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The Inhibition Effect of Succinic Acid on Corrosion of Low Carbon Steel in Hydrochloric Acid at Different Temperatures

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Abstract
The corrosion inhibition of ASTM-A240 201 Stainless Steel sheets (LCS) in 1M HCl solution in the presence of Succinic acid at temperature (20,30,40,50,60)°C at concentration between (0.1-10) ppm for two hours were studied using weight loss method. Results show that the inhibition efficiency was increased with the increase of inhibitor concentration and increased with the increase of temperature up to 60ºC . Activation parameters of the corrosion process such as activation energies E_a, activation enthalpies ΔH, and activation entropies ΔS, were calculated. The adsorption of inhibitor follows Langmuir isotherm. Maximum inhibition efficiency obtained was about 96% at 60ºC in the 10 ppm inhibitor concentration
Keywords: Corrosion, Corrosion Rate, Weight loss method, Inhibitor, Corrosion Inhibition, Inhibitor Efficiency, LCS (low carbon steel) , green corrosion inhibitors.

1. Introduction

Corrosion inhibitors are widely used in industry to reduce the corrosion rate of metals and alloys in contact with aggressive environments. Most of the corrosion inhibitors are synthetic chemicals, expensive, and very hazardous to environments. Therefore, it is desirable to source for environmentally safe inhibitors [1-2]. There are some reports on the inhibition effects of non-toxic compounds on the corrosion of metals. We have recently reported the inhibition effect of amino acids on the steel [1-3] and aluminum [4] corrosion in acidic media. The inhibition effects of some non-toxic organic compounds have been also reported for steel corrosion [5,6] but they are expensive.

Metals and alloy are exposed to the action of acid in industry, Processes in which acids play a very important part are acid pickling, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing and acid descaling [7]. The exposure can be most sever but in many cases.

Currently, research in corrosion is oriented to the development of "green corrosion inhibitors", compounds with good inhibition efficiency but low risk of environmental pollution [8-9-10-11]. Inorganic compounds such as chromate, dichromate, nitrite and nitrate are widely used as corrosion inhibitors in several media and for different metals and alloys [12].

Recently, it has been shown that SA acts as a mixed-type inhibitor for low carbon steel LCS corrosion in hydrochloric acid solutions [13-14]. Therefore, little seems to be published using SA as a corrosion inhibitor for LCS in acid media, and to our knowledge, no results have been reported and discussed in hydrochloric acid solutions at different temperatures .

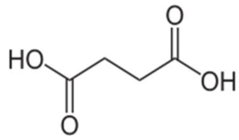
The aim of this study was to investigate the inhibition effect of Succinic Acid as a cheap, raw and non-toxic corrosion inhibitor on steel corrosion in hydrochloric acid. The weight loss measurements were used to evaluate the inhibition efficiencies. In addition, the effect of temperature on inhibition behavior of the inhibitor was also studied.

2. Experimental Work:

2.1. Materials and samples:

2.1.1. Succinic Acid:

Succinic acid (SA) is a water-soluble compound whose molecule has desirable characteristics for an acid inhibitor. However, its effect on corrosion processes of metals and alloys has not been extensively reported [13].
The concentrations of inhibitor were chosen as 0. 1,0. 5, 1,5 and 10 ppm at different temperatures.



Succinic acid formula

2.1.2. Low Carbon Steel:

The material of electrodes used was ASTM-A240 201 Stainless Steel sheets (LCS), of chemical composition (wt %) .

Table 1. Composition in wt% of the LCS used in this study

C	Mg	P	Cr	Ni	Si	N	S	Fe
0.12	6.5	0.06	19.6	4.4	0.75	0.25	0.03	Bal.

2.2. Experimental Procedure Weight loss Measurement:
The working electrode employed in this work is made from ASTM-A240 201 Stainless Steel sheets (LCS) of composition (wt%) presented in Table 1. For weight loss measurements, corrosion inhibition tests were performed using rectangular coupons measuring (20×15×2.8) mm prepared from LCS sheets. These coupons were first briefly ground with emery paper, subsequently polished with emery paper, washed with deionized water, degreased with absolute ethanol, dried, and then rinsed with deionized water rapidly, followed by immediate rinsing with absolute ethanol. The weight loss (in mpy) was determined at different temperatures (20,30,40,50 and 60) ◦C by weighing the cleaned samples before and after hanging the coupon into 250 cm^3 of the corrosive solution in (400 ml) beakers, namely 1.0M HCl (in open air) in the absence and presence of various concentrations of SA at different temperatures .
After the time elapsed the cleaning procedure consisted of wiping the coupons with a paper tissue and washing with distilled water and acetone, followed by oven drying and left in a desiccators over silica gel for 1hr.

3. Results and Discussion :
3.1. Weight loss technique:
Corrosion Rate (CR) calculations from weight loss data was performed according to the following equation:

$$CR=(K\times\Delta W)/(d\times A\times t)\ \frac{K\times\Delta W}{d\times A\times t}\ \frac{K\times\Delta W}{d\times A\times t}\ \frac{K\times\Delta W}{d\times A\times t} \quad \ldots\ldots\ldots\ldots\ldots\ldots.. \quad (1)$$

Where
ΔW :is the weight loss (g)
d : is the steel density (g/cm^3) =7.81 (g/cm^3)
A : is the steel area (cm^2)
t : is the time of Experiment (h)
K : is constant =3.45 x 10^6
The surface coverage (Θ) and inhibition efficiency, IE% were calculated from the weight loss measurements using the following equations, respectively

$$\Theta\ =[1-(CR_{inh}/CR_{free})]1-\frac{(CR)inh}{(CR)free} \quad \ldots\ldots\ldots\ldots\ldots\ldots.. \ (2)$$

$$IE\% =[1-(CR_{inh}/CR_{free})]\times 100 \quad \ldots\ldots\ldots\ldots \ (3)$$

Where $(CR)_{free}$, $(CR)_{inh}$, are the corrosion rate (mpy) in the HCl solution in absence and presence of Succinic Acid as inhibitor of different concentrations at different temperatures.
The corrosion rates of carbon steel corrosion in absence of inhibitor in 1M HCl acid increased from (149.3 to 4835.16) mpy as the temperature increased from 20 to 60 °C .Figure 1, shows the variation of corrosion rate with temperature.

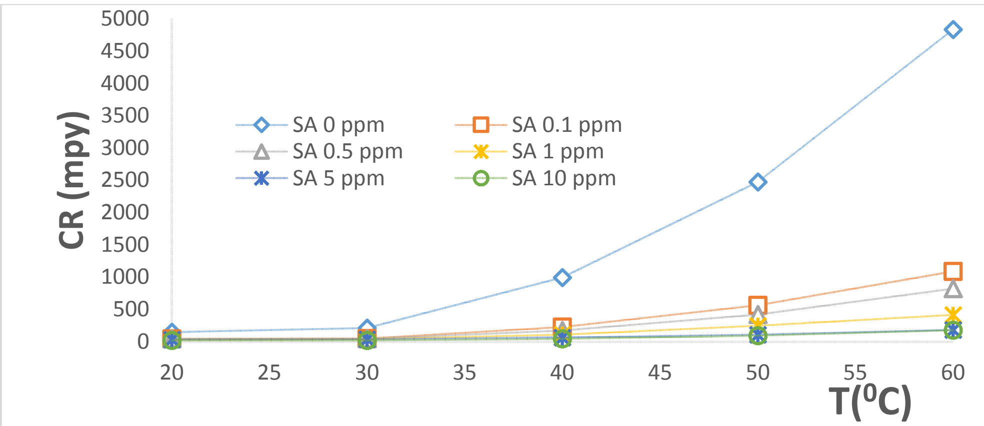


Fig. 1 Effect of Temperature on Corrosion Rate of Carbon Steel in 1M HCl at different concentrations of inhibitor.

Table 2, effect of temperature on the corrosion rate (mpy) of carbon steel in 1M HCl acid in absence and presence of Succinic Acid as corrosion inhibition.

SA conc.		Temperature (°C)				
		20	30	40	50	60
Nil	CR	149.29611	212.0683	995.8729	2471.8686	4835.1583
	ϴ	--	--	--	--	--
	IE%	--	--	--	--	--
0.1 ppm	CR	46.9485	49.7101	229.2189	566.1431	1090.8611
	ϴ	0.6855	0.7656	0.7698	0.7710	0.7744
	IE%	68.5535	76.5594	76.9831	77.0966	77.4390
0.5 ppm	CR	44.1868	46.9485	171.2238	419.7744	820.2171
	ϴ	0.7040	0.7786	0.8281	0.8302	0.8304
	IE%	70.4033	77.8616	82.8067	83.0179	83.0364
1 ppm	CR	35.9018	38.6634	107.7053	245.7890	414.2511
	ϴ	0.7595	0.8177	0.8918	0.9006	0.9143
	IE%	75.9527	81.7684	89.1848	90.0566	91.4325
5 ppm	CR	22.2302	40.0209	62.8900	111.4869	185.8114
	ϴ	0.8511	0.8113	0.9368	0.9549	0.9616
	IE%	85.1099	87.9800	93.6849	95.4898	96.1571
10 ppm	CR	19.3317	22.0934	44.1868	96.6586	179.5088
	ϴ	0.8705	0.8958	0.9556	0.9609	0.9629
	IE%	87.0514	89.5819	95.5630	96.0897	96.2874

The corrosion rate in 1M HCl increases sharply with increasing temperature.

Addition of Succinic Acid as inhibitor reduce corrosion rate generally. Table 2, shows the variation in corrosion rate with the inhibitor concentration at various temperature levels. It is clear that the corrosion rate decreases with increasing the concentration of inhibitor at any used temperature, the effect of Temperature on corrosion rate for different concentrations of inhibitor is expressed in Figure 1.This Figure shows that the corrosion rate increases with increasing temperature at all studied inhibitor concentration.

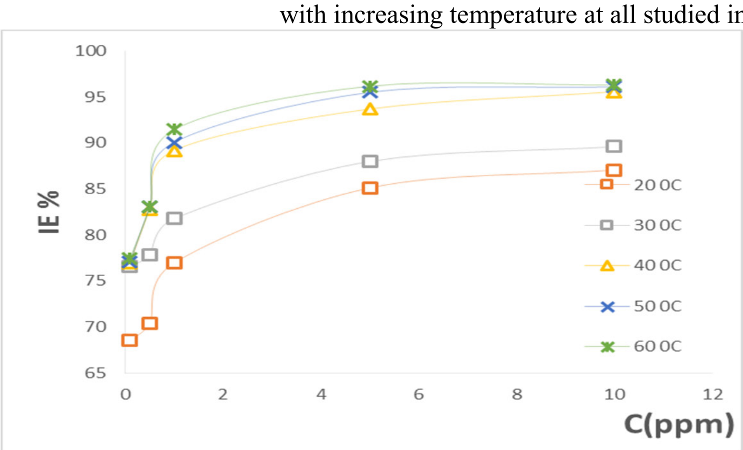


Fig. 2 Variation of Inhibition Efficiency with Inhibitor Concentration at Different Temperature.

Values of inhibition efficiency increase with increasing inhibitor concentration. Figure 2, shows the variation of inhibition efficiency with inhibitor concentration. It varies as follows; from 68.55 to 77.44 % at 0.1 ppm inhibitor concentration , from 70.40 to 83.04% at 0.5 ppm ,from 75.95 to 91.43 % at 1 ppm ,from 75.75 to 96.16% at 5 ppm and from 87.05 to 96.29% at 10 ppm as the temperature increased from 20 up to 60 ^{0}C.

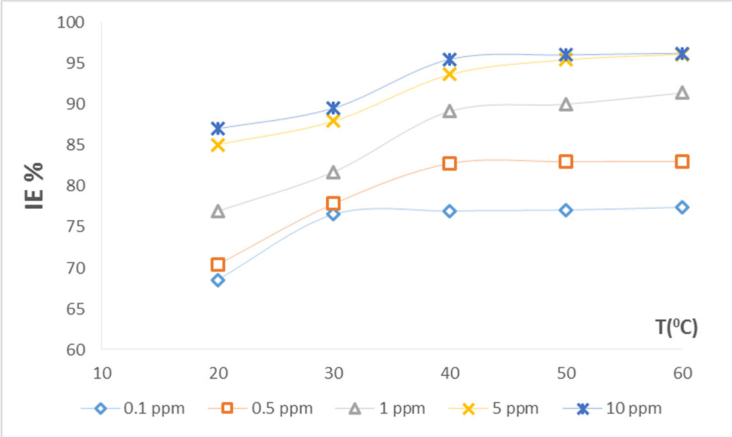


Fig.3 Effect of Temperature on Inhibition Efficiency at Different Inhibitor Concentration.

Figure 3, shows the effect of temperature on inhibition efficiency .Inhibition efficiency increase with increasing temperature up to 60 ^{0}C then the efficiency reaches a maximum value of 96.29 % at 60 ^{0}C for 10 ppm . This increase in inhibition efficiency with temperature is presumably due to an increase in adsorption of the inhibitor. This maybe explained due to the structure degradation of existing organic compounds in the inhibitor [15].

The plot of (IE %) vs. inhibitor concentration (ppm) Succinic Acid as corrosion inhibitor is found to generally increase with inhibitor concentration and approaches 96.29% in 1MHCl acid at 60 ^{0}C with 10 ppm of the inhibitor. While the lowest inhibition efficiency is 68.55 at 20^{0}C and 0.1 ppm inhibitor concentration it is shown in Fig 2.

3.2. Adsorption isotherm:

The corrosion rate data can be used to analyze the adsorption mechanism. The Langmuir isotherm was expressed as

$$\theta = \frac{KC}{1+KC} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where K is the equilibrium constant for the adsorption isotherm representing the degree of adsorption (i.e , the higher the value of K indicates that the inhibitor is strongly adsorbed on the metal surface). C is inhibitor concentration ppm and θ is the surface coverage. Rearranging equation will give :

$$\frac{C}{\theta} = \frac{1}{K} + C \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Figure 4, shows plots of C/Θ vs. C for Succinic Acid as corrosion inhibitor in 1M HCl acid at 20,30, 40, 50 and 60 ^{0}C. The data fit straight lines indicating that Succinic Acid is adsorbed according to the Langmuir adsorption isotherm from the intercept of straight line on the C/Θ axis; K values are to be calculated as given in Table 3.

Table 3. Equilibrium Constant for Langmuir Type Adsorption of the inhibitor in 1M HCl acid solution at different Temperatures

T (ºC)	Slope	K Value $(ppm)^{-1}$
20	1.06	8.1699
30	1.14	7.2411
40	1.11	14.0056
50	1.09	16.2337
60	1.1	18.4502

The rectilinear natures of figure 4 indicate an increase in adsorption with an increase in concentration of and that adsorption occurs in accordance with Langmuir adsorption equation. It is also noted in fig.4, that the lines accumulated and approximately looked like one line; this is due to the very close range of inhibition efficiency (68.55% – 96.29%).

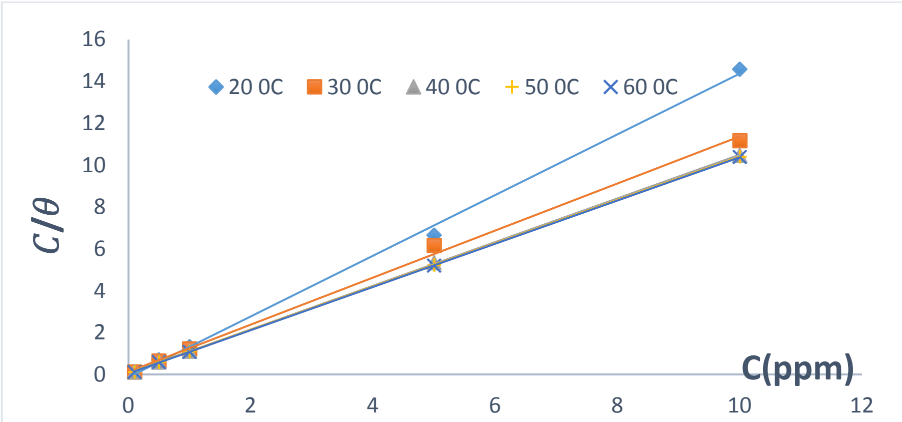


Fig. 4 Langmuir adsorption isotherm of SA on Low Carbon Steel in 1M HCl at Different Temperature

3.3. Thermodynamic parameters:

Activation energies of low carbon steel in 1M HCl in presence and absence of succinic Acid are calculated from Arrhenius plots fig **5**. It is observed that in uninhibited 1M HCl acid solution ,the activation energy of the dissolution process is (76.35kJ/mol). The relationship between the corrosion rate (CR) of carbon steel in acidic media and temperature (T) is often expressed by:

$$\log CR = \log A - \frac{E_a}{2.303\, RT} \quad \text{.................................(6)}$$

Where:
Ea is the apparent effective activation energy.
R the general gas constant
A the Arrhenius pre-exponential factor.
A plot of Log of Corrosion Rate obtained by weight loss measurement vs.1/T gave straight lines as shown in figure 5.

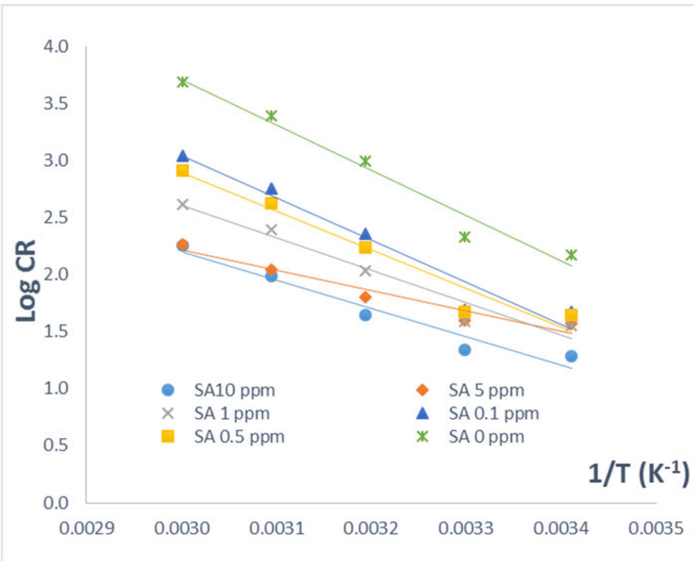


Fig. 5 Arrhenius plot for log corrosion rates (mpy) versus reciprocal of absolute temperature at different inhibitor concentration.

The values of activation energy (Ea) obtained from the slop of the lines are given in Table 3.
Some other activation parameters such as the enthalpy change of activation (ΔH) and entropy change of activation (ΔS) were obtained from the transition state equation which is an alternative formula for the Arrhenius equation[16]:

$$CR = \frac{RT}{Nh}\exp\left(\frac{\Delta S}{R}\right)\exp\left(\frac{-\Delta H}{RT}\right) \quad \text{.................................(7)}$$

Where:
h is the Plank's constant,(i.e., h = 6.626 × 10^{-34} Joule. Sec)
N the Avogadro number,(N = 6.023 ×10^{23} molecules g.mole^{-1}).

A plot of Log (CR/T) vs. 1/T should give a straight line.
Figure 6, with a slop of (-ΔH / 2.303 R)and an intercept of [(Log (R/N×h) + (ΔS/ 2.303 R)],from which the values of ΔS and ΔH were calculated .

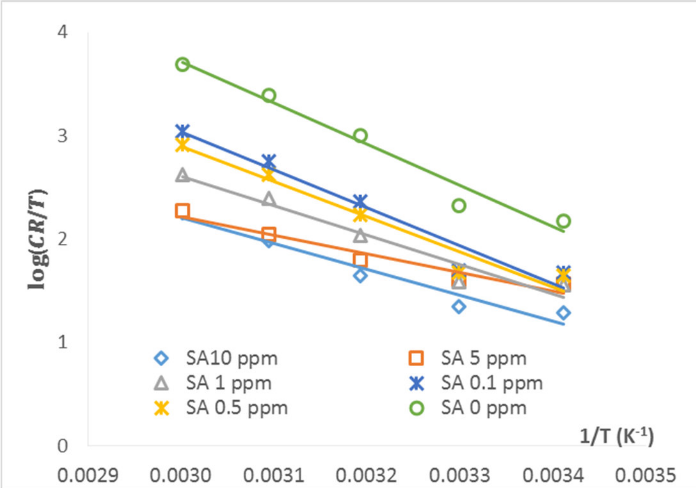


Fig. 6 Adsorption isotherm plot for Log (CR/T) of Low carbon steel Versus Reciprocal of Absolute Temperature in the presence and absence of Succinic Acid.

Table 4, thermodynamic activation parameters for carbon steel in 1N HCl in the absence and presence of inhibitor concentrations

C (ppm)	ΔH (kJ/mol)	$-\Delta S -$ ΔS (J/mol)	E_a (kJ/mol)
Nil.	73.7567	1.9196	76.3531
0.1 ppm	62.28373	3.277984	75.0509
0.5 ppm	59.62419	13.98313	67.7118
1 ppm	49.1756	50.87576	56.225
5 ppm	32.70332	107.8786	46.341
10 ppm	44.4386	73.00598	48.5609

These are listed in Table 4,The values of activation parameter (ΔH) in presence of inhibitor are less than that in the absence of inhibitor (nil) , these exhibit high inhibition efficiency at elevated temperature. The positive values of (ΔH) both in absence and presence of inhibitor reflect the endothermic nature of the steel dissolution process and means that the dissolution of steel is difficult.

It is also clear that the activation enthalpies vary in the same manner as the activation energies, supporting the proposed inhibition mechanism.

The values of activation ΔS in the absence and presence of inhibitor are large and negative. This indicates that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex.

It is obviously that the ΔS shifts to more negative values (more ordered behavior) with increasing inhibition efficiency, this can be explained that the inhibitor species may involved in the activated complex of the corrosion reaction leading to more ordered system [11].

These are listed in Table 4,The values of the Activation energies in presence of inhibitor are lower than uninhibited acid (76.36 kJ/mol) since only small differences are observed between the values of activation energy calculated **.**

At different concentration, the activation energy is considered to be essentially, constant (mean) value of 47.86kJ/mol for Succinic Acid independent of it's concentration..

Some authors have reported values of E_a < 80 kJ/mol as an indicator of physical adsorption, While value of E_a > 80 kJ/mol are related to chemical adsorption so the lower E_a in inhibited solutions compared to the uninhibited indicated of physical adsorption mechanism[10].

4. Conclusions

1- It was found that the activation energy in absence of inhibitor was (73.76 kJ/mol) .This value decreased down to 32.70 kJ/mol. This mean that the activation energy of the reaction is inhibitor concentration independent.
2. Succinic Acid is adsorbed according to the Langmuir adsorption isotherm
3. Inhibition efficiency increase with increasing temperature to 60°C and the efficiency increased with increase

inhibitor concentration.
4. The positive value of ΔH both in absence and presence of inhibitor reflect the endothermic nature of the steel dissolution process.
5. The values of ΔS are large and negative meaning that decrease in disordering takes place on going from reactants to the activated complex.
6. This investigation shows that Succinic Acid is an effective friendly inhibitor, Max. Efficiency obtained was a bout 96%.

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