Inhibition of acidic corrosion of iron by some Carrageenan compounds

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ABSTRACT

The corrosion inhibition of some sulfated water soluble natural polymer (carrageenan) compounds on the corrosion of iron in 1M HCl was studied using weight loss and galvanostatic polarization measurements. The percentage inhibition efficiency was found to increase with increasing concentration of inhibitor and with decreasing temperature. The inhibitive action of these compounds was discussed in terms of blocking the electrode surface by adsorption of the molecules. The adsorption process follows a Langmuir adsorption isotherm. The effect of temperature on the rate of corrosion in the absence and presence of these compounds was also, studied. Some activation thermodynamic parameters were calculated.

Keywords: Carrageenans, inhibitors, iron corrosion, adsorption.

INTRODUCTION

Iron is the most used of all the metals in several fields of industry. Iron and similar metals can be exposed to corrosion in connection with environmental conditions. The corrosion rate varies subject to structure of ions and molecules, kind of ion, concentration of ion, kind of solution and kind of materials[1,2]. Especially in environments containing Cl^{-} ions, corrosion of metals is unavoidable, as Cl^{-} ion is an active one, it forces oxide formation on metal surface. This increases the corrosion rate of metal[2].

Organic additives are commonly used to reduce the corrosion of iron in acidic medium[3-8]. The inhibition efficiency of such compounds may function by adsorption on the iron surface, the adsorption process depends mainly on certain physico-chemical properties of the molecules such as, functional groups, steric factors, aromaticity, electron density at the donor atoms, π- orbital character of donating electron[9,10] and also on the electronic structure of the molecules. The inhibition efficiency increases with increasing the number of atomic rings[11,12].
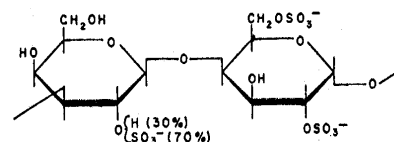
The aim of the present work is to study the inhibition action of some naturally occurring compounds known as carrageenans which produced from certain species of sea weeds to inhibit the corrosion of iron electrode in 1M HCl
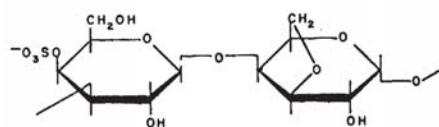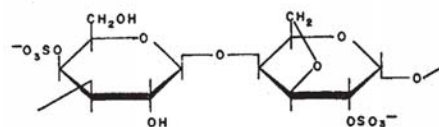
Fig. -1: Chemical structure of Carrageenan compounds

solution using weight loss and galvanostatic polarization technique. The effect of temperature on the dissolution of iron electrode in 1M HCl containing 500 ppm of the inhibitor used was also studied and some thermodynamic parameters were computed.

EXPERIMENTAL

The test electrode was made of iron obtained from Saudi iron and steel company and having the following chemical compositions (%) (C, 0.052, Mn 0.189, S 0.011, P 0.008, Si 0.011, Al 0.039, N 0.001, Cr 0.0128, Cu 0.04, Mo 0.024, Ni 0.0293 and remainder is Fe).

Iron sheets with dimension 2x2x0.1 cm were used for weight loss measurements. For galvanostatic polarization technique a cylindrical rod embedded in araldite with exposed surface area of 0.5 cm^2 was employed. Prior to each experiment, the surface of iron specimens were mechanically polished with different grades of emery paper, degreased with acetone and rinsed by distilled water.

For weight loss measurements, the cleaned Fe sheet was weighed before and after immersion in 50 ml of the test solution for a period of time up to 3 hours. The average weight loss for each two identical experiments was taken and expressed in mg cm^{-2}, the temperature was adjusted to 25 ± 0.1 °C using air thermostat.

The loss in weight of metal in the corrosive solution

$$\Delta W = W_B - W_A \qquad ...1$$

where

ΔW = Loss in mass of metal in the corrosive solution.

W_B = Weight of metal before exposure to the corrosive solution.

W_A = Weight of metal after exposure to the corrosive solution.

The corrosion rate R_{corr} was calculated from the following equation[13]:

$$...2$$

where,
S is the surface area (cm^2). t is the time (min), after 150 min.

The percentage inhibition efficiency (%I.E) of the selected carrageenans compounds were calculated using the following equation

$$\% \, I.E = \frac{R_{corr.free} - R_{corr.add}}{R_{corr.free}} \, x \, 100 \qquad ...3$$

where,
$R_{corr.add}$ and $R_{corr.free}$ are the corrosion rates of iron in the absence and presence of the carrageenan compounds, respectively.

For galvanostatic polarization measurements were carried out using Mensberger potentiostat galvanostatic PS6 with controlling measurements of potential and current density. Three compartments electrode (SCE) and a platinum foil auxiliary electrode was used.

The percentage inhibition efficiency (%I.E) of the selected carrageenan compounds were calculated using the following equation.

$$R_{corr} = \frac{L}{I} \frac{\Delta W}{S \, t} \qquad (2)$$

$$\% I.E = \frac{I_{add}}{I_{free}} \, 100 \qquad ...4$$

where,
I_{free} and I_{add} are the corrosion current densities in the absence and presence of the inhibitors, respectively.

RESULTS AND DISCUSSION

Weight loss measurements

Fig. 2 represents the relation between time and weight losses of iron coupons in 1M HCl solution devoid of and containing different concentrations of compounds III as an example. Similar curves were also obtained for other two compounds (not shown). Inspection of this figures reveals that, as the concentration of these compounds increases, the loss in weight of iron compounds decreases. This reflects that, these compounds acts as an inhibitor. The linear variation of weight loss with time in uninhibited and inhibited 1M HCl solution indicates the absence of insoluble
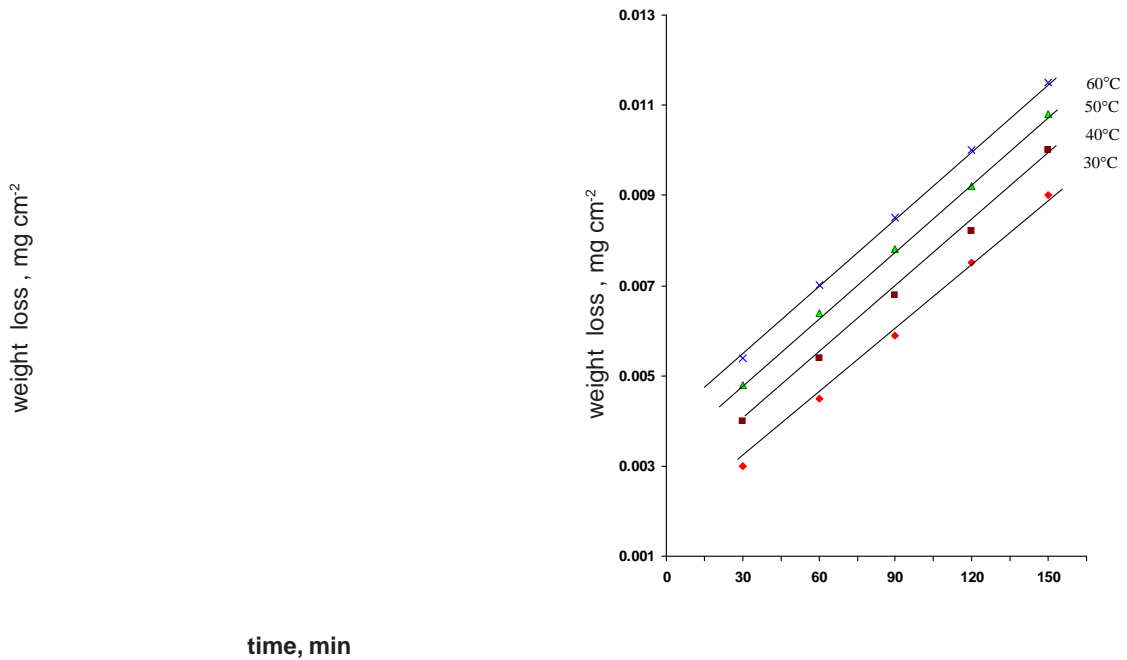
weight loss , mg cm^{-2}

60°C
50°C
40°C
30°C

time, min

Fig. - 2: Weight loss-time curves for the corrosion of iron electrode in 1M HCl in absence and presence of different concentrations of compound III.

1) 0 ppm   2) 100 ppm   3) 200 ppm
4) 300ppm   5) 400ppm   6) 500 ppm

Fig. - 3: Weight loss-time curves for the corrosion of iron electrode in 1M HCl containing 500 ppm of compound III at different temperatures

log R$_{corr}$, mg cm^{-2} min^{-1}
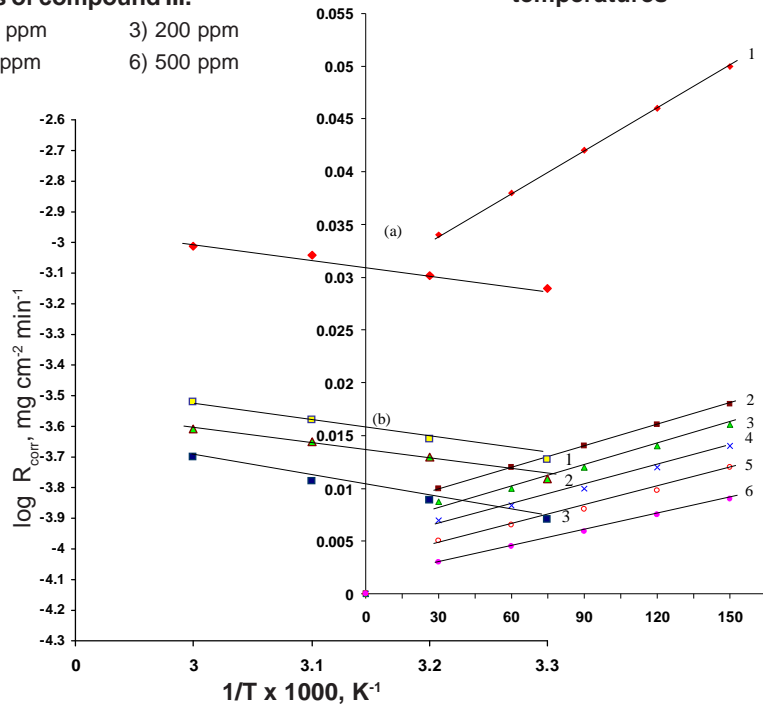
(a)

(b)

1
2
3

1
2
3
4
5
6

1/T x 1000, K^{-1}

Fig. -4: Relation between log R$_{corr}$ and the reciprocal of the absolute temperature of iron electrode in: a) 1M HCl, b) 1M HCl + 500 ppm of the studied compound
1) compound I   2) compound II   3) compound III

surface film during corrosion i.e. the inhibitor are first adsorbed on the metal surface and there after impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by uttering the mechanism of the anodic and cathodic processes.

The calculated values of inhibition efficiencies obtained from weight loss are listed in Table 1. It is obvious that the I.E increases with increasing the inhibitor concentrations, whereas decreases in the following order.

compound III > compound II > compound I

Effect of temperature

The effect of temperature on the corrosion rate of iron electrode in 1M HCl containing and devoid of 500 ppm of the studied these compounds was tested by weight loss measurements over a temperature range from 30-60°C.

Fig. 3 shows the weight loss-time curves of iron electrode in 1 M HCl containing 500 ppm of the compound III, at different temperatures. Similar curves were obtained for other two compounds I & II (not shown). It is clear that as the temperature increases the weight loss increases, the rate of corrosion increases and hence the inhibition efficiency decreases. This is due to desorption which is aided by increasing the temperature.

The activation energy (E_a) of the corrosion process was calculated using Arrhenius eq.[14]

$$...5$$

and the logarithmic form

$$\log R_{corr} = \log A - \frac{Ea}{2.303\ RT} \quad ...6$$

where,
R_{corr} is the rate of corrosion from weight loss, A, is Arrhenius constant , R is the gas constant and T is the absolute temperature.

Fig. 4 represents Arrhenius plot (log R_{corr} vs. I/T) for uninhibited and inhibited 1M HCl containing 500 ppm of the studied compounds. The values of E_a can be obtained from the slope of the straight lines and have been given in Table -2.

Inspection of Table -2 it is obvious that the values of E_a increases in the presence of the inhibitor. This is attributed to an appreciable decreases in the adsorption process of the inhibitors on the metal surface with increase of temperature and a corresponding increase in the reaction rate because of the greater area of the metal that is exposed to the acid[15].

The enthalpy change of activation (ΔH^*) and the entropy change of activation (ΔS^*) for dissolution of iron electrode in 1M HCl in presence and absence of 500 ppm of each used compound were obtained by applying the transition state equation[14].

$$R_{corr} = (\frac{RT}{Nh})\exp(\frac{\Delta S^*}{R})\exp^{(-\Delta H^*/RT)} \quad ...7$$

where
N is Avogadro number, h is Planck's constant. A plot of log (R_{corr}/T) vs (1/T) (Fig.5) should give straight line with a slope of (-ΔH^*/2.303 R) and an intercept of [log (R/Nh)-(ΔS^*/2.303R)]. The values of DH*--- and DS* are listed in Table -2.

$$R_{corr} = A\ e^{-Ea/RT} \quad (5$$

Inspection of Table it is clear that , the values of ΔH^* is positive. This reflect that the process of adsorption of the inhibitors on the iron surface is endothermic process. The values of ΔS^* is the presence and absence of the inhibitors is negative. This implies that the activated complex is the rate determining step and represents association rather than dissociation indicating that a decrease in disorder takes place on going from reactants to the activated complex[16].

Adsorption isotherm

The values of surface coverage θ for different concentrations of the studied compounds (I-III) at 25°C have been used to explain the best isotherm to determine the adsorption process. The adsorption of organic adsorbate on the surface of iron electrode is regarded as substitutional adsorption process between the organic compound in the aqueous phase (Org_{aq}) and the water molecule adsorbed on the electrode surface $(H_2O)_{ad}$[17].

$$Org_{aq} + XH_2O_{(ads)} \Leftrightarrow Org_{ad} + X\ H_2O_{(aq)} \quad ...8$$
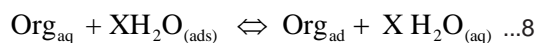
**Table -1: Effect of carrageenan compounds on corrosion rate (R$_{corr}$),
inhibition efficiency (%I.E) and surface coverage (θ) obtained from
weight loss measurements for dissolution of iron in 1M HCl.**

	R$_{corr}$ x 10^{-4}mg cm^{-2} min^{-1}	% I.E	θ
1 M HCl + compound I			
0 ppm compound I	6.94	-	-
100 ppm compound I	3.05	56.05	0.561
200 ppm compound I	2.77	60.08	0.601
300 ppm compound I	2.50	63.97	0.640
400 ppm compound I	2.22	68.01	0.680
500 ppm compound I	1.94	72.04	0.720
1 M HCl + compound II			
100 ppm compound II	2.63	62.10	0.621
200 ppm compound II	2.50	63.97	0.640
300 ppm compound II	2.22	68.01	0.680
400 ppm compound II	2.08	70.02	0.700
500 ppm compound II	1.66	76.08	0.761
1 M HCl + compound III			
100 ppm compound III	2.48	64.26	0.643
200 ppm compound III	2.25	67.57	0.676
300 ppm compound III	2.06	70.32	0.703
400 ppm compound III	1.72	75.21	0.752
500 ppm compound III	1.36	80.40	0.804

where,
X is the size ratio, that is the number of water molecules replaced by one organic molecules. Attempts were made to fit è values to various isotherm including Furmkin, Temkin, Freundilch and Langmuir isotherm. Plotting C/θ against C gave a straight line with unit slope value (Fig. 6) indicating the adsorption of carrageenan compounds on iron surface follows Langmuir adsorption isotherm.

From these results one can postulates that there is no interaction between the adsorbed species.

Galvanostatic polarization

The effect of carrageenan compounds on the anodic and cathodic polarization curves of iron electrode in 1 M HCl was studied. Fig. 7 shows the effect of increasing concentrations of compound III as an example. However, similar curves were

obtained for the other two compounds (not shown).

Inspection of Fig. 7 reveals that, the presence of increasing concentrations of carrageenan compound causes a marked decreases in corrosion rate i.e. shifts the anodic curves to more positive potentials and the cathodic curves to more negative potentials. This may be ascribed to the adsorption of the carrageenan compounds over the metal surface. The corrosion current density (I$_{corr}$) was determined from the intersection of the linear parts of the cathodic curves with the stationary corrosion potential (E$_{corr}$).

The electrochemical parameters such as, corrosion potential (E$_{corr}$), corrosion current density (I$_{corr}$) anodic and cathodic Tafel slopes (b$_a$&b$_c$) and inhibition efficiency (I.E) were calculated and given in Table 3. Inspection of the data cited in this Table reveals that , as the concentration of the additives
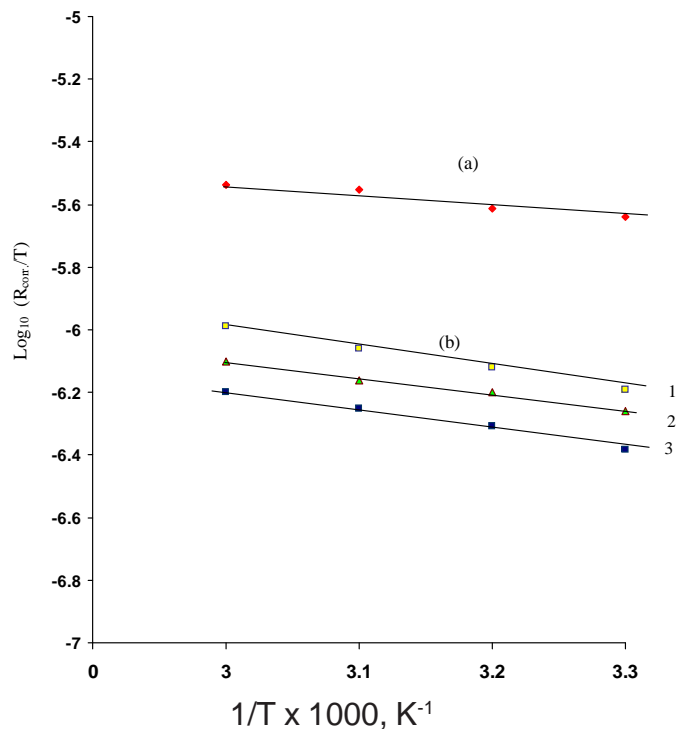
Fig. - 5: Transition state plot of the corrosion rate for iron electrode in 1M HCl in the absence and presence of the studied compounds. a) free   b) 1) compound I   2) compound II   3) compound III
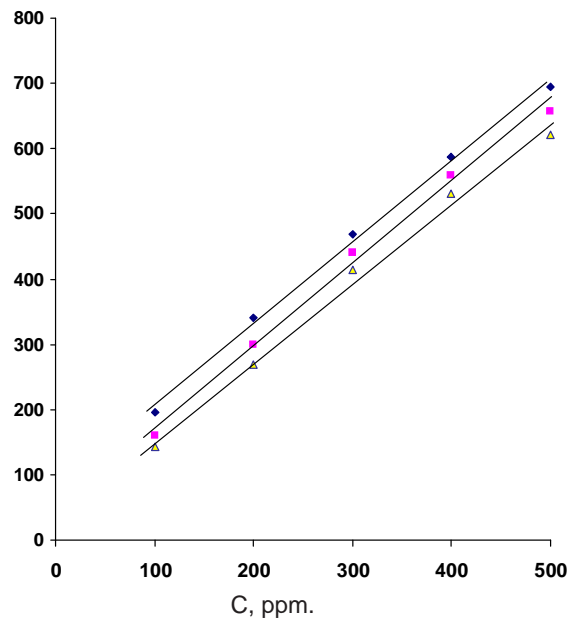
Fig. 6: Langmuir adsorption isotherm 1) compound I   2) compound II   3) compound III

**Table - 2: Activation parameters of the dissolution
of iron electrode in 1M HCl in the absence and
presence of 500ppm of the carrageenan compounds**

	Activation parameters		
	E_a° (KJ mol^{-1})	ΔH° (KJ mol^{-1})	$-\Delta S^\circ$ (J mol^{-1} k^{-1})
Free HCl	15.317	9.573	283.53
Compound I	19.147	11.488	291.19
Compound II	21.062	15.317	293.49
Compound III	22.976	17.230	295.02

**Table -3: Corrosion parameters obtained from galvanostatic polarization technique of iron
electrode in 1M HCl containing different concentrations of carrageenas compounds.**

Inhibitor conc., ppm	I_{corr}. (μAcm^{-2})	E_{corr}. mV(SEC)	β_a mV dec^{-1}	β_c mV dec^{-1}	θ	I.E
Compound I						
0	1.65	-530	163	-200	-	-
100	0.755	-276	166	-197	0.542	54.24
200	0.705	-278	154	-191	0.573	57.27
300	0.656	-274	157	-189	0.602	60.24
400	0.573	-270	166	-200	0.653	65.27
500	0.468	-261	160	-203	0.716	71.64
Compound II						
0	1.65	-530	163	-200	-	-
100	0.672	-320	153	-191	0.593	59.27
200	0.612	-305	147	-206	0.629	62.88
300	0.572	-295	161	-216	0.653	65.33
400	0.513	-282	154	-216	0.689	68.91
500	0.435	-268	165	-207	0.736	73.64
Compound III						
0	1.65	-530	163	-200	-	-
100	0.606	-315	165	-206	0.633	63.27
200	0.570	-306	158	-196	0.654	65.43
300	0.524	-297	164	-215	0.682	68.24
400	0.453	-281	156	-208	0.725	72.54
500	0.342	-278	160	-212	0.793	79.27

increases, the values of b_a & b_c are approximately constant suggesting the inhibiting action of these compounds by adsorption at the metal surface according to blocking adsorption mechanism. The values of E_{corr} is shifted to more positive potentials. This indicates that, this compounds are anodic inhibitors reducing the anodic reaction. The values of I_{corr} decreases and the values of I.E increases indicating the inhibiting effect of these compounds. The inhibition efficiencies of these compounds decreases in the following order:

compound III > compound II> compound I

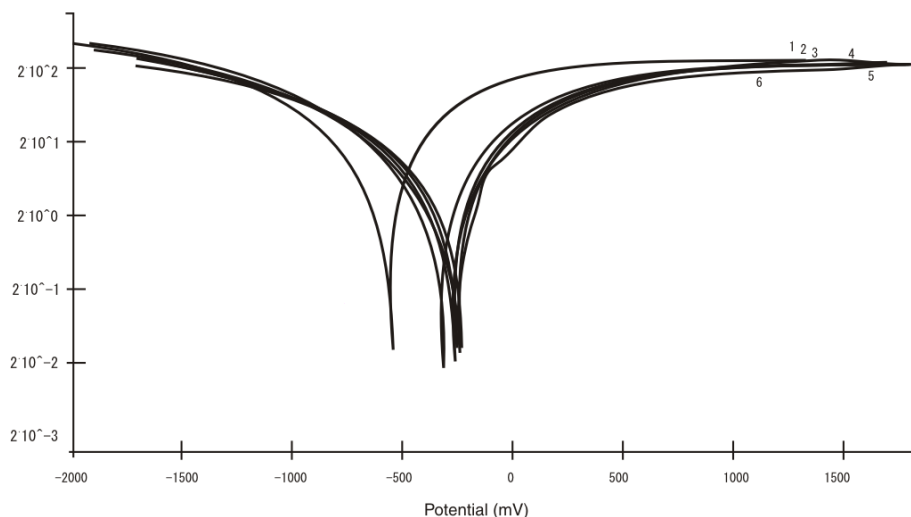which in consistent with that obtained from weight loss measurements.

**Fig. -7: Galvanostatic polarization curves for iron electrode in
1M HCI in absence and presence of different concentration of compound III
1) 0 ppm   2) 100 ppm   3) 200 ppm   4) 300 ppm   5) 400 ppm   6)500 ppm.**

Conclusions

1- The corrosion of iron electrode in 1M HCI is inhibited by addition of some carrageenan compounds.

2- The inhibition efficiency increases with increasing of the inhibitor concentrations and decreases with increasing of temperatures.

3- The inhibitive effect of these compounds is attributed to the adsorption on the metal surface.

4- The adsorption process follows Langmuir adsorption isotherm.

5- The inhibition efficiency from weight loss measurements agrees with those obtained from polarization measurements.

6- Investigated carrageenan compounds are anodic inhibitors reducing the anodic reaction.

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