Corrosion Inhibition of Mild-Steel in (1M) HCl using Spands Reagent

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ABSTRACT

The effect of Spands Reagent on the dissolution of Mild-steel in 1M HCl solution was studied using weight loss and galvanostatic polarization techniques. The inhibition efficiency of inhibitor increases with concentration to attain (75.26%) at concentration 1×10^{-2} M ,and standing time for 180 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 (64.53%) at concentration 1×10^{-2} M at 45°C and with standing time equal to 180 min. The effect of temperature on the rate of corrosion in the absence and presence of Spands Reagent was also studied. The Kinetic Parameters were 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, weight loss, galvanostatic polarization, Spands Reagent, Kinetic Parameters.**

1.INTRODUCTION

Acid solution are commonly used for removed of undesirable scale and rust in metal finishing industries, cleaning of boilers, and heat exchangers. Among these, hydrochloric acid is one of the most widely used agents in the process of acid pickling. Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solution to prevent unexpected metal dissolution and acid consumption[1]. A Mild- steel has been used widely in industry as material for reaction vessels, storage, tanks, etc. However, corrosion damage to mild steel causes heavy losses on the economy and potential problems in safety in work place[2,3].

Azo compound have attracted considerable attention due to their impressive and useful chemical and physical properties[4,5]. A part from their purely chemical interest, azo ligands have also received special attention because of their mixed soft-hard donor characters (O,N and S donor sites), versatile coordination behavior[6] pharmacological properties[7,8] and optical and thermal properties[9].

The aim of the present work is to study the inhibitive action of Spands Reagent toward the corrosion of Mild-steel in 1M hydrochloric acid using weight loss and galvanostatic polarization techniques. Moreover, the effect of temperature on the dissolution Mild-steel, as well as, on the inhibition efficiency of the studied compound was also investigated. The following Fig1 represent the structure of Spands Reagent 2-(p-sulphophenyl azo)-1,8-dihdroxynaphthalene-3,6-disulphonic acid trisodium salt

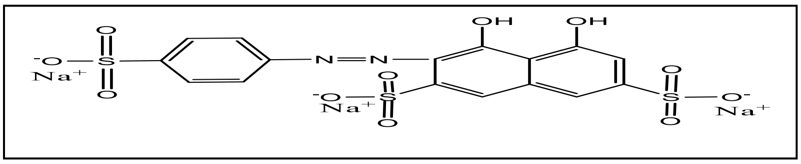

Fig1: The structure of Spands Reagent

2.Experimental method

The Mild-steel sample used coupons of with dimension of 3*2 *0.5 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. (1 M) A.R grade hydrochloric acid was used for preparing the corrosive solution. For weight loss experiments, the cleaned Mild-steel coupons were weighed before and after immersion in 25 ml of the test solution for a period of time 180 min. The weight loss for experiments was expressed in (gm). Galvanostatic polarization studies were carried out using Bank EIEIKTRONKIK INTELLGENT CONTROLS Model M Lab 200-Chemistry Department-College of Education for pure Sciences–Basrah University, 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

3. 1.Weight Loss Measurements

The percentage of inhibition efficiency %IE and surface coverage parameter (θ) and corrosion rate R_{corr} were determined by using following equation[10]:

$$\%IE = \left[\ 1 - \frac{Wadd}{Wfree}\right] \times 100 \quad ----------- \quad (1)$$

$$\theta = \left[1 - \frac{Wadd}{Wfree} \right] \qquad \text{-----------} \quad (2)$$

Where W_{free} and W_{add} are the weight losses of Mild-steel in absence and presence of inhibitors respectively.

$$R_{corr} = \frac{W*K}{A*D*t} \qquad \text{------------} \quad (3)$$

Where W: is the weight losses of metal(gram) , K: constant ($534*10^5$), A: sample area ($inch^2$), D: metal density (g/cm^3) and t: exposed time (hr).

The results of the measurements are shown in Tables 1 for the corrosion of Mild-steel in 1M HCl in the absence and in the presence of different concentrations of Spands Reagent at the temperature of 25°C. Fig2 represent the variation of the inhibition efficiency %IE as function of the time (180 min). The inhibition efficiency increased with increasing the inhibitor concentration.

Table 1: Effect of Spands Reagent on Dissolution Mild steel in 1M HCl

Conc. (M)	**Time (Min)**	**Wt-loss (gm)**	**Corr. Rate (mpy)**	**%IE**	**θ**
0	30	0.0024	123.82	-	-
	60	0.0032	82.51	-	-
	90	0.0055	94.55	-	-
	120	0.0063	81.22	-	-
	150	0.0073	75.29	-	-
	180	0.0093	79.93	-	-
1×10^{-4}	30	0.0011	56.75	54.16	0.5416
	60	0.0014	36.09	56.25	0.5625
	90	0.0022	37.82	60.00	0.6000
	120	0.0025	32.23	60.31	0.6031
	150	0.0028	28.88	61.64	0.6164
	180	0.0034	29.22	63.44	0.6344
1×10^{-3}	30	0.0010	51.59	58.33	0.5833
	60	0.0012	30.94	62.50	0.6250
	90	0.0020	34.38	63.63	0.6363
	120	0.0023	29.65	63.49	0.6349
	150	0.0025	25.78	65.75	0.6575
	180	0.0031	26.64	66.66	0.6666
1×10^{-2}	30	0.0007	36.11	70.83	0.7083
	60	0.0009	23.20	71.87	0.7187
	90	0.0015	25.78	72.72	0.7272
	120	0.0017	21.91	73.01	0.7301
	150	0.0019	19.59	73.97	0.7397
	180	0.0023	19.76	75.26	0.7526

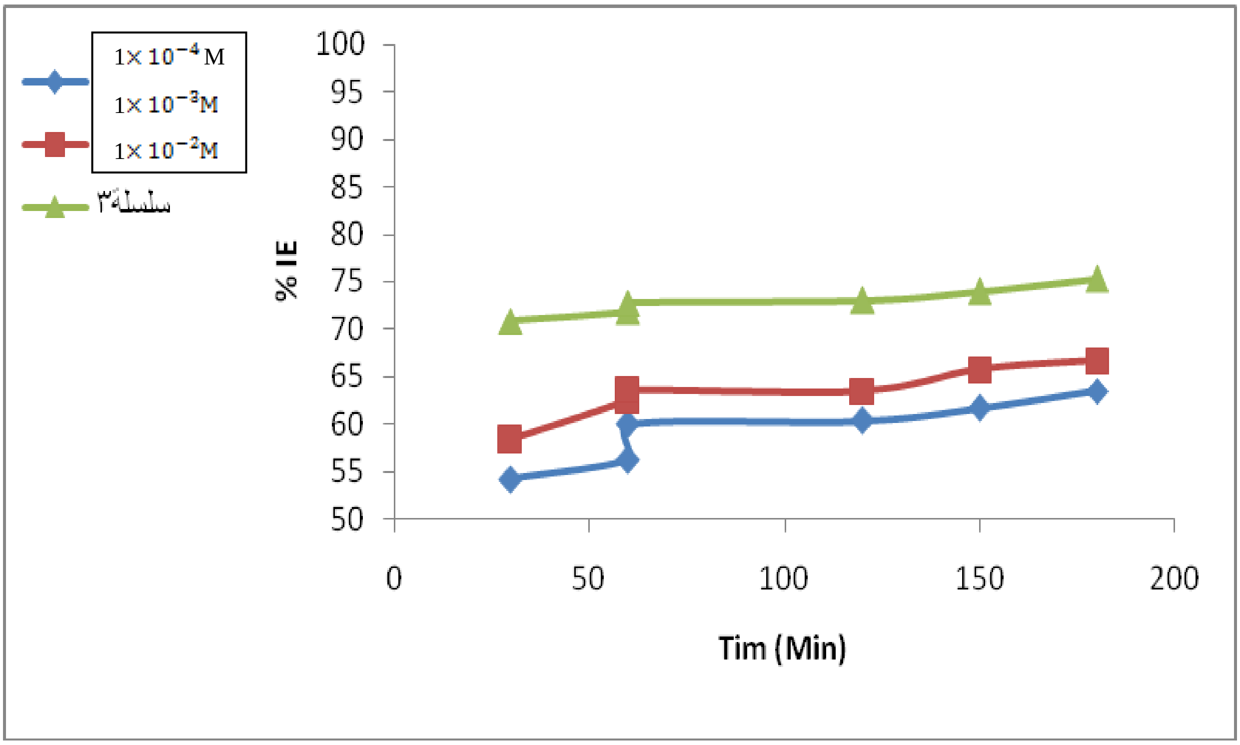

Fig2: Variation of the Inhibition Efficiency %IE as a function of the time in the presence of different concentrations of Spands Reagent at 25°C in 1M HCl

.3. 1. 2.Effect of Temperature

The influence of temperature on the behavior of Mild- steel/acid added of Spands Reagent at various concentrations is investigated by weight loss trends in the temperature range 25-45°C during 180 min of immersion. The variation of the inhibition efficiency of Spands Reagent with temperature is decreased with increasing temperature is suggestive physisorption mechanism which is effectively enhanced with increasing temperature[11]. The results of these measurements are shown in Tables2 . Figs3 represent the variation of the inhibition efficiency %IE as a function of the temperature .

Table 2: Effect of Spands Reagent on the dissolution Mild steel in 1M HCl in the different temperature

Conc. (M)	Temp (°C)	Wt-loss (gm)	Corr. Rate (mpy)	%IE	θ
0	25	0.0093	79.93	-	-
	35	0.0123	105.71	-	-
	45	0.0141	121.18	-	-
1×10^{-4}	25	0.0034	29.22	63.44	0.6344
	35	0.0050	42.97	59.34	0.5934
	45	0.0061	52.42	56.73	0.5673
1×10^{-3}	25	0.0031	26.64	66.66	0.6666
	35	0.0048	41.25	60.97	0.6097
	45	0.0058	49.85	58.86	0.5886
1×10^{-2}	25	0.0023	19.76	75.26	0.7526
	35	0.0038	32.66	69.10	0.6910
	45	0.0050	43.83	64.53	0.6453

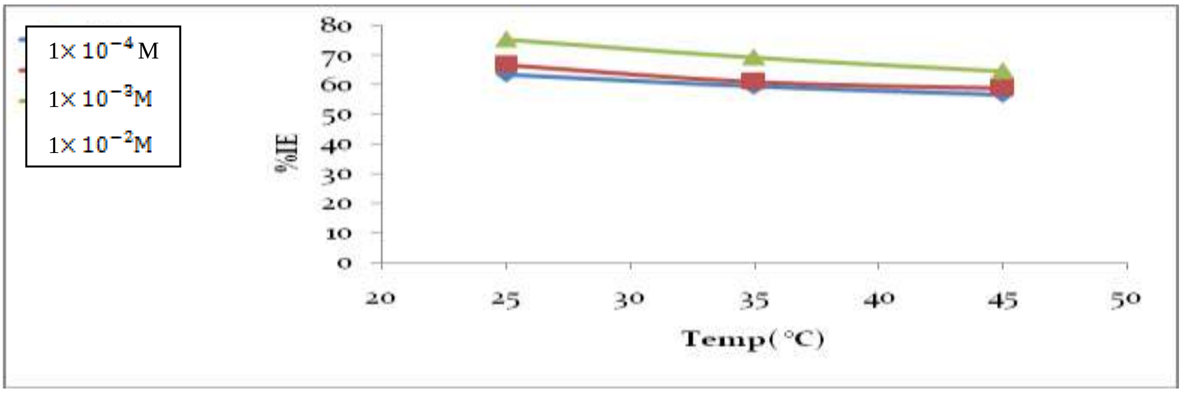

Fig3: Variation of the Inhibition Efficiency %IE as a function of the temperature in the presence of different concentrations of Spands Reagent in 1M HCl

3. 2 Kinetic Parameters

In order to obtain the effect of inhibitors on the kinetic parameters, gravimetric weight loss experiment were conducted at 25, 35 and 45°C in 1M HCl after 180 min of immersion in the absence and presence of Spands Reagent. The activation energy Ea of corrosion process was calculated using the following equation[12]:

$\ln(r_2/r_1) = (Ea\ (T_2-T_1)/R\ (T_2*T_1)$ ------------ (4)

Where

r_1= corrosion rate at 303 K

r_2= corrosion rate at 313 K

Ea= activation energy

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

T_1 and T_2= Absolute temperature (K)

Free energy of adsorption ΔG was calculated using the following equation[13]:

$\Delta G = -RT\ln[55.5\ \theta/C\ (1-\theta)]$ ---------- (5)

Where

θ = degree of coverage on the metal surface

C= concentration of inhibitor

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

T= Absolute temperature (K)

And For calculating the entropy ΔS and enthalpy ΔH apply the alternative formulation of the Arrhenius equation is the transition state equation[14]:

$Rcorr = \frac{RT}{Nh}\exp\left[\frac{\Delta S}{R}\right]\exp\left[-\frac{\Delta H}{RT}\right]$ ------------ (6)

Where

Rcorr= corrosion rate

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

T= temperature (K)

N= Avogadro 's number (6.2×10^{23})

h= plank 's constant (6.62×10^{-34} J.S)

The results of these measurements are shown in Tables3.

Table3 : kinetic parameters of Spands Reagent on the dissolution Mild steel in 1M HCl

Conc (M)	Temp (K)	Spands Reagent			
		Activation parameters ($KJmol^{-1}$)			
		Ea	ΔH	-ΔS	-ΔG
Blank		21.33	0.0140	0.1611	
1×10^{-4}	298	29.42	0.0201	0.1499	34.13
	308				34.83
	318				41.77
1×10^{-3}	298	33.36	0.0220	0.1432	23.07
	308				29.11
	318				29.82
1×10^{-2}	298	38.34	0.0290	0.1221	24.11
	308				24.13
	318				24.37

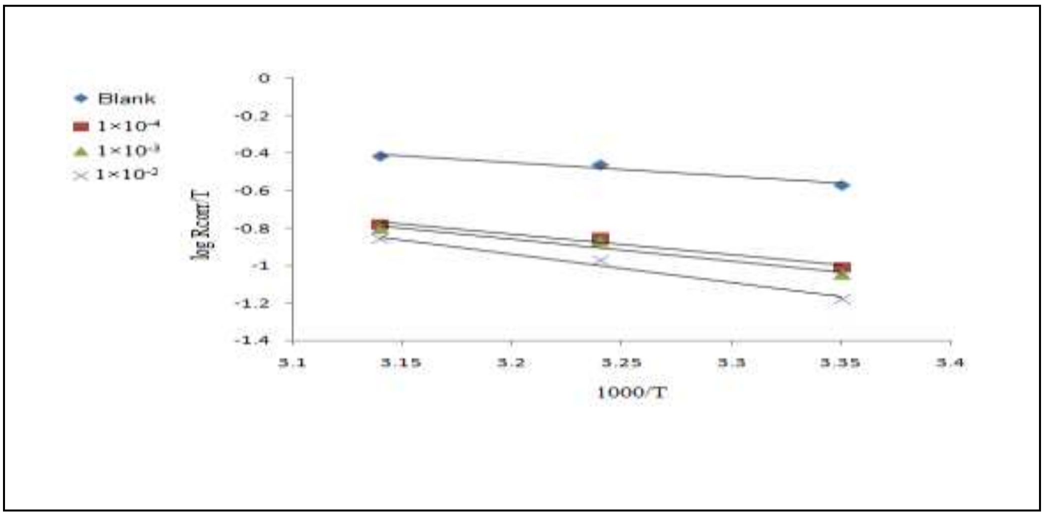

Fig4 : Arrhenius Plots Log R_{corr} ⁄ T) vs. 1⁄ T for Mild-steel in Different Additives of Inhibitor Spands Reagent

The values of Ea are give in Table3 the values of Ea increase in the presence of the inhibitors. This was attributed to an appreciable decrease in the adsorption process of the inhibitor on the metal surface with increase of temperature and corresponding increase in the reaction rate because of greater area of the metal that is exposed to HCl solution. Fig4: shows Arrhenius Plots Log R_{corr}/T) vs 1⁄T. Straight lines are obtained with a slop of (-ΔH/2.303R) and an intercept of (log R/Nh+ΔS/2.303R) from which the values of ΔH and ΔS are calculated and listed in Table3.

From inspection of Table (3) it is clear that the positive values of ΔH reflect that the process of adsorption of the inhibitors on the Mild–steel surface is an endothermic process. The value of ΔS in the presence and absence of the inhibitors are negative. This implies that the activation complex is the rate determining step representing association rather than dissociation, indicating that a decrease in disorder takes place on going from reactant to the activated complex[15].

The negative values of ΔG means that the adsorption of Spands Reagent on Mild-steel surface is a spontaneous process, and furthermore the negative values of ΔG also show the strong interaction of the inhibitor molecules on to the Mild-steel surface[16].

It was found that ΔG increases negatively with increasing the temperature. This phenomenon once again indicates that the adsorption is favourable with increasing experimental temperature and dominates on the desorption of the inhibitor from the Mild-steel surface[17].

.3. 3. Adsorption Isotherm

Adsorption isotherms are very important in understand the mechanism of inhibition of corrosion reaction. The most frequently used adsorption isotherm are Frundlich, Langmuir, Frumkin, and Temkin isotherm. The best fitted one follows Langmuir isotherm. Plotting (C/θ) versus concentration (C) give rise to straight lines as shown in Fig.5. The inhibitor Spands Reagent adsorbs on the Mild-steel surface according to the Langmuir kind isotherm model by the relation[18]:

$C/\theta = 1/K + C$ ------------- (7)

Where

K= is the equilibrium constant of the adsorption process.

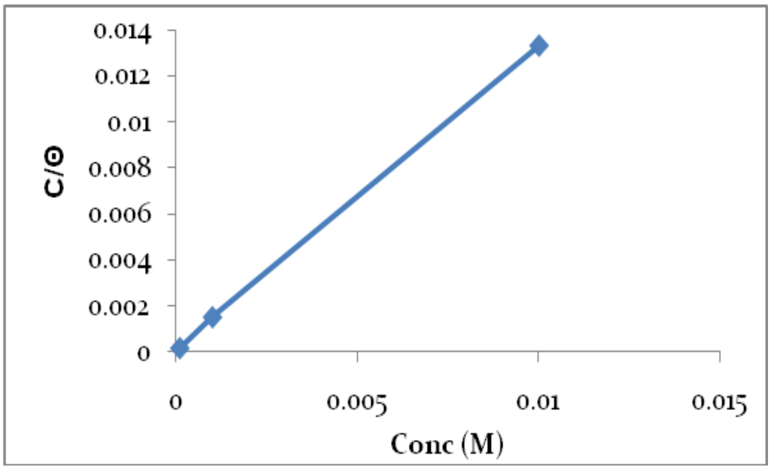

Fig5: Langmuir Adsorption Isotherm Model for Spands Reagent in1M HCl on the Surface of Mild- Steel

3 . 4. Polarization Measurements

Polarization behavior of Mild-steel in 1 M HCl in the presence and absence of Spands Reagent 25°C is shown in Fig.6.It was found that both anodic and cathodic reaction of Mild-steel electrode corrosion were inhibited with increasing concentration of inhibitor. These results suggest that not only the addition of inhibitor reduce anodic dissolution but als o retard the hydrogen evolution 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 Tables4 the results of electrochemical parameters. The addition of inhibitor causes a decrease of the current density, the maximum decrease in I_{corr} was observed for Spands Reagent. The E_{corr} values of Spands Reagent inhibitors were shifted slightly toward both cathodic and anodic directions and did not show any definite trend in 1 M HCl. This may be contributed to the mixed –type behavior of the studied inhibitors. Moreover, these inhibitor caused change in the anodic and Cathodic Tafel slope indicating that the inhibitor are affecting the anodic and cathodic reaction mechanism without blocking the reaction sites of Mild-steel surface. Inhibition efficiency (%IE) was calculated by the relation[19]:

$\%IE = [1 - \frac{I_{add}}{I_{free}}] \times 100$ ----------- (8)Where

I_{add} , I_{free} are the corrosion current in absence and presence of inhibitors.Data in Table 4 shows that the inhibition efficiency increased with increasing the inhibitor concentration , indicating the inhibiting effect of these compounds .

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Table 4 : The Values of corrosion parameters for the corrosion of Mild-steel in 1M HCl by galvanostatic polarization in presence (Spands Reagent)

Conc (M)	Icorr $\mu A/Cm^2$	Ecorr mV	βc $mV.dec^{-1}$	βa $mV.dec^{-1}$	IE %
0.00	210.0	-420.5	-111.0	98.8	–
1×10^{-4}	70.8	-448.1	-120.8	68.3	66.28
1×10^{-3}	65.9	-475.3	-118.5	60.9	68.61
1×10^{-2}	50.5	-461.0	-125.3	61.4	75.95

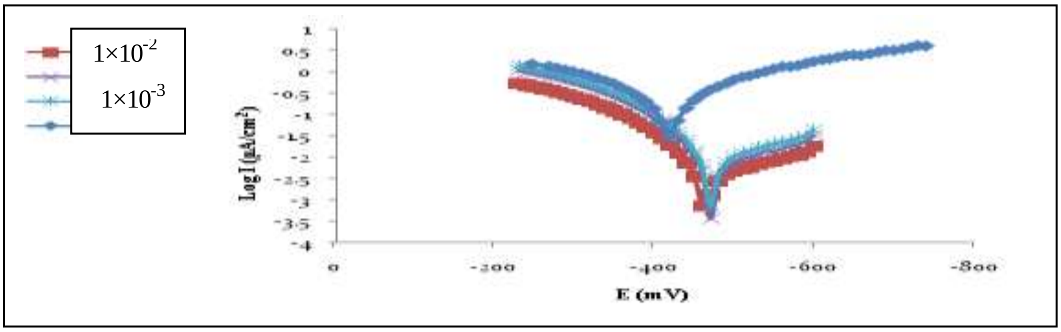
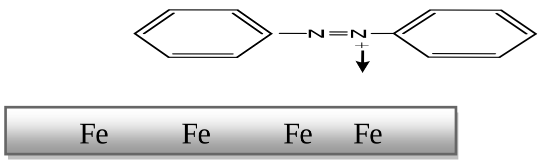


Fig6: Galvano static polarization curves of Mild-steel in 1M HCl in Presence Inhibitor Spands Reagent at 25°C

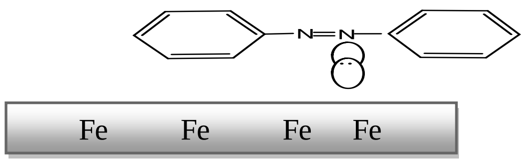
3. 5. Mechanism of Inhibition

From the results obtained from electrochemical and weight loss measurements , it was concluded that the (Spands Reagent) inhibit the corrosion of Mild-steel in 1M HCl by adsorption at Mild-steel solution interface. It is general assumption that the adsorption of organic molecules may adsorb on the metal surface in four types, namely[20,21].

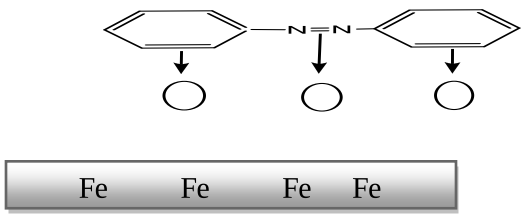
1-Electrostatic interaction between the charged molecules and the charged metal.



2- Interaction of unshared electron pairs in the molecule with metal.



3- Interaction of pi-electrons with the metal.



4-A combination of types (1,3).

4. Conclusions

The following conclusions could be predict from this study:

1- The corrosion of Mild-steel in 1M HCl is inhibited by the addition of Spands Reagent

2- The inhibition efficiency increases with increases in the concentration of these compounds.

3- The inhibition efficiency of Spands Reagent decreases with the temperature and the activation corrosion energy increases in presence of the inhibitor.

4- The inhibition of corrosion by Spands Reagent is due to physisorption adsorption on the metal surface.

5- Spands Reagent act as mixed type of inhibitors , and obey Langmuir adsorption isotherm .

5. References

1- Ashassi-sorkhabi . H, Seifzadeh . D and Hosseini . M . G, **Corrosion .Science** ,50, 3363-3370 (2008).

2- Migahed . M. A, Abdul- Raheim . A . M, Atta . A . M and Brostow . W, **Materials chemistry and physics**, 121, 208-214 (2010).

3- Asefi . D, Arami . M and Mahmoodi . N, **Corrsion Science**, 52, 3586-3598 (2010).

4- Ispir .E, **Dye pigment**, 82,13 (2009).

5- Khanmohammadi. H and Darvishpour . M, **Journal of Inorganic and Organometallic polymers and Materials**, 21,541(2011).

6- Dinc . H, aple, Toker . F, Durucasu . I , Avcibas . N, and Icli . I . S, **Dye pigment**, 75, 11 (2007).

7- Odabas . M, Og ˇlu, Albayrak . C , Özkanca . R, Aykan . F . Z and Lonecke . P, **Journal of Molecular structure**, 71, 840 (2007).

8- Zhang . D, Zang . M , Liu . Z, Xu . M, Li . F, Yi . T and Huang . C, **Tetrahedron Lett**, 47, 7093 (2006).

9-Pattanyak . P, Pratihar . J . L, Patra . D, Uranik . V . G and Chatto-padhyay .S, **Polyhedron,** 27, 2209 (2008).

10- Kadim . M . Y, Abdulsada . A . M and Alshawi J . M . S, **Journal of Basrah Researches ((Sciences)),** 40(3), 108-127(2014).

11- Abdallah . M, Fouda . A . S, Shama . S . A and Afifi . E . A, **African Journal of Pure and Applied Chemistry**, 2(9), 083-091 (2008).

12- Eddy. N .O and Odoemelam . S . A, **African Journal of Pure and Applied Chemistry**, 2, 132 (2008).

13- Hosseini . S . M . A , Azimi . A, Sheikhshoaei . I and Salari . M, **Journal of Iranian chemical Society**, 7, 799-806 (2010).

14- Noor . E . A and Al. Moubaraki . A . H, **Materials chemistry and physics**, 110,145-154 (2008).

15- Al-Juaid . S . S, **Portugaliae ElectrochimicaActa**, 25, 363-373 (2007).

16- Elachouir . M, Hajji . M . S, Salem . M, Kertit . S, Aride . J, Coudert . R and Essassi . E, **Corrosion**, 52, 103, (1996).

17- Savitri . B . V and Mayanna . S, **Indian Journal of chemical Technology**, 3, 256, (1996).

18- Langmuir . I and Amer . J, **chemical Society**, 39, 1848 (1947).

19- Zaafarany . I . A, **International Journal of Corrosion and Scale Inhibition** , 3(1), 12-27 (2014).

20- Li .X. H, Deng . S . D, Fu . H and Mu . G . N, **Journal Applied Electrochem**, 39.1125 (2009).

21- Lowmunkhong . P, Vngthararak . D and Sutthivaiyakit . P, **Corrosion Science**, 52, 30 (2010).