Available Online at http://www.recentscientific.com

International Journal of Recent Scientific Research
Vol. 6, Issue, 7, pp.5445-5453, July, 2015

International Journal of Recent Scientific Research

ISSN: 0976-3031

RESEARCH ARTICLE

SUDAN III AS CORROSION INHIBITOR FOR CARBON STEEL ST37-2 IN H_2SO_4SOLUTIONS

S.A .Hassan and A. K. Hadi*

Department of Chemistry, Faculty of Education for Girls ,University of Kufa, P.O. Box190 , Iraq
Al-Najaf –Al-Ashraf ,Iraq

ARTICLE INFO

Article History:

Received 14th, June, 2015
Received in revised form 23th, June, 2015
Accepted 13th, July, 2015
Published online 28th, July, 2015

Key words:

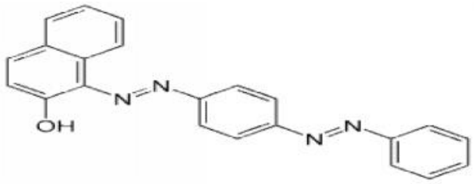
carbon steel(ST37-2) , Corrosion inhibition , Adsorption process, azo dyes ,sudan III

ABSTRACT

A study on the use of sudan III dye as corrosion inhibitor for carbon steel ST37-2 in aerated 0.01,0.5x10^{-5} M H_2SO_4solutions has been carried out by using potentiodynamic polarization technique. The corrosion parameters such as, corrosion rates, corrosion potential ,corrosion current ,inhibition efficiency and Tafel slopes were evaluated. The effect of temperature on the corrosion behaviour of carbon steel in H_2SO_4 solutions with and without addition of 5,25,50,100 and 150ppm of sudan III was studied in the temperature range 303-333 K. It was found that sudan III has been proved to be good inhibitor in 0.01 , 0.5x10^{-5}M H_2SO_4 attaining its highest efficiency, 50% and 99% respectively and though temperature rising. This reduction in the corrosion rate was due to the formation of an external layer formed by sudan III which was adsorbed physically and chemically on the carbon steel ST37-2 surface. Sudan III acted as a mixed type of inhibitor. Values of the activation energies (Ea), enthalpies (ΔH^*),Gibbs free energies (ΔG^*),entropies of activation (ΔS^*),besides the thermodynamic parameters of corrosion and adsorption provided evidence of the inhibitory effect of sudan III. Langmuir isotherm model fitted well the adsorption process onto carbon steel surface in H_2SO_4 solutions.

INTRODUCTION

Many authorities consider that the term corrosion is the degradation of a material's properties or mass over time due environmental effects. It is the natural tendency of a material's compositional elements to return to their most thermodynamically stable state. For most metallic materials, this means the formation of oxides or sulfides, or other basic metallic compounds generally considered to be ores. Under normal circumstances, iron and steel corrode in the presence of both oxygen and water. If either of these materials is absent, corrosion usually will not take place i.e.; only inert atmospheres andvacuumscan be considered free of corrosion for most metallic materials (1).In the field of corrosion science , the ferrous metals and alloys had the priority and the majority of corrosion studies deal with iron , cast iron , carbon steel , and various other iron alloys because. It is used in the manufacture of the most parts of the maritime transport , land transport as well as oil pipeline transport , structures of buildings and bridges. Also there are many industrial systems and commercial applications that inhibitors are applicable, such as cooling systems, refinery units, pipelines, chemicals, oil and gas production units , boilers and water processing ,paints ,pigments, lubricants, etc(2) .Corrosion inhibition of metals or alloys by organic compounds is a result of adsorption of organic molecules on the surface to forma protective thin film. This film reduces or prevents the corrosion of the metal or alloys. The inhibition ability depends on the nature of the metals or alloys , the chemical structure of the inhibitor and the type of corrosive media(3) . Many dyes and indicators are used in scientific research , home , industry and foodstuffs. (sudan III) dye is one of those which classified as synthetic azo-dye it has many industrial and scientific applications such as coloring of fuel and staining for microscopy (4). Sudan dye isused in plastics, oil and waxes due to its low cost and availability(5). Some studies in the literature have been studied the ability of some indicators ,organic dyes and drugs as corrosion inhibitors for various alloys and metals at different environments (6-12). Little studies on the interaction of(sudanIII) onto surfaces has been reported(13-15) .The aim of this research is concerned with the electrochemical study of carbon steel corrosion in H_2SO_4 solutions with and without addition of (5-150 ppm) of (sudan III) dye as inhibitor at different pH and temperatures under static conditions . The structure of the inhibitor molecule is given below(16):



---

*Corresponding author: **A. K. Hadi**
Department of Chemistry, Faculty of Education for Girls ,University of Kufa, P.O. Box190 , Iraq Al-Najaf –Al-Ashraf ,Iraq

Chemical structure of Sudan III. 1-(4-(phenyl diazenyl)phenyl) azonaphthalen-2-ol

Experimental

MATERIALS AND SOLUTIONS

Carbon steel electrodes

The carbon steel ST 37-2 specimen of composition (wt% : C max.0.17 %,Mn max. 1.40 %,P max 0.045 %,Si max.0.3% ,S max.0.045% and Fe max.98.04 %) was used for the study which have a rectangular form (2cm x 1.5cm x 0.2 cm) are polished with a series of emery papers of various grades from (100-1200) washed with distilled water, rinsed with acetone and drying at room temperature

Corrosive environment solutions

The aggressive solutions (0.01,0.5x10^{-5}M H_2SO_4) was prepared by dilution of analytical grade 98% H_2SO_4solution with distilled water.

Inhibitor Preparation

The concentration of (sudan III) employed ranged from (5 to 150 ppm) were prepared from analytical- grade of sudan III in 10 ml ethanol and complete the volume with distilled water.

polarization measurements

The electrochemical experiments were performed in a conventional three electrode electrolysis cylindrical pyrex glass cell. The working electrode was a carbon steel ST37-2 in the form of disc has a surface area of 1 cm^2, platinum electrode and calomel electrode were used as auxiliary and reference electrodes. The temperature is thermostatically controlled. The studies were performed by using potentiostat / galvanostat model M-Lab200 under computer control. The potentiodynamic current – potential curves were recorded by changing the electrode potential automatically from -300 mv to +300mv to at a scan rate of 2mvs-^{1}.Corrosion rate W ($g\cdot m^{-2}.day^{-1}$),inhibition efficiency (%IE), and the degree of surface coverage (Ө) were obtained by weight loss measurements and galvanostatic polarization by using the following equations(17-20) :

$\%IE = [I_{corr}-(I_{inh}/ I_{corr})] \times 100$

$\%IE = [W_{corr} – (W_{inh} /W_{corr})] \times 100$

$\%IE = [R_{p\ corr} – (R_{pinh} /R_{pcorr})] \times 100$

$\Theta = [W_{corr} –(W_{inh} /W_{corr})] = [I_{corr}- (I_{inh}/ I_{corr})] = [R_{p\ corr} – (R_{pinh} /R_{pcorr})]$

$\%IE = \Theta \times 100$

where I_{corr} ,I_{inh}Wcorr, Winh , $R_{p\ corr}$ and $R_{pinh}$are,current densities ,the corrosion rates and polarization resistance of the carbon steel in the absence and presence of the (sudan III), respectively.

RESULTS AND DISCUSSION

Effect of Sudan III Concentration

The effect of sudan III concentration on the weight loss results for carbon steel in 0.01, 0.5x10^{-5} M H2SO4 at the temperature range 303-333K are given Table 1, 2 where it can be seen in general that as the inhibitor concentration increases the weight loss decreases ,but in 0.01M H2SO4 with a further increase in the sudan III concentration (at 150ppm) the weight loss increase once again. Also it can be seen that the weight loss increases with increasing in the temperature, which might be due to inhibitor degradation with the temperature. Furthermore the values of inhibitor efficiency(IE%) at 303K in (0.01M H_2SO_4) increases from 27.7% to 50 % with increasing in sudan III concentration from 5 to 25ppm, and it remains constant up to 150ppm the (IE%) was decreased . while the inhibitor efficiency(IE%) at constant concentration decreases with increasing temperature which indicates that the increase in the corrosion rate.In 0.5x10^{-5} M H_2SO_4values of the inhibition efficiency (IE%) in general were independent on temperature and concentration, among the compounds studied (sudan III) exhibited the best performance in (0.5x10^{-5} M H_2SO_4) giving more than 99 % inhibition efficiency, generally we can interpretate this variation if consider the first step during the adsorption of an organic inhibitor on a metal surface usually involves replacement of water molecules adsorbed on the metal surfaceas shown in the following equations :(21)

$Sudan\ III\ sol. + xH_2O_{ads} sudanIII_{ads} + X\ H_2Osol$

$FeFe^{2+} + 2e \quad \Rightarrow$

The sudan III dye will combine with Fe^{2+} ions on steel surface, forming metal-inhibitor complexes:

$Fe^{2+} + sudIII_{ads}[Fe\text{-}sudanIII]_{ads}^{2+} \quad \longrightarrow$

The resulting complex, depending on its relative solubility, can either inhibit or catalyze further metal dissolution or increase its corrosion rate.

polarization measurements

Figures (1-8) show the typicalpolarization curves for carbon steel(ST 37-2)in (0.01 , 0.5x10^{-5}M H_2SO_4) in the absence and presence of different (sudan III) concentrations (5 – 150 ppm) at four temperatures in the range (303-333)K. In general it is clear from this Figures that both anodic metal dissolution and cathodic H_2 reduction reactions were inhibited when the (sudan III)was added and the cathodic polarization curves rise to parallel Tafel lines indicating that the hydrogen evolution reaction is activationcontrolled. The electrochemical parameterssuch as, corrosion potential (Ecorr.),corrosion current density(Icorr) , anodic and cathodicTafel slopes (βa, βc), degree of surface coverage and inhibition efficiency values were calculated and are given in Tables (1-2).It was observed from the data that (sudan III) addition caused a slightdeccrease in the corrosion current densities for carbon steel as the concentration increased at constant temperatures ,and increasing temperature at constant (sudan III) concentrations lead to increasein the I_{Corr} and shifted E_{Corr} to slightly active direction in both acid concentrations (0.01,

$0.5x10^{-5}$ MH_2SO_4). The values of theTafel slopes (βa and βc) varied with increasing in the temperature from (303 to 333)K. A departure in($β_a$ and $β_c$) may be attributed to the variation of the rate –determining step for the metal dissolution reaction or of a change in the mechanism of anodic and cathodic reaction. This results indicate that (sudan III) is adsorbed on the metal surface on the cathodic sites with resulting inhibition of hydrogen reductionand acts as a mixed type inhibitor. many researchers have been reported in literature this observation(22-24).

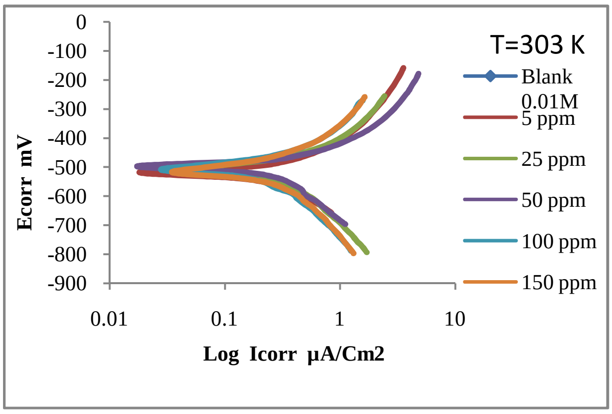


Figure1 Polarization curves of the carbon steel (ST 37-2) in (0.01 H_2SO_4)solution and in the presence of different concentrations of sudan I the temperature 303K.

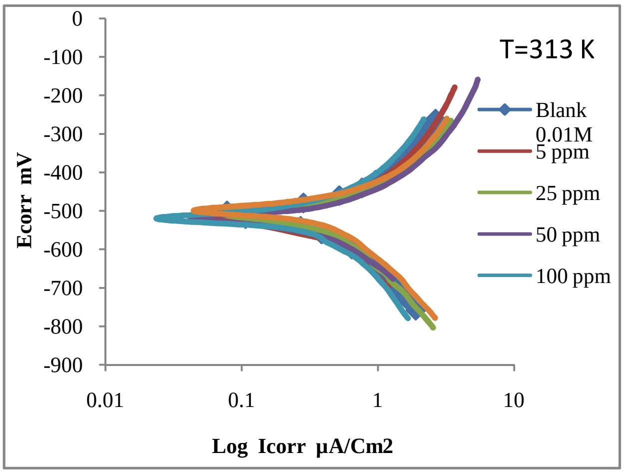


Figure 2 Polarization curves of the carbon steel (ST 37-2)in(0.01 M H_2SO_4)solution and in the presence of different concentrations sudan III dye at the temperature 313K..

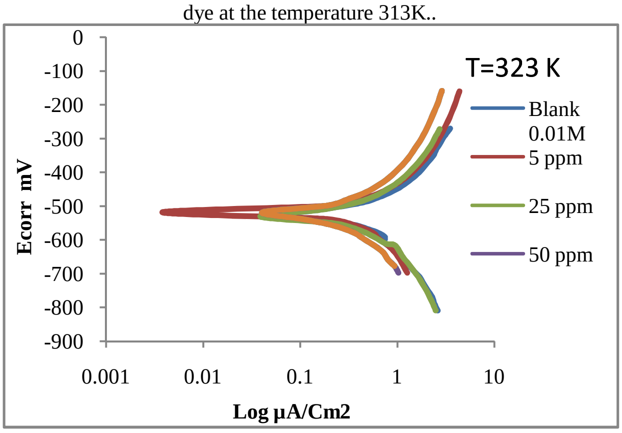


Figure 3 Polarization curves of the carbon steel (st 37-2) in(0.01 M H_2SO_4) solution and in the presence of different concentrations of (sudan III) dye at the temperature 323K .

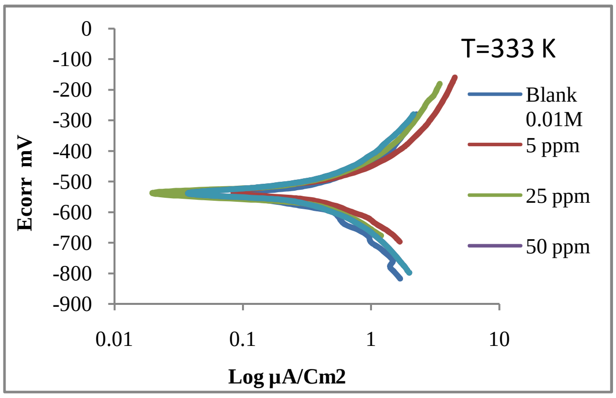


Figure 4 Polarization curves of the carbon steel (ST37-2) in(0.01 M H_2SO_4)insolution and inthe presence of different concentrations of sudan(sudanIII) dyeat the temperature333K.

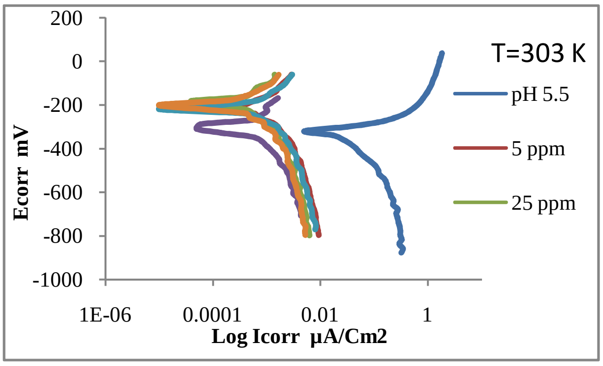


Figure 5 Polarization curves of the carbon steel (ST 37-2) in($0.5x10^{-5}$M H_2SO_4) solution and in the presence of different concentrations of sudan III dye at thetemperature 303K.

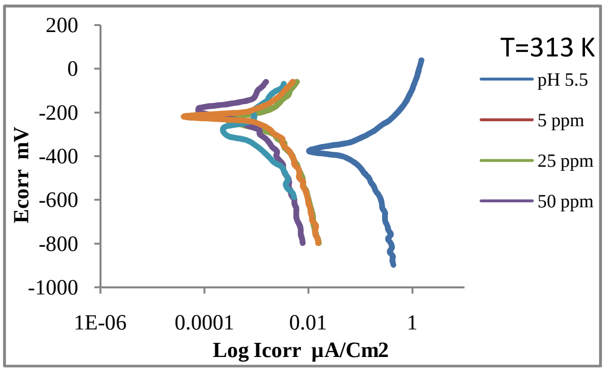


Figure 6 Polarization curves of the carbon steel (st 37-2) in ($0.5x10^{-5}$ M H_2SO_4) solution and in the presence of different concentrations of (sudan III) dye at the temperature 313K.

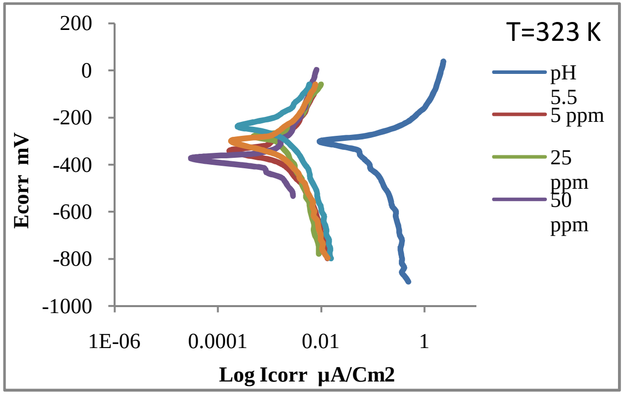


Figure 7 Polarization curves of the carbon steel (ST 37-2) in ($0.5x10^{-5}$M H_2SO_4) solution and in the presence of different concentrations of (sudan III)dye at the temperature 323K

Table 1 polarization parameters for the corrosion of carbon steel(ST37-2) by different concentrations of (Sudan III) in(0.01 M H_2SO_4) at the temperature range (303-333)K .

Tem. K	Inhibitor Con. PPM	E_{corr} mV	I_{corr} x10^{-6} A/Cm^2	β_c mV/Decade	β_a mV/Decade	Weight loss g/m^2.d	Penetration loss mm/y	IE %	θ
303	0	-503.7	301.00	-334.0	201.6	75.2	3.49	0	0
313		-517.7	384.33	-334.5	264.9	96.1	4.46	0	0
323		-519.7	451.24	-332.1	215.7	113	5.24	0	0
333		-539.0	496.48	-493	322.3	124	5.76	0	0
303	5	-513.4	217.53	-242.9	149.1	54.4	2.52	27.7	0.277
313		-516.3	260.82	-240.2	160.1	65.2	3.03	32.1	0.321
323		-523.8	280.48	-206.9	177.2	70.1	3.26	37.8	0.378
333		-5.36.4	310.72	-180.4	177.4	77.7	3.61	37.4	0.374
303	25	-511.1	150.23	150.1	130.1	37.6	1.74	50	0.50
313		-508.8	208.37	-165	110	52.1	2.42	45.7	0.457
323		-532.4	262.89	-172.4	189.8	65.7	3.05	41.7	0.417
333		-541.8	312.21	-160.6	167.8	78	3.62	37.1	0.371
303	50	-497.6	150.79	-180.5	91.3	37.7	1.75	49.9	0.499
313		-523.5	209.43	-167.8	130.7	52.4	2.43	45.5	0.455
323		-535.6	262.12	-242.8	254.7	65.5	3.04	41.9	0.419
333		-537.6	284.29	-213.4	206.5	71.1	3.30	42.7	0.427
303	100	-509.7	150.95	-229.1	164.4	37.7	1.75	49.8	0.498
313		-519.7	202.7	-191.2	181.1	50.7	2.35	47.4	0.474
323		-532.4	230.56	-170.1	179.1	57.6	2.68	48.9	0.489
333		-543.9	276.01	-182.7	165.5	69.0	3.20	44.4	0.444
303	150	-505.6	199.38	-308.5	198.2	49.8	2.31	33.7	0.337
313		-522.9	223.66	-176.9	129.4	55.9	2.6	41.8	0.418
323		-533.6	287.86	-253.3	224.36	72	3.34	36.2	0.362
333		-544.1	320.39	-253.8	271.7	80.1	3.72	35.4	0.354

Table 2 polarization parameters for the corrosion of carbon steel ST37-2 by different concentrations of (Sudan III) in (0.5x10^{-5} M H_2SO_4) at the temperature range (303-333)K .

Tem. K	Inhibitor Con. PPM	E_{corr} mV	I_{corr} x10^{-6} A/Cm^2	β_c mV/Decade	β_a mV/Decade	Weight loss g/m^2.d	Penetration loss mm/y	IE %	θ
303	0	-325.1	42.43	-399	94.6	10.6	0.493	0	0
313		-377.2	65.45	-372.2	197.8	16.4	0.760	0	0
323		-310	114.58	-820.1	157.2	28.6	1.33	0	0
333		-414.9	172.53	-435	173.8	43.1	2.00	0	0
303	5	-199.7	0.660	-268.5	199.6	0.165	0.00767	98.4	0.984
313		-242.9	0.748	-142.4	161.2	0.187	0.00868	98.8	0.988
323		-351	1.03	-224.9	239.1	0.258	0.012	99.1	0.991
333		-355.2	1.16	-160	179.8	0.289	0.0134	99.3	0.993
303	25	-187.6	0.283	-187.8	180.1	0.071	0.00329	99.3	0.993
313		-204.7	0.492	-246.8	300.7	0.123	0.00572	99.2	0.992
323		-302.1	1.09	-227.7	171.2	0.272	0.00126	99	0.99
333		-394.5	2.16	-330.9	390.2	0.539	0.0250	98.7	0.987
303	50	-314	0.354	-174.5	216.2	0.0886	0.00412	99.1	0.991
313		-280.6	0.481	-195.5	218.4	0.12	0.00559	99.2	0.992
323		-388.7	0.969	-275	339	0.242	0.0113	99.1	0.991
333		-417.6	1.32	-290.5	322.6	0.33	0.0153	99.2	0.992
303	100	-226.3	0.340	-105.8	151.9	0.0852	0.00396	99.1	0.991
313		-214.6	0.486	-119.8	114.1	0.120	0.00565	99.2	0.992
323		-239	0.921	-179.1	190.2	0.230	0.0107	99.1	0.991
333		-423.3	1.36	-162.8	151	0.339	0.0158	99.2	0.992
303	150	-193.6	0.213	-159.1	120.8	0.0534	0.00248	99.4	0.994
313		-194.4	0.367	-130.7	160.5	0.0918	0.00426	99.6	0.996
323		-318.6	0.557	-115.5	148.9	0.139	0.00647	99.5	0.995
333		-357	0.845	-202.4	206.9	0.211	0.00982	99.5	0.995

Values of the inhibition efficiency (IE%) were dependent on temperature , among the compounds studied (sudan III) exhibited the best performance in (0.5x10^{-5} M H_2SO_4) giving more than 99 % inhibition efficiency at the temperature range (303-333)K, while the values of inhibition efficiencies (IE%)in(0.01M H_2SO_4) decreases with increasing (sudan III)concentrations then almost becomes independent with increasing the concentration up to100 ppm then decreases , maximum efficiency percent attain to 50 at 303K and (sudan III) concentration is 25 ppm .

Kinetics of Corrosion

The effect of temperature on the rate of corrosion has been studied over the temperature range from (303to 333) K using the Arrehenus equation (20) :

$$\text{Log } i_{corr} = \log A - E_a/2.303RT$$

Where A is the Arrhenius constant, $E_a$activation energy, R the gas constant and T the absolute temperature of the solution . Figs (9 - 10) show the logarithms of(i_{corr})plotted against (1/T)for carbon steel (ST37-2) in(0.01 , 0.5x 10^{-5} M H_2SO_4)

in the presence of different concentrations of sudan III. The results are shown to be almost a linear dependence.

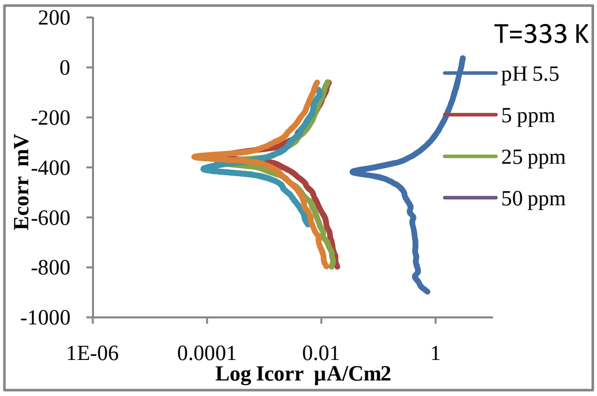


Figure 8 Polarization curves of the carbon steel (ST 37-2) in ($0.5x10^{-5}$ M H_2SO_4) solution and in the presence of different concentrations of (sudan III) dye at the temperature 333K.

In order to obtain more information on the corrosion process in free acid and in the presence of adsorbed sudan III dye , another activation parameters such as enthalpy of activation (ΔH^*), entropyof activation(ΔS^*) , Gibbs free energy of activation(ΔG^*) can be calculated using the relationships (19, 25-27):

$$i_{corr} = RT / Nh \exp(\Delta S^* / R) \exp(-\Delta H^* / RT)$$

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

Where N is Avogadro's number , h is Plank's constant . Figs.(11-12) show Log i_{corr} / T are plotted against (1 / T) ,the results are shown a linear relationship with a slopes ($-\Delta H^*/2.303$ R)andintercepts of (logR / Nh + $\Delta S^*/2.303$ R) . The values of activation parameters E_a ,A ,ΔS^* ,ΔG^* and ΔH^* are listed in Tables (3 - 4) The positive values of ΔH^* for dissolution reaction of carbon steel in 0.01 , $0.5x10^{-5}$ M H_2SO_4 in the presence and in the absence of sudan III show the endothermic nature of the dissolution process suggesting that the dissolution of carbon steel is slow (28).

The negative value of ΔS^*in the absence and presence implies that the activated complex is the rate determining step, which represents an association step rather than dissociation step. In the presence of the inhibitor, the values of ΔS^*increases and is generally interpreted as an increase in disorder as the reactants are converted to the activated complexes (29,30).

A linear relationship was found to exist between the experimental values of log A and the corresponding values of E_a for carbon steelST37-2 corrosion in different (sudan III) concentrations in(0.01 , 0.5 x 10^{-5} M H_2SO_4) as shown in Figs.(13 -14)which could be expressed as (26) :

$$\ln A = b + a E_a$$

Where a and b are constants .Such a relationship istermed a “compensation effect “which is observed in both homogeneous and heterogeneous catalysis when experimental Arrhenius parameters ,A and $E_a$obey a simple linear relationship. The effect is notced generally either for the same reaction and a group of similar catalysts or for the same catalyst and a family of similar reactions.

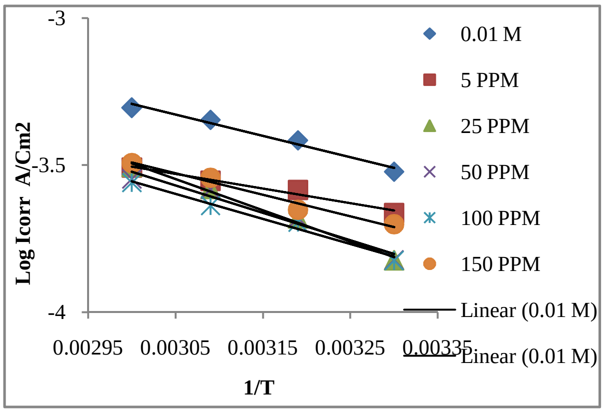


Figure 9 Arrhenius plot of the carbon steel(ST 37-2) in (0.01 M H_2SO_4) atvarious (sudan III) concentrations at the temperature range 303-333K.

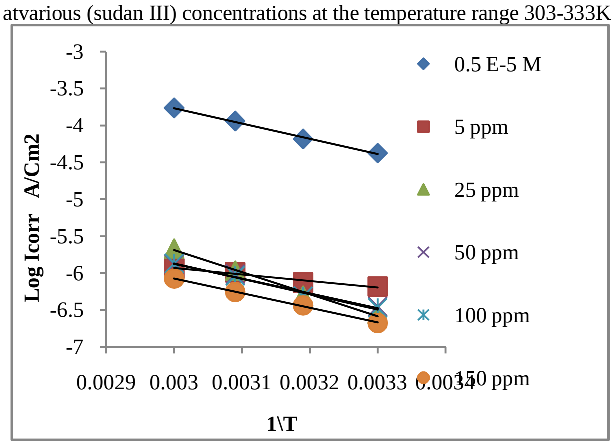


Figure 10 Arrhenius plot the carbon steel (ST37-2)in($0.5x10^{-5}$M H_2SO_4) at various(sudan III) concentrations at the temperature range 303-333K.

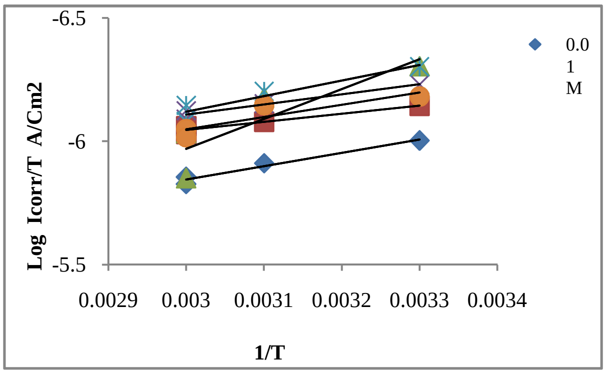


Figure 11 Relationship between Log icorr/T vs 1/T

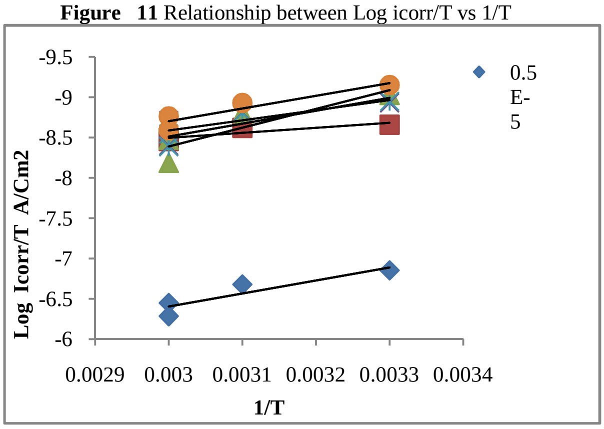


Figure 12 Relationship between Log icorr/T vs 1/T

Also the effect is describe the kinetics of catalytic and tarnishing reactions on metals(31)when such compensation operates, it is possible for striking variation in Ea. and log Athrough a series of surface sites on the metal to yield only a small variation in reactivity.

Table 3 Activation energy (Ea) ,Pre-exponential factor (A) for the corrosion of Carbon steel (ST37-2) in(0.010 , 5x10^{-5} M H_2SO_4) over temperature range(303-333) K and different (sudan III) concentration.

Media Con.M.	Inhibitor Con. Ppm	Ea. KJ.mol-1	A Molecule.Cm2.S-1
0.01	0	13.879	$4.74*10^{17}$
	5	9.525	$5.6*10^{16}$
	25	20.29119	$3.0432*10^{18}$
	50	17.83873	$1.1768*10^{16}$
	100	16.336	$6.346*10^{17}$
	150	13.977	$3.12*10^{17}$
0.5x10^{-5}	0	39.569	$1.709*10^{21}$
	5	16.691	$2.995*10^{15}$
	25	57.062	$1.126*10^{22}$
	50	38.543	$1.828*10^{18}$
	100	39.770	$1.445*10^{19}$
	150	37.907	$4.754*10^{18}$

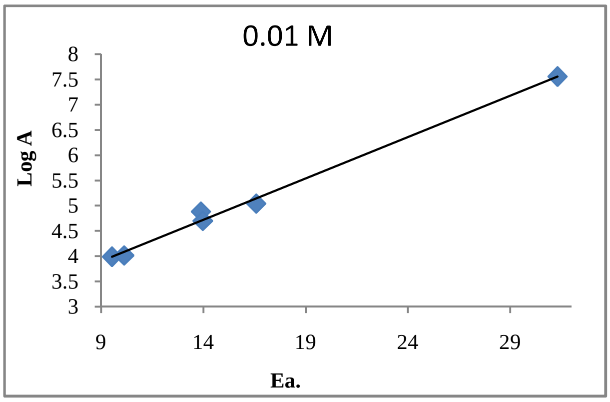


Figure 13 Eavalues are plotted vs. LogA for carbon steel corrosion in(0.01 M H_2SO_4)and different(sudan III) concentrations at the temperature range 303-333K.

Thermodynamics Parameters

Thermodynamics of corrosion

The change in Gibbs free energy (ΔG) for the corrosion of the carbon steel ST37-2 specimens in(0.01,0.5x10^{-5}M H_2SO_4)at a given temperature may be estimated from the equation: (32)

$$\Delta G = -nFE_{corr}$$

where n (which is considered to be equal to 2) is the number of electrons involved in the anodic process . From the values of ΔG at four different temperatures in the range (303 -333) K , the change in the enthalpy (ΔH) of corrosion process could be evaluated by using Gibbs-Helmholtz equation:(33)

$$[\frac{\partial \Delta G/T}{\partial T}]_P = -\frac{\Delta H}{T^2}$$

Which can be arranged as:

$$\frac{\Delta G}{T} = \frac{\Delta H}{T} + \text{con.}$$

Utilizing the values of ΔG and ΔH, it was possible to calculate the values of the change in the entropyΔS for the corrosion process using the well-known thermodynamic equation:

$$\Delta G = \Delta H - T\Delta S$$

The thermodynamic quantities ΔG,ΔS and ΔH for carbon steelST37-2corrosion in ,(0.01 , 0.5x10^{-5}M H_2SO_4)at four temperatures in the range(303- 333) K are given in the (Tables 5) , the result shows the negative values of ΔG that mean, the reaction occurring spontaneity and it is found that ΔG slightly increases with temperature .Negative and positive values of enthalpy changes (ΔH) have indicating the exothermic and endothermic nature for this reaction, exothermic process may involve either physisorption or chemisorption or of both the processes, while endothermic process is attributed to chemisorption. The positive value (ΔS) of shows the increased randomness at the metal/solution interface. This increase of disorder is due to more water molecules adsorbed on to the metal surface.

Table 4 Activation functions of the corrosion of carbon steel (ST37-2) in the different concentration of (sudan III) at 0.01 , 0.5x10^{-5} M H_2SO_4

Media Con. M.	Inhibitor Con. ppm	ΔH* KJ.mol^{-1}	ΔS* KJ.mol^{-1}.K^{-1}	ΔG* KJ.mol^{-1} 303 K	313 K	323 K	333 K
0.01	0	10.3434	-0.27782	94.52205	97.30023	100.0784	102.8566
	5	6.264119	-0.2939	95.31696	98.25599	101.195	104.1341
	25	15.68488	-0.26606	96.30107	98.96167	101.6223	104.2829
	50	14.24401	-0.27071	96.26872	98.97581	101.6829	104.39
	100	12.02894	-0.27804	96.27368	99.05403	101.8344	104.6147
	150	9.460933	-0.28438	95.62717	98.47094	101.3147	104.1585
0.5x10^{-5}	0	30.98677	-0.22661	99.65081	101.9169	104.1831	106.4492
	5	11.77911	-0.32427	110.032	113.2746	116.5173	119.76
	25	44.62264	-0.22367	112.3958	114.6325	116.8692	119.106
	50	29.9748	-0.26993	111.7636	114.4629	117.1622	119.8615
	100	30.80121	-0.26747	111.8452	114.5199	117.1946	119.8693
	150	30.20053	-0.27293	112.897	115.6263	118.3556	121.0848

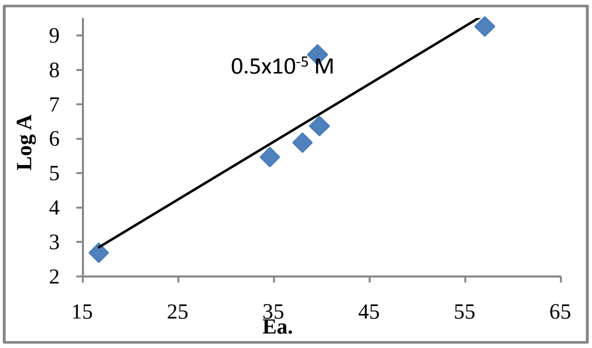


Figure 14 Ea values are plotted vs. LogAfor carbon steel corrosion in (0.5x10^{-5}M H_2SO_4) and different (sudan III) concentrations at the temperature range 303-333K.

Thermodynamic of Inhibition(Adsorption)

The adsorption behavior of sudan III can be described by physisorption and chemisorption and the mechanism was determined by fitting the surface coverage(Ɵ) values to Langmuiradsorption isotherm using the following equation(34):

$C_{inh}/\Theta \; = 1/K_{ads} + C$

where C_{inh} is the concentration of inhibitor, θ is the surface coverage.A plot of C_{inh}/θ values against the corresponding values of C_{inh}(Figs. 15,16)was found to be linear dependence at all temperature studied(Figs. 17 ,18). The equilibrium constant K_{ads} is related to the standard free energy of adsorption (ΔG_{ads}) as shown in the following equation (35) :

$K_{ads}= (1/55.5) \exp(-\Delta G_{ads}/RT)$

Adsorption enthalpy $\Delta H_{ads}$was calculated according to the Van't Hoff equation(29) :

$$\ln K_{ads} = -\frac{\Delta H_{ads}}{RT} + \text{constant}$$

Where R is the gas constant and T is the absolute temperature. The constant value of 55.5 is the concentration of water in solution in mol/cm3(36) .

The values of ΔG and ΔH, it was possible to calculate the values of the change in the entropy ΔS for the corrosion process using the well-known thermodynamic equation:

$\Delta G = \Delta H - T\Delta S$

Table 6 show the adsorption parameters of the interaction of sudan III with carbon steelST37-2 surface. The negative values of ΔGads reveals that the adsorption of sudan III molecules on the carbon steel surface is spontaneous (37) and the lower values (less than -20 kJmol^{-1} in 0.01M ,closely to -20 kJmol^{-1}in 0.5x10^{-5}M H_2SO_4) are consistent with the electrostatic interaction between the charged molecule and the charged metal. The estimated ΔG_{ads} values indicate that the adsorption mechanism of the sudan III may be a mixed type of physisorption and chemisorption . This phenomenon is often encountered in the literature (30,38-39).The negative values of ΔH_{ads}indicate that the adsorption of inhibitor is an exothermic process(40). Literature pointed out that an exothermic process signifies either physisorption or chemisorption while endothermic process is associated to chemisorption(41). In an exothermic process, chemisorption is distinguished from physisorption by considering the absolute value of a chemisorption process is higher than 40 kJ mol^{-1}(42). The ΔH°ads which obtained are -12.297 in 0.01M $H_2SO_4$and + 48.680 kJmol^{-1} in 0.5x10-5M H_2SO_4 respectively that mean physisorption and chemisorption occur.. On the other hand the adsorption of inhibitor molecules is accompanied by the negative and positive values of ΔS $_{ads}$, negative value means that adecrease in the system disorder takes place while positive values of ΔS $_{ads}$ might be explained by an ordered layer onto the steel surface and the adsorption of sudan III from the aqueous solution can be regarded as quasi-substitution process between the organic compound in the aqueous phase and water molecules at surface ,i.e the adsorption of sudan III is accompanied by desorption of water molecules from the surface (43-44). Generally the inhibition of the carbon steel ST37-2 corrosion is due to either the electrostatic interaction between the charged molecules and the charged metal (physisorption) or transfer charge from sudanIIImolecules to the metal surface to form a coordinate type of bond (chemisorption) (45,46).

Table 5 The thermodynamic functions of corrosion of carbon steel in solution (0.01, 0.5x10^{-5} M H_2SO_4) over the temperature range (303-333)K.

Media Con. M	**Tem. K**	**ΔG KJ.mol^{-1}**	**ΔH KJ.mol^{-1}**	**ΔS KJ.mol^{-1}.K^{-1}**
0.01	303	-97.2141	-31.252	0.216796
	313	-99.9161		0.218502
	323	-100.3021		0.212932
	333	-104.027		0.217724
0.5x10^{-5}	303	-62.7443	51.48	0.376978
	313	-72.7996		0.397059
	323	-59.83		0.344613
	333	-80.0757		0.395062

Table 6 The thermodynamic functions of Adsorption of (sudan III) dye onto carbon steel in (0.01 , 0.5x10^{-5} M H_2SO_4) over the temperature range (303-333) and (5-150ppm)sudan III concentrations.

Media Con. M.	**Tem. K**	**Kads.**	**ΔGads. KJ.mol^{-1}**	**ΔHads. KJ.K^{-1}.mol^{-1}**	**ΔSads. KJ.K^{-1}.mol^{-1}**
0.01	303 K	0.212743	-6.21717	-12.297	-0.02007
	313 K	0.208908	-6.37503		-0.01892
	323 K	0.145802	-5.6132		-0.02069
	333 K	0.147098	-5.81147		-0.01948
0.5x10^{-5}	303 K	9.90099	-15.8885	48.680	0.213097
	313 K	10.58201	-16.586		0.208517
	323 K	19.26782	-18.7247		0.208683
	333 K	57.47126	-22.3291		0.213241

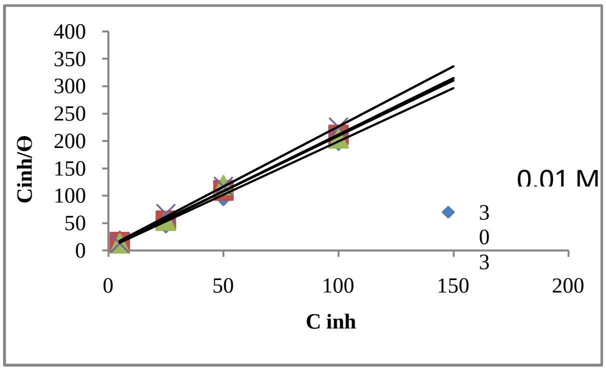


Figure 15 Langmuir adsorption isotherm for sudan III in 0.01 M H_2SO_4 at the temperaturerange303-333K

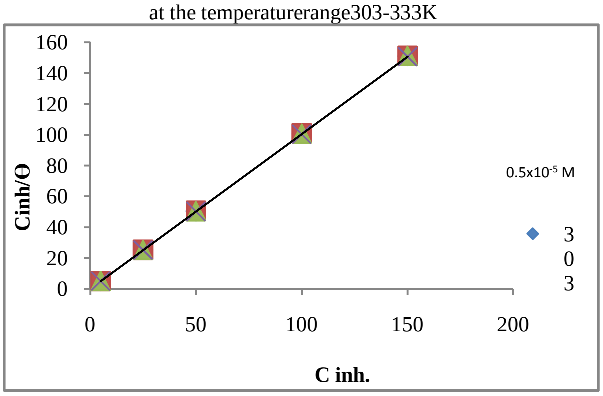


Figure16 Langmuir adsorption isotherm for (sudan III) in 0.5 x10^{-5}M H_2SO_4 at the temperaturerange303-333K.

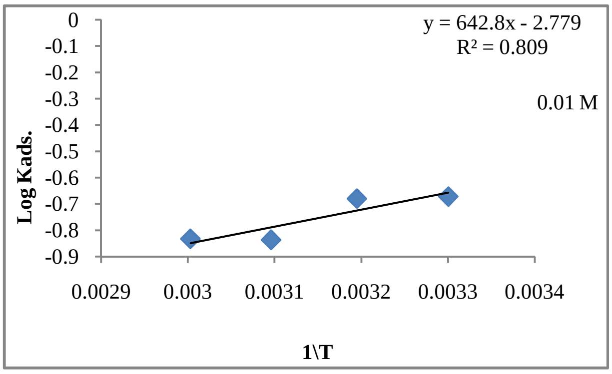


Figure 17 Variation of logK_{ads} with 1/T for carbon steel ST37-2 in 0.01M H_2SO_4 in the presence of sudan III dye

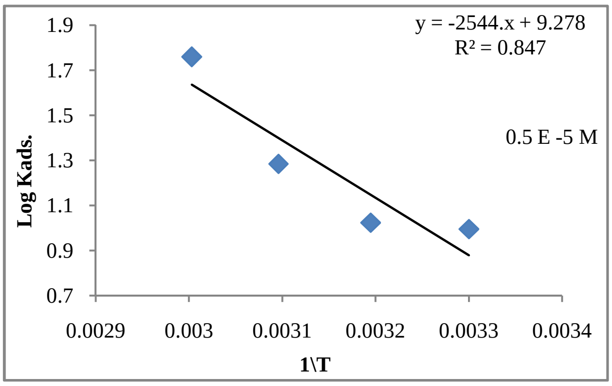


Figure 18 Variation of logK_{ads} with 1/T for carbon steel ST37-2 in 0.5x10^{-5}M H_2SO_4 in the presence of sudan III dye

CONCLUSION

For the present study the following conclusions are drawn:

1. The results showed the possibility of using(sudanIII) as corrosion inhibitor for carbon steel ST37-2 in H_2SO_4 solutions.
2. Values of the inhibition efficiency (IE%) were dependent on temperature , among the compounds studied (sudan III) exhibited the best performance in (0.5x10^{-5} M H_2SO_4) giving more than 99 % inhibition efficiency at the temperature range (303-333)K, while the values of inhibition efficiencies (IE%)in(0.01M H_2SO_4) increases with increasing (sudan III)concentrations then almost becomes independent with increasing the concentration up to 100ppm then decreeses , maximum efficiency percent attain to 50 at 303K and (sudan III) concentration is 25 ppm.
3. Polarization studies, kinetic and thermodynamic parameters show two types of adsorption can be considered. Physisorption and chemisorption.
4. The adsorption of sudan III on carbon steel ST37-2 surface was spontaneous and obeys Langmuir adsorption isotherm.
5. A linear relationship was found to exist between the experimental values of log A and the corresponding values of E_a for carbon steelST37-2 corrosion in different (sudan III) concentrations in(0.01 , 0.5 x 10^{-5} M H_2SO_4)..

References

1. SchweitzerP. A., Fundamentals of Metallic Corrosion,2nd Edition ,Tylor Francis Group Press U.S.A., 2007:1 .
2. SANYAL B., Organic compounds as corrosion inhibitors in different environments – A review, Progress in Organic Coatings,1981; 9:165-236.
3. Al-JuaidS. S., Mono Azo Dyes Compounds as Corrosion Inhibitors for Dissolution of Aluminium in Sodium Hydroxide Solutions, PortugaliaeElectrochimica. Acta.,2007; 25: 363-373
4. Hunger K., P. Mischke, W.Rieper, R. Raue, K.Kunde and A.Engel , Azo Dyes" in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2005; 245.
5. Refat N.A, Z.S. Ibrahim, G.G. Moustafa, K.Q. Sakamoto, M. Ishizuka and S.Fujita , The induction of cytochrome P450 1A1 by Sudan dyes , J. Biochem. Mol. Toxicol., 2008;22 (2): 77–84.
6. Liu R. Q., L. Xiang, and X. G. Zhang , Inhibition effect of methyl red on corrosion of steel in acidic solutions , Corrosion Protection, 2001; 22: 98–99.
7. Oguzie E. E., Influence of halide ions on the inhibitive effect of congo red dye on the corrosion of mild steel in sulphuric acid solution , Mater. Chemi. and Phys., 2004; 87(1):212–217.
8. Oguzie E. E., Corrosion inhibition of mild steel in hydrochloric acid solution by methylene blue dye , Mater. Lett., 2005; 59(8-9):1076–1079.
9. Oguzie E. E., C. Unaegbu, C. N. Ogukwe, B. N. Okolue, and A. I. Onuchukwu , Inhibition of mild steel corrosion in sulphuric acid using indigo dye and synergistic halide additives , Mater. Chemi. and Phys., 2004; 84(2-3):363–368.
10. Ebenso E. E., H. Alemu, S. A. Umoren, and I. B. Obot , Inhibition of mild steel corrosion in sulphuric acid using alizarin yellow GG dye and synergistic Iodide Additive, Inter. J. of Electrochem. Sci., 2008; 3: 1325–1339.
11. Onen A. I., O. N. Maitera , J. Joseph, and E. E. Ebenso , Corrosion inhibition potential and adsorption ehavior of bromophenol blue and thymol blue dyes on mild steel in acidic medium , *Inter. J. of Electrochem. Sci.*, 2011; 6(7) :2884–2897.
12. Deng S., X. Li, and H. Fu , Alizarin violet 3B as a novel corrosion inhibitor for steel in HCl, H_2SO_4 solutions , Corrosion Science, 2011; 53(11):3596–3602.
13. Abu-Alruba, S. S., M. W. Amerb and S. A. Alkahtania , Adsorption of the Sudan dye (III) in methanol using activated carbon, J. of Adv. In Chem., 2014;10(10):3291 -3302.
14. LiC., L. Chenand X. You ,Extraction of Sudan dyes from environmental water by hemimicelles-based magnetic titanium dioxide nanoparticles , Environ. Sci. and Pollu . Res.,2014; 21(21): 12382-12389
15. Pasupathy A., S.Nirmala, G.Abirami, A.Satish and R.P. Milton , Sudan-III Dye as a Novel Corrosion Inhibitor for Zinc Metal in Acidic Solutions , Inter. J. of Sci. and Res. Publi., 2014; 4(3): 1-3.
16. S.Ananthkuma r , Dr., A.Sankar and S.Rameshkumar , Corrosion Inhibition Of Mild Steel In 0.5 M H_2SO_4 By

1-(2-Methyl-4-(2-Methylphenyldiazenyl) Phenyl) Azonapthalen-2- , Amer. J. of Eng. Res., 2013; 2(9) :17-22.

17. ObotI.B. andN.O. Obi-Egbed , Anti-corrosive properties of xanthone on mild steel corrosion in sulphuric acid: Experimental and theoretical investigations ,Curr. Appl. Phys.,2011; 11(I3): 382–392.
18. Nwabanne J.T. and V.N.Okafor ,Adsorption and Thermodynamic Study of the Inhibition of Corrosion Of Mild Steel In H_2SO_4 Medium Using vernoniaamygdalina , J.of.Mine.andMat.Chara. and Eng.,2012; 11 :885-890.
19. Bouklah M. and B.Hammouti , Thermodynamic Characterisation of Steel Corrosion for the Corrosion Inhibition of Steel in Sulphuric Acid Solutions by Artemisia, Port. Elec.Acta.,2006;24 : 457- 468.
20. Ozkir D., E.Bayol, A.AligurtenandY.Surme ,Thermodynamic Study and Electrochemical Investigation of Calcein as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution, J.Chil.Chem.Soc.,2013;58(4):2158- 2167.
21. Rodriguez-Clemente1E., J.G. Gonzalez-Rodriguez1 and M. G. Valladares-Cisneros ,Allium sativum as Corrosion Inhibitor for Carbon Steel in Sulfuric Acid, Int. J. Electrochem. Sci., 2014; 9 : 5924 – 5936.
22. AhamadI., R. Prasad and M.A. Quraishi ,Adsorption and inhibitive properties of some new Mannich bases of Isatin derivatives on corrosion of mild steelin acidic media, Corr. Sci.,2010; 52(4) : 1472–1481.
23. QuraishiM.A and Danish Jamal ,Dianils as new and effective corrosion inhibitors for mild steel in acidic solutions , J.Mater. Chem. Phys., 2003; 78(3) : 608–613.
24. M.Bockris J.O. and A.K.N.Reddy ,Modern Electrochemistry (PhenumPress, New York ,1970;Vol.2 : 83
25. Li X. ,S. Deng, G. Mu, H. Fu and F.Yang , Inhibition effect of nonionic surfactant on the corrosion of cold rolled steel in hydrochloric acid , Corrosion Science ,2008; 50(2) :420–430
26. Aljourani J.,K.Raessi and M.A.Golozara, Benzimidazole and its derivatives as corrosion inhibitors for mildsteel in 1M HCl solution,Corr.Sci.,2009;51:1836 -1843.
27. Patterson W.R. and J.J.Rooney , An explanation of Compensation effect in Catalysis,J.of Catal.,1994; 146:310-312.
28. Guan N. M., L. Xueming and L. Fei, Synergistic inhibition between *o*-phenanthroline and chloride ion on cold rolled steel corrosion in phosphoric acid , Mater. Chem. Phys., 2004; 86(1) :59-68.
29. Ouali I. El, B. Hammouti, A. Aouniti, Y. Ramli, M. Azougagh, E. M. Essassi and M. Bouachrine,, Thermodynamic characterisation of steel corrosion in HCl in the presence of 2-phenylthieno (3, 2-b) quinoxaline,J. Mater. Envir. Sci.,2010; 1(1) :1-8.
30. Elaib -T.Heakal.F.,A.S.Fouda and S.S.Zahran, Environmentally safe Protection of Carbon Steel Corrosion in Sulfuric Acid by Thiouracil Compounds , Int.J. of Electrchem.Sci., 2015; 10 : 1595-1615.
31. Al-Haidari Y.K., J.M.Saleh, Studies of Adsorption and Corrosion Inhibition of Some OrganicSulphur Compounds on Some Metals and Alloys ,J. of Chem.Soc.,1988;54 :189.
32. Bradford S. A.,Corrosion Control ,2nd , Canada ,2001; Chapter 2, :7.
33. El-Hajjaj F., R.A. Belkhmima, B. Zerga1, M. Sfaira1, M. Tale1, M. EbnTouhami , B. Hammouti, S.S. Al-Deyab and E. Ebenso **,**Temperature Performance of a ThioneQuinoxaline Compound as Mild Steel Corrosion Inhibitor in Hydrochloric Acid Medium,Int. J. Electrochem. Sci., 2014; 9 : 4721 – 4731.
34. I.langmuir,J.Am.Chem.Soc.1947 ,39,1848
35. Fekry A.M. and M.A. Ameer ,Corrosion inhibition of mild steel in acidic media using newly **s**ynthesized heterocyclic organic molecules. *International Journal of Hydrogen Energy* ,2010; 35: 7641-7651.
36. Olivares O, N.V. Likhanova, B. Gomez, J. Navarrete, M.E. Lianos-Serrano, E. Arce and J.M Hallen , Electrochemical and XPS studies of decylamides of α-amino acids adsorption on carbon steel in acidic environment, Appli. Sur. Sci., 2006; 252 : 2894-2909.
37. Migahed. M.A. ,Electrochemical investigation of the corrosion behaviour of mild steel in 2 M HCl solution in presence of 1-dodecyl-4-methoxy pyridinium bromide , Mater .Chem. Phy., 2005; 93(1):48–53.
38. Dahmani M , A. Et-Touhami, S.S Al-Deyab, B. Hammouti , A. and Bouyanzer Corrosion Inhibition of C38 Steel in 1M HCl: A Comparative Study of Black Pepper Extract and Its Isolated Piperine, *Inte. J. of Electrochem.* Sci., 2010; 5 : 1060-1069.
39. BouklahM., N. Benchat, B. Hammouti, A. Aouniti and S. Kertit'm ,Thermodynamic characterisation of steel corrosion and inhibitor adsorption of pyridazine compounds in 0.5 M H_2SO_4, Materials Letters, 2006 ; 60(15) : 1901–1905
40. Gomma G.K ., M.H. Wahdan, Schiff bases as corrosion inhibitors for aluminium in hydrochloric acid solution., Mater. Chem. Phys., 1995 ; 39 (3) : 209 -213.
41. *Durnie W. , R.De Marco, A. Jefferson, and B. Kinsella, Development of a Structure‐Activity Relationship for Oil Field Corrosion Inhibitors, J. Electrochem. Soc., 1999; 146(5): 1751-1756*
42. Martinez S. and I. Stern ,Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in the low carbon steel mimosa tannin sulfuric acid system, Appl. Surf. Sci., 2002 ; 199 (1-4) : 83-89.
43. Singh A. K., S. K. Shukla , and M. A. Quraishi , Corrosion Behaviour of Mild Steel in Sulphuric Acid Solution in Presence of Ceftazidime, Int. J. Electrochem. Sci., 2011;(6): 5802 - 5814
44. Al Hamzi A. H., H. Zarrok, A. Zarrouk, , R. Salghi, B. Hammouti, S. S. Al-Deyab, M. Bouachrine, A. Amine and F. Guenoun ,The Role of Acridin-9(10*H*)-one in the Inhibition of Carbon Steel Corrosion: Thermodynamic, Electrochemical and DFT Studies, Int. J. Electrochem. Sci., 2013; 8: 2586 – 2605
45. Donahue F.M. and K. Nobe ,Theory of Organic Corrosion Inhibitors.Adsorption and Linear FreeEnergy Relationships, *J. Electrochem. Soc.,* 1965; 112: 886-891
46. Khamis E., F. Bellucci, R. M. Latanision, and E. S. H. El-Ashry , Acid Corrosion Inhibition of Nickel by 2-(Triphenosphoranylidene) Succinic Anhydride, Corrosion, 1991; 47(9): 677-686