Electrochemical, Theoretical And Surface Morphological Investigation Of Chitosan Schiff Base As Potential Corrosion Inhibitor For Mild Steel In Hydrochloric Acid Solution

R. Menaka[1], D. Lakshmi[2], S. Subhashini[3*]
[1]Research Scholar, Department of Chemistry, Avinashilingam Institute for Home science and Higher Education for Women University, Coimbatore 641 043, India
[2]Research Scholar, Department of Physics, Avinashilingam Institute for Home science and Higher Education
for Women University, Coimbatore 641 043, India
[3]Research Scholar, Department of Chemistry, Avinashilingam Institute for Home science and Higher Education for Women University, Coimbatore 641 043, India
*subhash.sethu@gmail.com

Abstract:

Chitosan, a versatile biopolymer was modified into its Schiff base derivative with Vanillin by condensation reaction.Elemental, spectral and SEM analysis of Chitosan vanillin Schiff base (ChVSB) confirmed the incorporation of vanillin groups onto the Chitosan backbone through imine linkages. The thermal stability of the ChVSB was analyzed by thermogravimetric analysis. The corrosion inhibition performance of ChVSB was explored for mild steel in 1M HCl solution using electrochemical impedance spectroscopy and potentiodynamic polarization methods at higher temperature range of 313-343K. Inhibition efficiency of the inhibitor increased with increase in concentration of all the studied concentration within the range of 100- 1500ppm. The Schiff base inhibitor showed better inhibition performance at the concentration of 1500ppm by forming protective layer on the metal surface. Electrochemical impedance spectroscopy analysis (EIS) revealed an increase in polarization resistance due to the adsorbed inhibitor molecules. Potentiodynamic polarization analysis revealed that ChVSB behaved as a mixed type inhibitor. The protective film formed on the metal was stable till 323K and then tend to desorbed at higher temperatures. The adsorption behaviour of the Chitosan Schiff base on the metal surface was monitored by cyclic voltammetric studies. The reduction in OQ-t plot after the addition of ChVSB indicated the reduction in corrosion rate. Surface morphology of the protective layer was examined by FTIR, scanning electron microscopy and atomic force spectroscopy. The inhibition mechanism of the inhibitor molecule was proposed in the light of the quantum chemical calculations using DFT. From the quantum chemical results, HOMO orbitals located on the –HC=N and –OH groups of Chitosan Schiff base and also the presence of mulliken charges on the heteroatoms clearly confirmed the formation of strong adsorption bond through chemical interaction with the empty d orbitals of the metal atom. Thus, the synthesized Chitosan derivative can be suggested as better corrosion inhibitor for the mild steel in acid medium.

Keywords: Chitosan Schiff base, Vanillin, cyclic voltammetry studies, FTIR, SEM.

1. Introduction

Corrosion is an environmental problem in which the metals tend to oxidize electrochemically and degrade from its original state. Corrosion of metals has a high impact since metals are widely used in industrial and structural applications. Metals when exposed to aggressive environment like acids, leads to high susceptibility of corrosion along with considerable economic losses and safety hazards. Since corrosion is the electrochemical reaction between the metal and corrosive media anticorrosion materials ie., corrosion inhibitors

come into play to minimize the occurrence of electrochemical reactions at the metal/solution interface. Numerous studies showed that using inhibitors found to be one of the most efficient and technologically simple methods for protection in closed systems, especially in acidic media. Polymers and polymer composites were being reported as better choice for corrosion inhibitors because of their large molecular size and multiple adsorption sites blanket the metal surface from corrosive media. Over the past few years, there has been intolerance towards the usage of organic, inorganic and synthetic polymeric inhibitor molecules due to their toxic nature. Obviously, the need of an hour is to switch over to the eco-friendly inhibitors. Tremendous numbers of eco-friendly inhibitors so called "green inhibitors" have been identified and reported so far. Among various eco-friendly inhibitors, natural polymers ie biopolymers have received a considerable attention because of their biocompatibility and biodegradability.

In the present study, attempts have been made to prepare an eco-friendly inhibitor with high efficiency.Chitosan is the natural polymer and deacetylated product of chitin. It has received a considerable attention in many fields because of its properties of biocompatibility, biodegradability, multifunctionality and low toxicity.In recent years, studies on Chitosan, modified Chitosan derivatives and Schiff bases of chitosan have been attempted and reported as corrosion inhibitors by the researchers. Chemical modification of Chitosan into Schiff bases has improved its corrosion inhibition efficiency to higher extent because of the presence of imine group and benzene ring in the aldehyde that helps in enhancing the performance of Chitosan derivative. Performance of the Chitosan Schiff base as corrosion inhibitor was evaluated by potentiodynamic polarization and electrochemical impedance spectroscopic techniques. Surface analytical techniques were also carried out to confirm the inhibitive action of Chitosan derivative for inhibition studies.

2. Experimental

2.1 Materials

Commercially available mild steel (MS) of composition C-0.106 %, Mn-0.196 %, P-0.027 %, Cr-0.022 %, S-0.016 %, Ni-0.012 %, Si-0.006 %, Mo-0.003 %, and remainder Fe was used for the corrosion measurement studies. The MS specimen of 1 cm^2 coupons fixed to brass rod was used for the electrochemical studies.

2.2 Synthesis of Chitosan Vanillin Schiff base (ChVSB)

Chitosan Vanillin schiffbase (ChVSB) was synthesized by stirring the mixture of chitosan suspension (1g in 1% acetic acid) and Vanillin (1mL) in ethanol (10mL) at room temperature for 7 h. The obtained yellow solution was kept overnight. The Schiff base formed was precipitated using acetone, washed several times with acetone to remove the unreacted compounds and then dried under vaccum. The scheme of the synthesis of chitosan derivative is shown in Figure 1.

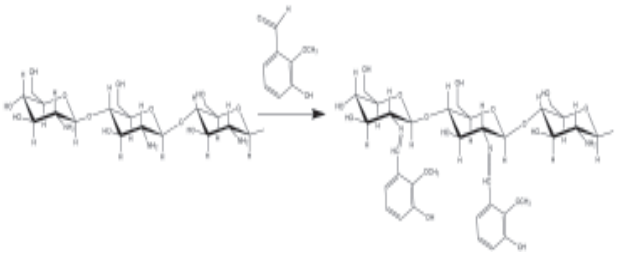


Figure 1- Synthesis scheme of ChVSB

2.3 Characterization of Chitosan Schiff base (ChVSB)

Synthesized ChVSB was characterized using Fourier transform infrared spectroscopy (FTIR) (Schimadzu IR affinity 1). The elemental composition was calculated using Elemental vario EL III. Thermogravimetric analysis for chitosan and its Schiff base was carried out using thermogravimetric analyzer (EXSTAR SII TG/DTA 6300). UV spectra were recorded using UV spectrophotometer 2202 (systronics). The surface morphology of the ChVSB was observed using scanning electron microscopy (JEOL JSM-6490LA).

2.4 Corrosion monitoring techniques- Electrochemical methods.

Electrochemical measurements were performed in a conventional three electrode glass cell consisting of mild steel substrate of 1cm^2 exposed area as working electrode, a platinum electrode as counter electrode and a saturated calomel electrode as reference electrode using Frequency Response Analyzer (Solartron 1280B) supported with Corrware and Zplot softwares. Potentiodynamic polarization curves were obtained from anodic potential of -0.1V to cathodic potential of -1 V versus open circuit potential at a sweep rate of 2 mV/s. The experiments were carried out at atmospheric conditions without any stirring. The anodic and cathodic curves of the Tafel plots were extrapolated to obtain corrosion current densities (Icorr). The inhibition efficiency was calculated using the Eq.(1),

$$IE(\%) = \frac{I\text{-}ocorr - Icorr}{Icorr} X\ 100 \circledcirc (1)$$

where I^{o}corr and Icorr are the corrosion current densities in the absence and presence of inhibitor, respectively.

EIS measurements were carried out at a frequency range of 20 kHz to 0.1Hz by applying AC amplitude of 10mV. The results were collected using Z plot software and interpreted with Z view

software. Nyquist plot represents the results obtained from EIS measurements. The charge transfer resistance (Rct) and capacitance of double layer (Cdl) were calculated from the Nyquist plot. The inhibition efficiency can be calculated using Eq.(2),

$$IE(\%) = \frac{Rct - Rct_{ll}}{Rct} X\ 100 \circledcirc (2)$$

where Rct and Rct' are the charge transfer resistance of the inhibited and uninhibited solutions respectively.

2.5 Adsorption monitoring technique- Cyclic Voltammetric studies

To examine the adsorption effect of Chitosan Schiff base on the metal surface cyclic voltammetric studies were carried out using Bio-Logic SP-150 electrochemical system.

2.6 Surface Analytical techniques

The protective layer formed on the mild steel surface was analyzed using FTIR (Schimadzu IR affinity 1), Scanning electron microscopy (JEOL JSM-6490LA) andAtomic force spectroscopy (A.P.E research, model A100, Italy). All the surface analytical techniques were performed as Ex-situ type of analysis by immersing the samples in the absence and presence of the inhibitor solution of 1500ppm for about 6 hours at room temperature.

2.7 Theoretical studies- DFT method

Gas phase geometry optimization and quantum chemical calculations were performed using Density functional theory (DFT) and the 6-311G (d,p) basis set. Becke's Three parameter Hybrid Functional together with the Lee- Yang- Parr correlation functional theory (B3LYP) was selected for the calculations using Gaussian 03 program package.

3. Results and Discussion

3.1 Characterization of Chitosan Schiff bases (ChVSB)

UV- visible spectra of ChVSB shown in Figure exhibit a broad peak at 215-350nm. This region corresponds to n- n* transition suggesting the presence of n bond (–N=CH) formed due to condensation of aldehydes into the chitosan matrix. The FTIR spectra of chitosan and ChVSB are shown in Figure. FTIR spectrum of ChVSB shows similar peaks that present in the chitosan spectrum along with some new peaks. The characteristic peak at 1638.78 cm^{-1} is attributed to the C=N vibrations of imines. The peak appears at 1531.65 cm^{-1} corresponds to the C=C stretching in the aromatic ring of the aldehyde. These results confirm the successful anchoring of vanillin onto the chitosan backbone and formation of biopolymeric Schiff base.

The formation of Schiff base (ChVSB) was further confirmed by the elemental analysis. The elemental compositions of the Chitosan and the Chitosan Schiff base are presented in the Table

1. The increase in carbon, hydrogen content of the Schiff base derivative suggests the condensation of vanillin on the chitosan chain. The increase in the C/N ratio also confirms the substitution.

Thermogravimetric analysis of the Chitosan vanillin Schiff base was conducted to measure their weight loss at different temperatures in the heating range of 40° - 550 °C at a heating rate of 10°C per minute. TG curve of chitosan and Schiff base polymer exhibits two degradation stages which are shown in Figure. The first degradation step is due to loss of water molecule. The second degradation step occurs in the range of 220-310°C is due to depolymerization of Schiff bases. The main thermal degradation step of ChVSB indicates that Schiff base polymer is less stable than chitosan. The instability of the Schiff base polymer compared to chitosan may be due to the anchoring of vanillin groups on the chitosan matrix.

The scanning electron micrographs of chitosan and chitosan Schiff bases depicted in Fig.5 gives a clear difference between them. The SEM image of chitosan exhibited a nonporous, smooth and flat membranous phase while the chitosan Schiff base (ChVSB) exhibited porous and layered structures. The change in the morphology of the Schiff base polymer can be attributed to the chemical modification of chitosan by anchoring of vanillin molecules..

3.2 Corrosion monitoring techniques

Electrochemical behaviour of theChitosan Schiff base was investigated using Potentiodynamic polarization method at various temperatures (313-343 K). The polarization data obtained at 313-343 K for 1500ppm is listed in Table 1.It is clear that the concentration has a positive effect on the IE and a highest IE was obtained for 1500 ppm of inhibitor for all studied inhibitors.Table reveals that the IE (derived from I_{corr} and Rp) increases with temperature till 323 K for the studied inhibitor. This confirms that the film forming property of the Chitosan favours in the formation of stable adsorptive film on the metal surface till 323 K. The slight fall in the IE is observed in the temperatures 333 K and 343 K, though the better IE is produced. The decrease in IE is due to the disturbed stability of the adsorbed film on the metal surface because of the induced polarization combined with high temperature. The inhibitive action of Chitosan Schiff base mainly attributed to the presence of –HC=N groups in the polymer matrix along with n-electron clouds present in the anchoring groups of aldehydes. Moreover, the longer molecular size ensures the greater adsorption on the MS steel surface and decreases the effective area for corrosion reaction by blocking the reaction sites.

The Nyquist plots for mild steel obtained in the absence and presence of the inhibitor at optimum concentrations at various temperatures are given in Figure . The impedance parameters for the

Table 1: Polarization parameters for the ChVSB for concentration of 1500 ppm at 313 – 343 K

Inhibitor system at 1500ppm	Temp	b_a (V/dec)	b_c (V/dec)	I_{corr} (mA/cm²)	IE Icorr (%)	Rp ϕιcm²	IE Rp ϕιcm²	Ecorr (mV/SCE)
ChVSB	303	0.102	0.078	0.371	91.11	30.791	78.86	-476.16
	313	0.109	0.090	0.104	98.68	29.7	85.47	-477.32
	323	0.197	0.151	1.502	91.34	25.236	87.62	-488.84
	333	0.111	0.129	1.662	86.57	14.127	85.19	-491.83
	343	0.159	0.162	3.738	82.28	4.5464	68.92	-483.29

investigated Chitosan Schiff bases at various temperatures were calculated and are presented in Table.Impedance plots of the inhibitors represent single capacitive loop and one time constant in the Bode-phase plot in the temperature range studied. The diameter of the semicircle increases till 323 K and then tends to decrease with rise in temperature. This can be attributed to the resistive nature of the inhibitor film formed on the metal surface towards higher temperature. The decrease in diameter of the semicircle can be acclaimed to the adsorption–desorption equilibrium towards desorption and roughening of the metal surface which results from enhanced corrosion.From the impedance parameters of the Chitosan Schiff base polymer, the increase in CPE was observed which may be due to the shifting of adsorption/desorption equilibrium towards desorption. The increase in n values with temperature reflects that the electrode surface is more homogeneous after the adsorption of Schiff base polymers. The IE calculated from R_p is listed in Table. All the investigated polymers found to follow the same trend in the IE. The IE of the Schiff base polymers are highly effective till 323 /ith increase in

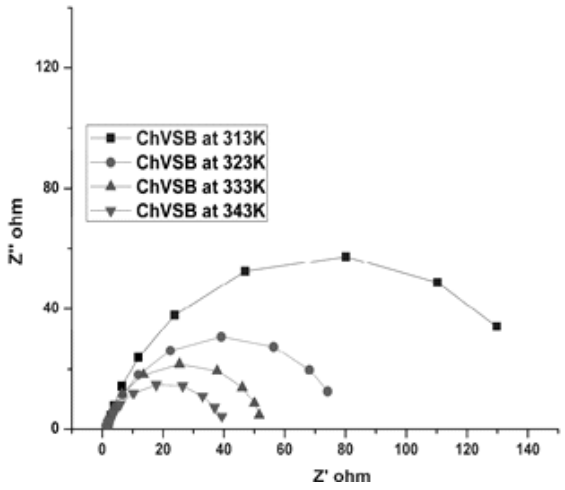


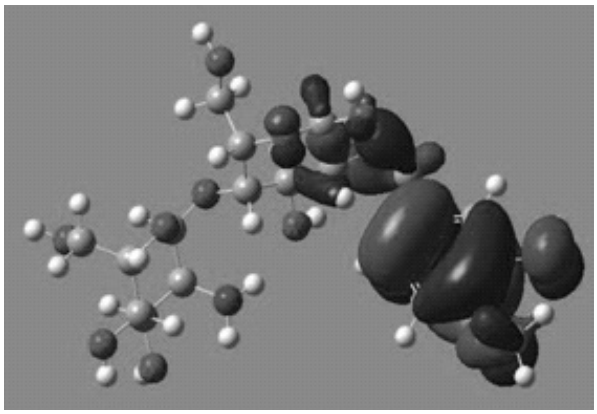
Figure 1: Nyquist plots for optimum concentration (1500ppm) of ChVSB at different temperatures

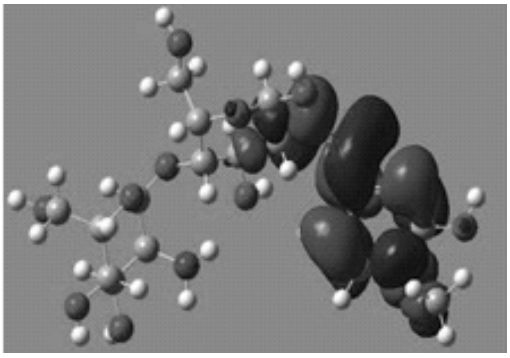
3.3 Surface Analytical techniques

Atomic force microscopy is a powerful technique to examine the adsorbed film formed on the metal surface from nano to micro scale. The microstructures has been achieved using the three dimensional and two dimensional surface topography of mild steel specimens immersed in HCl and in presence and absence of inhibitors. Therecorded three dimensionaland two dimensionalAFM images of MS sample in 1M HCl are shown in Fig.a and b. Some defected sites, number of protrusions and mountain like structures could be seen in the AFM images of metal surface due to the rapid attack of acid (Fig.a). The rough surface of the metal with some cracks and pores could be observed in the two dimensional image (Fig. 8b) which also augments the dissolution of metal in the acid solution [40]. In the presence of ChVSB, the surface roughness is visibly reduced which could be atrributed to the inhibition efficiency of the schiff base polymer. The three dimensional and two dimensional AFM image of metal surface exposed to ChVSB (Fig. a and b) is smooth which could be attributed to the more compact and homogeneous film formation by the inhibitors on the metal surface.

3.4 Theoretical studies

The HOMO electron density surface of the Chitosan Schiff bases reveal that the electron rich sites present in them from which the electrons could be donated to suitable vacant d- orbitals of the metal surface. The LUMO electron density surface point outs the electron deficient sites of the Chitosan Schiff bases and these regions have greater chances of accepting electrons from the occupied orbitals of the metal surface.





Frontier molecular orbital distribution – ChVSB

It could be seen that the HOMO and LUMO orbitals of the Chitosan Schiff bases (ChVSB, ChPSB) are found on the imine (-C=N-) substituted glucopyranose ring and the anchoring aldehydeic groups. The HOMO orbitals of Chitosan Schiff bases are mainly located on the pi- orbitals and the electron densities are distributed over the phenyl ring of the substituted aldehyde compounds. The HOMO orbitals of these Schiff base compounds found extend to the C=C n - electron centres of glucopyranose rings and also to the electron donating $-CH_3$ and –OH substituents on the phenyl ring in case of the ChVSB. This may give an idea of flat or parallel adsorption of the inhibitor molecules onto the metal surface. This should be the reason for the strong interaction with the metal surface and thereby giving high inhibition efficiency.

4. Conclusions:

Chitosan vanillin Schiff base was successfully prepared by anchoring vanillin groups into the Chitosan matrix. Performance of Chitosan Schiff base in inhibition of mild steel corrosion exhibited it as efficient inhibitor in 1M HCl. Polarization studies showed that the ChVSB as mixed type inhibitor. Its inhibition efficiency increased with the inhibitor concentration. Surface techniques clearly pointed the formation of protective film on the metal surface. Also, quantum studies supported the experimental results.

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