Research Article

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Electrochemical studies of the synergistic combination effect of thymus mastichina and illicium verum essential oil extracts on the corrosion inhibition of low carbon steel in dilute acid solution

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Abstract: Inhibition effect of the synergistic combination of thymus mastichina and illicium verum oil extracts (TMAV) on the corrosion inhibition of low carbon steel in 0.5 M H_2SO_4 and HCl solution was studied by weight loss analysis, potentiodynamic polarization, open circuit potential measurement, ATF-FTIR spectroscopy, and optical microscopy and macroscopic characterization. Results from weight loss shows TMAV performed more effectively in H_2SO_4 solution compared to HCl with optimal inhibition efficiency of 81.24% and 68.33%. Effective inhibition performance was observed at all TMAV concentration in H_2SO_4 compared to HCl where TMAV performed poorly until 5% concentration. The optimal inhibition performances from potentiodynamic polarization are 80.85% and 70.43%. The corresponding corrosion current density and polarization resistance are $7.16 \times 10^{-5} \text{ A/cm}^2$ and $8.01 \times 10^5 \text{ A/cm}^2$, and 331.73 Ω and 284 Ω . TMAV exhibited mixed type inhibition effect in both acid solutions, strongly influencing the anodic-cathodic plot configurations with respect to concentration. Open circuit potential plots without TMAV were significantly electronegative compared to the plots at 1% and 5% TMAV concentration which were relative electropositive due to decreased thermodynamic tendency of the carbon steel to corrode. The corresponding plots at 1% and 5% TMAV concentration from HCl solution were thermodynamically unstable with significant active-passive corrosion behaviour. TMAV inhibited through chemisorption adsorption according to Langmuir

and Freudlich adsorption isotherms in H_2SO_4 solution, and Frumkin and Freundlich adsorption isotherms in HCl solution with correlation coefficient values between 0.7 and 0.9. FTIR spectroscopic analysis exposed the functional groups and atomic bonds responsible for corrosion inhibition.

Keywords: corrosion; essential oils; adsorption; inhibitor; carbon steel

1 Introduction

Corrosion is the progressive oxidation and degradation of metallic and non-metallic materials by chemical and/or electrochemical interaction reaction with their environment [1–3]. Refined metals being in a higher energy state release energy thus reverting to their natural chemically combined state of lower energy in the form of ores and stable compounds [4, 5]. Corrosion damage has been a major economic and industrial problem necessitating research into solutions to mitigate it. Structural damage and damages to equipment and components made of metals and alloys is prevalent in construction plants, petrochemical refining, mining of ores, fertilizer production, energy generation etc. leading to flow interruptions, toxic leakages, plant shutdowns, industrial downtime, and high cost of repair and maintenance due to corrosion [6]. A report in 2000 showed that approximately 3.1% of U.S total GDP was spent on corrosion repairs, maintenance and prevention [7]. Mitigating the adverse effect of corrosion involves reducing material losses resulting from the corrosion of metallic parts by the most effective and economical method, and sustaining safety of operating equipment which may fail, collapse or breakdown due to corrosion such as in pressure vessels and boilers [8]. There are numerous corrosion control and prevention methods

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but the most cost effective is the application of corrosion inhibitors [9–17]. Corrosion inhibitors are grouped into classes such as anodic inhibitors, cathodic inhibitors, passivating inhibitors, film forming inhibitors, vapor phase inhibitors and adsorption based inhibitors. Carbon steel has extensive industrial application due to their ease of production and fabrication, cost of production, recyclability and availability in the form of beams, plates, bars and pipes, nuts and bolts. It is used in environments where it is exposed to the electrochemical action of corrosive anions. As a result of their weak corrosion resistance despite their high structural strength, the steel corrodes easily. Research on the corrosion inhibition performance of essential oil extract has shown them to be promising non-toxic compounds for corrosion inhibition with mixed corrosion results [18–26]. Synergistic combination effect of essential oils on corrosion inhibition has been proven to be more effective on singular oil extracts [27, 28]. *Thymus mastichina* is a plant species within the family Lamiaceae. It is aromatic in nature whose essential oil constituents is a complex aggregation of volatile terpenes. The oil has effective decongestive, antiseptic, antispasmodic, sedative, analgesic and antifungal properties. *Illicium verum* is a highly fragrant oil applied in cooking, perfumery, soaps, toothpastes, mouthwashes, and skin creams. The plant is majorly used for extraction of shikimic acid, a chemical intermediate in the synthesis of oseltamivir. In contribution to the research on corrosion inhibition of metallic alloys, this manuscript focusses on the corrosion inhibition performance of the admixture of *thymus mastichina* and *illicium verum* essential oil extracts on mild steel in dilute H_2SO_4 and HCl solutions.

2 Experimental methods

2.1 Material

Low carbon steel (LCS) rod procured from Lagos, Nigeria was analysed at the Materials Characterization Laboratory, Department of Mechanical Engineering, Covenant University, Ota, Ogun State, Nigeria. The elemental contents are shown in Table 1. LCS with diameter of 0.6 cm was cut and sectioned into 6 test specimens with average length of 6 mm. *Thymus mastichina* and *illicium verum* essential oil

extracts obtained from NOW Foods, USA have a combined molar mass of 2351.6 g/cm^3 [29, 30]. The combined extracts were evaluated for synergistic corrosion inhibition effect on LCS corrosion. The extracts, symbolized as TMAV were added to (ratio 1:1) 0.5 M H_2SO_4 (98% analar grade) and HCl solution (37% analar grade) in volumetric concentrations of 1%, 2%, 3%, 4% and 5% TMAV concentration per 200 mL of the acid electrolytes electrolyte.

Weight loss analysis was done by immersion of the LCS specimens in the acid-inhibitor electrolyte at specific TMAV concentrations. LCS specimens were weighed every 24 h for 480 h. Corrosion rate ($\hat{C}_R$) was determined from the equation below;

$$\hat{C}_R = \left[\frac{87.6W}{DAT} \right] \quad (1)$$

W (mg) indicates weight loss, A indicates LCS surface area (cm^2) and T (h) indicates exposure time. Inhibition efficiency (η), % was calculated as follows;

$$\eta = \left[\frac{W_1 - W_2}{W_1} \right] \times 100 \quad (2)$$

W_1 and W_2 represent weight loss in the presence and without predetermined additions of TMAV. Potentiodynamic polarization was done using triple electrode configuration (Pt counter electrode, LCS specimen electrode and Ag/AgCl reference electrode) placed inside a lucid container filled with the acid inhibitor electrolyte and linked to Digi-Ivy potentiostat. LCS specimen electrode was mounted in Versocit acrylic paste which hardened after 10 mins with visible surface area of 1.13 cm^2 for the steel. LCS was grinded with abrasive papers (80, 120, 220, 800 and 1000 grits) before polishing with $6\mu\text{m}$ diamond liquid solution. The potentiostat was interfaced with computer for real-time monitoring from -1.5V to $+1.5\text{V}$ at sweep rate of 0.0015V/s . Corrosion current density (J_{CD}) and corrosion potential (E_{CP}) were computed from the Tafel plots. Corrosion rate (C_R) was calculated as follows;

$$\hat{C}_R = \frac{0.00327 \times J_{CD} \times Q_{WT}}{D} \quad (3)$$

Where D (g/cm^3) indicates density and Q_{WT} (g) indicates LCS equivalent weight in grams. Inhibition efficiency (η) was computed from the equation below;

$$\eta = 1 - \left[\frac{\hat{C}_2}{\hat{C}_1} \right] \times 100 \quad (4)$$

Table 1: Elemental content (wt. %) of LCS

Element	C	Si	Mn	P	S	Cu	Ni	Al	Fe
Composition	0.40%	0.17%	0.44%	0.01%	0.01%	0.08%	0.01%	0.03%	Balance

$\hat{C}_1$ and $\hat{C}_2$ represents corrosion rate with and without TMAV concentrations. Open circuit potential measurements of LCS surface in the acid-inhibitor solution were performed at a step potential of 0.1 V s^{-1} for 5400 s using Digi-ivy potentiostat. Optical microscopic and macroscopic characterization of LCS surface before and after corrosion test was done with the aid of Omax trinocular metallurgical microscope.

3 Results and discussion

3.1 Potentiodynamic polarization studies

Potentiodynamic polarization plots of LCS corrosion at specific TMAV concentration in 1 M H_2SO_4 and HCl solution are shown in Figures 1(a) and 1(b). Tables 2 and 3 shows the potentiodynamic polarization data obtained.

Figure 2, 3(a) and 3(b), and 4(a) and 4(b) shows the optical microscopy images of LCS before polarization test, after polarization in H_2SO_4 and HCl solution without TMAV compound, and after corrosion at 5% TMAV concentration in H_2SO_4 and HCl solution. The slopes of the anodic-cathodic polarization plot at 0% TMAV in both acids are visibly higher than the slopes obtained at specific TMAV concentration due to the effect of SO_4^{2-} and Cl^- anions on the redox electrochemical processes occurring on LCS surface. The corrosion rate of MS at 0% TMAV in H_2SO_4 and HCl solution are 4.27 mm/y and 3.09 mm/y corresponding to corrosion current density of $3.74 \times 10^{-4} \text{ A/cm}^2$ and $2.71 \times 10^{-4} \text{ A/cm}^2$, and polarization resistance of 40.75 Ω and 83.93 Ω . The accelerated corrosion of LCS results in surface deterioration shown in Figure 3(a) and 3(b) due to oxidation reactions. Corrosion pits, localized surface deterioration and interconnecting grooves are visible on Figure 3(b) while Figure 3(a) shows general surface deterioration. The addition of TMAV in H_2SO_4 solution

Figure 1: LCS potentiodynamic polarization plots in (a) 0.5 M H_2SO_4 solution and (b) 0.5 M HCl solution at specific TMAV concentration

Table 2: Potentiodynamic polarization data for LCS corrosion in 1 M H₂SO₄ at specific TMAV concentration

Sample	TMAV Conc. (%)	LCS C_R (mm/y)	TMAV ξ_F (%)	C_I (A)	C_J (A/cm ²)	C_P (V)	R_p (Ω)	B_c (V/dec)	B_a (V/dec)
A	0	4.27	0	4.23E-04	3.74E-04	-0.423	40.75	-7.679	15.750
B	1	1.61	62.39	1.59E-04	1.41E-04	-0.453	199.20	-6.446	10.944
C	2	1.20	71.92	1.19E-04	1.05E-04	-0.411	256.33	-5.464	17.137
D	3	1.10	74.23	1.09E-04	9.64E-05	-0.434	289.00	-4.237	21.030
E	4	0.90	78.93	8.91E-05	7.88E-05	-0.399	305.00	-5.865	24.900
F	5	0.82	80.85	8.10E-05	7.16E-05	-0.425	331.73	-4.029	20.807

Table 3: Potentiodynamic polarization data for LCS corrosion in 1 M HCl at specific TMAV concentration

Sample	TMAV Conc. (%)	LCS C_R (mm/y)	TMAV ξ_F (%)	C_I (A)	C_J (A/cm ²)	C_P (V)	R_p (Ω)	B_c (V/dec)	B_a (V/dec)
A	0	3.09	0	3.06E-04	2.71E-04	-0.440	83.93	-8.590	18.020
B	1	2.49	19.47	2.46E-04	2.18E-04	-0.479	104.50	-8.810	14.410
C	2	2.20	28.65	2.18E-04	1.93E-04	-0.464	125.70	-7.828	15.910
D	3	2.03	34.21	2.01E-04	1.78E-04	-0.456	144.50	-6.367	17.130
E	4	1.54	50.18	1.52E-04	1.35E-04	-0.478	181.00	-9.065	27.970
F	5	0.91	70.43	9.05E-05	8.01E-05	-0.453	284.00	-6.327	18.570

Figure 2: Optical image of LCS surface before polarization

caused a significant decrease in anodic-cathodic polarization slopes though the effect is limited on the anodic slopes at 1% TMAV (H₂SO₄). The decrease in polarization slope in H₂SO₄ is more prevalent on the cathodic portion signifying strong influence on the O₂ reduction and H₂ evolution reactions. This phenomenon shows modification of the corrosive medium, increase in surface impedance of the steel and selective precipitation onto the active sites on the steel. Significant TMAV effect on the anodic portion of the polarization plot with respect to concentration shows adsorption through surface coverage dominated the anodic inhibition mechanism. At 1% TMAV, the corrosion rate of LCS decreases to 1.61 mm/y at 62.39% inhibition efficiency, corresponding to corrosion current density of 1.41×10^{-4} A/cm². Increase in TMAV concentration results in increase in inhibition efficiency and decrease in corrosion rate culminating at corrosion rate of 0.82 mm/y and inhibition ef-

(a)

(b)

Figure 3: Optical images of LCS surface after polarization from (a) H₂SO₄ solution and (b) HCl solution at 0% TMAV concentration

iciency of 80.85% (5% TMAV concentration). The corresponding image at this concentration (Figure 4(a)) show slightly improved morphology. The mild surface deterioration is due to initial adsorption of SO₄²⁻ ions before electrostatic attraction of protonated TMAV molecules onto the steel surface.

Figure 4: Optical images of LCS surface after polarization from (a) H_2SO_4 solution and (b) HCl solution at 5% TMAV concentration

The performance of TMAV in HCl solution significantly contrasts its performance in H_2SO_4 solution. This assertion is also proven from the image in Figure 4(b) which contrasts Figure 4(a). Effective corrosion inhibition was attained at 5% TMAV concentration with corrosion rate of 0.91 mm/y and inhibition efficiency of 70.43%. This value is significantly lower than the value obtained in H_2SO_4 solution due to differences in the electrochemical action of the corrosive species. Secondly TMAV at lower concentration is unable to counteract the electrochemical action of Cl^- anions until 5% concentration. This shows Cl^- anions are capable of diffusing through the protective barriers of TMAV HCl solution compared to H_2SO_4 . Observation of the corrosion potential values at specific TMAV concentration and comparing to corrosion potential at 0% TMAV gives maximum potential difference of 0.030 V in H_2SO_4 and 0.039 V in HCl solutions signifying mixed inhibition effect of TMAV in both acids.

3.2 Weight loss measurement

The plots of LCS corrosion rate versus exposure time in H_2SO_4 and HCl solution are shown in Figures 5(a) and 5(b) while Figure 6(a) and 6(b) shows the plots of TMAV inhibition efficiency versus exposure time in H_2SO_4 and HCl solution. Table 4 shows the data obtained from weight loss measurement at 480 h of exposure. Figure 7(a) to 8(b) shows the optical macroscopic images of LCS before corrosion, after corrosion from H_2SO_4 solution, after corro-

Figure 5: Plot of LCS corrosion rate versus exposure time at 0% – 5% TMAV concentration in (a) H_2SO_4 and (b) HCl

sion from HCl solution, after corrosion from H_2SO_4 /TMAV solution and after corrosion from HCl /TMAV solution at mag. $\times 20$. Observation of Figure 5(a) and 5(b) shows the significant difference between the plot at 0% TMAV and plots at specific TMAV concentration. At 0% TMAV the plots initiated at 0.0788 mm/y and 0.0679 mm/y (at 24 h in H_2SO_4 and HCl solution), and decreased with exposure time due to dilution of the static electrolyte solution with the corrosion product, culminating at 0.0101 mm/y and 0.0054 mm/y. The optical macroscopic images in Figure 7(b) and 7(c) show the morphological deterioration of the steel due to the electrochemical action of SO_4^{2-} and Cl^- anions on LCS surface. Significant decrease in corrosion rate was observed in both plots at specific TMAV concentration. However, observation of the plot at 1% TMAV (Figure 5(a)) show increase in corrosion rate from 120 h compared to the plots at higher TMAV concentration. This is due to inability of the inhibitor molecules to sufficiently hinder the electrochemical action of SO_4^{2-} anions in the

Table 4: Results obtained from weight loss measurement at 480 h of exposure

H₂SO₄					
LCS Samples	Weight Loss (g)	TMAV Concentration (%)	TMAV Concentration (M)	Corrosion Rate (mm/y)	TMAV Inhibition Efficiency (%)
A	3.110	0	0	10.091	0
B	2.173	1	0.0043	7.050	30.13
C	0.765	2	0.0085	2.483	75.40
D	0.757	3	0.0128	2.458	75.64
E	0.689	4	0.0170	2.235	77.86
F	0.583	5	0.0213	1.893	81.24

HCl					
LCS Samples	Weight Loss (g)	TMAV Concentration (%)	TMAV Concentration (M)	Corrosion Rate (mm/y)	TMAV Inhibition Efficiency (%)
A	1.656	0	0	5.372	0
B	1.468	1	0.0043	4.762	11.36
C	1.380	2	0.0085	4.478	16.64
D	1.244	3	0.0128	4.036	24.87
E	0.964	4	0.0170	3.129	41.75
F	0.524	5	0.0213	1.702	68.33

Figure 6: Plot of TMAV inhibition efficiency versus exposure time at 0% – 5% TMAV concentration in (a) H₂SO₄ and (b) HCl

acid inhibitor electrolyte. As a result, the anions react with LCS surface at weak portions of the protective covering. Beyond 1% TMAV (Figure 5(a)), the plot configuration shows significant decrease in corrosion rate and are generally the same signifying effective and consistent inhibition performance. The plot configuration in Figure 5(b) varies with respect to TMAV concentration signifying concentration dependent action of TMAV in HCl solution.

Observation of Figure 6(a) and 6(b) gives further insight to the inhibition performance of TMAV in H₂SO₄ and

HCl solutions. The plots configuration in both figures show relative decrease in inhibition efficiency values with respect to exposure time. Observation of Figure 6(a) shows the extent of decrease at 1% TMAV is significant culminating at 30.13% inhibition value (480 h) which is quite poor and unable to protect LCS surface. The plots at higher TMAV configuration slightly decreased with respect to exposure time culminating at values between 75.40% and 81.24% (2% – 5% TMAV concentration). The plot configuration in Figure 6(b) shows more significant decrease in

(a)

(a)

(b)

(b)

Figure 7: Optical macroscopic image of LCS (a) before corrosion test, (b) after corrosion from 0.5 M H_2SO_4 solution and after corrosion from 0.5 M HCl solution (mag. $\times 20$)

Figure 8: Optical macroscopic image of LCS (a) after corrosion from 0.5 M H_2SO_4 /TMAV solution and (b) after corrosion from 0.5 M HCl /TMAV solution (mag. $\times 20$)

inhibition efficiency with respect to exposure time and TMAV concentration. The final values from 1% TMAV to 4% TMAV are 11.36%, 16.64%, 24.87% and 41.75% which are below the values for effective corrosion inhibition. At 5% TMAV, the inhibition efficiency is 68.33% which is a marginal improvement but shows TMAV oil extract is insufficient to effectively inhibit LCS corrosion in HCl solution compared to its effective corrosion inhibition performance in H_2SO_4 solution. The optical macroscopic images shown in Figure 8(a) and 8(b) presents an improved morphology compared to the images earlier observed in the absence of TMAV. The images in Figure 8(a) and 8(b) aligns with the inhibition performance of TMAV signifying TMAV hinders the action of the corrosive species on the steel surface.

3.3 Adsorption isotherm and corrosion thermodynamics

The corrosion inhibition mechanism of TMAV on LCS in H_2SO_4 and HCl solution is further understood from mathematical models and curves that show the variation of the amount of inhibitor molecular species adsorbed unto the steel at equilibrium and constant temperature [31]. During corrosion inhibition reactions mechanisms, protonated TMAV molecules diffuse from the aqueous phase unto the solid phase. Results from potentiodynamic study shows TMAV exhibited mixed type inhibition mechanism *i.e.* corrosion inhibition through surface coverage and selective precipitation. The mechanism occurs through electrostatic

attraction covalent adsorption and adsorption through vander waals forces. Adsorption involves concentration of inhibitor molecules from the aqueous phase onto the charged metal surface. Results from weight loss measurement were evaluated with some adsorption isotherms and the resulting correlation coefficient was used to determine the isotherms most applicable. Langmuir, and Freundlich gave the highest correlation coefficient values in H_2SO_4 , while Frumkin and Freundlich gave the highest correlation coefficient values in HCl as shown in Table 5 below.

Table 5: Comparison of correlation coefficient values of Langmuir, Frumkin, Freundlich and Temkin adsorption isotherms from H_2SO_4 and HCl solution

Adsorption Isotherms	H_2SO_4 Solution	HCl Solution
Langmuir	0.8406	-
Frumkin	-	0.9211
Freundlich	0.7917	0.7480

The Langmuir and Freundlich isotherms from H_2SO_4 solution are shown Figures 9(a) and 9(b). Langmuir isotherm states that fixed number of adsorption sites exist on metallic surfaces with one molecular layer of adsorbed inhibitor molecules with fixed quantity of energy among the molecules under dynamic equilibrium conditions with respect to the equation below;

$$\theta = \left[\frac{K_{ads} C_{TMAV}}{1 + K_{ads} C_{TMAV}} \right] \quad (5)$$

K_{ads} is the equilibrium constant of adsorption during the inhibition process. C_{TMAV} is the molar concentration of TMAV compound. The Freundlich isotherm focusses on adsorbed molecular interaction on metallic surfaces and the lateral interaction effect between them [32]. The Freundlich equation is shown below;

$$\theta = KC^n \quad (6)$$

$$\log \theta = n \log C + \log K_{ads} \quad (7)$$

n represents the constant for the characteristics of adsorbed TMAV molecule.

The Frumkin and Freundlich isotherms from HCl solution are shown Figures 10(a) and 10(b). The Frumkin isotherm states that the surface coverage on heterogeneous metallic surfaces is uniform at high molecular concentrations and is subject to the potential of the metallic surface. The effect of lateral interaction among the inhibitor molecules is significant and quantitative with re-

Figure 9: Adsorption isotherm plot (a) Langmuir isotherm and (b) Frumkin isotherm in H_2SO_4 solution

spect to the equation below;

$$\log \left[C_{TMAV} * \left(\frac{\theta}{1 - \theta} \right) \right] = 2.303 \log K_{ads} + 2\alpha\theta \quad (8)$$

α is the lateral interaction parameter.

Calculated results of Gibbs free energy (ΔG) for TMAV adsorption onto LCS surface in H_2SO_4 and HCl solution are shown in Table 5. The results were determined from equation 9. The equilibrium constant of adsorption (K_{ads}) for H_2SO_4 was determined from Langmuir equation while the corresponding values in HCl were determined from Freundlich equation due to their high correlation coefficient values with respect to the equation below;

$$\Delta G_{ads} = -2.303RT \log [55.5K_{ads}] \quad (9)$$

55.5 indicates the molar concentration of H_2O in the solution, R is the universal gas constant, T is the abso-

Figure 10: Adsorption isotherm plots (a) Frumkin isotherm and (b) Freundlich isotherm in HCl solution

Table 6: Results of Gibbs free energy (ΔG) and equilibrium constant of adsorption (K_{ads}) in for TMAV adsorption in H_2SO_4 and HCl solution

H_2SO_4				
LCS Samples	TMAV Concentration (M)	Surface Coverage (θ)	Equilibrium Constant of adsorption (K)	Gibbs Free Energy, ΔG ($KJmol^{-1}$)
A	0	0	0	0
B	0.004	0.301	101419.9	-38.52
C	0.009	0.754	360301.0	-41.66
D	0.013	0.756	243439.6	-40.69
E	0.017	0.779	206695.6	-40.28
F	0.021	0.812	203654.8	-40.24
HCl				
LCS Samples	TMAV Concentration (M)	Surface Coverage (θ)	Equilibrium Constant of adsorption (K)	Gibbs Free Energy, ΔG ($KJmol^{-1}$)
A	0	0	0	0
B	0.004	0.114	959811.7	-44.09
C	0.009	0.166	185613.8	-40.01
D	0.013	0.249	84881.4	-38.08
E	0.017	0.418	61487.1	-37.28
F	0.021	0.683	52437.9	-36.88

lute temperature. The ΔG values from both acids shows chemisorption adsorption of TMAV molecules onto LCS surface wherewith strong electrostatic attraction and covalent bonding between the protonated TMAV molecules and valence electrons of LCS are prevalent [33]. The values show H_2O molecules from the aqueous acid media were effectively replaced by TMAV molecules thus limiting the electrochemical action of SO_4^{2-} and Cl^- ions in the solution. The ΔG values in both solutions ranges from (lowest to highest) $-36.88 KJmol^{-1}$ to $-44.09 KJmol^{-1}$ sig-

nifying chemisorption. The higher value of ΔG in HCl at some TMAV concentrations despite its lower corrosion rate is due to the higher electronegativity of Cl^- ions in the acid solution which strongly attracts the protonated TMAV molecules. However, according to Freundlich isotherm it is probable that the strength of lateral attraction among the inhibitor molecules influenced the performance of the inhibitor in HCl solution compared to its performance in H_2SO_4 solution.

3.4 ATF-FTIR spectroscopy analysis

Identification of the functional groups (atomic bonds) present within protonated molecules of TMAV and responsible for its corrosion inhibition performance on LCS in H_2SO_4 and HCl solution was done through ATF-FTIR spectroscopic analysis and the results compared with the theoretical IR Table [34–36]. The IR spectra of TMAV/0.5 M H_2SO_4 and TMAV/0.5 M HCl solutions before and after the corrosion test are shown in Figure 11(a) and 11(b). The spectra diagrams between initial wavelengths of 600 cm^{-1} and 665.48 cm^{-1} , and final wavelengths of 3344 cm^{-1} and 3464 cm^{-1} . Observation of the IR spectra peaks before corrosion in Figure 11(a) and 11(b) shows that they have significantly reduced after corrosion test due to chemisorption adsorption during the corrosion inhibition mechanism. The peaks on the spectra plot of TMAV/ H_2SO_4 before corrosion [Figure 8(a)] at wavelengths of 600 cm^{-1} , 1052 cm^{-1} , 1212 cm^{-1} , 1640 cm^{-1} , 2000 cm^{-1} , 2354 cm^{-1} and 3292 cm^{-1} has transmittance of 12.837%, 27.960%,

24.129%, 12.178%, 36.224%, 24.820% and 3.374%. The corresponding plot of TMAV/ H_2SO_4 after corrosion shows significant decrease in corresponding transmittance (0.089%, 0.301%, 0.214%, 0.249%, 2.536%, 1.523% and 0.02%) due to decrease in concentration of functional groups of C–Br stretch, C–N stretch, $\text{C}=\text{C}$ stretch, O–H stretch, H-bonded, N–H stretch, O–H stretch and $\text{C}(\text{triple bond})\text{C}$ –H:C–H stretch (alkyl halides, aliphatic amines, alkenes, alcohols, phenols primary, secondary amines, amides, carboxylic acids and alkynes terminal) within the inhibitor compound which adsorbed onto the steel surface stifling the redox electrochemical process responsible for corrosion. Similar observation occurred on the plots in Figure 11(b) at generally similar wavelength with the same atomic bonds and functional groups. However, the decrease in transmittance was quite lower at 2.301%, 5.655%, 2.01%, 6.14% and 0.08% compared to the observation in H_2SO_4 solution signifying relatively weaker adsorption onto LCS in HCl solution. This is probably responsible for the lower inhibition efficiency values of TMAV in HCl solution compared to the values in H_2SO_4 solution.

Figure 11: IR spectra of TMAV/acid solution before and after corrosion test from (a) H_2SO_4 solution and (b) HCl solution

3.5 Open circuit potential measurement

Open circuit potential plots of LCS corrosion in TMAV/ H_2SO_4 and TMAV/ HCl solution at 0%, 1% and 5% TMAV concentration are shown in Figures 12(a) and 12(b). Observation of the plot in Figure 12(a) shows the significant variation in plot configuration with respect to TMAV concentration and corrosion potentials. The plot at 0% TMAV in H_2SO_4 solution is the most electronegative throughout the exposure hours. The plot initiated at -0.485 V at gradually progressed to electropositive values till 1805 s (-0.465 V) due to miniature resistance to corrosion resulting from the formation of porous oxides on the steel surface. At 1805s the plot attained relative thermodynamic stability before attaining final potential of -0.463 at 5400s. At 1% TMAV concentration, significant potential shift occurred due to enhanced corrosion resistance of the steel surface in the presence of TMAV inhibitor molecules. The potential plot initiated at -0.454 V (0s) and sharply shifted electropositive direction to -0.443 V at 100s due to instantaneous alteration of the redox electrochemical process induced by the action of SO_4^{2-} ions. Beyond this point, there was no significant shift in corrosion potential. However, the plot configuration shows the thermodynamic condition on the steel surface in the presence of the TMAV is unstable. Potential transients are visible throughout the plot though the plot is significantly electropositive compared to the plot at 0% TMAV. The potential transient is

due to slight breakage/weakening of the protective covering offered by the presence of TMAV molecules on the steel surface. The plot at 5% TMAV was thermodynamically unstable for 2105s (-0.462 V). This observation is probably due to lateral interaction among TMAV molecules which affects its molecular cohesion, hence its stability on the steel surface. Beyond 2105s, the plot showed where thermodynamically stable with miniature potential transients.

The plot at 0% TMAV concentration in Figure 12(b) exhibited similar configuration to its counterpart in Figure 12(a), initiating at -0.498 V (0s) and sharply increasing in the electronegative direction before attaining thermodynamic stability at 2520s (-0.477 V). Final value of -0.476 V was attained at 5400s. The plot showed thermodynamic stability. However, plots at 1% and 5% TMAV concentration were thermodynamically unstable for the reasons ear-

lier explained though the difference between the plot configurations (1% and 5% TMAV) is due to the aggregation of the inhibitor molecules on LCS surface influenced by the concentration of the molecules. Though in HCl solution, the effect of Cl^- ions was significant. The small size of Cl^- ions compared to SO_4^{2-} ions enables easier diffusion unto the steel surface. Secondly Cl^- ions are more reactive which tends to be localized. As a result, competitive adsorption between the Cl^- ions, TMAV molecules and dissolved O_2 influence the mechanism of electrochemical reaction on the steel surface. Hence TMAV while providing substantial corrosion protection of LCS surface, it must be noted that the protective covering by TMAV are thermodynamically unstable.

4 Conclusion

The combined admixture of thymus mastichina and illium verum essential oil extracts effectively inhibited the corrosion of low carbon steel in dilute H_2SO_4 and HCl solution. The oil extracts performed more effectively in H_2SO_4 solution at all concentrations with inhibition performance independent of inhibitor concentration. The mixed type inhibition performance exhibited by the oil extracts significantly influenced the surface oxidation and reduction corrosion reactions. Corrosion inhibition of the extracts was determined to be through chemisorption adsorption mechanism. Images of inhibited and non-inhibited steel significantly contrast each other.

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Figure 12: Open circuit potential plots LCS corrosion in (a) H_2SO_4 solution and (b) HCl solution at 0%, 1% and 5% TMAV concentration

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