

# Mild Steel Corrosion Mitigation in Sulphuric Acid via Benign Isolated Phytochemicals from *Viscum album*

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## Abstract

We present the evaluation of four Eco-friendly corrosion inhibitors for the corrosion mitigation of mild steel in acid media. The corrosion inhibition of mild steel by ethanol extracts from *Viscum album* (EEVA) and some of its isolated phytochemical components; phytates extract (PEVA), saponins extract (SEVA), and flavonoids extracts (FEVA) have been studied using gravimetric and gasometric techniques. The results of the study reveal that these ecofriendly and benign extracts function as good inhibitors for mild steel corrosion in sulphuric acid. Inhibition efficiency of the extracts increases with inhibitor concentration and temperature rise. The trend of inhibition efficiency in lower inhibitor concentration is EEVA > PEVA > SEVA > FEVA and at higher concentration, the order was SEVA > PEVA > EEVA > FEVA. The presence of the plant extracts decreases the corrosion activation energy in the solution which indicates chemical adsorption mechanism. The adsorption of the components of the extracts is consistent with Temkin isotherm. The interaction between the isolated extracts is synergistic at lower inhibitor concentration and antagonistic at higher concentrations. The  $K_{ads}$  values for PEVA and SEVA are higher than those of EEVA and FEVA. This implies that PEVA and SEVA are more efficiently adsorbed on the mild steel surface.

## Keywords

Acid Corrosion, Mild Steel, *Viscum album*, Corrosion Inhibition, Phytochemicals

## 1. Introduction

Mild steel has been extensively used under different conditions in chemical and

allied industries in handling alkaline, acid and salt solutions. Sulphate ions in aqueous media are particularly aggressive and accelerate corrosion. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. Green corrosion inhibitors are ecofriendly and biodegradable and do not contain heavy metals or other toxic compounds. Inhibitors in this class are those that are environmentally friendly and are obtained from natural products such as plant extracts [1]. The use of natural products as corrosion inhibitors has been widely reported by several authors. The extracts from leaves, seeds, bark, roots and fruits of plants have been reported to inhibit metallic corrosion in acidic media [2]-[11]. *Viscum album* (Mistletoe) is a common bushy plant of the family Loranthaceae, which grows as an epiphyte on the branches of deciduous trees. The plant is widely distributed in tropical and subtropical Africa, in Asia and in Europe [12]. The plant is used in the treatment of nervous complaints, bleeding and tumors [12] [13]. The extracts from the leaves stimulate insulin secretion from pancreas cells and help in the treatment of arthritis [14] [15] [16] [17] [18]. This medicinal plant is believed to be rich in nitrogen, sulphuric and oxygen containing organic compounds thus could exhibit a very strong inhibitive effect on corrosion of steel. These compounds provide good adsorption sites unto the metal surface via the residual lone pair of electrons on the hetero atoms present in their molecular structure.

Over the past decades, researchers have concentrated on the use of different parts of plant extracts as corrosion inhibitors in various media. The inhibitive effect has always been attributed to active phytochemicals (glycosides, phytates, saponins, flavonoids and tannins amongst others) in the extracts [18]-[24]. This research assertion is rather general as there is no experimental evidence indicating the phytochemical that contributes majorly to the inhibitory properties of the extracts. Also little is known about the synergistic and antagonistic effects of these phytochemicals in the extract. This work presents results of experiments designed to investigate the corrosion inhibition performance of the isolated phytochemicals in *Viscum album* leaves on mild steel corrosion in  $H_2SO_4$  solutions using gasometric and weight loss techniques. This is in order to ascertain the major active component responsible for the corrosion inhibition and to gain more understanding of the synergistic/antagonistic relationships between the extracts. For the purpose of this study, the phytochemicals that were isolated are phytates, saponins and flavonoids.

## 2. Experimental

### 2.1. Materials Preparation

The mild steel sheet used for the study were of composition (wt %) Mn (0.64), P (0.06), C (0.19), S (0.05), Ni (0.09), Cr (0.08), Mo (0.02), Cu (0.27), Si (0.26) and the rest Fe. The sheet was cut into coupons of dimension  $2 \times 0.08 \times 5$  cm and  $4 \times 0.08 \times 5$  for the hydrogen evolution and weight loss measurements. Before measurements the mild steel coupons were mechanically polished with series of

emery paper of up to 400 grits, degreased with absolute ethanol, dried in acetone and preserved in desiccators. Distilled water was used to prepare all experimental solutions. All other chemicals used were of Analar grade and all weighing was done with Mettler P 1210 digital analytical balance.

## 2.2. Preparation of Plant Extracts

The required plant parts *Viscum album* (Mistletoe) was collected from a local bush in Ikot Ekpene, Akwa Ibom State, Nigeria. These were cut into small chips and dried in an N53C—Genlab laboratory oven at 323 K and ground into powder form. 80 g of the powder was extracted continually with 250 cm<sup>3</sup> of absolute ethanol in a soxhlet extractor for 24 hours. The extracted jell was heated in a water bath (at 333 K) until most of the ethanol evaporated. 10 g of the ethanol extract was dissolved in 1 liter of 5.0 M H<sub>2</sub>SO<sub>4</sub> solution. The resultant solution was kept for 24 hours, filtered and stored. From the stock solution (10.0 g/L), inhibitor test solutions were prepared at concentrations of 0.5, 1.0, 2.5, 4.0, 5.0 and 7.5 g/L. Phytochemical screening was carried out on the ethanol extracts of *Viscum album* following the methods previously described by [16] and Trease & Evans [17]. The plant extracts were screened for alkaloids, saponins, tannins, flavonoids, phytates, phenols, oxalate and glycosides. The same procedure was repeated to obtain various concentrations of PEVA, SEVA and FEVA. Gasometric and weight loss experiments were then carried out using different concentrations of the extracts at different temperatures.

## 2.3. Hydrogen Evolution Technique

Gasometric assembly was used for the measurement of hydrogen gas evolution from corrosion reaction. The assembly was coupled and the connections were greased to avoid the escape of the gas. 100 cm<sup>3</sup> of the corroder (5.0 M H<sub>2</sub>SO<sub>4</sub> solution) was introduced into the reaction chamber connected to a burette through a delivery tube. A sample of the polished mild steel coupon was dropped into the solution and the reaction chamber quickly closed to prevent any escape of hydrogen. The volume of the hydrogen gas evolved from the corrosion reaction was monitored by the depression (in cm<sup>3</sup>) in the paraffin oil level. This depression in the paraffin oil level was recorded every minute for 60 minutes (1 hour). The same experiment was repeated in the presence of 0.5, 1.0, 2.5, 4.0, 5.0, 7.5 and 10.0 g/L ethanol extracts of *Viscum album* (EEVA) at 303 K. Also the experiments were carried out with 2.5 g/L EEVA at 313, 323 and 333 ± 2 K. The same experiment was repeated in the presence of different concentrations (0.5, 1.0 and 2.5 g/L) of SEVA, FEVA and PEVA at 303 K. Then also, the experiments were repeated with 2.5 g/L of each extract at 313, 323 and 333 ± 2 K.

## 2.4. Weight Loss Technique

In the weight loss experiment, a weighed mild steel coupon was suspended in a beaker containing 100 cm<sup>3</sup> of 5.0 M H<sub>2</sub>SO<sub>4</sub> solution with the aid of glass rod and

hook at room temperature. The mild steel coupon was completely immersed in the solution and after 1 hour the mild steel coupon was retrieved, washed, scrubbed with bristle brush by immersing it in 20% NaOH containing 20 g of zinc-dust. After washing, the mild steel coupon was rinsed with absolute ethanol, dipped in acetone, air dried, re-weighed and re-immersed in the corrodent. The weight loss of the mild steel coupon was evaluated in grams as the difference between the initial and final weight of the coupon. This process was repeated progressively for 6 hours. The same experimental procedure was carried out in the presence of ethanol extracts of *Viscum album* using concentrations of 0.5, 1.0, 2.5, 4.0, 5.0, 7.5 and 10.0 g/L. Experiments were carried out on mild steel coupons at room temperature 303 K only for the weight loss study.

### 3. Results and Discussion

#### 3.1. Phytochemical Screening Results

Phytochemical screening was carried out on the ethanol extracts of *Viscum album*. The results obtained are shown in **Table 1** and this indicates that the plant extracts contain glycosides, phytates, saponins, flavonoids and tannins. These compounds are heterogeneous organic compounds containing nitrogen, oxygen, sulphur and/or aromatic ring in the molecular structures. Organic heterogeneous compounds containing these elements have been reported to be efficient corrosion inhibitors [19] [24]. Thus, in the systems studied, these compounds are believed to contribute significantly to the inhibition of the corrosion reaction of the mild steel in acid media.

#### 3.2. Weight Loss

The variation of the weight loss for mild steel coupons with immersion time in 5.0 M H<sub>2</sub>SO<sub>4</sub> solutions in the absence and presence of EEVA at 303 K is shown in **Table 2**. From the results, it is observed that weight loss increases with time but decrease with increase in the concentration of the extracts. This behavior reflects the inhibitory effect of the extract toward the acid corrosion of the steel.

**Table 1.** Phytochemical screening of *Viscum album*.

Phytochemicals	Test	Concentration/(%)
Alkaloids	–	ND
Oxalate	–	ND
Tannins	+	1.44%
Saponins	+	14.4
Flavonoids	++	14.0
Phenol	–	ND
Phytates	++	12.00
Glycosides	++	18.43

Notes: +; moderately present in the extracts, ++; highly present, –; absent in the extract and ND, not determined.

**Table 2.** Weight loss of mild steel in the presence and absence (blank) of EEVA in 5.0 M H<sub>2</sub>SO<sub>4</sub> at 303 K.

Time/(hours)	Weight loss/(mg/cm <sup>3</sup> )							
	Blank	0.5 g/L	1.0 g/L	2.5 g/L	4.0 g/L	5.0 g/L	7.5 g/L	10.0 g/L
1	0.272	0.202	0.167	0.124	0.091	0.084	0.063	0.011
2	0.522	0.372	0.385	0.186	0.133	0.105	0.091	0.072
3	0.903	0.653	0.564	0.242	0.172	0.143	0.104	0.083
4	1.336	0.950	0.829	0.340	0.222	0.209	0.131	0.092
5	1.817	1.303	1.095	0.443	0.276	0.221	0.143	0.103
6	2.306	1.684	1.397	0.595	0.337	0.260	0.170	0.116

The rates of corrosion (in mg cm<sup>-2</sup>.hr<sup>-1</sup>) of the mild steel in the acid medium in the absence and presence of the plant extracts are presented in **Table 3**. It is clearly seen that the corrosion rate decreases with increase in the inhibitor concentration, indicating that the extent of inhibition is dependent on the amount of extract present. From the corrosion rate values, the inhibition efficiency (%*I*) was determined using Equation (1).

$$\% I = \frac{(CR_{\text{blank}} - CR_{\text{inh}}) \times 100}{CR_{\text{blank}}} \quad (1)$$

where  $CR_{\text{blank}}$  and  $CR_{\text{inh}}$  are the corrosion rates in the absence and presence of the plant extracts. The results obtained are given in **Table 3**. It is observed that the inhibition efficiency increases as the added inhibitor concentrations are increased. This suggests that the phytochemical components of the extracts are adsorbed onto the mild steel surface resulting in the blocking of the reaction sites, thus protecting the mild steel surface from the attack of the corrosion active ions in the acid medium.

### 3.3. Hydrogen Evolution

The acid corrosion of mild steel is characterized by evolution of hydrogen and the rate of corrosion is proportional to the amount of hydrogen evolved [5] [7], thus the volume of hydrogen evolved ( $V_H$ ) during the corrosion of mild steel in 5.0 M H<sub>2</sub>SO<sub>4</sub> solutions in the absence and presence of the ethanol extracts from *Viscum album* at 303 K as a function of time is depicted in **Figure 1**. The presence of the extract decreases the volume of hydrogen evolved during the corrosion reaction compared to the blank system. Also, similar trends were obtained at 313 K, 323 K and 333 K during the corrosion reaction for the extract of *Viscum album* with a concentration of 0.5, 1.0, 2.5, and 5.0 g/L. The rate of hydrogen evolved was deduced from the slopes of the plots in **Figure 1** and that for the elevated temperatures [18] and presented in **Table 4**. It is seen that the rate of hydrogen evolution decreases with increase in the extract concentrations and temperature. From the rate of hydrogen evolution, the inhibition efficiencies were determined using Equation (2). The results obtained are shown in **Table 4** at 303 K and **Table 5** at (313, 323 and 333 K). The inhibition efficiency was

**Table 3.** Corrosion rate ( $CR$ ), Surface coverage ( $\theta$ ) and inhibition efficiency (%) for mild steel in the presence and absence of EEVA in 5.0 M  $H_2SO_4$  at 303 K.

Concentration (g/L)	Corrosion rate (mg/cm <sup>2</sup> /hr)	Surface coverage ( $\theta$ )	Inhibition efficiency (%)
Blank	0.0100	0.28	28
0.5	0.0072	0.41	41
1.0	0.0059	0.78	78
2.5	0.0022	0.88	88
4.0	0.0012	0.91	91
5.0	0.0009	0.95	95
7.5	0.0005	0.96	96
10.0	0.0004	1.00	99.99

**Table 4.** Calculated values of the rate of hydrogen evolution ( $R_H$ ), surface coverage ( $\theta$ ) and inhibition efficiency (%) for mild in 5.0 M  $H_2SO_4$  solution in the absence (blank) and presence of EEVA at 303.

Concentration (g/L)	$R_H$ (cm/min)	$\theta$	%I
Blank	0.0346	-	-
0.5	0.0278	0.196	19.7
1.0	0.0191	0.447	44.8
2.5	0.0118	0.658	65.9
4.0	0.0091	0.736	73.7
5.0	0.0073	0.789	78.9
7.5	0.0047	0.864	86.4
10.0	0.0044	0.872	87.3

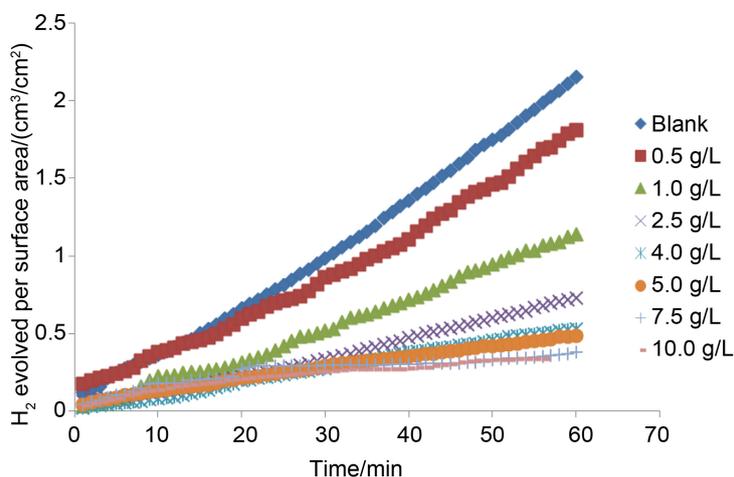
**Table 5.** Calculated values of the rate of hydrogen evolution ( $R_H$ ), surface coverage ( $\theta$ ) and inhibition efficiency (%) for mild steel in 5.0 M  $H_2SO_4$  solution containing, EEVA at 313, 323 and 333 K.

Conc. g/L	$R_H$ (cm/min)			$\theta$			%I		
	313 K	323 K	333 K	313 K	323 K	333 K	313 K	323 K	333 K
Blank	0.1209	0.2397	0.3297	-	-	-	-	-	-
0.5	0.0633	0.1147	0.1227	0.476	0.521	0.627	47.6	52.1	62.8
1.0	0.0375	0.0695	0.0900	0.689	0.710	0.727	68.9	71.0	72.7
2.5	0.0135	0.0229	0.0269	0.888	0.904	0.918	88.8	90.4	91.8

observed to increase with an increase in the extracts concentration and temperature (Table 5). This observation however, suggests a chemical interaction between the metal surface and the phyto chemical components of EEVA.

$$\% I = \frac{(R_{HB} - R_{HI}) \times 100}{R_{HB}} \quad (2)$$

where  $R_{HB}$  and  $R_{HI}$  are the rates of hydrogen evolution in the absence and presence



**Figure 1.** Variation of the volume of hydrogen evolved ( $V_H$ ) with time for mild steel in the presence and absence of different concentrations of EEVA in 5.0 M  $H_2SO_4$  solution at 303 K.

of plant extract. From the rate of hydrogen evolution, the inhibition efficiencies of different concentrations of flavonoids extract of *Viscum album* (FEVA), saponins extracts of *Viscum album* (SEVA), phytates extracts of *Viscum album* (PEVA) in 5.0 M  $H_2SO_4$  solution at 303 K were determined and presented in **Table 6**. The results obtained indicate that inhibition efficiencies generally increased with increase in extracts concentration for all the extracts. The highest inhibition efficiency of 85.3% obtained at 5.0 g/L SEVA, indicates that the dominant inhibitive effect of *Viscum album* may be attributed to SEVA while the lowest %*I* of 0.9% was obtained at 1.0 g/L of FEVA. The Inhibition efficiency of EEVA was generally higher than that of SEVA, FEVA and PEVA at lower concentrations (0.5 - 2.5 g/L), this suggests a synergistic interaction between the phytochemicals in *Viscum album* at low concentration. However, at higher concentrations of 5.0 g/L the efficiency of PEVA (81.5%) and SEVA (85.3%) became more pronounced.

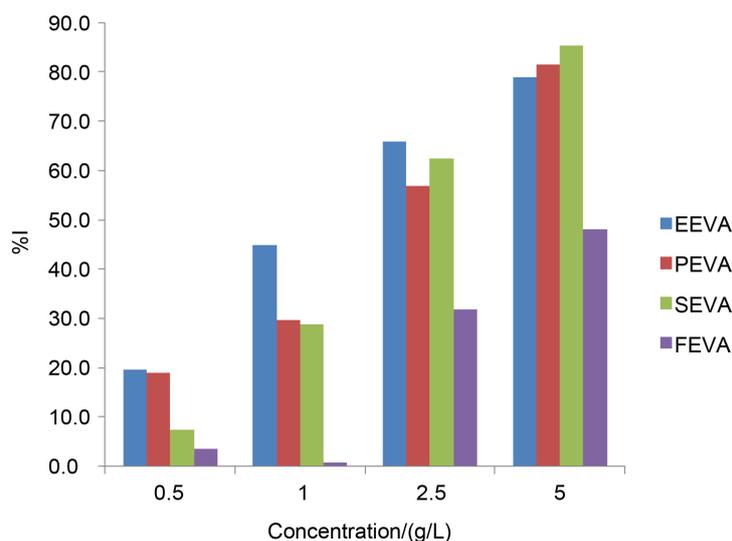
Comparison of the variation of inhibition efficiency with inhibitor concentration for EEVA, PEVA, SEVA and FEVA in 5.0 M  $H_2SO_4$  at 303 K is presented in **Figure 2**. The order of the efficiency at low concentrations obey the following trend EEVA > PEVA > SEVA > FEVA and at higher concentration the order was SEVA > PEVA > EEVA > FEVA. This indicates synergism at lower concentration and the opposite at higher concentration.

The volume of hydrogen evolved during corrosion of mild steel in 5.0 M  $H_2SO_4$  containing 2.5 g/L of PEVA at different temperatures is shown in **Figure 3**. From this figure, it is seen that the volume of hydrogen gas evolved increases with increase in temperature. Similar trends were obtained for FEVA and SEVA as shown in **Figure 4** and **Figure 5**.

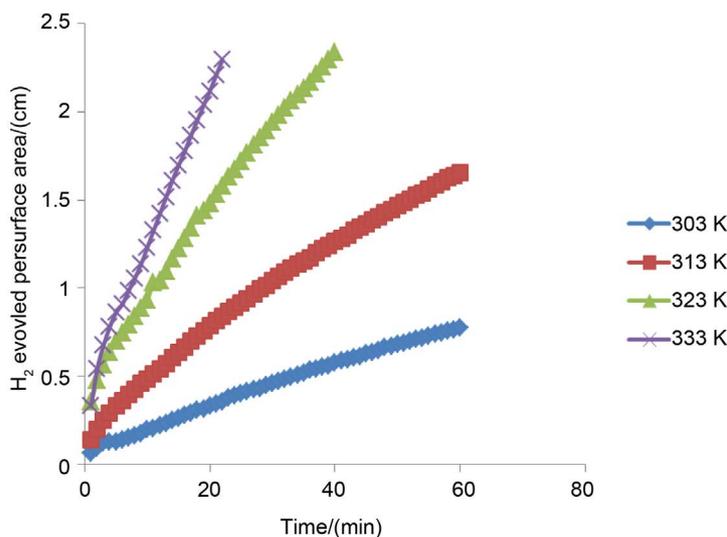
This is attributed to the increase in reaction rate which is known to increase with temperature. At elevated temperatures more of the reactant molecules gain enough energy required to overcome the energy barrier need to form products,

**Table 6.** Rate of hydrogen evolution ( $R_H$ ) Surface Coverage ( $\theta$ ) and Inhibition Efficiency (% $I$ ) of different concentrations of EEVA, SEVA, PEVA, FEVA in 5.0 M  $H_2SO_4$  solution at 303°C.

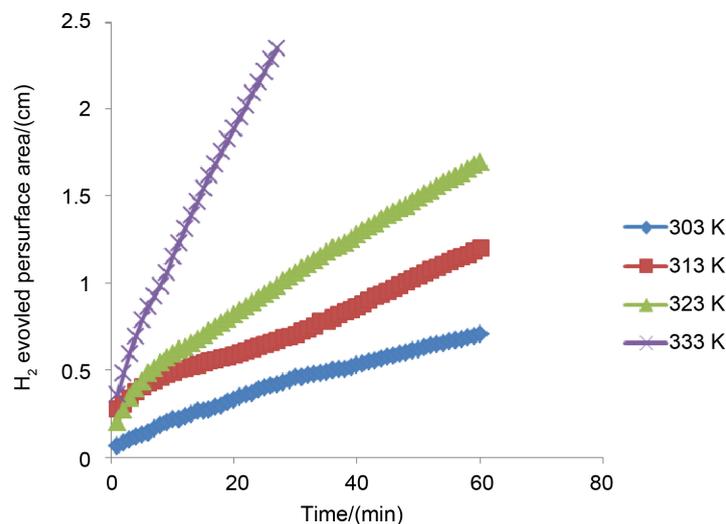
Conc (g/L)	Corrosion Rate/(cm/min)					$\theta$				% $I$			
Blank	EEVA	PEVA	SEVA	FEVA	EEVA	PEVA	SEVA	FEVA	EEVA	PEVA	SEVA	FEVA	
0.5	0.0346	0.0278	0.0280	0.0320	0.0334	0.20	0.19	0.08	0.03	19.7	19.1	7.5	3.5
1.0	0.0346	0.0191	0.0243	0.0246	0.0343	0.45	0.30	0.29	0.01	44.8	29.8	28.9	0.9
2.5	0.0346	0.0118	0.0149	0.0130	0.0236	0.66	0.57	0.62	0.32	65.9	56.9	62.4	31.8
5.0	0.0346	0.0073	0.0064	0.0051	0.0180	0.79	0.82	0.85	0.48	78.9	81.5	85.3	48.0



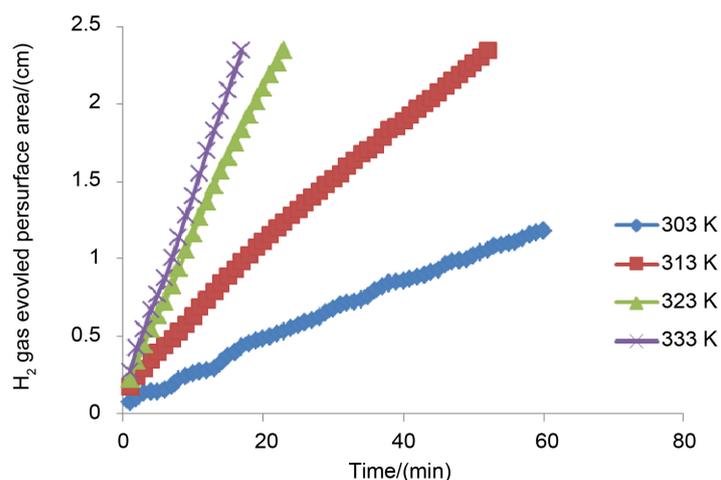
**Figure 2.** Comparison of the variation of inhibition efficiency with inhibitor concentration for EEVA, PEVA, SEVA and FEVA in 5.0 M  $H_2SO_4$  at 303 K.



**Figure 3.** Variation of hydrogen gas evolved ( $V_H$ ) with time for mild steel in 5.0 M  $H_2SO_4$  solution containing 2.5 g/L of PEVA at different temperatures.



**Figure 4.** Variation of hydrogen gas evolved ( $V_H$ ) with time for mild steel in 5.0 M  $H_2SO_4$  solution containing 2.5 g/L of SEVA at different temperatures.



**Figure 5.** Variation of hydrogen gas evolved ( $V_H$ ) with time for mild steel in 5.0 M  $H_2SO_4$  solution containing 2.5 g/L of FEVA at different temperatures.

thus leading to the higher rates of hydrogen evolution. From the rate of hydrogen evolution, the inhibition efficiencies for mild steel in 5.0 M  $H_2SO_4$  solution in the absence (blank) and presence of 2.5 g/L of EEVA, FEVA, PEVA and SEVA at different temperatures were determined and presented in **Table 7**. The results obtained indicate that the inhibition efficiencies increase with an increase in temperature. The maximum % $I$ , 91.8% was obtained at 333 K for 2.5 g/L concentration of EEVA and the minimum 31.4% at 303 K for 2.5 g/L concentration of FEVA. This suggests adsorption of the extracts via chemical interactions between the heterogeneous inhibitor molecules and the metal surface. The inhibitory effects observed for all the extracts can be attributed to the presence of hetero atoms in the molecular structure of the phytochemicals which provide good

**Table 7.** The rate of hydrogen evolution ( $R_H$ ), Surface Coverage ( $\theta$ ) and Inhibition Efficiency (%) for mild steel in 5 M  $H_2SO_4$  solution in the absence and presence of 2.5 g/L of EEVA, PEVA, SEVA and FEVA at different temperatures.

Temp	$R_H$ /(cm/min)				$\theta$				%I				
	Blank	EEVA	PEVA	SEVA	FEVA	EEVA	PEVA	SEVA	FEVA	EEVA	PEVA	SEVA	FEVA
303	0.0346	0.0118	0.0149	0.013	0.0236	0.66	0.57	0.62	0.31	65.9	56.9	62.4	31.9
313	0.1209	0.0135	0.0306	0.018	0.0518	0.87	0.66	0.72	0.32	87.4	66.2	71.9	32.4
323	0.1797	0.0227	0.0607	0.029	0.1214	0.89	0.67	0.84	0.51	88.9	66.8	83.9	51.1
333	0.3297	0.0269	0.1094	0.093	0.1612	0.91	0.75	0.85	0.57	91.8	74.7	85.1	57.1

adsorption sites unto the metal surface [20].

### 3.4. Adsorption Consideration

The observed corrosion inhibition of mild steel in 5.0 M  $H_2SO_4$  solutions in the absence and presence of EEVA, PEVA, SEVA and FEVA can be explained by the adsorption of the components of the plant extract on the metal surface. The surface coverage values obtained from this study were applied to different adsorption isotherm equations. From the results, it was found that the experimental data fitted the Temkin adsorption isotherm shown in **Figure 6** which may be formulated by Equation (3).

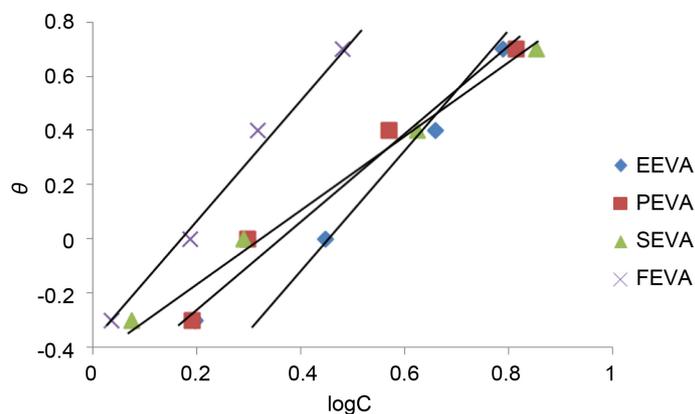
$$f(\theta, x) \exp(-2a\theta) = K_{ads} C \quad (3)$$

where,  $f(\theta, x)$  is the configuration factor which depends upon the physical model and the assumption underlying the derivation of the isotherm,  $c$  is the inhibitor concentration,  $\theta$  is the degree of surface coverage and  $K_{ads}$  is the adsorption-desorption equilibrium constant, and “ $a$ ” is an interaction parameter. The calculated values of  $K_{ads}$  and “ $a$ ” are as shown in **Table 8**. The positive values of “ $a$ ” indicate attractive forces between adsorbed molecules while negative values indicate repulsive forces between the adsorbed molecules.

It can be seen in **Table 8** that the value of “ $a$ ” is negative indicating that repulsion exists in the adsorption layer. It can also be observed from **Table 8** that the correlation factors ( $R^2$ ) for the isotherms in the presence of EEVA and SEVA are 0.9804 and 0.9990. This value is close to unity, signifying adherence to the principles underlying the derivation of the Temkin adsorption isotherm. It is generally known that  $K_{ads}$  denotes the strength between the adsorbate and adsorbent. Large values of  $K_{ads}$  imply more efficient adsorption and hence better inhibition efficiency [7]. In the present case,  $K_{ads}$  values for PEVA and SEVA is higher than those of EEVA and FEVA. This implies that PEVA and SEVA are better adsorbed [7].

### 3.5. Activation Parameters

The rate of a chemical reaction increases with increase in temperature. Increase in temperature was found to increase the inhibition efficiencies of the plant



**Figure 6.** Temkin adsorption isotherm for mild steel in the presence of EEVA, PEVA, FEVA and SEVA at 303 K.

**Table 8.** Temkin isotherm parameters for the adsorption of EEVA, SEVA, PEVA and FEVA on mild steel.

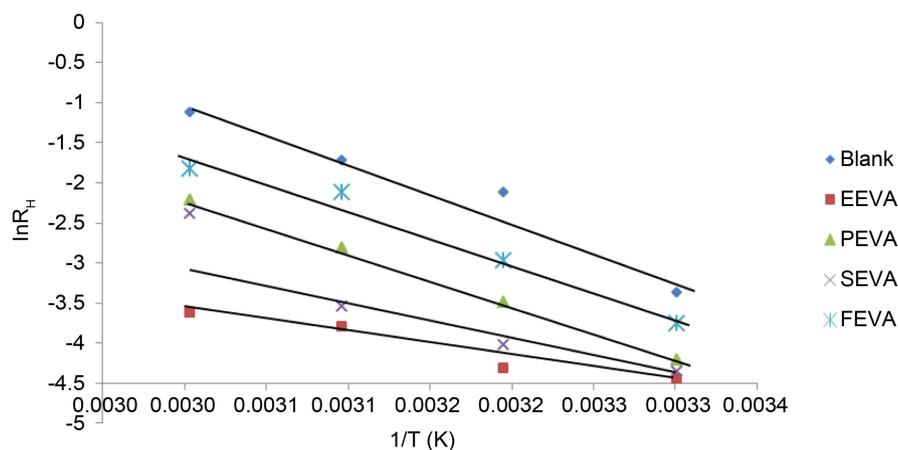
Parameter	EEVA	PEVA	SEVA	FEVA
$R^2$	0.9804	0.9787	0.9990	0.9913
$a$	-0.8395	-0.7740	-0.6355	-1.1553
$K_{ads}$	0.3197	0.4431	0.5126	0.4062

extracts indicating chemical adsorption. In order to further support that chemisorption is proposed, the activation parameters for the mild steel in 5.0 M  $H_2SO_4$  solutions in the absence and presence of the extracts from *Viscum album* were calculated using the Arrhenius equation and the transition state equation given by Equations (4) and (5), respectively.

$$K = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

$$K = \frac{RT}{Nh} \exp\left(\frac{\Delta S^0}{R}\right) \exp\left(-\frac{\Delta H^0}{RT}\right) \quad (5)$$

where,  $R$  is the universal gas constant,  $N$  is the Avogadro number,  $h$  is the Planck's constant,  $E_a$  is the activation energy,  $T$  is the absolute temperature, and  $\Delta H^0$  and  $\Delta S^0$  are the standard enthalpy and entropy of activation, respectively. The values of  $K$  were taken to be equal to the rate of hydrogen evolution [18] [19]. The Arrhenius plot of  $\log K$  versus  $1/T$ , for mild steel in 5.0 M  $H_2SO_4$  solutions containing EEVA, PEVA, FEVA and SEVA shown in Figure 7 gave straight lines. The calculated activation energies obtained from the slope of the plots are listed in Table 9. The results showed that  $E_a$  value in the presence of EEVA, PEVA, FEVA and SEVA is lower compared to the blank system. This behavior is an indication of chemical adsorption of the inhibitor on the surface of the metal [20] [21]. The lower  $E_a$  value in the presence of the inhibitor indicates that the inhibitor will be effective at higher temperature and efficiencies will increase at low temperature. The enthalpy and the entropy of activation



**Figure 7.** Arrhenius plot for mild steel in the presence of EEVA, PEVA, FEVA and SEVA.

**Table 9.** Thermodynamic parameters for the corrosion of mild in the presence of EEVA, PEVA, FEVA and SEVA.

Parameters	Blank	EEVA	PEVA	SEVA	FEVA
$\ln A$	20.29	5.45	18.01	16.50	18.43
$E_a$ (kJ/mol)	60.37	25.06	55.95	52.99	55.70
$\Delta H^\ddagger$ (kJ/mol)	57.73	22.42	53.31	50.35	53.06
$\Delta S^\ddagger$ (kJ/mol)	-80.93	-208.40	-103.98	-116.56	-100.49

values for the dissolution of mild steel in 5.0 M  $H_2SO_4$  solutions obtained from linear transition state plots of  $\log(K/T)$  data versus  $1/T$  shown in **Figure 8** are presented in **Table 9**. The lower value for  $\Delta H^\ddagger$  in the presence of the plant extract is indicative of lower protection efficiency observed for the system.

Generally, the positive value of  $\Delta H^\ddagger$  obtained indicates an endothermic nature of the dissolution of mild steel in the presence of the inhibitors. The endothermic adsorption process can be attributable to chemisorption [22].

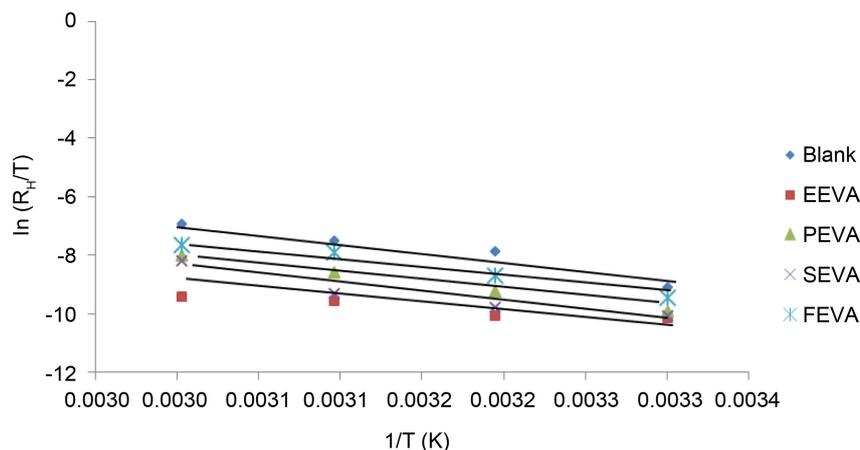
The  $\Delta S^\ddagger$  value in the absence and presence of plant extract is negative. This implies that the activation complex in the rate determining step represents association rather than dissolution step, meaning that a decrease in disordering takes place on going from reactants to the activated complex. The negative value for entropy also indicates the non-spontaneous nature of the dissolution as a result of the addition of the inhibitors [23] [24] [25].

## 4. Conclusions

The following conclusions have been drawn from the results obtained:

1) The ethanol extracts from *Viscum album* exhibit inhibitive action on corrosion of mild steel in sulphuric acid. The inhibition efficiencies increased with increase in extracts concentration and increased with temperature.

2) Experimental data obtained in this study fits well into the Temkin adsorption isotherm equation. The corrosion inhibition is due to the chemical adsorption



**Figure 8.** Transition state plots for mild steel in the presence of EEVA, PEVA, FEVA and SEVA.

of the inhibitor on the metal surface blocking its active sites by the phenomenon of chemical adsorption.

3) The order of the efficiency at low concentrations follows the trend, EEVA > PEVA > SEVA > FEVA while at higher concentration the trend was SEVA > PEVA > EEVA > FEVA.

4) The interaction between the isolated extracts is synergistic at lower inhibitor concentration and antagonistic at higher concentrations. The  $K_{ads}$  values for PEVA and SEVA are higher than those of EEVA and FEVA. This implies that PEVA and SEVA are more efficiently adsorbed on the mild steel surface.

5) The next phase of this research is to carry out molecular dynamic simulations of these appraised phytochemicals in order to clear certain aspects of the corrosion inhibition mechanism by the extracts.

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