EUROPEAN JOURNAL OF BIOMEDICAL AND PHARMACEUTICAL SCIENCES
http://www.ejbps.com

ISSN 2349-8870
Volume: 3
Issue: 8
475-492
Year: 2016

SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY STUDY OF SOME BIS-AZO DYES AND THEIR COMPLEXES AND THE USE OF BIS-AZO DYES AS CORROSION INHIBITORS FOR CARBON –STEEL IN ACIDIC MEDIA

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Article Received on 20/06/2016 **Article Revised on 11/07/2016** **Article Accepted on 01/08/2016**

ABSTRACT

Two bis- azo dyes derived from para and ortho phenylenediamine and 3-ethoxy salicylaldehyde and new chelate complexes of Ni(II) that were prepared by reacting ion with the bis-azo dyes .The ratios of metal: ligand obtained were (1:1) for all complexes.The prepared compounds were identified by CHNS analysis FT-IR, ^{1}H-NMR , and Mass spectroscopy. The prepared azo dyes were studied as corrosion inhibitors in 0.5M HCl solution by the weight loss and galvanostatic polarization techniques. The inhibition efficiency of inhibitor increases with concentration to attain (86.47%,88.26%) of A1 and A2 at concentration 5× 10−3 M ,time 5 hr and temperature 303K. Temperature effect on the corrosion behavior was studied at temperature ranged from 303-333 K, The efficiency of inhibitors was decreased as the temperature increases. The effect of temperature on the rate of corrosion in the absence and presence of these compounds was also studied.The activation energies, enthalpies and entropies of the dissolution process and the free energies and adsorption equilibrium constant for the adsorption process were determined and discussed. Also studied the biological activity compounds of Azo dyes.

KEYWORDS: Azo dyes, corrosion, Tafel, thermodynamic properties.

1. INTRODUCTION

Azo compounds are a very important class of chemical compounds receiving attention in scientific research. They are highly colored and have been used as dyes and pigments for a long time.[1-3] Furthermore, they have been widely studied because of their excellent thermal and optical properties in applications such as optical recording medium[4-7], toner[8,9], ink-jet printing[10], and oil-soluble lightfast dyes.[11] The finishing of fibrous materials in order to impart simultaneously with antimicrobial properties is of great interest.[12]

The corrosion

The use of inhibitors is one of the most practical methods for protecting materials against corrosion, especially in acidic media.[13] Acid solutions are widely used in industry, some of the important fields of applications being acid pickling of iron and steel, chemical cleaning and processing, or production and oil well acidification. The damage by corrosion generates not only high cost for inspection, repairing and replacement, but also these constitute a public risk, thus there is a necessity of developing novel substances that behave like corrosion inhibitors especially in acid media[14] – most well – known acid inhibitor are organic compounds containing nitrogen, sulphur, and oxygen atoms. Organic inhibitors react by adsorption on a metallic surface. Water molecules at metallic surface are replaced by organic inhibitor molecules. In the case of chemisorption, the formation of a bond between the metal and organic inhibitor impedes the anodic and cathodic processes, thereby protecting the metal surface.[15] Because organic inhibitors act by adsorption on the metal surface, the efficiency of these compounds depend strongly on their ability to form complexes with the metal. Both π electrons and polar groups containing sulfur, oxygen and/or nitrogen are fundamental characteristics of this type of inhibitor. The polar functional groups are usually considered the chelation center for chemical adsorption.[16] The aim of the present work is to study the inhibitive action of some newly prepared bis azo dye compounds toward the corrosion of c-steel in 0.5M hydrochloric acid 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 compounds was also investigated and some thermodynamic parameters were computed ,As Well as prepared two of the complexes azo dyes and studied of biological activity of these compounds.

2. Experimental part

Melting points were determined by open capillary and are uncorrected. The CHNS analysis measurements for

the synthesized compounds were performed by using (Thermofinigan) at the analytical Laboratory of Tehran University /Iran and ^{1}H-NMR spectra performed by using Bruker DRX System Al500(500MHZ), at the analytical Laboratory of Sanati Sharif University /Iran. DMSO-d6 was used as a solvent and TMS as an internal standard.

IR spectra were recorded using CsI disc on ShimadzuFTIR-spectrometer at Chemistry Department, , College of Science, Thi-Qar University and Mass spectra of the synthesized compounds were carried out using Work mass selective Detector –5973 of Iran / Tehran University. Molar Electrical Conductivity of the complexes prepared recorded by using Inolabcond720 in asolvent DMSO.

3. Synthesis of azo dyes

General procedure for the preparation of the compounds

The azo dyes compounds, **A1:**6,6'-(1E,1'E)-1,4-phenylenebis(diazene-2,1-diyl)bis(3-ethoxy-2-hydroxybenzaldehyde), **A2:**6,6'-(1E,1'E)-1,2-phenylenebis(diazene-2,1-diyl)bis(3-ethoxy-2-hydroxybenzaldehyde) were prepared using the same method.

Amixture of P- phenylenediamine (1.08 gm, 10mmol),water(20ml) and concentrated hydrochloric acid (5.24ml,60mmol) was stirred until a clear solution was obtained. The mixture was cooled to 0–5 ^{o}C and a solution of sodium nitrite (1.52 g, 22 mmol) in water (10 mL) was then added dropwise, maintaining the temperature below 5 ^{o}C. The resulting mixture was stirred for an additional 1h. 3-ethoxy salicylaldehyde (3.323gm, 20mmol) was dissolved in 8 mL aqueous NaOH (20 mmol) solution cooled to 0–5 ^{o}C in an ice bath. This solution was then gradually added to the solution of the cooled diazonium chloride and the resulting mixture was continually stirred at 0–5 ^{o}C for 2h. The mixture was left overnight. The resulting crude precipitate was filtered by acidification and washed several times with cold water, dried under vacuum, and then recrystallized from Athyl acetate. The other azo compound of A2 was synthesized in the same manner using O- phenylenediamine, as shown in Scheme 1. The physical properties of the prepared azo dyes were listed in Table 1.

2-2 Solution preparation

The aggressive solutions, 0.5M HCl, were prepared by the dilution of AR grade 37% HCl in distilled water. The different concentrations of bis azo dye compound were prepared by dissolving a certain amount of each compound in 0.5M HCl to obtain the following conc. ($1x10^{-4}$, $5x10^{-4}$, $1x10^{-3}$ and $5x10^{-4}$M).

2-3 Weight loss measuremen

Specimens of carbon low steel used in this study had the following Chemical composition (wt%): C(0.20), Si(0.24) Ni(0.15), Cu(0.18),Cr(0.10), Mn(0.44), S(0.05), P(0.05) and (98.25). The weight loss tests were performed on metallic samples of carbon low steel with dimensions of 3.5cm ×0.4cm. The specimens were polished mechanically using SiC emery papers of grade 220, 400 and 600, washed thoroughly with distilled water and degreased with ethanol and acetone.[17] After weighing accurately, the specimens were immersed in 50ml of 0.5M HCl with and without addition of different concentrations of azo dyes inhibitor after different time (1-5) hr, the strips were taken out washed, dried and weighed accurately. Duplicate experiments were performed in each and the mean value of the weight loss was reported. Inhibition efficiency E%, surface coverage (θ)by using the following equation.[18]

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

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

Where W_{add} and W_{free} are the weight loss values in presence and in the absence of inhibitor, respectively.
specimens the corrosion rate was calculated using the following relationship[19]

Corrosion rate (mpy) =

$$\frac{\text{???}}{D \cdot T \cdot A} \quad (3)$$

W: weight loss in milligram
D: density of specimen g/cm3
A: area of specimen in square inch (noting that 1 in2 = 6.5416 cm2.)
T: exposure time in hours
mpy = mils per year (1mil =1inch /1000)

2.4. Electrochemical measurements

Galvanostatic polarization studies were carried out using Bank EIEIKTRONKIK INTELLGENT CONTROLS Model MLab 200-Chemistry Department-College of Science–Baghdad University, for calculation of electrochemical parameters Three compartment cell with a saturated calomel electrode (Reference electrode), platinum for auxiliary electrode and working electrode. The linear Tafel segment of cathodic and anodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (*Icorr*). The inhibition efficiency was evaluated from the calculated *Icorr* values using the relationship.[20]

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

Where I_{add} and I_{free} are the corrosion current in the absence and in the presence of inhibitor, respectively.

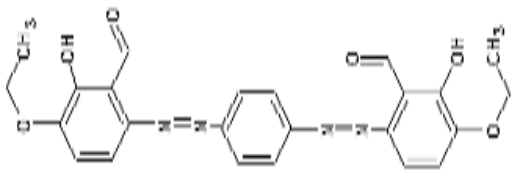
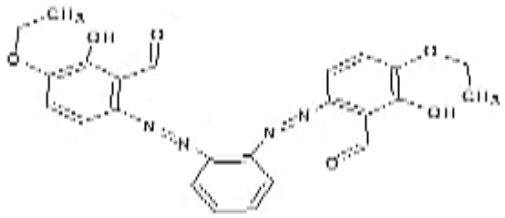
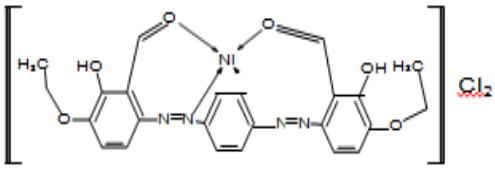
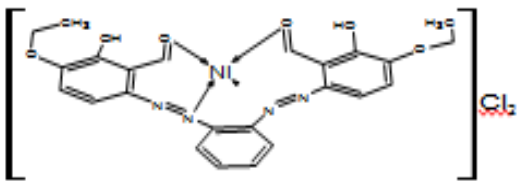
2.5. Synthesis of complexes

Asolution of nickel(II)chloride (0.0274 gm-1.66×10^{-4} mol) in 10ml of MeOH was added to amagnetically stirred 15ml MeOH solution containing the ligand A1 and A2 (0.0766 gm-1.66 $\times10^{-4}$ mol) .The resulting mixture was refluxed for 2h on water bath.After cooling,the complex precipitated out,which was filtered off,washed several times with EtOH and dried in vacuo.

2.6. Antibacterial activity

The study of antibacterial activity of the dyes prepared and complexes with nickel (II). Laboratory strains of 3 bacterial species which included Gram-positive bacteria, viz. Staphylococcus Aurens and two Gram–nagative bacterial, vis. Escherichia coli, **Pseudomons** aeruginosa, the samples was determined by the agar well diffusion method[21], and prepared the samples 0.05 gm for 1ml by using asolvent DMSO.

Table 1: The physical properties of the prepared azo dyes and complex.

Compd.	*Chemical structure*	Physical stat	Color	Melting point
A1		Powder	Reddish brown	79-80
A2		Powder	Light brown	72-74
A1-Ni		Powder	Dark brown	116-120
A2-Ni		Powder	Yellowish brown	112-114

3. RESULTS AND DISCUSSION

3.1. Elemental analyses

The elemental analyses of the prepared azo compounds are shown in Table 2 respectively. The measured values are in good agreement with the calculated values.

Table 2: CHN analysis of azo compounds.

Compound	Theoretical Data			Practical Data		
	C %	C %	H %	N %	H %	N %
$C_{24}H_{22}N_4O_6$	62.33	62.25	4.83	12.01	4.79	12.12
$C_{24}H_{22}N_4O_6$	62.33	62.21	4.88	12.03	4.79	12.12

3.2. FT-IR Spectra

FT-IR Spectra of the synthesized compounds were carried out using CsI disc method. The Spectra were shown in Figures 1-4 and the characterized bands were given in Table 3:

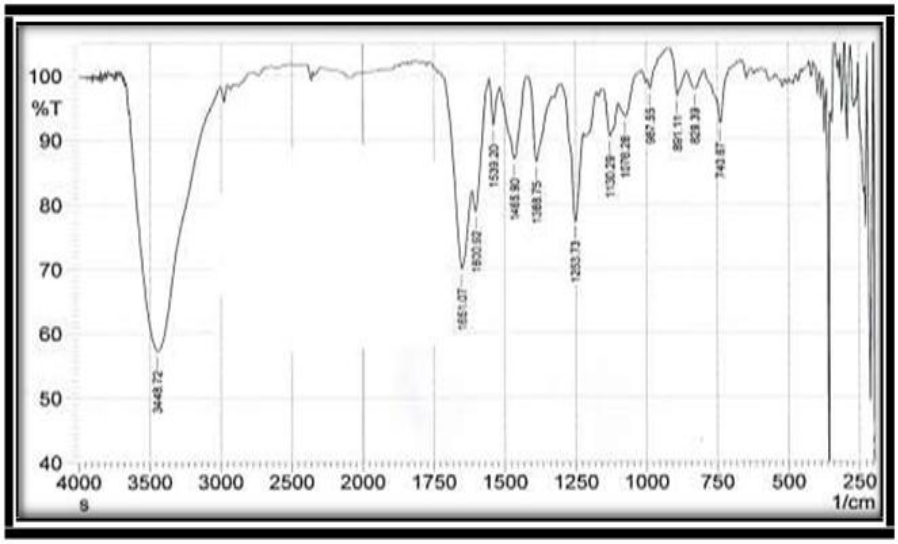


Figure 1: FT-IR Spectrum of A1 compound

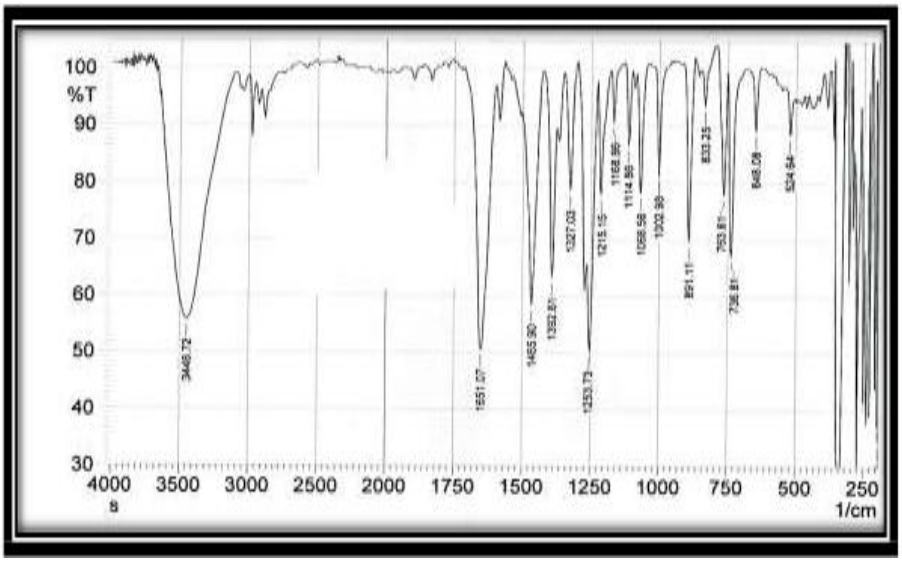


Figure 2: FT-IR Spectrum of A2 compound

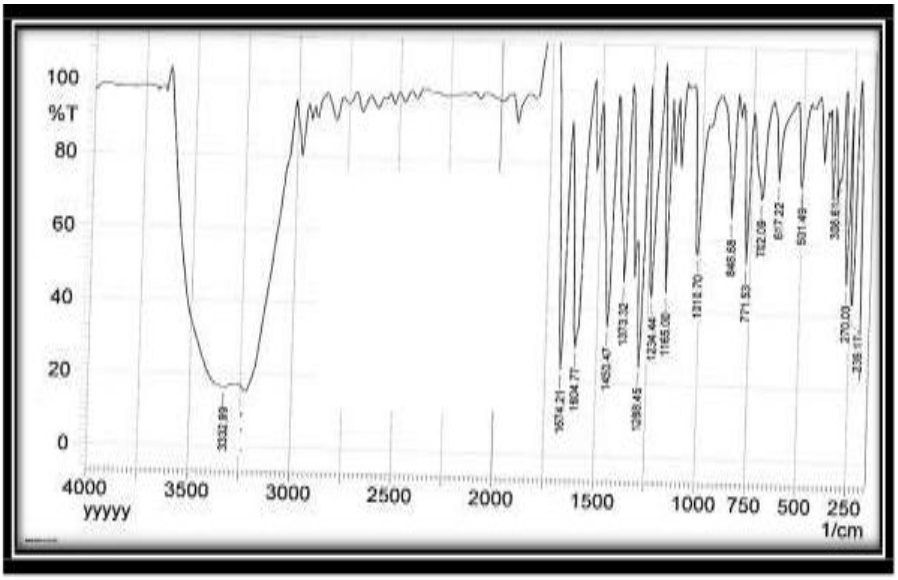


Figure 3: FT-IR Spectrum of(A1-Ni) complex

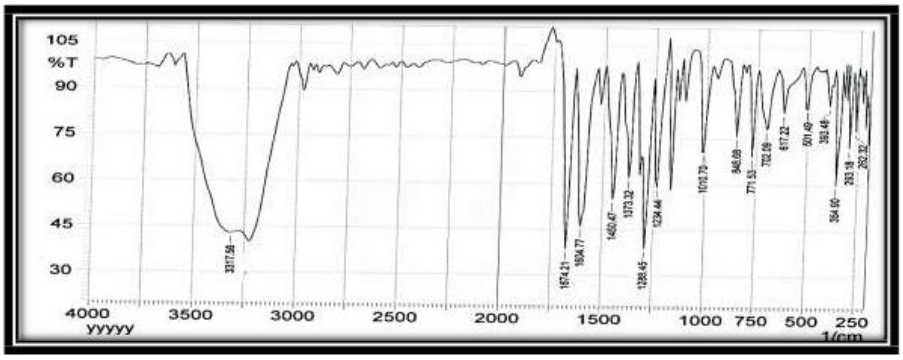


Figure 4: FT-IR Spectrum of (A2-Ni) complex

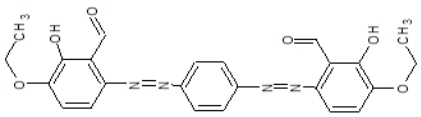
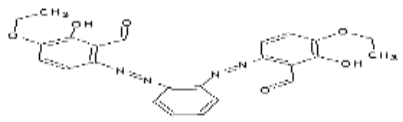
Table 3: Characterized Bands in FT-IR Spectra for Prepared Azo Dyes

Comp.	ν O-H (cm^{-1})	ν C-H Arom. (cm^{-1})	ν C-H Aliph. (cm^{-1})	ν C=C (cm^{-1})	ν N=N (cm^{-1})	ν C-N (cm^{-1})	ν M-N (cm^{-1})	ν M-O (cm^{-1})
A1	3448br	3057w	2965w	1539w	1465s	1253s	……..	……
A2	3448br	3087w	2912w	1545w	1465s	1215s	…….	……
[Ni(A1)]Cl_2	3332br	3045w	2928m	1545w	1450s	1288s	501m	354w
[Ni(A2)]Cl_2	3317br	3045w	2928m	1530w	1450s	1288s	501m	393m

3.3. ^{1}H-NMR

^{1}H-NMR spectra of the prepared bis azo dyes were performed in deuterated dimethyl sulfoxide solutions with tetramethylsaline as an internal standard. All these spectra showed a peak at 2.5 ppm which was due to DMSO solvent. Figures 5 and 6 represent the ^{1}H-NMR spectra of the bis azo compounds and Table 4 represents the data of these Figures.

Table (5): H^1 NMR for the prepared bis azo dyes in DMSO

Comp.	Chemical structure	Chemical shift (δ ppm)
A1		**7.322-8.036(m,8H,Ar-H)** 9.202,10.488(S,2H,CHO,OH) 3.602(S,4H,CH_2) 1.606(S,6H,CH_3)
A2		7.340-8.039(m,8H,Ar-H) 9.255,10.504(S,2H,CHO,OH) 3.682(S,4H,CH_2) 1.611(S,6H,CH_3)

S=singlet, m=multiple

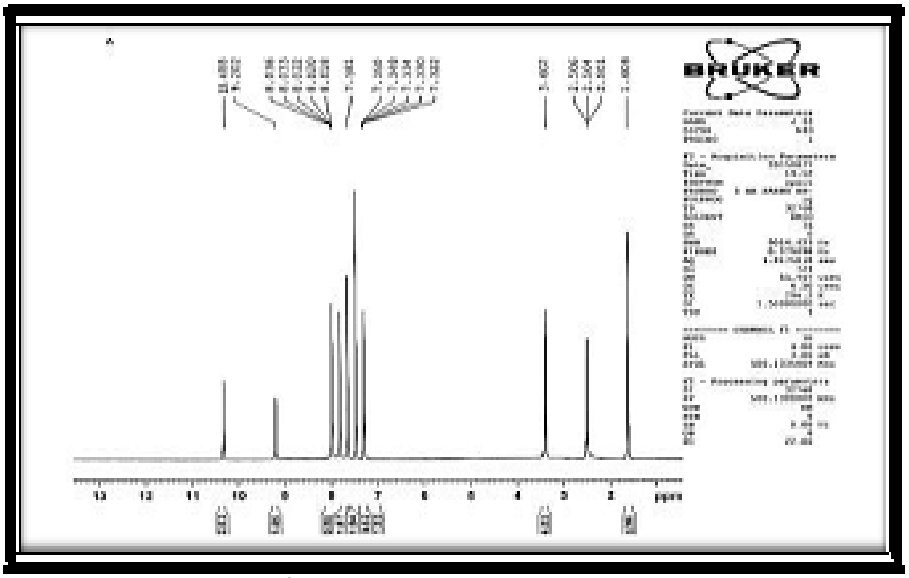


Figure 5: ^{1}H-NMR spectrum of the A1 compound

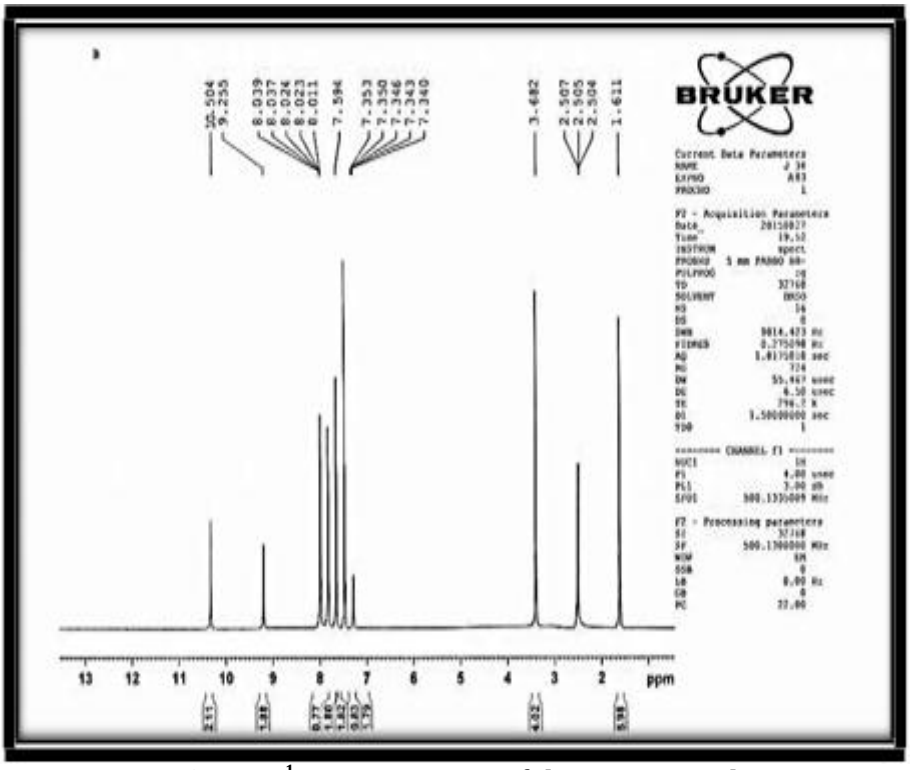


Figure 6: ^{1}H-NMR spectrum of the A2 compound

3.4. Mass Spectra

Mass spectra of the prepared inhibitors showed molecular ion peak (M^{+}) at 462, which corresponds to the molecular formula of inhibitor (A1) and at 462 which corresponds to the molecular formula of inhibitor (A2) and at 592 which corresponds to the molecular formula of [Ni(A1)]Cl2 and [Ni(A2)]Cl2. Mass spectra of A1, A2 and complexes are shown in Figs 7, 8,9 and 10.

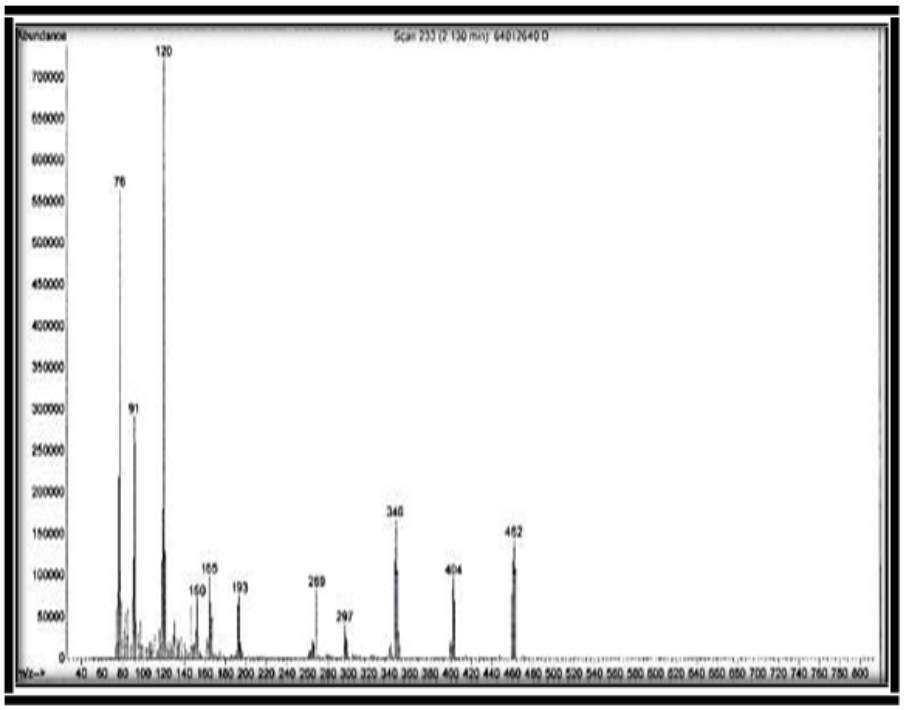


Figure 7: Mass Spectra of A1

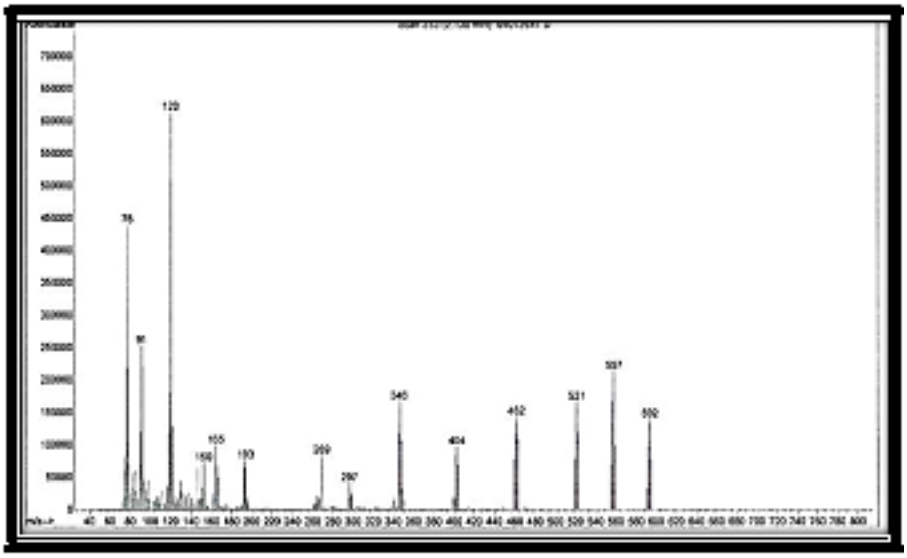


Figure8: Mass Spectra of [Ni(A1)]Cl_2

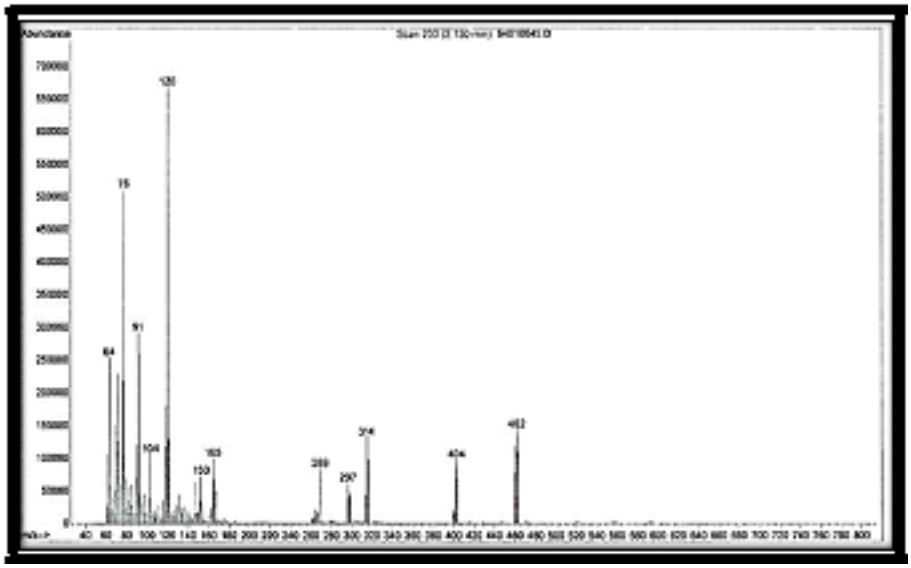


Figure 9: Mass Spectra of A2

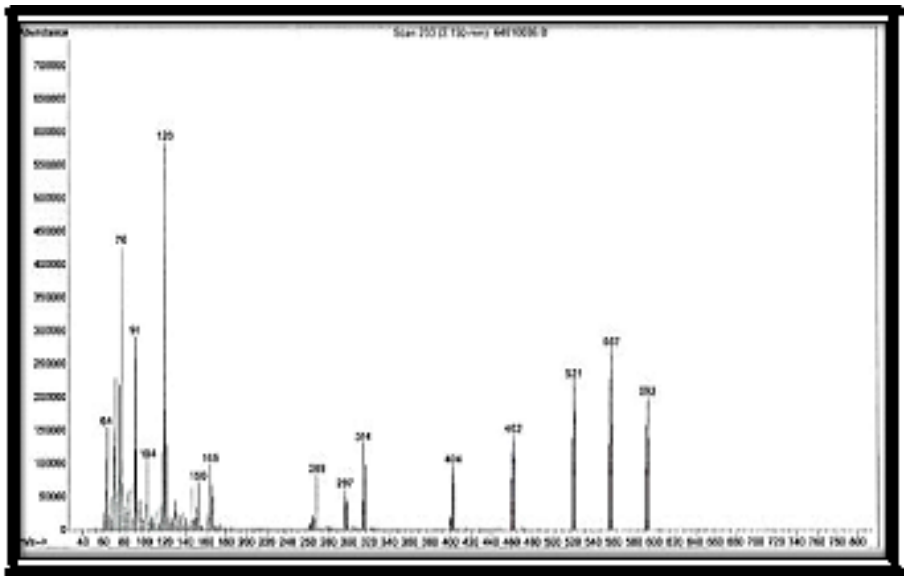


Figure10: Mass Spectra of [Ni(A2)]Cl_2

3.5. Weight loss measurements

Effect of immersing time, the inhibition efficiency values of mild steel with the addition of azo dyes at fixed temperature are presented in Tables 6 and 7. From these tables, it can be seen that inhibition efficiency values at fixed inhibitor concentration were increased as the immersing time increased. This result is due to the fact that the adsorption amount and coverage of inhibitor on mild steel surface increases. Figures 11 and 12 represent the variation of the inhibition efficiency IE% as function of the time, and effect of temperature, inhibition efficiencies obtained from weight loss measurement for the different inhibitor concentrations in 0.5 M HCl are shown in Figures 13 and 14. From these figures, it can be seen that the inhibition efficiency decreased with increasing temperature, which indicates desorption of inhibitor molecule.[22] As shown in Tables 8 and 9. The inhibition efficiency increasing by increasing the concentration of inhibitor, and the best concentration is $5x10^{-3}$ M.

Table 6: Effect of azo dye com`pound A1 on the dissolution of C-steel in 0.5M HCl at different immersing time

(Time)hr	1				2				3				4				5			
(Conc) M	Wt-loss gm	(Rcorr) mpy	% IE	θ	Wt-loss gm	(Rcorr) mpy	% IE	θ	Wt-loss gm	(Rcorr) mpy	% IE	θ	Wt-loss gm	(Rcorr) mpy	% IE	θ	Wt-loss gm	(Rcorr) mpy	% IE	θ
blank	0.0088	218.47	-	-	0.0254	315.30	-	-	0.0382	316.12	-	-	0.0580	359.98	-	-	0.0673	334.16	-	-
1× –––	0.0064	158.89	27.27	0.2727	0.0104	129.09	59.05	0.5905	0.0152	125.78	60.20	0.6020	0.0204	126.61	64.82	0.6482	0.0217	107.04	67.75	0.6775
5× –––	0.oo6	148.96	31.81	0.3181	0.0099	122.89	61.02	0.6102	0.0122	100.96	68.06	0.6806	0.0173	107.37	70.17	0.7017	0.0198	98.31	70.57	0.7057
1× –––	0.0054	134.06	38.63	0.3863	0.0091	112.96	64.17	0.6417	0.0101	83.58	73.56	0.7356	0.0123	76.34	78.79	0.7879	0.0132	65.54	80.38	0.8038
5× –––	0.0031	76.96	64.77	0.6477	0.0059	73.23	76.77	0.7677	0.0074	61.23	80.60	0.8060	0.0083	51.51	85.68	0.8568	0.0091	45.18	86.47	0.8647

Table 7: Effect of azo dye compound A2 on the dissolution of C-steel in 0.5M HCl at different immersing time

(Time hr)	1				2				3				4				5			
(Conc M)	Wt-loss gm	(Rcorr Mpy)	% IE	θ	Wt-loss gm	(Rcorr mpy)	% IE	θ	Wt-loss gm	(Rcorr mpy)	% IE	θ	Wt-loss gm	(Rcorr mpy)	% IE	θ	Wt-loss gm	(Rcorr mpy)	% IE	θ
blank	0.0088	218.47	-	-	0.0254	315.30	-	-	0.0382	316.12	-	-	0.0580	359.98	-	-	0.0673	334.16	-	-
1× –––	0.0059	146.47	32.95	0.3295	0.0086	106.75	66.14	0.6614	0.012	99.30	68.58	0.6858	0.0136	84.41	76.55	0.7655	0.0142	70.50	78.90	0.7890
5× –––	0.0053	131.58	39.77	0.3977	0.0075	93.10	70.47	0.7047	0.0098	81.10	74.34	0.7434	0.0119	73.85	79.48	0.7948	0.0128	63.55	80.90	0.8098
1× –––	0.0048	119.16	45.45	0.4545	0.0069	85.65	72.83	0.7283	0.0092	76.13	75.91	0.7591	0.0101	62.68	82.58	0.8258	0.0115	57.10	82.91	0.8291
5× –––	0.0024	59.58	72.72	0.7272	0.0041	50.89	83.85	0.8385	0.0054	44.68	85.86	0.8586	0.0075	46.55	87.06	0.8706	0.0079	39.22	88.26	0.8826

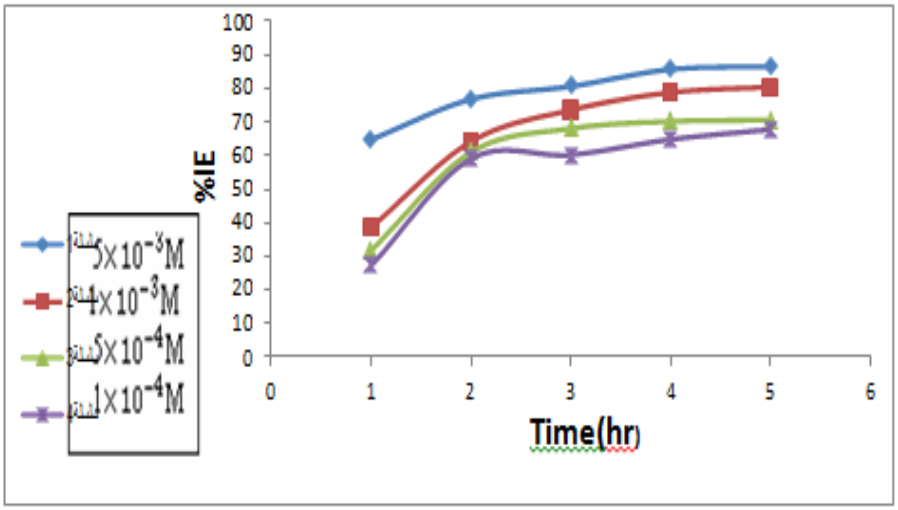


Figure 11: Variation of the Inhibition Efficiency %IE as a Function of the Time in the Presence of Different Concentrations of A1 at 30°C.

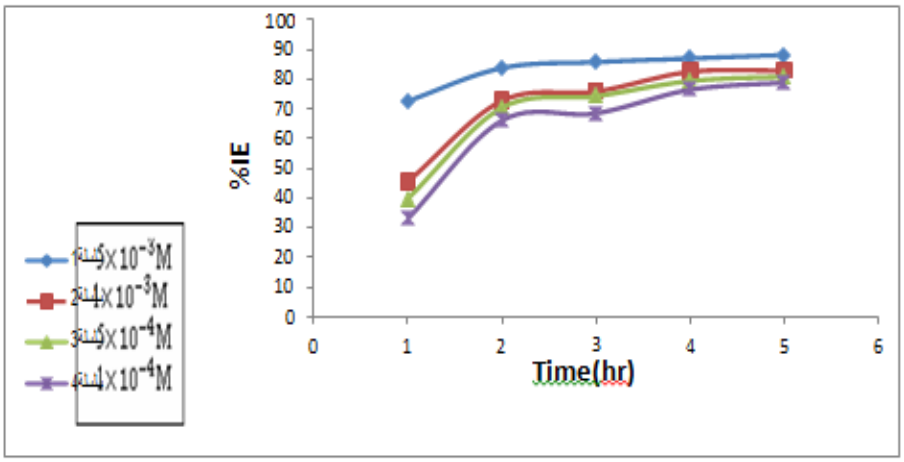


Figure 12: Variation of the Inhibition Efficiency %IE as a Function of the Time in the Presence of Different Concentrations of A2 at 30°C

Table 8: Effect of azo dye compound A1 on the dissolution of C-steel in 0.5M HCl at different temperature

Temp°C	303				313				323				333			
(Conc) M)	Wt-loss gm	(Rcorr) mpy	% IE	Θ	Wt-loss gm	(Rcorr) mpy	% IE	Θ	Wt-loss gm	(Rcorr) mpy)	% IE	Θ	Wt-loss gm	(Rcorr) mpy	% IE	Θ
Blank	0.0673	334.16	-	-	0.1000	496.53	-	-	0.4571	2269.66	-	-	0.6430	3192.72	-	-
1× ��⁻¹	0.0217	107.74	67.75	0.6775	0.0411	204.07	58.90	0.5890	0.1892	939.44	58.60	0.5860	0.3407	1691.69	47.01	0.4701
5× ��⁻¹	0.0198	98.31	70.57	0.7057	0.0319	158.39	68.10	0.6810	0.1568	778.56	65.69	0.6569	0.3085	1531.81	52.02	0.5202
1× ��⁻¹	0.0132	65.54	80.38	0.8038	0.0298	147.96	70.20	0.7020	0.1542	765.65	66.26	0.6626	0.2456	1219.49	61.80	0.6180
5× ��⁻¹	0.0091	45.18	86.47	0.8647	0.0157	77.95	84.30	0.8430	0.0737	365.94	83.87	0.8387	0.1116	554.13	82.64	0.8264

Table 9: Effect of azo dye compound A2 on the dissolution of C-steel in 0.5M HCl at different temperature

Temp°C	303	313	323	333												
(Conc M)	Wt-loss gm	(Rcorr) mpy	% IE	*Θ*	Wt-loss gm	(Rcorr) mpy	% IE	Θ	Wt-loss gm	(Rcorr) mpy	% IE	Θ	Wt-loss gm	(Rcorr) mpy	% IE	Θ
blank	0.0673	334.16	-	-	01000	496.53	-	-	0.4571	2269.66	-	-	0.6430	3192.72	-	-
1× ��⁻¹	0.0142	70.50	78.90	0.7890	0.0259	128.60	74.10	0.7410	0.1197	594.35	73.81	0.7381	0.1695	841.62	73.63	0.7363
5× ��⁻¹	0.0128	63.55	80.98	0.8098	0.0231	114.69	76.90	0.7690	0.1060	526.32	76.81	0.7681	0.1612	800.41	74.93	0.7493
1× ��⁻¹	0.0115	57.10	82.91	0.8291	0.0189	93.84	81.10	0.8110	0.0875	434.46	80.85	0.8085	0.1316	653.44	79.53	0.7953
5× ��⁻¹	0.0079	39.22	88.26	0.8826	0.0128	63.55	87.20	0.8720	0.0602	298.91	86.83	0.8683	0.0936	464.75	85.44	0.8544

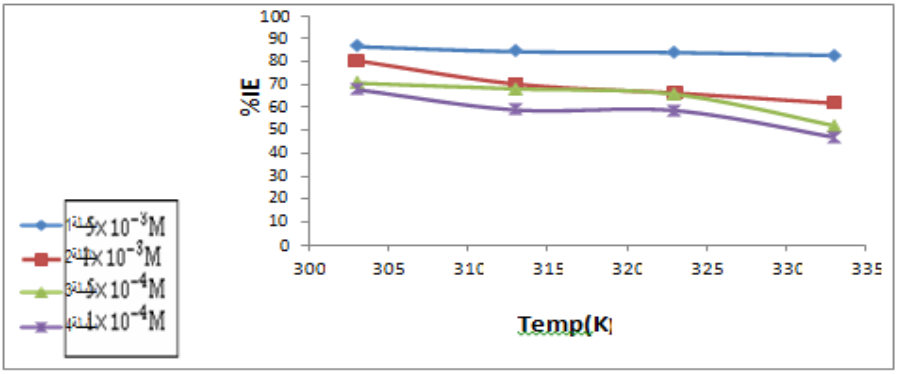


Figure13: Variation of the Inhibition Efficiency %IE as a Function of the Temperature in the Presence of Different Concentrations of A1

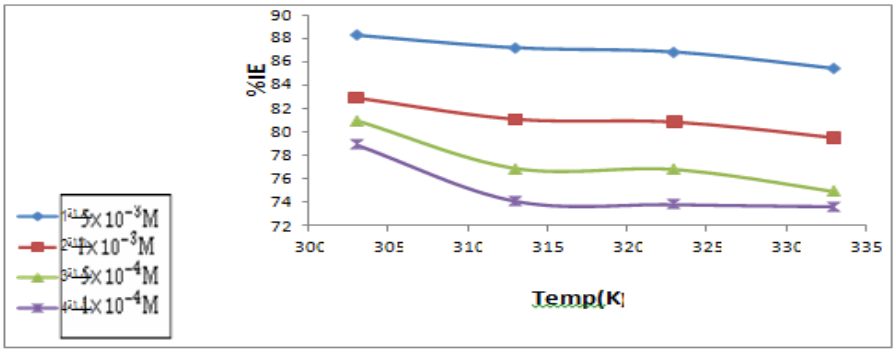


Figure14: Variation of the Inhibition Efficiency %IE as a Function of the Temperature in the Presence of Different Concentrations of A2

3.6. Kinetic parameters

The activation energy Ea of corrosion process was calculated using the following equation[23,24]

$$CR_{Corr} = A \exp(-Ea/RT) \quad \text{.....(5)}$$

$$\text{Log(CR2Corr / CR1Corr)=)Ea/ 2.303R)×)1 /T1-1 / T2) ..... (6)}$$

Where

RCorr Corrosion Rate, A Arrhenius factor, Ea Activation energy

Figure15,16 represent the relation between log Rcorr. vs. 1/T for metals in 0.5M HCl in the absence and presence nhibitor. Inspection of Table 10 reveal that, the activation energy increases in presence of the inhibitor and consequently the rate of corrosion reaction is decreased. Thus the activation energy values support the fact that the inhibitor was physically adsorbed on the metal surface in all media. The activation energies were also observed to increase with increasing in the concentration of the extract, indicating that there is increasing ease of adsorption of the inhibitors with increasing concentration. This is in accordance with the results.[25,26] It has been reported that when the values of Ea> 80 kJ/mol it indicates chemical adsorption whereas Ea< 80 kJ/mol infers physical adsorption.[27,28] In the present study, a physical adsorption mechanism is proposed since the values for the Ea are less than 80 kJ/mol.

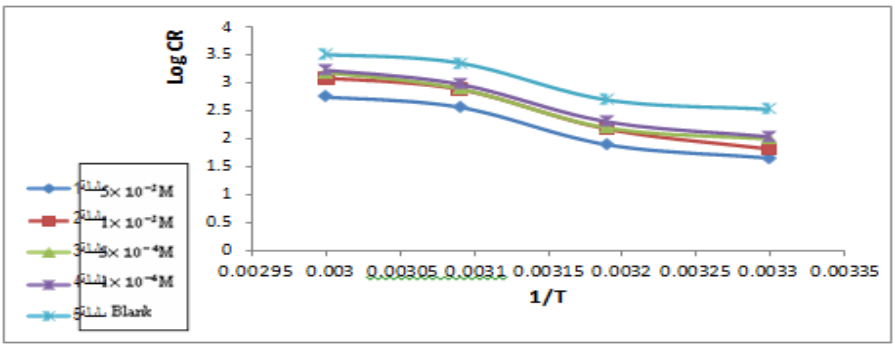


Figure 15: Arrhenius plots Log Rcorr. Versus 1/T at different concentration of A1

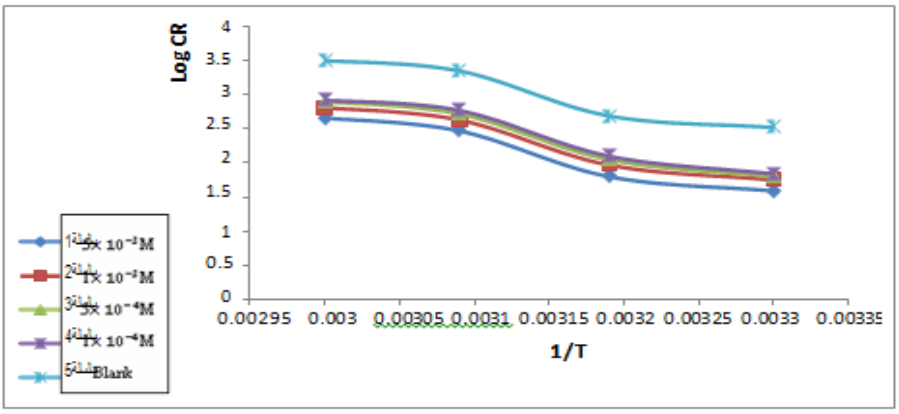


Figure 16: Arrhenius plots Log Rcorr. versus 1/T at different concentration of A2

Thermodynamic parameters enthalpy (ΔH) and entropy (ΔS) of activation of corrosion process may be evaluated from the effect of temperature. The enthalpy and entropy of activation of corrosion process was calculated from the equation:

$$RCorr = RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT) \quad \text{.....(7)}$$

where h is Planck's constant, N is the Avogadro's number, ΔS is the entropy of activation and ΔH is the enthalpy of activation.

Figure 17,18 signify the relation between log (RCorr / T) vs. 1/ T for metal in 0.5M HCl in absence and presence of various concentrations the inhibitor. Straight lines were obtained with slope equal to (– ΔH / 2.303 RT) and an intercept of log[(R/Nh) + (ΔS/2.303R)]. The calculated values of the apparent activation enthalpies ΔH and activation entropies, ΔS are given in Table 10. Enthalpy of activation of absolute values lower than 41.86kJmol^{-1} indicates physical adsorption, and values approaching 100 kJmol^{-1} indicate chemical adsorption.[29]

In this study, the values of ΔH are lower than 41.86 kJ mol^{-1} confirming physical adsorption. The positive signs of ΔH reflect the endothermic nature of the metal corrosion process.[30,31] The values of the entropy change of activation (ΔS) in the absence and presence of the inhibitor is large and negative; this indicates that the activated complex in the rate-determining step represents an association rather than dissociation step. The activated molecules were in higher order state than that at the initial state.[32]

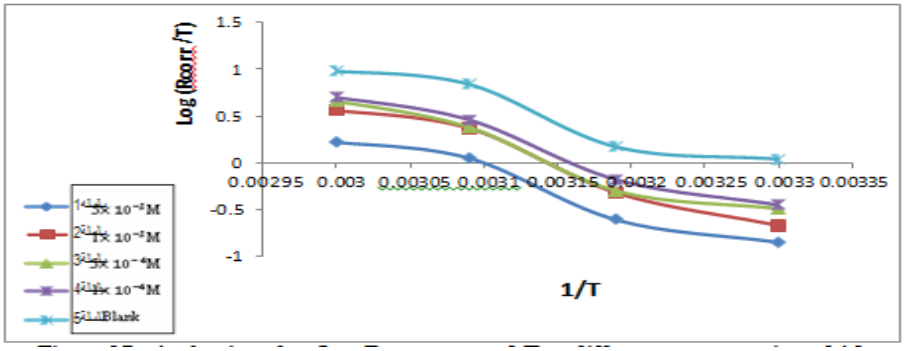


Figure 17: Arrhenius plots Log Rcorr. versus 1/T at different concentration of A1

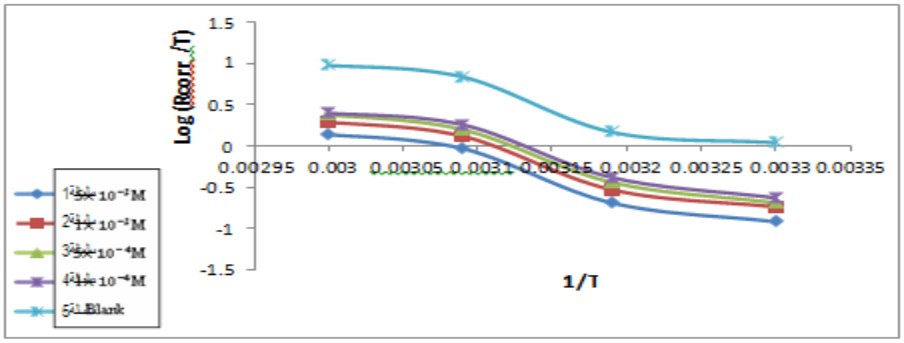


Figure 18: Arrhenius plots Log (Rcorr./T) versus 1/T at different concentration of A2

Table 10: Activation energy, the enthalpy ΔH of activation and the entropy of activation of bis azo inhibitors

(Conc M)	A1			A2			A3			A4		
	Activation parameters ($KJmol^{-1}$)			Activation parameters ($KJmol^{-1}$)			Activation parameters ($KJmol^{-1}$)			Activation parameters ($KJmol^{-1}$)		
	Ea	ΔH	- ΔS	Ea	ΔH	- ΔS	Ea	ΔH	- ΔS	Ea	ΔH	- ΔS
Blank	16.21	13.60	0.1519	16.21	13.60	0.1519	16.21	13.60	0.1519	16.21	13.60	0.1519
1× ◆◆⁻◆	26.32	23.71	0.1278	24.76	22.15	0.1365	24.08	21.47	0.1384	28.04	25.43	0.2094
5× ◆◆⁻◆	19.69	17.08	0.1504	24.31	21.70	0.1389	21.45	18.84	0.1474	27.19	24.58	0.1294
1× ◆◆⁻◆	33.54	30.93	0.2101	20.46	17.85	0.1526	20.46	17.85	0.1513	31.07	28.46	0.2115
5× ◆◆⁻◆	22.43	19.82	0.1479	19.95	17.34	0.1573	24.08	21.47	0.1427	24.08	21.47	0.1437

3.7. Adsorption isotherms

The values of surface coverage (θ) at different concentrations of azo dyes in 0.5 M HCl acid in the temperature range (303–333 K) were calculated to explain the best isotherm to determine the adsorption process from the experimental data obtained. Attempts were made to fit these θ values to various isotherm including Frumkin, Langmuir, Temkin, Freundlich isotherms. Byfar, the experimental data the results were best fitted by Langmuir adsorption isotherm equation.[33]

$$C / \Theta = \frac{1}{K} + C \qquad \text{..... (8)}$$

where C: is the inhibitor concentration
Θ: is the degree of surface coverage of the inhibitor
Kads. is the equilibrium constant of the adsorption process.

The *K* value is related to the Gibbs free energy of adsorption, ΔG°ads, according to the following equation[34]

$$\Delta G_{ads} = -RT[55.5\ K_{ads}] \qquad \text{..... (9)}$$

where 55.5 is the molar concentration of water in the bulk solution in mol L^{-1}, R is the universal gas constant and T is the absolute temperature.

Figures 17 and 18 show the relationship between C/θ and C at temperature ranges studied, which indicates that the adsorption of azo dyes follows Langmuir adsorption isotherm, which means that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species. The calculated values of k and ΔG° of the adsorption reaction of metal are shown in Table 11, the values of ΔG°ads around -20kJ/mol or lower are consistent with physicsorption, while those around -40kJ/mol or higher involve chemisorptions.[35] The result is presented in Table 11. The values ΔGads are negative and less than -40 $kJmol^{-1}$. The positive values of adsorption equilibrium constant Kads imply a better adsorption, which leads to an increase in the inhibition efficiency.[36] The adsorption equilibrium constant Kads decreases with increase temperature. The result interactions between the adsorbed molecules and the metal surface are weakens and consequently, the adsorbed molecules could become easily removable. Such data explains the decrease in the inhibition efficiency with increasing temperature.[37]

Table 11: equilibrium constant K and the free energy of adsorption ΔGads of bis azo inhibitors

	A1		*A2*		*A3*		*A4*	
(Temp K)	(K_{ads} mol^{-1})	- ΔG_{ads} ($KJmol^{-1}$)	(Kads mol^{-1})	- ΔG_{ads} ($KJmol^{-1}$)	(Kads mol^{-1})	– (ΔG_{ads}) $KJmol^{-1}$	(Kads Mol^{-1})	– ΔG_{ads} ($KJmol^{-1}$)
303	1278	28.01	1503	28.43	1311	28.08	1503	28.43
313	1073	28.57	1362	29.19	1050	28.52	1208	28.88
323	1039	`29.37	1318	30.01	970	29.18	1182	29.72
333	952	30.00	1173	30.58	914	29.89	967	30.05

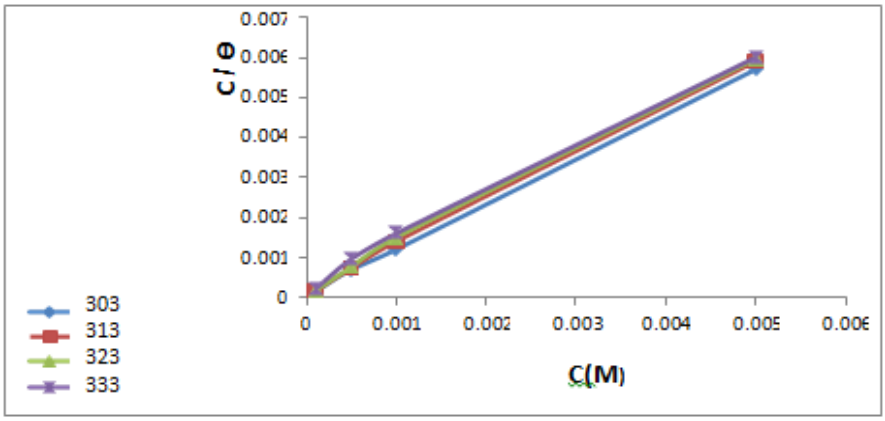


Figure 19: Langmuir adsorption isotherm of the used inhibitors A1 at different temperature

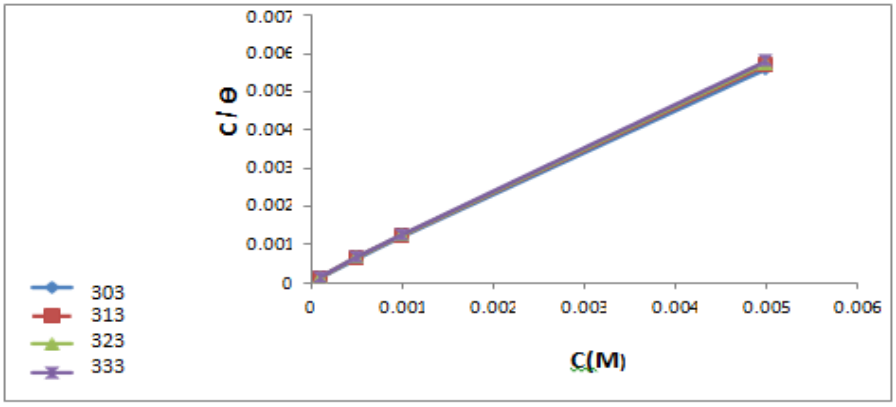


Figure 20: Langmuir adsorption isotherm of the used inhibitors A2 at different temperature

3.8. Potentiodynamic polarization measurements

Polarization behavior of C-steel in 0.5M HCl in the presence and absence of azo dyes compounds at 30°C is shown in Figs.[21-29] 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 but also retard the hydrogen evolution reaction. Electrochemical parameters such as corrosion potential (Ecorr), corrosion current density (Icorr), Cathodic Tafel constant (βc) and anodic Tafel constant (βa) were calculated from Tafel plots. In Tables 12 and 13 represents the results of electrochemical parameters. The addition of inhibitors causes a decrease of the current density, the maximum decrease in Icorr was observed for (A2). The *E*corr values of A1and A2 inhibitors were shifted slightly toward both Cathodic and anodic directions and did not show any definite trend in 0.5M HCl. This may be contributed to the mixed –type behavior of the studied inhibitors.[33,38] 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. Data in Table 12 and 13 shows that the inhibition efficiency increased with increasing the inhibitor concentration, indicating the inhibiting effect of these compounds.

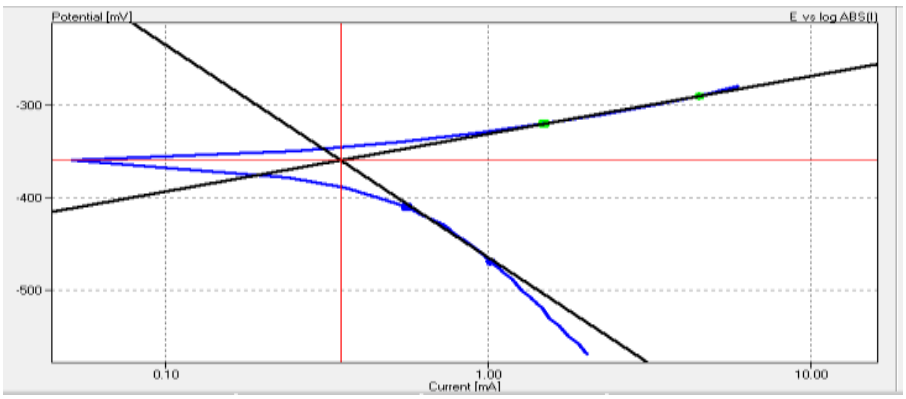


Figure 21: Galvano Static Polarization Curve of C-steel in 0.5M HCl in Absence Inhibitor at 30°C

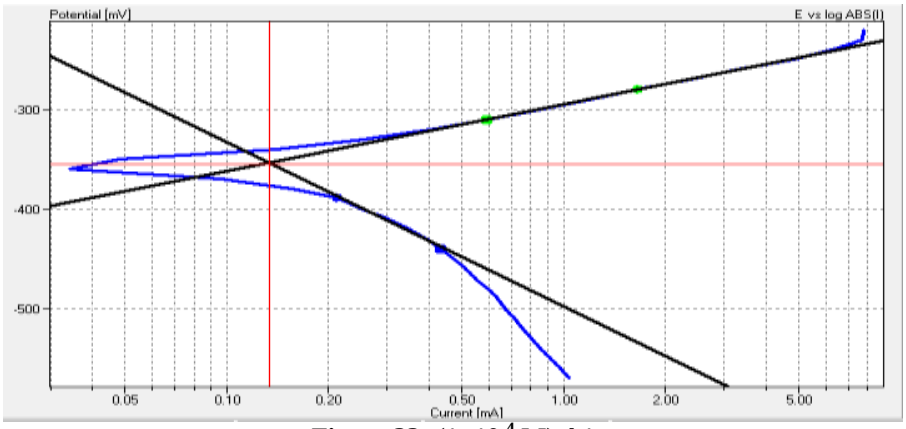


Figure 22: (1×10^{-4} M) A1

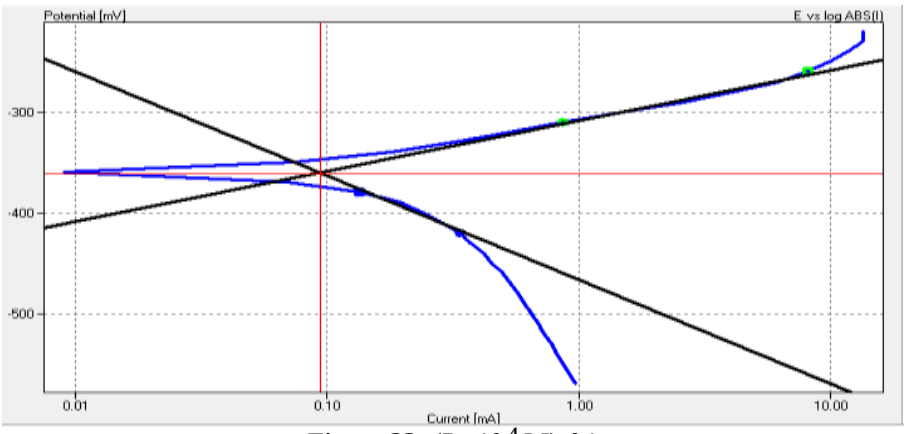


Figure 23: (5×10^{-4} M) A1

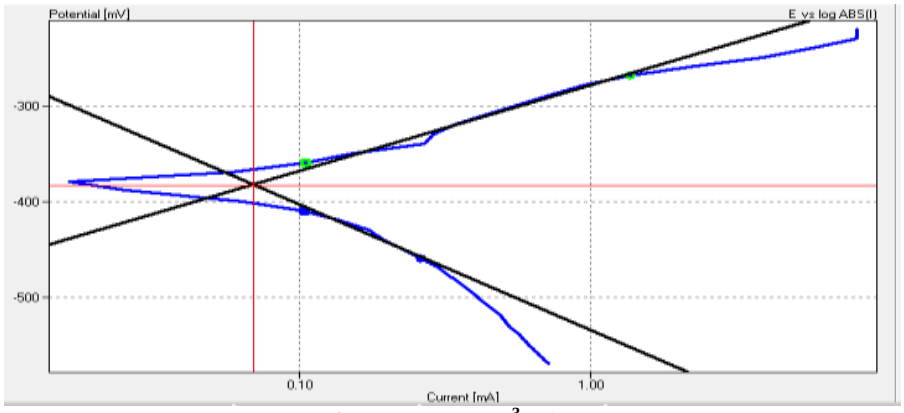


Figure 24: (1×10^{-3} M)A1

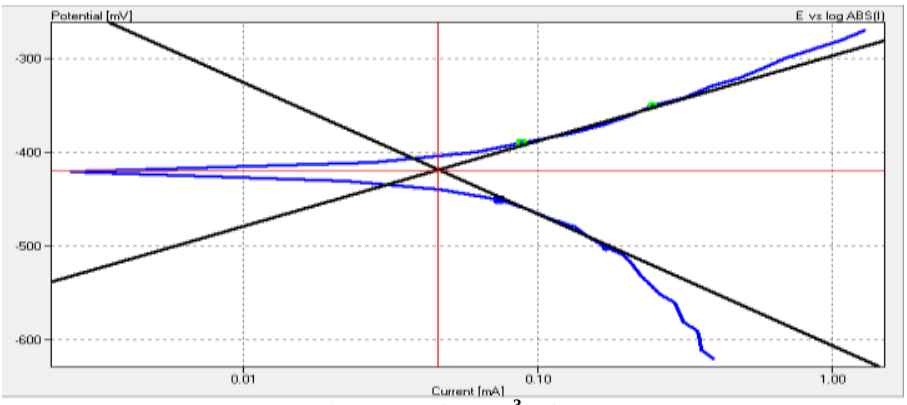


Figure 25: (5×10^{-3} M)A1

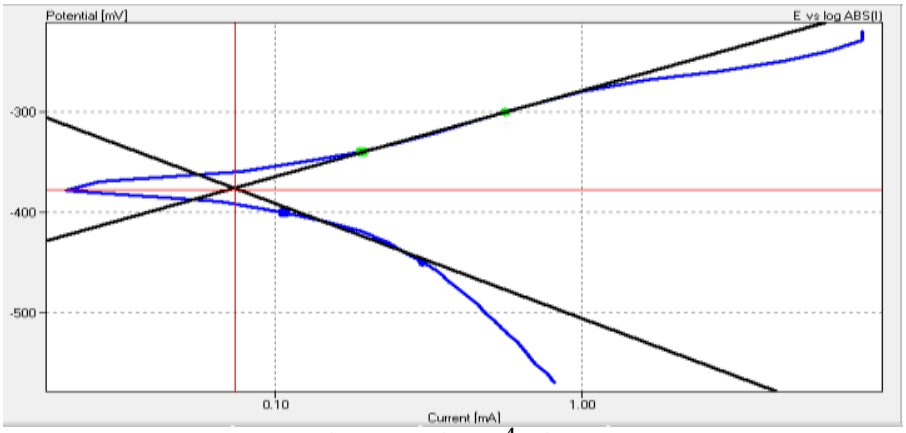


Figure 26: (1×10^{-4} M) A2

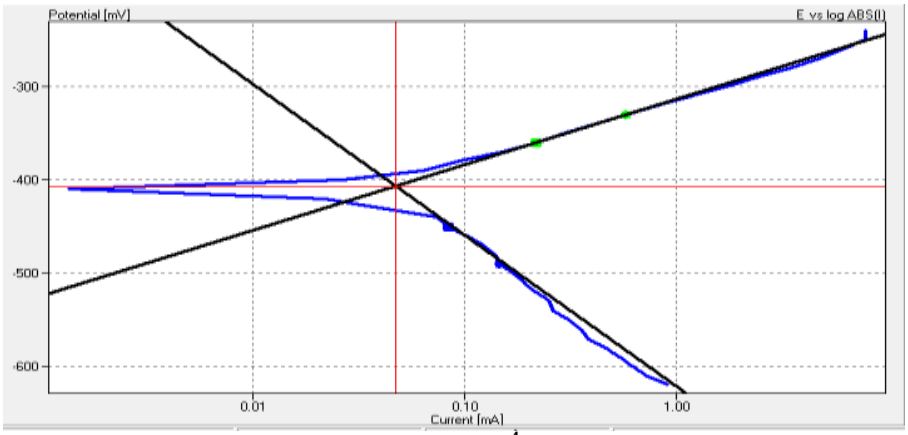


Figure 27: (5×10^{-4} M) A2

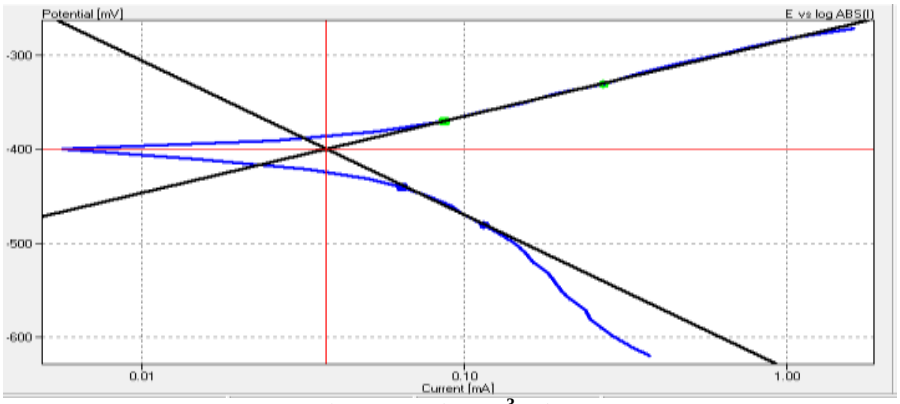


Figure 28: (1×10^{-3} M)A2

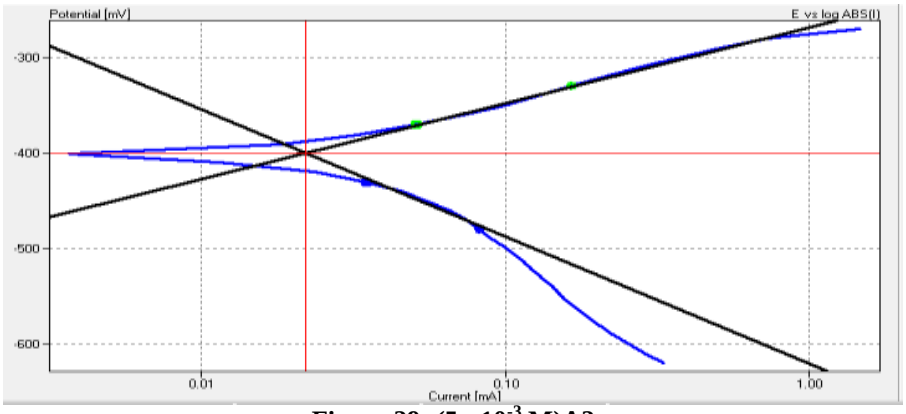


Figure 29: (5×10^{-3} M)A2

Table 12: The Values of Corrosion Parameters for the Corrosion of C-steel in 0.5M HCl by Galvanostatic Polarization in absence Presence A1

(Conc M)	Icorr µA / Cm^2	Ecorr mV	βc mV/Dec	βa mV/Dec	%IE
blank	349.90	-359.9	-230.2	62.4	_
1× ��$^{-}$$^{\square}$	133.54	-353.5	-164.8	67.1	61.83
5× ��$^{-}$$^{\square}$	93.57	-360.4	-103.3	50.0	73.25
1× ��$^{-}$$^{\square}$	69.22	-382.5	-131.2	89.6	80.21
5× ��$^{-}$$^{\square}$	46.03	-418.6	-140.2	90.9	86.84

Table 13: The Values of Corrosion Parameters for the Corrosion of C-steel in 0.5M HCl by Galvanostatic Polarization in Presence A2

(Conc M)	Icorr µA / Cm^2	Ecorr mV	βc mV/Dec	βa mV/Dec	%IE
blank	349.90	-359.9	-230.2	62.4	_
1×10^{-4}	73.79	-376.2	-114.6	85.6	78.91
5×10^{-4}	46.89	-406.6	-161.6	70.2	86.59
1×10^{-3}	37.39	-399.5	-164.1	81.6	89.31
5×10^{-3}	22.08	-400.1	-133.1	79.3	93.68

3.9. Molar Conductivity

The measurement of molar conductivity for the ionic from of acompound in solution is completed for [Ni(II)] with the ligand (A1,A2) and the result is reported in the table 14.

Table 14:-Conductivity measurement values of ligand's complexes (A1,A2) at 298K and using DMSO as solvent

Complex Number	Complexes	Λ m($S.cm^2.mole^{-1}$)	Electrolyte
1	[Ni(A1)]Cl_2	76	1:2
2	[Ni(A2)]Cl_2	79	1:2

3.10. Antibacterial activity

Studying of the growth inhibition against three types of pathogenic bacteria namely for some pigments lecture(A1,A2) and their complexes by using diffusion method and measurement inhibition zone by using (DMSO) as a solvent, using in this study three types from bacterial two its Gram negative bacterial strains, Escherichia coli, Pseudomonas Aeruginosa and the other is Gram positive bacterial strains, Staphylococcus aureus, Bacillus, We notice that the biological activity against this bacterial showed a positivity results. Ciprofloxacin were used as standard bactericide and compared inhibition this bacterial with Ciprofloxacin.

Table 15:- Antibacterial activity of bis azo dyes and Nickle(II) Complexes

Compound	Icon in the dish	Inhibition zone (mm)		
		Escherica coli	Staphylococcs aureus	Pseudomonas earuginosa
A1	1	18	10	……
A2	2	32	30	25
[Ni(A2)]Cl_2	3	…….	……	…….
[Ni(A1)]Cl_2	4	22	……..	18
Cipr.	Cipr.	28	30	31

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