Investigations on the corrosion inhibitive characteristics of novel polyesters for mild steel in acid media

A.Kiruthika, P.Sounthari, K.Parameswari, S.Chitra

ABSTRACT-The adsorption and inhibitive properties of polyesters formed by the condensation reaction between terephthaloyl chloride and 4, 4' -bis(hydroxyl thioureaazo) biphenyl sulphonediamine monomer[STTP]/ schiff base formed between 4,4'-diamino biphenylsulphone and 4-hydroxy benzaldehyde and vanillin [SBTP,SVTP] for the corrosion of mild steel in 1M H_2SO_4 were studied using weight loss, Impedance spectra and potentiodynamic polarization methods. The protection efficiency increased with increase in inhibitor concentration. The effect of temperature on the corrosion behavior of mild steel was studied in the temperature range 303 K -333 K for 1M H_2SO_4 containing an optimum concentration of the synthesized polymers. Polarization studies show that the polymers function as mixed inhibitors but predominantly control the cathodic reaction. AC impedance spectra and SEM studies reveal the formation of a protective film on the metal surface. The adsorption of the polymers on the steel surface was in agreement with Langmuir isotherm.

Keywords: Corrosion, Polyesters, Polarization, protection efficiency, SEM

1 INTRODUCTION:

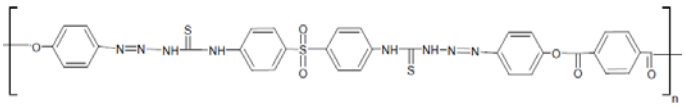
Corrosion is degradation of materials properties due to interactions with their environments and corrosion of most metals is inevitable. Corrosion control of metals is an important activity of technical, economic, environmental and aesthetical importance. The use of inhibitors is one of the best options of protecting metals against corrosion [1-4]. Corrosion inhibitors act via adsorption of their molecules on the corroding metal surface, and the efficiency of inhibition depends on the mechanical, structural, and chemical characteristics of the adsorption layers formed under a particular condition.

Polymers are used as corrosion inhibitors because they occupy a large surface area thereby blanketing the surface and protecting the metal from corrosive agents present in the solution. The inhibitive power of the polymers is related structurally to the rings and heteroatoms which are the major active centers of adsorption [5]. The aim of the present work is to study the inhibiting effect of the synthesized polymers on the corrosion of mild steel in 1M H_2SO_4in the temperature range 303-333K

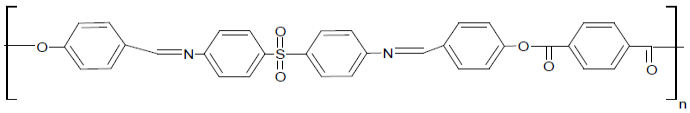
2 MATERIALS AND METHODS

2.1 Synthesis of inhibitor:

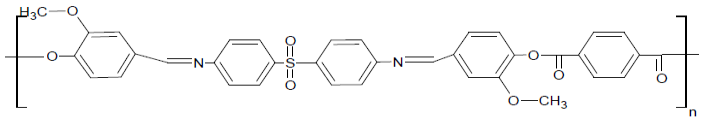
The polyesters were synthesized bypolycondensation reaction of diolmonomers anddiacid chlorides.



STTP



SBTP



SVTP

Structure of the polymers

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The polymers were characterized by FTIR spectra (Thermonicolet FTIR spectrometer) using the solid polymer as KBr disc.

For the weight loss measurements rectangular mild steel specimens (Composition: carbon-0.084%, Mn-0.369%, P-0.025%, Cr-0.022%, Ni-0.013% and Fe-remainder) of size 2.5cm X 1cm X 0.1cm were used. The specimens were cleaned in pickling solution of HCl washed with water and dried. The specimens were thenpolished using emery sheets, degreased with trichloroethylene, dried and stored in a desiccator.

2.2. Weight loss measurements:

Varying concentrations of the inhibitor solutions were prepared in 1M Sulphuric acid (100 ml) and kept in a thermostat maintained at desired temperature. The pre-weighed MS plates were immersed in the inhibitor solution at 30±1°C for 3 hours and for 1 hour at higher temperatures. The plates were then, dried and reweighed. From the loss in mass the percentage IE of the inhibitors were calculated.

2.3. Electrochemical studies:

A conventional three electrode cell assembly was used with mild steel rod as the working electrode,platinum wire as the counter electrode and saturated calomel as the reference electrode. The working electrode has an exposed area 0.785cm^2.The electrochemical experiments were performed with Iviumcompact stat potentiostat/ galvanostat. The data were collected and analysed by Ivium soft- software. The polarization curves were obtained by changing the electrode potential from -200 to +200mv with respect to open circuit potential at a scan rate of 1mv/sec. The linear Tafel segments of the anodic and cathodic curves were extrapolated to obtain corrosion potential (E_{corr}) and corrosion current density (I_{corr}).EIS measurements were carried out in the frequency range 10KHz to 0.01Hz with amplitude of 10mv peak-to-peak using AC signal at the OCP.

2.4. Morphological Investigation

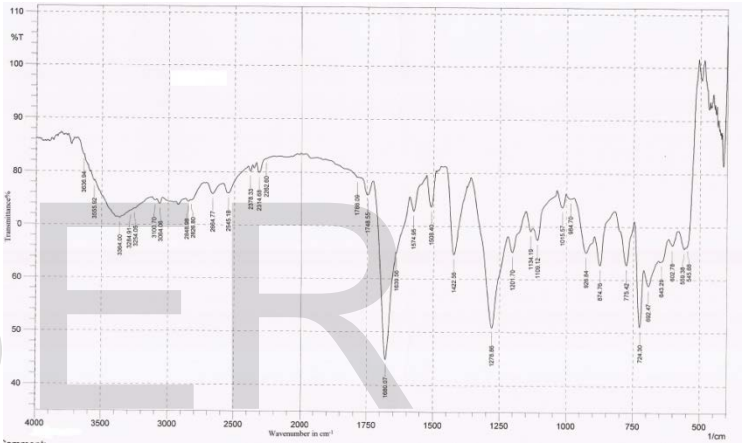
The surface morphology of the uninhibited and inhibited mild steel samples was investigated using the scanning electron microscopy(Medzer biomedical research microscope).

3. RESULTS AND DISCUSSION

3.1. IR data:

The synthesized polymers were characterized by FTIR spectra.Typical IR spectrum of STTP is shown in Fig.1. All the three polymers displayed a moderate bands around 1750 cm$^{-1,}$ 1278 cm^{-1} and 1422 cm^{-1} characteristic of –C=O- group of ester, symmetric and asymmetric –S=O group respectively. The STTP showed bands around 750 cm^{-1}, 1414 cm^{-1}, corresponding to –C=S and N=N groups. Both SBTP and SVTPexhibit a band in the region 1600 cm^{-1} indicating the presence of azomethine linkage. SVTP exhibits an additional band around2923cm^{-1}which is due to the presenceof methoxy group.

Figure:1 IR spectrum of STTP



3.2. Weight loss measurements:

The weight loss of the mild steel samples in 1M H_2SO_4 in the absence and in the presence of various concentrations of the polymers were determined after 3 hours of immersion at 30±1°C.The values of corrosion rate and inhibition efficiency were calculated using the following equations,

$$\text{Corrosion rate} = \frac{KW}{ATD}$$

Where,

R= gas constant; W = weight loss in g; A = surface area in cm^2;

T = exposure time in hours;

K = constant;

D = density of sample in g/cc.

Table:1 Inhibition efficiencies at various concentrations of the inhibitors for corrosion of mild steel in 1M H2SO4 obtained by weight loss measurement at 30±1 C

$$\% \text{ Inhibition Efficiency} = \frac{W^0 - W}{W^0} \times 100$$

Where,

W^o= Weight loss of the uninhibited system; W= Weight loss of the inhibited system

Inhibitor	Concentration (ppm)	Weight loss (g)	Inhibition Efficiency (%)	Degree of surface coverage (θ)	Corrosion rate (mpy)
STTP	Blank	0.1828	-	-	230.0081
	10	0.1781	2.57	0.0257	224.09433
	100	0.0248	86.43	0.8643	31.2046
	500	0.0009	99.51	0.9951	1.132425
	1000	0.0001	99.95	0.9995	0.125825
SBTP	Blank	0.1828	-	-	230.0081
	10	0.1389	24.02	0.2402	174.77093
	100	0.0323	82.33	0.8233	40.641475
	500	0.0028	98.47	0.9847	3.5231
	1000	0.0036	98.03	0.9803	4.5297
SVTP	Blank	0.1828	-	-	230.0081
	10	0.1105	39.55	0.3955	139.03663
	100	0.0585	68.00	0.6800	73.607625
	500	0.0273	85.07	0.8507	34.350225
	1000	0.0257	85.94	0.8594	32.337025

The values of corrosion rate obtained from weight loss measurements recorded in table-1 clearly show that corrosion rate decreases as the concentration of the polymer increases. The dependence of % IE on concentration shows that % IE reached the optimum value at a polymer concentration of 1000ppm.

3.3. Adsorption isotherm:

Basic information on the interaction between the inhibitors and mild steel is provided by adsorption isotherm. Two types of interactions can describe the adsorption of organic compounds; viz. physical adsorption and chemical adsorption. These are influenced by the chemical structure of the inhibitor, the type of electrolyte,the charge and nature of the metal

A plot of C/Θ against C (Fig.2) is found to be linear, showing that the adsorption of the inhibitors on mild steel obeys Langmuir adsorption isotherm confirming to monolayer adsorption.

The kinetic thermodynamic model of Flory – Huggins accounts for the degree of surface coverage characteristics of adsorbate on the adsorbent. A Plot of log(C/Θ) against log (1-Θ) (Fig.3)was shown to be linear indicating that each molecule of the inhibitor occupies one active site on the metal surface.

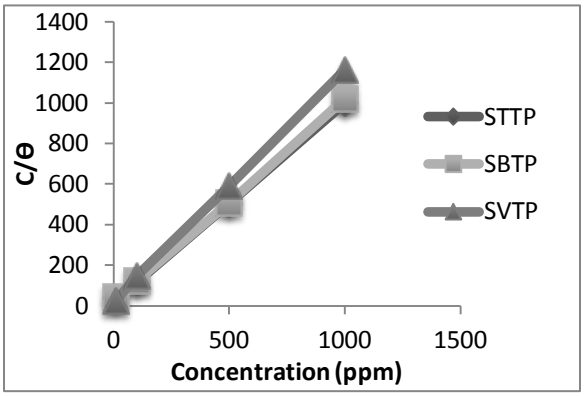


Figure: 2 Langmuir plot

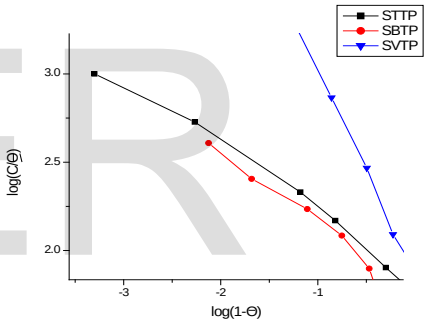


Figure: 3Flory –Huggins model

3.4. Effect of temperature:

Table-2 shows the result due to the influence of temperature on the performance of the inhibitors.

The inhibition efficiency decreased with increase in temperature indicating that the inhibitor molecules are physically adsorbed.

Table 2: Inhibition efficiencies of the inhibitors for corrosion of mild steel in 1M H2SO4 obtained by weight loss measurement at higher temperature at highest concentration

Name of the inhibitor	Temperature (K)	Weight loss (g)	Inhibition efficiency (%)	Corrosion rate (mpy)
Blank	303	0.0609	-	76627.43
	313	0.1152	-	144950.4
	323	0.1443	-	181565.5
	333	0.2486	-	312801
STTP	303	0.0001	99.95	41.944
	313	0.0247	78.56	31078.7
	323	0.0586	59.39	73733.27
	333	0.1997	19.67	251271.9
SBTP	303	0.0012	98.03	1509.9
	313	0.0055	95.23	6920.375
	323	0.0217	84.96	27304.03
	333	0.0436	82.45	54859.7
SVTP	303	0.00325	94.67	4026.4
	313	0.01155	89.97	14469.88
	323	0.0359	75.12	45171.18
	333	0.07677	69.12	96633.6

Inhibitor	-ΔHads kJ/mol	-ΔSads kJ/mol	Ea (J)
Blank	-	-	37.32601
STTP	1134.8	3.247	269.7751
SBTP	412.9	0.668	102.32
SVTP	317.7	1.653	89.76476

Analysis of the Table 2 shows that for STTP, the inhibition efficiency decreased to 19% at 60˚C. Shetty et al[6] have reported that stability of the inhibitor molecule in the corroding medium may become the determining factor, for example, molecules such as thioacetamide decompose readily in an acidic environment.

Papavinasam[7] has also observed that the nature of the inhibitor initially present inacid solutions may change with time as a consequence of chemical or electrochemical reactions. He has found thatdiphenylsulphoxide undergoes electrochemical reaction at the metal surface to produce diphenylsulphide which is more effective than diphenylsulphoxide. On the contrary, the reduction of thiourea and its methyl and ethyl derivatives give rise to HS- which accelerates corrosion. Poor efficiency of STTP at higher temperature may be attributed to the reduction of thiourea moieties (along the polymer chain) in the acid medium in the presence of iron at higher temperature which might have resulted in the formation of sulphide which accelerate corrosion and decreases the efficiency.

For the other two polymers(SBTP and SVTP) the inhibition efficiency reached a value of 85% and 69% at 60˚C showing their effectiveness even at higher temperature.

The temperature increases the rate of all electrochemical processes and influences adsorption equilibrium and kinetics. Weight loss studies at higher temperature allow the determination of activation energy and other thermodynamic activation functions in the absence and presence of the polymers. The activation energy for the corrosion processcan be calculated by applying the Arrhenius equation,

Corrosion rate = A exp (-Ea/RT)

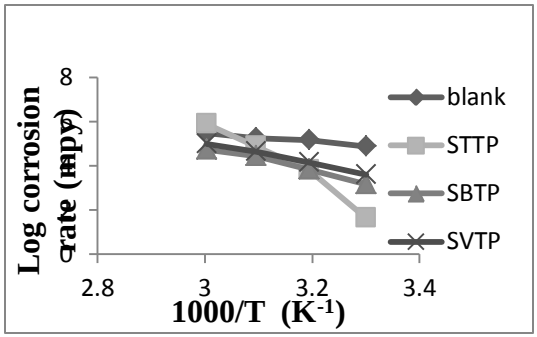


Figure 4: Arrhenius plot

Where Ea represents the apparent activation energy, R the gas constant, T the absolute temperature, A the pre-exponential factor.

Arrhenius plots were constructed for mild steel in 1M H2SO4 containing various concentrations of the polymers. The values of Ea were calculated from the plots(Fig-4) and are listed in Table 3.The higher values of Ea in presence of the inhibitors than in its absence can be interpreted as an indication of physical adsorption [3].

Table 3:Activation energy and free energy of adsorption of the inhibitors

Table 4:Thermodynamic parameters for adsorption of the inhibitors on the mild steel

Inhibitor	-ΔG°ads kJ/mol			
	303 K	313 K	323 K	333 K
Blank	-	-	-	-
STTP	25.7767	41.7759	44.0749	44.2684
SBTP	34.9842	38.3651	42.3687	44.0247
SVTP	37.4042	40.1516	43.39	45.1011

The free energy of adsorption ΔG^0_{ads} has been calculated from the equilibrium constant of adsorption using the equation

$$K = \frac{I}{55.5} Exp\left[\frac{-\Delta G^0_{ads}}{RT}\right]$$

$$K = \frac{\theta}{C(1-\theta)} and$$

$$\Delta G^0_{ads} = -RT \ln(55.5K)$$

The negative value of the free energy of adsorption ensures spontaneity of the adsorption process and stability of the adsorbed layer on the mild steel surface.

The stability of the adsorbed layer decreases with increase in temperature .This is also confirmed by the decrease in absolute value of ΔG^0_{ads} with the rise in temperature[8]. The absolute values of $\Delta G^0_{ads}$are less than the threshold value -40kJ/mol required for chemical adsorption indicating that the inhibitor molecules are physically adsorbed on the mild steel surface[9].

Electrochemical studies:

(i). Polarization studies:

The influence of the polymers on the kinetics of cathodic and anodic corrosion reactions was analyzed bypotentiodynamic polarization studies. Fig.5 shows the polarization curves for mild steel in $1MH_2SO_4$ containing various concentrations of STTP and in blank acid.

It is apparent from the figure that the addition of STTP shifts E_{corr} slightly in the negative direction ~40mV or less and reduced the current density.The observed variation in E_{corr} is much less than ±85mV and hence it cannot be classified as anodic or cathodic inhibitor[10].

Further the presence of these polymers influences both ba and bc values which indicates that these polymers inhibit both the reduction of hydrogen ion as well as the dissolution of metal. The % IE values of the polymers calculated from I_{corr} values are listed in Table 5.

The value of % I.E increased with increase in concentration which is in agreement with weight loss studies.

Table 5: Potentiodynamic polarization data of mild steel in 1M H_2SO_4 containingvarious concentrations of the polymers

Inhibitor	Inhibitor Concentration (mM)	Tafel slopes (mv / dec) ba	bc	Ecorr (mV)	Icorr (µAmp/ cm²)	Inhibition Efficiency (%)
	Blank	52	112	-467.40	568.4	-
STTP	10	67	142	-483.10	232.8	59.04
	100	63	142	-481.80	172.6	69.63
	1000	49	151	-470.50	124.1	78.17
SBTP	10	61	163	-485.80	200.7	64.69
	100	50	155	-478.70	188.4	66.85
	1000	51	153	-479.90	145.7	74.37
SVTP	10	59	117	-503.8	423	25.58
	100	49	131	-488.8	239	57.95
	1000	39	228	-428.3	193	66.04

(ii). Electrochemical Impedance spectroscopy:

EIS measurements were performed to evaluate the impedance parameters of the mild steel – sulphuric acid interface in the absence and presence of various concentrations of the polymers. Fig 6 illustrates the Nyquist plots obtained at 0, 10, 100, 1000ppm of STTP. The EIS data were analyzed in terms of equivalent circuit as shown in Fig below.

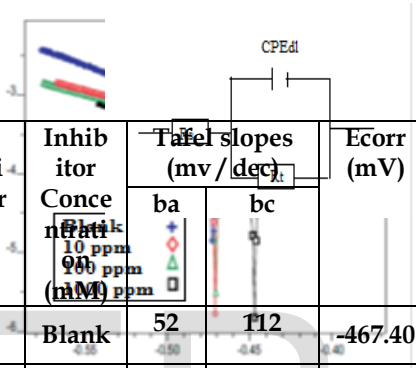


Figure 5: Tafel polarization plot for Mild Steel In STTP - Acid Solution

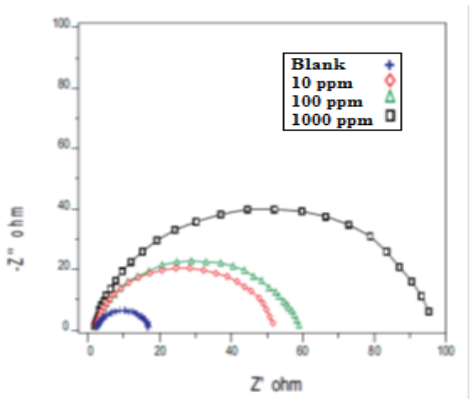


Figure 6: Nyquist plot for Mild Steel In STTP – Acid Solution

Table 6: Impedance parameters of Mild Steel at various concentrationsof polymers in H_2SO_4

It is a parallel combination of charge transfer resistance $R_t$and constant phase element of double layer CPE_{dl} both inseries with the solution resistanceR_s.

The impedance spectra exhibit a single semi-circle. It is clearly seen that the addition of increasing concentrations of the inhibitor causes an increase in the diameter of the semi-circle. The values of $R_t$and C_{dl} calculated from the Nyquist plots are given in Table 6.

Inhibitor	Inhibitor concentration (ppm)	R_t (ohm)	Cdl (µF/ cm²)	Inhibition Efficiency (%)
Blank	-	11.3	33.6	-
STTP	10	45.4	24	75.11
	100	81.1	23.3	86.07
	1000	86.3	20.9	86.91
SBTP	10	26.2	30.4	57.25
	100	37.99	23.9	70.52
	1000	53.9	20.9	79.22
SVTP	10	42.6	22.3	73.47
	100	51.1	25.2	77.89
	1000	79.9	11.7	85.86

The presence of polymers enhanced the value of R_t in acid solution. The increase in the value of R_t with the inhibitor concentration led to the increase in the Inhibition efficiency. Similarly the double layer capacitance decreases in the presence of inhibitors. The decrease in C_{dl} suggests that the adsorption of the inhibitors takes place on the metal surface from acid solution.

SEM Studies:

SEM photographs were taken for the selected sample (STTP) to monitor the effect of corrosion on the morphological properties of mild steel.Fig 7 show the SEM image of mild steel surface immersed in blank 1M H_2SO_4 and 1M H_2SO_4 containing10 and 1000 ppm of STTP .The morphology of mild steel specimen in the absence of inhibitor is very rough and the surface is damaged due to metal dissolution. But the presence of 10ppm polymer suppresses the corrosion rate and the surface damage has been diminished considerably. At 1000ppm of STTP it is found that the surface smoothness was improved and the metal surface is free from corrosion due to better coverage of the metal surface.

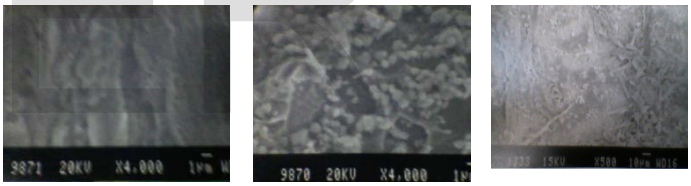


Figure 7: SEM images of the mild steel specimens in the absence and presence of 100 and 1000 ppm inhibitor (STTP) respectively.

Molecular structure and corrosion inhibition:

Comparison of the inhibition efficiency of the three polymers for the corrosion of mild steel in 1M H_2SO_4 obtained by all the methods show the following order,

STTP>SBTP>SVTP

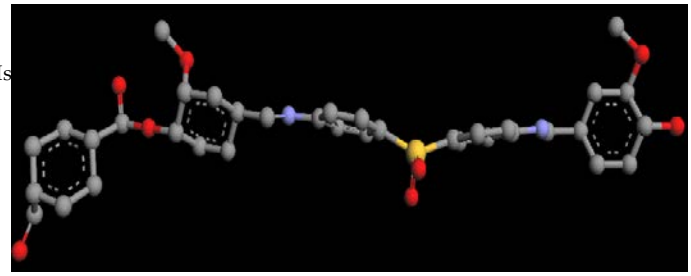
The inhibition effect of these compounds is attributed to the adsorption of the polymers on the metal surface. The adsorption is assumed to take place through the heteroatoms and the phenyl rings present on the polymer chain backbone.

SVTP containing electron releasing methoxysubstituent (σ=-0.27) is actually expected to enhance the electron density on the aromatic ring and to increase the inhibition efficiency. But it shows lower inhibition efficiency (85% at 1000 ppm). A possible explanation for this is that the –OCH3 substituent located on the polymer chain generates a steric effect which perturbs the geometry of the polymeric chain and avoids complete coverage of metallic surface. This results in a decrease in the protection of mild steel against its dissolution. A similar explanation was offered by Rosa Vera et al[11] for the high degree of protection of polyanilinethan that of poly(o-methoxyaniline).SVTP which shows the stericeffect due to methoxygroup on the geometry of the polymer.

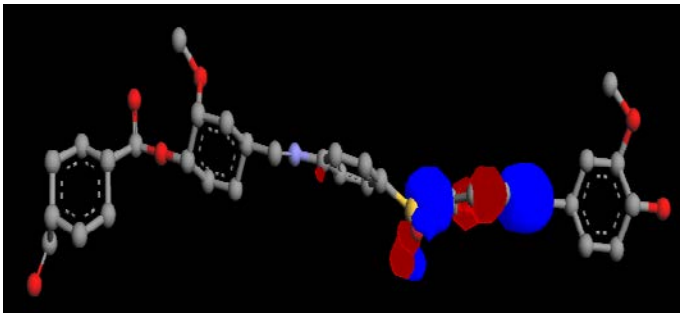
Computational studies:

Table 7: Parameters derived from computational studies

	Core repulsion (au)	geometry Energy (kcal/mol)	(kcal/mol)
STTP			29
SBTP	1414.62	-132469.7915	26206.8769
SVTP	1696.42	-131644.6731	47643.4700



Electron density map



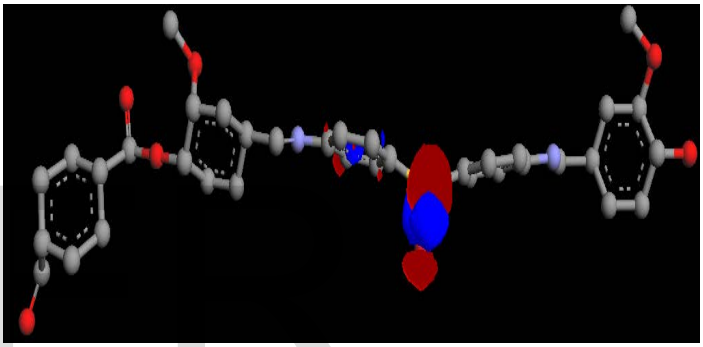
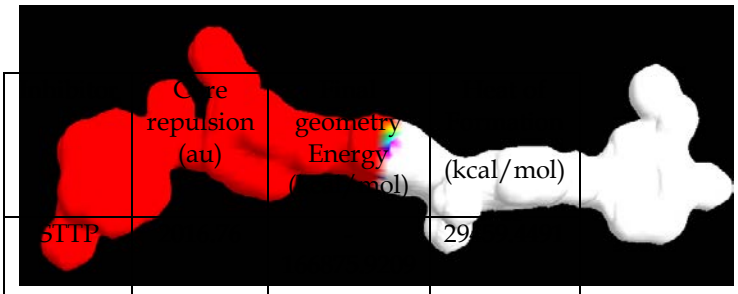


Figure 8: Optimized geometry, HOMO, LUMO and electron density map of SVTP

Optimized geometry

HOMO

LUMO



CONCLUSION: The optimized geometry of thepolymersalc

- Three polymers Viz. STTP,SBTP and SVTP have been synthesized and evaluated as good corrosion inhibitors for mild steel in 1M sulphuric acid.
- The order of inhibition efficiency, STTP> SBTP> SVTP
- The inhibition efficiency increases with increase in concentration and decreases with increase in temperature.
- The polymers behave as mixed type and obey Langmuir adsorption isotherm.

ACKNOWLEDGEMENT

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