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Titanium (IV) Oxide as Corrosion Inhibitor for Aluminium and Mild Steel in Acidic Medium

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The behaviour of titanium(iv) oxide, TO as a corrosion inhibitor of aluminium and mild steel in H_2SO_4 solutions has been investigated using the "Absorbance difference" technique at 303K and 313K. The percentage inhibition efficiencies (%IE) increased with concentration of TO and decrease with increasing temperature in the order: 59.62 % MS < 73.34 % Al. The activation energy, E_a of aluminium (Al) and mild steel (MS) corrosion increased with increasing concentration. The experimental results fit the Langmuir adsorption isotherm. Physisorption mechanism has been proposed for the inhibitor based on the E_a values ($E_a \approx 9.82$ kJmol^{-1} for Al and $E_a \approx 7.18$ kJmol^{-1}for MS). The negative values of heat of adsorption, Q_{ads} obtained in this study implies that the adsorption of TO molecules on the Al and MS surfaces is spontaneous.

Keywords: Titanium (iv) oxide, corrosion inhibitor, aluminium, mild steel, absorbance difference, physisorption

1. INTRODUCTION

Titanium (iv) oxide, TO is a white, very stable solid which occurs naturally as the mineral rutile. It is obtained in pure form by dissolving in conc. H_2SO_4 [1]. Large quantities of TO are used as white pigment in paint manufacture. TO, is also used in making "Indian paper" (a thin tough printing paper made opaque by the TO filter).

Aluminium and its alloys are generally light, cheap, good conductors of heat and electricity and resist corrosion at moderate temperatures. Aluminium alloys are therefore used widely as materials for cooking utensils, electricity cables, bottle tops, food and beverage containers, roofing sheets e.t.c [2].

Mild steel (an alloy of iron, carbon, manganese, e.t.c) is fairly ductile and malleable. It can be forged but not hardened by heat [3]. Mild steel is generally used in making bolts, girders, machine parts, boiler plates, rivets, pipelines etc [4]. An oxide film of iron (α-Fe_2O_3) is formed on the mild steel surface at moderate temperatures. Bottle tops of most alcoholic and non-alcoholic drinks, industrial machine parts e.t.c are found to corrode rapidly in moist air thus constituting a health hazard to the end users. Although the oil and gas, beverage and metallurgical industries sink large sums of money in trying to control corrosion of their engine parts and products, the problem still persists. In some chemical industries, equipment becomes obsolete after a few years owing to development of corrosion. The need to research into the field of corrosion inhibition and inherent consequences therefore becomes necessary.

Various methods namely weight loss and gasometric [5-19], electrochemical and analytical [10], hydrogen permeation [11] and polarization [12] have been employed in corrosion inhibition studies. Studies on corrosion inhibition of aluminium/alloys, mild steel, copper, zinc e.t.c in acid media have been carried out. Synthetic compounds [10, 14-15], natural products [7, 16-17] and dyes [8, 18-20] have been investigated and reported as good corrosion inhibitors to mention but a few. This study is therefore aimed at determining the inhibitory properties of titanium (IV) oxide, TO on the corrosion of aluminium and mild steel in H_2SO_4 at 303 and 313K using the absorbance difference technique. The findings reported in this paper forms part of an extensive data base on inhibition profiles of inorganic compounds used as corrosion inhibitors for metals and alloys in acidic/alkaline media.

2. EXPERIMENTAL

2.1. Material Preparation

The aluminium sheets (gauge 9 type, thickness of 0.09cm and purity 0f 97.8%Al) and mild steel sheets (composition of C=0.07%, P=0.08%, Mn=0.34% and Fe=99.51% with thickness of 0.07cm) were obtained locally. The aluminium and mild steel sheets used were mechanically press cut into 5.0cm x 4.0cm coupons and used without further polishing [8].They were, however, degreased in absolute ethanol, dried in propanone and stored in moisture free desiccators before corrosion studies commenced. The average mass of the coupons used was 6.59-6.63g and the total surface area of the coupons exposed was 20.0cm^2. Titanium (IV) Oxide, TO and other reagents/compounds, sulphuric acid used for the study were all BDH grade chemicals. The TO was recrystallized twice in absolute ethanol before use. A concentration range of 1x 10^{-4} – 1x 10^{-3} moldm^{-3} of TO, was prepared and used as inhibitor at 303 and 313K while concentrations of 0.20-1.00 moldm^{-3} H_2SO_4 were prepared and used as corrodent.

2.2. Absorbance difference Measurements

The absorbance difference measurements were done in accordance with an earlier report [21] using UV/Visible spectrophotometer (Jenway, Model 6405).

The percentage inhibition efficiency (%IE) was calculated using the formula:

$$\%\mathrm{IE} = \frac{A_0 - A_1}{A_0} \ \mathrm{x}100 \qquad (1)$$

where A_o and A_1 are absorbance differences for aluminium and mild steel in the absence and presence of the inhibitors in H_2SO_4 solutions at the same temperature and wavelength [21].

The degree of surface coverage (θ) at each concentration of the inhibitor was obtained from the expression below [20]:

$$\theta = \left[1 - \left(\frac{A_1}{A_0}\right)\right] \qquad (2)$$

The corrosion rates of aluminium and mild steel in different concentrations of acid and inhibitor were determined from the absorbance difference technique using the relation:

$$\text{Corrosion rate } (\mathrm{Adm^{-2}day^{-1}} \text{ or Add}) = \Delta\mathrm{A}/\mathbf{dat} \qquad (3)$$

where ΔA = absorbance difference, **d =** density of the metal/alloy, **a** = area of specimen (Al or mild steel) and **t =** time of exposure (hours).

The activation energy values obtained in the study were computed from the transformed Arrhenius equation:

$$\mathrm{Ea} = \left(2.303R\frac{T_1T_2}{T_2 - T_1}\right)\left(\log\frac{\rho_2}{\rho_1}\right) \qquad (4)$$

where R is the molar gas constant, ρ_1 and ρ_2 are corrosion rates at T_1 and T_2 respectively [22].

The values of heat of adsorption, Q_{ads}, for the study were determined from the following expression:

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right]x\left(\frac{T_{1X}T_2}{T_2 - T_1}\right)kJmol^{-1} \qquad (5)$$

where θ_1 and θ_2 are degree of surface coverage at 303K and 313K respectively [23].

3. RESULTS AND DISCUSSION

3.1. Influence of Corrodent Concentration on Aluminium and Mild Steel Corrosion

The results obtained from the study (Table 1 and Fig.1) show that there is an increase in absorbance difference (Ad) and corrosion rate (Abs.dm^2.day^{-1}) with increasing acid (H_2SO_4) concentration and temperature.

Table 1. Corrosion Parameters for Aluminium and Mild Steel in 1MH_2SO_4 containing TO from Absorbance difference Measurements

System	Absorbance Difference		Corrosion Rate (A_{dd}) x10^{-5}		Inhibition Efficiency (%I_E)		Surface Coverage (Θ)	
	303K	313K	303K	313K	303K	313K	303K	313K
Blank	0.408(0.604)	0.431(0.630)	1.13(1.37)	1.20(1.43)	-(-)	-(-)	-(-)	-(-)
0.0001M TO	**0.153(0.308)**	**0.171(0.334)**	**0.43(0.70)**	**0.48(0.76)**	**61.49(48.27)**	**59.17(46.32)**	**0.63(0.49)**	**0.60(0.47)**
0.0003M TO	**0.146(0.296)**	**0.165(0.321)**	**0.41(0.67)**	**0.46(0.73)**	**63.38(50.43)**	**60.62(48.42)**	**0.64(0.51)**	**0.62(0.49)**
0.0005M TO	**0.141(0.281)**	**0.157(0.310)**	**0.39(0.64)**	**0.44(0.70)**	**64.49(52.89)**	**62.55(50.17)**	**0.65(0.54)**	**0.64(0.51)**
0.0007M TO	**0.115(0.268)**	**0.128(0.298)**	**0.32(0.61)**	**0.36(0.67)**	**71.06(55.03)**	**69.34(52.03)**	**0.72(0.55)**	**0.70(0.53)**
0.001M TO	**0.106(0.241)**	**0.123(0.268)**	**0.29(0.55)**	**0.34(0.61)**	**73.34(59.62)**	**70.55(56.73)**	**0.74(0.60)**	**0.72(0.58)**

All the values in parentheses represent data for Mild Steel Corrosion.

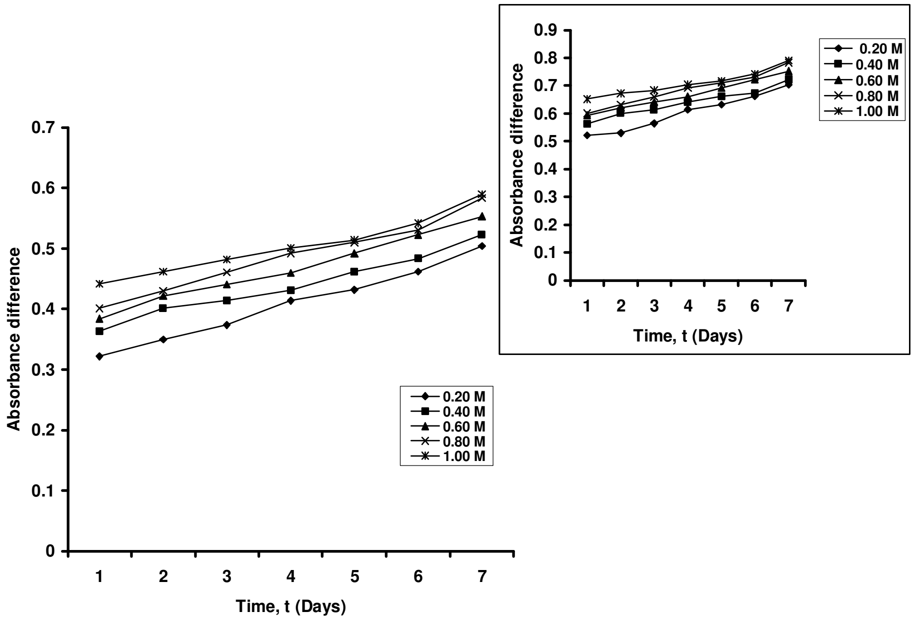

Figure 1. Variation of Absorbance difference (Ad) with Time, t (Days) for Aluminium Corrosion in different concentrations of H_2SO_4 at 303K. Inset shows Variation of Absorbance difference (Ad) with Time, t (Days) for Mild steel Corrosion in different concentrations of H_2SO_4 at 303K.

Similar observation has been made by several authors using other methods [14, 24-25]. This is due to the fact that rates of chemical reactions generally increase with increasing acid concentration and temperature. The observed trend can also be attributed to the increase in rate of ionization and diffusion of active species in the corrosion process.

3.2. Effect of Inhibitor Concentration on Inhibition Efficiency

Table 1 and Fig. 2 show that the inhibition efficiency (%IE) of the compound, TO studied increases with increasing inhibitor concentration and at low temperature. Absorbance difference was observed to be lowest at 0.001M TO (highest concentration of inhibitor studied). This indicates that TO actually inhibit the corrosion of aluminium and mild steel to an appreciable extent compared to the H_2SO_4 (blank) alone.

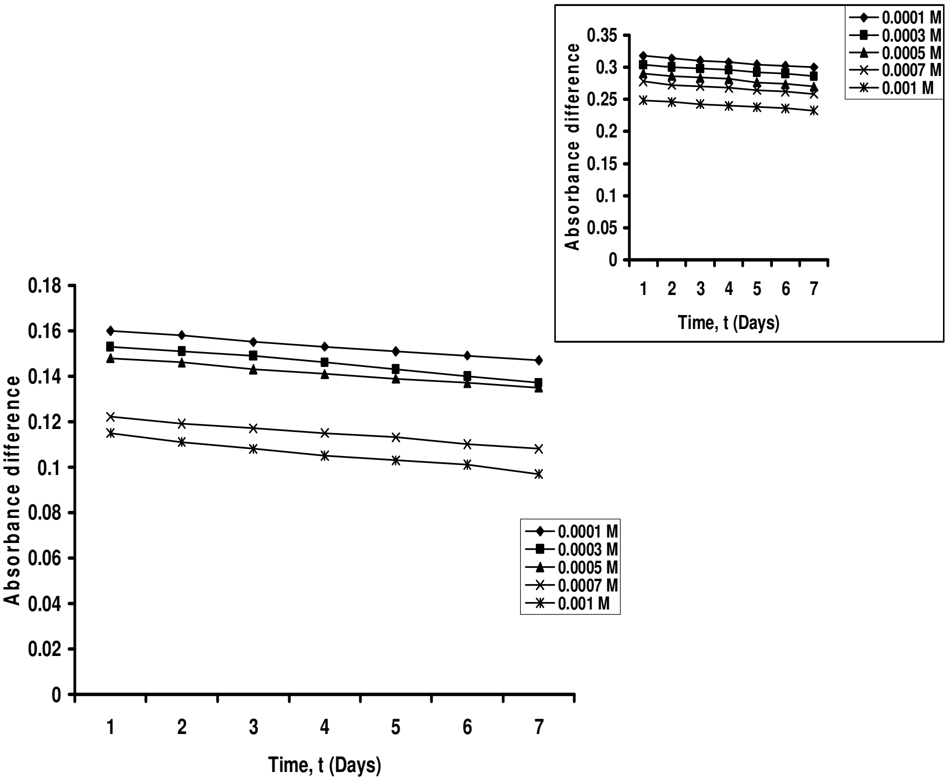

Figure 2. Absorbance difference (Ad) versus Time, t (Days) for Aluminium Corrosion in 1M H_2SO_4 with different concentrations of TO at 303K. Inset shows Absorbance difference (Ad) versus Time, t (Days) for Mild steel Corrosion in 1MH_2SO_4 with different concentrations of TO at 303K.

TO was observed to inhibit better, generally at higher concentrations at both temperatures. The inhibition efficiency (%IE) and the surface coverage (θ) (Table 1) for aluminium and mild steel corrosion were found to increase while corrosion rates decreased with increasing concentration at 303K in the order: 0.001M TO [73.34% IE (0.29 x 10^{-5}Add)] Al > [59.62% I_E (0.55 x 10^{-5}Add)] MS.

The fact that inhibition efficiency decreased with increasing temperature (303 – 313K) signifies that the inhibitor (TO) function effectively at lower temperatures. It also indicates that the time lags for the adsorption and desorption of the inhibitor molecules on the aluminium and mild steel surfaces become shorter.

The effectiveness of this compound as an inhibitor may be attributed to the presence of the lone pair of electrons from oxygen. These lone pair of electrons is delocalized and hence produces resonance stabilization energy which stabilizes the compound. At 313K, the inhibition efficiency of the inhibitor was observed to decrease probably due to the fact that an increase in temperature decreases the rate of adsorption for physically adsorbed species as a result of the weakening of Vander Waal's forces of attraction and constant bombardment of the molecules. This assertion is supported by other similar studies [15, 26].

3.3. Thermodynamic Considerations

The corrosion process kinetics acquire the character of a diffusion process, in which at higher temperature, the quantity of inhibitor molecules present at the metal surface is lower than at lower temperatures. The enhancement of inhibition efficiency at lower temperatures may be due to high activation energy available for adsorption, and the higher rate of diffusion of inhibitor molecules. This assertion is strongly supported by Ebenso *et al* [8].

Table 2. Thermodynamic Data for Aluminium and Mild Steel Corrosion in $1MH_2SO_4$ containing TO from Absorbance Difference Measurements

System	Activation Energy, Ea ($kJmol^{-1}$) 303K 313K	Heat of Adsorption, Q_{ads} ($kJmol^{-1}$) 303K 313K
Blank	**4.74(3.38)**	**-(-)**
0.0001M TO	**8.68(6.49)**	**-10.00(-6.32)**
0.0003M TO	**9.08(6.76)**	**-6.77(-6.31)**
0.0005M TO	**9.51(7.07)**	**-3.44(-9.49)**
0.0007M TO	**9.29(7.40)**	**-7.66(-6.35)**
0.001M TO	**12.54(8.17)**	**-8.01(-6.52)**
Average	**9.82(7.18)**	**-7.18(-7.00)**

All the values in parentheses represent data for Mild Steel Corrosion

Tables 2 shows calculated values of activation energy, Ea and heat of adsorption, Q_{ads} for aluminium and mild steel corrosion in $1MH_2SO_4$ and the inhibitor (TO) for different systems. Linear plots were obtained from graphs of Log. Ad against time (days) (Fig. 3a for H_2SO_4 and Fig.3b for aluminium and mild steel corrosion in 1M H_2SO_4 containing TO at 303K). This implies that the inhibition process follow first order kinetics. The extent of inhibition decreased with increasing temperature because of desorption of the inhibitor molecules. The fact that there is little difference in

E_a values (Table 2) shows the behaviour of TO may be likened to that of stable poisons in heterogeneous catalysis. This observation is also held by Wahaab *et al* [28], and Ebenso *et al*, [29].

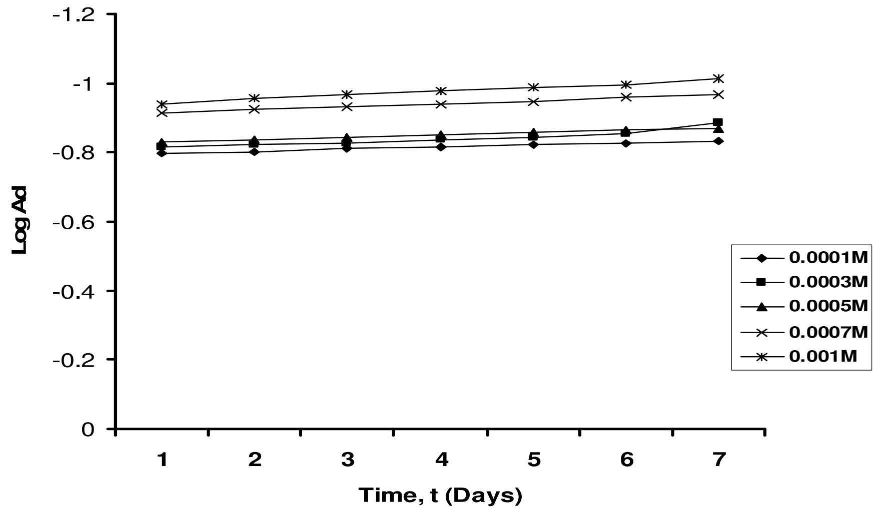

Figure 3. a)Plot of Log Ad versus Time, t (Days) for Aluminium corrosion in different concentrations of Inhibitor (TO) at 303K.

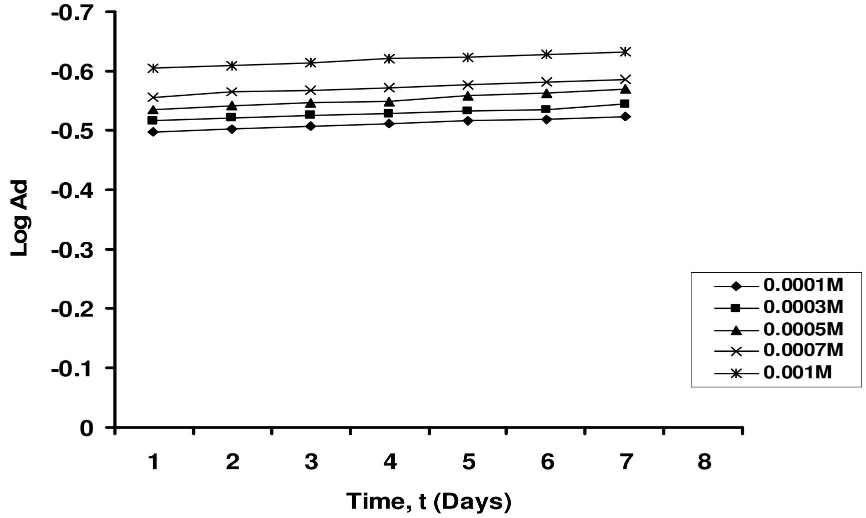

Figure 3. b)Plot of Log Ad versus Time, t (Days) for Mild Steel corrosion in different concentrations of Inhibitor (TO) at 303K.

The results show that the activation energy of the process is higher in the presence of the inhibitor than in its absence indicating physical adsorption on aluminium and mild steel. TO retards corrosion at ordinary temperatures but inhibition is considerably reduced at elevated temperatures. This assertion agrees with the findings of Ekpe *et al*, [15] and Ebenso *et al* [29].

From Table 2, it is evident that in all cases, the Q_{ads} values are negative and range from -10.00 to – 8.01 for aluminium and -6.32 to -6.52 kJmol^{-1} for mild steel. The negative Q_{ads} values indicate that adsorption and inhibition efficiency (Table 1) decreases with rise in temperature which confirms the findings of Bhajiwala and Vashi [30]. The negative values of Q_{ads} also imply that the adsorption of the inhibitor molecules on aluminium and mild steel is spontaneous and this is a strong characteristic of strong interaction with the metal / alloy surfaces. The action of TO as an inhibitor may therefore be due to the type of interaction between the inhibitor and aluminium and mild steel surfaces. This interaction causes a change on the surfaces available for the process or in the electrochemical process mechanism.

3.4. Adsorption Considerations

Most authors of papers on kinetics and mechanism of corrosion inhibition of metals in acidic solutions by organic/inorganic compounds agree that inhibition results from the adsorption of molecules or ions but the detailed mechanism of this phenomenon is still very unclear [8]. The action of organic/inorganic inhibitors is dependent on the type of interaction between the metal / alloy surface. This interaction(s) may lead to changes in electrochemical process mechanism. From the corrosion rates and / or surface coverage (θ) for different inhibitor concentrations, the respective adsorption isotherm may be obtained.

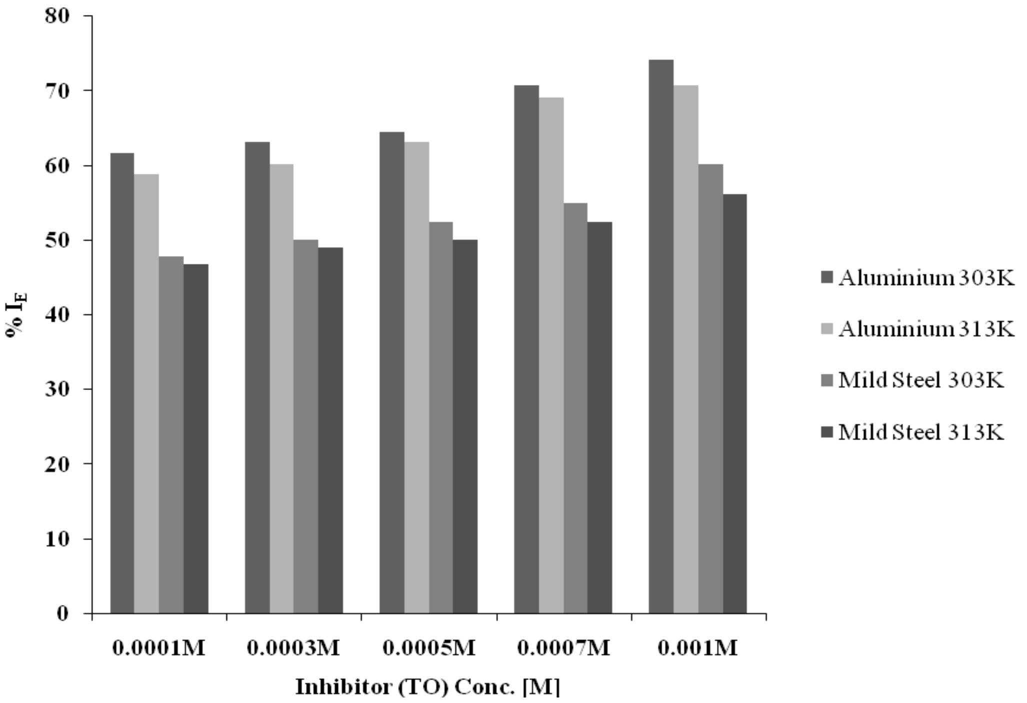

Figure 4. Plot of Inhibition efficiency versus concentration of TO for aluminium and mild steel at 303 and 313K.

An inspection of Table 1 and Figs. 4, reveals that inhibition efficiencies (%IE) and surface coverage (θ) increase with increasing inhibitor concentration and decrease with increase in temperature. The greater E_a values observed for inhibited than uninhibited solutions is suggestive of physical adsorption mechanism. The E_a values of aluminium were found to be higher than those for mild steel but generally less than $40 kJmol^{-1}$. As temperature rises, adsorption decreases. Therefore, the isotherms of high temperatures (313K) are below isotherms of lower temperatures (303K). For physical adsorption, the plot of 313K is under that of 303K as shown in Fig. 4 for aluminium and mild steel corrosion respectively. The extent of adsorption of inhibitor molecules on aluminium and mild steel surfaces was further established by plotting values of "C"eq/θ against values of 'C' at 303K and 313K (Fig. 5). It was found that experimental data obtained within the temperature range fits Langmuir adsorption isotherm given by equation (6) below:

$$\text{“C”eq}/\theta = \alpha\,\text{'C'} + \beta \qquad (6)$$

where Ceq is the equilibrium concentration (concentration at which no more absorbance was observed); C is the inhibitor concentration; θ is the surface coverage calculated from equation (2); α is the slope called the binding force and β is the Langmuir constant which is the adsorptive capacity [26].

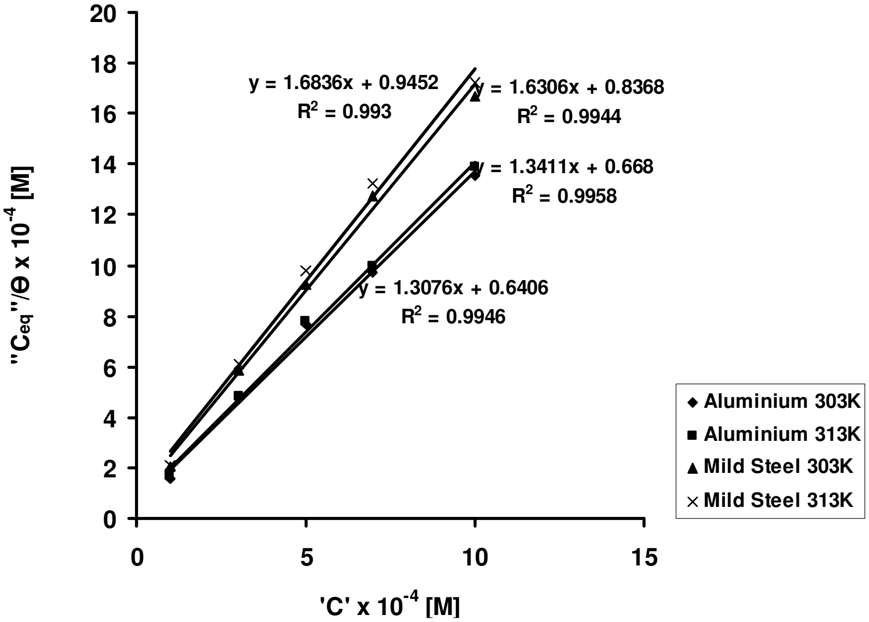

Figure 5. Langmuir adsorption isotherm plot of C/Θ versus 'C' for Aluminium and Mild Steel Corrosion in 1M H_2SO_4 containing TO at 303K and 313K

The slopes obtained from the plots are very close to unity. This is because the interactions between the adsorbed species on the metal surface and those between the adsorbed organic molecules with polar atoms or groups on the anodic and cathodic sites of the metal play important roles in the process. These interactions may be mutually attractive or repulsive. The fact that Q_{ads} are all negative is an indication that the interactions on the metallic surfaces are mainly attractive. This view is supported by Yadav [23]. More over, corrosion inhibition is generally believed to be due to the formation and maintenance of a protective film on metal/ alloy surface. The results plotted in Fig 5 suggest that the inhibitor cover both the anodic as well as the cathodic regions through general adsorption following Langmuir isotherms.

The inhibition effectiveness of TO may be attributed to the stable oxide layer formed around the metal/alloy surfaces. TO have a tetragonal structure in which each Ti^{4+} ion is surrounded by six O^{2-} ions arranged octahedrally. The structure may also be regarded as a distorted body-centred cubic arrangement of Ti^{4+} ions with O^{2-} ions in positions of three fold co-ordination [1]. The high co-ordination number (8 or 6) of Ti (in TO) is an evidence of ionic binding between TO molecules and aluminium and mild steel surfaces respectively. This ionic coverage is continuously renewed to protect these metals from the corrosive environment thereby enhancing the inhibitory properties of TO.

4. CONCLUSIONS

The following conclusions are drawn on the basis of this study: The corrosion rate increases with increase in H_2SO_4 concentration and with temperature. Generally, TO is a good inhibitor for the corrosion of mild steel and aluminium. The inhibition efficiency (%IE) of TO increases while corrosion rate (Add) decreases with increase in inhibitor concentration but decreases with increase in temperature. The E_a values obtained in the presence and absence of inhibitor are below 40 $kJmol^{-1}$(average E_a of 9.82 $kJmol^{-1}$ for aluminium and 7.18 $kJmol^{-1}$ for mild steel) which implies that the inhibition is by physical adsorption. The values of Q_{ads} obtained between 303K and 313K are all negative indicating that the inhibitor is strongly adsorbed on aluminium and mild steel surfaces and that the adsorption is spontaneous. The data obtained from this study fit well into the Langmuir adsorption isotherm.

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