Preparation and Characterization of New Azo Dye and its use as a corrosion inhibitor in (1 M) HCl

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A R T I C L E   I N F O

A B S T R A C T

The azo dye N-{4-hydroxy-3-[(E)-(4-hydroxyphenyl) diazenyl]phenyl} acetamide The dye features infrared spectroscopy, HNMR spectrometry, and mass spectrometry. Inhibitor A2 has been evaluated to be an effective corrosive compound at different concentrations and temperatures. Effective measurements of dynamic polarization were used. We note from the results that increasing the inhibitory concentration (A2) leads to an increase in inhibition while increasing the temperature leads to a decrease in it, as the highest inhibition efficiency (91%) was obtained at a concentration of 5*10-3 at a temperature of 298 K.

1. Introduction

Corrosion is the destructive attack of a metal by its environment. Metal corrosion is a major industrial problem that has attracted the attention of many researchers in recent years [1]. One of the most common processes in the field of corrosion prevention and control is the use of inhibitors. Corrosion inhibitors can be defined generally as a substance when added at a low concentration to an aggressive environment that significantly reduces the rate of corrosion of the exposed metal. In that environment. Corrosion inhibitors can be divided into two main types,[2] those that promote the formation of an original protective oxide layer with an oxidizing effect and those that prevent corrosion by selectively adsorbing on the metal surface and creating a barrier that prevents the corrosive agent from reaching the surface. In general, corrosion can be inhibited [3]. by adding a chemical compound that prevents the oxidation of the metal. Azo dyes have been used as effective inhibitors of corrosion in metals. It can effectively reduce or prevent the corrosion effects of metals and metal alloys by creating a protective layer that reduces many corrosive agents from reaching the metal surface [4]. The aim of this research is to inhibit the corrosion of carbon steel in hydrochloric acid medium by using a new azo dye.

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2. Experimental

The melting points of azo dyes were discovered. using Buchi B190K. The IR spectrum was carried out on the aFT-IR-8400S. Infrared Fourier Transform Spectrophotometer Shimadzu (Japan) by using a KBr disc in the range (600 – 4000) cm^{-1} . The UV-Visible spectrum was done using ethanol (1 x 10^{-4} M). The IR, UV-Visible spectrophotometer and melting point were completed by the Chemistry Department–Education College of pure science–Basrah University, Iraq. The correct mass spectrum and the 1H NMR were measured at Tehran University.

2.1.Preparation of N-{4-hydroxy-3-[(E)-(4-hydroxyphenyl)diazenyl]phenyl} acetamide (A$_2$ in spectrum figure)

The azo dye was prepared using of *3-amino phenol* (0.005 mol., 0.744g), with (1.05 mL) conc. HCl in separate deaker followed by adding solution of NaNO$_2$ was prepared by dissolving (0.9 g) in (5 mL) of distilled water, the NaNO$_2$ solution was then added to the 1st beaker. The resulting diazonium salt was then added to N-Hydroxy-N-(4-hydroxyphenyl) acetamide (0.003 mol., 0.4535 g) in 25% sodium hydroxide solution

2.2.Corrosion Rate Measurement Apparatus:

Use a device Bank Eieiktronkik Intelligent Controls Type M lab 200(2007) Germany In measuring the rate of corrosion of the carbon steel alloy used in this study and in the acidic medium and at different temperatures in the Analytical Chemistry Research Laboratory/College of Education for Pure Sciences/University of Basrah.

2.3.Alloys used:

In this study, an alloy of carbon steel N-80 was used, which was supplied by the Basrah Oil Company (B.O.C). It contains the elements listed in the proportions of their components in the following table: 10 mL of distilled water. Then, the And in a study conducted by the researcher (Hadi Thamer Obaid) who studied the azo dye

**Table 1.** Ratios of the components of carbon steel (N-80).

Element	C	Mn	S	P	Fe
Percentage%	0.3	1.2	0.06	0.05	98.39

3-((*E*)-(2-hydroxy-4-methylphenyl)diazenyl)-1-((*E*)-((2-hydroxy-5-methylphenyl)imino)methyl)naphthalen-2-ol

And its use as a corrosion inhibitor, dynamic data was applied to investigate the corrosion inhibition efficacy of carbon steel. The study was carried out at different temperatures and with different concentrations and the results showed that when the temperature rises above 298K, the inhibition efficacy decreases. The improvement in efficiency can be attributed to the adsorption of the inhibitor molecules, which form a dense preservative film on the metal surface [5]

3. Results and Discussion

The azo dye was prepared according to the following scheme
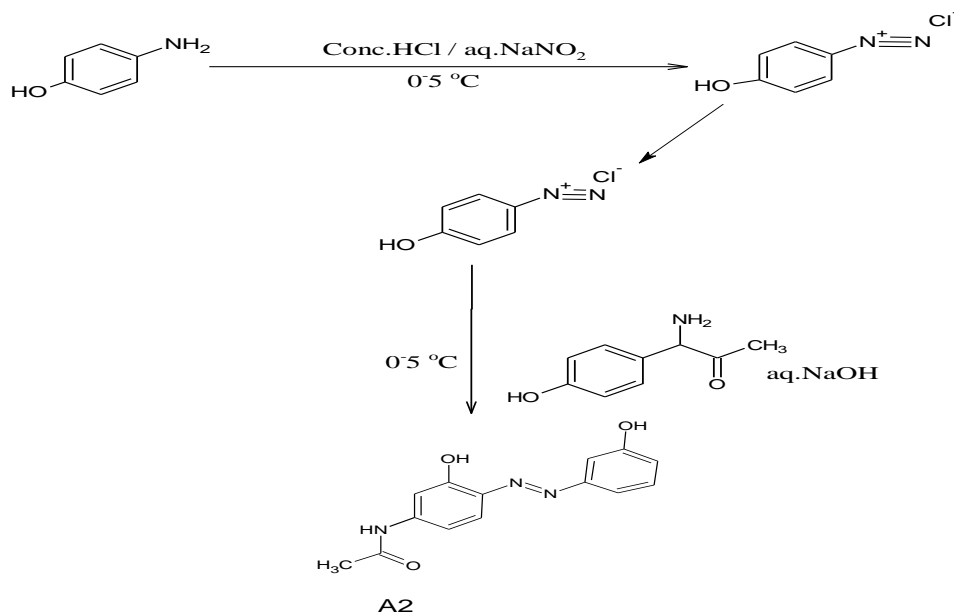
Scheme (1) Preparation of a new azo dye.

The dye was derived from paracetamol, this dye was diagnosed using infrared spectroscopy, proton nuclear magnetic resonance and mass spectrometry. The (N-H) amplitude vibration beam (N-H) at $3475.73 cm^{-1}$, $3562.88 cm^{-1}$ The (O-H) group amplitude vibration beam is shown at the 3414.00cm group amplitude vibration beam (C=O) is shown at the 1616.53cm position.
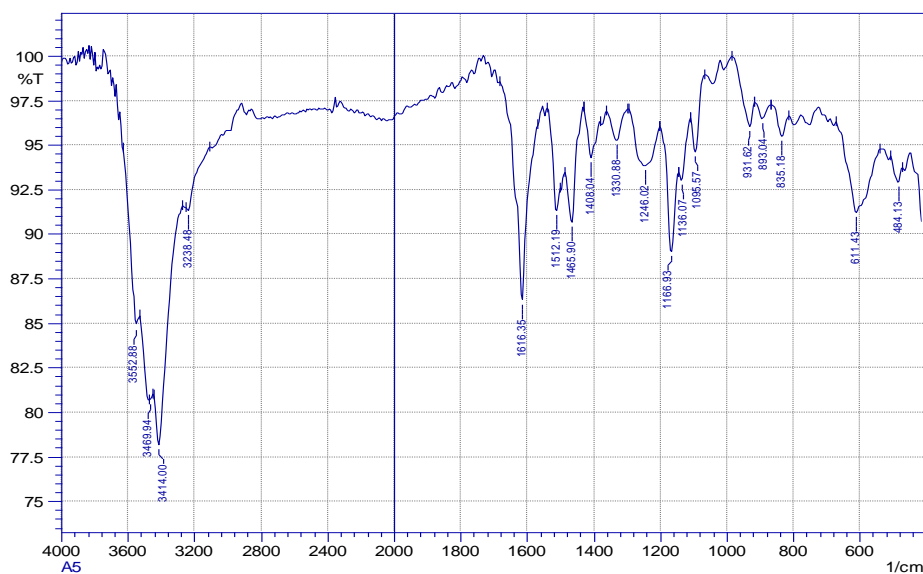

Fig. 1. FT-IR Spectrum of A2compound.

The H-NMR spectrum of the spectrum of the dye (A2) as shown in Fig. 2 was characterized by the appearance of a signal at displacement (10.80 ppm) belonging to the NH group and a signal at(9.57 ppm) belonging to the phenolic OH group. It is also characterized by the appearance of a displacement of the aromatic rings8.93 -7.10 (7H, Ar-<u>H</u>).
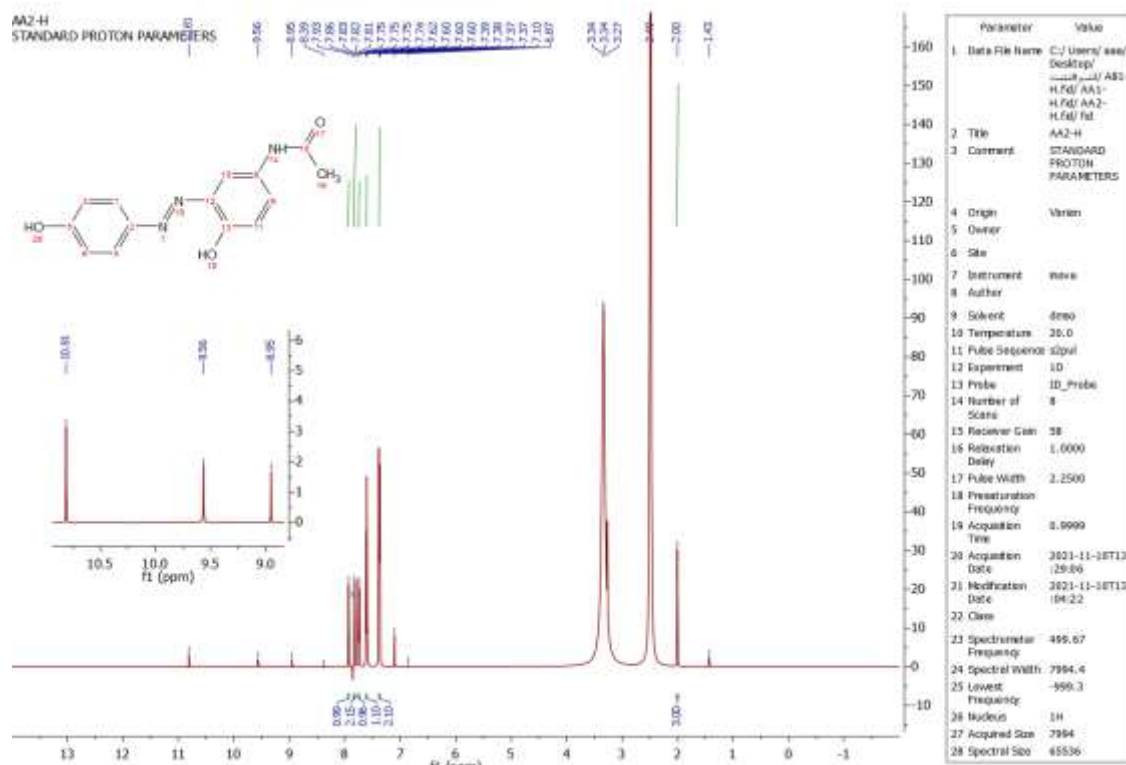
Fig. 2. 1 H-NMR spectrum of the A₂ compound.

The mass spectrum of dye A2 in Fig. 3 indicates the appearance of the molecular ion peak at m/z = 270, which theoretically agrees with the molecular weight of the compound   M.wt = 270.65 g/mol, and the spectrum indicates the appearance of the base ion peak at m /z=63 g/mol
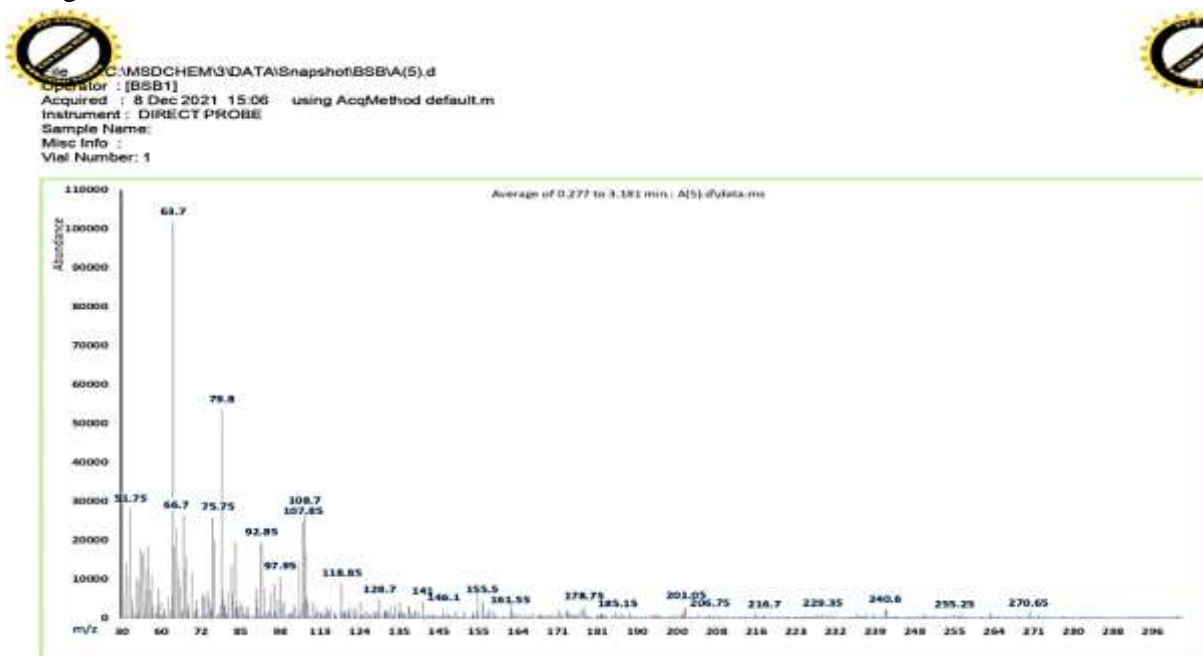

Fig. 3. The mass spectrum of the azo dyes (A₂).

3.1. Electrochemical corrosion rate measurement

The measuring cell of a wear rate measuring device, consisting of three electrodes, the first of which is the working electrode, was used. It is the model's carrying electrode, and the second electrode is an auxiliary electrode made of graphite. Finally, the standard calomel electrode serves as the reference electrode. The measuring cell is prepared by connecting the model (carbon steel) to the working electrode, filling the cell with (100ml) of (1M HCl) solution, and connecting the cell to the device. The required information, which includes the start and end of the effort as well as the reaction time, is included after the experiment, which takes 15-20 minutes. The results are presented in the form of a graph.

3.2. The study of dynamic polarization:

The study included the use of azo dye new prepared from a pharmaceutical preparation as a corrosion inhibitor for carbon steel alloy with the acidic medium (1M) of hydrochloric acid The erosion velocity was measured by polarization curves method (Extrapolation Tafel plot) at different temperatures (298,308,318K) with different concentrations. According to the law

$$CR = K \times \frac{I_{corr}}{\rho} \times E.W \tag{1}$$

The results showed that the azo dye inhibits the corrosion process by reducing the intensity[6] of the corrosion current I_{corr} of carbon steel in the presence of an inhibitor A comparison of its values in the absence of inhibitors, . As for the inhibition efficiency (% E), it was found that it increases with the increase in the concentration of the inhibitor for each temperature,[7] and in general it was noted that the inhibition efficiency decreases with the increase in temperature for one concentration of the inhibitory substance.[8] The relationship between concentration and percentage is a positive relationshipThe percentage values of the inhibition efficiency indicate that the inhibition efficiency of the dy e (A2) was 91%, which was the highest at a concentration (5 x 10-3 M) and at a degree of 298 K. This can be explained by the presence of a group (-CH3) in the compound (A2), which activates the ring as it is one of the electron-motive groups, as well as the presence of an (OH-) group in the ortho and close to the azo group, which facilitates the bonding process with the metal-metal. Which increases the efficiency of inhibition he results are shown in the Table 2.

Table 2. Polarization curves data for corrosion of carbon steel alloy with different concentrations of inhibitor (A2) in (1M) hydrochloric acid solution and in the thermal range (298-318).

Temp(K)	InhibitorConc.(M)	E_{corr} (mV)	CR (Mpy)	Icorr ($\mu A/Cm^{2)}$	βa (mv/Dec)	βc (mv/Dec)	% (IE).	θ
298		-479.3	11.46	25.17	243.6	-256.2	0	0
308	blank	-494.6	21.16	44.84	327.3	-273.0	0	0
318		-476.0	30.82	67.67	340.9	-330.9	0	0
298		-511.7	5.41	11.89	233.1	-222.2	52.7	0.52
308	$1*10^{-4}$	-494	10.45	22.95	253.5	-231.4	48.8	0.48
318		-518.2	17.30	31.96	383.2	-315.6	43.8	0.43
298		-496.6	2.93	6.45	212.2	-206.4	74.3	0.74
308	$5*10^{-4}$	-496.9	6.35	13.94	285.0	-253.3	68.9	0.68
318		-485.8	12.02	26.39	178.7	-171.4	61.0	0.61
298		-456.2	1.94	4.27	143.6	-202.4	83.0	0.83
308	$1*10^{-3}$	-483.4	4.95	10.88	210.1	-191.5	75.7	0.75
318		-473.1	9.40	20.64	215.9	-211.1	69.4	0.69
298		-433.1	1.19	2.02	95.9	-173.1	91.9	0.91
308	$5*10^{-3}$	-473.2	3.46	7.60	171.0	-189.1	83	0.83
318		-463.3	5.14	18.70	163.5	-174.7	72	0.72

3.3. Study the effect of temperature

At temperatures ranging from 298 to 318 k, the effect of temperature on the corrosion characteristics of carbon steel in free and inhibited solutions of 1 M hydrochloric acid was investigated. As for the retarding efficiency (% E) It was found that it increases with the

increase in the concentration of the inhibitor for each temperature, and in general it was noted that the inhibition efficiency decreases with the increase in temperature for one concentration of the inhibitory substance Fig. 1 shows the effect of temperature on carbon steel corrosion inhibition effectiveness in 1 M hydrochloric acid in the presence of different inhibitor concentrations. Fig. 7 (a2)
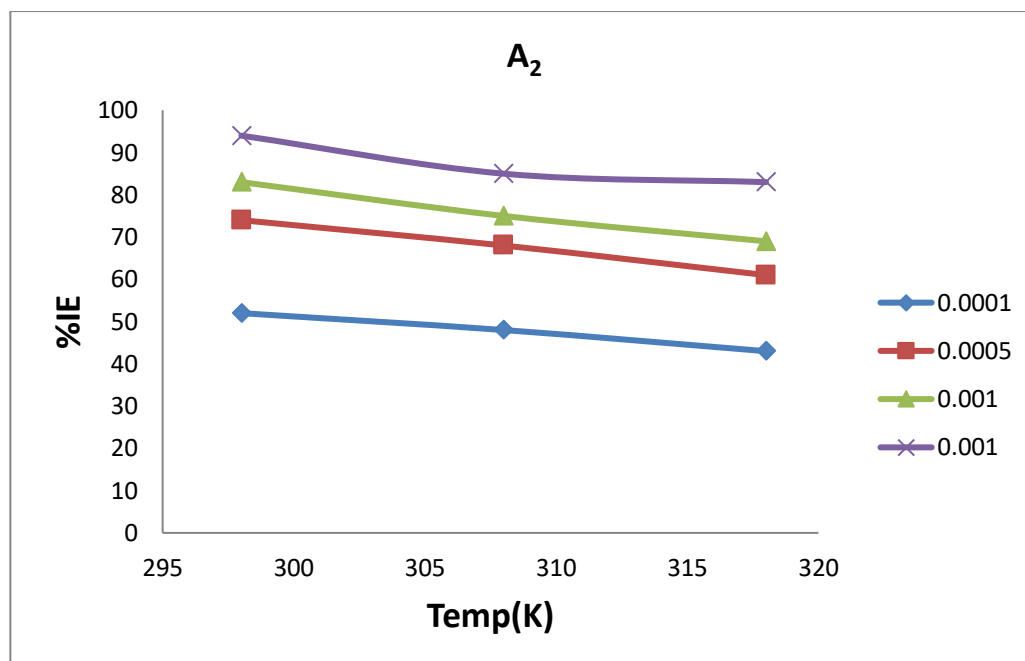

Fig. 7. The relationship between inhibition efficiency and temperature in acidic solutions of different concentrations of inhibitor a2 and in the thermal range K (298-318).

3.4. Studying the kinetic variables of the corrosion process

In an acidic environment of (1M) hydrochloric acid and in the presence and absence of inhibitors with different concentrations, the corrosion reaction of carbon steel was studied, where temperature has an effect on the corrosion rate of carbon steel was investigated in the thermal range (318-298K). Calculate the activation energy (Ea), as shown in the following equation [9].

$$\text{Log I}_{\text{corr}} = \text{Log A} \frac{-\text{Ea}}{2.303 \text{ RT}} \tag{2}$$

When drawing the relationship between Log Icorr against 1/T as shown in Fig. 8, and Table 3 a straight line is obtained and from the slope of. The curve the activation energy is calculated, where (-Ea)/(2.303 R))) The slope of the linear relationship, and Log A represents their intersection with the axis From Eq. (3-8) The kinetic functions (ΔS*,ΔH*) of the activated complex were calculated, which provide information on how the corrosion inhibitor activated complex is formed in an acidic medium.

$$\text{Log} \frac{\text{Icorr}}{\text{T}} = \text{Log} \frac{\text{R}}{\text{N h}} + \left(\frac{\Delta \text{S}^*}{2.303} \right) - \left(\frac{\Delta \text{H}^*}{2.303 \text{ RT}} \right) \tag{3}$$

When drawing the relationship we get a linear relationship whose slope is 2.303 R (-ΔH*/ where ΔH* is calculated and is an intercept. Its axis is [(Log R/hN+((ΔS*)/(2.303 R)] from which is calculatedΔS * From the values of the intersection of the axis and the slope, ΔG*can be calculated according to the equation [10]

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{4}$$

Observing the results, we discover that the activation energy with the inhibitor present is greater than in the absence of the inhibitor, indicating a high energy barrier for the corrosion process with the inhibitor present or the formation of a thin layer of the inhibitor added on the surface of the carbon steel., which in turn prevents the interaction of the charge from the metal surface.[11] The positive values of the activation enthalpy (ΔH*) indicate that the reaction is endothermic in nature and that it increases with increasing concentration of the inhibitor compared to its absence. This means that the reaction of the dissolution of carbon steel in hydrochloric acid (1M) is endothermic and the dissociation process is difficult .The negative value of the activation entropy (ΔS*) is higher in the presence of the inhibitor, which indicates that the adsorption of reactants as inhibitors that turn into adsorbed active complexes on the surface of carbon steel alloy is more stable. And the positive values of free activation energy (ΔG*)indicate that The reaction is not spontaneous and these values are higher in the presence of the inhibitor.[12].

Table 3. Values of the functions Ea, ΔS*, ΔH*, ΔG* in the presence and absence of the inhibitor (A2) at different concentrations and temperatures in the acidic medium.

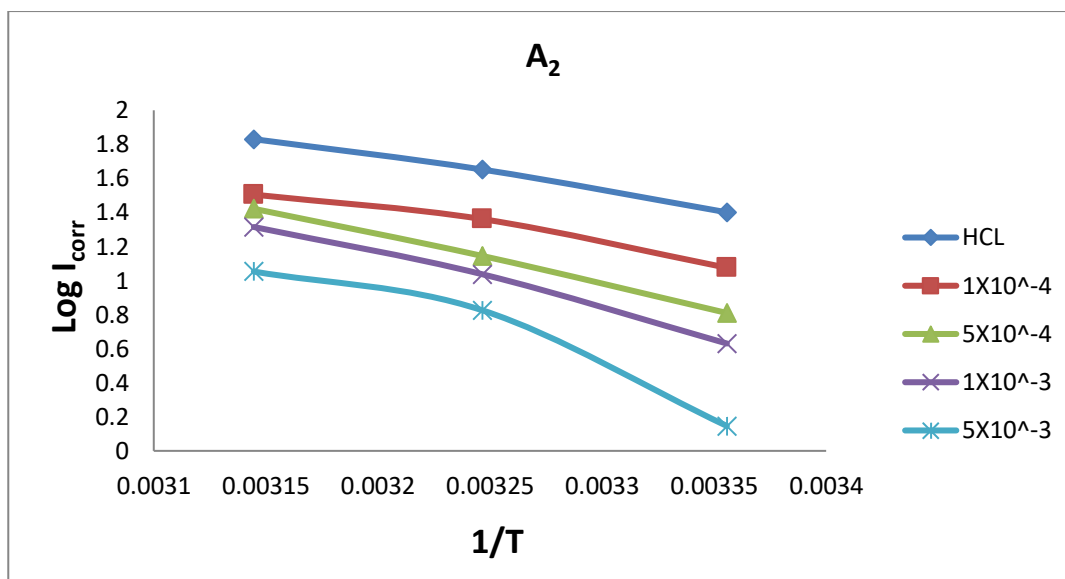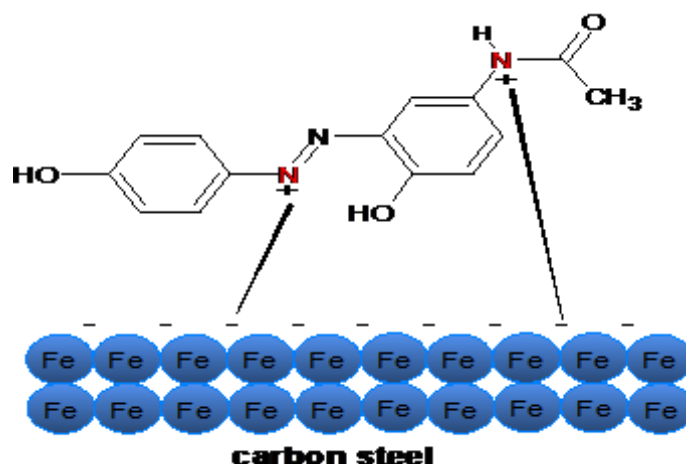| Comp	Conc (M)	Ea (K.Jmol^{-1}).		ΔH* (K.Jmol^{-1}).	ΔS* (K.Jmol^{-1}). T (298K)	ΔG* (K.Jmol^{-1}). T (308K)	T (318K).
HCl	1	39.02	36.466	-0.266	38.496	38.565	38.633
	1x10-4	44.54	36.52	-0.257	36.607	36.607	36.609
	5x10-4	51.56	52.99	-0.252	59.437	59.235	59.437
A$_2$	1x10-3	53.41	59.62	-0.241	69.012	69.327	69.642
	5x10-3	75.13	80.13	-0.192	104.064	104.867	105.670

Fig. 8. Arinos' relationship with the absence and presence of inhibitor A2)) and in the thermal range (298-318)K.

3.5 inhibition mechanism

The mechanism of inhibiting the azo dye compound used as a corrosion inhibitor for carbon steel –N 80 can be explained by one of the following proposed mechanisms: [13-14] The first mechanism: the possibility of overlapping the free electron pairs (Lone pairs) on the oxygen atoms and the nitrogen atoms of the azo group with the d-orbitalate present in the iron atoms of the carbon steel surface. Forming covalent coordination bonds that enable it to adhere to the surface and form a protective layer, which is a (coordination complex) that prevents The arrival of the corrosive substance to the surface. Hence, it reduces chemical corrosion and this interference potential is classified as (chemical adsorption).[15]
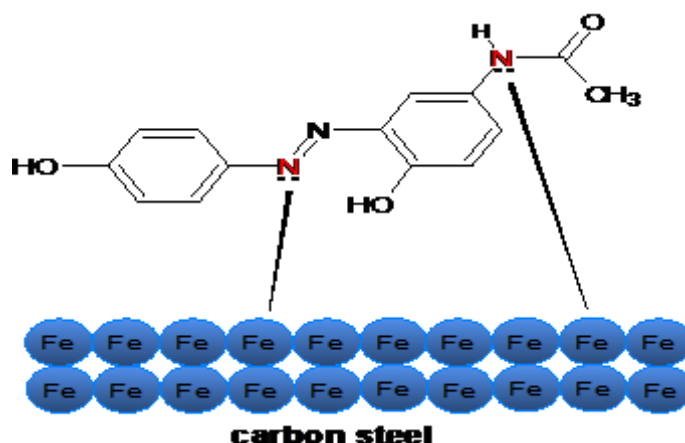
The second mechanical: the possibility of electrostatic attraction (physical adsorption) between some positively charged inhibitor molecules with the negative charge on the surface of the carbon steel alloy. This is due to the possibility of protonation on the nitrogen atoms in the azo group.[16-17]

The third mechanical: the possibility of electrons overlapping π bonds with d orbitals, which leads to the formation of a protective layer that prevents corrosive substances from reaching the surface of the metal[18]
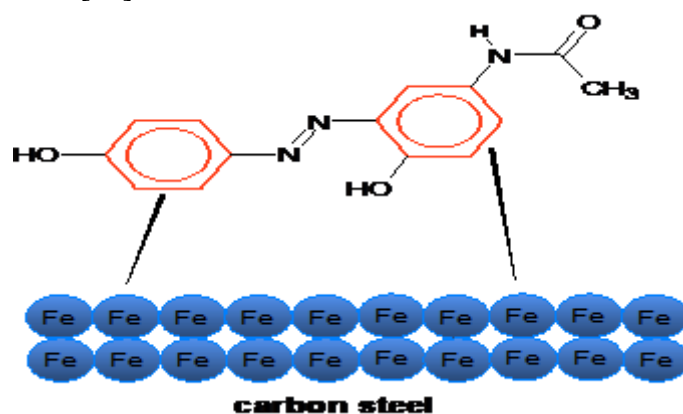
4. Conclusion

A compound (A2) has been synthesized, the inhibition efficiency of A2for carbon steel corrosion in 1 M HCl was investigated, High inhibition efficiency was recorded (91%) at $5*10^{-3}$ M concentration. Thermodynamic studies proved that A2is adsorptive inhibitor and their adsorption process obeys the Langmuir's adsorption isotherm, and is spontaneous. The values of the standard free energies of adsorption indicate that inhibitors are adsorbed on carbon steel in 1 M HCl through chemical mechanism. Such high corrosion inhibition efficiency with such low concentration make A2 an excellent carbon steel corrosion inhibitor with environmental and economic advantages.

5. References

[1] Kornev, F. Saprykin, G. Lobanova, V. Ushakov, S. Spark, Journal of Electrostatics **96**, 111 (2018).
[2] A Al-Amiery, A.B. Mohamad, A.A. H Kadhum, L.M. Shaker, W.N.R.W. Isahak, M. S.Takriff, Scientific Reports **12**(1), 1 (2022).
[3] S. Tanwer, S. Kumar Shukla, Current Research in Green and Sustainable Chemistry **5**, 100227 (2022).
[4] S.K. Shukla, M.A. Quraishi, E.E. Ebenso, International Journal of Electrochemical Science **6**, 2912 (2011).
[5] H.T. Obaid, M.Y. Kadhum, A.S. Abdulnabi, Materials Today: Proceedings **60**(3), 1394 (2022).
[6] Y.S. Choi, J.G. Kim, Corrosion **56**(12), 1202 (2000).
[7] L. Zheng, J. Landan, N.S. Matin, G.A. Thomas, K. Liu. Corrosion Science **106**, 281 (2016).

[8] S. Abdul Nabi, M.Y. Kadhum, A.A. Hussain, International Journal of Science and Research (IJSR) **8**(6), 1746 (2019).

[9] S.S. Al-Juaid, Portugaliae Electrochimica Acta **25**(3), 363 (2007).

[10] M. Bouklah, B. Hammouti, Portugaliae Electrochimica Acta 24(4), 457 (2006).

[11] S.M. Merdas, Annals of the Romanian Society for Cell Biology **25**(4), 910 (2021).

[12] Ghames, T. Douadi, S. Issaadi, L. Sibous, K. I. Alaoui, M. Taleb, S. Chafaa, International Journal of electrochemical science **12**, 4867 (2017).

[13] M. Mohammed, F. Almashal, J. Jassem, Egyptian Journal of Chemistry, 64(1), 47 (2021).

[14] Q.Q. Liao, Z.W. Yue, D. Yang, Z.H. Wang, Z.H. Li, H.H. Ge, Y.J. Li, Thin Solid Films **519**(19), 6492 (2011).

[15] Doner, R. Solmaz, M. Ozcan, G. Kardaş, Corrosion science **53**(9), 2902 (2011).

[16] G. Khan, W.J. Basirun, S.N. Kazi, P. Ahmed, L. Magaji, S.M. Ahmed, G.M. Khan, M.A. Rehman, A.B.B.M. Badry, Journal of colloid and interface science **502**(15), 134 (2017).

[17] P. Kumari, P. Shetty, Nagalaxmi, D. Sunil, Surface Engineering and Applied Electrochemistry **56**(5), 624 (2020).

[18] H.K. Dhaef, R.H. Al-Asadi, A.A. Shenta, M.K. Mohammed, Indonesian Journal of Chemistry **21**(5), 1212 (2021).

تحضير وتشخيص صبغة آزو جديدة واستخدامها كمثبط للتآكل في (1مولاري) حامض الهيدروكلوريك

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الملخص	معلومات البحث

صبغة الازو ن-(4-هيدروكسي-3-4)-(E)]-هيدروكيسي فينيل)ديازينيل فينيل)[استياميد شخصت الصبغة بمطياف الأشعة تحت الحمراء ، وقياس طيف HNMR ، وقياس طيف الكتلة. تم تقييم المثبط A2 على أنه مركب فعال للتآكل بتراكيز ودرجات حرارة مختلفة. تم استخدام قياسات فعالة للاستقطاب الديناميكي. نلاحظ من النتائج أن زيادة التركيز المثبط (A2) يؤدي إلى زيادة التثبيط بينما تؤدي زيادة درجة الحرارة إلى انخفاضه ، حيث تم الحصول على أعلى كفاءة تثبيط (91٪) بتركيز 5*10-3 عند درجة حرارة 298كلفن.

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