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A study of quantum and electrochemical investigation for a sample of mild steel in HCl-CO_2 system.

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ABSTRACT

2-(1-Naphthylamino)ethylamine 2HCl(NNED) was examined as a novel corrosion inhibitor for a sample of mild steel in 1 HCl in the presence of carbon dioxide by employing the potentio-dynamic polarization method as well as the AM1 calculations, and an analysis surface technique, (SEM-EDX). It is observed from the experimental results the efficiency of corrosion inhibitor, which acts as "mixed-type inhibitor" with dominant cathodic control, increases with concentration at a particular temperature. The adsorption of (NNED) on the mild steel electrode conforms with "Langmuir adsorption isotherm". Thermodynamic and kinetic parameters demonstration that the adsorption of (NNED) inhibitor on metal surface includes conjointly adsorption kinds. , (SEM-EDX) analysis displays a great enhancement for metal surface morphology with (NNED) inhibitor. The electronic properties were calculated using the AM1 forcefield for the possible optimized structures, and these support the experimental data to protect mild steel and prevent corrosion process.

Keywords: NNED inhibitor, mild steel, AM1 method, SEM-EDX characterization, corrosion inhibition.

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INTRODUCTION

Fe and its alloys as mild steel that utilized mainly in several engineering implementations, for instance in constructional supplies, due to the benefit of their properties which include the high compliance and low cost [1,2]. They are often used as the material forming the main tubular passage through which fluids flow in pipelines in the oil transport industry [3]. The consideration of iron alloys is an important topic in a theoretical concern as well the enormous practical fields, so, has got a large scope of interest [4,5]. The acid solutions (hydrochloric acid is one of the most hazardous) which used for acidifying processes in oil wells, pickling, cleaning and removal of remain deposition [6–8]. However, most acidic media cause damage to the resources, resulting in great economic losses [9]. This problem cannot be avoided, and organic compounds are commonly used as inhibitors to prevent and control it. Thus, the investigation from the corrosion associated with materials (e.g. iron and its alloys in acidic media) and the search for corrosion inhibition by using organic compounds is a very interesting and attractive as a field of research both from a fundamental academic or industrial point of view [10–12].The use of inhibitors is one of the most practical means on a large-scale in such situations [9,13] and it is becoming increasingly popular. The addition of small compounds in the aggressive medium allows them to migrate and retard the corrosion process of metal by counter-acting the attack by acids. It is recognized that hetero-organic materials, or those which contain conjugated multiple bonds, are effective, as the nitrogen, oxygen and/or sulfur atoms in their structures, [3,14,15] may act as centers of the adsorption of the organic compounds as corrosion inhibitors [1,3,16–24]. There are a number of reports in the literature outlining the investigation into the corrosion inhibition of mild steel in HCl solution. More recent studies have included the derivatives of benzimidazole [3,28,32,35], antipyrine [1], pyrimidine [28], thiazole [29], benzamides [30], fluconazol [31], indoloimidazoline [32], 1-butyl-3-methylimidazolium tetrachloroferrate [33], novel hydrazides [34], 3,4-diaminobenzonitrile [35], cupral inhibitors [12], benzothiazole [36], Cefradine [37], 5-(4-Dimethylaminobenzylidene) rhodanine [38] as corrosion inhibitors. The aim of present study focuses on the investigation of the potential of 2-(1-Naphthylamino)ethylamine 2HCl (NNED) as a good inhibitor for corrosion of mild steel type in aggressive and corrosive conditions: in 1 molar of HCl solution saturated with carbon dioxide at a range of temperatures (303.15–318.15) K ±1. The efficacy of the treatment is measured by using a potentiodynamic electrochemical method and scanning electron spectroscopy (SEM) with the benefit of the X-ray dispersive electron (EDX) technique. Similarly, AM1 routine is applied to approve the correlation of (NNED) structure of inhibitors with experimental results and the compatibility between them.

EXPERIMENTAL METHODS

Electrochemical measurements

Specimens of mild steel (1.0 cm × 1.0 cm) were prepared with a 1 cm^2 surface area exposed to a corrosive aqueous solution of hydrochloric acid (1 M) and the remainder of the body of the sample was covered by a cured epoxy resin. Before any electrochemical tests were performed, the specimen was prepared according to followed work steps[12] and set aside for analysis. A series freshly prepared solutions of N-(1-naphthyl)ethylenediamine dihydrochloride (Sigma-Aldrich) were prepared (in different concentrations) and transferred to the corrosion cell. Carbon dioxide was then passed through each test solution for one hour. The corrosion cell comprised three electrodes: the mild steel (MS) sample as the (WE) working electrode, "(SCE)asaturated Calomel electrode" as a reference electrode and a "platinum electrode" as anauxiliary electrode in the electrochemical circuit. The electrode terminals were connected to an electrochemical instrument using a Gamry interface /Potentiostat/Galvanostat/ZRA to achieve the run test after set experiment parameters. To obtain the electrochemical parameters from the polarization scan curves Echem Analyst software package (v 6.33) was used the at the polarized electrode ±100 mV with respect to free corrosion potential value. Full details are reported elsewhere [12,23,34,35,39]. Additionally, polarization resistance (Rp) values were measured at 318.15 K with an interval time 10 min. to understand the effectiveness of corrosion inhibitor by performing the RE/EC routine with respect to the "Tafel slopes" close to 0.0.12 V decade^{-1}.

SEM-EDX analysis

The morphology of surface electrode and the chemical composition of the protective film that formed on its surface were inspected by (SEM-EDX) measurements, with and without 2-(1-Naphthylamino)ethylamine 2HCl(NNED) inhibitor (2.8 mM) in hydrochloric acid solution (1M) saturated with carbon dioxide at 303.15 K after completion of ten hours of immersion time. The SEM measurements were performed using a ZEISS Sigma 300 type microscope at an accelerating voltage 15 kV with a resolution of less than 2 nm

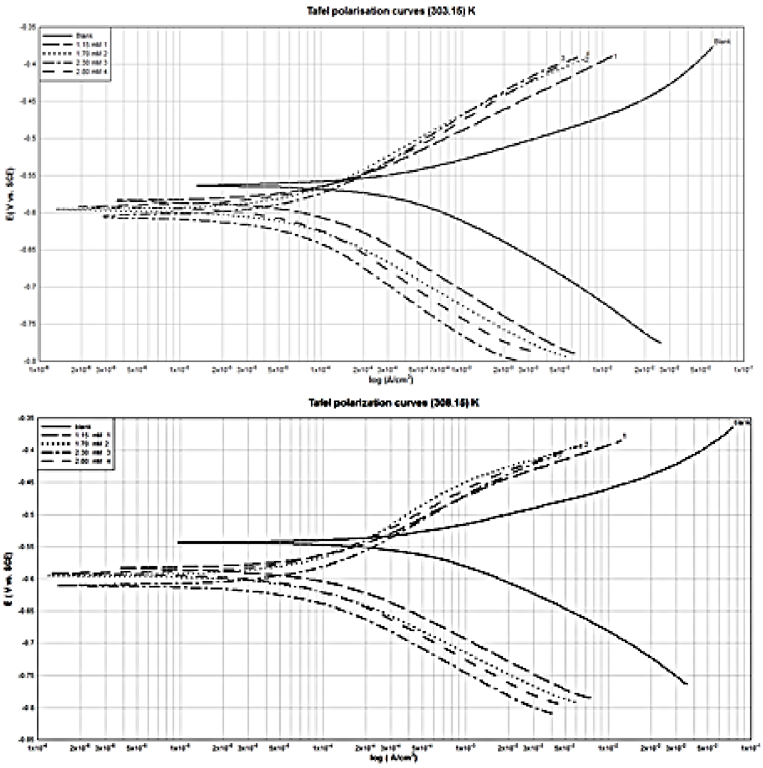
Computational treatments

The quantum chemical calculations were performed by employing the restricted Hartre-Fock method with AM1 parameterization [40–44] (SCF-RHF) and the optimized structure of the 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor was simulated with the COSOM routine [45] which permitted the study of the solvent effect by using the VAMP model as a package in Material Studio (v. 8.0.34) from Accelrys Inc. Quantum chemical parameters were estimated for optimized geometrical inhibitor structure, including the "lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO)", respectively as well as the Mulliken atomic charges of hetro-atoms. These theoretical calculations have been confirmed the validity of the electrochemical findings.

RESULTS AND DISCUSSION

Polarization Scan Results

Potentiodynamic scan curves of specimen electrode in 1 molar of hydrochloric acid solution with and without the 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor at different concentrations in the existence of carbon dioxide over a range of temperatures (303.15–318.15) K are illustrated in Fig. 1. As was mentioned in experimental section, the electrochemical parameters, such as the "corrosion current density ($i_{corr..}$), corrosion potential ($E_{corr.}$), anodic Tafel slope (β_a), cathodic Tafel slope(β_c)" were calculated from the Tafel polarization curves (TPC) by the extrapolation method with respect of the free corrosion potential with high significant (and a high degree of confidence). In contrast, the transfer coefficients for the cathodic and anodic processes [46–48] (α_a) and (α_c),respectively were estimated by the equation (1) as well as using the degree of coverage area (θ) and the percentage of corrosion inhibition ($\eta\%$)[49] according to the equations (2 and (3),respectively. Table 1 shows the all parameters.



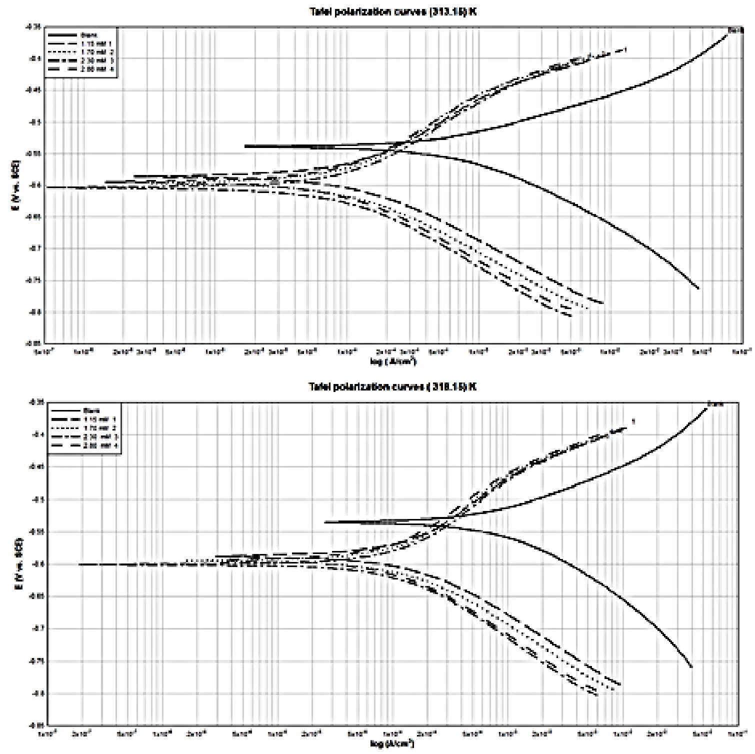


Fig (1): TPC for MS in 1 molar of HCl (in the presence of carbon dioxide at various concentrations of 2-(1-Naphthylamino) ethylamine 2HCl (NNED)inhibitor and different temperatures.

$$\alpha_a = \frac{2.303\ RT}{b_a\ F} \quad ; \quad \alpha_c = \frac{2.303\ RT}{b_c\ F} \text{............}(1)$$

$$\theta = \frac{i_{corr.uninh.} - i_{corr.inhib.}}{i_{corr.uninh.}} \text{........................}(2)$$

$$\eta\% = \theta \times 100 \text{..........................}(3)$$

Where " R, T, and F are the absolute gas constant, temperature degree and the Faraday constant " , respectively and the symbols of equations (2) and (3) are defined as the "corrosion current density" for the blank solution and "corrosion current density"with2-(1-Naphthylamino) ethylamine 2HCl (NNED)at particular temperature ($i_{icorr.uninh.}$) and ($i_{icorr.inhib.}$), respectively. The polarization curves, resulting from the presence of the 2-(1-Naphthylamino) ethylamine 2HCl (NNED)inhibitor, drifted towards the cathodic region at the temperature ranges and are asymmetric. The curves in without 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor are depicted in Fig. 1 and Table 1. Furthermore, the cathodic polarized region is well defined and was raised apparently as parallel lines demonstrating that the reaction of "hydrogen evolution" comes under effective control [50] which indications a reduction in the "cathodic current densities" with increasing 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor concentration. Instead, the minor change in the anodic polarized branch of the polarization scan curve is shown in Fig 1 and it appears restricted. The appearance of the anodic curves in this style indicates the deposition of the impurities and the products of thecorrosion process on the surface electrode and the formation of a film which has non-passive characteristics [51]. At first glance, these results show that the adsorption of2-(1-Naphthylamino) ethylamine 2HCl (NNED)molecules occurs on the surface of the MS electrode at the site active of the cathodic areas and hence the inhibition of corrosion process takes place. Similarly, it is evidenced from data in Table 1 that the values for the degree of coverage degree and the efficiency of inhibition corrosion are increased with increasing 2-(1-Naphthylamino) ethylamine 2HCl (NNED)concentration at a particular temperature. This indicates that the molecules of 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor adsorb on MS surface electrode. It appears (Fig.1) that the nature of the potentiodynamic scan curves remains similar with and without 2-(1-Naphthylamino) ethylamine 2HCl (NNED)with a shift in the corrosion current density towards the lower values and hence the mechanism for the retardation of corrosion remains the same mechanism in the aggressive acidic medium.

Table (1): Electrochemical parameters at various concentrations of 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor and different temperatures in the presence of carbon dioxide in 1 molar of HCl solution.

Temperature (K)	$i_{corr.}$ μA/cm²	- E_{corr} mV	β_a mV/decade	β_c mV/decade	Corrosion Rate (mpy)	$\alpha_a \times 10^{-1}$	$\alpha_c \times 10^{-1}$	θ	η%
Blank 1 M HCl									
303.15	333	563.0	62.40	98.40	152.3	4.42	2.80	-	-
308.15	435	543.0	62.10	95.90	199.5	4.52	2.92	-	-
313.15	646	539.0	70.90	99.90	295.8	4.02	2.85	-	-
318.15	816	535.0	80.90	105.5	373.9	3.41	2.62	-	-
1.15 mM									
303.15	117	584.0	101.1	131.4	53.41	2.73	2.10	0.648	64.8
308.15	131	584.0	130.1	123.9	59.81	2.16	2.26	0.698	69.8
313.15	144	586.0	149.3	119.0	66.14	1.91	2.40	0.777	77.7
318.15	175	588.0	168.8	115.3	80.10	1.63	2.39	0.785	78.5
1.7 mM									
303.15	86.7	596.0	126.0	123.8	39.71	2.19	2.23	0.739	73.9
308.15	115	595.0	172.0	130.1	52.64	1.63	2.16	0.735	73.5
313.15	146	596.0	187.1	130.8	66.70	1.52	2.18	0.773	77.3
318.15	169	595.0	188.2	124.0	77.42	1.47	2.23	0.792	79.2
2.3 mM									
303.15	86.4	606.0	128.1	165.0	39.60	2.15	1.67	0.740	74.0
308.15	100	610.0	143.5	138.2	45.80	1.95	2.03	0.770	77.0
313.15	128	604.0	158.6	140.7	58.50	1.80	2.03	0.801	80.1
318.15	161	601.0	172.1	142.8	73.80	1.60	1.93	0.802	80.2
2.8 mM									
303.15	97.6	591.0	111.2	173.5	44.71	2.48	1.59	0.706	70.6
308.15	99.3	591.0	132.0	134.1	48.10	2.12	2.09	0.778	77.8
313.15	116	594.0	154.2	135.7	53.30	1.85	2.10	0.820	82.0
318.15	131	594.0	166.5	128.8	60.02	1.66	2.14	0.839	83.9

These results along with the values of the "Tafel slopes for both the cathodic and anodic reactions", and the corresponding transfer coefficients (α_a) and (α_c) values, are offered in Table 1. These information illustration the Tafel slopes and transfer coefficients values depart from the 0.120 V decade^{-1} (120 m V decade^{-1})and 0.5 [52–54] indicating that the nature of "rate determining step" varies from a charge transfer process to electrochemical desorption [55–58]. The corrosion potential values are somewhat changed in the presence of 2-(1-Naphthylamino) ethylamine 2HCl (NNED), indicating that it acts as "mixed-type inhibitor" by affecting both the "cathodic and anodic reactions" on the surface of the MS electrode [59]. It is noted that the corrosion potential values did not exceed ± 85 mV/SCE [60] which is consistent with its classification as a "mixed–type". Thus, the maximum offsets of $E_{corr.}$ values in present work were 31 mV/SCE at 303.15 K and more than 55 mV/ SCE at 318.15 K. However, the minor drift of corrosion potential values towards the negative direction following the addition of 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor into the aggressive media signifies that cathodic control on the overall reaction is predominant.

Kinetic and thermodynamic considerations

The kinetic and thermodynamic parameters are played a big role of understanding how the corrosion inhibitors are working. So, a study was made of the effect of temperature on corrosion inhibition by 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor for MS electrode in the 1M HCl solution with carbon dioxide from 303.15 K to 318.15 K. The activation energy (E_a) energy for the dissolution of MS electrode in an aggressive HCl solution was estimated by calculating the corrosion rate values ($Corr.Rate$) shown in Table 1. The latter can be determined by the Arrhenius equation [61–63] as expressed in the following.

$$log \ (Corr.Rate) = \frac{-E_a}{2.303 \ RT} + log \ A \quad .... (4)$$

Where A is the "pre –exponential parameter" and the other symbols in equation (4) are mentioned earlier in the present paper. The kinetic values are collected in Table (2) and Fig.2 and represent the logarithmic relationship between the corrosion rate and the inverse of the "absolute temperature (Kelvin^{-1})" in the absence and the presence of 2-(1-Naphthylamino) ethylamine 2HCl (NNED). It is manifest from the results, the values of (E_a) are lower in the uninhibited solution from the blank solution, which demonstrates that the adsorption process has occurred [64] and is consistent with a reduction in the energy barrier for the formation of ferrous ions. The latter interact with the 2-(1-Naphthylamino) ethylamine 2HCl (NNED)and hence form the "protective layer" on the MS surface as stated in previous documents [3,65,66]. Table (1) displays that the η% increases with an increase in the temperature range. This behaviour follows the "second type of Radovici classification"[66,67] for the relationship between the$\eta\%$ percentage as a function of temperature.

Table 2: Kinetic and thermodynamic values of MS specimen in 1 molar of HCl (saturated with CO_2) at various concentrations of 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor and different temperatures.

Kinetic parameters				
Conc. inh. (mM)	E_a (kJ/mol)	A (mg/cm^2)	r^2	
Blank	49.5463	1.08×10^{11}	0.995	
1.15	35.9872	7.90×10^{9}	0.986	
1.70	33.8316	9.30×10^{7}	0.992	
2.30	21.0723	2.81×10^{5}	0.992	
2.80	15.7910	621.74	0.993	
Thermodynamic parameters				
Temperature (K)	slope	$K_{adsorp.}$ M^{-1}	$-\Delta G_{adsorp.}$ kJ/mol	r^2
303.15	1.325	3351.85	30.5870	0.992
308.15	1.175	5566.03	32.3911	0.999
313.15	1.166	5841.88	33.0426	0.999
318.15	1.143	6631.43	33.9056	0.998

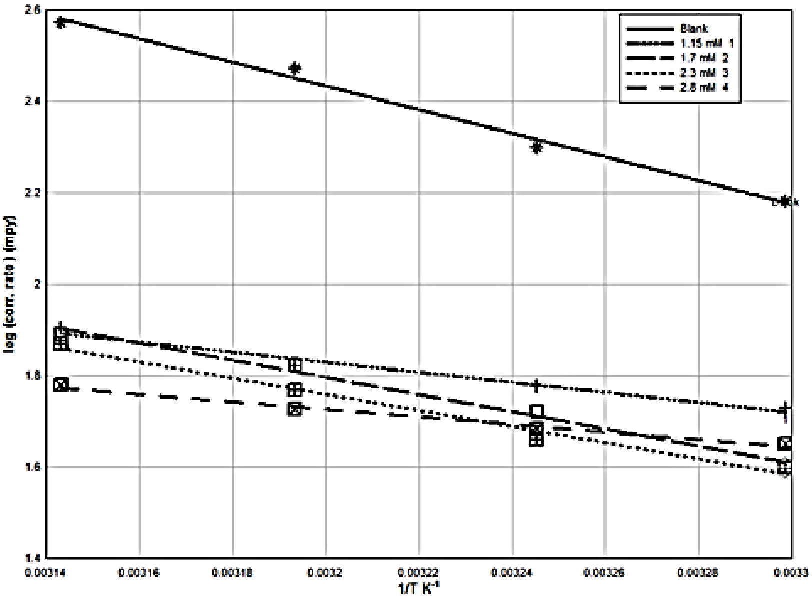


Fig (2): "Arrhenius plots" of "log (corr. rate) (mpy) versus 1/T (K^{-1})" at various concentrations of 2-(1-Naphthylamino) ethylamine 2HCl (NNED)inhibitor in the presence of carbon dioxide.

This behaviour has been explained by some authors [68,69] of whom perhaps the most important was Ivanov [70,71] who showed that the increase in the $\eta\%$with temperature follows the change in nature of adsorption process type. This means that at low temperature the inhibitor molecules begin the physical adsorption process whereas, the chemical adsorption is favoured when temperature increases causing the enhancement reported by other authors [69,72]. Considering the Arrhenius equation (Eq. 4), it is found the other parameters may be introduced as evidence with understanding of the activation energy value. For instance, the pre – exponential factor is a parameter whose scale indicates the "number of active sites" on the MS surface electrode in a heterogeneous reaction [73,74]. This is illustrated in Table (2), where the A values are decreased to below 650 (mg/cm^2) in an inhibited solution, following the addition of the 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor. It is suggested that this is due to the active sites of lower activation energy value becoming blocked, leaving the remaining sites uncovered on the surface of the electrode, which may be occupied through the corrosion process. This observation was confirmed via the existence of a linear relationship between the (E_a) and the $log\ A$ values [75] with high correlation factor, 0.999 (Fig.3) This indicates the "compensation effect" that describe the kinetics of heterogeneous reactions on the metal’s surface [12,75,76].

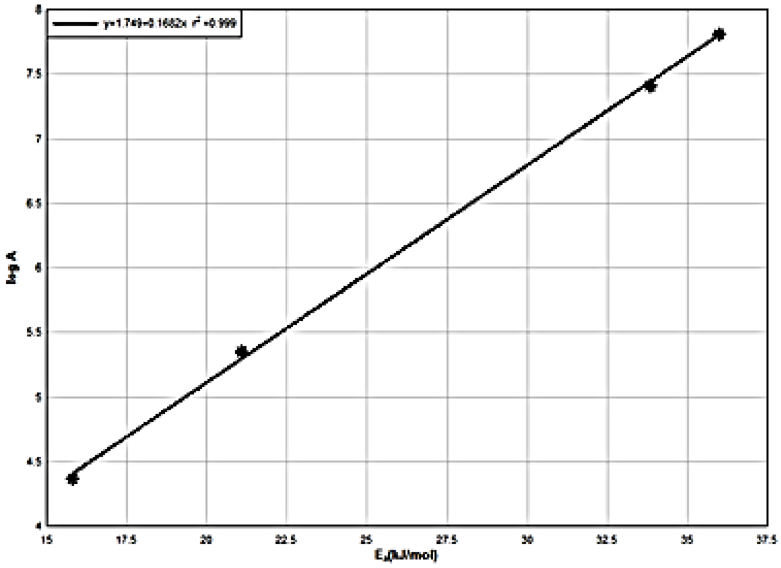


Fig (3): linear relationship between the (E_a) and the $log\ A$ values.

Finally, The capability of 2-(1-Naphthylamino) ethylamine 2HCl (NNED) compound when used as an inhibitor demonstrates good efficiency under the study conditions at high temperature. This was investigated through measurements of the polarization resistance (Rp) and the corrosion rate at 318.15 K at different time intervals at various concentrations of 2-(1-Naphthylamino) ethylamine 2HCl (NNED)inhibitor by the Rp-EC trend technique (see experimental section). Clearly that the average value of Rp increases with increasing 2-(1-Naphthylamino) ethylamine 2HCl (NNED)inhibitor concentration throughout the selected time as is shown in Fig. 4. Furthermore, the corrosion rate declined and Rp increased with time at a particular temperature (Fig 4) in the inhibited solution that supports adsorb of the inhibitor molecule in chemisorption process.

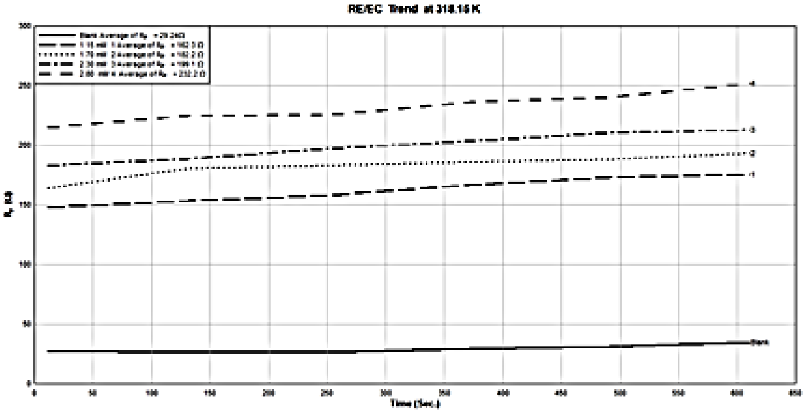


Fig (4): The relationship between the Rp (Ohm) and the time (sec.) for MS electrode at high temperature.

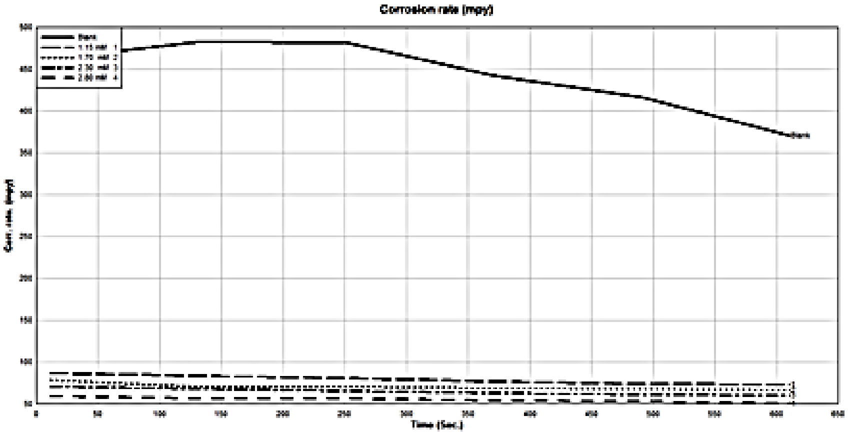


Fig (4): The relationship between the "corrosion rate (mpy) and the time (sec.)" for MS electrode at high temperature.

To gain a grasp of the nature of the interaction between 2-(1-Naphthylamino) ethylamine 2HCl (NNED)and MS surface, the commonly utilized isotherm models are those of "Langmuir, Temkin, Flory-Huggins, Bockris-Swinkel, and Frumkin"[66,77,78]. Consequently, the direct relationship between the surface coverage values which are displayed in Table 1 with the various concentrations at fixed temperature was verified graphically via a plot these data to find a suitable isotherm model by the least squares method with a high significant correlation value (r^2). Thus, the best linear plot was obtained with high (r^2) value for the present experimental results with the Langmuir equation (5). So, the Langmuir parameters are collected in Table (2) and graphically in Fig. 5 .

$$\frac{C_{inhib.}}{\theta} = \frac{1}{K_{adsorp.}} + C_{inhib.} \text{ .... } (5)$$

The symbols $C_{inhib.}$ and $K_{adsorp.}$ refer to the concentration of 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor in 1molar of hydrochloric acid in carbon dioxide at specific temperatures and the equilibrium constant which relates with the adsorption-desorption processes, respectively. It is noticeable from the data in Table 2 that the equilibrium constant $K_{adsorp.}$ values increase with a rise in temperature because of the greater number of interactions between the "electrical double layer" and the 2-(1-Naphthylamino) ethylamine 2HCl (NNED)molecules at the interface boundary (surface electrode/solution). This leads, in turn, to better corrosion inhibition and an enhancement in the number of 2-(1-Naphthylamino) ethylamine 2HCl (NNED)molecules participating in chemical adsorption on the MS surface and with an increase in temperature will reinforce the process of adsorption [79]. Clearly, the values of slopes deviate from unity as is shown in Table 2, due to the interaction of the adsorbed 2-(1-Naphthylamino) ethylamine 2HCl (NNED)molecules between those on the heterogeneous MS surface [80]in addition to the changes in a heat associated with the adsorption process which occurs with the increase in the θ value[81–83]. Furthermore, importantly estimation the "Gibbs free energy" for adsorption of the 2-(1-Naphthylamino) ethylamine 2HCl (NNED)by using the following equation (6)[79].

$$\Delta G_{adsorp.} = -RT\ ln\left(55.5\ K_{adsorp.} \right) \ldots\ldots\ (6)$$

Where, "$\Delta G_{adsorp.}$ is the Gibbs free energy of adsorption" for the inhibitor molecules and "the value of 55.5 refers to the concentration of water in mol L^{-1}"". The negative sign obtained for all values of "Gibbs free energy" implies the spontaneity for the adsorption process of inhibitor as well as enhancing the stability of a film layer on the MS surface. The $\Delta G_{adsorp.}$values decrease as the temperature increases and this behaviour indicates that the adsorption of 2-(1-Naphthylamino) ethylamine 2HCl (NNED)inhibitor on mild steel is an endothermic process [84,85]. Besides, the values of around -32 kJ mol^{-1} (Table 2) support the adsorption of 2-(1-Naphthylamino) ethylamine 2HCl (NNED)molecules on MS surface via both types of adsorption process models through the electrostatic interactions of $\pi -$ electrons in "naphthalene aromatic rings" and the charge transfer process of N atoms. Furthermore, the adsorption of 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor on the MS surface in 1 molar of HCl of hydrochloric acid saturated carbon dioxide is reinforced by the SEM-EDX measurements and AM1 parameterization along with presenting the mechanism of corrosion inhibition.

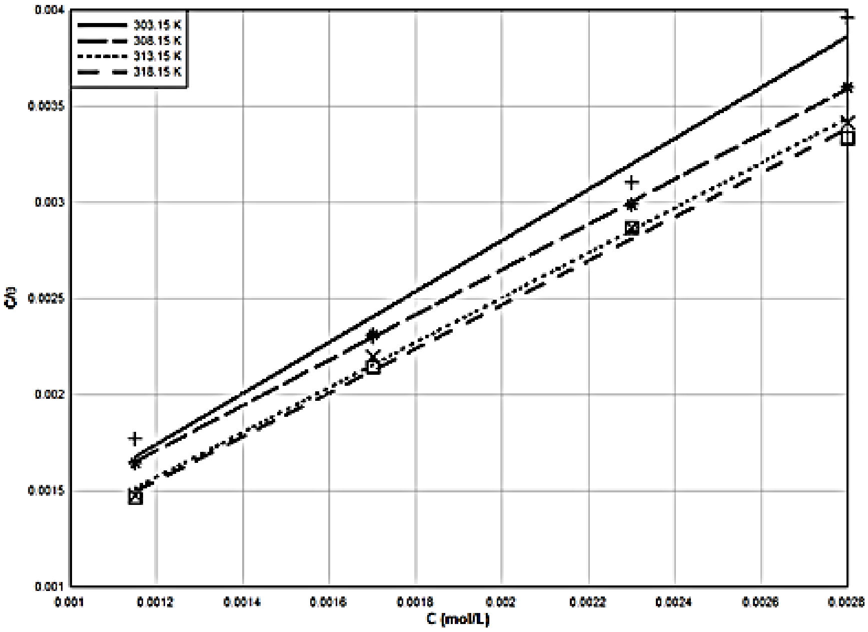


Fig (5): "Langmuir adsorption isotherm" of the 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor.

SEM and EDX analysis characterization

The morphologies of the surfaces of MS surface specimens were inspected using the scanning electron microscope technique supported with EDX analysis and confirms the efficiency the 2-(1-Naphthylamino) ethylamine 2HCl (NNED), so the SEM-EDX images for the uninhibited solution (one molar of hydrochloric acid solution) saturate with carbon dioxide and with 2.8 mM from the N-(1-naphthyl)ethylenediamine dihydrochloride inhibitor in 303.15 K are depicted in Fig. (6a,d), respectively. Clearly from the Fig. 6a, the surface is extremely damaged and has the appearance of cavities and deep pits (because of the action of the chloride and carbonate ions) without the of 2-(1-Naphthylamino) ethylamine 2HCl (NNED)inhibitor. It is obviously noticeable that the corrosion process products in the existence of carbon dioxide cover the whole MS surface and appear to be lighter coloured in addition to the appearance of the lines from the polishing treatment before the immersion process. However, in the presence of2-(1-Naphthylamino) ethylamine 2HCl (NNED)(Fig. 6b), the surface of the mild steel seems less damaged and not affected by the aggressive solution and clearly even the polishing lines have disappeared (along with the defects such as pits, gullies and cracks) consequently of the formation of a "protective layer" on MS surface. This becomes an insulation layer which appears as a bold colour of showing the inhibitor molecules repelling the attacked of the hydrochloric acidic solution that deforms the metal surface via chloride ions. So, the corrosion rate is reduced to minimum levels and leads to a smooth electrode surface morphology and a reduction in the iron band according to EDX analysis (Fig. 6b). It can be concluded that the film layer is very fine with strong adhesion formed between the 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor film and MS electrode.

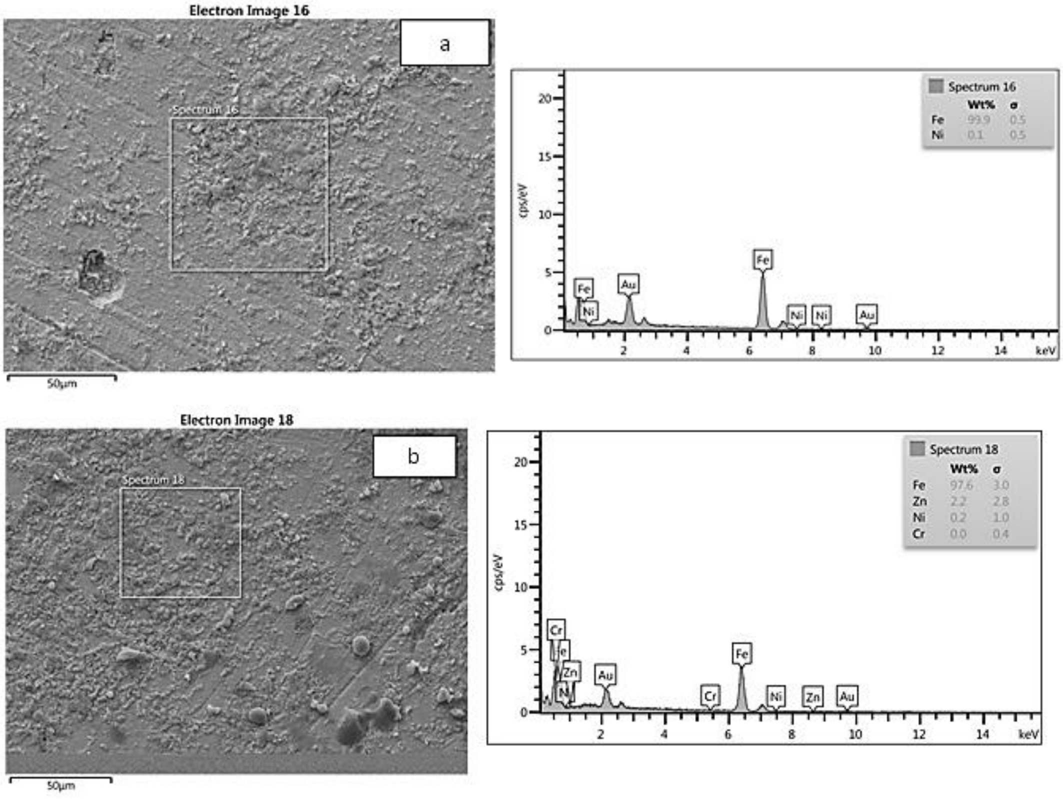


Fig 6 (a) : SEM image and EDX analysis of MS morphology without2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor and (b) : SEM image and EDX analysis of MS surface morphology in the presence of 2.8 mM 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor.

AM1 calculations

It is recognized today that the quantum chemical calculations are potentially powerful new tools to design and develop new corrosion inhibitors based on the best geometrical structure for the corrosion inhibitor, as well as using computational methods[86–90] to enhance and reinforce the experimental methods used inspect the degree to which they react with metal surfaces via acceptor–donor interactions. So, the theory of frontier orbital is valuable for predicting the active sites in the "adsorption process" to adsorb the2-(1-Naphthylamino) ethylamine 2HCl (NNED) molecules on the MS surface and responsible for the interactions taking place between them. [91]. The electronic parameters were estimated by performing the AM1 semi-empirical method to achieve an optimized structure of 2-(1-Naphthylamino) ethylamine 2HCl (NNED)with the lowest energy. For this structure, "the highest occupied molecular orbital (E_{HOMO}) , lowest unoccupied molecular orbital (E_{LUMO})" (Fig 7), and Mulliken atomic charges were calculated when considering the influence of water on the whole corrosion reaction, particularly its subsequent displacement from the electrode's surface when the ions have achieved more hydration as chloride ions. Moreover, this method enables a study a large number of cases that could occur to achieve corrosion inhibition by looking about the possible structures that are believed to participate and retard the corrosion rate (leading to a better understanding of the mechanism of inhibition).

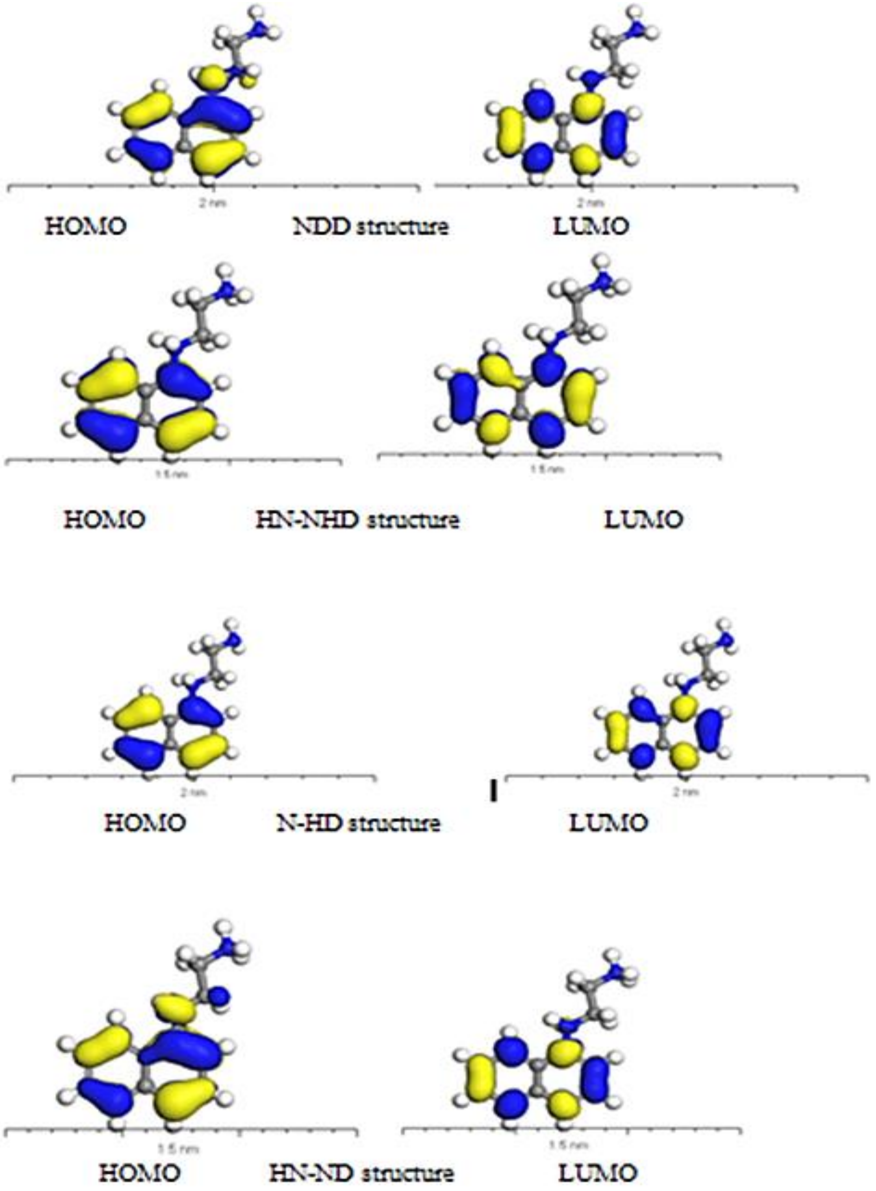


Fig (7): HOMO and LUMO for the (NDD),(HN-NHD),(N-HD), and(HN-ND)structures.

Table 3 shows the electronic properties that carried out in AM1 method for the 2-(1-Naphthylamino) ethylamine 2HCl (NNED) molecular structure with other structures (NDD, HN-NHD, N-HD, and HN-ND) that includes protonation of the nitrogen atom/atoms along with neglecting the effects of the hydrochloride molecules to achieve acceptable convergence for the optimized geometric structure. Furthermore, it is useful to calculate the "energy gap (ΔE) "and the values of the" fraction of transferred electrons (ΔN)"[91–95] that correlate with the effectiveness of corrosion inhibitor. Table 3 shows that the values of (E_{HOMO}) for the two nitrogen atoms and the protonated middle nitrogen atom of the inhibitor structures are higher, indicating the structures have a tendency towards donating the electrons for a given acceptor molecule. The unoccupied d-orbital iron and associated expectation that the corrosion inhibition will be higher [96], corresponds to a reduction in the (E_{LUMO}) values for accepting the electron density from the metal orbitals. Thus, The lowering in important parameters such as (ΔE) and (ΔN) reveal to improve in the $\eta\%$. Thus, in the present study the two, protonated nitrogen atoms in the inhibitor structure which display lower values, indicate that it sorbs more easily on MS surface than when it carried a negative charge. Additionally, the ability of the 2-(1-Naphthylamino) ethylamine 2HCl (NNED)to be adsorb on the mild steel is also associated with the nature of the charges on the nitrogen atoms. When the atoms display the highest partial atomic charge then it becomes easiest to donate its electron to the empty d-orbital [97]. So, Table 3 depicts the nitrogen atoms in other possible structures that have higher Mulliken atomic charges, which are also able to participate in the formation of a bond [98] by donating the electronic ion pair, a condition that is not inconsistent with the (ΔE) and (ΔN) values.

Table (3): Quantum chemical parameters for the NND,HN-NHD,N-NHD and HN-ND possible structures of corrosion inhibitor.

Electronic properties	NND Structure point group (C1)	HN-NHD Structure point group (C1)	N-NHD Structure point group (C1)	HN-ND Structure point group (C1)
HOMO (eV)	-8.530	-9.368	-9.335	-8.552
LUMO (eV)	-0.599	-1.079	-1.039	-0.61
Mulliken atomic charge 1N	-0.420	-0.204	-0.204	-0.445
Mulliken atomic charge 2N	-0.535	-0.300	-0.533	-0.299
ΔE (eV)	7.931	8.289	8.296	7.942
ΔN	0.307086	0.21432	0.218539	0.304583

Mechanism of inhibition of the (NDDE) inhibitor:

To expound the inhibiting action of 2-(1-Naphthylamino) ethylamine 2HCl (NNED)in one molar of HCl saturated with carbon dioxide, one must note the main reactions that occur on MS electrode, this means that complicated electrochemical reactions participate together depending on the temperature, pressure and the acidity of the medium. In general, carbon dioxide is not aggressive and the corrosion takes place through carbonic acid (a weak acid) as shown in equations (7)and (8) [99]. Thus, the corrosion process is characterized in the presence of CO_2 by pitting – a type of corrosion due to the generation of negatively-charged ions such as carbonate, oxide, and hydroxide which damage the surface of MS sample along with the effectiveness of chloride ions (hydrochloric acid solution) and source of the hydrogen ions. This is in contrast with reports in other publications, which specify that the corrosion reaction mainly occurs in the corrosion cell involve the reaction of the iron metal with hydrogen ions to evolve hydrogen gas and liberate the free iron ions according to equation (9)[99–101] in highly aggressive, acidic media with pH of less than 4.

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} \quad \dots\dots\dots \quad (7)$$

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO^-_{3(aq)} + H^+_{(aq)} \quad \dots\dots\dots.(8)$$

$$Fe_{(s)} + 2H^+_{(aq)} \rightleftharpoons Fe^{2+}_{(aq)} + H_{2(g)} \dots\dots\dots\dots\dots\dots(9)$$

So, the main cathodic reaction comes from the reduction of the hydrogen ions to form the hydrogen ions (equation 10) besides the possible cathodic reactions as shown in equations (10 and 11 a,b and c)[102]. This may be happen considering all possibilities of cathodic reactions that generate negative ions whereas, the anodic reaction occurs in a one-step (equation 12) [103]

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \dots\dots\dots\dots\dots..(10)$$

$$HCO^-_{3(sol.)} + e^- \longrightarrow H_{adsor.} + CO^{2-}_3 \dots\dots\dots\dots\dots\dots\dots\dots..\dots\dots(11a)$$

$$HCO^-_{3(near\ the\ electrode)} + H_{adsor.} + e^- \longrightarrow H_2\uparrow + CO^{2-}_3 \dots\dots\dots\dots\dots(11b)$$

$$H_2CO_{3(solu.)} + e^- \rightarrow H_{(adsor.)} + HCO^-_{3(adsor.)} \dots\dots\dots\dots\dots(11c)$$

$$\mathrm{Fe} \rightleftharpoons \mathrm{Fe}^{2+} + 2e^{-} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

The above equations indicate that anions (e.g. commonly chloride ions in corrosive solutions) confer a negative charge to the surface of MS electrode (initially, the MS has a positive charge in acidic media [4,85,104]) at the electrical double layer which facilitates the adsorption of the protonated of 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor molecules by the "electrostatic interaction (physical adsorption)". The 2-(1-Naphthylamino) ethylamine 2HCl (NNED) inhibitor may undergo adsorption on MS electrode via the electron pairs on the nitrogen atoms in addition to by the "π-electrons of the aromatic rings" of the naphthalene. The adsorption process takes places through the interactions between the HOMO of the 2-(1-Naphthylamino) ethylamine 2HCl (NNED) the electron donor (Lewis acid) and the "vacant d-orbitals" of MS (iron metal), which acts as a "Lewis base" for accepting electron density in the LUMO to achieve the formation of a bond. The latter interaction with filled s-orbital, which is attributable to the elemental iron element. These interpretations are supported by both the experimental results and theoretical calculations, and are consistent with previous reports [105–106]

CONCLUSIONS

The experimental data and quantum chemical calculations have been summarized and the following salient points can be stated:

1- The results revealed that 2-(1-Naphthylamino) ethylamine 2HCl (NNED) acts as a excellent inhibitor and is effective for the inhibition of corrosion in a 1 molar of HCl acidic solution in the presence carbon dioxide over the temperature range (303.15-318.15)K.

2- The information contained in the potentiodynamic polarization curves confirmed the behaviour of the NDDE inhibitor as mixed-type with the cathodic reaction predominant.

3- The temperature influence on the inhibitory action was examined at various temperatures so as to estimate the both parameters kinetic and thermodynamic, such as the "energy activation "and the "Gibbs' free energy" values in addition to the adsorption equilibrium constant (the latter refers to the inhibition validity under the present conditions).

4- The data obtained from SEM-EDX analysis demonstrate that the adsorption of NDDE occurs on MS surface and results in an improvement in the surface morphology. This yields sufficient protection by forming a "protective film" on MS surface.

5- Electronic properties indicators support the experimental results and suggest that the NDDE inhibitor undergoes protonation. Furthermore, the mechanism of corrosion inhibition has been established and is explained on the basis of the electrostatic interactions and acceptor-donor reactions taking place between inhibitor and the mild steel surface.

REFERENCES

[1] El-Haddad MN, Elattar KM.. Int J Ind Chem 2015;6:105–17. doi:10.1007/s40090-015-0037-9.

[2] Quraishi MA, Jamal D, Corrosion 2000;77:1–4.

[3] Yadav M, Behera D, Kumar S, Sinha RR.. Ind Eng Chem Res 2013;52:6318–28. doi:10.1021/ie400099q.

[4] Jyothi S, Ravichandran J. Acta Metall Sin (English Lett 2014;27:969–80. doi:10.1007/s40195-014-0107-6.

[5] Pavithra MK, Venkatesha T V, Kumar MKP, Tondan HC.Corros Sci 2012;60:104–11. doi:10.1016/j.corsci.2012.04.003.

[6] Zhang QB, Hua YX. Electrochim Acta 2009;54:1881–7.

[7] Sardar N, Ali H. Corrosion 2002;58:317–21.

[8] Ahamad I, Quraishi MA. Corros Sci 2009;51:2006–13. doi:10.1016/j.corsci.2009.05.026.

[9] Solmaz R, Karda G, Ya B, Erbil M. 1 2005;41:628–32.

[10] Bouayed M, Rabaa H, Srhiri a., Saillard J-Y, Bachir AB, Beuze AL. Corros Sci 1998;41:501–17. doi:10.1016/S0010-938X(98)00133-4.

[11] Li W, He Q, Pei C, Hou B. Electrochim Acta 2007;52:6386–94. doi:10.1016/j.electacta.2007.04.077.

[12] Qhatan AY, Adel A, others. Mod Appl Sci 2016;10:82.

[13] Quraishi MA, Jamal D.Mater Chem Phys 2003;78:608–13. doi:10.1016/S0254-0584(02)00002-0.

[14] Antonijevic MM, Bogdanovic GD, Radovanovic MB, Petrovic MB, Stamenkovic AT.. Int J Electrochem Sci 2009;4:654–61.

[15] Selvi ST, Raman V, Rajendran N. 2003:1175–82.

[16] Obot IB, Ebenso EE, Kabanda MM. Biochem Pharmacol 2013. doi:10.1016/j.jece.2013.06.007.

[17] Zhang S, Tao Z, Li W, Hou B. Appl Surf Sci 2009;255:6757–63. doi:10.1016/j.apsusc.2008.09.089.

[18] Liu B-Y, Liu Z, Han G-C, Li Y-H. Thin Solid Films 2011;519:7836–44. doi:10.1016/j.tsf.2011.06.002.

[19] El-Haddad MN, Elattar KM. Res Chem Intermed 2013;39:3135–49. doi:10.1007/s11164-012-0826-0.

[20] Yadav DK, Quraishi MA, Maiti B. Corros Sci 2012;55:254–66. doi:10.1016/j.corsci.2011.10.030.

[21] Pournazari S, Moayed MH, Rahimizadeh M. Corros Sci 2013;71:20–31. doi:10.1016/j.corsci.2013.01.019.

[22] Hassan HH. Electrochim Acta 2007;53:1722–30. doi:10.1016/j.electacta.2007.08.021.

[23] Obot IB, Gasem ZM. Corros Sci 2014;83:359–66. doi:10.1016/j.corsci.2014.03.008.

[24] Hu J, Zeng D, Zhang Z, Shi T, Song GL, Guo X. Corros Sci 2013;74:35–43. doi:10.1016/j.corsci.2013.04.005.

[25] DUTTA A, PANJA SS, NANDI MM, SUKUL D. J Chem Sci 2015;127:921–9. doi:10.1007/s12039-015-0850-x.

[26] Zhang D, Tang Y, Qi S, Dong D, Cang H, Lu G. Corros Sci 2015:2–7. doi:10.1016/j.corsci.2015.10.002.

[27] Obayes HR, Alwan GH, Alobaidy AHM, Al-Amiery A a, Kadhum AAH, Mohamad AB. Chem Cent J 2014;8:21. doi:10.1186/1752-153X-8-21.

[28] Shojaie F, Mirzai-Baghini N. Int J Ind Chem 2015;6:297–310. doi:10.1007/s40090-015-0052-x.

[29] Berisha A, Podvorica FI, Mehmeti V, Syla F, Vataj D. 2015;34:287–94.

[30] Belfilali I, Chetouani a., Hammouti B, Louhibi S, Aouniti a., Al-Deyab SS. Res Chem Intermed 2013;40:1069–88. doi:10.1007/s11164-013-1022-6.

[31] Yadav M, Behera D, Kumar S, Yadav P. Chem Eng Commun 2015;202:303–15. doi:10.1080/00986445.2013.841148.

[32] Ramkumar S, Nalini D. Orient J Chem 2015;31:1057–64. doi:10.13005/ojc/310255.

[33] Ullah S, Bustam MA, Shariff AM, Gonfa G, Izzat K. Appl Surf Sci 2016;365:76–83. doi:10.1016/j.apsusc.2015.12.232.

[34] Abdallah ZA, Mohamed Ahmed MS, Saleh MM. Mater Chem Phys 2016;174:91–9. doi:10.1016/j.matchemphys.2016.02.055.

[35] Sığırcık G, Tüken T, Erbil M. Corros Sci 2016;102:437–45. doi:http://dx.doi.org/10.1016/j.corsci.2015.10.036.

[36] Jafari H, Akbarzade K, Danaee I. Arab J Chem 2014:1–8. doi:10.1016/j.arabjc.2014.11.018.

[37] Singh AK, Singh AK, Ebenso EE. Int J Electrochem Sci 2014;9:352–64.

[38] Solmaz R. Corros Sci 2014;79:169–76. doi:10.1016/j.corsci.2013.11.001.

[39] Thanapackiam P, Rameshkumar S, Subramanian SS, Mallaiya K. Mater Chem Phys 2016;174:129–37.

[40] Kayi H, Clark T. J Mol Model 2009;15:295–308. doi:10.1007/s00894-008-0419-4.

[41] Dewar MJS, Thiel W. Ground states of molecules. 38. J Am Chem Soc 1977;99:4899–907. doi:10.1021/ja00457a004.

[42] Dewar MJS, Yuan Y. 1990:3881–90.

[43] Dewar MJS, Jie C, Yu J. SAM1; Tetrahedron 1993;49:5003. doi:10.1016/S0040-4020(01)81868-8.

[44] Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP. J Am Chem Soc 1985;107:3902–9. doi:10.1021/ja00299a024.

[45] Kamel AM, Zandi KS, Massefski WW. J Pharm Biomed Anal 2003;31:1211–22. doi:10.1016/S0731-7085(03)00025-6.

[46] Loose WS, Uhling HH. The corrosion handbook. Wiley, New York, 1948) P 1948;218.

[47] Studies G, The OF, Of K, Copper THEC. Galvanostatic Studies of the Kinetics of Deposition and Dissolution in the Copper Copper 1958:1586–601.

[48] Vetter KJ, Gorn F. Electrochim Acta 1973;18:321–6. doi:10.1016/0013-4686(73)80036-2.

[49] Stanly Jacob K, Parameswaran G. Corros Sci 2010;52:224–8. doi:10.1016/j.corsci.2009.09.007.

[50] Benabdellah M, Tounsi A, Khaled KF, Hammouti B. Thermodynamic, Arab J Chem 2011;4:17–24. doi:10.1016/j.arabjc.2010.06.010.

[51] Amin MA, Khaled KF, Fadl-Allah SA. Corros Sci 2010;52:140–51. doi:10.1016/j.corsci.2009.08.055.

[52] Kear G, Barker BD, Walsh FC. Corros Sci 2004;46:109–35. doi:10.1016/S0010-938X(02)00257-3.

[53] Holmes PR, Crundwell FK. Geochim Cosmochim Acta 2000;64:263–74. doi:10.1016/S0016-7037(99)00296-3.

[54] Aramaki K. Corros Sci 2001;43:2201–15. doi:10.1016/S0010-938X(00)00189-X.

[55] de Souza FS, Spinelli A. Corros Sci 2009;51:642–9. doi:10.1016/j.corsci.2008.12.013.

[56] Conway BE, Angerstein-Kozlowska H. Acc Chem Res 1981;14:49–56. doi:10.1021/ar00062a004.

[57] Krishtalik LI. Charge transfer reactions in electrochemical and chemical processes. Springer Science & Business Media; 2012.

[58] Conway BE. Electrochemical supercapacitors: scientific fundamentals and technological applications. Springer Science & Business Media; 2013.

[59] Jayaperumal D. Mater Chem Phys 2010;119:478–84. doi:10.1016/j.matchemphys.2009.09.028.

[60] Ferreira ES, Giacomelli C, Giacomelli FC, Spinelli A. Mater Chem Phys 2004;83:129–34. doi:10.1016/j.matchemphys.2003.09.020.

[61] Laidler KJ. The development of the Arrhenius equation. J Chem Educ 1984;61:494–8. doi:10.1021/ed061p494.

[62] Mathur PB, Vasudevan T. Reaction Rate Studies for the Corrosion of Metals in Acids--I , Iron in Mineral Acids * 1982;38.

[63] Gao G, Liang C. Electrochim Acta 2007;52:4554–9. doi:10.1016/j.electacta.2006.12.058.

[64] Dehri İ, Özcan M. Mater Chem Phys 2006;98:316–23. doi:10.1016/j.matchemphys.2005.09.020.

[65] Ashassi-Sorkhabi H, Shaabani B, Seifzadeh D. Appl Surf Sci 2005;239:154–64.

[66] Amin MA, Ahmed MA, Arida HA, Arslan T, Saracoglu M, Kandemirli F. Corros Sci 2011;53:540–8. doi:10.1016/j.corsci.2010.09.019.

[67] Journal C. 8th European Symposium on Corrosion Inhibitors. Br Corros J 1995;30:267–74. doi:10.1179/bcj.1995.30.4.267.

[68] Szauer T, Brandt A. Electrochim Acta 1981;26:1253–6. doi:10.1016/0013-4686(81)85107-9.

[69] Martinez S, Stern I. Appl Surf Sci 2002;199:83–9. doi:10.1016/S0169-4332(02)00546-9.

[70] Ivanov ES, Brodskii ML, Timonin A V. Metallurgist 2009;53:421–8. doi:10.1007/s11015-009-9200-x.

[71] Ivanov ES. Inhibitors of Corrosion of Metals in Acid Media, Metallurgy, Handbook in Accordance with the State Service of Standard Reference Data 1986.

[72] Rosenfeld IL. Inhibitors of corrosion. Khimiya, Moscow 1977.

[73] Popova A. Temperature effect on mild steel corrosion in acid media in presence of azoles 2007;49:2144–58. doi:10.1016/j.corsci.2006.10.020.

[74] Popova A, Sokolova E, Raicheva S, Christov M. A Corros Sci 2003;45:33–58. doi:10.1016/S0010-938X(02)00072-0.

[75] Bond GC. Catalysis by metals. Academic Press; 1962.

[76] Al-haydari YK, Saleh JM, Matloob MH. Adsorption and Decompositlon of Hydrazine on Metal Films of Iron, Nickel, and Copper 1985;223:3286–90.

[77] Dhar P. ON THE FORM OF ADSORPTION ISOTHERMS FOR SUBSTITUTIONAL OF MOLECULES OF DIFFERENT SIZES 1973;18:789–98.

[78] Jimbo H. 0. IKEDA, H. JIMBO and H. TAMUEL4 Department of Applied Chemistry, Faculty of Engineerins 565 (Japan) Osaka 1982;137:127–41.

[79] Do DD. Adsorption Analysis: Equilibria and Kinetics:(With CD Containing Computer Matlab Programs). vol. 2. World Scientific; 1998.

[80] Migahed MA, Farag AA, Elsaed SM, Kamal R, El-Bary HA. Corrosion Chem Eng Commun 2012;199:1335–56. doi:10.1080/00986445.2012.662922.

[81] Chakrabarty C, Singh MM, Yadav PNS. V Agarwal C. Trans SAEST 1983;18:15.

[82] Oguzie EE, Okolue BN, Ebenso EE, Onuoha GN, Onuchukwu AI. Mater Chem Phys 2004;87:394–401. doi:10.1016/j.matchemphys.2004.06.003.

[83] Oguzie EE, Onuoha GN, Onuchukwu a. I. Mater Chem Phys 2005;89:305–11. doi:10.1016/j.matchemphys.2004.09.004.

[84] Negm NA, Elkholy YM, Zahran MK, Tawfik SM. Corros Sci 2010;52:3523–36. doi:10.1016/j.corsci.2010.07.001.

[85] Sakunthala P, Vivekananthan SS, Gopiraman M, Sulochana N, Vincent AR. J Surfactants Deterg 2012:1–13. doi:10.1007/s11743-012-1405-5.

[86] Shanshal MA, Al MA, Yusof QA. 2016;7:166–76. doi:10.5155/eurjchem.7.2.166.

[87] Yousif QA. Structure and the Corrosion Inhibiting Effect of Some 2010;13:14–23.

[88] Yousif QA. Quantum Chemical Study on some substituted thiourea as corrosion inhibition for aluminum n.d.

[89] Borówko M. Computational methods in surface and colloid science. CRC Press; 2000.

[90] Shanshal MA, Yousif QA. 2014;17:61–70.

[91] Fang J, Li J. J Mol Struct THEOCHEM 2002;593:179–85. doi:10.1016/S0166-1280(02)00316-0.

[92] Kokalj A. Chem Phys 2012;393:1–12. doi:10.1016/j.chemphys.2011.10.021.

[93] Pearson RG. Inorg Chem 1988;27:734–40. doi:10.1021/ic00277a030.

[94] Pearson RG. J Chem Educ 1987;64:561. doi:10.1021/ed064p561.
[95] Pearson RG. Proc Natl Acad Sci U S A 1986;83:8440–1. doi:10.1073/pnas.83.22.8440.
[96] Zhao P, Liang Q, Li Y. Appl Surf Sci 2005;252:1596–607. doi:10.1016/j.apsusc.2005.02.121.
[97] Martinez S. Mater Chem Phys 2003;77:97–102. doi:10.1016/S0254-0584(01)00569-7.
[98] Xia S, Qiu M, Yu L, Liu F, Zhao H. Corros Sci 2008;50:2021–9. doi:10.1016/j.corsci.2008.04.021.
[99] Jawich MWS, Oweimreen GA, Ali SA. Corros Sci 2012;65:104–12. doi:10.1016/j.corsci.2012.08.001.
[100] Sun W, Corrosion 2009;65:291–307. doi:10.5006/1.3319134.
[101] Yousif QA, Al-zhara AA. 2016;11:12619–30.
[102] Moiseeva LS. Prot Met 2005;41:76–83. doi:10.1007/s11124-005-0011-6.
[103] Popoola L, Grema A, Latinwo G, Gutti B, Balogun A. Int J Ind Chem 2013;4:35. doi:10.1186/2228-5547-4-35.
[104] Li Y, Zhao P, Liang Q, Hou B. 2005;252:1245–53. doi:10.1016/j.apsusc.2005.02.094.
[105] Obot IB, Obi-Egbedi NO. Corros Sci 2010;52:198–204. doi:10.1016/j.corsci.2009.09.002.
[106] Bouklah M, Hammouti B, Aouniti A, Benhadda T. 2004;49:225–8. doi:10.1016/j.porgcoat.2003.09.014.