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The Inhibition of Corrosion of Aluminium in 1 M Hydrochloric Acid Solution with Ethanol Extract of Vinegar (*Rhustyphina*) Leaf

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Abstract

The corrosion inhibition of aluminium using ethanol extract of vinegar leave (EEVL) in 1 M HCl solution was investigated by weight loss method at temperatures: $30^{o}C$, $40^{o}C$, and $50^{o}C$. The results showed that corrosion rate was significantly reduced in the presence of the extract. Inhibition efficiency was also found to have increased with increase in the concentration of the extract. The maximum inhibition efficiency of 92% was obtained at 50% v/v inhibitor concentration. The reduction in corrosion rate was due to the adsorption of the extract on the metal surface as revealed by Langmuir adsorption isotherm plot.

1. Introduction

Corrosion or wearing away of materials such as metallic industrial and engineering equipment is a major problem today, as it retards the growth of the industries by trimming down profit margin through huge expenditure on corrosion control. Metals such as steel, copper, aluminium etc. used in equipment construction, corrode because they tend to move from thermodynamically less stable state to a more stable state.

Aluminium is an important metal with the following properties: good electrical and thermal conductivities, low cost, low density, high ductility and tensile strength. As a result of this, it has found a good application in construction industries such as the fabrication of automobiles, aviation, electronic devices, pipelines, machineries and household appliances (Sherifa and Su-Moon, 2005). Therefore, aluminium protection against acid corrosion is of great economic importance. Aluminium corrodes by losing three electrons and going into solution as a positive ion:

$Al \rightarrow 3e^{-} + Al^{3+}$ in the presence of acid. Similar results were obtained by other authors such as Kalada et al., (2011), James and Akaranta, (2009) and Orubite et al., (2007).

Acids and high temperature are among other things the major causes of corrosion. Aluminium, despite its great applications suffers severe corrosion in the presence of acids such as HCl. This can occur as HCl is used for industrial cleaning, de-scaling and other industrial chemical processes (Oforka, 2004).

The heavy loss of metals when in contact with acids can be minimized to a great extend through the use of corrosion inhibitors which are mostly inorganic and organic compounds (Deepa and Selvaraj, 2011). The inhibitors are adsorbed on the surface of the metal forming a protective layer which prevents corrosion. In the wake of this, scientists and engineers swung into research for organic and inorganic inhibitors with lots of the inhibitors having adverse effect on the environment (Quraishi et al., 2009). Thus the focus of this research on vinegar leaf extract a natural extract which could inhibit corrosion to a high degree without destructive effects to the environment.

Vinegar tree is known in both French and German with a common species name as Sumac VinaigrierEssigbaum. It was originally introduced as Staghorn Sumac in the 17th century to Europe where it became a popular garden plant. It is a deciduous shrub or a small tree of 5m tall by 6m broad. Staghorn Sumac or Stag's horn Sumach (*Rhustyphina*) is a species of flowering plant in the family Anacardiaceae, native to eastern North America. It is primarily found in Southeastern Canada, the Northeastern and Midwestern

United States and the Appalachian Mountains.(United State Geological Survey, 2008). It is widely cultivated as an ornamental plant throughout the temperate world, but has other uses such as: It is used as fuel for smokers by beekeepers when dried, it can be prepared as pink lemonade for drinking, it can be used as natural dye and as mordant. The tree is rich in tannins which could be responsible for its corrosion inhibition property.

According to literature, the search for a suitable extract for corrosion management of different metals has been on. Plant extracts like aqueous extract of fenugreek leaves was investigated by Noor, (2007), aqueous extract of Olives leaves (El-Etre, 2007), *Sansevieria Trifasciata* extract (Oguzie, 2007).

2. Experimental

2.1. Methods

Fresh leave of *Rhustyphina* commonly known as vinegar was obtained from Ibiakpan Community, Ikot Ekpene Local Government Area in Akwa Ibom State, Nigeria and was transported safely to Laboratory for extraction.

2.2. Material Preparation

2.2.1. Preparation of Leave Extract

The vinegar leaves were dried and ground properly; 103.1941 g of the leave were soaked with 500 ml of ethanol, shaken properly and allowed to stand for 7 days. Ethanol volume was checked constantly within the period. Resultant solution was filtered and more volume of ethanol was added to the leave and allowed to stand for one hour. It was filtered again, more volume of ethanol added continuously to the leave until the required volume of the leaf extract was obtained, the total volume of ethanol used was 1,750 ml. This was used as the stock solution from which 10% v/v, 20% v/v, 30% v/v, 40% v/v, and 50% v/v concentrations of the inhibitor were prepared.

2.2.2. Preparation of the Aluminium Coupons

Rectangular specimens of aluminium were cut into dimensions; 4.0 cm x 4.0 cm x 0.01 cm. A perforation of about 2 mm in diameter near the upper edge was done to allow passage of rubber thread for suspension of the metal into acid solution. The specimens were cut from the centre of the aluminium sheet and thoroughly cleaned, buffed and rubbed with emery paper to obtain a mirror-like spotless surface. Then washed in absolute ethanol, degreased by rinsing in acetone, dried and stored in a desiccator to prevent contact with moisture before use.

2.2.3. Weight Loss Determination

The aluminium coupons kept in the desiccators were carefully weighed. Each coupon was placed into a 100ml beaker container containing different concentrations of the inhibitor prepared with 1 M HCl as stated above. The aluminium coupons were placed in the test solution with the aid of rubber thread and was allowed for 30 minutes after which it was retrieved washed, dried, reweighed, and placed back into the test solution for the next 30 minutes. The experiment was carried out for eight replicate values at the temperature of 30°C and repeated at temperatures of 40°C and 50°C. The temperature was regulated using a thermostatic water bath and the results were recorded and analyzed accordingly.

3. Results and Discussions

The gradual increase in weight loss of aluminium coupons especially in the blank acid solution (one without the inhibitor) as time progressed is shown in Figure1,this indicates that aluminium corrodes in 1 M HCl. The corrosion could be attributed to the presence of air, water and H^+ from the acid (James and Akaranta, 2009). Aluminium is generally known to possess a protective oxide when it comes in contact with oxygen in the presence of water; this oxide naturally reduces the corrosion of aluminium at a pH above 4.

The observation from the experiment shows that in 1 M HCl solution, the aluminium oxide dissolves, thereby exposing the aluminium to corrosion.

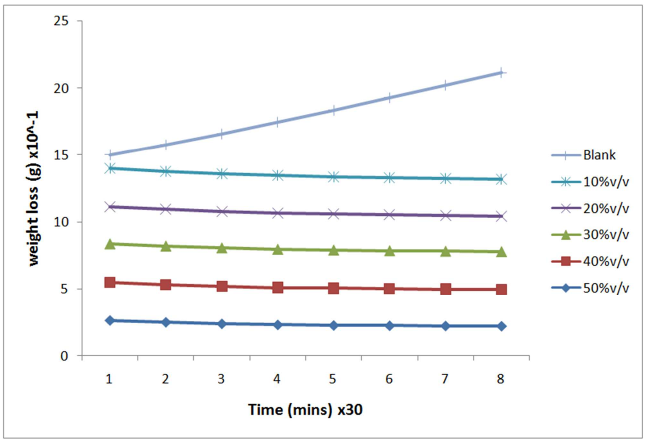

Figure 1. *Weight Loss(g) of Aluminium in 1 M HCl with Various Concentrations of Ethanol Extract of Vinegar Leaf at 30°C.*

However, the corrosion was highly minimized by the presence of ethanol extract of vinegar leaf (EEVL) serving as an inhibitor. This was shown by the decrease in the weight loss of the metal. All solutions containing EEVL inhibited corrosion according to their percentage concentration. The weight loss appeared almost constant in all the solutions containing the inhibitor as shown in Figure 1.

Figure 2 revealed that the value of the percentage inhibition efficiency increased proportionally to the concentrations of the EEVL.

The percentage inhibition efficiency was calculated using

$$\%\, Inhibition Efficiency = \frac{\Delta W_b - \Delta W_i}{\Delta W_b} \times 100 \qquad (1)$$

Where; ΔW_b and ΔW_i are the weight loss data of the metal coupons in the absence and presence of the EEVL inhibitor respectively as previously used by Orubite and Oforka, (2004). The likely reason for the observed high level of percentage inhibition efficiency (92%) obtained is attributed to the chemical composition of vinegar plant. The vinegar plant extract contains photochemical rich in heteroatoms and aromatic ring containing pi-electrons. It is these heteroatoms and the presence of high electron density that make the electrostatic attraction between the aluminium surface and inhibitor active site possible (Abiola and Oforka, 2004; Abiola and Tobun, 2010).

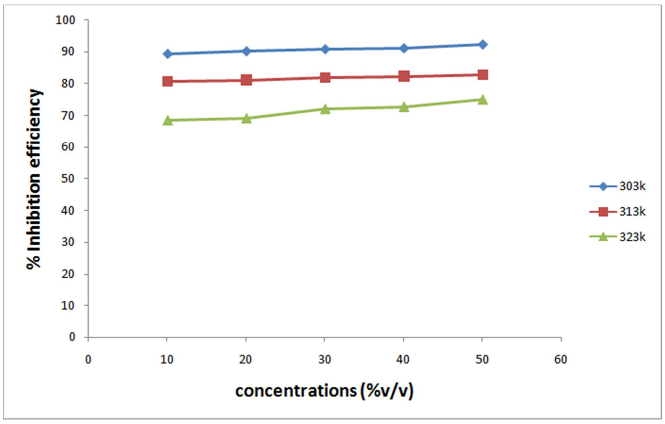

Figure 2. *% Inhibition efficiency of Ethanol Extract of Vinegar Leaf at various temperatures in 1 M HCl*

It was further observed that, increase in temperature was inversely proportional to the percentage inhibition efficiency value (Figure 3). This observation was attributed to the general rule guiding the rate of chemical reaction, which says that chemical reaction increases with increase in temperature, this was also reported by James and Akaranta, (2009) and Orubite et al., (2007).

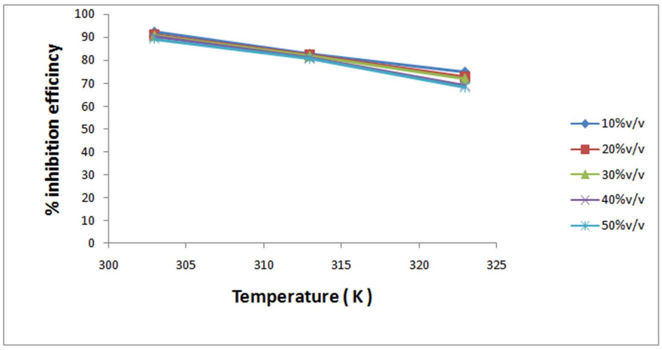

Figure 3. *% Inhibition efficiency ofEthanol Extract of Vinegar Leaf of different concentrations monitored at increasing temperatures in 1 M HCl solution.*

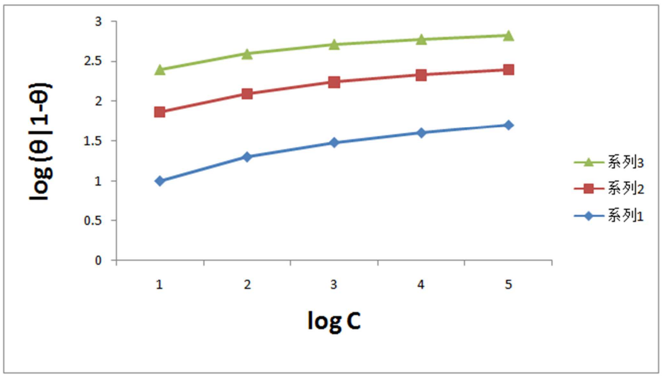

Figure 4. *Langmuir adsorption isotherm plot for EEVL adsorption on aluminium in 1 M HCl medium at different temperatures (^{o}C).*

The plot in Figure 4 showed a very close to perfect Langmuir isotherm at the different temperatures though with little deviation, suggesting a minimal degree of the adsorbed inhibitor molecules interacting among themselves, Sethi et al., (2007), Devender et al., (2010).

This could be interpreted as a very strong physical adsorption. The decrease in the inhibition efficiency with increase in temperature further supported the proposed physical adsorption of EEVL on aluminium in 1 M HCl.

Table 1. *The kinetic parameters defining the performance of Ethanol Extract of Vinegar Leaf inhibitor on aluminium corrosion in 1M HCl solution.*

Inhibitor conc.(%v/v)	Rate constant(K)(Min^{-1}) x 10 $^{-4}$			Half Life ($t_{1/2}$) (Min) x 10^3			Activation Energy (kJmol^{-1}) 30°C - 40°C	Activation Energy (kJmol^{-1}) 40°C – 50°C
	303K	313K	323K	303K	313K	323K		
10	9.02*	2.89	3.27	7.68	2.40	2.12	21.7 2	21.40
20	1.02	2.93	3.71	6.79	2.37	1.87		
30	1.04	2.95	3.92	6.66	2.35	1.77		
40	1.15	3.00	4.08	6.03	2.31	1.70		
50	1.23	3.10	4.20	5.63	2.24	1.65		

* → 10^{-5}

Table 2. *More kinetic parameters of Ethanol Extract of Vinegar Leaf inhibitor on aluminium corrosion in 1M HCl solution.*

Concentration	**Surface coverage θ**			**Corrosion rate(mdd)mgdm^{-2}day^{-1} x10^{3}**			**Corrosion rate (mm/year)**		
	303K	**313K**	**323K**	**303K**	**313K**	**323K**	**303K**	**313K**	**323K**
10	0.88	0.77	0.63	2.58	5.52	7.31	26.54	57.81	74.20
20	0.86	0.76	0.60	3.05	5.74	7.92	31.01	59.84	82.73
30	0.85	0.75	0.58	3.19	5.98	8.32	32.13	62.10	88.46
40	0.84	0.74	0.56	3.39	6.21	8.74	35.06	62.83	90.60
50	0.83	0.73	0.54	3.60	6.45	9.11	36.41	70.86	95.16

Looking at Tables 1 and 2 above it would be observed that parameters such as the Rate constant(K) and the half life($t_{1/2}$) of the inhibitor both decreased with increase in temperature indicating the reduction in strength of adsorption with increase in temperature this further supports the fact that adsorption is temperature dependence; as temperature rises the quantity adsorbed decreased, Orubite et al., (2007). The activation energy Ea was calculated using the integrated form of Arrhenius equation as follows:

$$E_a = \frac{2.303RT_1T_2(\log k_2/k_1)}{T_2 - T_1} \quad (2)$$

Where T_1 and T_2 are the initial and final temperatures respectively, while K_1 and K_2 are the rate constants at T_1 and T_2 respectively. R is the gas constant = 8.314 Jmol^{-1} K^{-1}. The values obtained were shown in Figure 1. Similar results were obtained by Orubite and Oforka, (2004).

The half life values were calculated using the equation

$$t_{1/2} = \frac{0.693}{k} \quad (3)$$

Where K is the rate constant

The surface coverage (θ) was observed to increase with increase in the concentration of EEVL, showing that more adsorption took place at high concentration but decrease with temperature, due to the reason mentioned earlier above.

$$CR = \frac{\Delta W}{Area(cm^2)\times day} \quad (4)$$

Was used to calculate the corrosion rate above.

Table 3. *Free Energy of Adsorption ΔG_{ads}*

Free Energy of Adsorption ΔG_{ads} (kJmol^{-1})			
concentration	**303K**	**313K**	**323K**
10	-10.26	-11.94	-13.06
20	-8.84	-10.21	-11.26
30	-7.96	-9.23	-10.23
40	-7.37	-8.55	-9.49
50	-6.93	-8.03	-8.91

The kinetic parameters such as ΔG_{ads} Table 3.which is high above -20 KJmol^{-1} at all temperatures is another parameter that is indicative of physical adsorption of the inhibitor on the metal surface, (Orubite and Oforka 2004). This could be supported by the fact that the percentage inhibition efficiency is inversely proportional to temperature Figure 3. The negative free energy of adsorption also shows the spontaneous adsorption of the inhibitor, (Abiola et al., 2007).

4. Conclusion

The studied EELV inhibited the corrosion of aluminium in 1M HCl at temperatures 30°C, 40°C and 50°C through a strong physical adsorption to the aluminium surface. The calculated values of Gibbs free energy of adsorption were negative, this confirmed that adsorption process is spontaneous.

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