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ISSN: 2278-1862

Journal of Applicable Chemistry

2018, 7 (6): 1713-1727

(International Peer Reviewed Journal)

Inhibition Effect of 4-{[4-(dimethylamino)benzylidene]amino}-5-methyl-4H-1,2,4-triazole-3-thiol on the Corrosion of Maraging Steel in 1.5M HCl

Rachael Natash Mary[1], Ronald Nazareth[1] and P. A.Suchetan[2*]

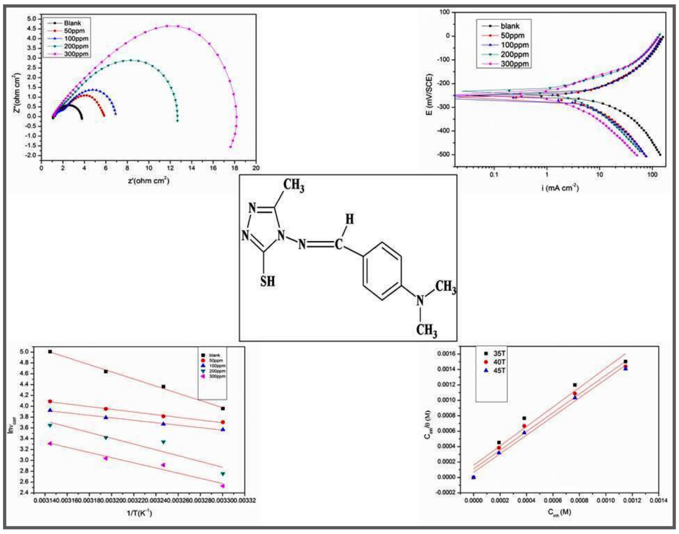
1. Department of Chemistry, St. Aloysius College, Mangaluru-575003, INDIA
2. Department of Studies and Research in Chemistry, University College of Science,
Tumkur University, Tumkur-572103, INDIA
E-mail:pasuchetan@gmail.com

Accepted on 14th November, 2018

ABSTRACT

The inhibition effect of the synthesized Schiff base, (4-{[4-(dimethylamino)benzylidene]amino}-5-methyl-4H-1,2,4-triazole-3-thiol)[DBAMTT]on corrosion of maraging steel in 1.5M HCl was evaluated using electrochemical techniques such as potentiodynamic polarization and electro-chemical impedance spectroscopy (EIS). Results showed that, with increase in temperature and concentration of the inhibitor there was an increase in inhibition efficiency. DBAMTT acts as a mixed type inhibitor. Adsorption of the inhibitor on the metal surface follows Langmuir adsorption isotherm. Corrosion activation and thermodynamic parameters were calculated. Scanning electron microscope technology with Energy dispersive X-ray spectroscopy (SEM-EDX) was used to study the surface morphology of maraging steel.

Graphical Abstract



Keywords: : Corrosion inhibition, Maraging Steel, Schiff base, Hydrochloric acid Potentiodynamic polarization, EIS.

INTRODUCTION

Corrosion is a destructive phenomenon, chemical or electrochemical, which can attack any metal or alloy through reaction by the surrounding environment and in extreme cases may cause structural failure. Metals and alloys are used in variety of activities and applications, and are susceptible to corrosion due to their thermodynamic instability, especially, in an aggressive media.

Maraging steel was developed in 1960s for applications requiring ultrahigh strength in combination with good fracture toughness. The alloy is a low carbon steel that classically contain about 18 wt % Ni, substantial amounts of Co and Mo together with small additions of Ti. However, depending on the demands dedicated by the application, the composition of the material can be modified [**1**]. They have higher modulus of elasticity and lower thermal expansion coefficient. Another important property is its better thermal conductivity, which reduces surface temperature during thermal loading and lowers thermal stresses [**2**]. Maraging steels have been extensively used in a variety of applications due to their attractive combination of properties such as high strength, moderate toughness and good weld ability [**3**]. Due to the low carbon content, maraging steels have good machinability. Its strength and malleability allow it to be used in the preparation of rocket and missile skins in aerospace industries, engine components like crankshafts and gears, bearings, submarine hulls, surgical components, nuclear and gas turbine applications [**4**]. Maraging steels were found to be less susceptible to hydrogen embrittlement than common high-strength steels owing to significantly low diffusion of hydrogen in them [**5**]. Maraging steel is an alloy which is very prone to corrosion particularly in acidic medium. Maraging steels come in contact with acids during pickling, acid cleaning, acid descaling and oil well acidizing and the use of inhibitors to control the destructive attack of acid environment on metals in the above processes is found to have widespread applications [**6**].

Organic compounds containing polar functions with oxygen, nitrogen, or sulfur atoms have been widely studied as corrosion inhibitors. These compounds act as efficient inhibitors by adsorbing on the metal surface in which polar groups act as adsorption centers. The extent of adsorption of an inhibitor depends on many factors such as the nature and the surface charge of the metal, the mode of adsorption of the inhibitor, the inhibitor’s chemical structure, and the type of the aggressive solution.

The efficient adsorption may be due to the pi electrons and multiple bonds of the aromatic system or the presence of electronegative atoms (O or N) in the inhibitors molecular structure [**7-10**]. Availability of π electrons due to the presence of multiple bonds or aromatic rings in the inhibitors molecule would facilitate electron interaction with d-orbital of iron. Schiff’s bases have been reported to act as good corrosion inhibitors due to presence of polar –CH=N- bond which act as adsorption center during adsorption of Schiff bases on the metal surface.

The effect of 3,4dimethoxybenzaldehyde thiosemicarbazone [**11**] and diacetylmonoximethiosemi carbazone [**12**] in 0.5 M sulphuric acid medium on corrosion of aged maraging steel was studied [**11**] and reported to have good inhibitor efficiency. The effect of 2-(4-chlorophenyl)-2-oxoethyl benzoate in 1.0 M sulphuric acid medium [**13**] and effect of 1(2E)-1-(4-aminophenyl)-3-(2-thienyl)prop-2-en-1-one in 1.5 M hydrochloric acid medium [**14**] on corrosion of maraging steel under weld aged conditions was studied and have good inhibition efficiency. Influence of 2,5-bis (3,4,5-trimethoxy phenyl)-1,3,4- oxadiazole (BTPO) on 18 Ni M250 grade welded maraging steel in 1.0 M sulphuric acid medium was studied [**15**]. The inhibition efficiency of the inhibitor increases with increase in its concentration and decreases with the increase in temperature. Adsorption was found to be through physical adsorption and followed Langmuir adsorption isotherm [**15**].

MATERIALS AND METHODS

Studies were carried out using a specimen of Maraging Steel (18%Ni M250 Grade).Table 1 shows the percentage composition of 18% Ni M250 Grade Maraging Steel.

Table 1. Percentage Composition of 18%Ni M250 Grade Maraging Steel

Element	Composition	Element	Composition
C	0.015%	Ti	0.3-0.6%
Ni	17-19%	Al	0.05-0.15%
Mo	4.6-5.2%	Mn	0.1%
Co	7-8.5%	P	0.01%
Si	0.1%	S	0.01%
O	30ppm	N	30ppm
H	2.0ppm	Fe	Balance

Preparation of the test coupons: The working electrode used for electrochemical studies was cut from a plate into a rod and sealed with epoxy resin in such a way that the area exposed to the acid medium was 0.8910 cm^2. The test coupon was polished as per standard metallographic practice by subjecting it to belt grinding followed by polishing it on emery papers of grades 180, 400, 600, 800,1000, 1200, 1500, 2000 and finally on polishing wheel using legated alumina abrasive to obtain mirror finish. It was then washed with distilled water, degreased with acetone, and dried before immersing it in the acid medium in the presence and absence of the inhibitor.

Medium: The corrosive medium used for the study was 1.5M hydrochloric acid solution and standard solution of this acid was prepared by diluting Analar grade hydrochloric acid using double distilled water. The inhibitor concentrations employed for the study was 50, 100, 200 and 300ppm. Solutions of the inhibitor with the above concentrations were prepared in 1.5M HCl solution. Analysis was carried out using calibrated thermostat at temperatures 30, 35, 40 and 45^{o}C (± 0.5^{o}C).

Synthesis of (4-{[4-(dimethylamino)benzylidene]amino}-5-methyl-4H-1,2,4-triazole-3-thiol): Thiocarbohydrazide (TCH) was prepared by the method proposed by Audrieth *et al* [16]. Triazole was prepared by refluxing TCH with glacial acetic acid for 4h according to the procedure given by Dhaka *et al* [17]. The synthesized triazole was refluxed with N,N-dimethyl amino benzaldehyde in the presence of absolute alcohol containing 3 drops of sulphuric acid to obtain the required Schiff base, (4-{[4-(dimethylamino)benzylidene]amino}-5-methyl-4*H*-1,2,4-triazole-3-thiol)[16, 17].The product formed was filtered dried and recrystallized from ethanol. Melting point of the synthesized inhibitor was in the range 205-210°C. The product was characterized by IR studies. Chemicals required for inhibitor synthesis were of analytical reagent grade. FTIR spectrum of the Schiff base is shown in figure 1.

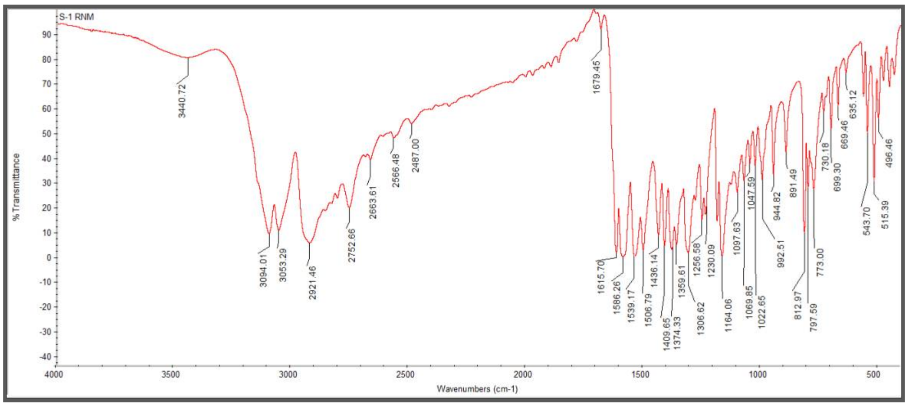
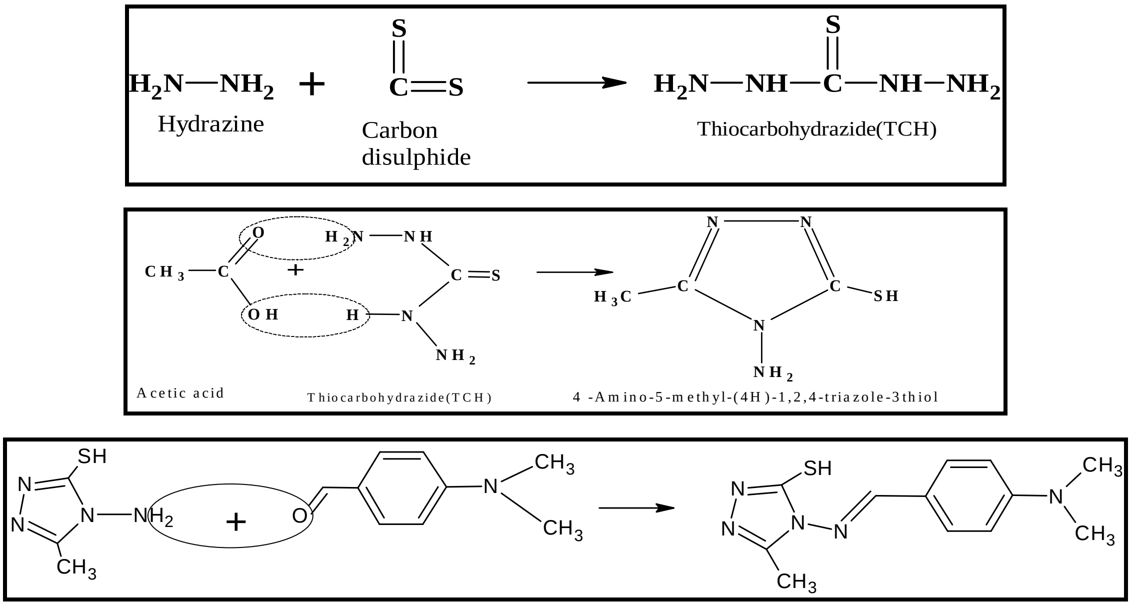


Figure 1. FTIR spectrum of the Schiff base.

The Inhibitor preparation scheme 1 is shown below



Scheme 1.: Triazole N, N-dimethyl amino benzaldehyde Schiff Base.

Electrochemical measurements: Electrochemical measurements were carried out using an electrochemical work station, Gill AC having ACM instrument Version 5 software. The arrangement used was a conventional three-electrode compartment glass cell. A platinum counter electrode, a reference Saturated Calomel electrode (SCE) and the working electrode were placed inside the three-electrode glass cell. Tafel polarization studies were carried out immediately after EIS studies on the same electrode without any further surface treatment.

Tafel Polarization Studies: Finely polished maraging steel specimen with exposure area of 0.8910 $cm^2$was exposed to acid corrosion medium of 1.5MHCl in the presence and absence of the inhibitor at different temperatures (30-45°C) and allowed to attain a steady state open circuit potential (OCP).In order to record the potentiodynamic current-potential curves, the specimen was polarized to -250mV cathodically and +250mV anodically with respect to OCP at a sweep rate of 1 $mV\ s^{-1}$.

Electrochemical Impedance spectroscopy Studies (EIS): EIS technique was also used to study the corrosion behavior of the specimen. The impedance measurements were carried out in the frequency range of 10KHz to 0.01Hz by applying a small amplitude AC signal of 10mV to the electrochemical system. Impedance data was analyzed using Nyquist plots. The double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) were calculated from the Nyquist plots.

Scanning Electron Microscopy -Energy Dispersive X-Ray Spectroscopy (SEM-EDX): The surface morphology of marging steel specimen immersed in 1.5MHCl solution in the presence and absence of the inhibitor was evaluated using SEM-EDX analysis (Carl Zeiss, USA) and (Oxford Instruments).

RESULTS AND DISCUSSION

Tafel Polarization Measurements: Tafel polarization curves of maraging steel specimen in 1.5M HCl solution using different inhibitor concentration (50, 100, 200 and 300 ppm) at different temperatures (30-45°C) were recorded and results were tabulated. Figure 2 shows the Tafel polarization curves for corrosion of maraging steel in 1.5M HCl at 45°C using different inhibitor concentrations. Similar curves were obtained at other temperatures too.

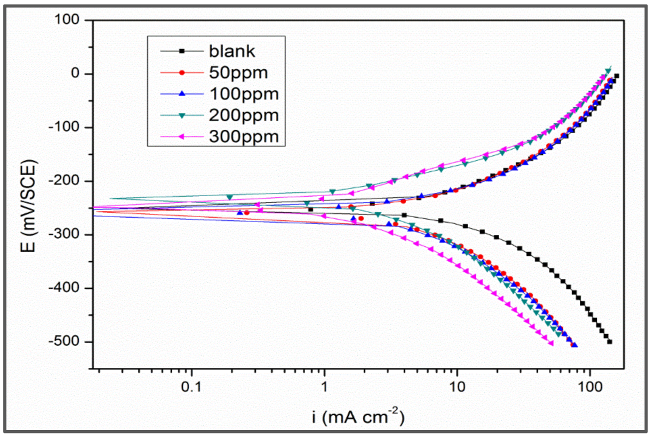


Figure 2. Tafel Polarization curves for the corrosion of Maraging Steel in 1.5M HCl containing different concentrations of inhibitor at 45°C.

The corrosion rate was calculated using equation (1) [18]

$$\upsilon_{corr}(mmy^{-1}) = \frac{3270\times M\times i_{corr}}{\rho\times Z} \qquad (1)$$

Where, 3270 is a constant that defines unit of corrosion rate, i_{corr} is corrosion current density, ρ is the density of corroding material, M is the atomic mass of the metal and Z is number of electrons transferred per atom. The inhibition efficiency was calculated from equation (2).

$$\eta(\%) = \frac{i_{corr}-i_{corr(inh)}}{i_{corr}} \times 100 \qquad (2)$$

Where, i_{corr} and $i_{corr(inh)}$ are corrosion current densities obtained in uninhibited and inhibited solutions.

From the tafel polarization curves, Electrochemical parameters namely Corrosion potential (E_{corr}), Corrosion current density (i_{corr}) , Cathodic and Anodic Tafel slopes (β_c and β_a) and Inhbition efficiency (η) were recorded and are listed in table 2.

Maraging steel shows corrosion in 1.5M HCl solution. According to the data in table 2 it is observed that the presence of the inhibitor has some effect on the corrosion inhibition of maraging steel specimen. Inhibited solution shows a decrease in the corrosion rate compared to the uninhibited solution. A shift of the polarization curves to low current density region indicates decrease in corrosion rate (**ν_{corr}**). With the increase in temperature and concentration of the inhibitor there is an increase in inhibition efficiency.

For an inhibitor to be considered distinctively as cathodic or anodic type, the displacement in corrosion potential (E_{corr}) should me more than ± 85mV with respect to the corrosion potential of the blank. The present study indicates no definite shift in the (E_{corr}) values showing maximum displacement of about ± 33mV. This suggests that both anodic and cathodic polarization profiles are influenced simultaneously and the inhibitor can be considered as a mixed type inhibitor affecting both metal dissolution and hydrogen evolution reactions [19]. From figure 2, it is observed that that cathodic Tafel slope does not differ much with increase in inhibitor concentration indicating that hydrogen evolution is activation controlled and presence of inhibitor does not change the mechanism of cathodic hydrogen evolution reaction [20, 21].

Table 2. Results of Tafel Polarization studies on Maraging Steel in 1.5MHCl containing different concentrations of the inhibitor

Temperature °C	Conc. of Inhibitor (ppm)	E_{corr} (mV/SCE)	β_a (mV dec^{-1})	β_c (mV dec^{-1})	i_{corr} (mA cm^{-2})	v_{corr}(mm y^{-1})	η(%)
30	Blank	-261.9	124.13	15.38	4.1773	52.350962	
	50	-257.91	97.739	139.31	3.2475	40.698477	22.25
	100	-257.99	92.145	146.01	2.831	35.478795	32.25
	200	-228.4	85.135	151.79	1.2557	15.736744	69.93
	300	-230.17	83.436	154.43	0.999138	12.521457	76.08
35	Blank	-255.54	13742	161.1	6.258	78.426812	
	50	-256.58	106.49	166.23	3.6164	45.321624	42.21
	100	-255.244	93.354	150.34	3.1329	39.262281	49.93
	200	-227.23	98.69	157.67	2.2584	28.302830	63.91
	300	-224.18	90.014	130.96	1.4703	18.432431	76.49
40	Blank	-225.68	149.24	165.54	8.2733	103.68305	
	50	-256.86	114.1	172.52	4.481	51.985020	49.86
	100	-257.25	95.564	156.28	3.5294	44.231318	57.33
	200	-235.14	108.46	191.28	2.4456	30.648867	70.43
	300	-231.83	96.778	163.75	1.6637	20.849902	79.89
45	Blank	-249.18	178.52	183.79	11.929	149.49719	
	50	-257.24	109.03	169.95	4.684	59.758774	60.02
	100	-258.49	96.83	160.53	4.0382	50.607726	66.14
	200	-231.65	8.874	174.96	3.0724	38.504080	74.24
	300	-249.46	104.22	160.69	2.1873	27.411787	81.66

Electrochemical Impedance Spectroscopy: Electrochemical impedance spectroscopy (EIS) is a technique, which can be used to determine the characteristics and kinetics of electrochemical processes occurring at the metal solution interfaces. Corrosion inhibition of maraging steel in 1.5 M HCl solution in the presence and absence of inhibitor was investigated by electrochemical impedance spectroscopy measurements. The nyquist plots for maraging steel in 1.5M HCl at 45°C using different inhibitor concentrations are given in figure 3. Similar plots were obtained at other temperatures too. Figure 3 indicates that corrosion rate decreases with increase in concentration of the inhibitor, as in nyquists plots, the diameter of the semicircle increases with the increase in concentration of the inhibitor [22].

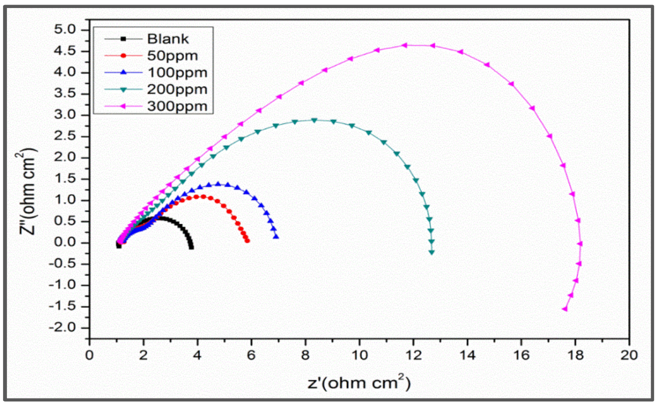


Figure 3. EIS curves for the corrosion of Maraging Steel in 1.5M HCl containing different concentrations of inhibitor at Temperature 45°C.

Impedance parameters recorded from nyqyists plots are given in table 3. Nyquist plots are semicircular both in presence and absence of inhibitor indicating that the inhibitor does not change the reaction mechanism of corrosion sample in acid medium and corrosion of the sample is controlled by charge transfer process. Nyquist plots are not perfect semicircles and this deviation is due to surface heterogeneity which is due to surface roughness, dislocation, distribution of active sites or adsorption of molecules. R_{ct} values increases with increase in concentration of the inhibitor and this increase is because the inhibitor molecules adsorb on the metal surface by replacing the water molecules forming a protective film on the metal surface [23, 24].

Table 3. Results of Tafel polarization studies on Maraging Steel in 1.5M HCl containing different concentrations of the inhibitor

Temperature °C	Conc. of Inhibitor (ppm)	R_{ct} (ohm cm^2)	C_{dl} (F)	Efficiency η (%)
30	Blank	7.71	0.045	
	50	8.96	0.119	13.98
	100	12.2	0.1125	36.80
	200	18.5	0.02554	58.32
	300	25.8	0.02829	70.11
35	Blank	5.91	0.0974	
	50	7.5	0.0804	21.2
	100	9.4	0.1149	37.12
	200	16.3	0.0309	63.74
	300	27.3	0.0428	78.35
40	Blank	4.57	0.1186	
	50	6.63	0.096	31.07
	100	8.57	0.1048	46.67
	200	14.7	0.0266	68.91
	300	23.4	0.02933	80.47
45	Blank	3.25	0.1885	
	50	5.08	0.105	36.02
	100	7.45	0.1224	56.37
	200	13.5	0.0304	75.92
	300	17.9	0.0129	81.84

As R_{ct} is inversely proportional to the corrosion current density, inhibitor efficiency, η (%), was calculated from the following relationship:

$$\eta(\%) = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \qquad (3)$$

Where, $R_{ct(inh)}$ and R_{ct} are the charge transfer resistances obtained in inhibited and uninhibited solutions, respectively. The corrosion current density i_{corr} can be calculated using the charge transfer resistance value, R_{ct}, using with the Stern–Geary equation (4) [25].

$$i_{corr} = \frac{b_a b_c}{2.303\,(b_a + b_c)R_{ct}} \qquad (4)$$

Nyuist plots consisted of a semi-circular capacitive loop. These Nyquist spectra were fitted to the best equivalent circuit model, R (QR), represented in figure 4 and this was done using ZSimpWin 3.21 software. The equivalent circuit is a parallel combination of charge-transfer resistance (R_{ct}) and constant phase element corresponding to double layer (CPE, Q) both in series with solution resistance (Rs). The CPE element is used to explain depression of the capacitance semicircle. The CPE impedance (Z_{CPE}) is given by the expression

$$Z_{CPE} = \frac{1}{Q} \text{x} \frac{1}{(j\omega)^n} \qquad (5)$$

Where, Q is the CPE coefficient, n is the CPE exponent, ω is the angular frequency (ω= 2Πf, where f is the AC frequency) and j is the imaginary unit.

CPE behaves like an ideal double layer capacitance (C_{dl}) when the value of n is 1. The Correction of capacitance to its real value is calculated using equation (6) [14].

$$C_{dl} = Q(\omega_{max})^{n-1} \qquad (6)$$

Where, ω_{max} is the frequency at which the imaginary part of impedance ($-Z_i$) has a maximum [26].

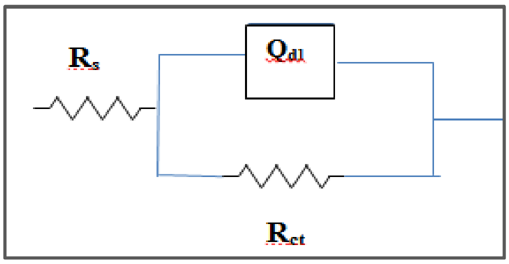


Figure 4. Equivalent circuit used to fit experimental EIS data.

Effect of Temperature: Temperature is an important parameter in studies on material corrosion. The dependence of temperature on corrosion rate and inhibition efficiency reveals valuable kinetic and thermodynamic parameters and this contributes in determining the type of adsorption of the studied inhibitors.

The value of activation energy, E_a was calculated using Arrhenius equation, (7).

$$ln(v_{corr}) = B - \frac{E_a}{RT} \qquad (7)$$

Where, B is a constant which depends on the metal type, R is universal gas constant and T is the absolute temperature. The plot of $ln\ (v_{corr})$vs reciprocal of absolute temperature (1/T) gives a straight line with slope $=\frac{Ea}{R}$, from which the activation energy values for the corrosion process was calculated. Figure 5 represents the Arrhenius plots for the corrosion of maraging steel using different inhibitor concentrations in 1.5M HCl.

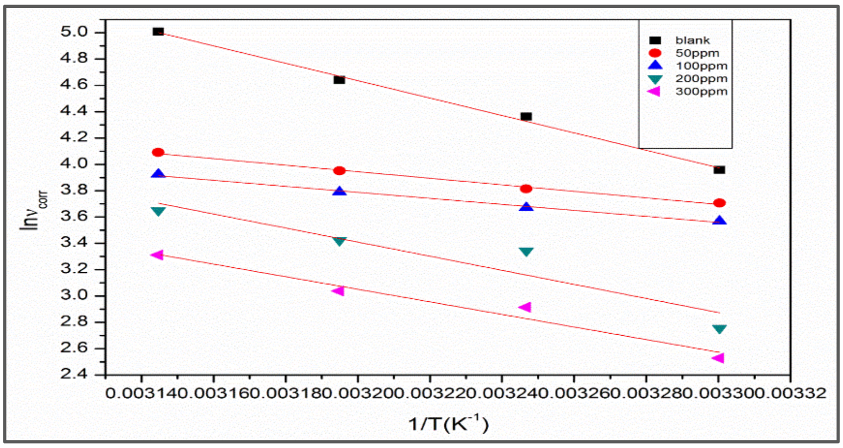


Figure 5. Arrhenius plots for corrosion of Maraging Steel in 1.5M HCl containing different concentrations of inhibitor.

The enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activation values for the corrosion process was calculated from transition state equation (8).

$$\upsilon_{corr} = \frac{RT}{Nh}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(\frac{-\Delta H^{\neq}}{RT}\right) \qquad (8)$$

Where, h is Planck's constant and N is Avagadro's number. A plot of $\ln(\upsilon_{corr} / T)$ vs 1/T gives a straight line with slope = $-\Delta H^{\#}/R$ and intercept = $\ln (R/ Nh) + \Delta S^{\#}/R$. Figure 6 represents the plot of $\ln(\upsilon_{corr} / T)$ vs 1/Tfor the corrosion of maraging steel using different inhibitor concentrations in 1.5M HCl. The activation parameters were recorded and are shown in table 4.

Table 4. Activation parameters for the corrosion of Maraging Steel in 1.5MHCl containing different concentrations of inhibitor

Concentration of Inhibitor (ppm)	E_a ($kJ\ mol^{-1}$)	$\Delta H^{\neq}$ ($kJ\ mol^{-1}$)	$\Delta S^{\neq}$ ($J\ mol^{-1}\ K^{-1}$)
Blank	54.91	52.33	-39.27
50	0.64	18.06	-192.38
100	18.96	16.38	-193.19
200	44.46	41.88	-183.75
300	39.68	37.1	-185.95

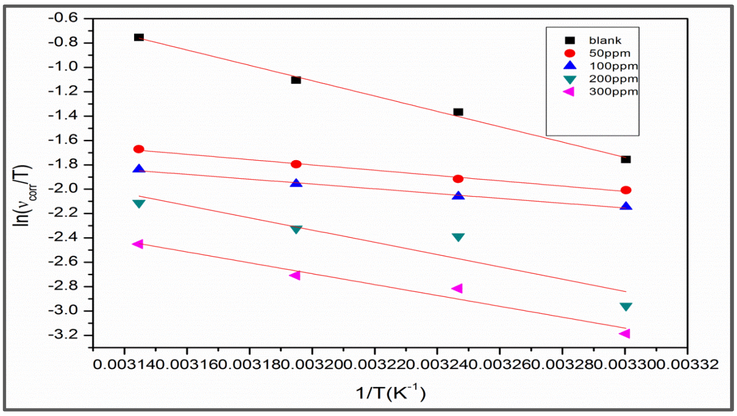


Figure 6. Plots of $\ln(\nu_{corr}/T)$ vs 1/T for corrosion of Maraging Steel in 1.5M HCl containing different concentrations of inhibitor.

It is found that the values of E_a for inhibited solutions are lower than that for uninhibited solutions. The decrease of activation energy may be due to slow rate of inhibitor adsorption. Studies have shown that lower values for E_a in inhibited solutions compared to blank is indicative of chemisorption mechanism [27]. The corrosion reaction is endothermic in nature indicative of positive values of enthalpy. The negative values of entropy of activation implies that activated complex in the rate determining step represents an association rather than dissociation, resulting in decrease in randomness on going from reactant to activated complex.

Adsorption Isotherm: Adsorption isotherms provide information about the interaction between the inhibitor molecule and metal surface. Adsorption of an organic inhibitor on the metal solution interface is considered as a substitution process between organic molecule in aqueous solution (Org_{aq})and water molecules on metal surface(H_2O_{ads}) [28] which can be represented as

$$Org_{(aq)} + \chi H_2O_{(ads)} \longleftrightarrow Org_{(ads)} + \chi H_2O_{(aq)}$$

Where, $Org_{(aq)}$ and $Org_{(ads)}$ are organic molecules in aqueous solution and adsorbed on metal surface, $H_2O_{(ads)}$and $H_2O_{(aq)}$are water molecules on metal surface and in solution and χ represents number of water molecules replaced by one molecule of organic adsorbate.

The surface coverage (θ) was calculated from potentiodynamic polarization data using the equation (9) [29]

$$\theta = \frac{\eta\ (\%)}{100} \qquad (9)$$

Where, η (%) is thepercentage inhibition efficiency, the values of θ at different inhibitor concentrations in solution (C_{inh}) were applied to various isotherms namely Langmuir, Temkin, Frumkin and Florye Huggins isotherms, It was observed that, the data was in good agreement with the Langmuir adsorption isotherm, which is given by the relation (10).

$$\frac{C_{inh}}{\theta} = C(inh) + \frac{1}{K} \qquad (10)$$

Where, K is the adsorption/desorption equilibrium constant,C_{inh} is the corrosion inhibitor concentration in the solution and θ is the surface coverage. The plot of C_{inh}/θ versus C_{inh} gives a straight line with an intercept of 1/K. The Langmuir adsorption isotherms for the adsorption of DBAMTT on the maraging steel surface are shown in figure 7.

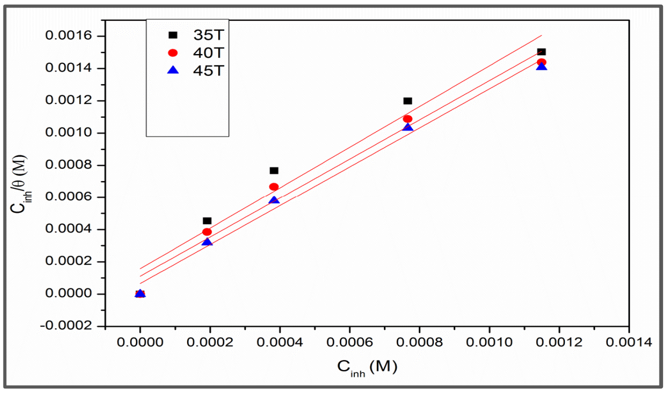


Figure 7. Langmuir adsorption Isotherms for adsorption of DBAMTT on maraging steel in 1.5MHClsolutionat different temperatures.

The standard free energy of adsorption (ΔG^o_{ads}) was calculated using equation11 [22].

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G^o_{ads}}{RT}\right) \qquad (11)$$

Where, value 55.5 is the concentration of water in solution in mol dm^{3-1}, R is the universal gas constant and T is the absolute temperature. Figure 8 represents a plot of (ΔG^o_{ads}) vs T, from which standard enthalpy of adsorption (ΔH^o_{ads}) and standard entropies of adsorption (ΔS^o_{ads}) were obtained from thermodynamic equation (12). The thermodynamic data obtained are recorded in table 5.

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \qquad (12)$$

Table 5. Thermodynamic parameters for adsorption of DBAMTT on surface of maraging steel in 1.5M HCl at different temperatures.

Temperature °C	**ΔG^o_{ads} (kJ mol^{-1})**	**ΔH^o_{ads} (kJmol^{-1})**	**ΔS^o_{ads} (J $mol^{-1}K^{-1}$)**
35	-32.71	71.13	336.91
40	-34.15		
45	-36.08		

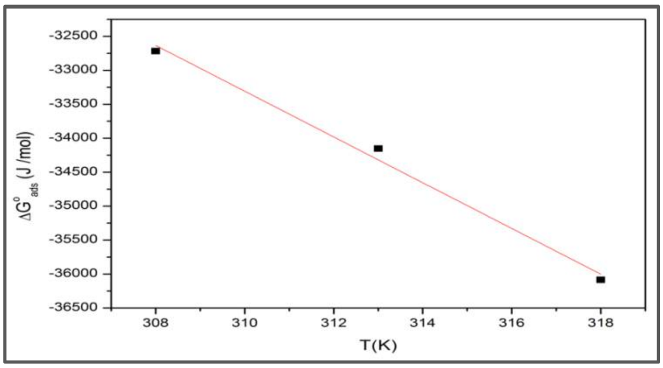


Figure 8. Plot of (ΔG^o_{ads})vs T for adsorption of DBAMTT on maraging steel in 1.5M HCl.

The negative values of ΔG^o_{ads} indicate that the adsorption is a spontaneous process. Generally the values of ΔG^o_{ads} less than -20 kJ mol^{-1} are consistent with physisorption, while that greater than-40 kJ mol^{-1} are corresponding to chemisorptions [30, 31]. In the present study the values of ΔG^o_{ads} obtained range between -32.71 and -36.08, indicating both physical and chemical adsorption behavior of DBAMTT on the metal surface. These values indicate that the adsorption process may involve complex interactions involving both physical and chemical adsorption of the inhibitor [26]. Positive ΔH^o_{ads} values indicates endothermic nature of adsorption and hence chemisorption. Positive value of ΔS^o_{ads} indicates that there is increase in entropy during adsorption process.

Corrosion Inhibition Mechanism: Inhibitors function by adsorbing on the metal surface and this is the basis for explaining the inhibition mechanism. Adsorption of the inhibitor on the metal surface is due to the presence of electronegative atoms like nitrogen, oxygen and presence of pi electron cloud in the aromatic ring of the molecule. The effectiveness of the inhibitor is determined by the degree of adsorption and this is attributed to size, orientation, shape and electrical charge on the molecule.

In acidic solution, the following mechanism is proposed for the corrosion of iron and steel [32].

$$Fe + H_2O \leftrightarrow H^+ + FeOH_{ads} + e^-$$

$$FeOH_{ads} \rightarrow FeOH^+ + e^- \text{ (rate determining step)}$$

$$FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$$

The cathodic hydrogen evolution follows the steps:

$$Fe + H^+ \leftrightarrow (FeH^+)_{ads}$$

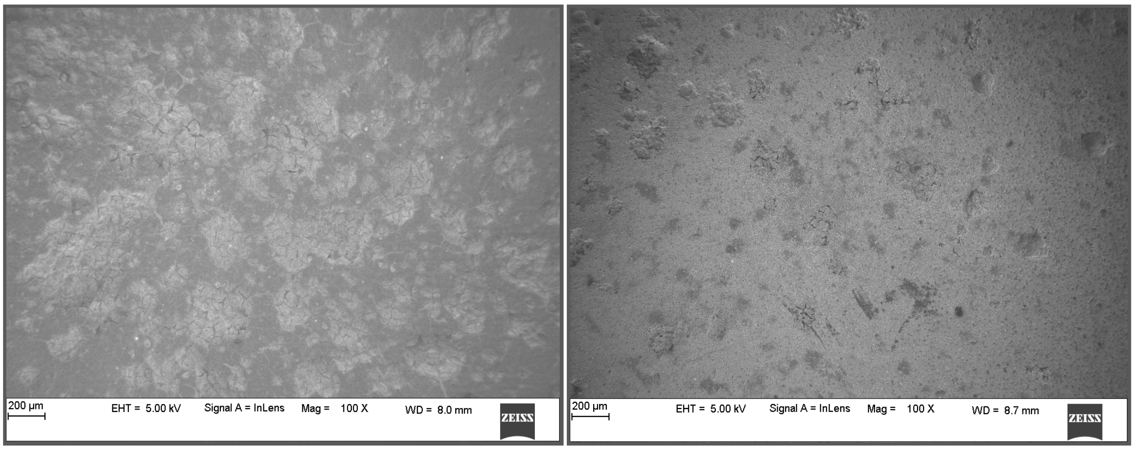
$$(FeH^+)_{ads} + e^- \leftrightarrow (FeH)_{ads}$$

$$(FeH)_{ads} + H^+ + e^- \rightarrow Fe + H_2$$

In acidic solutions DBAMTT exists partly as protonated species and partly as neutral molecules. Two modes of adsorption can be considered. In acidic solutions metal surface bears a positive charge [12, 33, 34]. The adsorption of negatively charged chloride ions from the solution on the metal surface results in the metal surface being negatively charged and facilitates electrostatic interaction between positively charged inhibitor and negatively charged metal surface causing physical adsorption. The vacant adsorption sites on the metal surface may also be occupied by neutral inhibitor molecules through the chemisorption mode involving the displacement of water molecules from the metal surface and sharing of electrons by the hetero atoms like nitrogen and/or sulphur with iron. Chemisorption is also possible by the donor–acceptor interactions between π electrons of the aromatic ring and the vacant d orbitals of iron, providing another mode of protection [35].

(SEM-EDX) studies: SEM/EDX investigations were carried out to differentiate the surface morphology and identify the composition of uninhibited and inhibited samples of maraging steel immersed in 1.5M HCl solution.

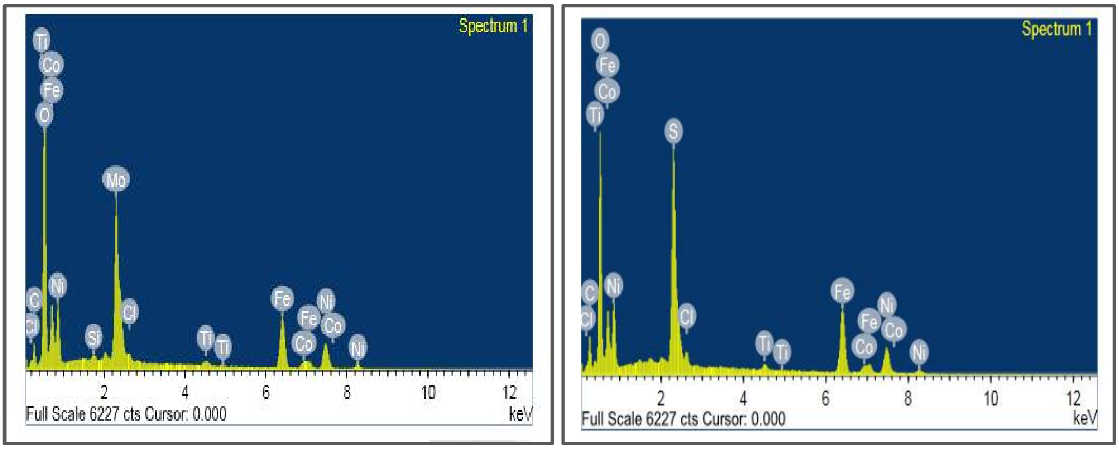
Figure 9 (a) represents maraging steel specimen immersed in 1.5MHCl solution and indicates that the surface has been damaged due to corrosion. Figure 9 (b) represents maraging steel specimen immersed in 1.5MHCl solution containing inhibitor and indicates that the surface has corroded less as the inhibitor has formed a film on the metal surface.



(a) (b)

Figure 9. SEM images of the surface of maraging steel after immersion in 1.5M HCl: (a) in the absence and (b) in the presence of DBAMTT.

The EDX spectra of the two samples are shown below. Figure 10 (a) represents EDX spectrum of uninhibited sample where there is absence of peak due to sulphur. The presence of a peak corresponding to sulphur is seen in the EDX spectrum of inhibited sample represented in figure 10 (b) and this indicates the adsorption of the sulphur-containing inhibitor on the metal surface.



(a) (b)

Figure 10. EDX spectrum of maraging steel after immersion in 1.5MHCl (a) in the absence and (b) in the presence of DBAMTT.

APPLICATION

The study of corrosion inhibition efficiency of [DBAMTT] reveals that such compounds on certain minor structural modifications (such as change of substituent) can be converted into a potential candidate for inhibiting corrosion in maraging steel in acid media.

CONCLUSION

The following conclusions were drawn based on the present study

1. DBAMTT functions as a good inhibitor for the corrosion of maraging steel in 1.5M HCl solution.
2. There was an increase in inhibition efficiency with increase in temperature and concentration of the inhibitor.
3. Adsorption of DBAMTT obeys Langmuir Adsorption Isotherm.
4. DBAMTT acts as a mixed type inhibitor.
5. Adsorption of the inhibitor is mainly through Chemisorption.
6. SEM /EDX studies reveal changes in surface morphology of uninhibited and inhibited samples of maraging steel.
7. Results obtained from Tafel polaristion studies and EIS studies are in good agreement with each other.

ACKNOWLEDGEMENTS

The authors are thankful to the Department of Chemistry, St. Aloysius College, Mangaluru, for providing laboratory facilities. PAS acknowledges Tumkur University for recognizing him as Ph.D. supervisor.

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