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Adsorption and Thermodynamic studies on acid corrosion of Mild Steel in the presence of additives

Mukta Sharma[1] **and Gurmeet Singh**[2]

[1]*Department of Chemistry, Faculty of Engineering & Technology, MRIU, Faridabad - 121001, India*
[2]*Department of Chemistry, Delhi University, Delhi-110007, India*
E-mail: muktapragya@gmail.com

Abstract

The effect of surfactants on corrosion of mild steel in 1N Sulphuric acid was studied using these techniques namely Galvanostatic and Temperature kinetic studies. Corrosion of mild steel in the presence of aerated acid systems increases with rise in temperature. The kinetics of adsorption and corrosion rates of Cetyl Trimethyl Ammonium Bromide (CTAB) and Sodium dodecyl sulphate (SDS), has been examined on the basis of heat of adsorption and activation energy values calculated from Langmuir's adsorption isotherm and the Arrhenius equation. The parameters so obtained were used to explain the effectiveness of inhibitor when present in different concentrations. The results obtained revealed that these act as efficient inhibitors and show very good inhibition efficiency.

Key words: Corrosion inhibitors, Surfactants, Mild Steel, Adsorption.

Introduction

Mild Steel is widely used in variety of industries especially for structural applications. It may come in contact with various acid solutions and corrodes heavily during chemical processes like acid cleaning, transportation of acids, storage of acids, etc. Corrosion of mild steel in the presence of aerated acid systems increases with rise in temperature. The effect of temperature on acid corrosion of metals in the presence and absence of surfactants has been studied by the number of investigators [1-4]. A variety of N containing organic compounds and O containing compounds have been reported as corrosion inhibitors for mild steel.]. Allyl triphenyl phosphonium bromide[5] acts as efficient inhibitor for mild steel in sulphuric acid. The kinetics of adsorption and corrosion rates has been examined on the basis of heat of adsorption and activation energy values calculated from Langmuir's adsorption isotherm and the Arrhenius equation [6]. Some of the additives do not confirm to Langmuirian behavior instead they adsorb on the metal surface according to other types of isotherms, e.g. Frumkin's isotherm, Temkin's isotherm and Freundlich's isotherm. In the presence of additives, viz., CTAB and SDS, the corrosion reactions become more complicated because of multi-layer adsorption of these additives over the corroding surface. In the present work, adsorption behavior has been studied using Langmuir's, Temkin's and Freundlich's isotherms.

$$[\theta / (1 - \theta)] = A\ C \exp(-Q / RT)$$

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- θ), a fraction that reacts with acid as it does in the absence of inhibitor, 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 maintained over mild steel surface, Langmuir's adsorption can be written as

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

Therefore, a plot of Log [θ / (1 – θ)] vs. Log C at constant temperature should be a straight line. Similarly a plot of Log [θ/(1–θ)] vs. 1/T at constant temperature 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

$$\text{Log}\ i_c = A / T + B$$

where, A and B are corrosion constants.

For the corrosion process the value of effective activation energy, E_{eff}. can be written as

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

The effective activation energy can be calculated from the slope of the plot of log $i_{corr.}$ vs. 1/T at constant inhibitor concentration. The Langmuir's isotherm ignores the possibility that the initial overlayer may act as a substrate for the further adsorption. Another assumption of this isotherm is the independence and equivalence of adsorption sites. The deviation from the Langmuir's expression can often be traced to the failure of these assumptions e.g. the enthalpy of adsorption often becomes less negative as θ increases, which suggests that the energetically most favourable sites are occupied first. Various attempts have been made to take these variations into account .The Temkin's isotherm,

$$\theta = a \ln (b_c),$$

where, a and b are constants, corresponds to supposing that the adsorption enthalpy changes linearly with concentration. The Freundlich's isotherm,

$$\theta = k\, c^{1/n} ,$$

corresponds to a logarithmic change. Different isotherms agree with experiment more or less over restricted ranges of concentration but they remain largely empirical. To evaluate the nature and strength of adsorption, the experimental data is fitted to the isotherm and from the best fit the surface coverage and thermodynamic data for adsorption can be evaluated.

Experimental

Materials

Flat mild steel of size 1cm X 1cm (with data C= 0.15%, Si = 0.8%, S = 0.025%, P = 0.025%, Mn = 0.02%) was used. The solutions used for the corrosion studies were prepared in conductivity water. Sulphuric acid (E Merck, India) was used for the preparation of solutions. Sodium dodecyl sulphate (SDS) was obtained from Fluka. All reagents were used as received and were of analytical grade.

Preparation of working Electrode

A square mild steel rod soldered on one end with an insulated Copper wire and carefully coated with an epoxy resin (araldite) leaving the circular flat surface exposed uncoated for the corrosion studies. The exposed metal surface was then abraded with different grades of emery papers of variety 150, 320, 400, 600 and 1200 respectively. This was finally polished by 4/0 polishing paper to mirror like surface followed by washing and dried in a desiccator for twenty-four hours. These mild steel coupons were used as working electrodes for the corrosion studies immediately.

Galvanostatic Polarization Studies

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

For a number of times for each set and the reproducible data have been recorded.

Results and Discussion

Galvanostatic polarization studies

Galvanostatic cathodic and anodic polarization studies on Mild Steel in 1N H_2SO_4 in the presence and absence of SDS at different temperatures, viz., 308 K, 318 K, 328 K and 338 K have been studied. The effect of change in concentrations of SDS on Tafel Polarization curves for mild steel has also been studied. Figs.1-5 show the plots of Logarithms of true current density against the corresponding electrode potential for mild steel in H_2SO_4 in the presence and absence of SDS at different temperatures, which are measured against SCE. The electrochemical parameters so obtained are listed in Table 1. It is clear from the table that SDS inhibits corrosion of mild steel to different extent when present in different concentrations. The variation in the inhibitor concentration is found to cause considerable change in the corrosion current. The increase in concentration of SDS leads to low value of corrosion current (i_{corr}). The percentage decrease in corrosion current was found to increase with respect to increase in concentration of surfactant. The effect is most pronounced at concentration 10^{-3} M.

It is further seen that at a given inhibitor concentration, the corrosion current is higher at higher temperatures and this trend 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. At the highest temperature, i.e., at 338 K, the inhibition efficiency is reduced to 49.88% as compared to that of 87.41% at 308 K for 10^{-3} M. SDS has produced no appreciable shift in open circuit potential towards any direction. This indicates that this additive acts as the mixed type inhibitor and influences both the cathodic and anodic partial processes to an equal extent.

Temperature Kinetics studies on Acid Corrosion of Mild Steel in the presence of CTAB.

Since the corrosion rates are directly related to corrosion current, the inhibition efficiencies (I%) for different concentrations of CTAB at 308 K, 318 K, 328K and 338K were calculated and tabulated in Table 1. The graph of I% vs. log C for CTAB at four temperatures is shown in Fig.1. Figs 2 and 3 show the graph of Log ($\theta/1-\theta$) is Log C and I/T respectively whereas the variation of corrosion current with temperature as shown in Fig. 4. Temkin’s and Freundlich’s isotherms are drawn and depicted in Figs. 5 and 6 respectively. It can be seen from Fig. 1 that the efficiency increases with the increase in concentration and decrease with the increase in temperature from 308K to 338K. The plots of Log $(\theta/(1-\theta))$ vs. Log C should be a straight line but as shown in Fig. 2, the curves are straight line over certain range of concentration but no general agreement with simple Langmuir's adsorption isotherm can be claimed over a wide range of concentrations Langmuir's general adsorption theory is inadequate to explain because of the tendency to adsorb in a multi -layered manner. In order to obtain an approximate average heat of adsorption (Q) of CTAB over metal surface in IN Sulphuric acid the plots of Log $(\theta/1-\theta)$ vs. 1/T can be used as given in Fig. 3. The values of Q are calculated from straight-line portions of the curve for the various concentrations of the inhibitor and are reported in Table 2.

The shifting of potential to more cathodic values is indicative of anodic polarization if accompanied by a decrease in the corrosion rate. Thus, the action of many inhibitors at the anodic areas (anodic inhibitors) has been shown by means of potential.

Therefore, the adsorption of the inhibitor at elevated temperatures are hindered by two processes viz.,

a. time lag between the process of adsorption and desorption, becomes shorter at higher temperatures; and
b. the molecular film gets deprotonated which leads to desorption leading to enhanced corrosion.

Calculations reveal that the values of Q support chemisorption process and this is the reason that I% remains as 92% at 308 K at highest concentration. From the plots of Log i_{con} vs. I/T, shown in Fig. 4, the effective activation energies can be calculated at different concentrations. In the present case, the effective activation energies are found to be higher than the activation energy of the corrosion process in IN sulphuric acid except at 10^{-5} M concentration. This behavior reveals that CTAB molecules are very well adsorbed over the metal surface at lower temperatures. This indicates that CTAB belongs to first category of inhibitors as classified by Putilova. This type of inhibitor retards the corrosion at ordinary temperature but they do not perform as well at elevated temperatures.

Therefore, from above results, it can be seen that this inhibitor is very well adsorbed over the metal surface at all concentrations but only at lower temperature i.e. 308 K. The strong adsorption covers the surface forming a barrier of inhibition very high (due to chemisorption). The two processes that govern the adsorption of CTAB at a particular temperature are:

- Ion-pair adsorption between protonated molecules and the negatively charged metal surface (as per galvanostatic results too), and
- By interaction through a lone pair of electrons on N atom of the additive and positively charged metal surface.

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

The various plots for SDS are given in Figs. 7 - 12 The plots of Log (θ/1-θ) vs. 1/T and Log i_{corr} vs. 1/T in Figs. 9 and 10 curves show that Langmuir's general adsorption theory as discussed earlier in the case of CTAB is inadequate in explaining the above results at all temperatures and concentrations. The additive is unable to maintain mono-layer adsorption and tends to be multi-layer adsorption. Heats of adsorption and effective activation energies are calculated from the slopes of the straight line portions of Figs. 9 and 10 respectively and reported in Table 4.

The values of heat of adsorption may be regarded as one representing chemisorption for all concentrations. From surface coverage vs. Log C curves, it becomes clear that this additive is uniformly adsorbed over the metal surface at all the three concentrations. This coverage decreases with increase in temperature as is obvious from the same plot once again. 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 once again 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.11 and 12 also reveal a similar trend of adsorption isotherm at all temperatures and concentrations at which the study has been carried out.

It can be concluded from Fig.7 (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 $(M\ \text{-}OH\text{-}In)_{ads.}$

In the above case, also there is intermixing of adsorption various species during oxygen reduction reactions and metal dissolution reactions. This should result in change in the adsorption mechanism by giving irregular trend in the various Tafel slopes. This trend as is revealed from the Tafel slope values as indeed irregular as indicated in Table 3. A zig-zag structure of this additive shows that at higher concentrations, the molecules can align better to cover a fairly large number of active sites leading to higher inhibition efficiency. As the concentration of the additive is reduced at covers the surface to a considerably less extent, which results in lower inhibition efficiency. Here, also it has been seen that the adsorption is very strong and is mainly chemisorption as revealed from the entries in Table 4 but for any given concentration, inhibition efficiency decreases with increase in temperature which again is due to the shortening of time-lag between adsorption and desorption.

Conclusions

These inhibitors namely CTAB and SDS are found to be very effective inhibitors for the corrosion of mild steel from 35°C to 65°C particularly at 10^{-3}M concentration of inhibitor. Langmuir's adsorption theory is inadequate in explaining the results over wide range of concentrations. These inhibitors show multi-layer adsorption particularly at higher concentrations. The inhibition action is mainly due to their adsorption through the long chain interactions assisted by lone-pair of electrons present on heteroatoms (N, S) present in CTAB and SDS respectively; The value of heat of adsorption, Q and effective activation energies, E_{eff} indicate that all the inhibitors are chemisorbed on the mild steel.

Table 1 Corrosion parameters of Mild Steel in IN H_2SO_4 in the presence of CTAB.

Temp. (K)	Conc. (mol l^{-1})	i_{corr} (mA cm^{-2})	Log (i_{corr})	I%	θ	θ/1-θ
308	10^{-3}	0.100	2.0	92.0	0.920	11.5
	10^{-5}	0.3160	2.5	74.90	0.749	2.90
	10^{-7}	0.5012	2.7	60.19	0.601	1.50
	H_2SO_4	1.259	3.1	---	---	---
318	10^{-3}	0.1995	2.3	84.15	0.841	5.28
	10^{-5}	0.6310	2.8	74.48	0.744	2.90
	10^{-7}	1.000	3.0	60.12	0.601	1.50
	H_2SO_4	2.512	3.4	---	---	---
328	10^{-3}	1.259	3.1	68.37	0.683	2.15
	10^{-5}	1.585	3.2	60.18	0.601	1.80
	10^{-7}	2.512	3.4	36.90	0.369	0.58
	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	0.26
	H_2SO_4	6.310	3.8	---	---	---

Table 2 Calculated Values of Q and E_{eff} for the corrosion of Mild Steel in IN H_2SO_4 in the presence of CTAB.

Concentration (mol l^{-1})	-Q (Kcal mol^{-1})	E_{eff} (Kcal mol^{-1})
10^{-3}	63.82	21.79
10^{-5}	29.45	8.71
10^{-7}	41.02	13.72
H_2SO_4	----	10.75

Table 3 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	θ/1-θ
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	---	---	---

Table 4 Calculated values of Q and $E_{eff.}$ for the corrosion of Mild Steel in IN H_2SO_4 in the presence of SDS.

Concentration (mol l^{-1})	-Q (Kcal mol^{-1})	E_{eff} (Kcal mol^{-1})
10^{-3}	74.46	23.96
10^{-5}	42.50	16.01
10^{-7}	76.50	20.8
H_2SO_4	---	11.44

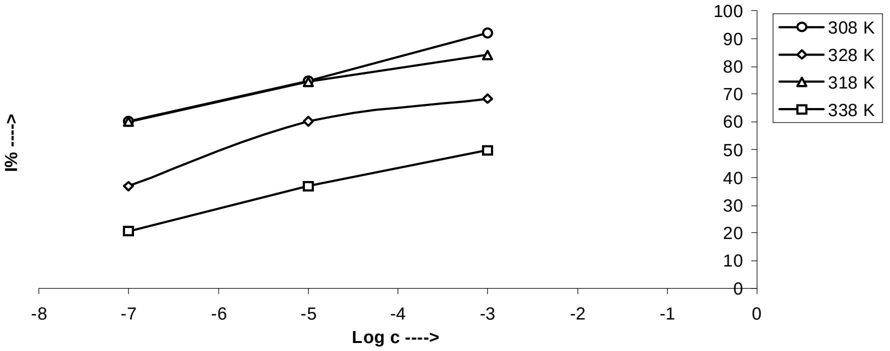

Fig. 1 Inhibition Efficiency vs. concentration of CTAB at different temperatures

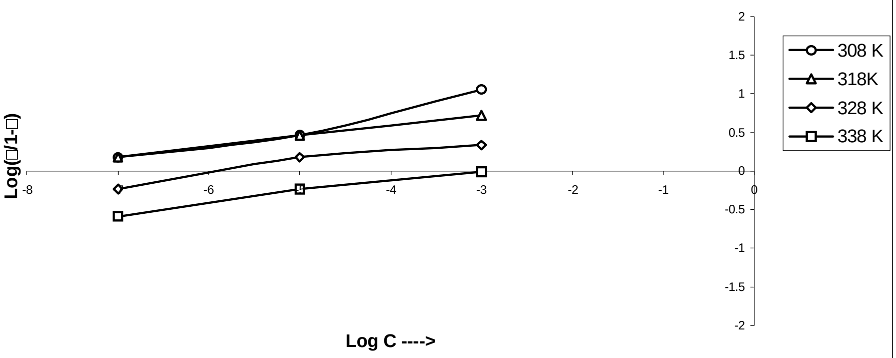

Fig. 2 Variation of surface coverage vs. concentration of CTAB at different temperatures

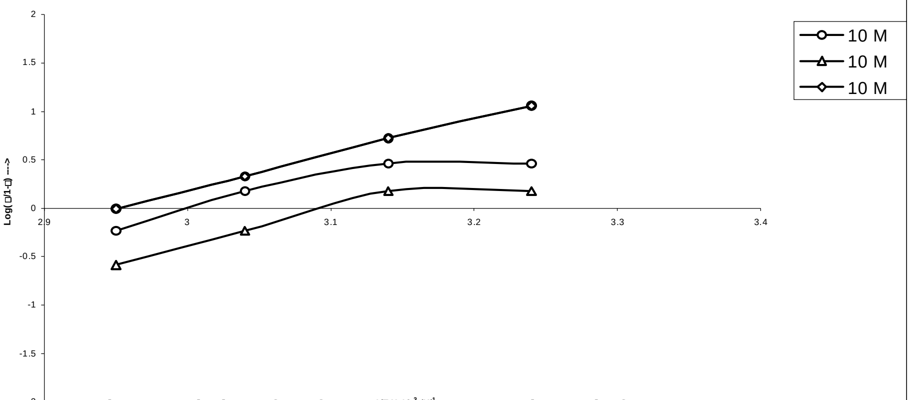

Fig. 3 Variation of surface coverage vs. reciprocal of temperature at different concentrations of CTAB

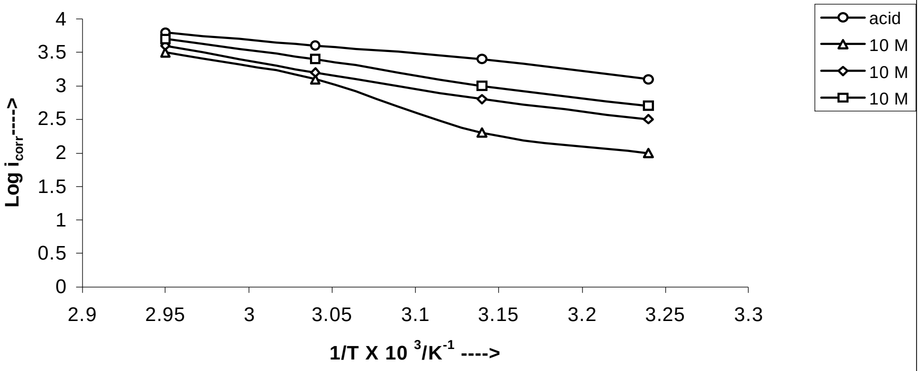

Fig. 4 Variation of corrosion current vs. reciprocal of temperature at different concentrations of CTAB

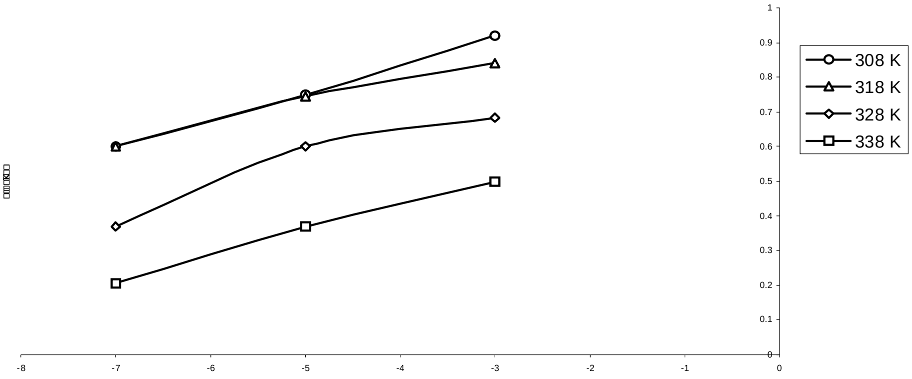

Fig. 5 Surface coverage vs. concentration of CTAB at different temperatures (Temkin's Isotherm)

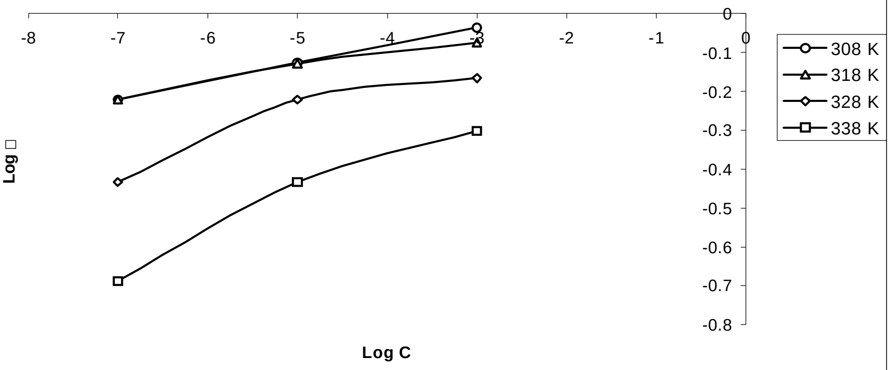

Fig. 6 Surface coverage vs. concentration of CTAB at different temperatures (Freundlich's Isotherm)

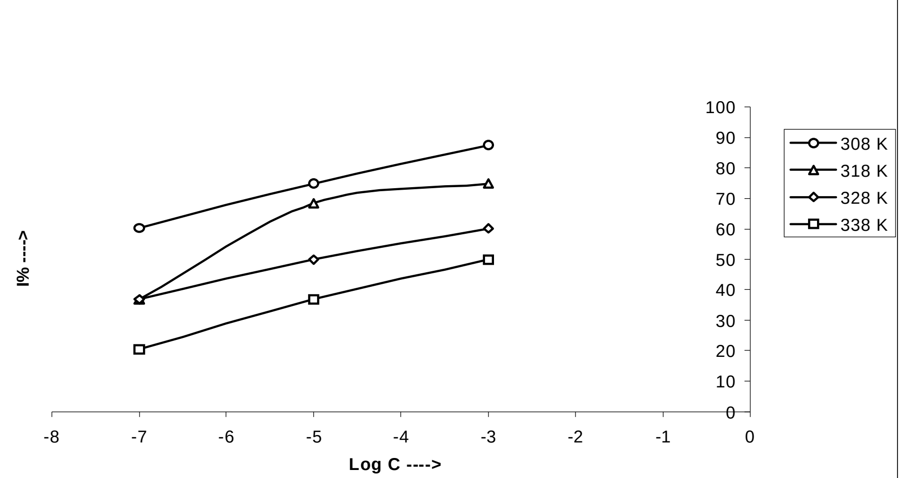

Fig. 7 Inhibition Efficiency vs. concentration of SDS at different temperatures

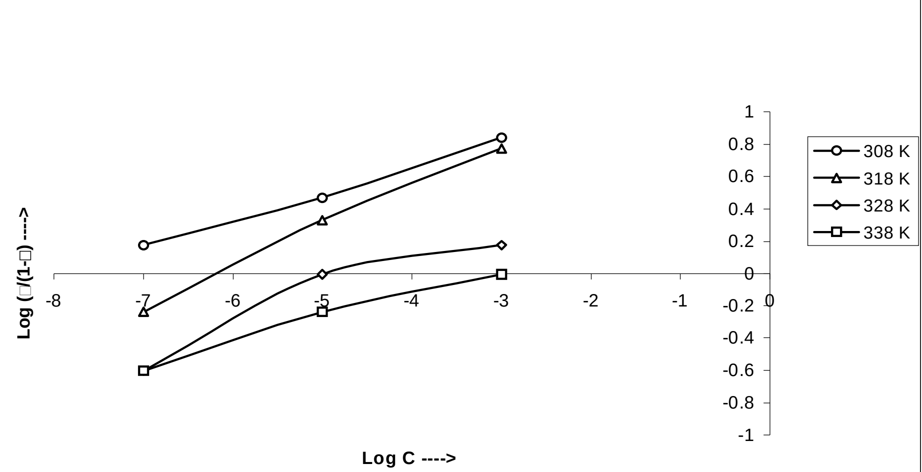

Fig. 8 Variation of surface coverage vs. concentration of SDS at different temperatures

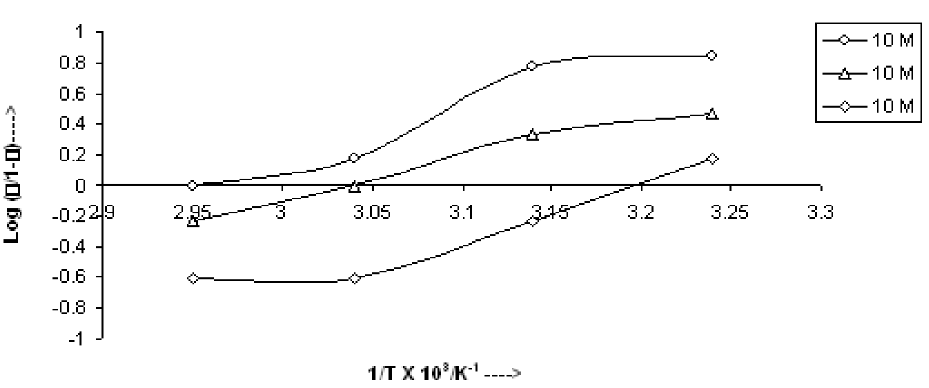

Fig. 9 Variation of surface coverage vs. reciprocal of temperature at different concentrations of SDS

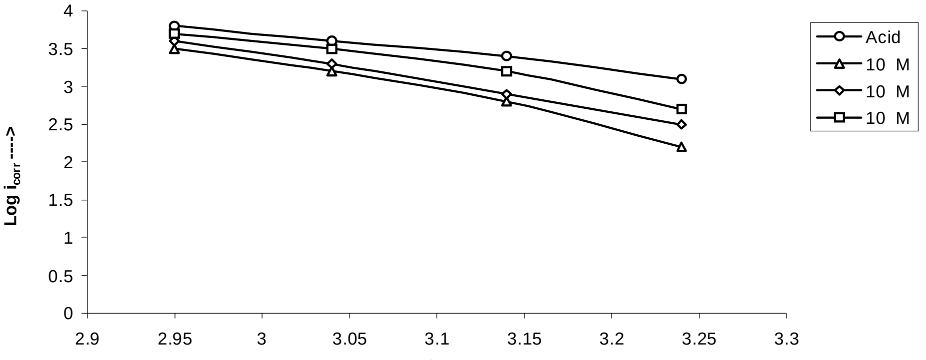

Fig.10 Variation of corrosion current vs. reciprocal of temperature at different concentrations of SDS

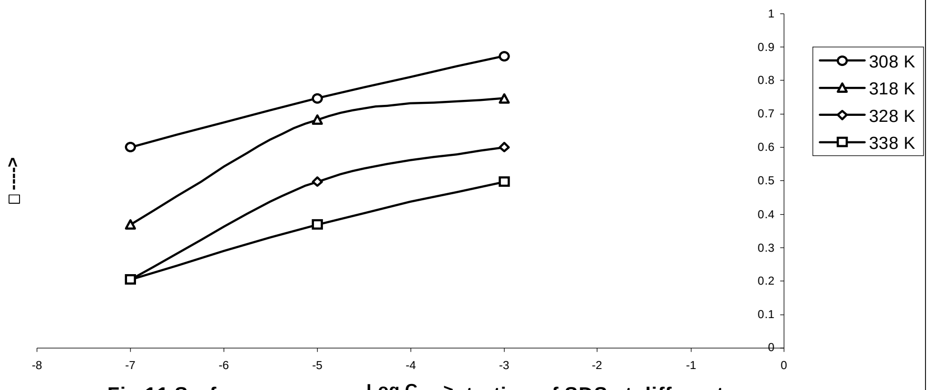

Fig 11 Surface coverage vs. concentration of SDS at different temperatures(Temkin's Isotherm)

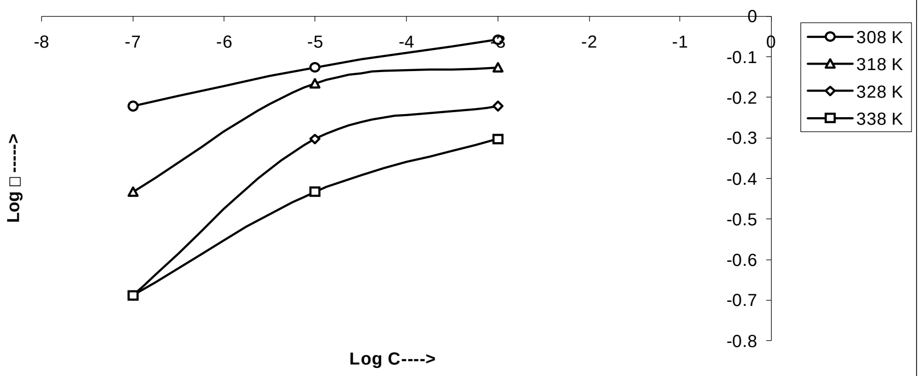

Fig. 12 Surface coverage vs. concentration of SDS at different temperatures (Freundlich's Isotherm)

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