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Characterization and synthesis of some new Schiff bases and their potential applications

Mayada Talib Mohammed* 🆔 |**Wadhah Naji Al-Sieadi** |**Oday H. R. Al-jeilawi**

Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq

In this present work, [4,4`-(biphenyl-4,4`-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(2-methoxyphenl)(**A₁**),4,4`-(biphenyl-4,4`-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol(**A₂**),1,1`-(biphenyl-4,4`-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene) dinaphthalen-2-ol (**A₃**)]C.S was prepared in 3.5% NaCl. Corrosion prevention at (293-323) K has been studied by using electrochemical measurements. It shows that the utilized inhibitors are of mixed type based on the polarization curves. The results indicated that the inhibition efficiency changes were used with a change according to the functional groups on the benzene ring and through the electrochemical technique. Temperature increases with corrosion current (icorr) and potential (Ecorr) and decreases with CS covered by Schiff bases in the presence of inhibitors and temperatures decrease with efficiency (% PE) of CS in the absence and presence of inhibitors and using several techniques including infrared (FT-IR), scanning electron microscopy (SEM) and atomic force microscopy (AFM). Kinetic and thermodynamic activation parameters (Ea, A, ΔH*, S*, G*) were calculated for prepared vehicles. Then, the biological activity of the prepared compound (A₁-A₃) showed its efficiency with the use of Gram-positive and Gram-negative bacteria (*Staphylococcus aureus, Staph.aure*) and (*Escherichia coli, E.coli*), as well.

*Corresponding Author:

Mayada Talib Mohammed

Email:
mayada.mohammed1105@sc.uobaghdad.edu.iq

Tel.: +9647711230526

Introduction

Corrosion is defined as the interaction of metals with their environment [1], and surface damage or degradation of a metal in the aggressive environment. It involves chemical or electrochemical oxidation processes, transferring electrons of metals to their environment and undergoing a valency change from zero to positive. The environments include liquid, gas, and a mixture of liquid soil. The so-called environments' electrolytes have their own higher conductivity for electron transport [2]. The scientific and logical classification of corrosion processes, although not easy in any way, because there is an enormous diversity in corrosion environments and diversity in corrosion reactions, but there is classification of corrosion reactions divided into "wet" or "dry" is now wide. In general, these terms are commonly used. The term "wet" for all reactions includes in which an aqueous solution participates in the functioning of the

reaction mechanism; the term "dry" implies the absence of water or aqueous solution [3]. To reduce corrosion and prevent gas hydrates forming in the tubes, the researchers dried the films by using new techniques [4]. Carbon steel is one of the most important materials applied in industry, which is used as a raw material and manufactured by alloying many iron and carbon with very small amounts of other presented metals [5,6]. Carbon steels are considered to have good properties, for example CS welding, as well as low cost [6]. C.S also reveals other good qualities which are prominent for its application in diverse section such as industry, oil and gas [6-9]. In many other industries, organic acids are used to clean and remove scale from steel substrates or work to melt aggregate and remove mud for easy access to crude oil [10], thus carbon steel is frequently used in drilling oil in wells erodes pipes due to harsh effects erosion processes. Corrosion has significant damages which affect important areas, including conservation, economy and safety. It is important to reduce corrosion by using several methods as adding inhibitors that are mixed cathodic and anodic by adding organic materials or by coating carbon steel [10-13]. There are many organic materials that can be used as inhibitors to reduce corrosion in saline media [14]. Studies are performed on the base mineral Schiff due to its diverse chemical and physical properties, as well as the use of the Schiff base in color photography [15]. Studies have been carried out on the mineral Schiff base due to its diverse chemical and physical properties, in addition to the use of the Schiff base in color photography [16], and Schiff bases were used as antioxidants prepared with creatinine from the reaction of aromatic aldehydes with a few drops of glacial acetic acid as a catalyst in ethanol [17]. Schiff bases for inorganic compounds and transition metal chelates of Mn(II), Ni(II) and Cu(II) are considered to exhibit analgesic, inflammatory and antimicrobial activities [18]. Schiff bases with organic and inorganic compounds having optical and linear properties are one of the important compounds which have an important role in biological activities [19]. Schiff bases for inorganic compounds depend on the complex structure and Schiff bases have a number of their coordination complexes with antimicrobial, antifungal, and anticancer capabilities [20,21].

Experimental part

Electrochemical synthesis of 4,4`-(biphenyl-4,4`-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(2-methoxyphenl)(A_1), 4,4`-(biphenyl-4,4`-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)diphenol (A_2),1,1`-(biphenyl-4,4`-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)dinaphthalen-2-ol (A_3). On the surface of carbon steel immersed in brine, as depicted in Figure 1. The cell contains the solution and the power source, and contains two electrodes so that the electrodes are polished with silicon carbide (800, 1200 and 2000 mesh grains) of varying roughness, and then washed. These electrodes are made by distilled water and acetone and dried in a desiccator [22]. The rest of the wear cell consists of the working and galvanic electrode, the platinum as the axillary electrode, and the saturated calomel electrode (SCE) as the reference electrode. The cathodic and anodic polarization curves of carbon steel in 3.5% NaCl solution were studied in the temperature range from 293 K to 323 K.
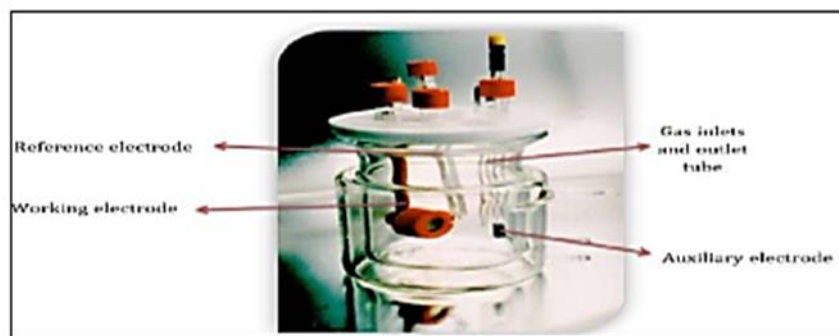
**FIGURE 1** The corrosion cell

Results and discussion

Mechanism for preparation of compounds (A₁-A₃)

These compounds which synthesized by a nucliuphilic addition of different substituted amines to aldehyde in the presence of glacialacetic acid as illustrated in Equation 1. The first step is the formation of carbcation which is attacked by the nitrogen lone pair in the amine forming the intermediate hemi aminal (β-hydroxy amine) which is stabilized by losing a water equivalent to form Schiff bases [23] as displayed in Scheme 1.
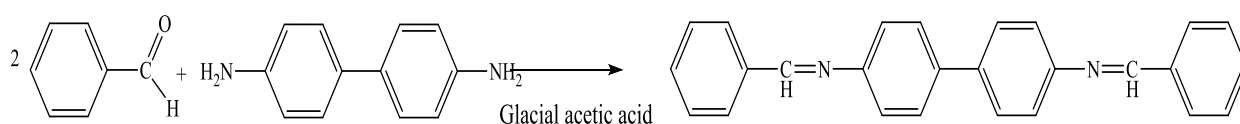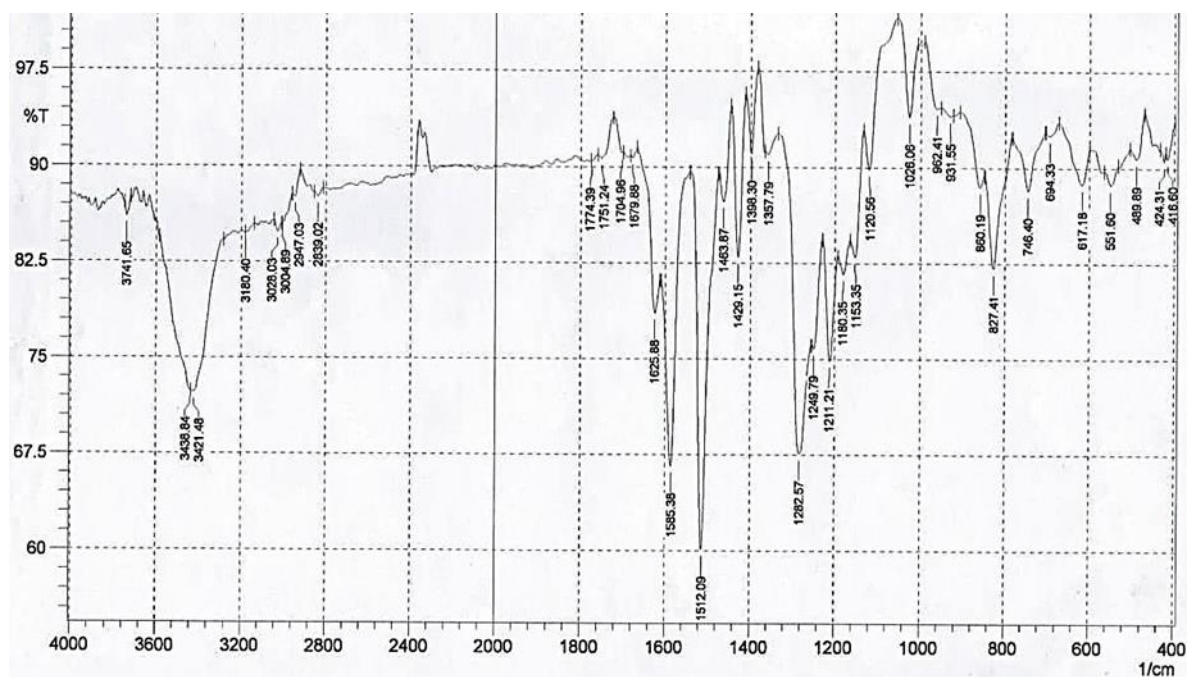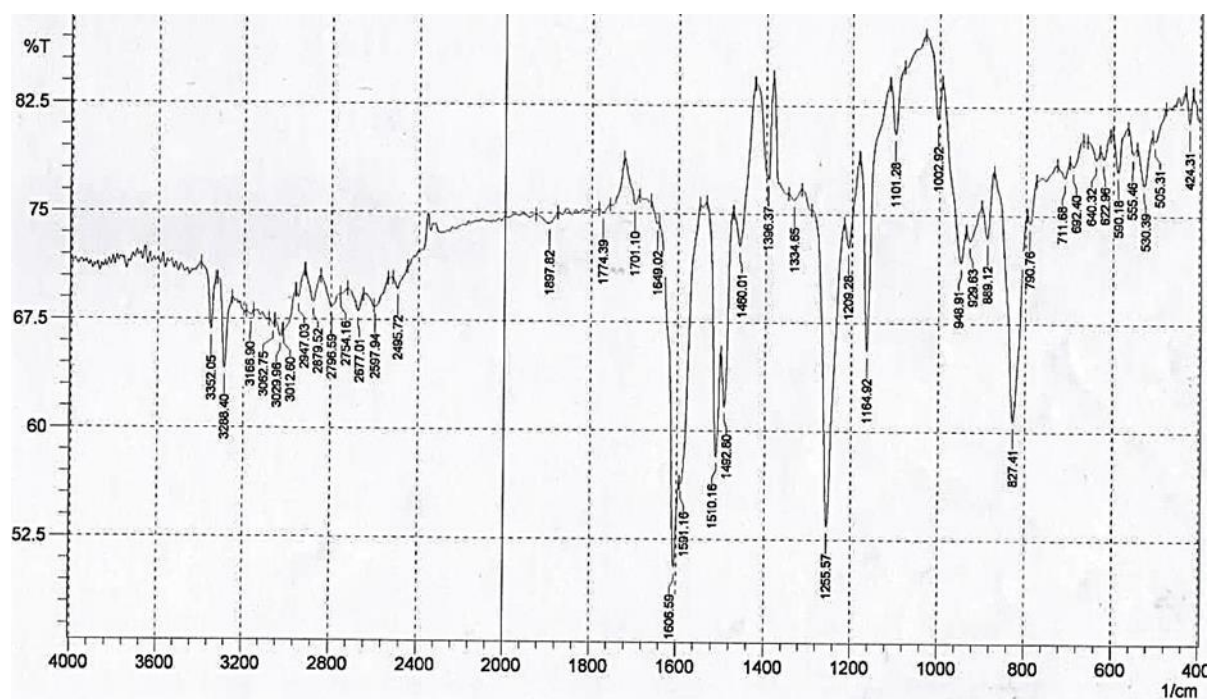

EQUATION 1 Preparation of compounds (A1-A3)
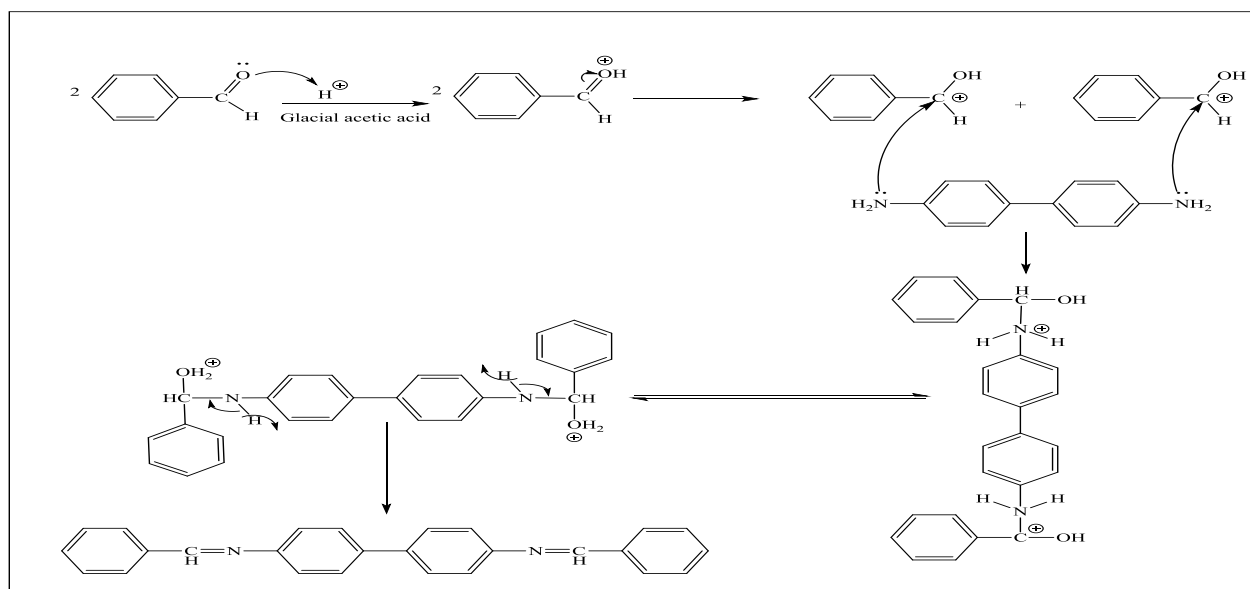
SCHEME 1 Preparation mechanism of compounds (A₁-A₃)

Fourier transmission infrared region(FT-IR) Spectroscopy of the compounds (A₁-A₃)

The spectral results of the compounds (A₁-A₃) showed clear differences indicating the occurrence of the Schiff base reaction.

FIGURE 2 FT-IR spectrum of compound (A₁)

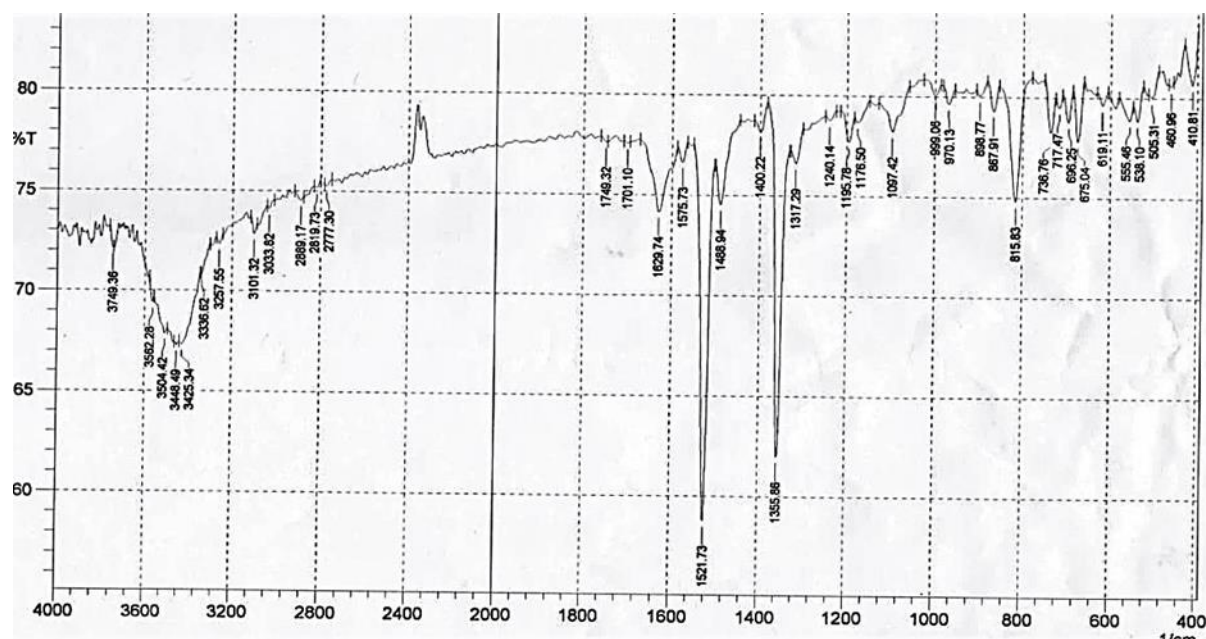**FIGURE 3** FT-IR spectrum of compound (A₂)

FIGURE 4 FT-IR spectrum of compound (A₃)

The FT-IR spectrum illustrates the main difference in the groups in terms of the absence of the carbonyl band and the presence of other bands indicating the presence of imine group v (C=N) at 1662-1606 cm⁻¹. According to Figures 2-4, the band appeared at 1701-1708 cm⁻¹ for v (C=O) of the carbonyl group, the band of v (O-H appeared at ٣٤38-3288cm⁻¹, the band of aromatic v (C=C) appeared at 1591-1510 cm⁻¹[24-26].

Atomic force microscope (AFM)

The results indicate the surface morphology of C.S immersed in 3.5% NaCl solution with and without inhibitors by using atomic force microscopy (AFM) in these numbers (5a-n). The average roughness is clearly shown in the Figure (5a,b). The CS sample was significantly damaged by NaCl attack on the CS surface, (Ra), (Rq), (Ry) for 8.1 nm CS, 4.11 nm and 42.8 nm, respectively, the average roughness will increase by exposing the steel surface to immersion in 3.5% NaCl with inhibitor [27] as clearly demonstrated in Table 1. The values increase in the compounds (A₁-A₃) without corrosion, then we notice a decrease in the values after exposure to carbon steel to corrosion. Also, the average roughness is indicated on the CS surface, (Ra) for 53.8 nm CS, 23.1 nm and 30.9 nm, respectively. These images reveal the presence of agglomeration of the compounds, along with the smooth layers produced. As in AFM analysis, it represents mean roughness (Ra) and root mean (Rq). These parameters are more commonly used in describing the surface roughness of the prepared compounds. The values of Rq and Ra were obtained as in Table 1. The results showed (increase in smoothness) in the composite (A₂) for the surface of the sample CS with the presence of the inhibitor before and after exposure to abrasion, as well as the result of reducing the grain size [28].

TABLE 1 Average grain size (Ry), average roughness (Ra) and rms roughness (Rq) of C.S by (A_1-A_3) compounds with and without of inhibitor

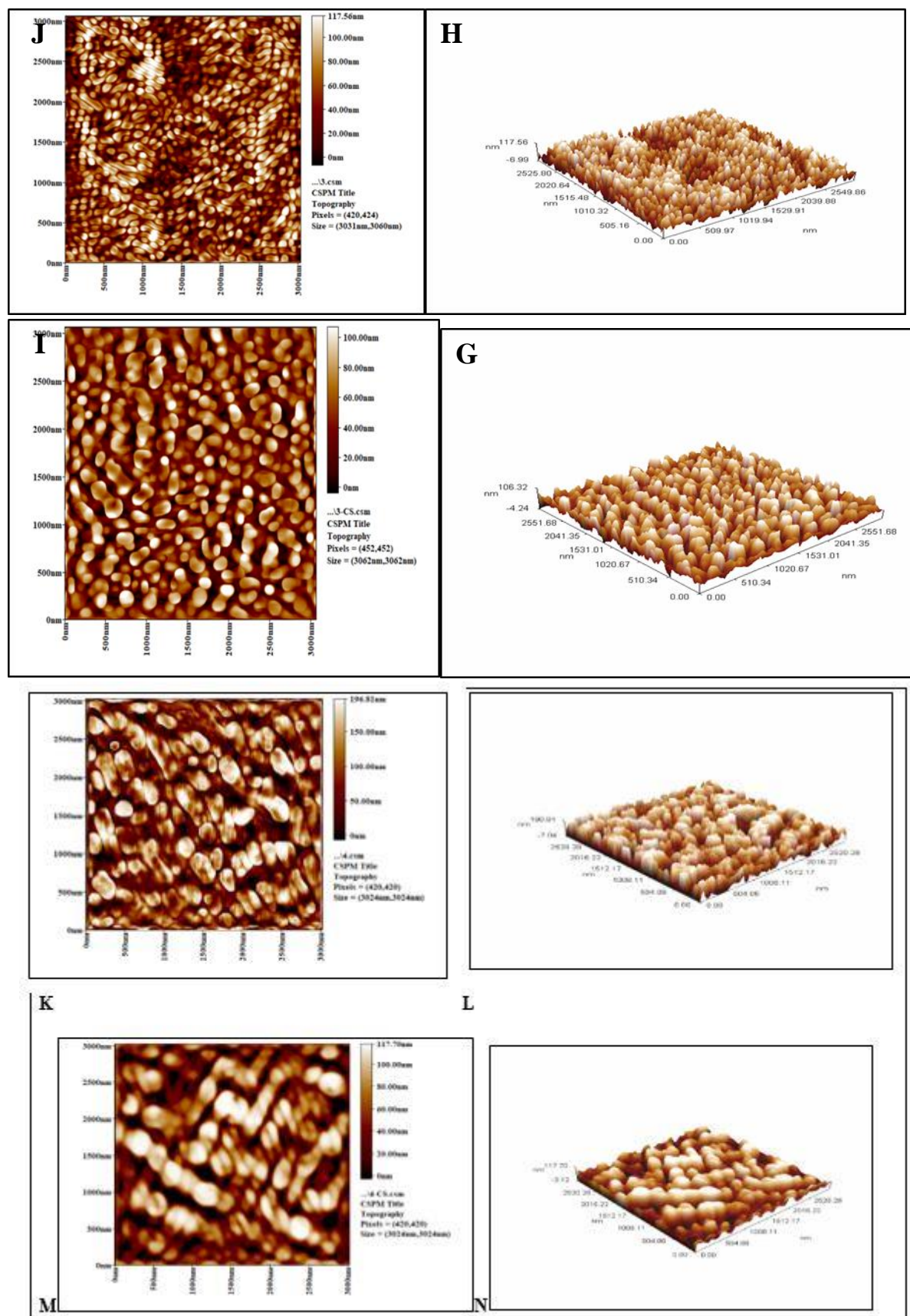| Compounds	Ra (nm)	Rq (nm)	Ry (nm)
C.S	8.1	4.11	42.8
A_1 without corrosion	53.8	63.7	285
A_1 with corrosion C.S	53.9	62.3	211
A_2 without corrosion	26.6	31.4	125
A_2 with corrosion C.S	23.1	27.5	111
A_3 without corrosion	51.7	59.8	204
A_3 with corrosion C.S	30.9	35.9	121
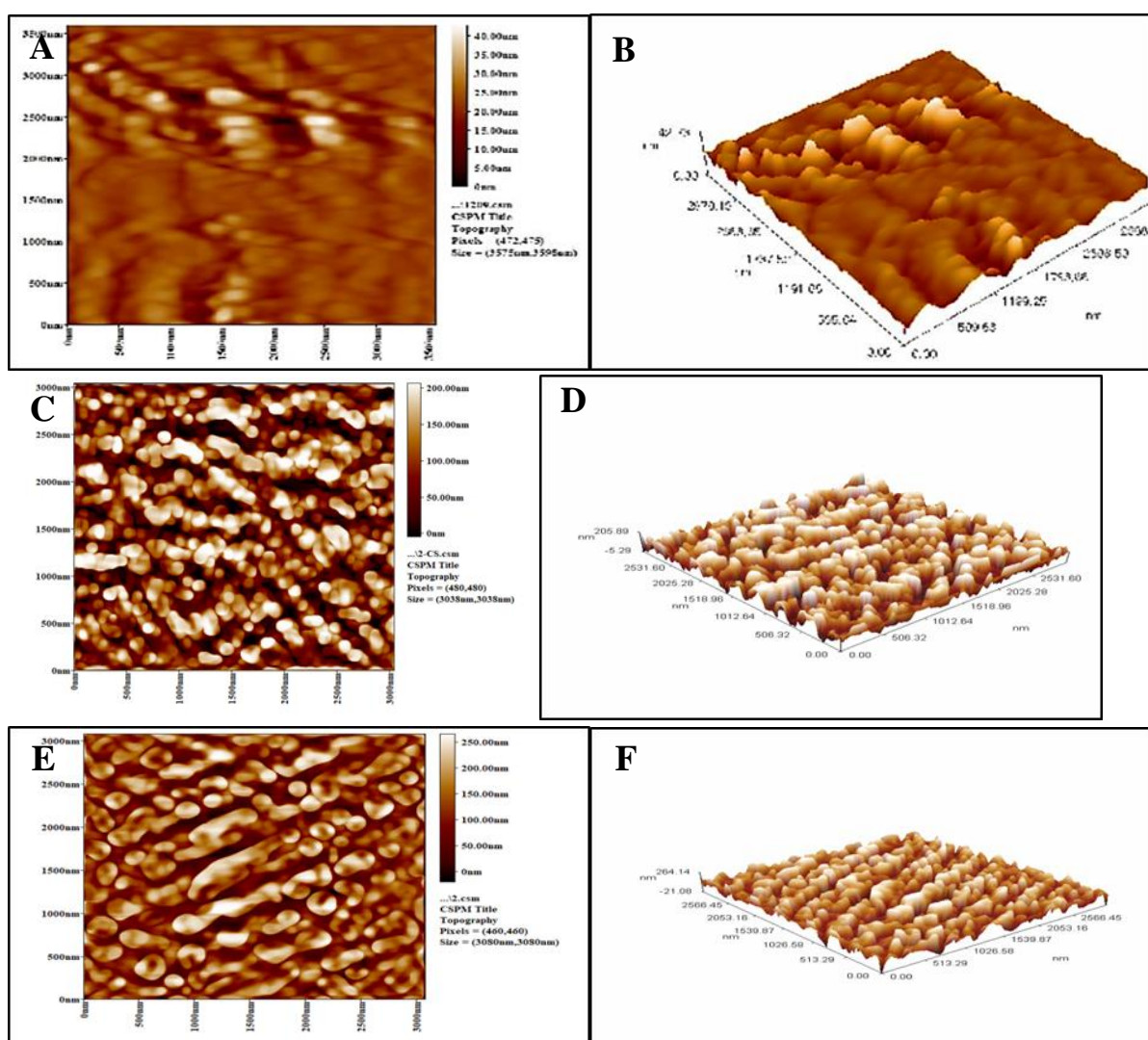
FIGURE 5 Images AFM AFM images, (A, B) carbon steel, (C,D) without corrosion and with corrosion (E,F) for compound(A1)& (J,H) without corrosion and with corrosion (I,G) for compound(A₂) and (K,L) without corrosion and with corrosion (N,M) for compound (A₃).

Scanning electron microscopy (SEM)

Figure (6-a), the surface severely damaged by immersing carbon steel in 3.5% NaCl solution uncoated inhibitor indicates significant corrosion. In the absence of the inhibitor, Figure (6-b), with the presence of the inhibitor noted the improvement of the metal surface significantly with an increase in its smoothness compared to Figure (6-a), which leads to a decrease in the rate of metal corrosion. The improvement is due to the formation of a coating layer in the shape of the inhibitor surface of carbon steel, which is responsible for preventing corrosion [29].
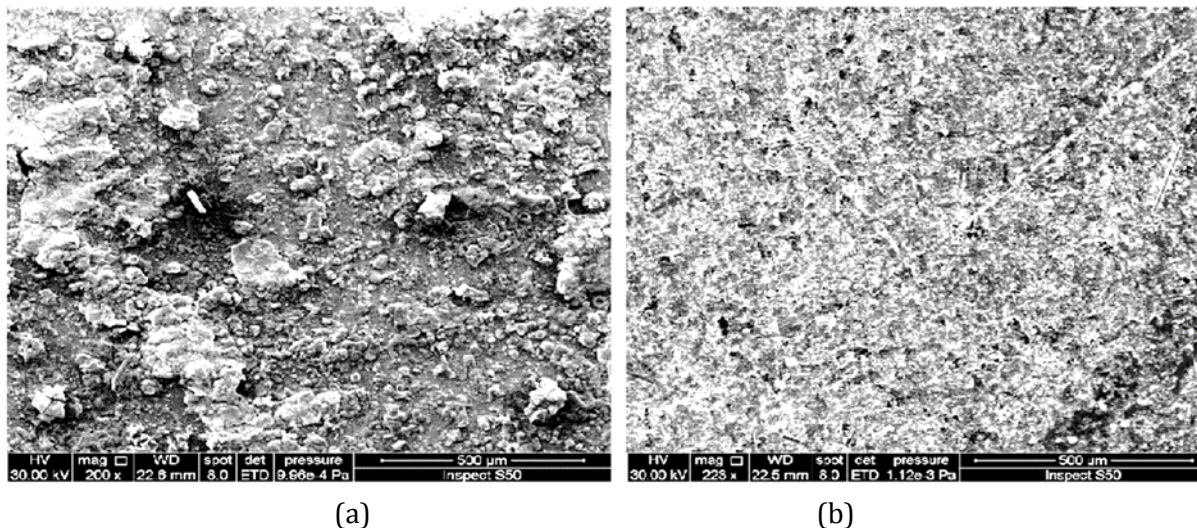
(a)	(b)

FIGURE 6 Surface image SEM of C.S in a 3.5% NaCl solution at 293 K (a) C.S immersion without inhibitor (b) the compound (A_1) with inhibitor

Potentiostate polarization curve

By extrapolating the anodic as well as cathodic Tafel curves, the data parameters were obtained as in Table 2 and Figure 7. It was revealed that for CS immersed in 3.5% NaCl solution uncoated, the corrosion current (icorr) and corrosion potential (Ecorr) as well as through Tafel slopes can be increased and obtained anodic and cathodic values (ba, bc). Table 2 indicates all the data mentioned and the protection efficiency %PE. Tafel showed that the Ecorr corrosion potential of the CS coated and immersed in the saline medium shifts to a higher position compared to the uncoated C.S, [30]. The protection efficiency (% PE) can also be calculated by the following equation [31]:

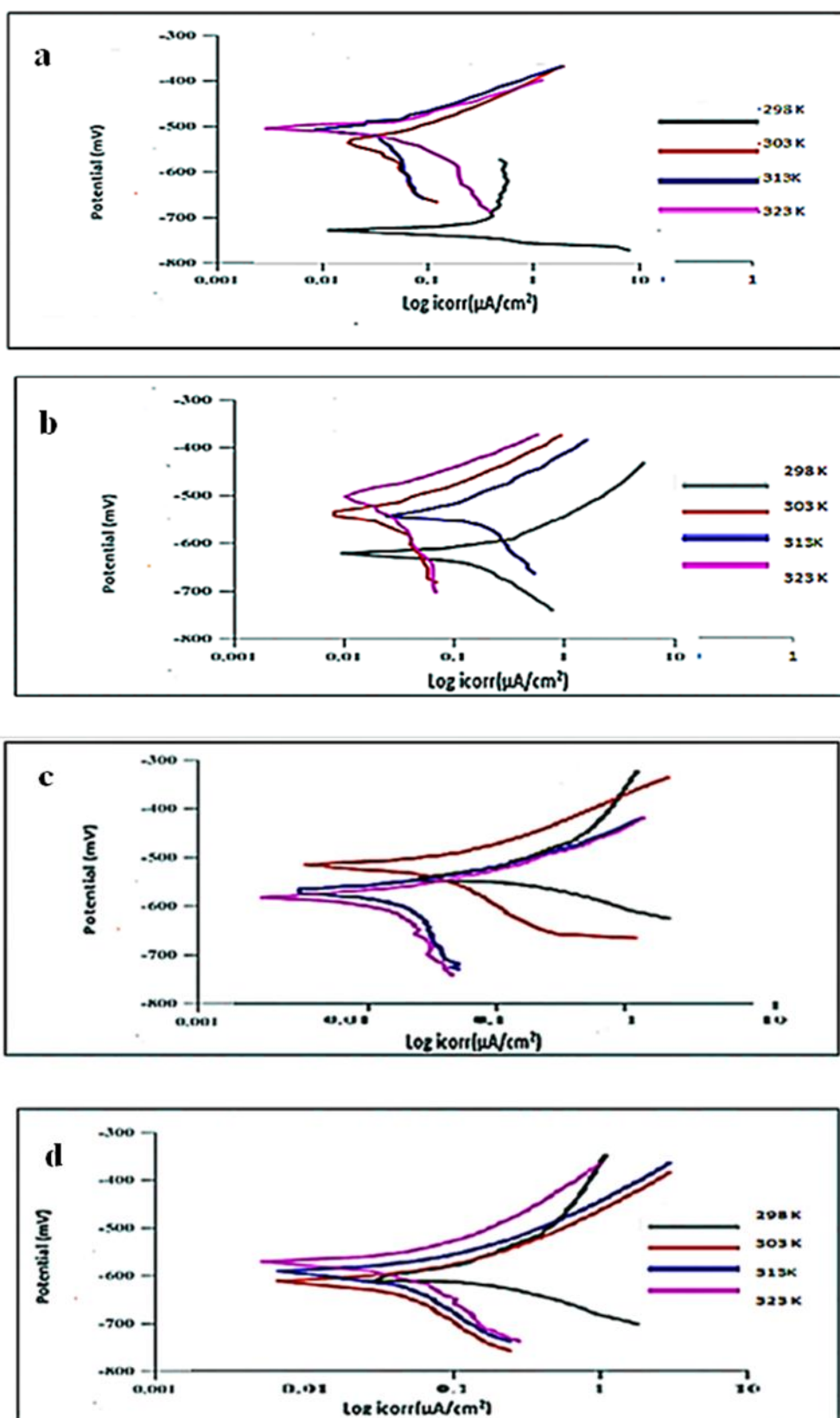%PE = [I corr (uncoated) – I corr (coated)] / [I corr (uncoated)] * 100   (3)

FIGURE 7 Curves Polarization for corrosion of a) without coated C.S, b) coated C.S with compound (A$_1$), c) coated C.S with compound (A$_2$),d) coated C.S with compound (A$_3$)

TABLE 2 Corrosion data of C.S in 3.5 % NaCl in blank and presence of several temperature 293-323K

Coating	T(K)	-Ecorr (mV)	icorr (µA/cm2)	-βc (mV/sec)	βa (mV/sec)	PE%	
Blank	293	621.0	121.7	146.9	82.1		
	303	785.7	164.5	26.3	73.8		
	313	608.0	191.1	102.0	31.2		
	323	667.2	195.2	129.9	82.3		
Compound (A₁)	293	483.1	20.48	358.3	55.9	83.170	0.832
	303	498.1	32.53	115.4	68.5	80.229	0.802
	313	598.0	42.01	222.6	92.3	78.024	0.780
	323	543.2	45.56	148.2	88.3	77.16٠	0.771
Compound (A₂)	293	562.9	24.6٠	231.5	79.6	79.785	0.798
	308	491.3	36.09	426.4	91.6	78.063	0.781
	313	598.0	42.01	222.6	92.3	78.024	0.780
	323	591.4	48.19	276.6	92.6	77.09٠	0.770
Compound (A₃)	293	537.3	27.44	377.0	102.7	77.451	0.775
	303	530.0	41.84	434.4	106.8	74.570	0.746
	313	622.9	55.16	138.8	61.4	71.145	0.712
	323	578.8	46.33	432.1	89.54	71.057	0.710

Temperature effect on the corrosion of C.S

The Arrenhius equation was studied and calculated for the prepared compounds and also, the thermodynamic parameters were obtained by first determining the activation energy from the following relationship which represents between the reciprocal of the absolute temperature (1/T) Log CR and [32], as displayed in Figure 8:

$$\text{Log (Icorr)} = \text{Log A} - Ea / 2.303\ RT \qquad (4)$$

Where Ea: Activation energy, A: pre-exponential factor, C.R: corrosion rate, R: Gas constant (8.314 $JK^{-1}mol^{-1}$), T: Absolute temperature (K).
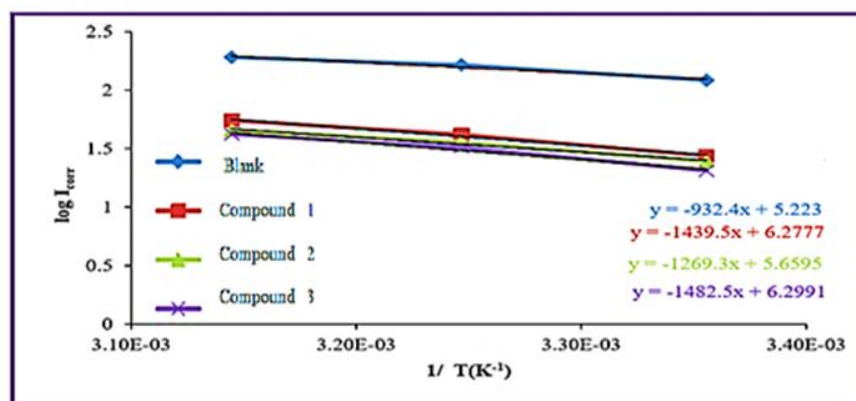
FIGURE 8 Plot of log 1/T for vs. Icorr the compounds (A_1-A_3) in the absence inhibitor and presence of the inhibitors in 3.5% NaCl solution

TABLE 3 The thermodynamic parameters for the corrosion of the blank and coated C.S with a compound in the presence and absence of the inhibitor in 3.5% NaCl solution

Coating.	Ea KJ mol^{-1}	A Molecules cm^{-2} S^{-1}	R^2
Blank	7.37	$5.60*10^{28}$	0.78
Compound(A_1)	18.07	$8.80*10^{27}$	0.73
Compound(A_2)	22.94	$4.32*10^{28}$	0.99
Compound(A_3)	23.22	$3.75*10^{28}$	0.94

While, in the following equation is expressed the transition state [33]:

$$\text{Log }(I_{corr}/T) = \text{Log }(R/Nh) + \Delta S^*/2.303\,R - \Delta H^*/2.303\,RT \qquad (5)$$

In which, the entropy and enthalpy of activation (ΔS^*, ΔH^*), h: Planks constant (6.626×10^{-34} J.S) and N: Avagadrous number (6.022×10^{23} mol). While the relationship between the reciprocal of absolute temperature (1/T) log and (CR/T) can be represented, as in Figure 9. So that the intercept (Log (R/Nh) + $\Delta S^*/2.303R$) can represent either the slope represents $\Delta H^*/2.303R$). The following equation determined the free energy of activation:
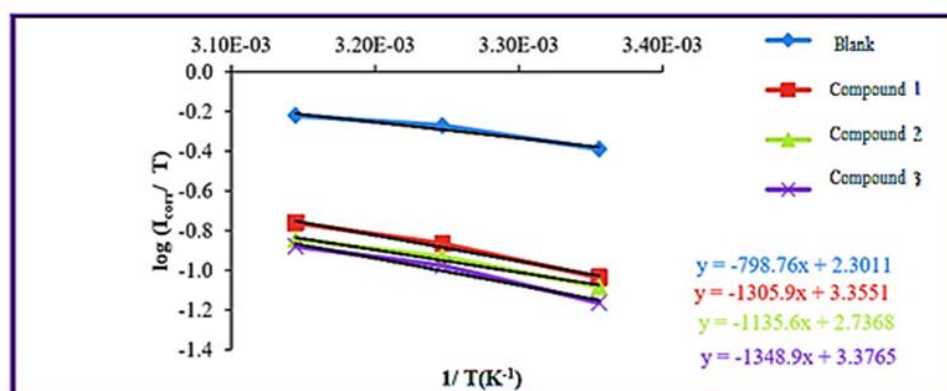
$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (6)$$

FIGURE 9 Plot of 1/T vs. log icorr/T for the compounds(A1-A3) in the presence of the inhibitors and blank in 3.5% NaCl solution

TABLE 4 Transition state thermodynamic at several temperatures for the corrosion of the blank and coated C.S with a compound in the with and without of the inhibitors in 3.5% NaCl solution

Coating.	ΔG/ kJ mol^{-1}				ΔH^* kJ mol^{-1}	$-\Delta S^*$ J mol^{-1}.K^{-1}	R^2
	298K	303K	313K	323K			
Blank	68.25	70.42	72.58	74.75	4.711	216.864	0.80
Compound(A$_1$)	72.09	74.02	75.96	77.89	15.396	193.501	0.67
Compound(A$_2$)	73.03	74.83	76.64	78.44	20.203	180.317	0.99
Compound(A$_3$)	73.66	75.50	77.33	79.17	20.547	181.303	0.93

The thermodynamic activation parameters showed higher values for C.S coated compounds (A$_1$-A$_3$) than for uncoated C.S. This leads to an increase in the energy barrier activation and entropy values for all coated and uncoated CS (A$_1$-A$_3$) compounds indicating that the compound activated in the rate-limiting step was achieved in a bonding rather than a dissociation step [34]. Positive values for the activation of free energy appeared, as depicted in Table 4. Also, almost little change appears with increasing temperature, which indicates that the possibility of its formation decreases with increasing temperature due to the instability of the formed compound [34].

Antimicrobial activity

The bands inhibition of the prepared compounds (A$_1$-A$_3$) was examined on positive and second-negative bacteria (S. aureus and E. coli) and they were prepared at a concentration of 800 mg/ml in the presence of the inhibitor, and dimethyl sulfoxide (DMSO) was used as a solvent for these materials. The results are included in Table 5 as follows.

TABLE 5 Inhibition zone values for the compounds (A$_1$-A$_3$) in the presence and absence of inhibitors

Coating	(S. aureus)	(E. coli)
DMSO	-	-
Compound(A$_1$)	25	30
Compound(A$_2$)	15	13
Compound(A$_3$)	10	9

The compounds showed excellent results, compared to DMSO, with two types of bacteria. The ability of these compounds to destroy these bacteria is a complex task formed between the cleaved DNA and the drug-bound topoisomerase. Its protection is the function of topoisomerase which is formed between these inhibitors and compounds that possess stabilizing properties and formed from DNA has a significant bad effect on cells, as it turns out that it has the ability to deal with the drug which destroys DNA [35]. The inhibitor plays a main role in pharmaceutical and biological applications against the emergence of antibiotic-resistant strains [36]. Organic compounds are effective as biocides [37].

Conclusion

The results show that there is an increase in temperature with the corrosion current (icorr) and also a decrease in temperature with CS covered with Schiff bases in the case of the presence of inhibitors and a decrease in

temperature with a decrease in the efficiency (% PE) of the uncoated and coated CS in the absence and presence of inhibitors and an increase temperature with (Ecorr) increases. A$_1$-coated CS has a top protective efficiency % (PE) than A$_2$-coated CS-coated CS. (AFM and SEM) gives an analysis to describe the surface of the steel and its CS protection, beside the corrosion resistance which occur due to the forming of a protective layer on the surface metal. It provides antimicrobial activity in contrast to two types of bacteria used, namely *S. aureus* and *E. coli*, as the inhibitors have strong activity against these types of bacteria.

Acknowledgements

Orcid:
Mayada Talib Mohammed:
https://orcid.org/0000-0003-0877-8784

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