Calcium D-Pantothenate as Green Corrosion Inhibitor on Mild Steel in 240 ppm NaCl Solution

Rajajeyaganthan Ramanathan, Albin Aloysius, Auxilia Christy, Noreen Anthony, Gangadhara Angajala

Abstract: Corrosion inhibition of mild steel in 240 ppm NaCl solution using Calcium D-Pantothenate (Vitamin B₅) as corrosion inhibitor is studied using electrochemical impedance, potentiodynamic polarization and weight loss studies. From the potentiodynamic polarization studies, i_{corr} (corrosion current density) decreases with increasing the concentration of vitamin $B_5(VB_5)$. The CR (corrosion rate) decreases and the IE (inhibition efficiency) of VB5 increases on increasing the concentration of VB_5. Surface investigation using SEM, EDX spectra, UV-Vis, FTIR, electrochemical impedance, potentiodynamic polarization and adsorption isotherm parameter of VB_5in 240 ppm NaCl solution shows that VB_5 can act asworthy corrosion inhibitors. Quantum chemical data obtained from density functional theory (DFT) calculations also agreed with the experimental outcomes.

Keywords : Pantothenic acid, Electrochemical impedance spectroscopy, Vitamin B5, Mild steel, Potentiodynamic polarization

I. INTRODUCTION

The cooling water circulation process is encountered with many challenges; among them, the most significant is corrosion of metal parts. Dissolved substances in cooling water may possibly have dangerous effects on the metals. Chloride ions present in the cooling water system is the cause for corrosion of iron. The mechanism of crevice and pitting corrosion are alike and it commonly occurs in NaCl system.[1] Sulfate and Chloride ions dangerously corrode the metals and even existence of 100 ppm NaCl in cooling water results in pitting corrosion of mild steel. Drugs and natural products in different environment of metals can act as corrosion inhibitors. Organic compounds with hetero atoms for example S, P, N, O and compounds with double (or) triple bonds prevent corrosion by surface adsorption.[2-4]Role of vitamins on metal corrosion and their inhibition efficiency in acid and chloride[5]medium were studied in detail. Among all vitamins, B vitamins are water-soluble and their role as corrosion inhibitors in NaCl medium is not studied well.

In the group of water soluble B vitamins, vitamin B_5 that is Calcium D-pantothenic acid (mentioned asVB_5) is vital in human health system. Animals require pantothenic acid to synthesize coenzyme-A (CoA), as well as to synthesize and metabolize proteins, carbohydrates, and fats. Little quantities of pantothenic acid are found in many foods and present in high amounts in liver, fortified grain cereals, dried mushrooms and in egg yolks. It is commonly found as its alcohol analog, the pro-vitamin panthenol (pantothenol), and as calcium pantothenate. The structure of vitamin B_5 is given in Figure 1. Pantothenic acid has amide linkage between pantoic acid and β-alanine. In this study UV-Vis, weight loss method, FT-IR, electrochemical impedance and potentiodynamic polarization is used to investigate the corrosion inhibition outcome of vitamin B_5 on mild steel in 240 ppm NaCl solution.
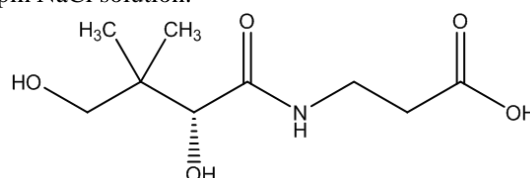

Figure 1. Structure of Pantothenic acid

II. EXPERIMENTAL

2.1. Materials

The mild steel was used as an experiment material having the composition of 0.06% P, 0.10% C, 0.026% S, 0.40% Mn and the balance of Fe. Mild steel of size 1 x 4 x 0.2 cm^3 were cut and their sides were scuffed with 150–600 sand emery paper. After that the mild steel was washed with acetone followed by distilled water before analysis. Vitamin B_5 was obtained from Loba Chemie, India. $FeSO_4$ and NaCl were purchased from Merck, India. To prepare vitamin B_5 solution,1g of vitamin B_5 is dissolved in distilled water and made up to 100 ml in a SMF using distilled water.

Rajajeyaganthan Ramanathan, Department of Chemistry, Kalasalingam Academy of Research and Education, Kalasalingam University, Krishnankoil 626126, Tamil Nadu, India. Email: r.rajajeyaganthan.r@klu.ac.in

Albin Aloysius*, Department of Chemistry, BWDA Arts & Science College, Kolliyangunam – 604304, Tamilnadu, India. Email: albin.aloysius@gmail.com

Auxilia Christy, Department of Chemistry, BWDA Arts & Science College, Kolliyangunam – 604304, Tamilnadu, India. Email: r.auxiliachristy@gmail.com

Noreen Anthony, Department of Chemistry, Holy Cross College, Tiruchirappalli – 620002, Tamilnadu, India. Email: noreencyril@gmail.com

Gangadhara Angajala, Department of Chemistry, Kalasalingam Academy of Research and Education, Kalasalingam University, Krishnankoil 626126, Tamil Nadu, India. Email: gangadharaangajala@gmail.com

Corrosion medium containing 240 ppm of NaCl was chosen, to study the inhibition efficiency of vitamin B_5. Vitamin B_5 concentration of 25, 50, 100, 150 and 200 ppm were used to find out inhibition efficiency and corrosion rate of mild steel in 240 ppm of NaCl medium. 300 ppm of ferrous ion solution was also prepared by dissolving the salt $FeSO_4$ in distilled water.

2.2. Weight loss method

All the tests were conducted at room temperature by hanging the mild steel coupons using glass hooks in 100 mL of 240 ppm NaCl medium with and without inhibitor vitamin B_5. After 24h of immersing, the mild steel coupons were taken out and washed with distilled water. Later it is allowed to air dry and weighed accurately.

From the weight loss study, corrosion rate CR, ($mg.dm^{-2}day^{-1}$) and the inhibition efficiency IE, (%) were calculated,

CR ($mg.dm^{-2}.day^{-1}$) = W = (M_1- M_2)/SP

where,

M_1– mass of the mild steel before corrosion,

M_2– mass of the mild steel after corrosion,

S – Surface area of the mild steel in dm^2,

P - Period of immersion in days,

W - Corrosion rate.

The IE was calculated by using the following equation:

IE (%) = [(W_0- W_i)/ W_0]*100

where,

W_0- corrosion rate of mild steel in the absence of inhibitor,

W_i - corrosion rate of mild steel in the presence of inhibitor,

The CR was calculated using the formula,

CR ($mg.dm^{-2}.day^{-1}$) =M_1-M_2 (mg)/ [0.096 (dm^2) x 1 day]

where, the surface area S takes the value of 0.096 dm^2.

2.3. Potentiodynamic polarization studies

Electrochemical investigations were conducted by means of three electrode cell assembly. The working electrode was mild steel with an unprotected external area of 1 cm^2. The mild steel was fixed using a holder and remaining zone was covered with an epoxy resin based coating. Platinum electrode and saturated calomel electrode were used as counter and reference electrode. The mild steel was dipped in the NaCl medium and open circuit potential was noted by using Princeton Applied Research (2 channels) analyzer. From the open circuit potential value, the Tafel polarization investigation were conducted at a scan ratio of 0.5 mV/s. Corrosion potential (E_{corr}) and Corrosion current (I_{corr}) were achieved by extrapolating the cathodic and anodic curves of Tafel plot. IE was calculated using relevant I_{corr} values. Electrochemical impedance studies were executed from 1 Hz to 1MHzfrequency range. The exposed surface area of mild steel to the corrosive solution for this study was 1 cm^2. The tests were conducted in the presence and absence of inhibitor with various concentrations in the 240 ppm NaCl solution.

2.4. Characterization of surface morphology

Surface morphology of the films was studied using scanning electron microscopy, SEM (TESCAN Vega 3) with electron speeding up between 5 and 15 kV.

2.5. Fourier transforms infrared (FT-IR) spectroscopy

Perkin Elmer Spectrum RX I with a spectral range of 4000 cm-1 to 400 cm-1was used to record the FT-IR spectra with a spectral resolution of 4 cm-1. After 24 h of immersion in 240 ppm NaCl medium, the mild steel were scrubbed with a little quantity of KBr powder and made into a disk for FTIR analysis.

2.6. UV-Visible spectroscopy

The UV-Visible absorption spectra of NaCl solution having various Vitamin B_5 concentrations and the similar solution with 300 ppm of ferrous ion were analyzed using PerkinElmer's Lambda 35 UV-Vis spectrophotometer with a spectral range of 190 nm to 1100 nm.

2.7. Computational methods

All DFT analysis was completed using Gaussian 03 software. The molecular structure optimization was done by quantum chemical calculations using density function theory (DFT)/B3LYP technique (Becke's three parameter hybrid Hartree-Fock and Lee-Yang-Par correlation functional theory) with basis set 6-31G*. Energy of lowest unoccupied molecular orbital (LUMO), highest occupied molecular orbital (HOMO) and dipole moment (μ), the energy gap between E_{LUMO} and E_{HOMO} ($\Delta E = E_{LUMO}$ - E_{HOMO}), and other data were acquired from the theoretical investigation for Vitamin B_5.

III. RESULT AND DISCUSSION

3.1. Weight Loss Measurement

The weight loss measurements data for corrosion of mild steel in 240 ppm NaCl solution in the presence and absence of different concentration of inhibitor are given in Table 1 and figures 2(a) and 2(b). For further discussion, vitamin B_5 is denoted as VB_5. Weight loss study shows that, when the concentration of the inhibitor increases the IE (%) also increases. The maximum IE 90.05% is achieved at 200 ppm of VB_5 solution after 24 h of immersion time of mild steel. In figure 2(a), when the inhibitor concentration increases, the IE (%) also increases, and reached a maximum IE (%) at 200 ppm inhibitor concentration. While increasing the inhibitor concentration further to 250 and 300 ppm, it does not show any considerable change in the IE(%). From figure 2(b), after 24 h of dipping time, the mild steel CR decreases from 14.46 $mgdm^{-2}day^{-1}$ to 3.913$mgdm^{-2}day^{-1}$ on the addition of 25 ppm to 200 ppm of inhibitor. The IE (%) increases from 63.23% to 90.05% may be due to the barrier effect of the metal surface by adsorption and film formation mechanisms, which reduces the active area of corrosion occurrence. From these outcomes, it is understood that the analyzed inhibitor VB_5 is rapidly adsorbed at the active sites of mild steel surface and accountable for anticorrosion activity.

3.2. pH Study

Corrosion rates of mild steel in 240 ppm NaCl solution decreases in the acidic pH range (from pH 2 to pH 7). After pH 7, the corrosion rate increases in the alkaline pH range (from pH 2 to pH 7). The pH studies were conducted for the VB_5 of 200 ppm concentration. Figure 3(a) and 3(b) showed the effect of pH on corrosion rate and inhibition efficiency.
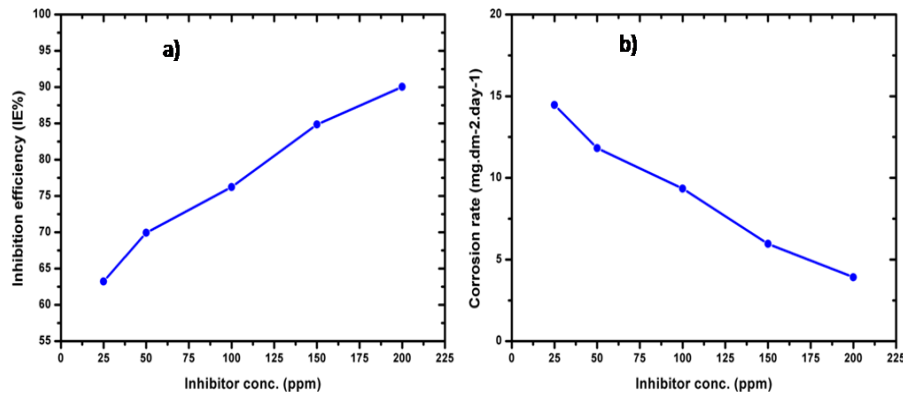
Figure 2. Weight loss curves of VB$_5$ in 240 ppm NaCl solution at RT: (a) variation of IE (%) with several concentrations of inhibitor and (b) variation of CR with several concentrations of inhibitor.

Table 1.Percentage IE(%) and CR values found from the weight loss of mild steel in 240 ppm NaCl solution in the absence and presence of VB$_5$

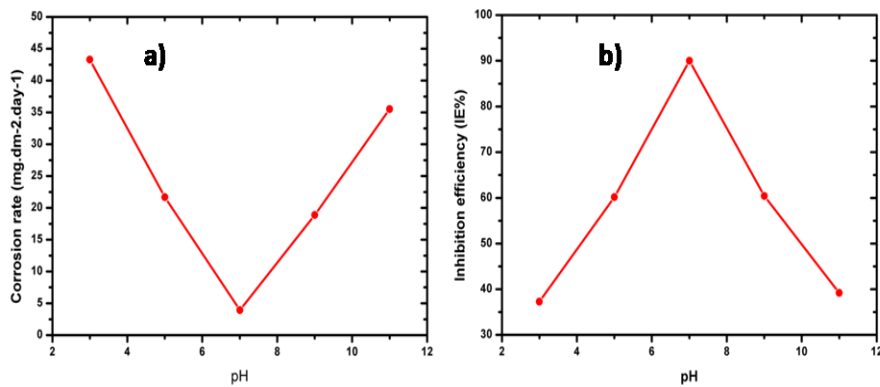| Conc. of VB$_5$ (ppm)	30°C		40°C		50°C		60°C	
	CR (mg.dm^{-2}.day^{-1})	IE (%)	CR (mg.dm^{-2}.day^{-1})	IE (%)	CR (mg.dm^{-2}.day^{-1})	IE (%)	CR (mg.dm^{-2}.day^{-1})	IE (%)
Blank	39.33	-	56.47	-	104.3	-	198.2	-
25	14.46	63.23	23.94	57.6	50.01	52.05	102.0	48.51
50	11.82	69.94	20.10	64.39	42.93	58.84	90.61	54.29
100	9.34	76.24	16.55	70.69	36.35	65.14	80.70	59.29
150	5.958	84.85	11.68	79.3	27.37	73.75	63.03	68.2
200	3.913	90.05	8.753	84.5	21.95	78.95	52.72	73.4

Figure 3. Plot of 200 ppm VB5 in 240 ppm NaCl solution at different pH: (a) variation of CR with different pH and (b) variation of IE (%) with different pH.

Table 2. Weight loss studies of mild steel in several pH in 240 ppm NaCl solution

pH	Weight loss (mg.dm^{-2})	CR (Blank) (mg.dm^{-2}.day^{-1})	CR (Inhibitors) (mg.dm^{-2}.day^{-1})	Surface coverage (θ)	IE (%)
3	4.3285	69.0272	43.2855	0.3729	37.29
5	2.1705	54.5118	21.7052	0.6018	60.18
7	0.3933	39.3324	3.9330	0.9000	90.00
9	1.8895	47.7066	18.8959	0.6039	60.39
11	3.5514	58.4114	35.5146	0.3919	39.19

3.3 Adsorption isotherm

Adsorption isotherms are significant in accepting the mechanism of corrosion inhibition reactions of metals. The most often used adsorption isotherms are the Temkin, Frumkin and Langmuir isotherms. Efforts to fit the data found from the weight loss technique into various adsorption isotherms make known that the data best fitted with the Langmuir adsorption isotherm. Assumptions of Langmuir show that the concentration of the adsorbate in the bulk of the electrolyte (C_{inh}) to the degree of surface coverage (θ) is given by the equation mentioned below:

$$(C_{inh} / \theta) = (1/ K_{ads}) + C_{inh}$$

where, K_{ads} is the equilibrium constant of adsorption. The linear regressions data's between C_{inh}/θ and C_{inh} are recorded in Table 3. Figure 4 shows the straight lines of C_{inh}/θ versus C_{inh} at various temperatures. From these results it is clear that linear regression coefficients (R) of all the data's are close to 1, it confirms the adsorption of VB_5 on the mild steel surface follows the Langmuir adsorption isotherm. The deviation of the slope of the plots from unity indicates nonideal simulating [6] and is unexpected from the Langmuir adsorption isotherm. It may be due to the interactions between the adsorbed species on the mild steel surface. The free energy of adsorption(ΔG^{o}_{ads}) and adsorption equilibrium constant (K_{ads}) were found out using the subsequent equation:

$$\Delta G^{o}_{ads} = -RT \ln (55.5\ K_{ads})$$

where, 55.5 is the concentration of water in solution in mol L^{-1} and R is the universal gas constant. Table 3, indicate that when increasing temperature, the K_{ads} decreases; which shows that inhibitor is powerfully adsorbed on the steel surface at a lower temperature. But at high temperature, inhibitor was desorbed from the metal surface. Usually, values of ΔG^{o}_{ads} around -20 kJ mol^{-1} or lower are reliable with the electrostatic interaction, and when it is around -40 kJ mol^{-1} or higher, then this is a chemical interaction [7]. At this point, the calculated ΔG^{o}_{ads} values are between -266.08 and -322.99 $kJmol^{-1}$, representing that the adsorption mechanism of VB_5 on mild steel in 240 ppm NaCl solution at the considered temperatures is mainly chemisorption. The negative values of ΔG^{o}_{ads} confirm that the adsorption of inhibitor molecule against the metal surface is a spontaneous process.

Table 3. Thermodynamic adsorption data for mild steel in 240 ppm of NaCl solution in the presence of 200 ppm of VB₅ at various temperatures

Temperature (K)	R^2	K_{ads} $(10^3$/ppm)	ΔG_{ads} $(kJmol^{-1})$
303	0.9944	52.36	-266.082
313	0.9935	45.07	-304.899
323	0.9925	38.38	-314.338
333	0.9904	34.43	-322.996

3.4 Potentiodynamic polarization

The corrosion of mild steel in NaCl solution is an electrochemical corrosion includes a simultaneous cathodic reduction reaction and anodic dissolution of mild steel. To understand the mechanism of corrosion, potentiodynamic polarization arcs of mild steel dipped in the presence and in absence of VB_5 at 30°C was taken and showed in Figure 5. It

shows both cathodic and anodic half-reactions of the mild steel corrosion in 240 ppm NaCl solution. From the extrapolation of linear Tafel segments in these Tafel curves of VB_5, the electrochemical corrosion data's such as corrosion current (I_{corr}), corrosion potential (E_{corr}), cathodic slope (β_c), surface coverage area (θ), anodic slope (β_a) and IE(%) were find out from Tafel plots and summarized in Table 4.
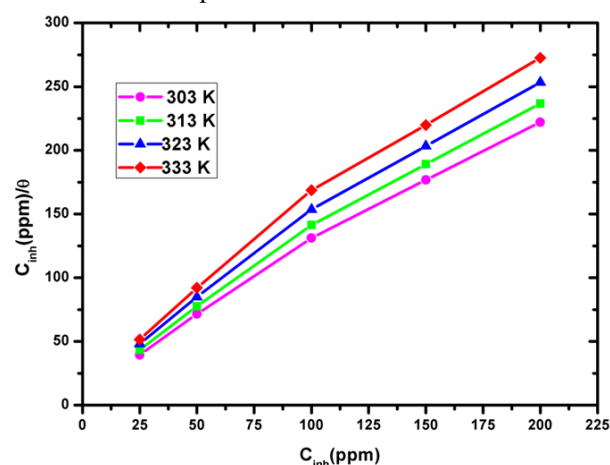

Figure 4. Langmuir adsorption isotherm plots for the adsorption of VB₅ in 240 ppm NaCl solution on the surface of mild steel.

The IE (%) was then find outfrom the following equation

$$IE\% = [(I°_{corr} - I_{corr}) /\ I°_{corr}] \times 100$$

where I_{corr} and $I°_{corr}$ are the corrosion current density values in the presence and absence of VB_5 correspondingly.

When the concentration of VB_5 increases from 25 to 200 ppm in the NaCl solution, the I_{corr} was reduced considerably and it touched the least value for 200 ppm of VB_5. The I_{corr} value reduces from 23.871 $\mu A/cm^{-2}$ for blank and reached the least value of -2.423 $\mu A/cm^{-2}$ for 200 ppm of VB_5. This recommends that both anodic and cathodic reaction were hindered by the inhibitor VB_5. The role of inhibitor was blocking the energetic pots and changing the mild steel surface. This is the cause for the shift of cathodic and anodic slope areas toward lower current densities. The IE (%) values gained from the polarization studies improved with increase in the concentration of the VB_5 added to the corrosion medium. This suggests that the corrosion inhibition was due to the development of the adsorption film of VB_5 on the mild steel surface. The IE (%) data received from polarization studies also support well with the data of weight loss techniques.The type of inhibitor VB_5 can be find out by connecting the corrosion potential (E_{corr}) values. Usually, if the value of E_{corr} is larger than 85 mV/SCE the inhibitor can be categorized as cathodic or anodic type and furthermore, if the value of E_{corr} is lesser than 85 mV/SCE the inhibitor can be categorized as mixed-type.[8]The tendency in the values of E_{corr} for VB_5 exhibited a variation less than

Table 4. Potentiodynamic polarization (PDP) data's for mild steel dipped in 240 ppm of NaCl solution in the absence and presence of VB$_5$.

Inhibitor concentration	Blank I$_{corr}$ (μAcm^{-2})	Inhibitor I$_{corr}$ (μAcm^{-2})	E$_{corr}$ (mV)/SCE	β_a (mV dec-1))	β_c (mV dec^{-1})	Surface coverage (θ)	IE$_{PDP}$ (%)	IE$_{WL}$ (%)
Blank	23.871	-	-316.816	162.689	128.447	0	-	-
VB$_5$								
25	23.871	-7.044	-260.028	92.204	94.747	0.7049	70.49	63.23
50	23.871	-6.324	-233.048	115.183	109.905	0.7350	73.50	69.94
100	23.871	-6.177	-233.391	99.665	72.339	0.7412	74.12	76.24
150	23.871	-4.222	-246.468	86.137	105.521	0.8231	82.31	84.85
200	23.871	-2.423	-261.482	62.977	58.265	0.8984	89.84	90.05

Table 5. Electrochemical impedance parameters obtained for mild steel dipped in 240 ppm of NaCl solution medium in the presence and absence of VB$_5$.

Inhibitor concentration (ppm)	R$_{ct(blank)}$ (Ω cm^2)	R$_{ct(i)}$ (Ω cm^2)	Y$_{max}$	C$_{dl}$ (μ F cm^{-2})	IE (%)	$\theta_{(imp)}$
VB5						
25	62.316	274.53	137.26	4.22562E-06	77.30	0.7730
50	62.316	347.82	173.91	2.63246E-06	82.08	0.8208
100	62.316	384.27	192.13	2.15674E-06	83.78	0.8378
150	62.316	443.48	221.74	1.61928E-06	85.94	0.8594
200	62.316	513.13	256.56	1.20953E-06	87.85	0.8785

85 mV/SCE and was within the range (-316.816 mv/SCE to -233.048 mV/SCE) of -83.768 mV/SCE for VB$_5$. This kind of activity of VB$_5$ was recognized as a mixed-type indicator in 240 ppm NaCl solution. On the other hand, the cathodic current densities were less sensitive and in the anodic range, a noteworthy increase in the anodic current densities compared to cathodic current densities for various concentration of VB$_5$ leads to the shift of the E$_{corr}$ in the direction of anodic direction. These observations conclude that addition of VB$_5$ in 240 ppm NaCl solution will reduce anodic dissolution of mild steel more than the cathodic reduction reaction. This shows that the VB$_5$act as mixed-type inhibitors but inhibits the corrosion mechanism by governing anodic reaction primarily in 240 ppm NaCl solution.
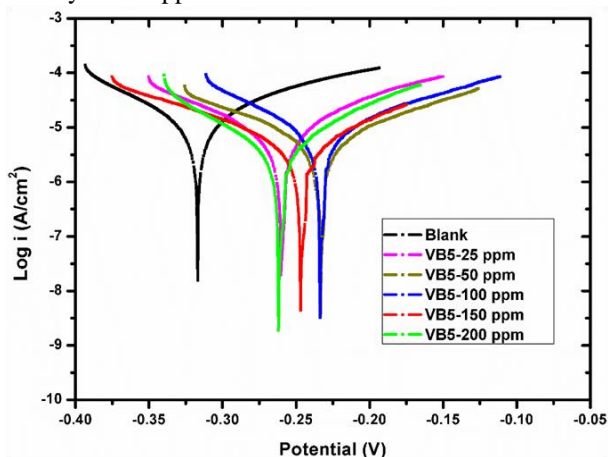

Figure 5. Potentiodynamic polarization curves for mild steel in 240 ppm NaCl solution in the absence and presence of VB$_5$.

3.5 Electrochemical impedance spectroscopy

The surface and kinetics nature of the corrosion of mild steel in 240 ppm NaCl solution in the presence and absence of VB$_5$at 30°C can be observed by means of electrochemical impedance spectroscopy and it is given in Nyquist plots in Figure 6. It gives the value of double layer capacitance (C$_{dl}$) and charge transfer resistance (R$_{ct}$) and it is given in Table 5. The nature of impedance can be explained based on Simple electrical equivalent circuit (figure. 7) using the resistance of charge transfer (R$_{ct}$), resistor (R$_s$) and CPE$_{dl}$ is the constant phase equivalent of double layer.

From the Nyquist plots, when VB$_5$concentration increases, the R$_{ct}$ value increases and C$_{dl}$ value decreases. It point out that there is a development of shielding film on the mild steel surface.[9] The IE (%) was finding out from R$_{ct}$ values from the given equation

$$IE\% = [(R_{ct(i)} - R_{ct(b)}) / R_{ct(i)}] \times 100)$$

where, uninhibited and inhibited charge transfer resistance were distinguished as R$_{ct(b)}$ and R$_{ct(i)}$, respectively. The data's of IE (%) were concise in Table 6. When the concentration of VB$_5$ increases, the value of IE (%) also increases. It is due to the increase in R$_{ct}$ value and the equivalent decrease in C$_{dl}$ values. C$_{dl}$ is associated with the thickness of the adsorbed shielding layer (d) by the following equation:

$$C_{dl} = (\varepsilon \varepsilon o A)/d$$

where, A is the surface area of the electrode, ε is the dielectric constant of the medium and ε_o is the free space permittivity.

3.6 Analysis of adsorbed film

The scratched samples collected from mild steel dipped in 240 ppm NaCl solution was labeled as "MS in Cl" and scratched samples collected from mild steel dipped in the same medium with VB$_5$ were labeled as "MS in VB$_5$+Cl" were used in the further discussion.

FTIR spectra in Figure 8 were recorded for MS in Cl, MS in VB$_5$+Cl and VB$_5$ samples. The strong peaks at 1656 cm^{-1} corresponding to –NC=O stretching frequency of VB$_5$ which is disappeared in MS in VB$_5$+Cl[10] and the strong peak at 1540 cm^{-1} and 1439 cm^{-1} is due to asymmetric and symmetric stretching of -CO-O-Ca$^+$ present in VB$_5$ and it is shifted to 1569 cm^{-1} and 1399 cm^{-1}, respectively in MS in VB$_5$+Cl.[11] The presence of strong peaks at 3402 cm^{-1} in MS in VB$_5$+Cl and their absence in VB$_5$ shows the formation of free acid in MS in VB$_5$+Cl [12] and the strong peak at 1087 cm^{-1}is due to C-N stretching in VB$_5$ that is shifted to 1126 cm^{-1}in MS in VB$_5$+Cl. The disappearance and shifting of the peaks mentioned above highlighted that some adsorption or interaction of VB$_5$ happened on the surface of the mild steel.
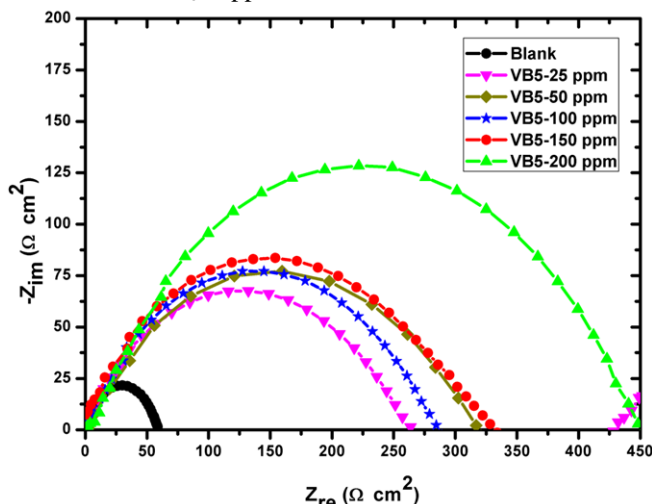

Figure 6. Nyquist plots for mild steel in 240 ppm NaCl solution medium in the presence and absence of VB$_5$.
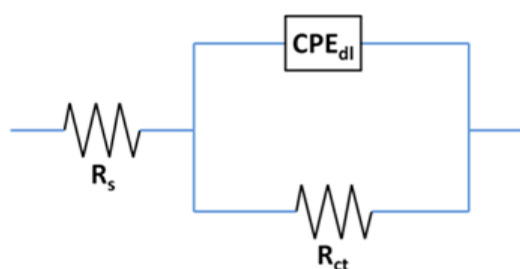

Figure 7. Equivalent electrical circuit used to fit the impedance spectra for mild steel in 240 ppm NaCl solution medium in the presence and absence of VB$_5$.

The UV-Vis spectroscopy is an appropriate technique for proof of identity of complex ions in solution. The change in the location of the absorption maximum shows the development of a complex among two species in solution. Pantothenic acid is not having sensitive UV absorption [13]. The UV-Vis absorption spectrum in figure 9 was taken for 240 ppm NaCl medium containing 200 ppm of VB$_5$ and 300 ppm of Fe (FeSO$_4$). The small shift (see figure 9) in the absorption band of VB$_5$ in Cl from the Fe^{2+} in VB$_5$+Cl clearly show that there is a complex formation between Fe^{2+} ion and VB$_5$.
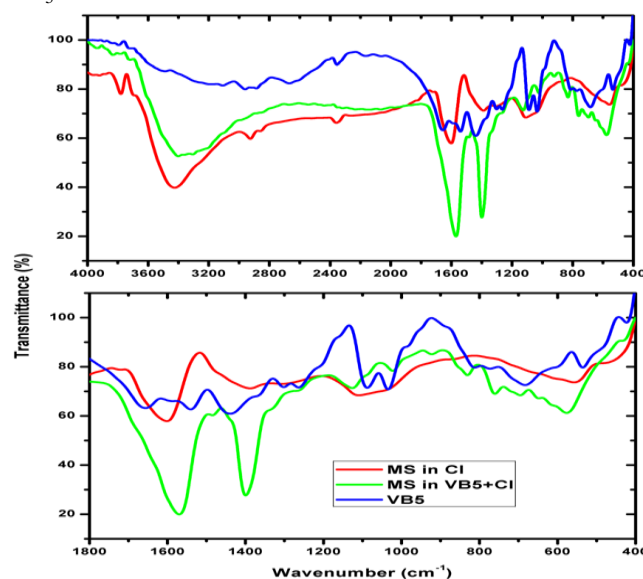

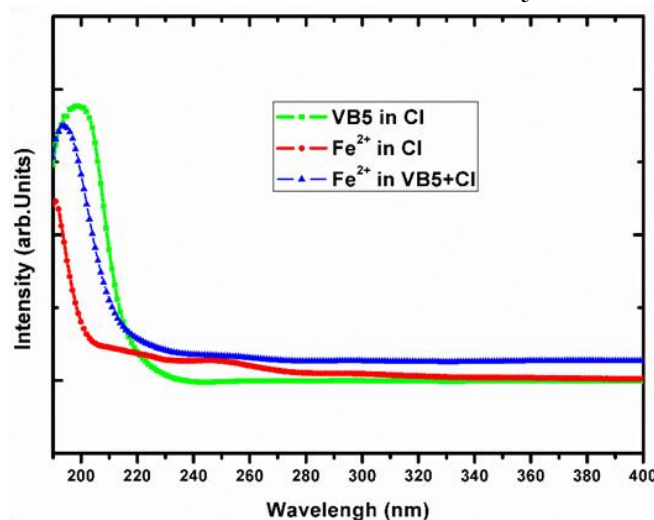**Figure 8. FTIR spectra of MS in chloride medium, MS in VB5 and chloride medium and VB$_5$.**

Figure 9.UV-Vis spectra for VB$_5$ system in 240 ppm NaCl medium.

3.7 Surface analysis

Scanning Electron Microscopy (SEM) pictures and their equivalent Energy Dispersive Spectroscopy (EDX) spectra were represented in figure 10 and figure 11. The flat surface was the mild steel surface before immersion (see Figure. 10(a)). Subsequent immersion in 240 ppm NaCl solution, the lumpiness due to depths was detected in the mild steel surface exposed in figure 10(b). Figure 10(c) denotes the pictures of mild steel dipped in the presence of VB$_5$.

On comparing the SEM pictures, it was apparent that the VB$_5$ was adsorbed on the surface of the mild steel which was shown by the smooth surface in the figure 10(c). The corresponding EDX spectra to the SEM image figures 10(a) to 10(c) were shown in figures 11(a) to 11(c). In figure 10(b), the presence of NaCl was accountable for the pitting in the mild steel. Sodium ions were proved to have no effect on the corrosion actions.

The absence of NaCl in figure 11(c) shows that the inhibitor VB$_5$ was adsorbed on the mild steel which was shown by the presence of oxygen and nitrogen in EDX

spectra (see Figure 11(c)) and smooth SEM images of VB_5 (see Figure 10(c)). The adsorbed film of VB_5 hindered the interaction of NaCl to the metal surface and prohibit the further corrosion of mild steel.
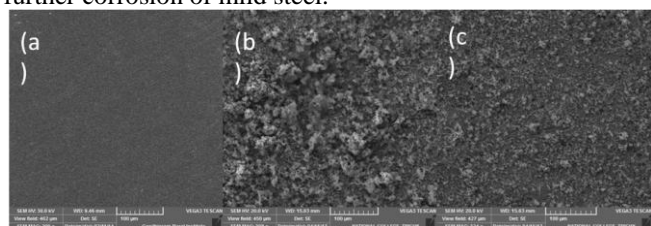

Figure 10. SEM pictures of surface of mild steel: a) polished mild steel, b) mild steel dipped in 240 ppm of NaCl solution and mild steel dipped in 240 ppm of NaCl solution in presence of c) VB_5.
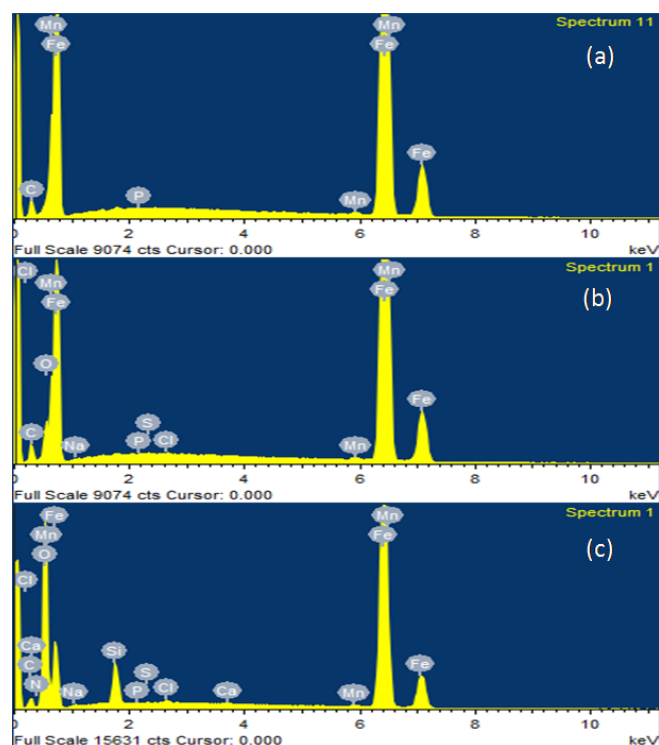

Figure 11. EDX spectra of the surface of mild steel: a) polished mild steel b) mild steel dipped in 240 ppm of NaCl solution and c) mild steel dipped in 240 ppm of NaCl solution in presence of VB_5.

3.8 Quantum chemical calculation

This theoretical method aids to discover the corrosion inhibition efficiency which be determined by the structure of the molecule. The calculated quantum chemical parameters connected to the inhibition effect of VB_5 such as energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy of the highest occupied molecular orbital (E_{HOMO}), the gap energy ΔE_{gap}, the electronegativity (χ), the total energy (E_T), the dipole moment (μ), the global softness (σ) and the global hardness (γ) were find out and given in Table 6. The optimized geometries for VB_5 (a); electrostatic potential surface of compound VB_5 (b); distribution of LUMO energy of VB_5 (c); and distribution of HOMO energy of VB_5 (d) were shown in figure 12.

A real corrosion inhibitor needs to give electrons to the empty d orbital of the metal for bonding and/or accept free electrons from the surface of the metal. The frontier molecular orbital are highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) which is participated in the bonding among the corrosion inhibitor and the metal surface.

Table 7. Quantum chemical data for VB_5 determined using DFT/B3LYP method.

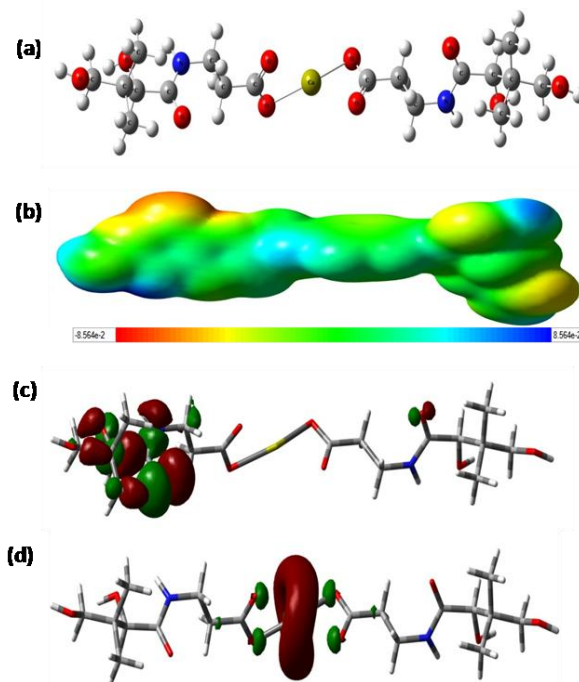| Vitamin	VB_5
E_{HOMO} (eV)	-6.424
E_{LUMO} (eV)	-0.834
ΔE_{gap} (eV)	5.590
μ (Debye)	6.009
x	3.629
Γ	2.795
σ	0.358
Total Energy (a.u)	-2244.97

Figure 12. The optimized geometries for VB_5 (a); electrostatic potential surface of compound VB_5 (b); distribution of LUMO energy of VB_5 (c); and distribution of HOMO energy of VB_5 (d).

The energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) of the corrosion inhibitor is reflected for the reactivity of the inhibitors on the metal surface. Higher energy of the HOMO (E_{HOMO}) point out the electron donating capability of the inhibitor to the vacant d-orbital of the metal and lower energy of the LUMO (E_{LUMO}) point out the electron accepting capability of the inhibitor from the metal. Higher the ΔE value suggests that the IE of the inhibitor is less due to low reactivity with the metal surface and lower the ΔE value indicates that the inhibitor is consuming higher IE due to great reactivity with metal surface. The dipole moment (μ) denotes the sharing of electrons in the molecular structure. High value of μ maybe rise the inhibitor adsorption over electronic force.[14]

The dipole moments of VB_5 is 6.009 Debye, which point out that there are strong dipole–dipole interactions among VB_5 and metal surface and electronegativity (x) denotes the electron drawing ability of the molecule. VB_5 have high electronegativity (3.629) so that VB_5 becomes adsorbed on the metal surface powerfully and has high IE. Global softness (σ) and Global hardness (γ) are

added important belongings to find out the reactivity of an inhibitor. The calculated data of softness indicates enhanced adsorption power of VB_5 on the metal.

IV. CONCLUSION

The calcium D-Pantothenic acid is act as commendable corrosion inhibitors on mild steel in 240 ppm NaCl solution. The values of the IE (%) of VB_5 attained from the weight loss technique at 240 ppm NaCl solution were 90.05%. It acts as mixed–type inhibitors without altering the mechanism of hydrogen evolution and it is confirmed by potentiodynamic polarization technique. In electrochemical impedance studies, when charge transfer resistance increases, the double layer capacitance decreases. This is due to the adsorption of VB_5 on the surface of mild steel. The development of Fe−VB_5 complex and adsorption of VB_5 on the mild steel surface was assured by UV−visible spectra and FT-IR spectra, respectively. The presence of nitrogen in EDX spectra confirmed the adsorption of VB_5 on the mild steel. The transformation in mild steel surface due to development of barrier film by VB_5 was confirmed by surface morphology of SEM image. IE of VB_5 was agreed on the base of the quantum chemical data such as E_{HOMO}, E_{LUMO}, ΔE, and μ and the studied inhibitors adsorb over the active centers (N and O atoms) of VB_5. The theoretical investigations are in close relationship with the experimental outcomes; it clearly shows that VB_5 act as good organic corrosion inhibitor.

REFERENCES

1. Szklarska-Smialowska, Z. and J. Mankowski, Crevice corrosion of stainless steels in sodium chloride solution. Corrosion Science, 1978. 18(11): p. 953-960.
2. Bouklah, M., et al., Thiophene derivatives as effective inhibitors for the corrosion of steel in 0.5 M H2SO4. Progress in Organic Coatings, 2004. 49(3): p. 225-228.
3. Al-Sarawy, A.A., A.S. Fouda, and W.A.S. El-Dein, Some thiazole derivatives as corrosion inhibitors for carbon steel in acidic medium. Desalination, 2008. 229(1–3): p. 279-293.
4. Albin Aloysius, A., Rajajeyaganthan Ramanathan, R.,Auxilia Christy, R., Sambath Baskaran, Noreen Anthony, Experimental and theoretical studies on the corrosion inhibition of vitamins – Thiamine hydrochloride or biotin in corrosion of mild steel in aqueous chloride environment. Egyptian Journal of Petroleum, 2018. 27: p. 371-381. http://dx.doi.org/10.1016/j.ejpe.2017.06.003
5. Malhotra, S. and G. Singh, Vitamins: potential inhibitors for nickel in acidic media. Surface Engineering, 2005. 21(3): p. 187-192.
6. W.A. Badawy, K.M. Ismail, A.M. Fathi, Electrochim.Corrosion control of Cu–Ni alloys in neutral chloride solutions by amino acids. Acta 51, 4182 (2006)
7. M. Hosseini, S.F.L. Mertens, M.R. Arshadi, Synergism and antagonism in carbon steel corrosion inhibition by sodium dodecylbenzenesulphonate and hexamethylenetetramine. Corros. Sci. 45, 1473 (2003)
8. Singh, A.K. and M.A. Quraishi, Investigation of adsorption of isoniazid derivatives at carbon steel/hydrochloric acid interface: Electrochemical and weight loss methods. Materials Chemistry and Physics, 2010. 123(2–3): p. 666-677.
9. Umoren, S.A., et al., Inhibition of carbon steel corrosion in H2SO4 solution by coconut coir dust extract obtained from different solvent systems and synergistic effect of iodide ions: Ethanol and acetone extracts. Journal of Environmental Chemical Engineering, 2014. 2(2): p. 1048-1060.
10. Refaat B. Hamed., Luc Henry., J. Ruben Gomez-Castellanos., Amina Asghar., Jürgen Brem., Timothy D. W. Claridge., and Christopher J. Schofield., Stereoselective Preparation of Lipidated Carboxymethyl-proline and Pipecolic acid Derivatives via Coupling of Engineered Crotonases with Alkylmalonyl-CoA Synthetases. Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry, 2013. 47(2): p. 8153-8284.
11. 11 Masayuki Nara, Hajime Torii, and Mitsuo Tasumi., Correlation between the Vibrational Frequencies of the Carboxylate Group and the Types of Its Coordination to a Metal Ion: An ab Initio Molecular Orbital Study. J. Phys. Chem, 1996. 100: p. 19812-19817.
12. Pandurang D. Pol, Chandrashekar P. Kathari and Sharanappa T. Nandibewoor., Kinetics of oxidative degradation of pantothenic acid by cerium(IV)in aqueous perchloric acid. Transition Metal Chemistry, 2002. 27: p. 807-812.
13. Pei Chen . Wayne R. Wolf, LC/UV/MS-MRM for the simultaneous determinationof water-soluble vitamins in multi-vitamin dietary supplements. Anal Bioanal Chem, 2007. 387: p. 2441-2448.
14. Zhang, F., et al., Performance and theoretical study on corrosion inhibition of 2-(4-pyridyl)-benzimidazole for carbon steel in hydrochloric acid. Corrosion Science, 2012. 61: p. 1-9.

AUTHORS PROFILE

Dr. Rajajeyagantha Ramanathan completed his B.Sc., Applied Sciences from Coimbatore Institute of Technology, Coimbatore and M.Sc., Applied Chemistry from National Institute of Technology, Tiruchirappalli. He was awarded "Best Outgoing Student" with a gold medal in M.Sc. He completed his Ph.D (Surface Science) under TWAS-CNPq fellowship from Federal University of Rio Grande do Sul, RS, Brazil.

Dr. A. Albin Aloysius completed his B.Sc., Chemistry from Pioneer Kumaraswamy College, Nagercoil and M.Sc., Chemistry from Annamalai University, Chidambaram. He completed his Ph.D in Corrosion Science from Bharathidasan University, Tamilnadu.

Mrs. R. Auxilia Christy completed her B.Sc., Chemistry from Holy cross College, Tiruchirappalli and M.Sc., Chemistry from Annamalai University, Chidambaram. She completed her M.phil., in Corrosion Science from Holy cross College, Tiruchirappalli.

Dr. Noreen Antony completed her B.Sc., Chemistry from Holy cross College, Tiruchirappalli and M.Sc., Chemistry from Seethalakshmi Ramaswami College, Tiruchirappalli,. She completed her M.Phil. In Corrosion Science from St. Joseph's College Tiruchirappalli She completed her Ph.D. in Corrosion Science from GTN Arts College, Dindigul, Tamilnadu.

Dr.Gangadhara Angajala is working as an Assistant professor in Department of Chemistry at Kalasalingam Academy of Research and Education. He completed his under-graduation in B.Sc with triple major at Government Degree College for Men, Anantapur, Andhra pradesh and his graduation with specialization in Pharmaceutical Chemistry at Vellore Institute of Technology, Tamil nadu. He obtained his Ph.D with specialization in Organic and Medicinal Chemistry from Vellore Institute of Technology.