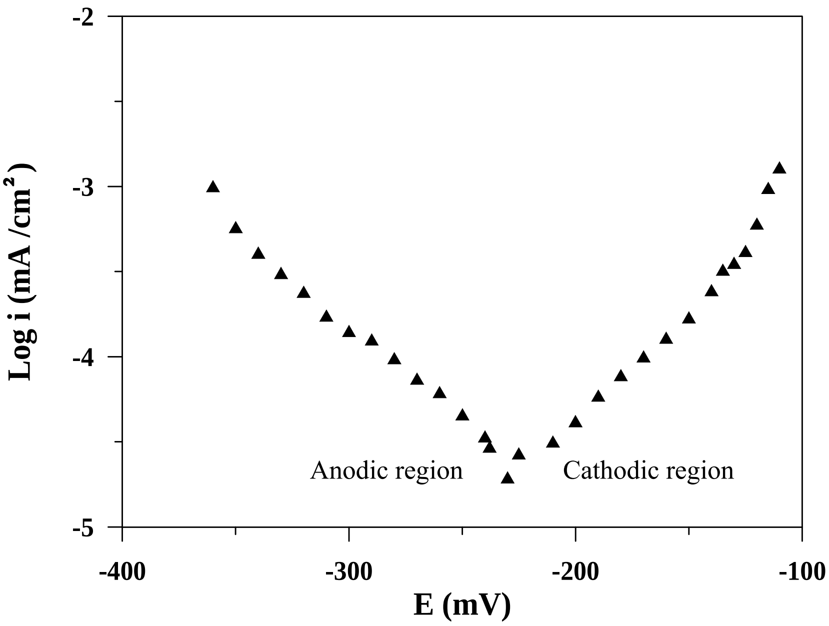

Fig.(5): Polarization curves for mild steel in potable water containing concentration (1 % v/v) of the inhibitor at T = 30°C.

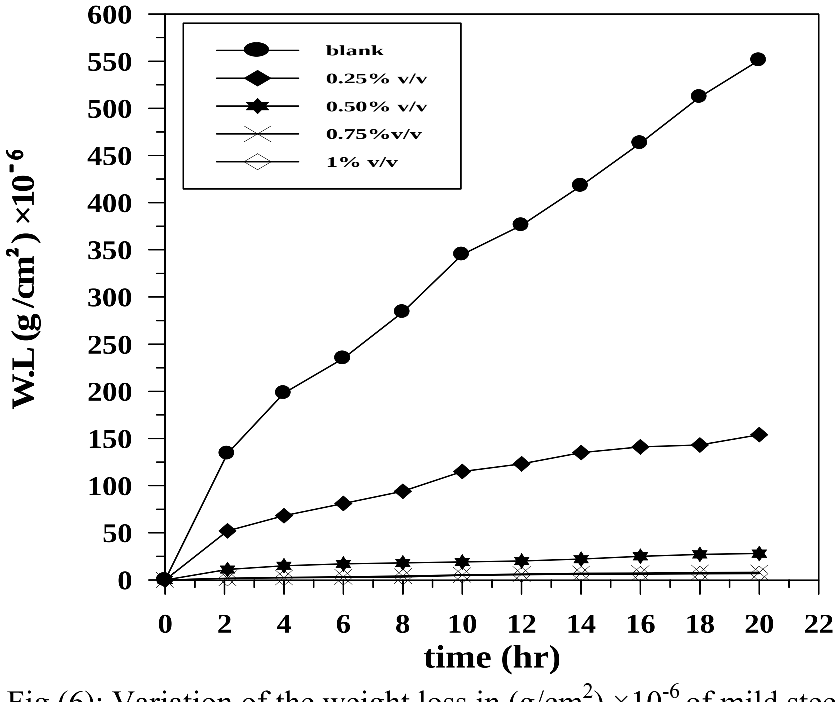

Fig.(6): Variation of the weight loss in (g/cm^2) $\times 10^{-6}$ of mild steel in potable water with and without the addition of different concentrations inhibitor with the immersion time at 30°C.

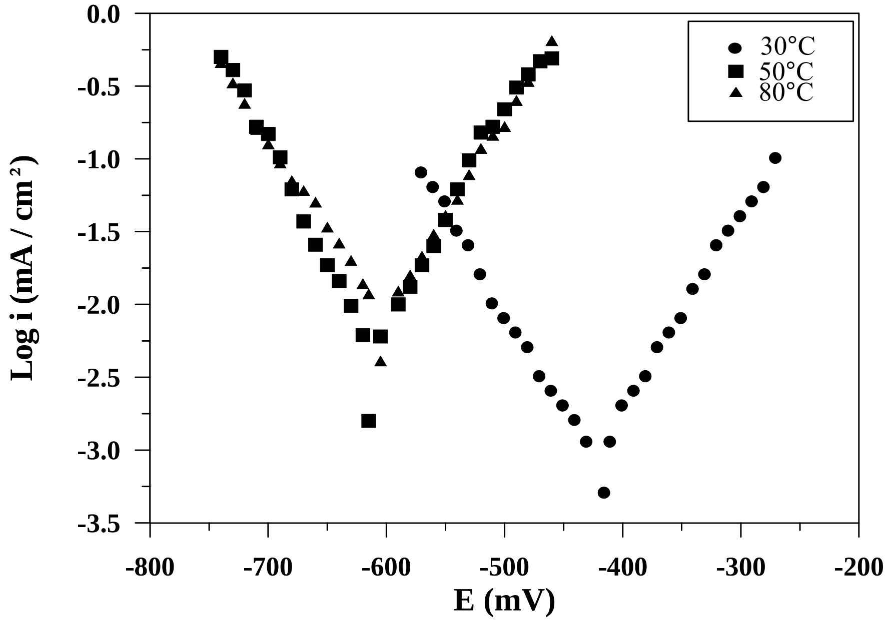

Fig.(7): Effect of temperature on polarization curves for mild steel in potable water .

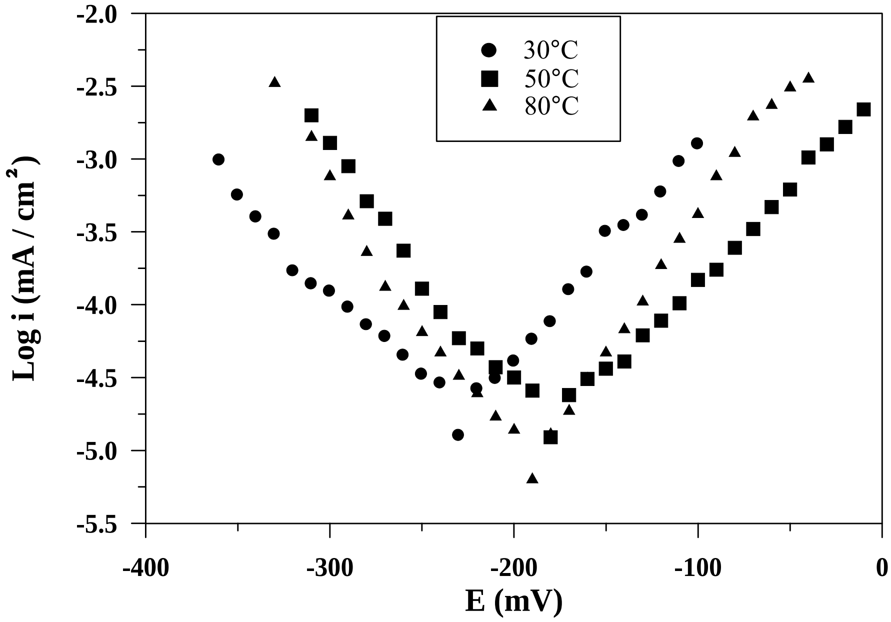

Fig.(8): Effect of temperature on polarization curves for mild steel in potable water containing concentration (1 % v/v) of the inhibitor.

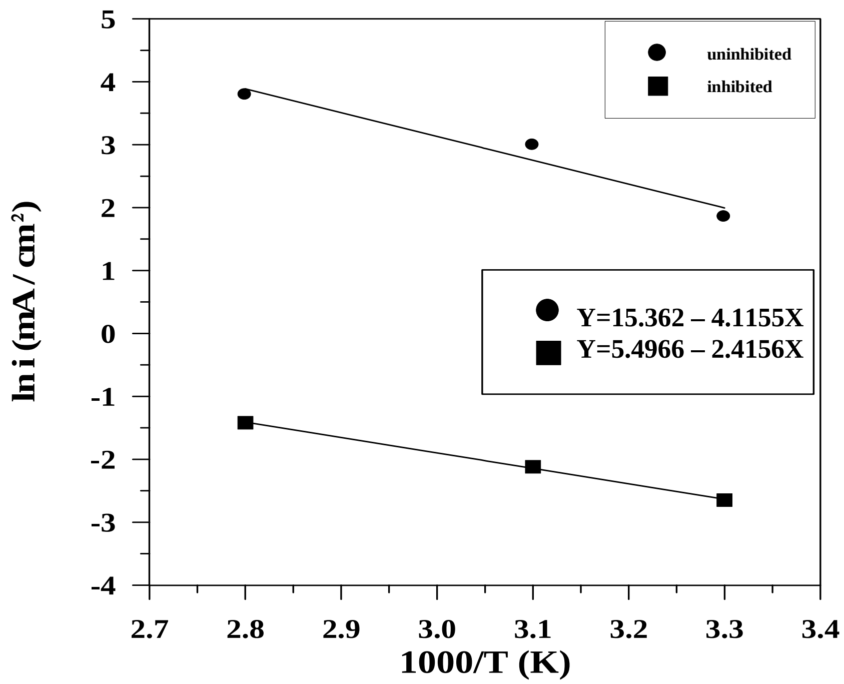

Fig.(9): Arrhenius plots for uninhibited and inhibited mild steel in potable water .