KHAYA SENEGALEASIS OIL AND AZADIRACHTA INDICA OIL (FATTY ACIDS) AS CORROSION INHIBITORS FOR MILD STEEL IN SULPHURIC ACID (H_2S0_4) SOLUTION

By

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ABSTRACT

Corrosion inhibitors namely Khaya Senegaleasis oil and Azadirachta indica oil fatty acids have been synthesized and their inhibitive performances towards the corrosion of mild steel in 0.5M sulphuric acid (H2S04) at room and elevated temperatures (30 to 80°C) have been investigated. Preliminary screening of the inhibition efficiency (IE) was carried out using weight- loss measurements technique. The inhibition efficiencies of the vegetable based fatty acids increase with increase in concentration at all temperatures considered. The trend of inhibition efficiency with temperature suggests that inhibitor molecules are adsorbed physically on the corroding metal surface which was assumed to occur via the adsorption of the fatty acid molecules on the metal surface. These results were further corroborated by some thermodynamic (kinetic and activation) parameters such as heat of adsorption, free energy of adsorption and activation energy for corrosion and adsorption processes evaluated from experimental data at the temperature studied khaya senegaleasis oil and azadirachta indica oil-fatty acids were found to obey Lamgmuir and Temkin adsorption Isotherms in the concentration rate investigated.

INTRODUCTION

The perennial problems of corrosion in most industries such as petrochemical, fertilizer, pharmaceutical and general process industries has led to the evolution of a number of methods aimed at controlling its deleterious effects since it is impracticable to eliminate corrosion.

A variety of organic compounds containing heteroatom such as 0, N. S, and multiple bonds in their molecules are of particular interest as they give better inhibition efficiency than those containing N, or S alone (Quraish et al, 2003).

Oils and fats are members of a class of naturally occurring compounds called lipids that are insoluble in water but soluble in organic solvents (Holman and Hill, 1983).

Oil are triesters of glycerol and various long CHAIN mono carboxylic /fatty acids (Quraishi, 2003). Esters are compounds which are found when the hydroxyl hydrogen atom in oxygen acids is replace by an alkyl group. Some of the fatty acids present in oils and fats, most of which have an even number of carbon atoms are saturated like lauric, myristic, palmitic and stearic acids while others are unsaturated e.g. oleic, linoleic and linolenic acids,

Khaya Senegaleasis oil, commonly referred to as Mahogany oil is composed mainly of Linoliec and linolenic acids, with traces of lauric, oleic acids (Yawas, 2003).

Azadirachta indica oil commonly called neem oil is composed also mainly of linolenic, linoleric and oleic acids with small amount of avachudic stearic and lignoceric acids (Yawas, 2003). Despite the importance of organic acids in industry, few corrosion studies involving these acids have been made (Quraishi, 2003).

In the present investigation we report the influence of two vegetable based fatty acids: namely khaya Senegaleassis oil and Azadirchta indica oil on the corrosion inhibition of mild steel in sulphuric acid, these vegetable based fatty acids, were chosen because they are more environmentally friendly, have low toxicity and are more cost effective than petroleum based products. Further more they possess non bonding electron pairs on the nitrogen atoms additional to the ?-electron of the phenyl and aromatic rings and the readily polarizable sulphur atoms that tend to induce greater adsorption of the compounds on the metal surface leading to higher efficiency (Quraishi, 2003; Ebenso et al., 1998).

MATERIALS AND METHOD

Chemical Composition

This was done at the Quality Control Laboratory, Universal, Steel Limited, Ikeja, Lagos, Nigeria. This was done to determine the elements present and their percentages in the steel pipes. A 20mm x 30mm piece of standard pipe samples was made. A pintopin spark was impressed on the sample using a solid technique optical emissions spectrograph. The reading was taken from a direct computerized spectrometer. The procedure was repeated four times and the mean value was obtained. The result of the compositional analysis is presented below.

Table 1:								
%C	%Si	%S	%P	%Zn	%Ca	%Pb	%Al	%Co
0.2752	0.1384	0.040	0.05	0.0170	0.0128	0.01732	0.0972	0.0218
%Si	%As	%W	%Cu	%V	%Cr	%Ni	%Mn	Fe.
0.0158	0.0461	0.01344	0.1649	0.0128	0.0248	0.1125	.09820	balance

Weight loss experiments were performed with specimens cut from an oil pipe obtained from NNPC having an average total geometric surface area of 10cm^2. The acid H_2S04 (Merck) of AR grade was used for preparing solutions. Double distilled water was used to prepare solutions of 0.5m H_2S04. The specimens were mechanically polished using different grades of emery paper (120, 400, 800, 1000 and 1200) and washed thoroughly with distilled water and degreased with acetone according to the method of NACE, (1984). Concentrations of the inhibitors (using ethanol as solvent) were prepared and used for the corrosion measurements at all temperatures

(30 80^{0}C) according to the method described elsewhere (Yawas, 2003). All reagents were of analar grade and doubly distilled water was used for preparation of all solutions.

RESULTS AND DISCUSSION

Inhibition Efficiency

The results are reported in Table 14 and Figures 19. As shown in figures, it was observed that in all the cases studied, the extent of inhibition increased with increase in concentration of inhibitors. These Figures also indicate that the corrosion rates of mild steel decreases with increase of the Azadirachta indica and khaya Senegaleasis oil inhibitors concentrations. As the concentration increases the protection efficiency increases until it reaches a maximum constant value corresponding to the critical micelle concentration

(Igwe et al., 1989, Ekpe et al., 1995, Okpala, 1997). An inhibitor's concentration as low as 2% causes high inhibition efficiency.

The inhibition efficiency was obtained form weight loss measurements at different

concentrations of the vegetable based fatty acid at 30°C, 50°C, 70°C and 80°C.

The percentage inhibition efficiency (*IE*) and surface coverage () of each concentration were calculated using the following equations:

$$IE = \frac{r_0 - r}{r_0} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

$$= \frac{r_0 - r}{r_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

The average corrosion rates were determined using the relation (Callister,

1997): corrosion rate (mm/yr)

$$= \frac{87.6W}{DAT} \quad \ldots\ldots\ldots\ldots\ldots\ldots 3$$

Where r_0 and r are the corrosion rates in the absence and presence of inhibitors, respectively. For the corrosion rate, w is weight loss in grammes, D is the density of metal in kg/cm^3, A is the total surface area in cm^2 and T is the exposure time in hours.

The influence of temperature at maximum concentration (5v/v%) on IE is shown in Figure 2-5. The inhibition efficiency decreases slightly with increase in temperature from 30°C to 80°C, which may be attributed to desorption of the inhibitor molecules from the metal surface at higher temperature and agrees with an earlier research (Atia et al., 2003).

The values of activation energy (E_a) were calculated using the Arrhenius equation (Ita, et al., 2001, Alia et al., 203). :

$$\ln \frac{r_2}{r_1} = -\frac{E_a \Delta T}{RT_1T_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where r_1 and r_2 are corrosion rates at temperature T_1 and T_2, respectively, $\Delta T = T_2 - T_1$. The free energy of absorption (ΔG_{ads}) at different temperatures was calculated from the equation (Abiola et al., 2003).

$$\Delta G_{ads} = -RT \ln(55.5\,K) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

Where $K = \theta/C(1-\theta)$, θ is the degree of surface coverage on the metal surface, c is the concentration of inhibitor (v/v%) and K is the equilibrium constant. The Ea values for inhibited systems are higher than those of uninhibited systems, indicating that all the inhibitors are more effective at room temperature (Saleh et al., 1980, Ekpe et al., 2001). The low and negative values of free energy of adsorption (ΔG_{ads}) indicate spontaneous adsorption of the inhibitor on the mild steel surface (Ekpe et al., 2001). The values of ΔG_{ads} for all the compounds are = - 40 KJ mol^{-1} indicating physical adsorption of the inhibitor molecules (Oki, 2004, Oni, 1992), and the negative values also

suggest a strong interaction of the inhibitor molecules on the mild steel surface (Saleh et al., 1980)..

The heats of adsorption Q_{ads} were calculated for the various inhibited systems using the equation (ebenso, 1998, Aku et al., 2005).

Q_{ads}, = 2.303R {log $e_2/1-e_1/1-e_1$)}x T_1T_2/T_2 T_1 (kJ mol^{-1}).....6

Where e_1 and e_2 are the surface coverage at temperatures T_1 and T_2 respectively. The mean value obtained was 10.17Jmol^{-1}. Such negative values of Q_{ads} indicate that inhibitor adsorption and hence efficiency decreased with rise in temperature.

Mechanism of Corrosion Inhibition

Inhibition of iron corrosion is attributed to the adsorption of the surfactant on the iron surface. At the concentration of 2v/v%, the monomers of the fatty acids adsorb at the surface individually with a low percent coverage. As the concentration increases, that is, in the range between 3% and 4% the start of the Plateau, the amount adsorbed increases leading to a higher degree of coverage and consequently higher corrosion inhibition. Adsorption is enhanced due to the inter-hydrophobic chain interaction. Such interaction assists the formation of a thin film of surfactant molecules at the iron surface. This film is of hydrophobic nature due to anchoring of the hydrophobic chains into the solution. At higher inhibitor concentration near the CMC, an efficiency plateau is obtained. This may be attributed to the formation of a bimolecular layer of surfactant through the interaction of the fatty acid chains by tail-tail orientation at the electrode-electrolyte interface (Atia, 2003, Oni, 1996). The bilayer is amenable to desorb away from the surface due to repulsion of the polar head group. Accordingly, and since at this concentration the monomers tend to form micellar aggregates, a plateau was obtained. The protection efficiency is seen to increase with concentration even with increase in temperature. This points to the capability of the surfactant to inhibit the corrosion of steel at low and relatively higher temperature.

It is well-known that the inhibitive action of organic compounds containing SN and /or O. is due to the formation of a co-ordinate type bond between the metal and the lone pair of electrons in the additive.

The adsorption of the vegetable based fatty acid derivatives on the metal surface can occur either directly on the basis of donor-acceptor interactions between the ? -electrons of the inhibitor and the vacant d-orbital of iron surface atoms or an interaction of inhibitor with already adsorbed sulphate irons as proposed earlier (Barnejee, 1985, Hucinska et al., 1993). The corrosion inhibition property of the vegetable based fatty acids can be attributed to the presence of heteroatom such as N, O. and of ? -electrons on aromatic nuclei. These factors play the vital role in the adsorption of the inhibitor on the metal surface. Khaya senegaleasis oil and azadirachta indica oil-fatty acids are potential corrosion inhibitors, since these compounds contain nitrogen and sulphur (Ebenso 1998, Loto, 1992 and Oni, 1997). However, studies on use of chelating agents as inhibitors especially those bearing nitrogen and sulphur as coordinating atoms, are few in the literature.

ABSORPTION CONSIDERATIONS

Corrosion inhibition occurs via absorption of inhibitor molecules on the metal surface following some known absorption isotherms. Thus surface coverage data are quite useful in deducing inhibitor absorption characteristics. For heterocyclic compounds, the degree of absorption depends primarily on the electronic structure of the molecule and absorption normally occurs with the aromatic ring parallel to the metal surface (Aku et al., 2005).

The degrees of surface coverage (0) corresponding to different concentrations of the fatty acids at different temperatures have been extracted to deduce the best isotherm. This has been sued in determining the extent and mode of absorption. The mechanism of corrosion inhibition may be explained on the basis of absorption behaviour (Aku, et al., 2005; Borode et al., 1999). The degrees of surface coverage () for different inhibitor concentrations were evaluated by the weight-loss method. Data were tested graphically by fitting to various isotherms. A plot of against log C was linear (Figure 8) suggesting that the absorption of the compounds on to the mild steel surface follows the Temkin absorption isotherm. The Temkin isotherm equation is

$$\beta C = \frac{\exp(a)-1}{1\ \exp[-a(1-)]} \quad \ldots\ldots\ldots\ldots\ldots 7$$

Where $\beta = (1/55.5)\ [\exp(-\Delta G_{ads}/RT)]$, G_{ads} is the free energy of adsorption, the surface coverage, C

the concentration of inhibitor, a the molecular interaction constant, and or a > 0 attraction and for a < 0 = > repulsion.

Conclusions

The main conclusions are:

1. All the vegetable based fatty acids show excellent performance as corrosion inhibitors in sulphuric acids.
2. All the acids inhibited well even at elevated temperatures (50 80^{0}C).
3. The inhibition is due to the absorption of vegetable based fatty acids on the steel surface and the blocking of active sites.
4. the high inhibitive efficiency of the fatty acids in the acidic solution can be associated with primary absorption of the fatty acids molecules which is follow by successive formation of further adsorption layers the participation of amines cations (Atia and Saleh, 2003)
5. Mechanism of physical absorption is proposed where the absorbed inhibitors molecules lie horizontally on the metal surface thus blocking the active sites.

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Table 2: Physico-chemical properties of oil

Parameter	Mahogany oil	Neem oil
Viscosity (mm^2/s)	7.1	6.2
Calorific value (kJ/kg)	44721	44259
Acid value (mg/g)	6.90	4.90
Ash content (%wt)	0.006	0.004
Carbon residue (%wt)	0.61	0.27
Water content (% wt)	0.026	0.24
Relative density (15°C/15°C)	0.920	0.876
Flash point (°C)	88	98
Oil %	30 %	30 %
Saponification value	192	190
Iodine	130	132
Refractive index (27°C)	1.463	1.470
Peroxide value	4.56	4.58
Unsaponifiable matter	o.58	o.45
Class of oil	Semi-drying	Semi-drying

Table 3: Trace metal composition of the oils (Mg/g)

Trace metal	Mahogany oil	Neem oil
Fe	0.0530	0.540
Pb	0.070	0.056
Cu	0.088	0.038
Mg	0.914	0.294
Mn	0.084	0.0196
Cr	0.620	0.251
Zn	1.00	0.692
Ni	0.683	0.417

. **Table 4: Kinetic Of Inhibitors In H_2s0_4 At 5% Concentration**

Medium	Activating Energy	Free Energy of adsorption (KJ/Mol)			Heat of Adsorption (J/Mol)
	Ea (KJ/Mol)	$_D$Gads T(50^{0}c)	$_D$Gads T_2 T,(70^{0}c)	$_D$Gads (80^{0}c)	Qads
0.5mH_2S0_4	466.149	-	-	-	-
Mahogany oil + 0.5mH_2S0_4	8.308	-25.536	-26.26	-27.54	8627.07
Neem oil + 0.5mH_2S0_4	2.575	-25.486	-26.09	-27.68	2322.46

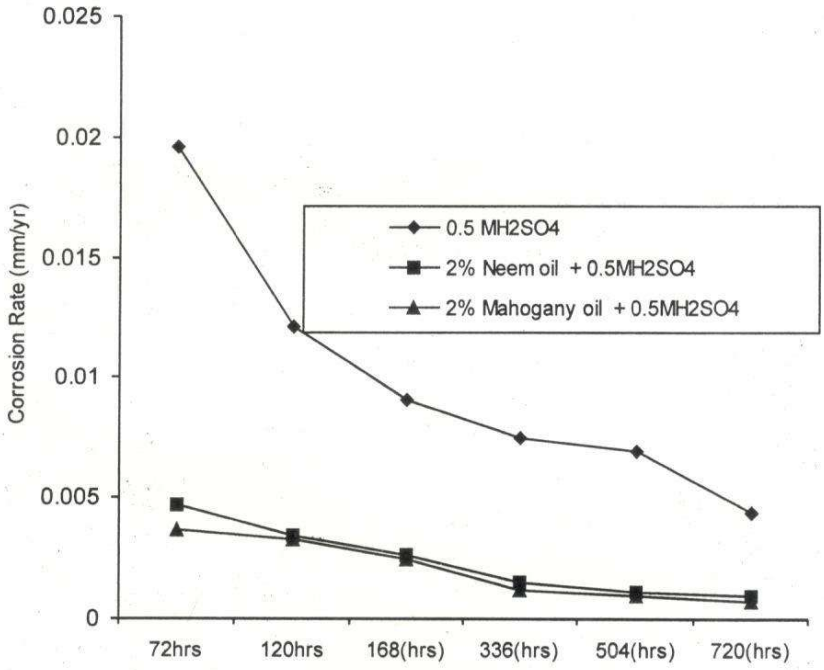

Fig. 1: Corrosion Rate against Time for2% oil + 0.5MHCl at 30^{0}C

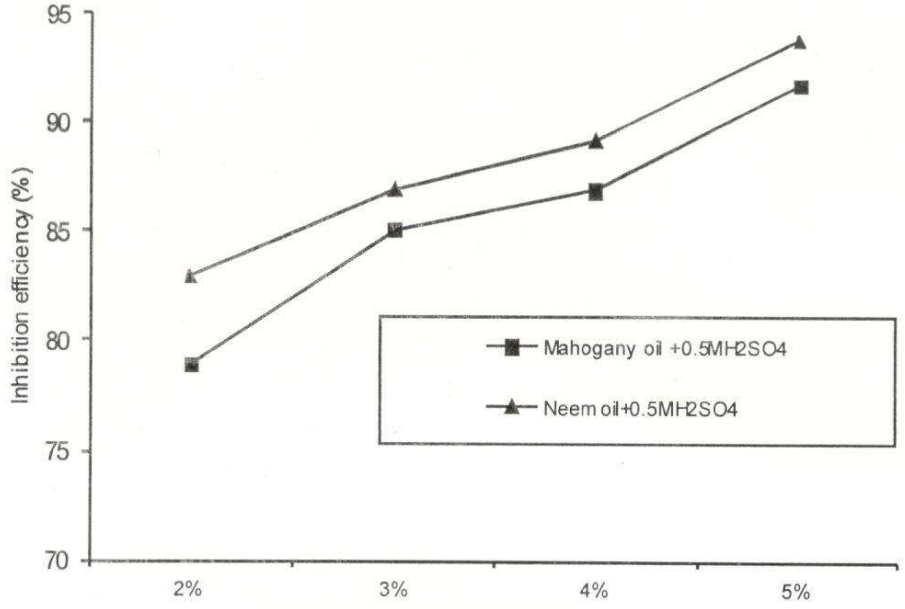

Fig. 2: Inhibition efficiency against concentration for oil + $0.5MH_2SO_4$ at 30^0C

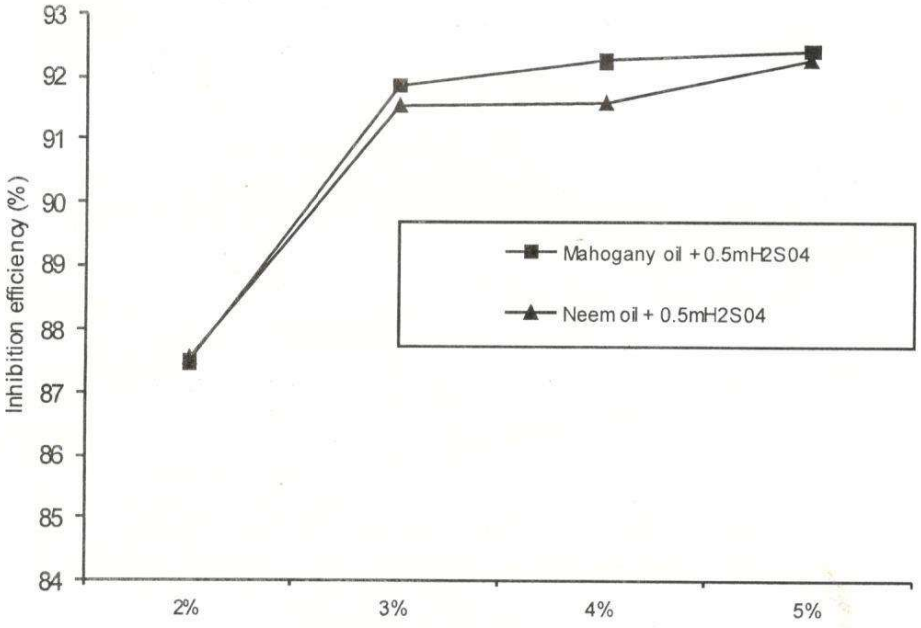

Fig. 3: Corrosion Rate against Time for Oil + $0.5MH_2SO_4$ at 50^0C

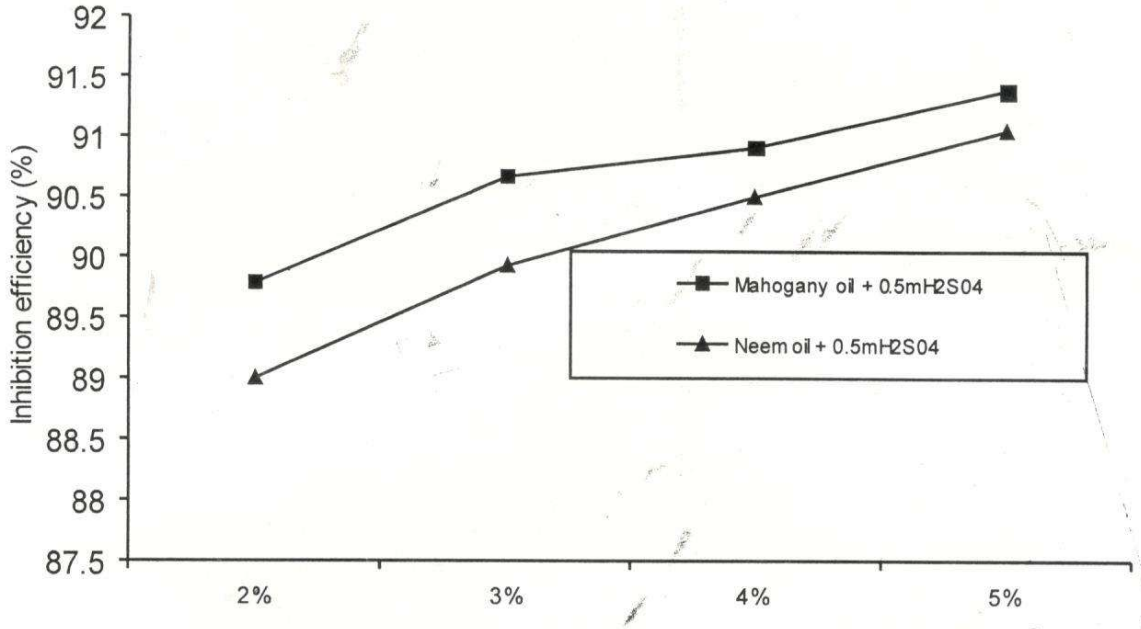

Fig. 4: Corrosion Rate against Time for Oil + 0.5MH_2SO_4 at 70^{0}C

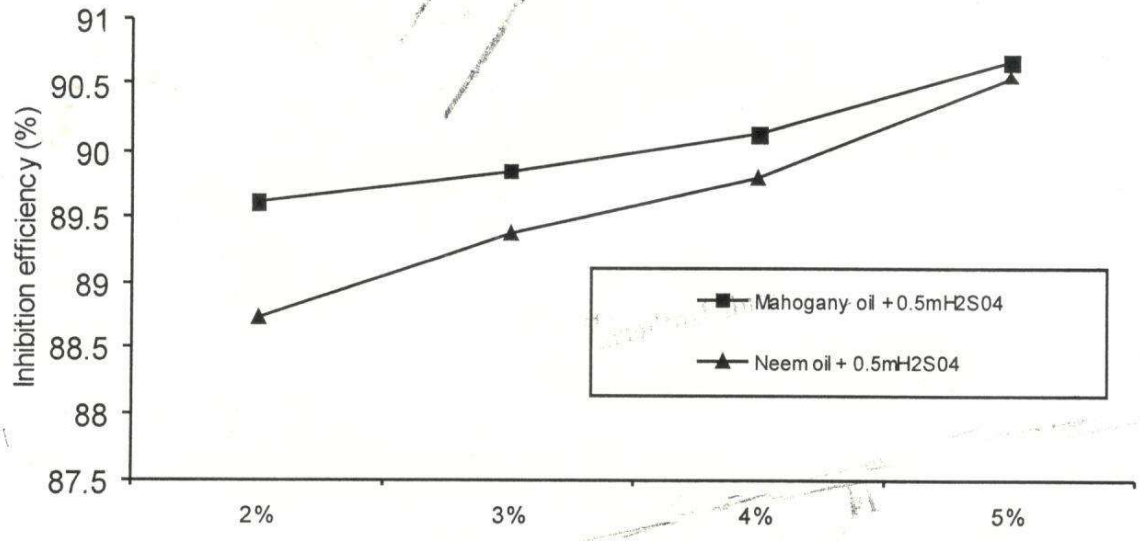

Fig. 5: Corrosion Rate against Time for Oil + 0.5MH_2SO_4 at 80^{0}C

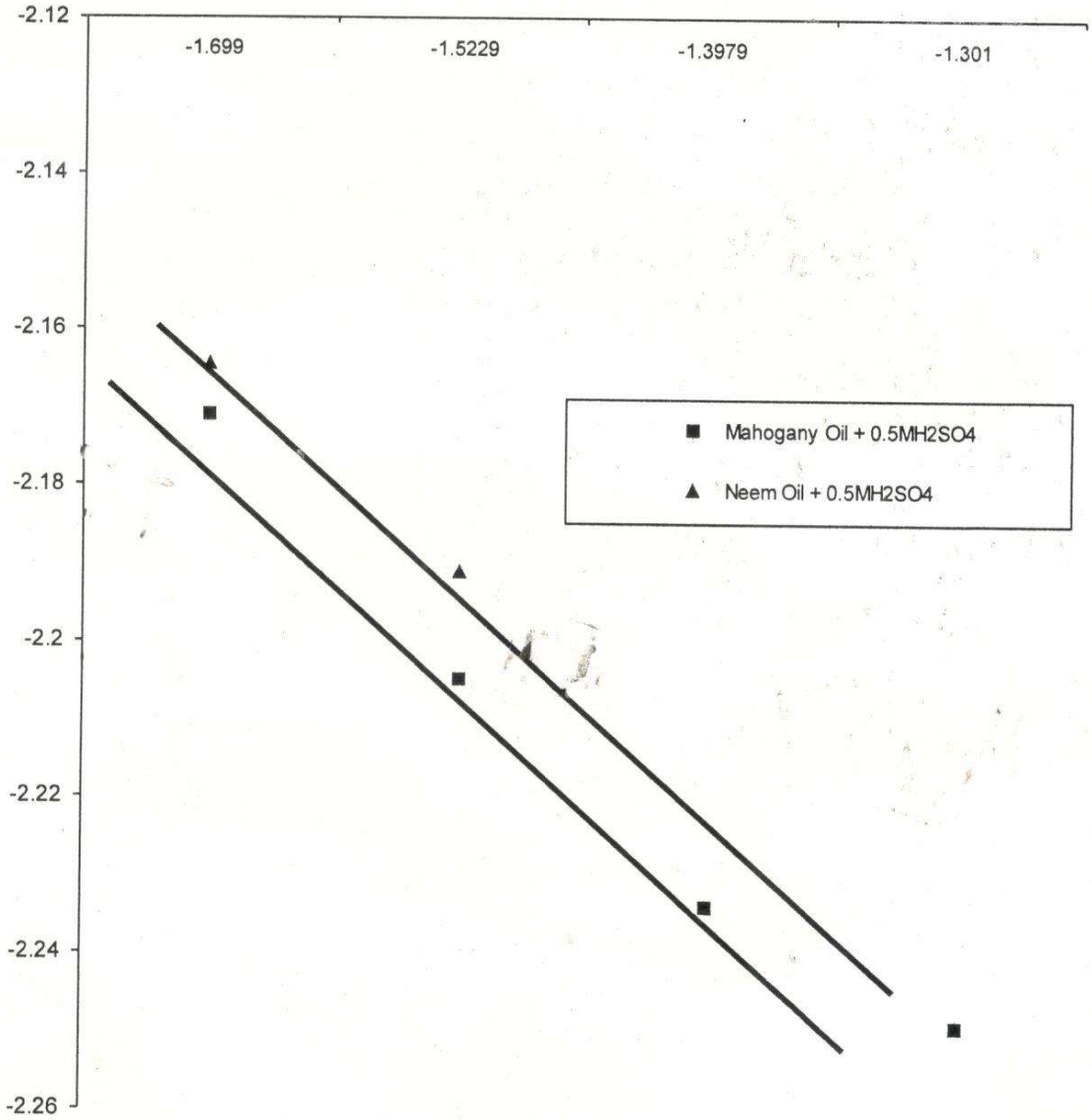

Fig. 6. Log /1- against log C for H_2SO_4 at 70°C Lamgmuir Isotherms

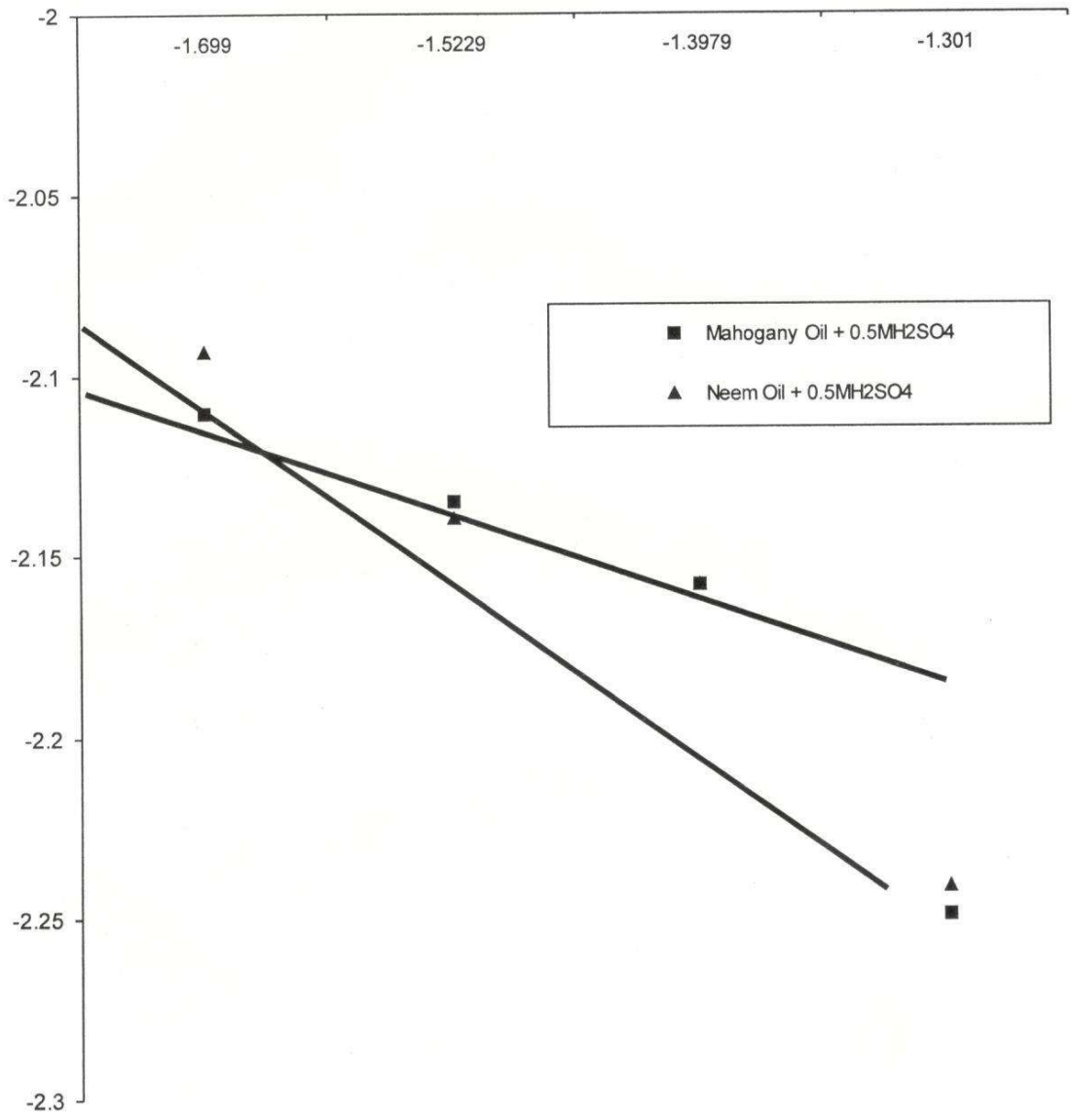

Fig. 7. Log /1- against log C for H_2SO_4 at 80^0C
Lamgmuir Isotherms

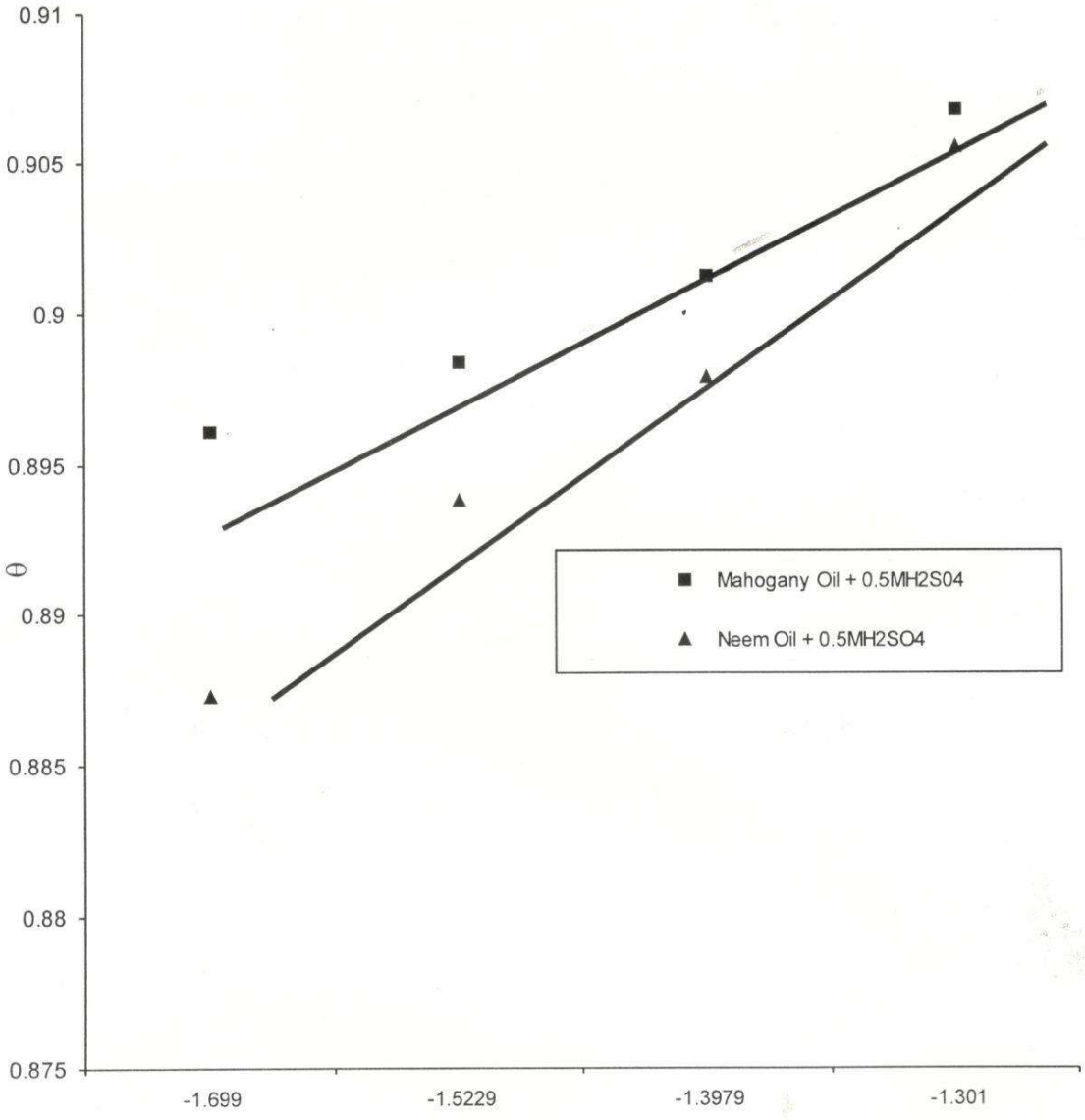

Fig. 8. θ against log C for H_2SO_4 at 70^0C Temkin's Isotherms

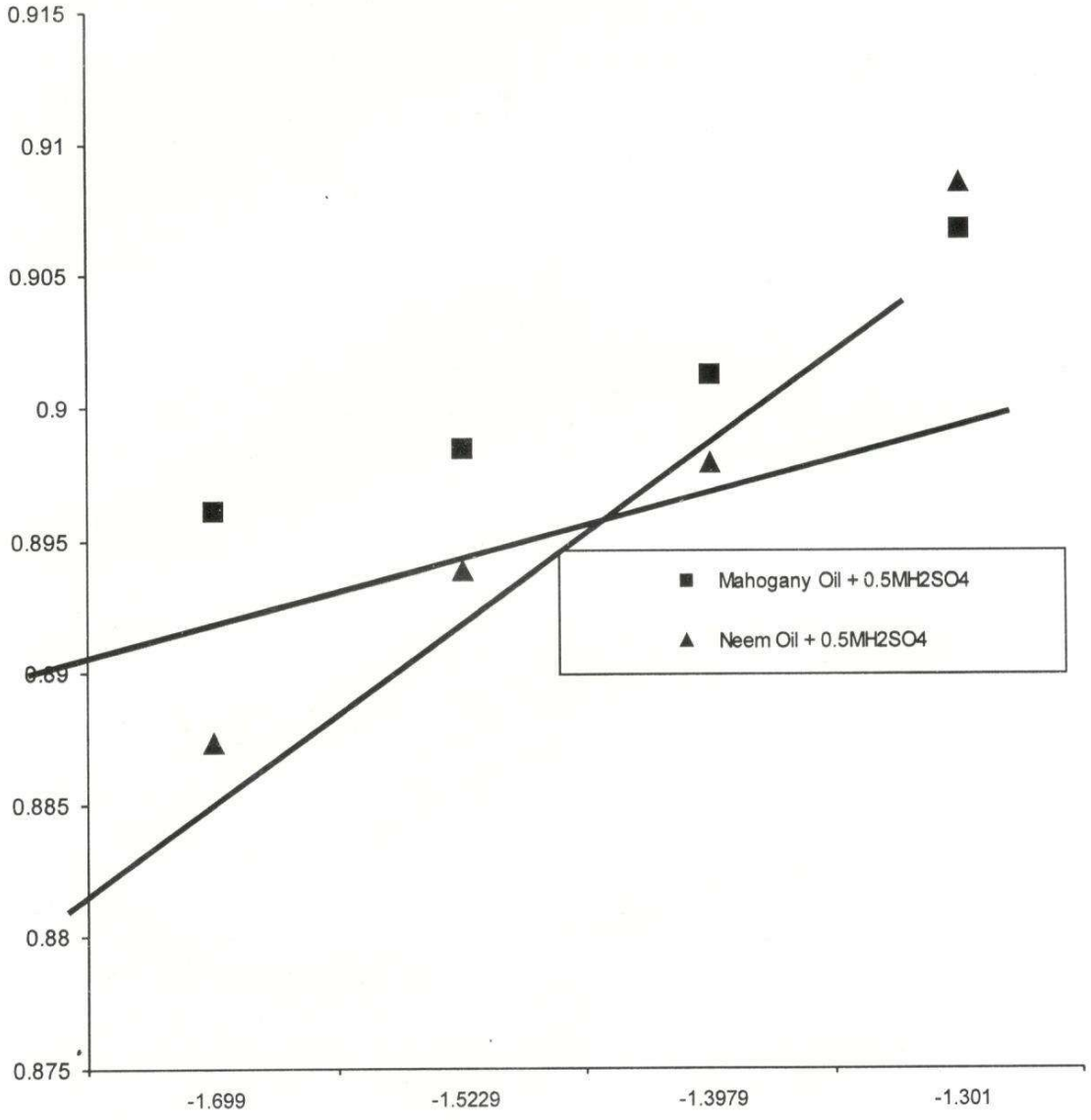

Fig. 9. against log C for H_2SO_4 at 80°C
Temkin's Isotherms