Behaviour of Micro-Alloying Carbon steel in acid containing Sauropus Androgynus leaves extract

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Abstract: *The Inhibitive nature of Sauropus Androgynus Leaves extract on Micro-Alloying Carbon Steel in 1.0N Hydrochloric acid has been investigated using vary the concentrations of inhibitor as well as Temperature by mass loss measurements. Derived result reveals that the percentage of inhibition efficiency increased with increase of inhibitor concentration and temperature. Thermodynamic parameters viz; Ea, ΔG_{ads}, ΔH_{ads} and ΔS) suggests that the adsorption of SAL extract is exothermic, spontaneous and chemisorptions process. It follows the Langmuir adsorption isotherm.*

Keywords: *Micro-Alloying Carbon Steel, Mass Loss, SAL, 1.0N HCl, Adsorption studies.*

1. Introduction:

Mild steel is most familiar material widely employed in a variety of industries in world wide. But the main problem of using this material undergoes dissolution in acidic solutions. In various industrial processes, acid solutions are commonly used for removal of rust and scale. Use of inhibitor is one of the best method to prevent metal dissolution is very common [1, 3]. Most of the well-known acid inhibitors are organic compounds containing hetero atoms viz; nitrogen, sulfur, oxygen, heterocyclic compounds with a polar functional group and conjugated double bond [4, 5]. These kinds of compounds are adsorbed on the metallic surface and block the active corrosion sites. Most of the synthetic chemicals are costly, toxic to both human being and the environment. In order to overcome these difficulties choosing the inhibition are plenty, cheap, nontoxic and environmentally friendly natural products as corrosion inhibitors. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants. Plant extracts are an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in nature. The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as “Green Inhibitors”. These inhibitors do not contain heavy metals or other toxic compounds. Recent studies using plants containing heteroatom such as oxygen, nitrogen and sulphur like, Punica granatum [6], Mentha pulegium [7], Cnidoscolus chayamansa [8], Solanum Torvum [9], Pisonia Grandis [10], mimusops elengi [11], Sauropus Androgynus [12], Kingiodendron pinnatum [13], Wrightia Tinctoria [14], Lagenaria Siceraria Peel [15], Tephrosia Purpurea [16], Alangium Salvifolium Leaves [17] have also been used for inhibition of corrosion. In continuous of our research work, the present investigation is the Sauropus Androgynus leaves extract used as corrosion inhibitor on micro-alloying carbon steel in 1.0N HCl have been investigated with various periods of contact and temperature using the mass loss measurements.

2.0 Materials and methods

2.1 Sauropus Androgynus leaves was used as a inhibitor

2.2 Stock solution of Sauropus Androgynus *Leaves* Extract:

Sauropus Androgynus leaves (SAL) was collected from the source and dried under shadow for about 15 days, grained well, then soaked in a solution of ethyl alcohol for about 48 hrs, Then it is filtered followed by evaporation in order to remove the alcohol solvent completely and the pure plant extract was collected. From this extract, different concentration of 10 to 1000ppm stock solution was prepared using double distilled water and used throughout our present investigation.

2.3 Specimen preparation

Rectangular specimen of Micro-alloying carbon Steel (MACS) was mechanically pressed cut to form different coupons, each of dimension exactly 20cm^2 (5x2x2cm)with emery wheel of 80 and 120 and degreased with trichloroethylene, washed with distilled water, cleaned and dried, then stored in desicator for our present study.

2.4 Mass loss method

In the mass loss measurements on MACS in triplicate were completely immersed in 100ml of the test solution in the presence and absence of the inhibitor. The metal specimens were withdrawn from the test solutions after 24 to 360 hrs exposure at room temperature and also measured temperature ranges from 313K to 333K. Mass loss was recorded as the difference in weight of the specimens before and after immersion using digital balance with sensitivity of ±1 mg. Tests were performed in triplicate to guarantee the reliability of the results and the mean value of the mass loss is reported. From the mass loss measurements, the corrosion rate was calculated using the following relationship.

$$\text{Corrosion Rate}(\text{mmpy}) = \frac{87.6 \times W}{DAT} \quad \text{--------------------- (1)}$$

[Where, mmpy = millimeter per year, W = Mass loss (mg), D = Density (gm/cm^3),

A = Area of specimen (cm^2), T = time in hours]

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using the following equations.

$$\%\,IE = \frac{W_1 - W_2}{W_1} \times 100 \quad \text{--------------------- (2)}$$

$$\theta = \frac{W_1 - W_2}{W_1} \quad \text{--------------------- (3)}$$

(Where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor respectively)

3.0 Results and Discussion

3.1 Effect of time variation

Anti-Corrosion behavior of MACS in 1.0N HCl containing the presence and absence of SAL extract with various exposure times (24hrs to 360 hrs) are shown in Table-1. Observed values are clearly indicates that the in presence of SAL extract, the corrosion rate moderately decreased from 1.5576 to 0.9764 mmpy for 24 hrs and 0.1239 to 0.0309 mmpy after 360 hrs with increase of inhibitor concentration (0 to 1000 ppm). The maximum of 75.06 % of inhibition efficiency is achieved after 360 hrs exposure time, suggests that the adsorption process occurs mainly due to the presence of active phytochemical constituents present in the inhibitor molecule especially hetero atom containing species and the metal ion from the surface of the metal.

Table-1. The corrosion parameters of MACS in 1.0N Hydrochloric acid containing various concentration of SAL inhibitor at different exposure time.

Conc. of inhibitors (ppm)	24 hrs		72 hrs		120 hrs		240 hrs		360 hrs	
	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E
0	1.5576	-	0.5347	-	0.3487	-	0.1836	-	0.1239	-

10	1.4414	7.46	0.4339	18.85	0.2789	20.01	0.1255	31.64	0.0883	28.73
50	1.2786	17.91	0.3952	26.08	0.2464	29.33	0.0999	45.58	0.0805	35.02
100	1.2089	22.38	0.3642	31.88	0.2324	33.35	0.0929	49.40	0.0681	45.00
500	1.1159	28.35	0.3099	42.04	0.1952	44.02	0.0743	59.53	0.0480	61.33
1000	0.9764	37.31	0.2712	49.27	0.1394	60.02	0.0557	69.66	0.0309	75.06

3.2. EFFECT OF TEMPERATURE

Dissolution behavior of micro-alloying Carbon Steel in 1.0N HCl containing various concentration of SAL extract at 303to 333K and the observed values are listed in Table-2. Observed results reveals that the corrosion rate decreased with increase of inhibitor concentrations and also increased with rise in Temperature from 303 to 333K. The maximum of 75% inhibition efficiency is achieved at 333K. However the value of inhibition efficiency is increased with rise in Temperature may suggests and support the facts that the process of adsorption follows **chemisorption**.

Table- 2. The corrosion parameters of MACS in 1.0N Hydrochloric acid containing various concentration of SAL inhibitor at different temperature after one hours exposure time.

Conc. of inhibitor (ppm)	303 K		313 K		333 K	
	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E
0	30.1299	-	33.4777	-	37.9414	-
10	26.7821	11.11	30.1299	10.00	25.1082	33.82
50	25.1082	16.66	23.9923	28.33	22.8764	39.70
100	21.7605	27.77	20.6445	38.33	21.2025	44.11
500	20.6445	31.48	17.8547	46.66	15.0649	60.29
1000	19.5286	35.18	13.3910	60.00	9.4853	75.00

3.3 ACTIVATION PARAMETERS ON THE INHIBITION PROCESS:

Usually, the temperature plays an important role to understanding the inhibitive mechanism of the corrosion process. To assess the effect of temperature, experiments were performed at 303K- 333K in uninhibited and inhibited solutions containing different concentrations of SAL and the corrosion rate was evaluated and the values are presented in Table-3. The relationship b/w the corrosion rate (CR) of MACS in acidic media and temperature (T) is expressed by the Arrhenius equation,

$$\text{Log CR} = -Ea/2.303RT + \log \lambda \text{ --------- } \rightarrow (1)$$

Where Ea is the apparent effective activation energy, R molar gas constant and λ is the Arrhenius pre- exponential factor.

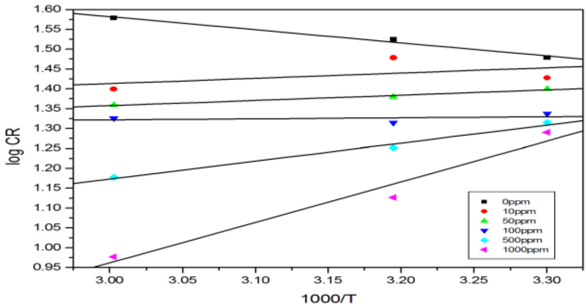


Fig-1. Arrhenius plot for MACS corrosion 1.0N HCl in the absence and presence of different concentration of SAL.

A plot of log (CR) obtained by weight loss measurement versus 1/T gave straight line with regression co-efficient (R^2) value close to unity as shown fig (1). The values of apparent activation energy (Ea) obtained from the slope (-Ea/2.303R) of the lines and the pre-exponential factor (λ) obtained from the intercept (logλ) are given in Table -3. It is evident from the Table that the apparent energy of activation decreased on addition of (SAL) in comparison to the uninhibited solution. These values ranged from 6.3281 to -19.5588 kJ/mol and are lower than the threshold value of 80kJ/mol required for chemical adsorption. This shows that the adsorption of ethanol extract of SAL on MACS surface is Physical adsorption. Decrease in the activation energy is attributed to appreciable increase in the adsorption of inhibitor on MACS surface by increase in the temperature. The increase in adsorption leads to decrease in corrosion rate due to the lesser exposed surface area of the MACS towards 1.0N HCl.

Table:3 Activation parameters of SAL in 1.0N HCl.

S.No	Concentration of SAL (ppm)	E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
1	0	6.3281	6.3281	178.3948
2	10	-2.5427	5.1946	148.5425
3	50	-2.5408	-5.1812	147.5143
4	100	-0.4997	-3.1439	152.9444
5	500	-8.6391	-11.2795	125.6885
6	1000	-19.5588	-22.2049	88.8685

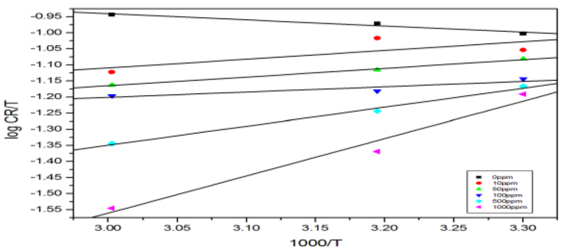


Figure-2 Transition state plot for MACS corrosion in 1.0N HCl in the absence & presence of different concentration of SAL.

The value of λ is also lower for inhibited solution than for the uninhibited solution. It is clear from equation (1) that corrosion rate is influenced by both Ea and λ. Moreover increase in the concentration of (SAL) in leads to an decrease in the value of Ea, indicating that the weak adsorption of the inhibitor molecules on the metal surface.

Experimental corrosion rate values evaluated from the weight loss data for MACS in 1.0N HCl in the presence and absence of SAL was used to determine the enthalpy of activation (ΔH) and apparent entropy of activation (ΔS) for the formation of the activation complex in the transition state equation (2). An alternative formula for the Arrhenius equation is the transition state equation

$$CR = RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT) \text{ --------------(2)}$$

A plot of log (CR/T) versus 1/T is shown is fig (2), a straight lines were obtained with slope (-ΔH/2.303R) and intercept of [log (R/Nh)+(ΔS/2.303R)], from which ΔH and ΔS were calculated and listed out in Table -3. The negative value of enthalpy of activation (ΔH) in the presence and absence of various concentration of inhibitor reflects that the exothermic natures of MACS. The values of entropy of activation (ΔS) listed in Table-3. It is clear that the entropy of activation decreased in the presence of the using inhibitor when compared to free acid solution. The decrease in the entropy of activation (ΔS) in the presence of inhibitor may decreases in the disordering on going from reactant to activated complex is difficult

3.4 Adsorption studies:

Process of adsorption are very important phenomeno to determine the corrosion rate of reaction mechanism. The most frequently use of isotherms are viz: Langmuir, Temkin, Frumkin, Flory- Huggins, Freund lich, Bockris-Swinkles, Hill-de Boer, Parson's and the El-Awady, thermodynamic-kinetic model.

3.4.1. Langmuir, Frumkin and Temkin Adsorption Isotherm

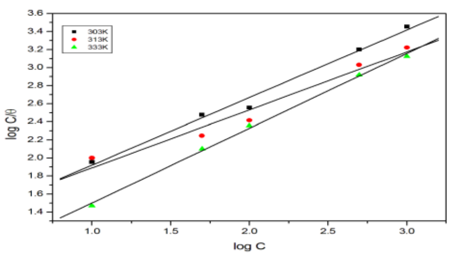
The Langmuir adsorption isotherm of SAL extract on MACS surface proceeded according to the following equation (7).

$$\log C/\theta = \log C - \log K \qquad \text{--------(7)}$$

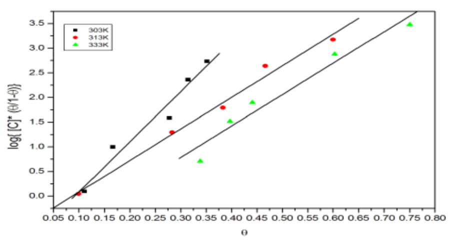
(Where θ is the degree of surface coverage, C is the concentration of the inhibitor solution and K is the equilibrium constant of adsorption of inhibitor on the metal surface).

By plotting the values of log(C/θ) Vs log C, linear plots are generated (fig-3). Inspection of this figure reveals that the experimental data fitted with the Langmuir adsorption isotherm, means that there is no interaction between the adsorbed species.

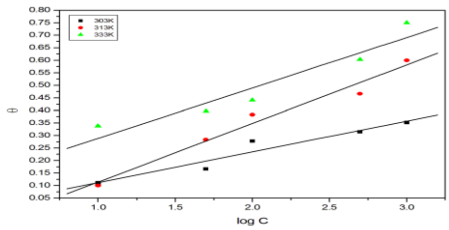
The Figs 3(a-c) shows Langmuir, Frumkin, and Temkin isotherm model respectively. The values of K, R^2 and ΔG_{ads} are derived from these adsorption isotherm at different temperature ranges from 303K to 333K are given in Table -4. The regression co-efficient values viz, El-Awady (R^2=0.9596) and Temkin (R^2=0.9684) Freundlich (R^2=0.9594), and Florry-Huggins (R^2=0.9319), Frumkin (0.9837) adsorption isotherm models and these observed values relatively far from unity as compared with the values obtained with Langmuir adsorption isotherm (R^2=0.9917) which is clearly indicate that the average value of regression co-efficient is almost close unity. Thus it is that the inhibitor obeys Langmuir adsorption isotherm.



(a)



(b)



(c)

Fig. 3 (a) Langmuir, (b) Frumkin, (c) Temkin isotherm for the adsorption of SAL inhibitor on MACS in 1.0N HCl.

3.4.2. Free energy of adsorption:

The equilibrium constant of adsorption for various plant extract on the surface of MACS is related to the free energy of adsorption ΔG_{ads} by equation (8).

$$\Delta G_{ads} = -2.303\ RT \log (55.5\ K) \qquad \text{---------------------------------- (8)}$$

(Where R is the gas constant, T is the temperature, K is the equilibrium constant of adsorption). The values of intercept (K) obtained from Langmuir, Frumkin, Temkin adsorption isotherm is substituted in equation (8) and the calculated values of ΔG_{ads} are placed in Table-4. In Langmuir adsorption, the negative values of ΔG_{ads} suggested that the adsorption of SAL extract onto MACS surface is a spontaneous process and the adsorbed layer is more stable one. Also shows that the values of the adsorption parameters α are positive suggest that the attractive behaviour of the inhibitor on the surface of MACS. The values of attractive parameter (a) are positive in all cases, indicating that no repulsion exists in the adsorption layer.

Table- 4 Langmuir, Frumkin and Temkin adsorption parameters for the adsorption of SAL inhibitor on MACS in 1.0N HCl.

Temp	Langmuir			Frumkin				Temkin			
	K	R^2	$-\Delta G_{ads}$ kJ/mol	K	R^2	A	$-\Delta G_{ads}$ kJ/mol	K	R^2	-a	$-\Delta G_{ads}$ kJ/mol
303K	14.8970	0.9943	-16.9254	0.3928	0.9800	5.09	7.7652	0.0004	0.9645	9.33	9.2471
313K	17.6970	0.9820	-17.4069	0.5718	0.9941	3.20	8.9987	0.0002	0.9865	4.93	11.2194
333K	4.7000	0.9990	-15.4069	0.3230	0.9770	3.18	7.9922	0.0021	0.9543	5.72	5.8547

4. CONCLUSIONS

Sauropus Androgynus leaves has shown excellent inhibition performance for MACS in 1.0N HCl environment. The inhibition efficiency increased with the increase of inhibitor concentration. The maximum inhibition efficiency was achieved 75.06%. Inhibition efficiency gradually increased with the rise in temperature ie, 35.18% to 75% for 303K and 333K respectively. The value of activation energy (E_a), enthalpy of adsorption (ΔH_{ads}) and free energy change (ΔG_{ads}) were indicates that the adsorption of inhibitor on metal surface follows physical, exothermic and spontaneous process respectively. The inhibitor is found to obey Langmuir adsorption isotherms.

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