Experimental Studies on Corrosion Inhibitive Effect of Surfactants

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Abstract

The corrosion inhibition performance on mild steel in acid solution was studied by different techniques. The inhibition efficiency of each inhibitor increased with increasing the concentration of inhibitor. The inhibition effect of Sodium dodecyl sulphate on corrosion of mild steel in acid solution was investigated using polarization studies. The inhibition efficiency was increased with an increase in inhibitors concentration but decreased with an increase in temperature. The mechanism of the inhibition process was also discussed with quantum chemical calculations of the investigated inhibitors. The inhibition efficiency of additives depends on factors which include the number of adsorption sites, charge density, molecular size and mode of interaction with the metal surface. The adsorption depends mainly on the electronic structure of the molecules. Recently, some work has been done on the theoretical prediction of corrosion inhibition efficiencies of some organic inhibitors, based on quantum chemical calculations. Although these semi-empirical calculations tend to be complex in case of large molecules, yet they are useful tools, which help in finding more effective corrosion inhibitors. The approach is based on correlation between the dependent variables (inhibition efficiencies) and the set of independent variables, viz., energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), dipole moments, etc.

Keywords: Corrosion inhibitors, Surfactants, Mild Steel, Adsorption, SDS

INTRODUCTION

Corrosion inhibitors are used for protection against corrosion in acidic media. For example the mild steel corrosion in acid solution are controlled effectively by using organic substances such as nitrogen (N), oxygen (O), Sulphur (S) as these get adsorbed on metal surface. The corrosion inhibition by surfactant molecules and the surfactant's ability to aggregate at interfaces is related to each other . Due to amphiphilic nature, the surfactants get adsorbed on surfaces and form aggregates with different methodologies which potentially provide different extent of corrosion inhibition. The most well known inhibitors are surfactants containing long chain of carbon atoms and heteroatoms like nitrogen, sulphur and oxygen atoms. .This article investigates the inhibition of corrosion of mild steel in acidic medium using Sodium dodecyl sulphate by using different techniques. The effectiveness of the inhibitor is explained on the basis of electrochemical parameters obtained from Galvanostatic studies. A clear understanding of the nature of adsorption on mild steel specimen exposed to the inhibited and uninhibited solutions of different concentrations has been made with the use of Scanning Electron Microscopy (SEM).

EXPERIMENTAL DETAILS

In the present study, flat mild steel coupon was used. The solutions used were prepared in conductivity water. Sodium dodecyl sulphate (SDS) was used. All reagents used in the study were of analytical grade. The working electrode was prepared using a square mild steel rod. Polishing was done using 4/0 polishing paper. These mild steel coupons were used as working electrodes for the corrosion studies immediately.
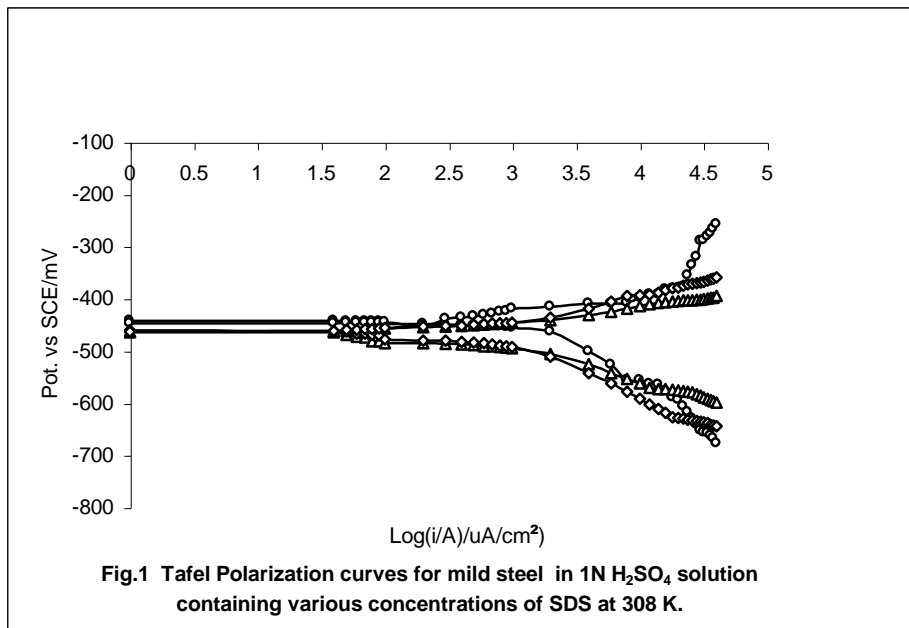
Galvanostatic Polarization Studies

The galvanostat assembled indigenously having the range of 10mA to 100mA was used to measure the potential of the metal electrode vs. reference electrode. A constant distance of approximately 1-2 mm between the tip of Luggin capillary and working electrode surface was maintained. The counter electrode used was of Platinum electrode. The potential of working electrode was measured against Saturated Calomel Electrode (SCE). Steady State potentials were achieved in three hours.
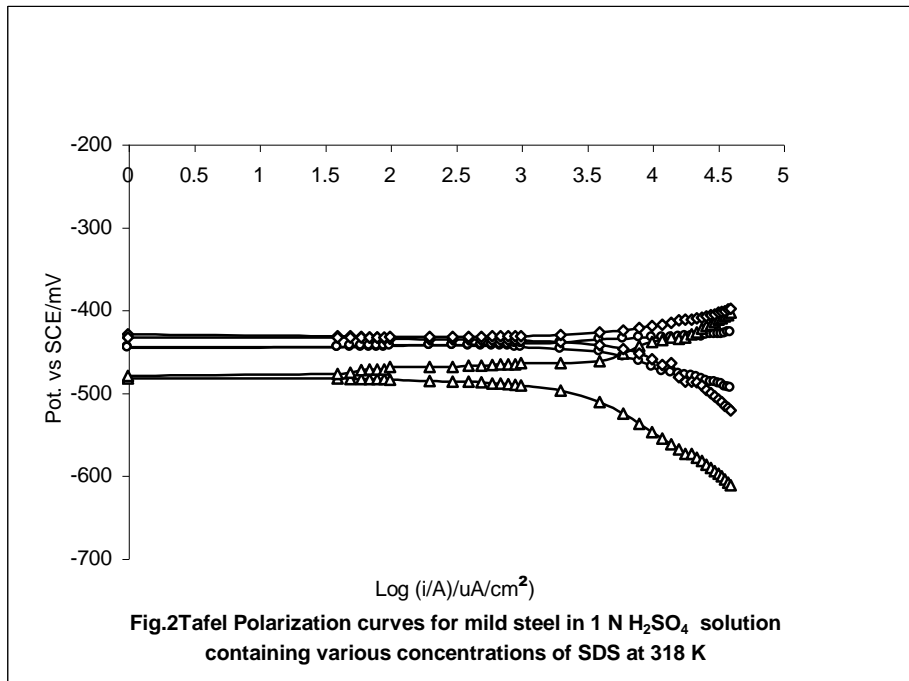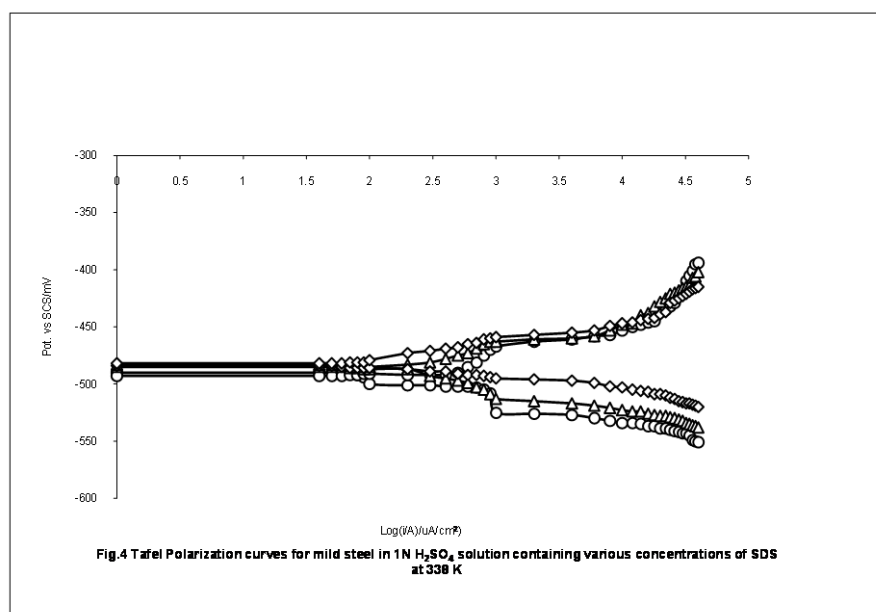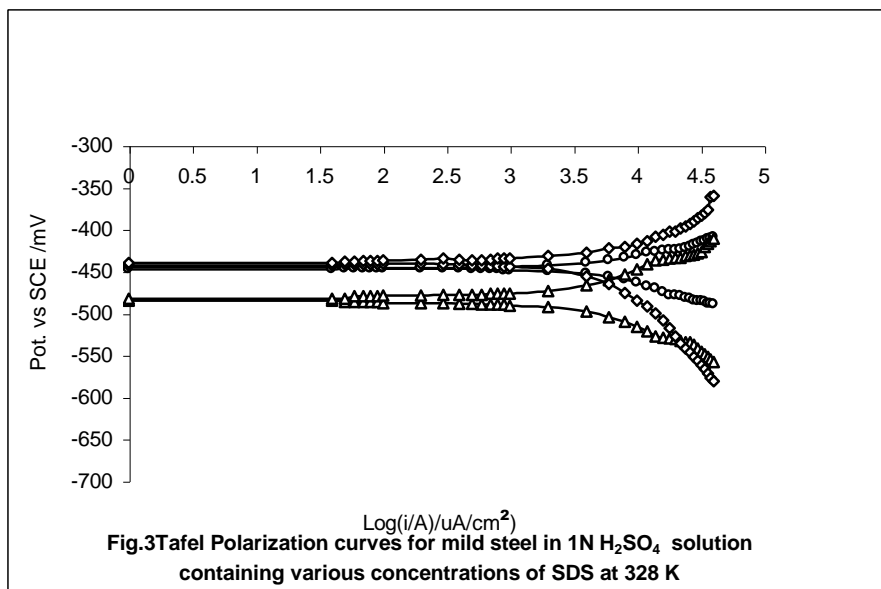
RESULTS AND DISCUSSION

Galvanostatic polarization studies

Galvanostatic studies on Mild Steel in 1N H_2SO_4 in the presence and absence of SDS at different temperatures. In the present study the change in concentrations of SDS effects on Tafel Polarization curves for mild steel has also been studied in Figs.1-4.

Fig.1 Tafel Polarization curves for mild steel in 1N H_2SO_4 solution containing various concentrations of SDS at 308 K.

☐- 0 M SDS   O- 10^{-3} M SDS

◇- 10^{-5} M SDS   Δ- 10^{-7} M SDS

Fig.2 Tafel Polarization curves for mild steel in 1 N H_2SO_4 solution containing various concentrations of SDS at 318 K

Fig.3 Tafel Polarization curves for mild steel in 1N H$_2$SO$_4$ solution containing various concentrations of SDS at 328 K

Fig.4 Tafel Polarization curves for mild steel in 1N H$_2$SO$_4$ solution containing various concentrations of SDS at 338 K

□- 0 M SDS   O- 10^{-3} M SDS
◇- 10^{-5} M SDS   Δ- 10^{-7} M SDS

The electrochemical parameters so obtained are listed in Table 1. In different concentrations SDS inhibits corrosion of mild steel to different extent. The percentage decrease in corrosion current was found to increase with respect to increase in concentration of surfactant. It is observed that at a given inhibitor concentration, the corrosion current is higher at higher temperatures and this behavior is observed at all concentrations of the inhibitor. At lower temperature, the decrease in corrosion

current with an increase in concentration of SDS is more pronounced than at higher temperature. For example, at 308 K, the corrosion current decreases from 1.259 mA/cm^2 for the uninhibited solution to 0.1585mA/cm^2 for the solution containing the inhibitor (10^{-3} M), while this change is from 6.310 mA/cm^2 to 3.162mA/cm^2 for the above inhibitor concentration at 338 K.

The inhibition efficiency is decreased to 49.88% at the highest temperature (338K) as compared to that of 87.41% at 308 K for 10^{-3} M SDS .This inhibitor is considered as mixed inhibitor.

Table 1: Corrosion Parameters of Mild Steel in 1N H$_2$SO$_4$ in presence of SDS

Temp. (K)	Conc. (mol l^{-1})	-E$_{corr}$ (mV)	I$_{corr}$ (mA/cm^2)	I(%)
308 K	10^{-3}	445.0	0.1585	87.41
	10^{-5}	464.0	0.3162	74.88
	10^{-7}	462.0	0.5012	60.19
	0	479.0	1.259	-
318 K	10^{-3}	445.5	0.6310	74.88
	10^{-5}	481.5	0.7943	68.37
	10^{-7}	432.0	1.585	36.90
	0	484.0	2.512	-
328 K	10^{-3}	446.5	1.585	60.18
	10^{-5}	484.0	1.995	49.88
	10^{-7}	441.5	3.162	20.57
	0	485.0	3.981	-
338 K	10^{-3}	480	3.162	49.88
	10^{-5}	485	3.981	36.90
	10^{-7}	486	5.012	20.57
	0	480	6.310	-

Temperature Kinetics Studies on Acid Corrosion of Mild Steel in the presence of SDS

A number of investigators have studied the effect of temperature on acid corrosion of metals in the presence and absence of surfactants[1-4] .The adsorption and corrosion rate kinetics has been examined using Langmuir's adsorption isotherm and the Arrhenius equation. Because of multi-layer adsorption of the additives, viz., SDS over the corroding surface the corrosion reactions become more complicated. Since the corrosion current is directly related to the corrosion rate at a particular temperature then I % can be represented as

$$I \% = (i_o - i_c) / i_o \times 100$$

where, i_o is the corrosion current in uninhibited solution and i_c is the corrosion current in inhibited solution.

If it is assumed that inhibitor gives a mono-layer adsorption covering at any instant, θ, a fraction of the metal surface covered in a uniform or random manner and the free surface, $(1-\theta)$, then

$$(1 - \theta) = i_c / i_o$$

and can be computed readily from the results within certain range of inhibitor concentrations and temperatures. When mono-layer adsorption is present over mild steel surface, Langmuir's adsorption can be written as

$$Log \ [\ \theta / (1 - \theta)] \ = Log \ A + Log \ C - (\ Q / 2.303 \ RT)$$

Therefore, a plot of $Log \ [\ \theta / (1 - \theta)]$ vs. $Log \ C$ at constant temperature should be a straight line. Similarly a plot of $Log \ [\theta/(1-\theta)]$ vs. $1/T$ should be a straight line with the slope of $-Q/2.303R$ from which the average heat of adsorption (Q) can be calculated. Since corrosion rates are directly related to corrosion currents, their dependence on temperature can be expressed by the equation

$$Log \ i_c = A / T + B$$

where, A and B are corrosion constants.

The value of effective activation energy, $E_{eff.}$ can be written as

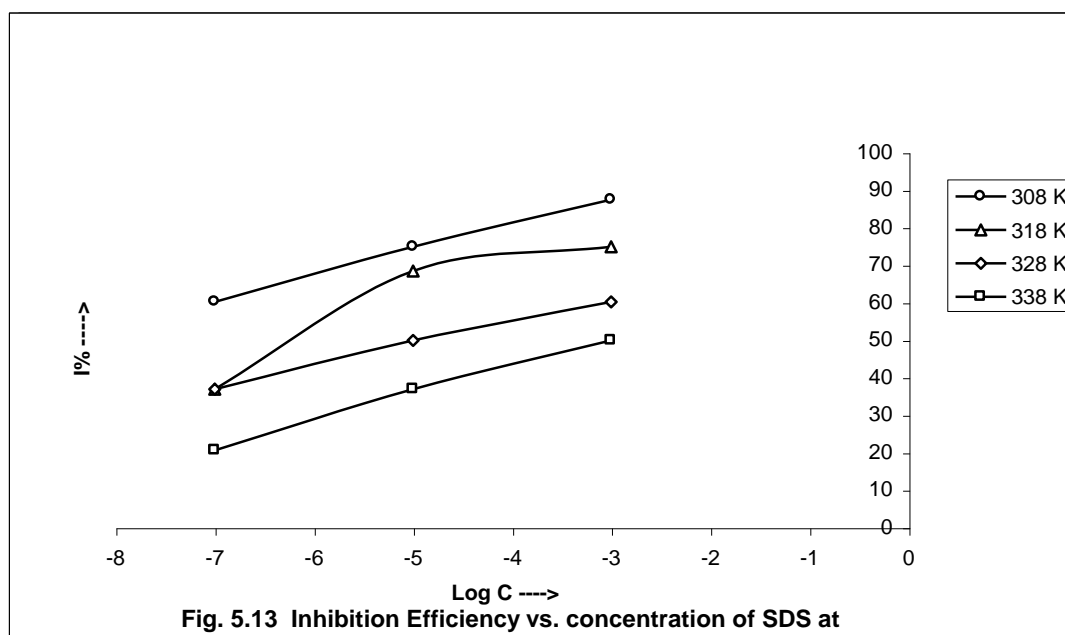$$E_{eff.} = - (2.303). (1.987) \ d \ (log \ i_c) \ /d \ (1/T)$$

In order to study the effects of SDS an acid corrosion of mild steel, the inhibition efficiencies and surface coverage at various temperatures viz. 308 K, 318 K, 328 K and 338 K were determined from the corrosion current values reported in Table 2.
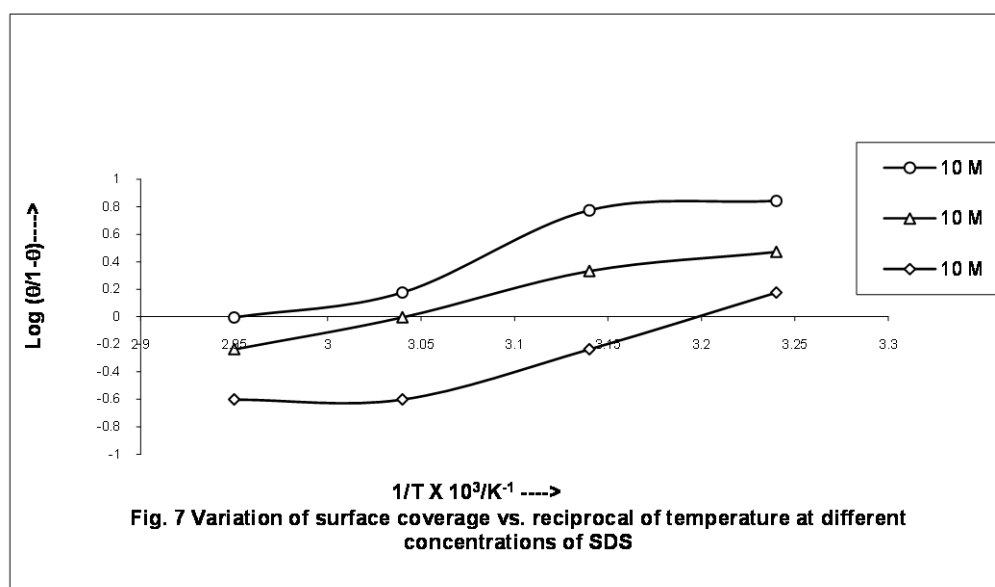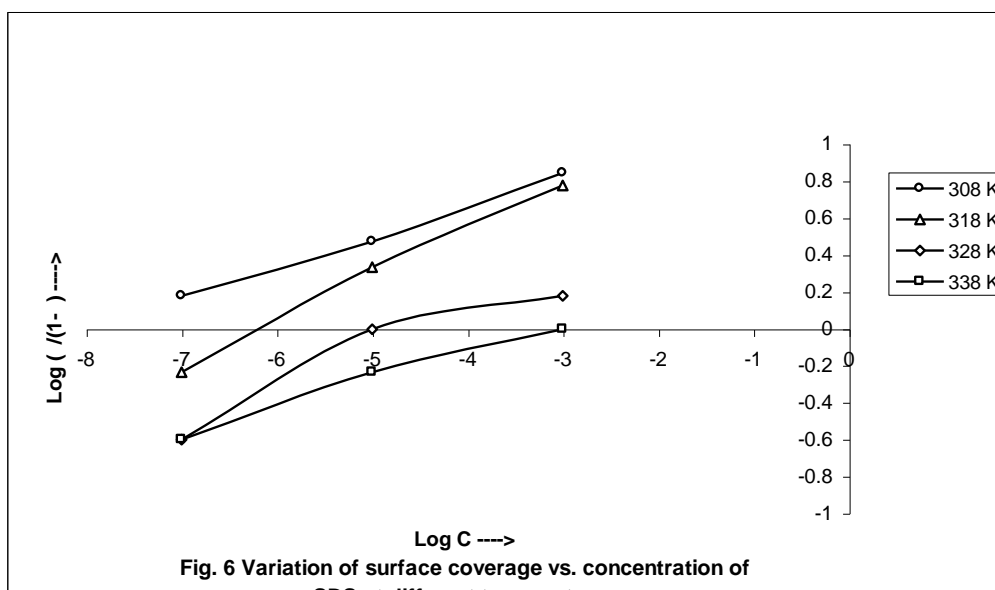
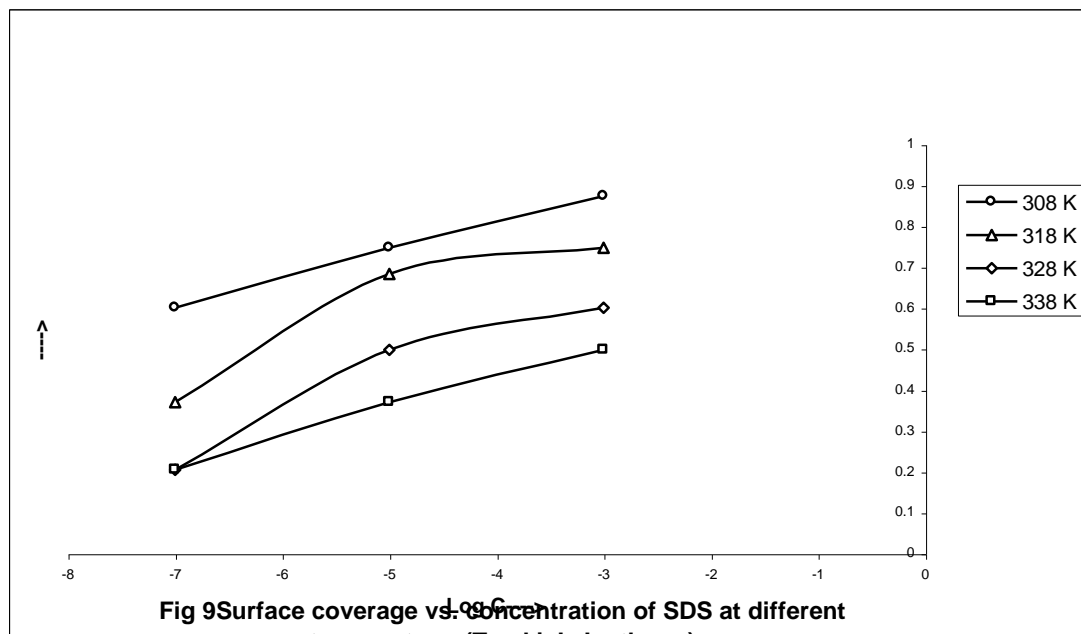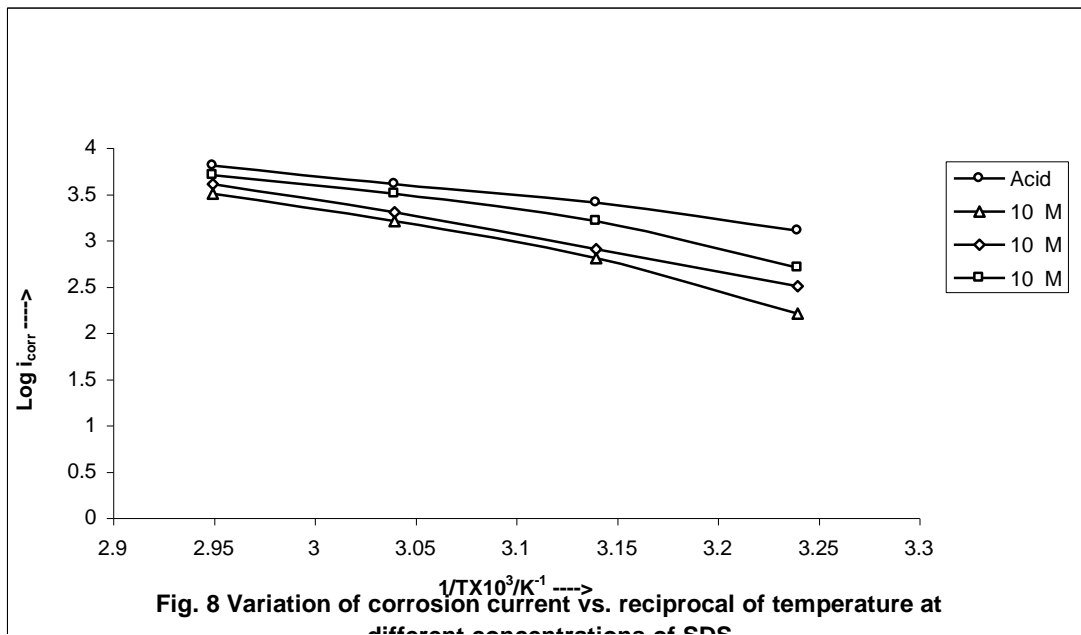**Table 2:** Corrosion parameters of Mild Steel in IN H_2SO_4 in the presence of SDS.

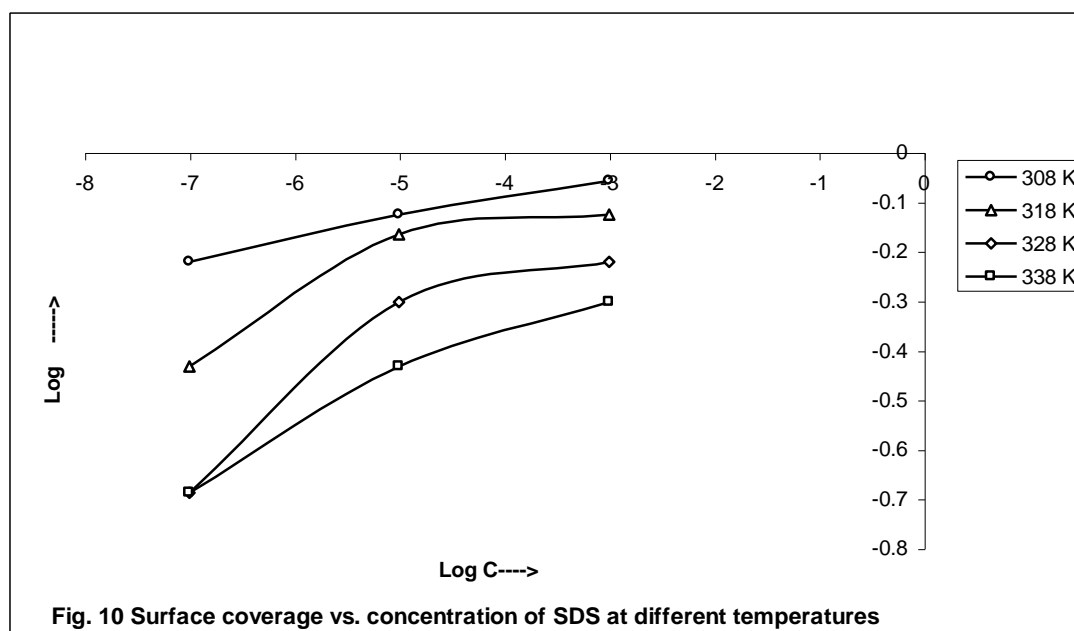| Temp. (K)	Conc. (mol l^{-1})	i_{corr} (mA cm^{-2})	Log (i_{corr})	I%	θ	$\theta/1-\theta$
308	10^{-3}	0.1585	2.2	87.41	0.874	6.93
	10^{-5}	0.3162	2.5	74.88	0.748	2.96
	10^{-7}	0.5012	2.7	60.19	0.601	1.50
	H_2SO_4	1.259	3.1	---	---	---
318	10^{-3}	0.6310	2.8	74.88	0.748	5.93
	10^{-5}	0.7943	2.9	68.37	0.683	2.15
	10^{-7}	1.585	3.2	36.90	0.369	0.58
	H_2SO_4	2.512	3.4	---	---	---
328	10^{-3}	1.585	3.2	60.18	0.601	1.50
	10^{-5}	1.995	3.3	49.88	0.498	0.99
	10^{-7}	3.162	3.5	20.57	0.205	0.25
	H_2SO_4	3.981	3.6	---	---	---
338	10^{-3}	3.162	3.5	49.88	0.498	0.99
	10^{-5}	3.981	3.6	36.90	0.369	0.58
	10^{-7}	5.012	3.7	20.57	0.205	0.25
	H_2SO_4	6.310	3.8	---	---	---

The graph of I% vs. log C for SDS at four temperatures is shown in Fig.5. The variation of corrosion current with temperature as shown in Fig. 8, Temkin's and Freundlich's isotherms are drawn and depicted in Figs. 9 and 10 respectively. From Fig. 5 it is clear with the increase in concentration, the efficiency increases and with the increase in temperature. from 308K to 338K, the efficiency decreases. As shown in Fig. 6, the curves are straight line over certain range of concentration . From the plots of Log i_{con} vs. I/T, shown in Fig. 8, the effective activation energies can be calculated at different concentrations The values of effective activation energies indicate higher values in the presence of inhibitors than in the absence of it. According to Putilova's classification this belongs to first category of inhibitors which retard the corrosion process at lower temperatures but this inhibition action is reduced considerably at higher temperatures. The corrosion behavior of mild steel at different temperatures in the presence of SDS as reported here reveals that the metal surface

and this coverage shows an almost uniform trend but not a linear relationship with inhibitor concentration. The surface coverage readily changes with the change in temperature and a uniform trend of less coverage at higher temperature can be seen for all concentrations. The two other isotherms, namely Temkin's and Freundlich's isotherms shown in figs also reveal a similar trend of adsorption isotherm at all temperatures and concentrations at which the study has been carried out. It can be observed from Fig. (I% vs. Log C) that this is fairly good inhibitor at lower temperatures and higher concentrations. Its performance decreases only at 338K and with decrease in concentration. The electrostatic interaction between the inhibitor and the metal surface probably lead to a barrier between the metal surface and reactive sites. This barrier or adsorption becomes weaker with increase in corrosion rates which is the case at lower concentrations. The other factor which inhibits during the anodic polarization in the formation of an adduct of the type $(M\text{-}In)_{ads}$ or $(M\text{-}In\text{-}OH)_{ads}$ or $(M\text{ -}OH\text{-}In)_{ads.}$

Fig. 5.13 Inhibition Efficiency vs. concentration of SDS at

Fig. 6 Variation of surface coverage vs. concentration of SDS at different temperatures

Fig. 7 Variation of surface coverage vs. reciprocal of temperature at different concentrations of SDS

Fig. 8 Variation of corrosion current vs. reciprocal of temperature at different concentrations of SDS

Fig 9 Surface coverage vs. concentration of SDS at different temperature (Freundrich isotherm)

Fig. 10 Surface coverage vs. concentration of SDS at different temperatures

Quantum Chemical Analysis

The relation between inhibition characterstics and quantum chemical data shows that Log i_{corr} mostly depends upon the energy of HOMO and LUMO[5-7] ·In addition, the data can also be related to dipole, charge on metal and the shapes of the additives. The energy of HOMO is the theoretical analogue of the ionization potential of the additive whereas the energy of LUMO represents electron affinity of the substance. In other words, good donors and bad acceptors of electrons are going to be efficient inhibitors. The higher the HOMO and lower the LUMO will be indicators of good inhibitors. Dipole charge values will also indicate that there is a possibility of donation of electrons to the metal surface. The optimized geometries have been carried out by using AM 1 method for the molecules. For these molecules, the various energetic and electronic parameters are given in Table 4.The various plots of electrostatic potential, HOMO, LUMO and optimized geometries of SDS are shown in Figs.11-14. The quantum chemical calculations help to explain the observed corrosion inhibition behavior of the additives as corrosion inhibitors. These studies eliminate the empirical approach of the research work in the field of corrosion inhibition and facilitate scientific studies in selection of new inhibitors. These will also be useful in designing the new inhibitors. These will also be useful in designing the new inhibitors with suitable substituents in the parent skeleton of the additive to increase the electron donation characterstics of the inhibitors for different environments on different surfaces.

Table 3 Calculated values of Q and E$_{eff.}$ for the corrosion of Mild Steel in IN H$_2$SO$_4$
in the presence of SDS.

Concentration(mol l^{-1})	-Q (Kcal mol^{-1})	E$_{eff}$ (Kcal mol^{-1})
10^{-3}	76.46	23.96
10^{-5}	72.50	20.12
10^{-7}	48.50	16.83 B
H$_2$SO$_4$	---	11.44

Table 4 Optimized AM1 Parameters for various inhibitors using Hyperchem 5.1

| Inhibitors → Parameters ↓	SDS
No. of electrons	103
Total Energy (a.u)	-123.40
Energy of HOMO (eV)	-11.1152
Energy of LUMO (eV)	0.3691
Binding Energy (Kcal mol^{-1})	-3845.46
Isolated Atomic Energy (Kcal mol-1)	-73583.6
Electronic Energy (Kcal mol-1)	-451921.5
Core-Core interaction (Kcal mol-1)	374492.45
Heat of formation (Kcal mol-1)	-187.60
Dipole (debyes)	4.217
Total charge on M	2.8695 (for S)
Molecular Point group	C$_1$
Inhibition energy (I%)	87.41
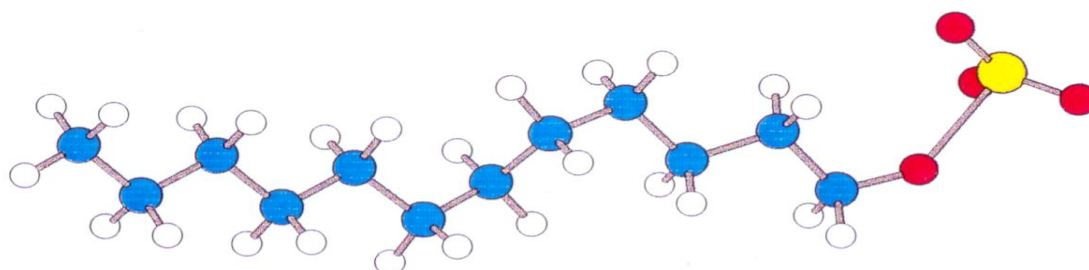
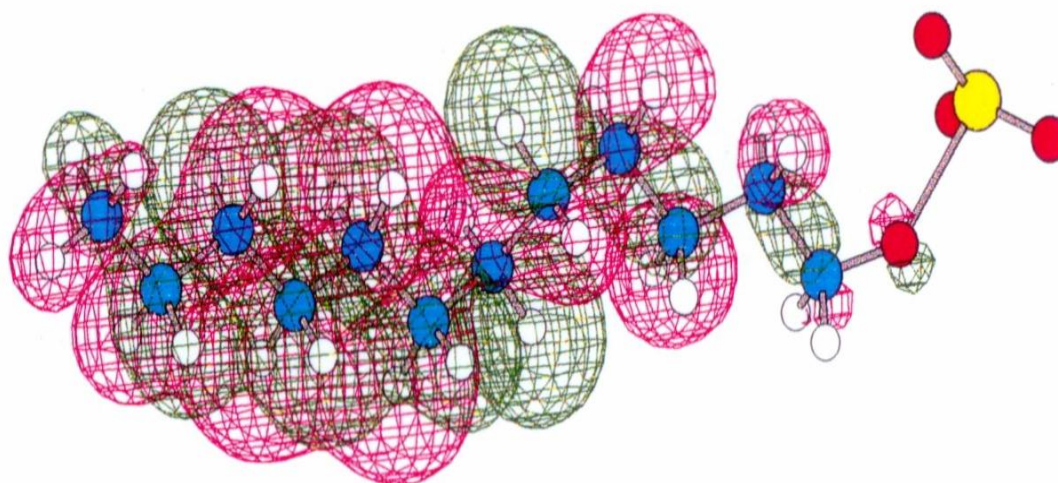**Fig. 11.** Ball and Stick Model of Optimized Geometry of SDS

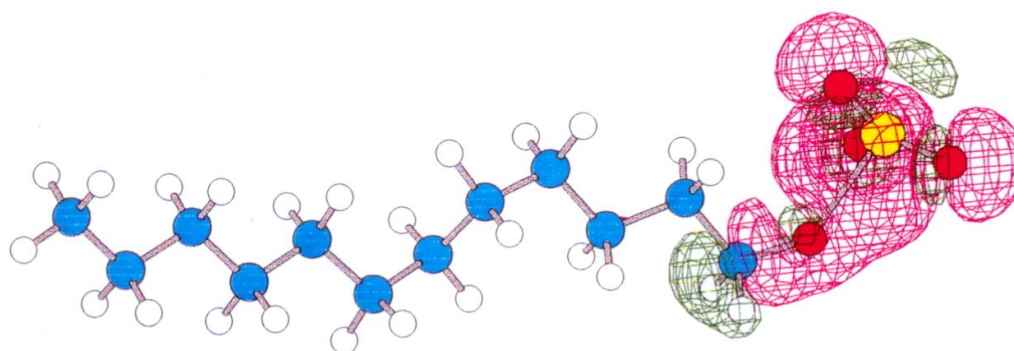**Fig 12.** 3-D Isosurface of Total Charge Density on SDS (HOMO)

Fig.13. 3–D Isosurface of Total Charge Density on SDS (LUMO)
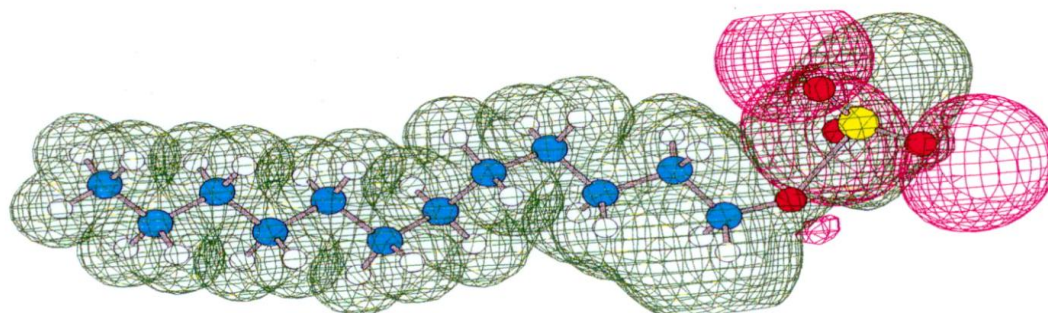
Fig .14. Electrostatic Potential mapped on to 3-D Charge Density Isosurface of SDS

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