Corrosion Inhibition of Carbon-Steel in (0.1M) HCl and NaCl using Sulfasalazine Drug

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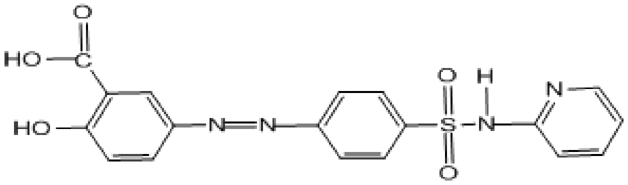
Abstract: ***Sulfasalazine drug (SS) was identified by CHN, FTIR, ^{1}HNMR and ^{13}CNMR techniques . The effect of Sulfasalazine on the dissolution of C-steel in 0.1M HCl and 0.1M NaCl solution was studied using weight loss and galvanostatic polarization techniques .The inhibition efficiency of inhibitor increases with concentration to attain (93.42%) in HCl and (79.31%) in NaCl at concentration 1×10^{-2} M ,and standing time for 240 min at 25°C. Temperature effect on the corrosion behavior was studied at temperature range from 25-45°C , the results showed that inhibition efficiency decreased with increasing temperature to attain (70.14%) in HCl and (50.92%) in NaCl concentration 1×10^{-2} M for both, at 45°C and with standing time equal to 240 min .The effect of temperature on the rate of corrosion in the absence and presence of Sulfasalazine (SS) drug was also studied. The activation energy was calculated and discussed .The polarization curves revealed that the studied inhibitor represent a mixed – type inhibitors .Adsorption of inhibitor was isotherm physisorption type.***

Keywords: Corrosion, Carbon steel, Sulfasalazine

1. Introduction

Corrosion is the destructive attacks of metals by its environment. Corrosion of metals is a major industrial problem that has attracted a lot of investigators in recent years (1).One of the most vital processes in the field of prevention of corrosion and its control is the use of organic inhibitors .The crucial part in the mechanistic aspect of such inhibitors is the specific interaction between certain functionalities in the inhibitors with the corrosion active centers on the metal surface. Heteroatoms such as nitrogen, oxygen, sulphur, present in the inhibitors play a leading role in this interaction by donating their free electron pairs(25). Hence most of the organic compounds containing these heteroatoms generally act as good inhibitors. In addition, compounds with multiple bonds behave as efficient inhibitors due to the availability of π-electrons for interaction with the metal surface. Certain inhibitors possess both the above tow features , availability of lone pair from heteroatom as well as π-electrons in the same molecule , and such compound show extraordinary inhibition characteristics(6). The aim of the present work is to study the inhibitive action of Sulfasalazine (SS) drug toward the corrosion of C-steel in 0.1M hydrochloric acid and sodium chloride solution using weight loss and galvanostatic polarization techniques. Moreover, the effect of temperature on the dissolution carbon steel, as well as, on the inhibition efficiency of the studied compound was also investigated. The following fig represent the structure of sulfasalazine((2-hydroxy -5- [(E)-2-{4-[(pyridine-2-yl) sulfamoyl] phenyl}diazen-1-yl] benzoic acid))



2. Experimental Method

The C-steel sample used (N-80) had the composition 0.3%C, 1.2%Mn, 0.05%P, 0.06%S and the remainder Fe coupons of C-steel with dimension of 2.1×2.4×0.1 cm were used for weight loss measurements. For galvanostatic studies a cylinder rod embedded in araldite with an expose surface area of (1cm^{2}) was used. The electrode surface was polished with different grades of emery paper, degreased with acetone, and rinsed with distilled water. (0.1 M) A.R grade hydrochloric acid and sodium chloride were used for preparing the corrosive solution. For weight loss experiments, the cleaned C-steel coupons were weighed before and after immersion in 25 ml of the test solution for a period of time 4 hrs. The weight loss for experiments was expressed in (gm). Galvanostatic polarization studies were carried out using Bank EIEIKTRONKIK INTELLGENT CONTROLS Model MLab 200- Department of Chemistry- College of Education for Pure Science- University of Basrah, for calculation of electrochemical parameters three compartment cell with a saturated calomel electrode (reference electrode), platinum for auxiliary electrode and working electrode was used.

3. Results and Discussion

Identification of Sulfasalazine

Identification of Sulfasalazine ((2-hydroxy -5- [(E)-2-{4-[(pyridine-2-yl) sulfamoyl] phenyl}diazen-1-yl]benzoic acid)). The chemical structure of Sulfasalazine was confirmed by the CHN , FTIR , ^{1}HNMR and ^{13}CNMR .

CHN analysis was recorded on ECS-4010 CHNSO Analyzer indicating the found percentages of carbon, hydrogen and nitrogen are equivalent to calculated values as (%H= $3.549_{(cal)}$, $3.59_{(found)}$. %C= $54.27_{(cal)}$, $54.31_{(found)}$. %N= $14.06_{(cal)}$, $14.12_{(found)}$). FTIR Spectrum of Sulfasalazine (SS) was carried out using (FT- IR- 8400S. Fourier Transform Infrared Spectrophotometer) Shimadzu (Japan). The Spectra were shown in Fig 1 and the characterized bands were given in Table 1. ^{1}HNMR and ^{13}CNMR spectra of Sulfasalazine in DMSO were recorded on Brucker Biospin GMBH (500 MHz) , indicating the signals of Sulfasalazine were in well agreement with its structure as shown in Figure 2, Figure 3 and Table 2

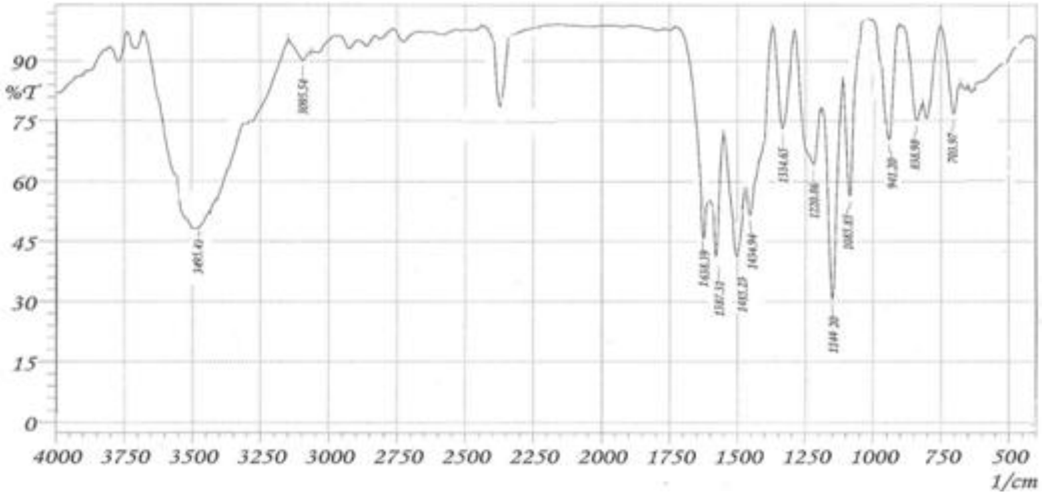


Figure 1: FTIR spectrum of Sulfasalazine

Table 1: Characterized Bands in FTIR spectrum for Sulfasalazine (SS)

Compound	υ OH, NH (cm^{-1})	υ CH Arom (cm^{-1})	υ -C=C- (cm^{-1})	υ -N=N- (cm^{-1})	υ C=O (cm^{-1})
SS	3495.41 b	3095.54 w	1485.23 w	1434.94 w	1638.39 s

b= broad, w= weak, s= strong

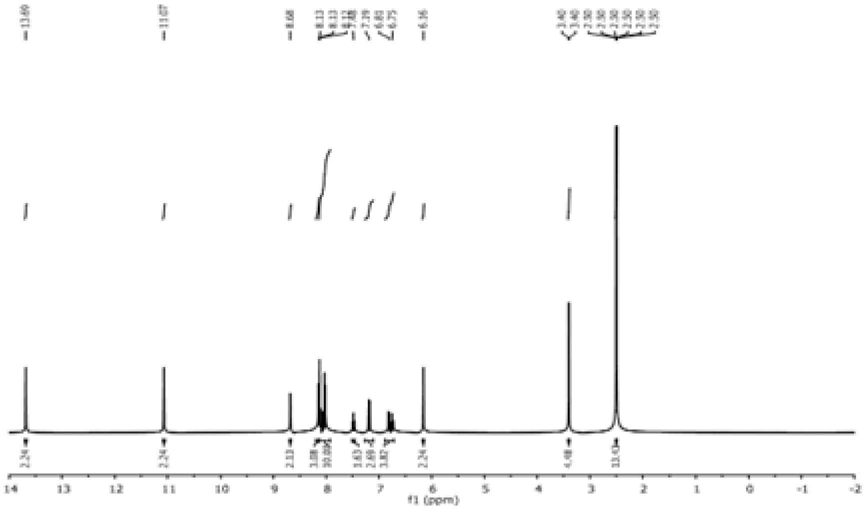


Figure 2: ^{1}HNMR spectrum of Sulfasalazine

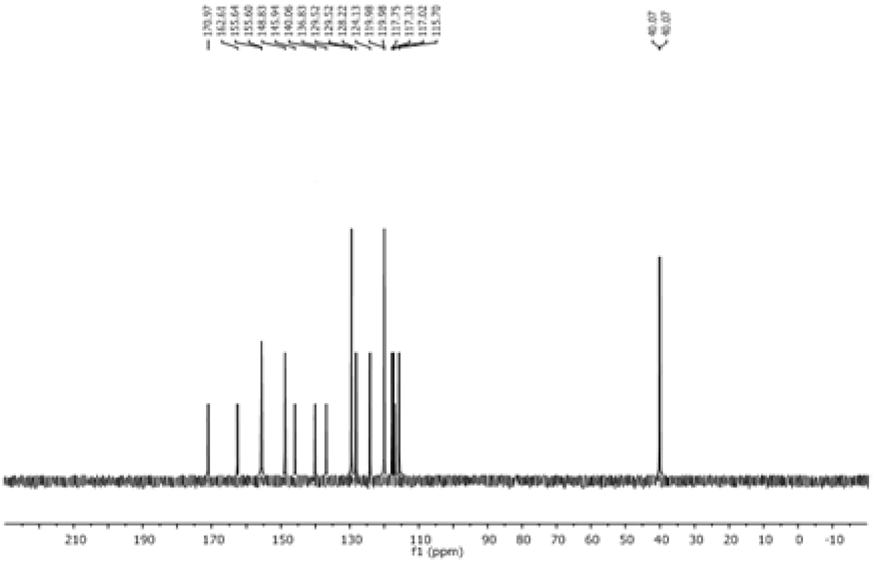


Figure 3: ^{13}CNMR spectrum of Sulfasalazine

Table 2: ^{1}HNMR and ^{13}CNMR data of Sulfasalazine (SS)

SS	Chemical shift δ (ppm)
^{1}HNMR	13.69 (1H ,OH $_{\text{phenolic}}$) , 11.07 (1H, OH $_{\text{carboxylic}}$) , 8.68-6.75(H$_{\text{aromatic}}$) , 6.16 (1H , NH) , 3.40 (H in H_2O presented in DMSO) , 2.5(6H , DMSO)
^{13}CNMR	170.97 (C=O) , 162.61(C-OH) , 155.64(C=N $_{\text{aromatic}}$) , 155.60 (C-N=N $_{\text{right}}$) ,148.83 (C-N $_{\text{aromatic}}$), 145.94 (C-N=N $_{\text{left}}$) ,140.06-115.70 (C $_{\text{aromatic}}$), 40.07 (C in DMSO)

Weight loss measurements

The results of the measurements are shown in Tables 3 and 4 for the corrosion of C-Steel in 0.1M HCl and NaCl in the absence and in the presence of different concentrations of Sulfasalazine (SS) at the temperature of 25°C.The percentage of inhibition efficiency %IE and surface coverage parameter θ which represents the part of the surface covered by the inhibitor molecules were calculated using the following equations$^{(7)}$:-

$$\%IE = [1 - \frac{W_{add}}{W_{free}}] \times 100 \quad \text{----------} \quad (1)$$

$$\theta = [1 - \frac{W_{add}}{W_{free}}] \quad \text{-----------} \quad (2)$$

Where W_{free} and W_{add} are the weight losses of C-Steel in absence and presence of inhibitors.

Figures 4 and 5 represent the variation of the inhibition efficiency %IE as function of the time (240 min). The inhibition efficiency increased with increasing the inhibitor concentration . The corrosion rate R_{corr} where calculated using the following equation$^{(8)}$:-

$$R_{corr} = \frac{\Delta W}{St} \quad \text{------------} \quad (3)$$

Where ΔW= is the weight losses of metal , S= is the surface area (cm^2), T= is the exposed time (min)

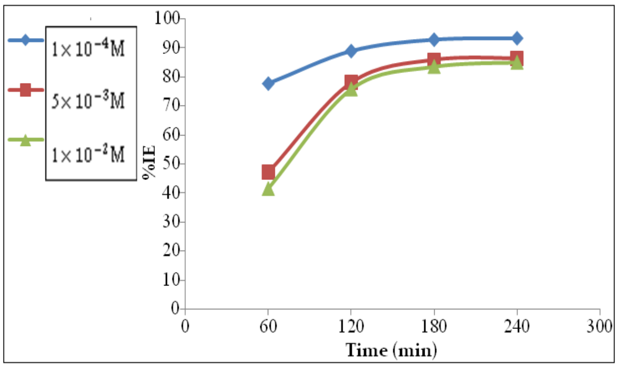


Figure 4: Variation of the Inhibition Efficiency %IE as a function of the time in the presence of different concentrations of (SS) at 25°C in 0.1M HCl

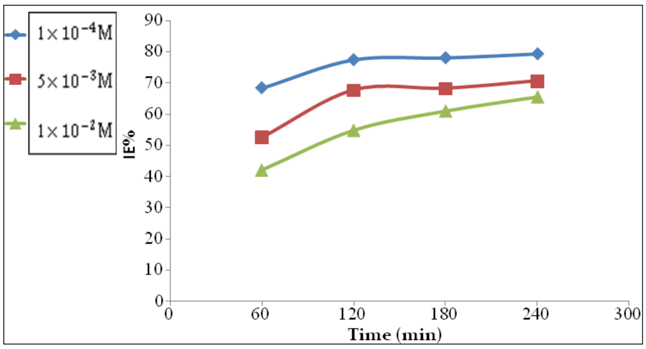


Figure 5: Variation of the Inhibition Efficiency %IE as a function of the time in the presence of different concentrations of (SS) at 25°C in 0.1M NaCl

Table 3: Effect of (SS) on the dissolution C- steel in 0.1M HCl

Time (Min)	60				120				180				240			
Conc (M)	Wt-loss gm	Rcorr $gm.cm^{-2}$ min^{-1}	IE %	Θ	Wt-loss gm	Rcorr $gm.cm^{-2}$ min^{-1}	IE %	Θ	Wt-loss gm	Rcorr $gm.cm^{-2}$ min^{-1}	IE %	Θ	Wt-loss gm	Rcorr $gm.cm^{-2}$. min^{-1}	IE %	Θ
0.00	0.0036	54.64 $\times 10^{-7}$	–	–	0.0091	69.06 $\times 10^{-7}$	–	–	0.0170	86.01 $\times 10^{-7}$	–	-	0.0213	90.04 $\times 10^{-7}$	–	–
1×10^{-4}	0.0021	31.87 $\times 10^{-7}$	41.60	0.4160	0.0022	16.69 $\times 10^{-7}$	75.82	0.7582	0.0028	14.16 $\times 10^{-7}$	83.52	0.8352	0.0032	12.14 $\times 10^{-7}$	84.97	0.8497
1×10^{-3}	0.0019	28.84 $\times 10^{-7}$	47.22	0.4722	0.0020	15.17 $\times 10^{-7}$	78.02	0.7802	0.0024	14.67 $\times 10^{-7}$	85.88	0.8588	0.0029	10^{-7} x11.00	86.38	0.8638
1×10^{-2}	0.0008	12.14 $\times 10^{-7}$	77.77	0.7777	0.0010	7.58 $\times 10^{-7}$	89.01	0.8901	0.0012	6.07 $\times 10^{-7}$	92.94	0.9294	0.0014	5.31 $\times 10^{-7}$	93.42	0.9342

Table 4: Effect of (SS) on the dissolution C- steel in 0.1M NaCl

Time (Min)	60				120				180				240			
Conc (M)	Wt-loss gm	Rcorr $gm.cm^{-2}.min^{-1}$	IE %	Θ	Wt-loss gm	Rcorr $gm.cm^{-2}.min^{-1}$	IE %	Θ	Wt-loss gm	Rcorr $gm.cm^{-2}.min^{-1}$	IE %	Θ	Wt-loss gm	Rcorr $gm.cm^{-2}.min^{-1}$	IE %	Θ
0.00	0.0019	20.84 $\times 10^{-7}$	-	–	0.0031	23.52 $\times 10^{-7}$	–	–	0.0041	25.74 $\times 10^{-7}$	–	–	0.0058	29.00 $\times 10^{-7}$	–	–
1×10^{-4}	0.0011	16.69 $\times 10^{-7}$	42.10	0.4210	0.0014	10.62 $\times 10^{-7}$	54.83	0.5483	0.0016	8.09 $\times 10^{-7}$	60.97	0.6097	0.0020	7.58 $\times 10^{-7}$	65.51	0.6551
1×10^{-3}	0.0009	10^{-7} 13.66×	52.63	0.5263	0.0010	75.80 $\times 10^{-8}$	67.79	0.6779	0.0013	65.70 $\times 10^{-8}$	68.29	0.6829	0.0017	10^{-8} 64.50×	70.68	0.7068
1×10^{-2}	0.0006	91.00 $\times 10^{-8}$	68.42	0.6842	0.0007	53.10 $\times 10^{-8}$	77.41	0.7741	0.0009	45.50 $\times 10^{-8}$	78.04	0.78041	0.0012	45.20 $\times 10^{-8}$	79.31	0.7931

Effect of temperature

The influence of temperature on the behavior of C- steel / acid and salt added of Sulfasalazine (SS) at various concentrations is investigated by weight loss trends in the temperature range 25-45°C during 4hrs of immersion. The variation of the inhibition efficiency of Sulfasalazine (SS) with temperature is decreased with increasing temperature is suggestive physisorption mechanism which is effectively enhanced with increasing temperature(9) . Figures 6 and 7 represent the variation of the inhibition efficiency %IE as a function of the temperature. The results of these measurements are shown in Tables 5 and 6.

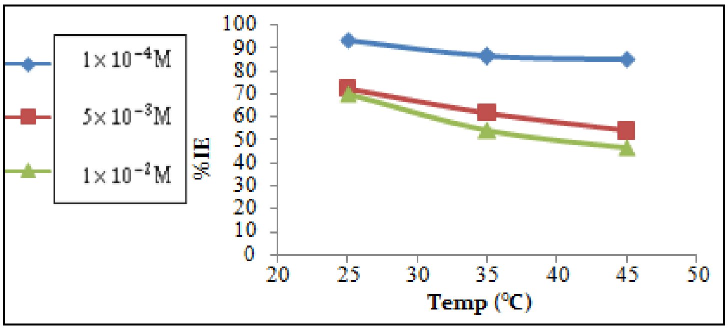


Figure 6: Variation of the Inhibition Efficiency %IE as a function of the temperature in the presence of different concentrations of (SS) in 0.1M HCl

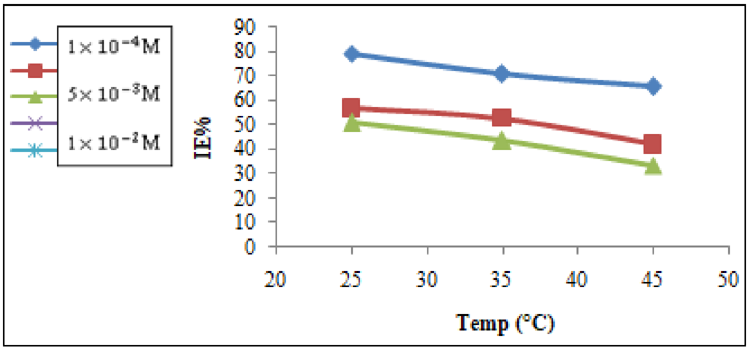


Figure 7: Variation of the Inhibition Efficiency %IE as a function of the temperature in the presence of different concentrations of (SS) in 0.1M NaCl

Table 5: Effect of (SS) on the dissolution C- steel in 0.1M HCl in the different temperature

Temp°C	25				35				45			
Conc (M)	Wt-loss gm	Rcorr gm.cm^{-2}.min^{-1}	IE %	Θ	Wt-loss gm	Rcorr gm.cm^{-2}.min^{-1}	IE %	Θ	Wt-loss gm	Rcorr gm.cm^{-2}.min^{-1}	IE %	Θ
0.00	0.0213	90.04$\times 10^{-7}$	_	_	0.0255	47.81 $\times 10^{-7}$	_	_	0.0402	15.25$\times 10^{-6}$	_	_
1$\times 10^{-4}$	0.0032	12.14$\times 10^{-7}$	84.97	0.8497	0.0118	22.00$\times 10^{-7}$	53.72	0.5372	0.0214	81.20 $\times 10^{-7}$	46.76	0.4676
1$\times 10^{-3}$	0.0029	10^{-7} 11.00×	86.38	0.8638	0.0097	18.21 $\times 10^{-7}$	61.96	0.6196	0.0183	69.44$\times 10^{-7}$	54.47	0.5447
1$\times 10^{-2}$	0.0014	5.31$\times 10^{-7}$	93.42	0.9342	0.0071	13.28$\times 10^{-7}$	72.56	0.7256	0.0120	45.53$\times$ 10^{-7}	70.14	0.7014

Table 6: Effect of (SS) on the dissolution C- steel in 0.1M NaCl in the different temperature

Temp°C	25				35				45			
Conc (M)	Wt-loss gm	Rcorr gm.cm^{-2}.min^{-1}	IE %	Θ	Wt-loss gm	Rcorr gm.cm^{-2}.min^{-1}	IE %	Θ	Wt-loss gm	Rcorr gm.cm^{-2}.min^{-1}	IE %	Θ
0.00	0.0058	29.00$\times 10^{-7}$	-	-	0.0095	36.05 $\times 10^{-7}$	-	_	0.0108	40.98$\times 10^{-7}$	-	-
1$\times 10^{-4}$	0.0020	7.58$\times 10^{-7}$	65.51	0.6551	0.0055	20.87$\times 10^{-7}$	42.10	0.4210	0.0072	27.32 $\times 10^{-7}$	33.33	0.3333
1$\times 10^{-3}$	0.0017	10^{-8} 64.50×	70.68	0.7068	0.0045	17.07 $\times 10^{-7}$	52.63	0.5263	0.0061	23.29 $\times 10^{-7}$	43.51	0.4351
1$\times 10^{-2}$	0.0012	45.20$\times 10^{-8}$	79.31	0.7931	0.0041	15.55$\times 10^{-7}$	56.86	0.5686	0.0053	20.11$\times$ 10^{-7}	50.92	0.5092

The activation energy Ea of corrosion process was calculated using the following equation$^{(10)}$:-

$$\ln(r_2/r_1) = (Ea\ (T_2-T_1)/R\ (T_2*T_1)\ \text{------}\quad (3)$$

Where

r_1= Corrosion rate at 303 K

r_2= Corrosion rate at 313 K

Ea= Activation energy

R= Gas constant (8.3143J.K^{-1}.mol^{-1})

$T_1$and T_2= Absolute temperature (K)

The values of activation energy Ea given in Table 7

Table 7: Activation energy for dissolution of C- Steel in 0.1M HCl and 0.1 M NaCl in the different concentration of (SS)

Conc. Of SS [M]	Activation energy KJ mol^{-1}	
	HCl (SS)	(SS) NaCl
0.00	41.51	13.62
1$\times 10^{-4}$	84.65	58.80
1$\times 10^{-3}$	72.58	50.58
1$\times 10^{-2}$	74.86	50.50

Radovici$^{(11)}$ classifies the inhibitors into 3 groups according to temperature effects :-

1) Inhibitors whose IE decreases with temperature increase and Ea greater than that in the uninhibited solution . This is can indication of physisorption .
2) Inhibitors whose IE does not change with the presence or absence of inhibitors.
3) Inhibitors whose IE increases with temperature and Ea is smaller for the inhibited solution, which is characteristic of chemisorption.

Also the interpreted the decreases of IE value with temperature increase as an indication for a physisorption type of adsorption$^{(12,13)}$. Therefore it can be concluded that Sulfasalazine (SS) are adsorbed on the C-steel surface by physisorption .

Polarization measurements

Polarization behavior of C-steel in 0.1M HCl and 0.1M NaCl in the presence and absence of Sulfasalazine (SS) at 25°C is shown in Figure 8 (A-H) where the x axis is current (μA/Cm^2) and axis y is voltage (mV). It was found that, both anodic and Cathodic reaction of C-steel electrode corrosion were inhibited with increasing concentration of synthesized inhibitors. These results suggest that not only the addition of synthesized inhibitors reduce anodic dissolution (anodic reaction) but also retard the hydrogen evolution reaction (Cathodic reaction). Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), Cathodic Tafel constant (βc) and anodic Tafel constant (βa) were calculated from Tafel plots. Data in Tables 7 and 8 represents the results of electrochemical parameters. The addition of inhibitors causes a decrease of the current density, the maximum decrease in I_{corr} was observed for (SS). The Ecorr values of (SS) inhibitor were shifted slightly toward both Cathodic and anodic directions and did not show any definite trend in 0.1M HCl and 0.1M NaCl. This may be contributed to the mixed –type behavior of the studied inhibitors. Moreover, these inhibitors caused change in the anodic and Cathodic Tafel slope indicating that, the inhibitors are affecting the anodic and Cathodic reaction mechanism without blocking the reaction sites of C-steel surface. Inhibition efficiency (%IE) was calculated by the relation$^{(14)}$:-

$$\%IE = [1 - \frac{I_{add}}{I_{free}}] \times 100 \quad \text{-------} \quad (4)$$

Where

I_{add} and I_{free} are the corrosion current in presence and absence of inhibitors. Data in Tables 8 and 9 shows that the inhibition efficiency increased with increasing the inhibitor concentration, indicating the inhibiting effect of these compound.

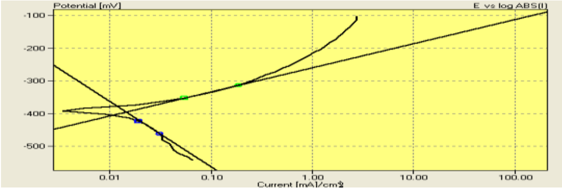


Figure 8 (A): Blank (0.1 M NaCl)

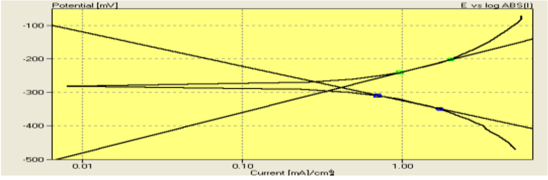


Figure 8 (B): Blank (0.1M HCl)

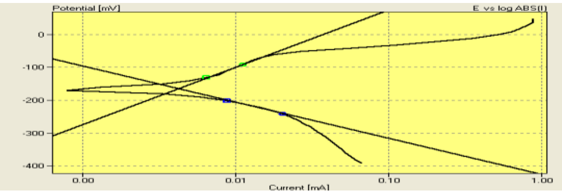


Figure 8 (C): 1×10^{-4}M of inhibitor

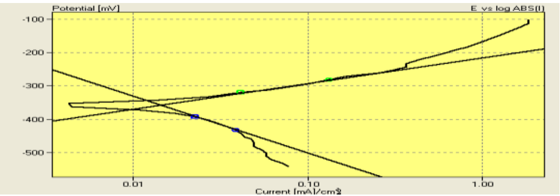


Figure 8 (D): 1×10^{-4}M of inhibitor

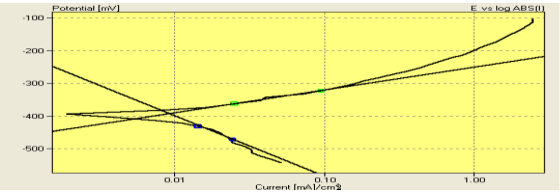


Figure 8 (E): 1×10^{-3}M of inhibitor

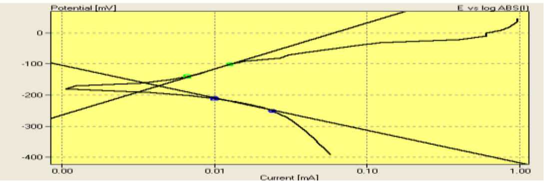


Figure 8 (F): 1×10^{-3}M of inhibitor

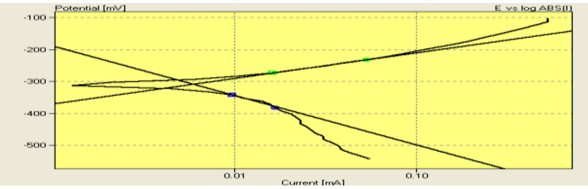


Figure 8 (G): 1×10^{-2}M of inhibitor

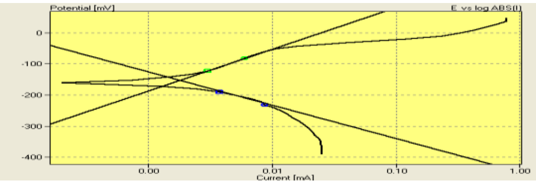


Figure 8 (H): 1×10^{-2}M of inhibitor

Figure 8 (A-H): Galvanostatic polarization curves of C-steel in 0.1M HCl and NaCl in Presence Inhibitor at 25°C

Table 8: The Values of corrosion parameters for the corrosion of C-steel in 0.1M HCl by galvanostatic polarization in presence (SS)

Conc (M)	Icorr μA/Cm^2	Ecorr mV	cβ mV.dec^{-1}	aβ mV.dec^{-1}	IE %
0.00	294.5	-330.9	-147.43	116.8	_
1×10^{-4}	61.20	-330.0	-75.0	54.0	79.22
5×10^{-3}	55.12	-297.7	-67.5	48.6	81.28
1×10^{-2}	40.01	-219.1	-49.0	35.3	86.41

Table 9: The Values of corrosion parameters for the corrosion of C-steel in 0.1M NaCl by galvanostatic polarization in presence (SS)

Conc (M)	Icorr μA/Cm^2	Ecorr mV	cβ mV.dec^{-1}	aβ mV.dec^{-1}	IE %
0.00	18.52	-165.5	-153.8	71.7	_
1×10^{-4}	7.43	-386.5	-194.0	99.2	59.88
5×10^{-3}	6.11	-317.8	-159.6	82.6	67.00
1×10^{-2}	4.21	-219.0	-109.9	56.9	77.26

4. Conclusions

The following conclusions could be predict from this study:-

1) The corrosion of C-steel in o.1M HCl and 0.1 NaCl is inhibited by the addition of Sulfasalazine (SS) drug.
2) The inhibition efficiency increases with increases in the concentration of Sulfasalazine (SS) drug.
3) The inhibition efficiency of Sulfasalazine (SS) drug decreases with the increases temperature and the activation corrosion energy increases in presence of the inhibitor.
4) The inhibition of corrosion by Sulfasalazine (SS) drug is due to physisorption on the metal surface.
5) Sulfasalazine (SS) drug act as mixed type of inhibitors.

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