

Research Article

Inhibitory Action of *Artemisia annua* Extracts and Artemisinin on the Corrosion of Mild Steel in H₂SO₄ Solution

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The action of ethanol (EEAA), acid (AEAA), and toluene (TEAA) extracts from *Artemisia annua* and Artemisinin (ATS) on mild steel corrosion in H₂SO₄ solutions was investigated using gravimetric and gasometric techniques. The extracts and ATS functioned as good inhibitors, and their inhibition efficiencies (%IE) followed the trend: EEAA > AEAA > TEAA > ATS. %IE increased with increase in inhibitors concentration and decreased with increase in temperature. The enhanced %IE values of the extracts were attributed to synergistic effect of the components of the plant extracts with ATS. The adsorption of the inhibitors was consistent with Langmuir isotherm. Physisorption is proposed as the mechanism of inhibition.

1. Introduction

Present trend in research on environmental friendly corrosion inhibitors is taking us back to exploring the use of natural products as possible sources of cheap, nontoxic, and ecofriendly corrosion inhibitors. These natural products are either synthesized or extracted from aromatic herbs, spices, and medicinal plants. Of increasing interest is the use of medicinal plant extracts as corrosion inhibitors for metals in acid solutions. This is because these plants serve as incredibly rich sources of naturally synthesized chemical compounds that are environmentally acceptable, inexpensive, readily available, and renewable sources of materials [1, 2]. These chemicals include alkaloids, flavonoids, terpenoids, glycosides, tannins, saponins, fats and oils, and carbohydrates, and so forth [3–11]. The complex composition of phytochemicals in plant extracts makes it difficult to attempt to assign the inhibition ability to a particular constituent. Some researchers have, however, ascribed the inhibition efficiency of these medicinal plants to their active components used for medical purposes [3]. We have recently attempted to

assign the inhibition ability to some constituents by studying the inhibitive effect of different parts of a given plant with variable concentrations of the phytochemicals on acid corrosion [4–7]. Another most probable method would be the use of different solvents in the extraction process and comparing their inhibition efficiencies. This is yet to be explored in most of the reported work on corrosion inhibition of plant extracts.

Artemisia annua is native to Asia, most probably China, but is currently cultivated in many countries including Nigeria, mainly as a source of artemisinin, an important natural sesquiterpene lactone with antimalarial effect against susceptible and multidrug resistant *Plasmodium* spp. The plant is a large shrub often reaching more than 2.0 m in height, usually single-stemmed with alternate branches. The leaves are deeply dissected and range from 2.5 to 5 cm in length.

A. annua contains at least 20 known sesquiterpenes including artemisinin (arteannuin A), arteannuin B, artemisitene, and artemisinin acid. Artemisinin content varies from as low as 0.01 to 1.5% of plant dry weight depending

TABLE 1: Chemical composition of the mild steel.

| Element | C | Si | Mn | S | P | Ni | Cr | Mo | Cu | Fe |
|-------------|------|------|------|------|------|------|------|------|------|---------|
| Composition | 0.19 | 0.26 | 0.64 | 0.05 | 0.06 | 0.09 | 0.08 | 0.02 | 0.27 | Balance |

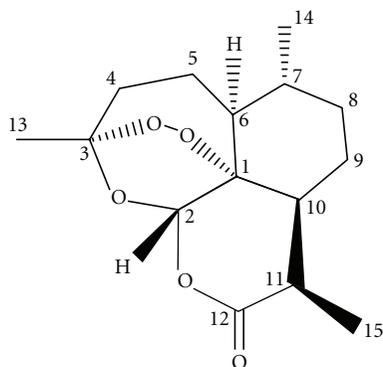


FIGURE 1: Structure of artemisinin.

on various factors such as the plant's origin, its stage of development, and the cultivation conditions [12–14]. This compound, isolated more than 50 years ago from *A. annua* by Chinese scientists searching for novel antimalarial drugs, has an unusual trioxane structure with seven stereogenic centers and tetracyclic framework (Figure 1) but lacks a nitrogen containing heterocyclic ring which is found in most antimalarial compounds. *A. annua* has also been shown to have a high content of flavonoid compounds, including the newly reported C-glycosyl flavonoids as a possible component of the antioxidant and antiviral activity [15].

In view of our interest in environmentally friendly corrosion inhibitor, the present study reports the inhibitory effect of acid (AEAA), ethanol (EEAA), and toluene (TEAA) extracts from *A. annua* and artemisinin (ATS) on mild steel corrosion in H_2SO_4 solutions using the weight loss and gasometric techniques.

2. Experimental Methods

The mild steel sheets used in this present work have the composition presented in Table 1. Before measurements, the mild steel coupons were mechanically polished with series of emery paper of variable grades starting with the coarsest and proceeding in steps to the finest (600) grade, degreased with absolute ethanol, dipped into acetone, and air-dried. The hydrogen evolution experiments were conducted on mild steel coupons of dimension $1.33 \times 0.08 \times 5.0$ cm (with a surface area of 14.008 cm^2), and, for the weight loss study, mild steel specimens of size $4.0 \times 0.08 \times 5.0$ cm (with a surface area of 41.44 cm^2) were used.

2.1. Preparation of Inhibitor Solutions. Dried leaves of *Artemisia annua* and artemisinin (ATS) used for this work were gotten from the Department of Genetics and Biotechnology, University of Calabar, Calabar, Nigeria. The leaves were ground into powder form. 80.0 g of the powder was

extracted continually with 250 cm^3 of the appropriate solvent (ethanol and toluene for the ethanol and toluene extracts, resp.) in a soxhlet extractor for 24 hours. After recovering most of the solvents, the extracts were heated on a water bath (at 60°C) until most of the solvents evaporated. 4.0 g of the extracts were soaked in 1 liter of 5 M H_2SO_4 and 1 M H_2SO_4 solutions for hydrogen evolution and weight loss measurements, respectively. The resultant solutions were kept for 24 hours, filtered, and stored. From the stock solutions (4.0 gL^{-1}), test solutions (concentrations of 0.1, 0.5, 1.0, 2.0 and 4.0 gL^{-1}) were prepared. Similar procedure was also carried out with 4.0 g of the powdered form of the leaves. For the ATS- H_2SO_4 solutions, 20, 50, 100, 200, and 400 mgL^{-1} ATS solutions were prepared in 5.0 M H_2SO_4 and 1.0 M H_2SO_4 solutions for hydrogen evolution and weight loss measurements, respectively.

2.2. Phytochemical Screening. Phytochemical screening was carried out on the extracts from *A. annua* following the methods described by Harbone [16], Sofowora [17], and Trease and Evans [18]. The plant extracts were screened for alkaloids, saponins, tannins, flavonoids, cardiac glycosides, and anthraquinones.

2.3. Weight Loss and Gasometric Measurements. The weight loss and gasometric measurements were carried out as previously described [19, 20]. However, experiments were conducted at 30°C for weight loss, and at 30° , 40° , 50° , and 60°C for gasometric measurements.

For the weight loss measurements, the mild steel coupons were each suspended and completely immersed in the test solutions (1 M H_2SO_4) with and without different concentrations of the plant extracts and artemisinin (ATS) with the help of glass hooks and rods for 7 days at $30 \pm 1^\circ\text{C}$. The coupons were retrieved at 24-hour intervals, washed several times in 20% sodium hydroxide solution containing 200 gL^{-1} of zinc dust until clean, dipped into acetone, air-dried, and reweighed [19, 20].

Gasometric technique is based on the principle that corrosion reactions in aqueous media are characterized by the evolution of gas resulting from the cathodic reaction of the corrosion process, which is proportional to the rate of corrosion [21]. The rate of evolution of the gas (R_H) was determined from the slope of the graph of volume of gas evolved per surface area versus immersion time and efficiencies (%IE) determined using

$$\%IE = \frac{R_{H_0} - R_{H_i}}{R_{H_0}} \times 100, \quad (1)$$

where R_{H_0} and R_{H_i} are the rates of hydrogen evolution per surface area in the absence and presence of the inhibiting molecules, respectively.

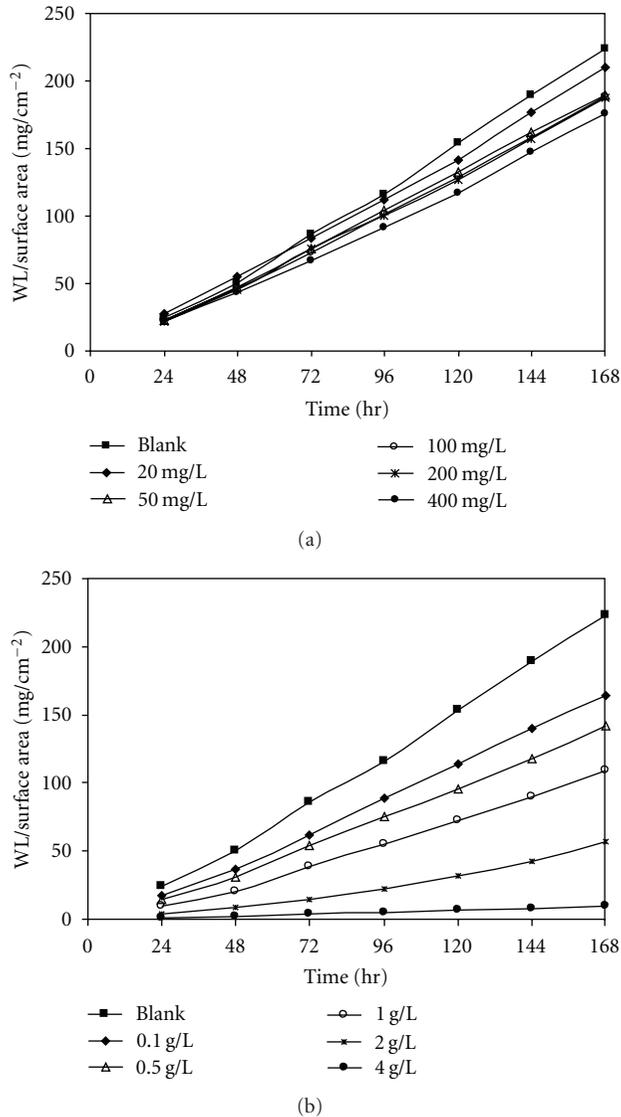


FIGURE 2: Variation of weight loss per surface area with time for mild steel in 1.0 M H_2SO_4 containing (a) ATS and (b) EEAA.

In determining the rate of hydrogen evolution per surface area, the contribution of other gases, including water vapour at especially higher temperature is assumed to be insignificant. This gasometric technique has been corroborated by other well-established corrosion rate determination techniques, including weight loss, thermometric, and electrochemical techniques [22–24]. The data presented in this work represents the average of two to three measurements from the weight loss and gasometric techniques.

3. Results and Discussion

3.1. Weight Loss Results. The variation of the weight loss (in $mg\ cm^{-2}$) of mild steel with immersion time in 1 M H_2SO_4 solutions in the absence and presence of ATS and EEAA at $30^\circ C$ is as shown in Figure 2. The weight loss

was observed to increase with increase in time but decrease with increase in the concentration of the inhibitors. This behaviour reflects the inhibitive effect of the inhibitors toward the acid corrosion of the steel. Similar trend was observed in the presence of the other plant extracts. The rate of corrosion (in $mg\ cm^{-2}h^{-1}$) of the mild steel in the acid medium determined from the slope of the plots is given in Table 2. It is clearly seen that the corrosion rate decreases with increase in the inhibitors concentration. This observed trend may result from the fact that adsorption and surface coverage increase with the increase in concentration; thus, the surface is separated from the medium. From the corrosion rate values, the inhibition efficiency (%IE) was determined using

$$\%IE = \frac{R_o - R_i}{R_o} \times 100, \quad (2)$$

where R_o and R_i are the corrosion rates in the absence and presence of the inhibiting molecules, respectively. The data are given in Table 2. It is observed that the inhibition efficiency increases as the added inhibitors concentrations are increased. It reaches 96% for $4.0\ gL^{-1}$ EEAA, 93% for $4.0\ gL^{-1}$ AEAA, and 24% for $400\ mgL^{-1}$ ATS.

3.2. Gasometric Technique. The effect of addition of the tested extracts (EEAA, AEAA, and TEAA) and ATS at different concentrations and temperatures on the corrosion of mild steel in 5 M H_2SO_4 was studied in more detail using the gas evolution method. The gas evolution technique is more suitable at a high corrodent concentration, while the weight loss method suffices for a low corrodent concentration [19]. Table 3 groups the corresponding values of rate of hydrogen evolved per surface area of the mild steel and the inhibition efficiency. It is clear that the presence of all tested extracts and ATS reduced the rate of hydrogen evolution per surface area and consequently the corrosion attack is inhibited. It is clearly seen that the rate of hydrogen evolution per surface area decreases with increase in the extracts and ATS concentrations. This trend as noted earlier may result from the fact that adsorption and surface coverage increases with the increase in the inhibitors concentration, thus, separating the surface of the metal from the medium [25–27]. It is also observed from Table 3 that the inhibition efficiencies follow the trend: EEAA > AEAA > TEAA > ATS. Similar trend was obtained at lower concentration of the acid via the weight loss method. The inhibition efficiency increases with the extracts and ATS concentrations to reach 96.73, 94.01, 86.10 and 44.41% for EEAA, AEAA, TEAA, and ATS, respectively. Figure 3 illustrates the comparison of the inhibition efficiencies of the extracts and ATS on the corrosion of mild steel in H_2SO_4 at $30^\circ C$.

3.3. Activation Parameters. Temperature can affect mild steel corrosion in acidic media in the presence and absence of inhibitor. To determine the action energy of the corrosion process, gasometric measurements were taken at various temperatures (30 – $60^\circ C$) in the presence and absence of the extracts and ATS. The corresponding results are also given in Table 3. From these results, we can deduce that the rate of

TABLE 2: Calculated values of the corrosion rate and inhibition efficiency for mild steel coupons in 1.0 M H₂SO₄ solutions in the absence and presence of inhibitors (using the weight loss technique).

| Inhibitor | System | Corrosion rates (mg cm ⁻² hr ⁻¹) | Inhibition efficiency (%) |
|-----------|--|---|---------------------------|
| | Blank | 1.406 | — |
| EEAA | 0.1 gL ⁻¹ EEAA + 5 M H ₂ SO ₄ | 1.040 | 26.00 |
| | 0.5 gL ⁻¹ EEAA + 5 M H ₂ SO ₄ | 0.886 | 37.02 |
| | 1.0 gL ⁻¹ EEAA + 5 M H ₂ SO ₄ | 0.703 | 50.01 |
| | 2.0 gL ⁻¹ EEAA + 5 M H ₂ SO ₄ | 0.366 | 74.00 |
| | 4.0 gL ⁻¹ EEAA + 5 M H ₂ SO ₄ | 0.064 | 95.48 |
| AEAA | 0.1 gL ⁻¹ AEAA + 5 M H ₂ SO ₄ | 0.886 | 37.02 |
| | 0.5 gL ⁻¹ AEAA + 5 M H ₂ SO ₄ | 0.515 | 63.35 |
| | 1.0 gL ⁻¹ AEAA + 5 M H ₂ SO ₄ | 0.414 | 70.55 |
| | 2.0 gL ⁻¹ AEAA + 5 M H ₂ SO ₄ | 0.206 | 85.36 |
| | 4.0 gL ⁻¹ AEAA + 5 M H ₂ SO ₄ | 0.105 | 92.54 |
| ATS | 20 mgL ⁻¹ ATS + 5 M H ₂ SO ₄ | 1.266 | 9.97 |
| | 50 mgL ⁻¹ ATS + 5 M H ₂ SO ₄ | 1.172 | 16.61 |
| | 100 mgL ⁻¹ ATS + 5 M H ₂ SO ₄ | 1.159 | 17.55 |
| | 200 mgL ⁻¹ ATS + 5 M H ₂ SO ₄ | 1.153 | 17.98 |
| | 400 mgL ⁻¹ ATS + 5 M H ₂ SO ₄ | 1.071 | 23.81 |

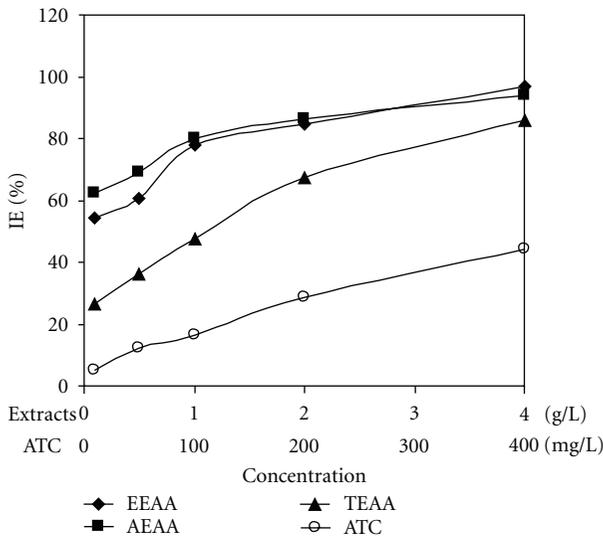


FIGURE 3: Variation of inhibition efficiency with extract concentration for mild steel in 5 M H₂SO₄ containing the inhibitors at 30°C.

hydrogen evolution per surface area increases with the rise of temperature. The inhibitive efficiencies of the inhibitors decrease with the rise of temperature.

Figure 4 shows Arrhenius plots for the mild steel in 5 M H₂SO₄ solutions in the absence and presence of EEAA. Similar plots were obtained in the presence of AEAA, TEAA, and ATS. The activation energies (E_a) can be expressed by the Arrhenius equation:

$$k = A \exp\left(\frac{-E_a}{RT}\right), \quad (3)$$

where T is the absolute temperature, A is the Arrhenius constant, and R is the universal gas constant. The values of k

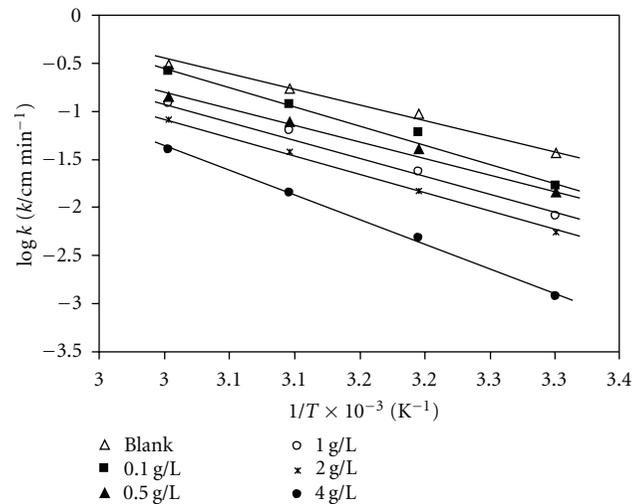


FIGURE 4: Arrhenius plots for the mild steel in 5 M H₂SO₄ in the absence (Blank) and presence of EEAA.

were taken to be equal to the rate of hydrogen evolution per surface area [4, 28–30]. The activation energies are given in Table 3. It is evident that the presence of inhibitor increases the activation energy. This may indicate the physical nature of adsorption mechanism [31, 32].

The enthalpy (ΔH^*) and entropy of activation (ΔS^*) were determined using the Eyring transition state equation (Figure 5 for EEAA):

$$k = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right), \quad (4)$$

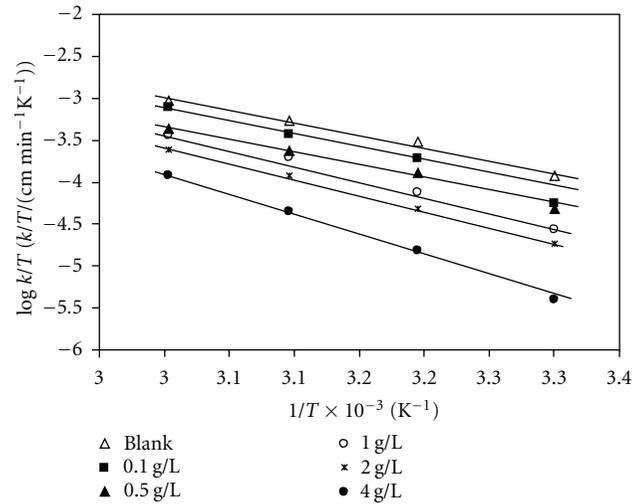
where N is the Avogadro's number, h is the Plank's constant, and ΔH^* and ΔS^* are the standard enthalpy and entropy

TABLE 3: Kinetics and activation parameters for mild steel coupons in 5.0 M H₂SO₄ solutions in the absence and presence of inhibitors (using the gasometric technique).

| System | Rate of hydrogen evolution (cm min ⁻¹) | | | | Inhibition efficiency (%) | | | | E_a (KJmol ⁻¹) | ΔH^* (KJmol ⁻¹) | ΔS^* (Jmol ⁻¹ K ⁻¹) |
|--|---|-------|-------|-------|---------------------------|-------|-------|-------|---------------------------------|--|--|
| | 30°C | 40°C | 50°C | 60°C | 30°C | 40°C | 50°C | 60°C | | | |
| 5 M H ₂ SO ₄ (blank) | 0.037 | 0.096 | 0.174 | 0.311 | — | — | — | — | 58.96 | 56.32 | -86.00 |
| 0.1 gL ⁻¹ EEAA + 5 M H ₂ SO ₄ | 0.017 | 0.060 | 0.119 | 0.257 | 54.50 | 37.70 | 31.70 | 17.27 | 74.83 | 72.19 | -39.82 |
| 0.5 gL ⁻¹ EEAA + 5 M H ₂ SO ₄ | 0.015 | 0.041 | 0.078 | 0.144 | 60.49 | 56.96 | 55.22 | 53.72 | 63.30 | 60.66 | -79.28 |
| 1.0 gL ⁻¹ EEAA + 5 M H ₂ SO ₄ | 0.008 | 0.023 | 0.064 | 0.120 | 77.93 | 75.71 | 63.40 | 61.27 | 76.55 | 73.91 | -40.73 |
| 2.0 gL ⁻¹ EEAA + 5 M H ₂ SO ₄ | 0.006 | 0.015 | 0.038 | 0.082 | 84.74 | 84.40 | 77.93 | 73.66 | 75.52 | 72.88 | -47.53 |
| 4.0 gL ⁻¹ EEAA + 5 M H ₂ SO ₄ | 0.001 | 0.005 | 0.014 | 0.039 | 96.73 | 94.97 | 91.82 | 87.33 | 97.12 | 94.48 | 11.34 |
| 0.1 gL ⁻¹ AEAA + 5 M H ₂ SO ₄ | 0.014 | 0.037 | 0.090 | 0.256 | 62.40 | 60.84 | 48.41 | 17.59 | 80.78 | 78.14 | -23.05 |
| 0.5 gL ⁻¹ AEAA + 5 M H ₂ SO ₄ | 0.011 | 0.032 | 0.082 | 0.168 | 68.94 | 66.18 | 52.91 | 46.06 | 75.58 | 72.94 | -41.17 |
| 1.0 gL ⁻¹ AEAA + 5 M H ₂ SO ₄ | 0.007 | 0.028 | 0.070 | 0.132 | 79.84 | 70.68 | 59.54 | 57.67 | 80.49 | 77.84 | -27.76 |
| 2.0 gL ⁻¹ AEAA + 5 M H ₂ SO ₄ | 0.005 | 0.018 | 0.047 | 0.090 | 86.38 | 81.05 | 73.20 | 70.96 | 81.03 | 78.39 | -29.39 |
| 4.0 gL ⁻¹ AEAA + 5 M H ₂ SO ₄ | 0.002 | 0.008 | 0.034 | 0.071 | 94.01 | 91.73 | 80.58 | 77.10 | 99.91 | 97.27 | 25.45 |
| 0.1 gL ⁻¹ TEAA + 5 M H ₂ SO ₄ | 0.027 | 0.079 | 0.149 | 0.286 | 26.43 | 17.17 | 14.18 | 7.91 | 64.93 | 62.29 | -68.71 |
| 0.5 gL ⁻¹ TEAA + 5 M H ₂ SO ₄ | 0.023 | 0.066 | 0.123 | 0.263 | 36.24 | 31.41 | 29.34 | 15.37 | 66.27 | 63.63 | -65.75 |
| 1.0 gL ⁻¹ TEAA + 5 M H ₂ SO ₄ | 0.019 | 0.052 | 0.102 | 0.204 | 47.68 | 45.86 | 41.10 | 34.26 | 65.37 | 62.73 | -70.39 |
| 2.0 gL ⁻¹ TEAA + 5 M H ₂ SO ₄ | 0.012 | 0.035 | 0.067 | 0.145 | 67.57 | 63.66 | 61.21 | 53.39 | 68.59 | 65.95 | -63.65 |
| 4.0 gL ⁻¹ TEAA + 5 M H ₂ SO ₄ | 0.005 | 0.016 | 0.039 | 0.079 | 86.10 | 83.66 | 77.75 | 74.69 | 76.65 | 74.01 | -44.14 |
| 20 mgL ⁻¹ ATS + 5 M H ₂ SO ₄ | 0.035 | 0.092 | 0.167 | 0.306 | 5.18 | 3.98 | 3.57 | 1.67 | 59.90 | 57.26 | -83.33 |
| 50 mgL ⁻¹ ATS + 5 M H ₂ SO ₄ | 0.032 | 0.087 | 0.159 | 0.286 | 12.26 | 9.01 | 8.53 | 7.91 | 60.23 | 57.59 | -82.80 |
| 100 mgL ⁻¹ ATS + 5 M H ₂ SO ₄ | 0.031 | 0.083 | 0.151 | 0.279 | 16.35 | 13.19 | 13.26 | 10.20 | 60.74 | 58.10 | -81.57 |
| 200 mgL ⁻¹ ATS + 5 M H ₂ SO ₄ | 0.026 | 0.071 | 0.145 | 0.265 | 28.61 | 25.86 | 16.54 | 14.73 | 64.42 | 61.79 | -70.80 |
| 400 mgL ⁻¹ ATS + 5 M H ₂ SO ₄ | 0.020 | 0.054 | 0.125 | 0.233 | 44.41 | 43.04 | 27.72 | 25.06 | 68.46 | 65.82 | -59.73 |

of activation, respectively. The data are given in Table 3. Inspection of Table 3 shows higher values for ΔH^* in the presence of the inhibitors, indicative of the higher protection efficiency observed for the system [28]. The ΔS^* values in the absence and presence of the inhibitors are negative. This implies that the activation complex in the rate determining step represents association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [33].

3.4. Adsorption Parameters. The inhibitive action of the plant extracts toward the acid corrosion of steel is attributed to the adsorption of ATS and the other components of the plant on the surface of the mild steel. The adsorbed layer acts as a barrier for mass and charge transfers, leading to a decrease in the corrosion rate. Thus, it follows that the inhibition efficiency (%IE) is directly proportional to the fraction of the surface covered by the adsorbed molecules (θ). Therefore, θ is calculated using the relation $\theta = \%IE/100$ [3]. The mode of variation of θ with the extract concentration specifies the adsorption isotherm that describes the system. The obtained θ values were applied to different adsorption isotherm equations and found to fit the Langmuir adsorption isotherm (Figure 6 for AEAA) with R^2 values of up to 0.9962 for EEAA, 0.9995 for AEAA, 0.9688 for TEAA, and 0.9026 for

FIGURE 5: Eyring transition state equation for the mild steel in 5 M H₂SO₄ in the absence (Blank) and presence of EEAA.

ATS. The Langmuir adsorption isotherm may be formulated as

$$\frac{c}{\theta} = c + \frac{1}{K}, \quad (5)$$

TABLE 4: Thermodynamic parameters for the adsorption of EEAA, AEAA, TEAA, and ATS on mild steel in 5 M H₂SO₄ (using the gasometric technique).

| Inhibitor | Equilibrium constant | | | | $\Delta H_{\text{ads}}^{\circ}$ (KJmol ⁻¹) | $\Delta S_{\text{ads}}^{\circ}$ (Jmol ⁻¹) |
|-----------|----------------------|------|------|------|--|---|
| | 30°C | 40°C | 50°C | 60°C | | |
| EEAA | 3.97 | 3.31 | 2.48 | 1.94 | -20.37 | -55.51 |
| AEAA | 5.92 | 4.42 | 3.27 | 2.03 | -29.41 | -81.89 |
| TEAA | 1.35 | 1.08 | 0.97 | 0.50 | -25.50 | -81.01 |
| ATC | 0.32 | 0.23 | 0.24 | 0.16 | -17.22 | -66.45 |

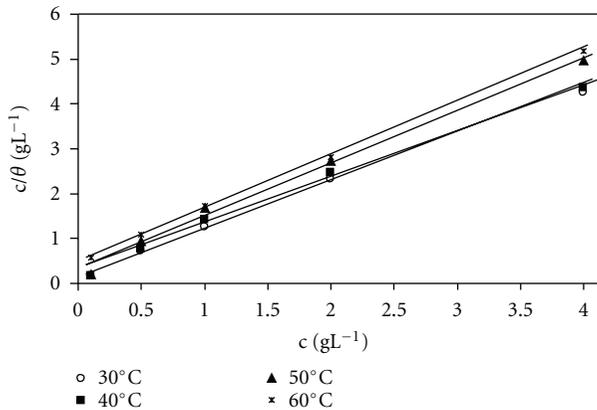


FIGURE 6: Langmuir adsorption isotherm for AEAA on mild steel in 5 M H₂SO₄.

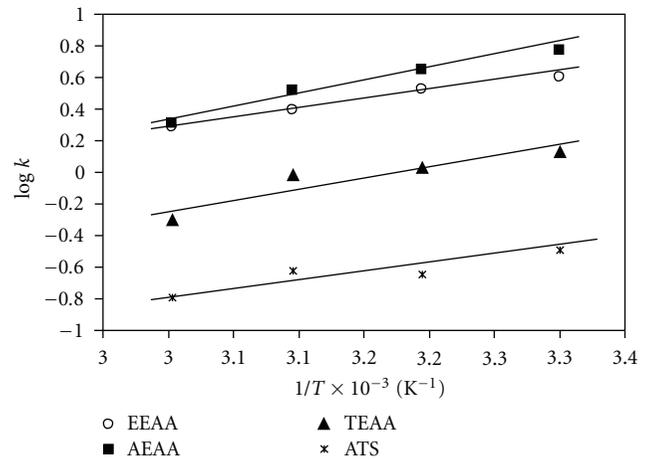


FIGURE 7: Curve fitting of log K data against $1/T$.

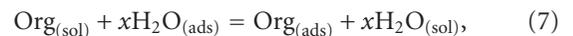
where c is inhibitor concentration, θ is the fraction of the surface covered by the adsorbed molecules, and K equals the equilibrium constant. The values of K obtained from the intercept of the isotherm plots are given in Table 4. K values are seen to decrease with increase in temperature suggesting that the inhibitors are physically adsorbed on the surface of the metal. From the dependence of the K values on temperature, the thermodynamic parameters $\Delta H_{\text{ads}}^{\circ}$ and $\Delta S_{\text{ads}}^{\circ}$ were obtained by linear least squares fits of the log K data against $1/T$ (Figure 7):

$$\log K = -\frac{\Delta H_{\text{ads}}^{\circ}}{RT} + \frac{\Delta S_{\text{ads}}^{\circ}}{R}. \quad (6)$$

The resultant values are given in Table 4. Generally, negative values of $\Delta H_{\text{ads}}^{\circ}$ were obtained indicating an exothermic adsorption process. The exothermic adsorption process signifies either physical or chemical adsorption, while endothermic adsorption process is attributable to chemisorption. In an exothermic process, physical adsorption is distinguished from chemisorption by considering the absolute value of adsorption enthalpy. Typically, enthalpy of physical adsorption process is lower than 80 KJmol⁻¹, while the enthalpy of chemisorption process approaches 100 KJmol⁻¹ [32]. The values of the obtained enthalpy therefore suggest physical adsorption of the inhibitors on the surface of the metal. Comparing the values of $\Delta H_{\text{ads}}^{\circ}$ obtained in this work with the values of ΔH^* (enthalpy of activation), it is observed that the latter are very much larger than those of $\Delta H_{\text{ads}}^{\circ}$. This has

been interpreted to indicate physical adsorption rather than chemisorption [28].

3.5. Mechanism of Inhibition. The adsorption of an organic adsorbate on a metal surface is generally regarded as a substitutional adsorption process between the organic molecule in the aqueous solution ($\text{Org}_{(\text{sol})}$) and water molecules adsorbed on the metallic surface ($\text{H}_2\text{O}_{(\text{ads})}$) [34]:



where x is the size ratio representing the number of water molecules replaced by one molecule of organic adsorbate. The adsorption of organic compounds can be described by two main types of interaction: physical adsorption and chemisorption. In general, the proceeding of physical adsorption requires the presence of both electrically charged surface of the metal and charged species in the bulk of the solution. Chemisorption process involves charge sharing or charge-transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond. This is possible in case of a positive as well as a negative charge on the surface. The presence of a transition metal, having vacant, low-energy electron orbital and of an inhibitor with molecules having relatively loosely bound electrons or heteroatoms with lone pair of electrons is necessary [35, 36].

The plant extracts under investigation contain ATS in variable concentrations (0.01 to 1.5% of plant dry weight) [12–15]. The compound inhibits the corrosion reaction to

TABLE 5: Phytochemical screening of the extracts from *A. Annuua*.

| Chemical constituent | Screening | | |
|----------------------|-----------|------|------|
| | EEAA | AEAA | TEAA |
| Alkaloids | + | – | – |
| Saponins | – | – | – |
| Flavonoids | ++ | + | – |
| Tannins | + | – | + |
| Glycosides | + | + | + |
| Anthraquinones | – | – | – |

Notes: +: present in the extracts, –: absent in the extracts.

an appreciable extent as shown in Tables 2 and 3. ATS is a slightly polar compound [12] and can adsorb directly on the positively charged mild steel surface. ATS has an unusual trioxane structure with seven stereogenic centers and tetracyclic framework (Figure 1). It is probable that the adsorbed molecule is oriented with three of the tetracyclic ring structures parallel to the metal surface, thereby creating a barrier for mass and charge transfers. This situation leads to the protection of the mild steel from the acid corrosive ions. Comparing the inhibition efficiencies of ATS with those of the plant extracts, it is evident that ATS has the least efficiency. In addition to ATS, the plant extracts contain other known sesquiterpenes (over 20) including arteannuin B, artemisitene and artemisinin acid, flavonoid compounds, and other naturally occurring organic compounds [12–15]. This large number of different chemical compounds may form adsorbed intermediates which may either inhibit (forming insoluble Fe-phytochemical complex) or catalyse further metal dissolution. From the observed results, it can be inferred that the insoluble Fe-phytochemical complexes dominate the adsorbed intermediates and thus the resultant inhibitive effects. Synergistic inhibition of the components of the plant extracts may also contribute to the enhanced inhibition efficiency when compared to that of ATS. In addition to the physical adsorption mechanism of inhibition of ATS and other components of the extracts, there could be chemical adsorption of some components of the extracts which may also enhance the inhibition ability of the plant extracts. However, from the study, it is evident that physical adsorption is the dominant mechanism of inhibition.

The results from the phytochemical screening of the extracts are shown in Table 5. It revealed that the composition of the extracts is dependent on the type of solvents used for the extraction process. EEAA is observed to contain alkaloids, appreciable quantities of flavonoids, tannins, and glycosides. Flavonoids and glycosides were detected in AEAA while tannins and glycosides were present in TEAA. The presence of more phytochemicals in EEAA, especially the alkaloids (which are nitrogen containing organic bases) and flavonoids compared to the other extracts may be responsible for the observed highest inhibition efficiency of EEAA. Comparing the phytochemical components of AEAA and TEAA, and relating them to their inhibition efficiencies, it could be inferred that the flavonoids inhibit better than the tannins thus the higher efficiency observed for AEAA. From

the observed phytochemical screening results and inhibition efficiencies, it could be concluded that the flavonoids are the principal phytochemicals in the extracts responsible for the inhibition ability of the plant. Synergism effects with other components of the plants, especially the alkaloids and tannins, may increase the inhibition efficiency to an appreciable extent, as observed for EEAA.

4. Conclusions

The ethanol (EEAA), acid (AEAA), and toluene (TEAA) extracts from the leaves of *Artemisia annua* and artemisinin (ATS) act as inhibitors for the corrosion of mild steel in H_2SO_4 solutions and the maximum inhibition efficiencies followed the trend: EEAA > AEAA > TEAA > ATS. The inhibition efficiency values increase with increase in concentration of the inhibitors and decrease with increase in temperature. The composition of the extracts as well as its inhibition efficiency is dependent on the type of solvents used for the extraction process. Synergistic inhibition of the components of the plant extracts with ATS is attributed to the enhanced inhibition efficiencies of the extracts. The adsorption of the inhibitors molecules was consistent with Langmuir adsorption isotherm, and physical adsorption is proposed as the dominant mechanism of inhibition.

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