Inhibition of Mild Steel Corrosion in Sulphuric Acid Using Alizarin Yellow GG Dye and Synergistic Iodide Additive

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The corrosion inhibition of mild steel in 2 M H_2SO_4 using Alizarin yellow GG (AYGG) (an azo dye) in the presence of iodide ions was studied at $30 – 60^oC$ using weight loss and hydrogen evolution methods. Results obtained showed that inhibition efficiency increased with increase in concentration of AYGG and decreased with increase in temperature. The inhibition efficiency of AYGG synergistically increased on addition of KI. The adsorption of AYGG alone and in combination with iodide ions on the metal surface is found to obey Temkin adsorption isotherm at all temperatures studied. Phenomenon of physical adsorption is proposed from the values of E_a and ΔG^o_{ads} obtained. Synergism parameter evaluated is found to be greater than unity for all concentrations of AYGG indicating that the enhanced inhibition efficiency of AYGG caused by addition of iodide ion is only due to synergism. Experimental results obtained indicate that the adsorption of AYGG and AYGG + KI onto mild steel surface is spontaneous.

1. INTRODUCTION

A survey of literature reveals that the applicability of organic compounds as corrosion inhibitors for mild steel in acidic media has been recognized for a long time. A large number of organic compounds, particularly those containing nitrogen, oxygen or sulphur in a conjugated system, are known to be applied as inhibitors to control acid corrosion of iron and steel. The inhibition process has been shown to occur via inhibitor adsorption isotherm and the efficiency of the inhibitors strongly depends on the structure and chemical characteristics of the adsorbed inhibitor layer formed under particular experimental conditions.

Although dyes have been extracted from natural sources for centuries, it was not until 1856 that a synthetic dye was produced commercially [1-3]. Different kinds of dyes are known viz. heterocyclic dyes (e.g. safranine T, methylene blue); xanthene dyes (e.g. eosin, thymol blue, phenolphthalein, phenol red) ; anthraquinone dyes (e.g. alixarin red S) and azo dyes (e.g. methyl red, congo red, methyl orange). Of all the dyes, azo dyes are a class of compounds that are strongly coloured. They can be intensely yellow, red, orange, blue or even green, depending on the exact structure of the molecule. Because of their colour, azo compounds are of tremendous importance as dyes. Infact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts [4]. Structural features in organic compounds that lead to colour are $>C = C<$, $-N = O$, $-N = N-$, aromatic rings, $>C = O$ and $-NO_2$. Most importantly, azo ($-N = N-$) and nitro ($-N = O$) groups invariably confer colour while the other groups do so under certain circumstances.

Dyes have been used to give multi-colour effects to anodized aluminium [5-10]. Cyanine dyes have been reported as efficient corrosion inhibitors on metal corrodent systems [11]. Green S and erythrosine dyes have been studied as potential inhibitors for mild steel corrosion in HCl [12]. A survey of the literature also reveals that the corrosion on aluminium in amine solutions by some dyes has been reported [13-20]. Preliminary experiments in our laboratories in an earlier study have shown, however, that some azo dyes (metanil yellow, naphthol blue black and solochrome dark blue) actually inhibit the corrosion of mild steel in HCl medium [21]. Some other studies by other research groups and from our laboratories recently reported also show that some organic dyes are quite effective in retarding the corrosion of mild steel and aluminium in acidic or basic environments [22-35]. This investigation is therefore part of an extensive on-going project in our laboratories to develop new classes of inhibitors from some dyes with low toxicity, good efficiency and also to further elucidate the mechanism of the inhibition process. Therefore, in continuation of our interest on the corrosion inhibiting characteristics of organic dyes, the present paper reports on the inhibiting action of Alizarin yellow GG (AYGG), $C_{13}H_8N_3NaO_6$ (an azo dye) [5-(3 – nitrophenylazo)- 2 – hydroxybenzoic acid sodium salt] shown below on the corrosion of mild steel in H_2SO_4 using the weight loss and hydrogen evolution techniques. The effect of changing the temperature of the medium as well as the addition of iodide ions on the corrosion rate and inhibition efficiency is also examined and discussed.
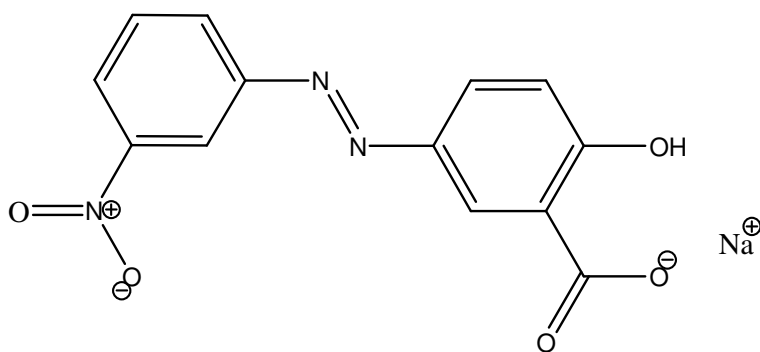
2. EXPERIMENTAL PART

The mild steel used in the study had the following composition (wt %), C (0.19), Si (0.26), Mn (0.64), S (0.05), P (0.06), Ni (0.09), Cr (0.08), Mo (0.02), Cu (0.27), and the remainder iron (Fe) and was obtained from Ejison Resources (Nig.) Ltd. The mild steel coupons were prepared, degreased and cleaned as previously reported [3-5]. The concentration of the blank corrodent, H_2SO_4 (BDH Chemical Supplies Laboratory, England) prepared and used was 2M. Alizarin yellow GG (AYGG), $C_{13}H_8N_3NaO_6$ (an azo dye) [5-(3 – nitrophenylazo)- 2 – hydroxybenzoic acid sodium salt] used, as inhibitor in the present study is a product of Merck Chemicals, UK and has a molecular weight of 309.21 g/mol. A stock solution of AYGG (0.005M) was prepared by weighing an appropriate amount of it and dissolved in 1 litre of 2M H_2SO_4. Other concentrations ($1x10^{-5}$ – $1x10^{-3}$ M) were obtained from the stock solution following serial dilution. The halide salt (KI) used was obtained from BDH Laboratory Supplies, England. Similarly, a stock solution of 0.1M was prepared by weighing an appropriate amount of the halide salt and dissolved in 1 litre of 2M H_2SO_4. However, 0.06M KI was used for the synergistic study. All preparations were carried out using deionized water. All chemicals and reagents used were of analytical grade. They were used as sourced without further preparation.

The apparatus and procedure followed for weight loss and hydrogen evolution methods were similar to that earlier reported [36-39]. In the weight loss method, the progress of the corrosion reaction was monitored by determining the weight loss of the coupons (obtained as the differences in the weight of the coupons after immersion in different solutions of the system and the original weight of the coupons) and careful measurement of the volume of hydrogen gas evolved for weight loss and hydrogen evolution methods respectively at fixed time intervals. In both techniques, the experiments were conducted in the temperature range 30 to 60°C at intervals of 10° maintained in a thermostated bath.

3. RESULTS AND DISCUSSION

3.1. Corrosion rates and inhibition efficiency

Figure 1 shows the plot of corrosion rate against inhibitor concentration for mild steel corrosion in 2 M H_2SO_4 at different temperatures (a) AYGG and (b) AYGG + KI from weight loss measurements. The figure reveals that the rate of corrosion of mild steel in 2 M H_2SO_4 decreases with increase in inhibitor concentrations at all the temperatures studied. The increase in inhibition efficiency with increase in concentration of the compound studied can be explained on the basis of increased adsorption of the compound on the metal surface. Further reduction in corrosion rate was observed on addition of 0.06 M KI to AYGG. The reduction in corrosion rate of AYGG when combined with iodide ions was found to be concentration dependent. Similar plot was obtained for mild steel corrosion in 2 M H_2SO_4 at different temperatures in the presence of different concentrations of the inhibitor using hydrogen evolution technique (Figure 2). The plot of inhibition efficiency against concentration for (a) AYGG and (b) AYGG + 0.06 M KI at different temperatures is shown in Figure 3. Inspection of the figure revealed that inhibition efficiency increases with increase in the

concentration of the inhibitor (AYGG) and decreases with increase in temperature. Decrease in inhibition efficiency with increase in temperature may be attributed to increase in the solubility of the protective films and of any reaction products precipitated on the surface of the metal that may otherwise inhibit the reaction. Ergun et al. [40] has attributed the inhibition efficiency decrease with rise in temperature to be due to an enhanced effect of temperature on the dissolution process of steel in acidic media and/or the partial desorption of the inhibitor from the metal surface. A similar trend has been reported elsewhere [41].
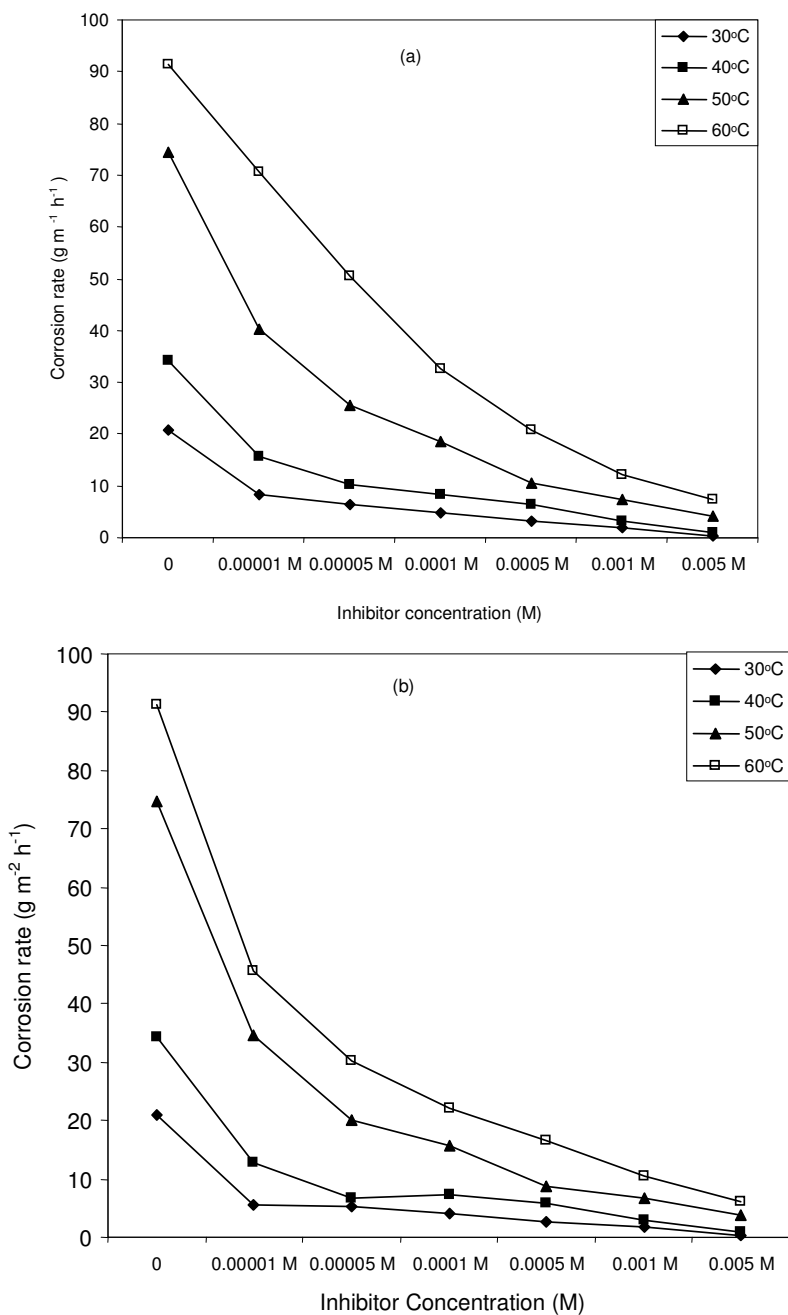

Figure 1. Plot of corrosion rate against inhibitor concentration for mild steel corrosion in 2M H_2SO_4 at different temperatures (a) inhibitor (AYGG) and (b) Inhibitor (AYGG) + KI from weight loss measurements.
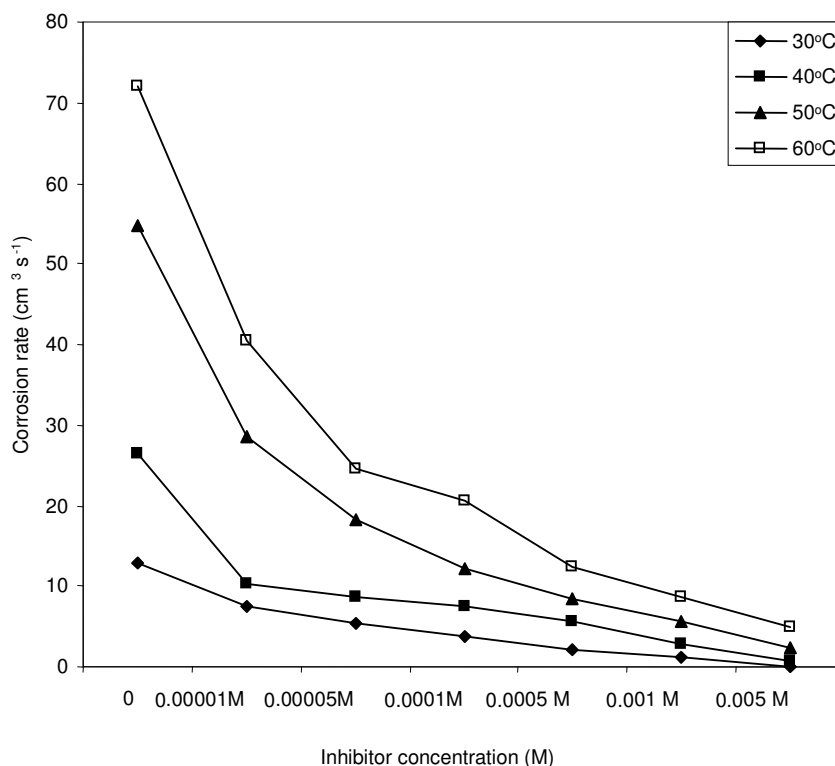
Figure 2. Plot of corrosion rate against inhibitor (AYGG) concentration for mild steel corrosion in 2M H$_2$SO$_4$ at different temperatures from hydrogen evolution measurements

As far as the inhibition process is concerned, it is generally assumed that the adsorption of the inhibitors at the metal/aggressive solution interface is the first step in the inhibition mechanism [42]. Considering the dependence of inhibition efficiency on the concentration as represented in Figures 2 and 3, it seems to be possible that the inhibitor acts by adsorbing and blocking the available active centre for steel dissolution. In other words, the inhibitor decreases the active centre for steel dissolution. The adsorption process is made possible due to the presence of heteroatoms such as N and O which are regarded as active adsorption centres. AYGG molecule contains nitrogen, oxygen, two phenyl rings with π electrons and N=N (azo group). The compound could be adsorbed by the interaction between the lone pair of electrons of the oxygen and nitrogen atoms or the electron rich π systems of the aromatic rings and the azo group and the mild steel surface. This process as earlier reported by Umoren and Ebenso [39] may be facilitated by the presence of vacant d- orbital of iron making the steel, as observed in d- group metals or transition element. In addition to the molecular form, AYGG can be present in protonated species in an acidic solution. The formation of positively charged protonated species facilitates adsorption of the compound on the metal surface through electrostatic interaction between the organic molecules and the metal surface [43].
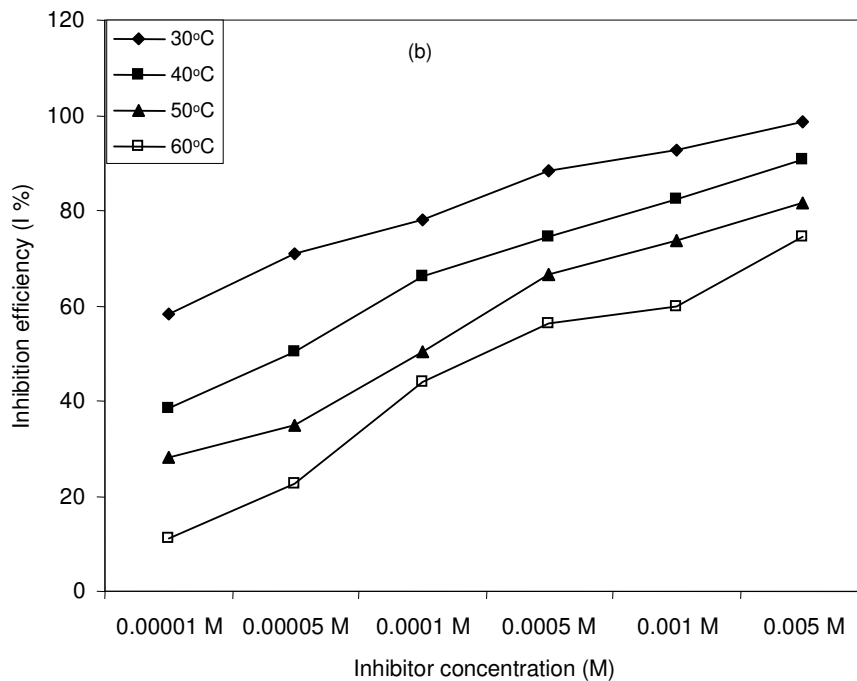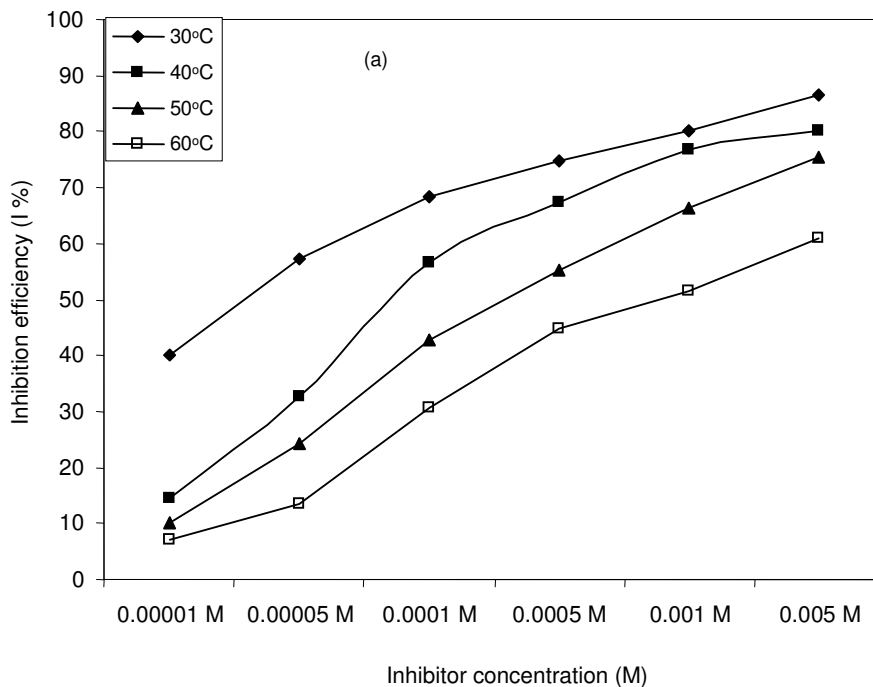
Figure 3. Plot of inhibition efficiency against extract concentration for mild steel corrosion in 2M H_2SO_4 containing (a) inhibitor (AYGG) and (b) inhibitor (AYGG) + 0.06 M KI at different temperatures.

3.2. Adsorption considerations

It has been reported that the adsorption of an organic compound onto the surface of a metal is dependent on the following physiochemical properties of the inhibitor molecule, such as steric factors, functional groups, electron density (i.e. charge distribution) at the donor atoms and π orbital character of donating electrons, and on the nature of substrate metals and the type of interaction between organic molecules and the metallic surface as well [44]. In other words, the efficiency of an organic compound as corrosion inhibitor depends not only on the characteristics of the environment in which it acts, the nature of the metal surface and electrochemical potential at the interface, but also on the structure of the inhibitor itself; which includes the number of adsorption active centres in the molecule, their charge density, the molecular size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metallic surface [45].

Adsorption isotherms are very important in understanding the mechanism of organo-electrochemical reactions [46]. In discussing adsorption isotherms, the degree of surface coverage values were obtained from weight loss measurements using the equation (θ = IE%/100). Attempts were made to fit (θ) values to the Thermodynamic-kinetic model of El-Awady et al, Freundlich, Temkin and Langmuir isotherms and the correlation coefficient (R^2) values were used to determine the best fit isotherm. By far, best results were obtained for the Temkin adsorption isotherm. The surface coverage values for AYGG were fitted into the Temkin adsorption isotherm model, which has the form:

$$\exp(-2a\theta) = KC \tag{1}$$

where 'a' is molecules interaction parameter, θ, is the degree of surface coverage, 'K' is equilibrium constant of adsorption process and 'C' is the concentration of the inhibitor. The plot of surface coverage as a function of logarithms of inhibitor concentration is shown in Figure 4 (Temkin adsorption isotherm). From the plot, straight lines were obtained with $R^2 > 0.9$ for both AYGG and AYGG + I⁻ indicating that the experimental data fit well into the Temkin adsorption isotherm. The calculated values of molecular parameter 'a' are negative in all cases [for both inhibitor (AYGG) and inhibitor (AYGG) + iodide mixture] showing that repulsion exists in the adsorption layer [47, 48]. The value of K decreases with increasing temperature suggesting that the inhibitor is physically adsorbed on the mild steel surface (see Table 1). Similar observation has been documented [39].

The free energy of adsorption is related to the equilibrium constant of adsorption, K by the following equation:

$$K = \frac{1}{55.5} \exp\left[\frac{-\Delta G^o_{ads}}{RT}\right] \tag{2}$$

The values of free energy of adsorption for AYGG in the temperature range 30-60 ^{o}C are shown in Table 1. The negative values indicate spontaneous adsorption of the inhibitor on the metal surface [39, 47]. The results in general indicate AYGG to be physically adsorbed on the metal surface. Generally, values of ΔG^o_{ads} up to –20 kJmol⁻¹ are consistent with electrostatic interaction between

charged molecules and a charged metal (which indicates physical adsorption) while those more negative than -40 kJmol^{-1} involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorption) [47].
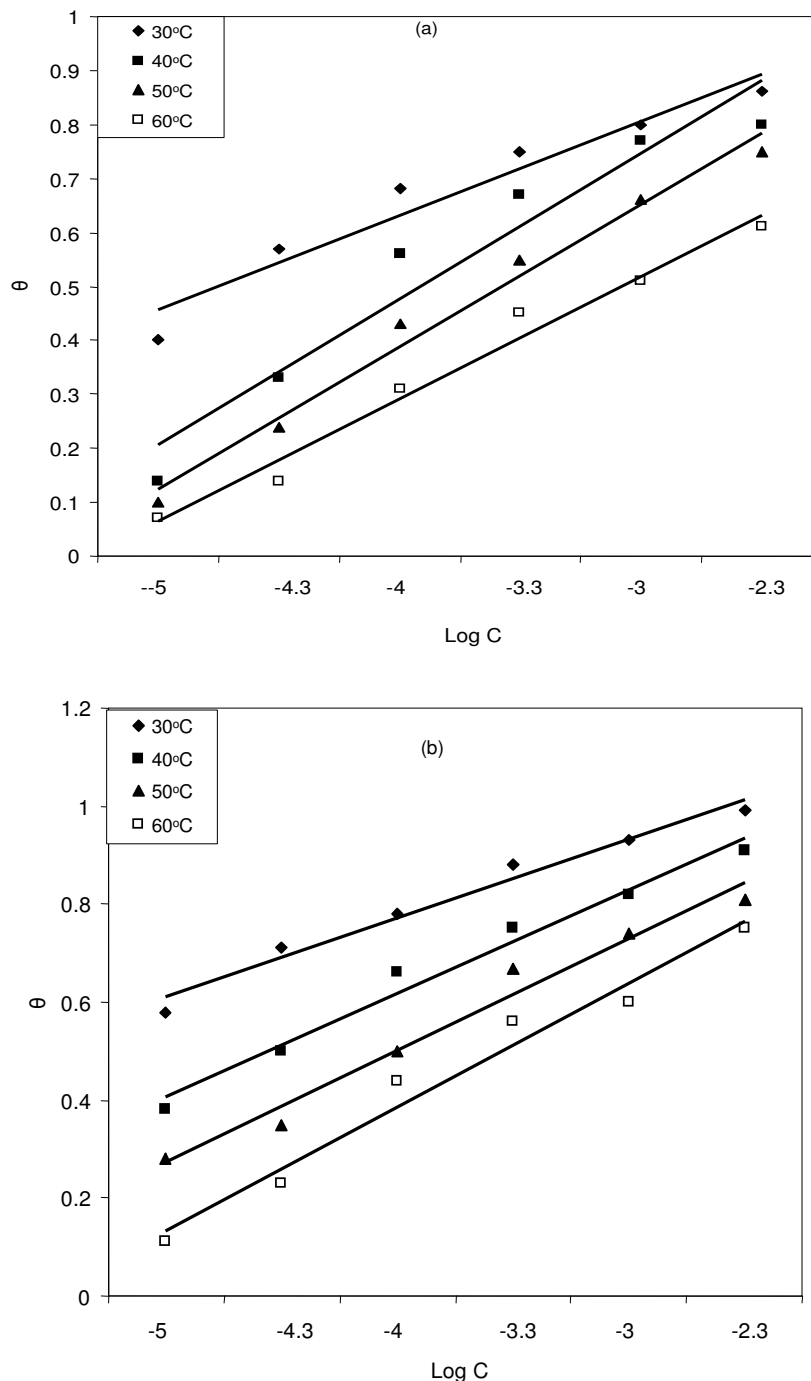

Figure 4. Temkin adsorption isotherm plot for mild steel corrosion in 2M H_2SO_4 containing (a) inhibitor(AYGG) and (b) inhibitor(AYGG) + 0.06 M KI at different temperatures.

Table 1. Adsorption parameters deduced from Temkin adsorption isotherm

inhibitor	Temperature (^{o}C)	Temkin isotherm			
		ΔG (kJ/mol)	a	K_{ads}	R^2
Inhibitor (AYGG)	30	-11.05	-0.019	1.45	0.94
	40	-10.63	-0.029	1.07	0.94
	50	-10.76	-0.029	0.99	0.98
	60	-10.98	-0.025	0.95	0.98
Inhibitor (AYGG) + KI	30	-11.45	-0.017	1.69	0.98
	40	-11.23	-0.023	1.35	0.98
	50	-11.21	-0.025	1.17	0.98
	60	-11.55	-0.027	1.17	0.98

3.3. Effect of temperature

The results obtained from temperature studies of the corrosion of mild steel in 2 M H_2SO_4 in the absence and presence of AYGG and AYGG + iodide mixtures in the temperature range 30-60 ^{o}C revealed that increasing temperature increases corrosion rate and decreases inhibition efficiency at all the concentrations studied. According to Dehri and Ozcan [49], the relationship between the temperature dependence of percent inhibition efficiency (IE %) of an inhibitor and the activation energy found in its presence was given as follows: (a) Inhibitors whose IE% decrease with temperature increase, the value of activation energy (E_a) found is greater than that in the uninhibited solution; (b) Inhibitors whose IE% does not change with temperature variation, the activation energy (E_a) does not change with the presence or absence of inhibitors; (c) Inhibitors whose IE% increases with temperature increase, the value of activation energy (E_a) found is less than that in the inhibited solution.

In an acidic solution the corrosion rate is related to temperature by the Arrhenius equation:

$$\log CR = \frac{-E_a}{2.303RT} + \log A \qquad (3)$$

where 'CR' is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor. Figure 5 shows the plot of log CR versus 1/T. Linear plots were obtained for both AYGG and AYGG + I^-. The values of E_a were computed from the slope of the straight lines and are listed in Table 2. It is clear from the table that E_a values in the presence of the additives are higher than that in the absence. The higher activation energies imply a slow reaction and that the reaction is very sensitive to temperature. Similar results have been reported elsewhere [50]. The increase in the activation energy in the presence of AYGG and AYGG + iodide mixtures signifies physical adsorption [51]. This conclusion is denoted by the decrease in inhibition

efficiency with increasing temperature. Enthalpy and entropy of activation ΔH^o and ΔS^o were obtained by applying the transition state equation:

$$CR = \left(\frac{RT}{Nh}\right)\exp\left(\frac{\Delta S^o}{R}\right)\exp\left(\frac{-\Delta H^o}{RT}\right)$$

(4)

Where h is the Planck's constant, N is the Avogadro's number, T is the absolute temperature, and R is the universal gas constant. Plots of Log (CR/T) as a function of 1/T were made (Figure 6).
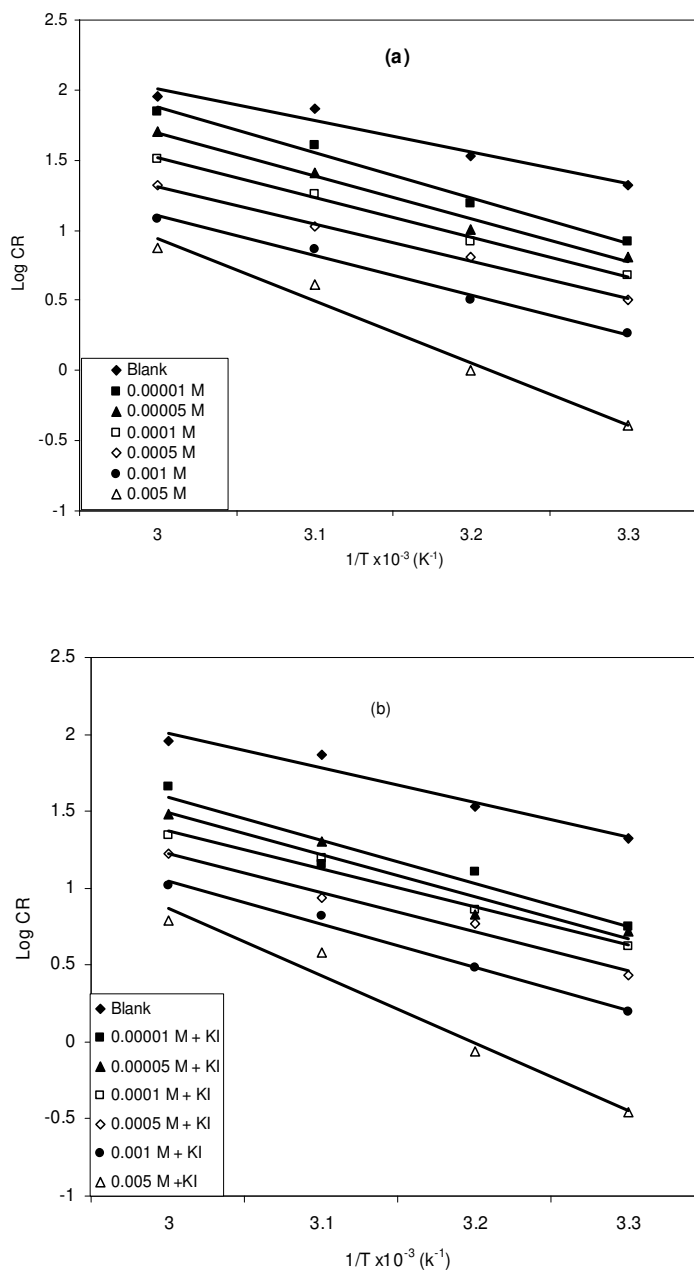

Figure 5. Arrhenius plot for mild steel corrosion in 2M H_2SO_4 in the absence and presence of different concentrations of (a) inhibitor (AYGG) (b) inhibitor (AYGG) + KI.
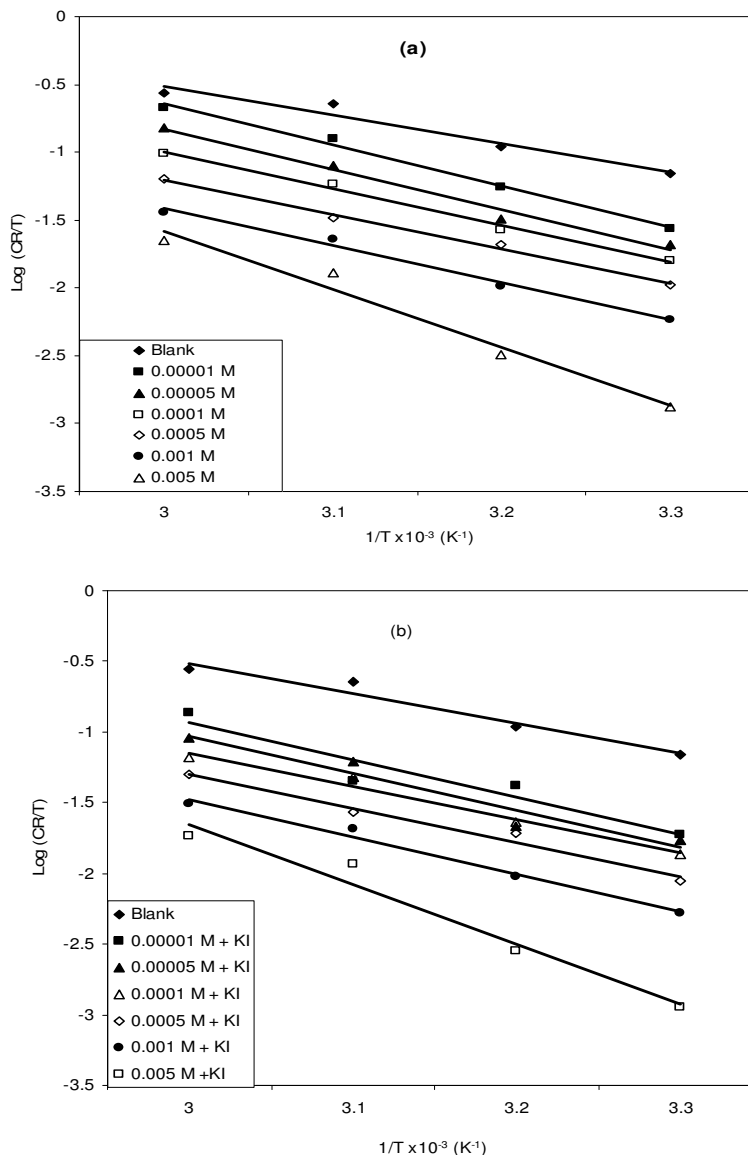
Figure 6. Transition state plot for mild steel corrosion in 2M H_2SO_4 in the absence and presence of different concentrations of (a) inhibitor (AYGG) and (b) inhibitor (AYGG) + KI.

Straight lines were obtained with a slope of $(-\Delta H^o/ R)$ and an intercept of $(\ln R/Nh + \Delta S^o/R)$ from which the values of ΔH^o and ΔS^o were calculated, and listed in Table 2. While an endothermic adsorption process $(\Delta H^o > 0)$ is attributed unequivocally to chemisorption, an exothermic adsorption process $(\Delta H^o < 0)$ may involve either physisorption or chemisorption or a mixture of both processes. In the present work, the negative value obtained may introduce both chemisorption and physisorption processes. This may be interpreted by the presence of both heteroatoms (nitrogen and oxygen atoms) which lead to coordinate bonds and aromatic rings which get physisorption. Also the negative values of ΔH^o show that the adsorption is exothermal with an ordered phenomenon ascribed by the negative

values of ΔS^o. This order may more probably be explained by the possibility of the formation of iron complex on the metal surface [52 - 58].

Table 2. Kinetic/thermodynamic parameters for mild steel corrosion in 2M H_2SO_4

System/concentration	Ea (kJ/mol)	$-\Delta H$ (kJ/mol)	$-\Delta S$ (J/mol/K)
Blank	0.520	0.488	5.74
0.00001M	0.739	0.698	6.51
0.0005 M	0.707	0.684	10.15
0.0001M	0.652	0.623	13.98
0.0005M	0.610	0.585	18.19
0.001M	0.647	0.626	22.11
0.005M	1.018	0.988	22.11
0.00001M +KI	0.640	0.608	12.83
0.0005 M + KI	0.633	0.603	14.65
0.0001M + KI	0.585	0.544	17.42
0.0005M + KI	0.573	0.533	20.29
0.001M + KI	0.645	0.608	23.26
0.005M + KI	1.011	0.972	23.65

3.4. Synergistic effect of KI addition

It is generally accepted that the presence of halide ions in acidic media synergistically increases the inhibition efficiency of some organic compounds. It is thought that the halide ions are able to improve adsorption of the organic cations by forming intermediate bridges between the positively charged metal surface and the positive end of the organic inhibitor. Corrosion inhibition synergism according to Oguzie et al. [59] results from increased surface coverage arising from ion-pair interactions between the organic cations and the anions. The synergistic ability of the halides increases in the order $Cl^- < Br^- < I^-$ [47], and is initiated by the specific adsorption of the anion onto the metal surface. The greater influence of the iodide ion is often attributed to its large ionic radius, high hydrophobicity, and low electronegativity, compared to the other halide ions [39].

The synergism parameter, S_1 was evaluated using the relationship given by Aramaki and Hackerman and reported elsewhere [39, 41]:

$$S_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \qquad (5)$$

where $I_{1+2} = (I_1 + I_2)$; I_1 = inhibition efficiency of the iodide; I_2 = inhibition efficiency of AYGG; I'_{1+2} = measured inhibition efficiency for AYGG in combination with iodide ions. This parameter was

evaluated from the inhibition efficiency values obtained from both the weight loss and hydrogen evolution measurements. The S_1 values for both methods employed as shown in Table 3 for different concentrations of AYGG are greater than unity. This indicates that the improved inhibition efficiency caused by the addition of iodide ions to AYGG is only due to synergistic effect. Similar results have been documented elsewhere [43, 54]. The synergistic effect between AYGG and KI can be explained by the fact that the addition of the KI component stabilized the adsorption of AYGG on the steel surface. This stabilization may be caused by the interaction between AYGG and I^- ions. Thus, the interaction enhances the inhibition efficiency to a considerable extent due to the increase of the surface coverage in the presence of iodide ions.

Table 3. Synergism parameter for different concentrations of the inhibitor (AYGG) at 30°C from the weight loss and hydrogen evolution methods.

Inhibitor (AYGG) concentration (M)	Synergism parameter,S_1	
	Weight loss	Hydrogen evolution
0.00001	1.11	1.17
0.00005	1.16	1.11
0.0001	1.12	1.15
0.0005	1.19	1.24
0.001	1.13	1.13
0.005	1.12	1.09

4. CONCLUSIONS

- Results from the two techniques employed show AYGG as effective inhibitor for the corrosion of mild steel in H_2SO_4.
- Increase in temperature increases corrosion rate but decreases the inhibition efficiency. Inhibition efficiency was found to increase with increase in concentration of AYGG.
- Synergistic effects between AYGG and KI have been observed. The addition of KI enhances the inhibition efficiency significantly.
- The adsorption of AYGG, KI and AYGG + KI on mild steel surface in 2M H_2SO_4 obeys Temkin adsorption isotherm.
- Phenomenon of physical adsorption is proposed from the obtained values of kinetic/thermodynamic parameters (E_a, ΔG^{o}_{ads}).

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