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Inhibitory effect and adsorption parameters of extract of leaves of *Portulaca oleracea* of corrosion of aluminium in H_2SO_4 solution

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ABSTRACT

The inhibitory effect of the extract of leaves of *Portulaca oleracea* on the corrosion of aluminium was investigated by the weight loss method at the temperature range of 305 K to 315 K in 2 M H_2SO_4 solution. The inhibition efficiency (IE %) was found to increase with increase in both the inhibitor concentration and temperature. The increase in IE% with rise in temperature is suggestive of chemical adsorption process. The unchanged value of activated energy, E_a , with change in concentration and increase in Gibbs free energy value with rise in temperature are further evidence supporting the proposed chemical adsorption mechanism. The evaluated heat of adsorption values are all positive, an indication that the heat of adsorption process onto aluminum surface is endothermic. The negative values of entropy of activation, ΔS^*_{ads} , signify that the activated complex in the rate-determining step represented an association, rather than dissociation. The data obtained best fitted the Langmuir, Freundlich, El-Awady and Temkin adsorption isotherms.

Keywords: Corrosion inhibition, aluminium, *Portulaca oleracea*, adsorption mechanism Adsorption isotherms

INTRODUCTION

Aluminium is second to iron in terms of application, among the metals. The metal and its alloys are extensively used in automotive, aviation and aerospace, ship building, military hardware and household appliances. In fact, the usefulness of aluminium and its alloys is due to their good physical and mechanical properties such as high strength-to-weight ratio ease of recycling, excellent machining properties and outstanding resistance to corrosion [1 - 3]. However, exposed of the metal to aggressive environments can lead to substantial loss due to corrosion [4].

Corrosion, an irreversible interfacial reaction of a material (metal, ceramic, and polymer) on exposure to aggressive environments, affects the performance efficiency of a material and also leads to reduction of its service life [5, 6]. A lot of technological efforts have and are still being developed to mitigate corrosion of service materials through proper selection of the materials, change in design philosophies and more importantly adoption of varied prevention techniques [6]. Aside the economic viewpoint, corrosion control is also important from environmental and aesthetical angles [7]. One of the methods usually employed to combat corrosion is the application of corrosion inhibitors and most of the well-known inhibitors are organic compounds. Naturally occurring substances, especially the plant extracts as inhibitors for corrosion process of materials, have continued to receive attention as replacement for synthetic ones, which have several detrimental effects on the environment and human beings, as well as factors like cost and renewability [8, 9]. Most of the effective and efficient organic inhibitors are those heteroatoms containing elements such as oxygen, nitrogen, sulphur, and phosphorus, in their structures, which allow them to be adsorbed onto the metal surface [10 -13]. Most inhibitors function by being adsorbed onto the metal surface to interact with anodic and/or cathodic reaction sites and influence the oxidation and reduction corrosion reaction, and prevent transportation of water and corrosion active species onto the metal surface [14 – 16].

In this work, the inhibitory effect of ethanol leaves extract of *Portulaca oleracea* on corrosion reaction of aluminium was investigated in the range of 305 K to 315 K in 2 M H₂SO₄ medium. Adsorption mechanisms were deduced through adsorption isotherms using data obtained therefrom. This submission is in furtherance of our contribution to the sustained global interest in the search for eco-friendly inhibitors for corrosion of metals.

MATERIALS AND METHODS

Commercial aluminium wire, obtained from open market, was melted in a furnace to get rid of impurities and moulded into desired sheet at Department of Mechanical Engineering, University of Agriculture, Makurdi-Nigeria. The sheets were mechanically press-cut to form coupons, each of the dimension 2.1x2.1 x 0.35 cm and a tiny hole drilled at the edge of each sample for the purpose of suspension in the corrodant. The coupons' surfaces were thoroughly polished to mirror finish using different grades of emery paper, washed with distilled water, degreased by washing with ethanol, dried with acetone, and then preserved in a desiccator. Subsequently, the initial weight of each coupon was taken. All reagents used in this study were of analar grade while doubly distilled water was used for all solution preparations.

The *Portulaca oleracea* leaves were soaked in absolute ethanol for 48 hours with occasional shaking and filtered thereafter using a cotton wool. The ethanol was evaporated from the filtrate in a thermostated water bath at about 351 K and the residue preserved in a desiccator. A 2 M H₂SO₄ solution was prepared and used as the blank and *Portulaca oleracea* leaves extract so obtained was then used to prepare solutions containing 0.1, 0.2, 0.3, 0.4, and 0.5 g/dm³ in 2 M H₂SO₄, respectively.

Weight Loss Measurement

In the weight loss experiment, 100 ml beaker containing 50 ml 2 M H₂SO₄, which acted as the corrodant was placed in the thermostated water bath at 305 K, with a coupon was suspended in it with the aid of a thread tied to retort stand. The coupon was retrieved from the corrodant solution after 8 hours of immersion and dipped immediately in saturated ammonium acetate solution to terminate the corrosion reaction, and was then washed several times with distilled water, dried in acetone and then kept in a desiccator to cool to ambient temperature and re-weighed. The weight loss, which is an average of triplicate measurements, is as given by equation (1) [14-16].

$$W = W_i - W_f \quad (1)$$

where W is the weight loss of the coupon in grams, W_i the initial weight and W_f the weight after retrieval. The procedure was then repeated at 307 K, 309 K, 311 K and 315 K and each of these served as the blank at the respective temperatures. The same procedure was repeated after the introduction of various concentrations of the inhibitor into the acid solution maintained at same temperatures.

Inhibition efficiency, surface coverage and corrosion rate

The inhibition efficiency, $IE\%$, was calculated using equation (2).

$$IE\% = \left[1 - \frac{W_1}{W_2}\right] \times 100 \quad (2)$$

where W_1 and W_2 are the weight losses in grams of aluminium coupon in the presence and absence of the inhibitor, respectively, in the acid solution at the same temperature. The degree of surface coverage, θ , is given by the equation (3) [16].

$$\theta = 1 - \frac{W_1}{W_2} \quad (3)$$

The corrosion rate, CR , of rate of the aluminium was determined for the immersion period from weight loss using equation (4) [7, 17, 18].

$$CR (mg\,cm^{-2}\,h^{-1}) = \frac{WL}{At} \quad (4)$$

where WL is the weight loss in milligrams (mg), A the coupon surface area in cm² and t the immersion time in hours.

RESULTS AND DISCUSSION

Effects of concentration of inhibitor and temperature on the corrosion of the metal in the acid solution

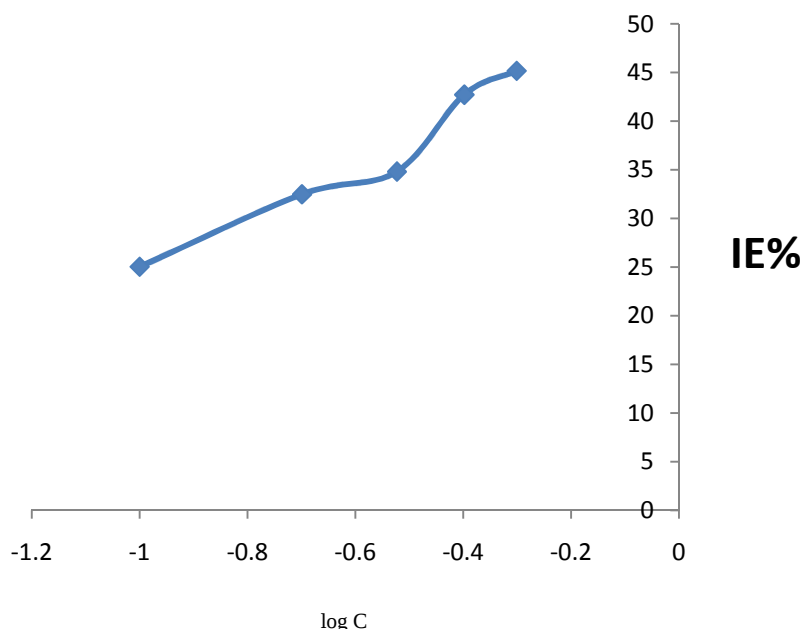
Table 1 shows that the corrosion rate is higher in the blank than in the presence of the extract and the rate decreased with increase in the extract concentration. The decrease in weight loss with increase in concentration of the extract depicts inhibitive propensity of the extract in this acid medium. However, the corrosion rate increased with increase in temperature. The S-shaped curve of figure 1, a plot of IE% against log of concentration (at 315 K), is an indication of the formation of a protective barrier by the inhibitor molecules on the aluminium surface and signifying inhibitive action of the extract [19, 20]. Inhibition efficiency, IE%, increases with increase in the both the concentration of the inhibitor and temperature (Table 2). The increase in IE% with rise in temperature is suggestive of chemical adsorption mechanism Chemisorption [21,22].

Table 1: Variation of corrosion rate with concentration and temperature

	Conc. (g/dm ³)			Corrosion Rate (mgcm ⁻² h ⁻¹)		
	305 K	307 K	309 K	311 K	313 K	315 K
Blank	0.0957	0.1382	0.1807	0.2232	0.2445	0.3295
0.1	0.0850	0.1169	0.1488	0.1807	0.1913	0.2338
0.2	0.0820	0.1129	0.1382	0.1701	0.1750	0.2225
0.3	0.0775	0.1063	0.1276	0.1594	0.1679	0.2115
0.4	0.0744	0.1032	0.1169	0.1460	0.1568	0.2020
0.5	0.0638	0.0892	0.1119	0.1359	0.1415	0.1807

Table 2: Values of inhibition efficiency, IE%, at various concentrations and temperatures

Conc. (g/dm ³)	IE%					
	305 K	307 K	309 K	311 K	313 K	315 K
0.1	11.11	15.38	17.65	19.05	21.74	29.03
0.2	14.32	18.31	23.53	23.81	28.43	32.47
0.3	19.02	23.08	29.41	28.57	31.33	35.81
0.4	22.22	25.33	32.29	34.46	35.87	38.71
0.5	24.33	30.33	38.08	39.10	42.13	45.16

**Fig. 1. A plot of IE % against log C at 315K****Activation energy and thermodynamic parameters for the inhibition process**

The value of apparent activation energy, E_a , was calculated using the Arrhenius equation as given by equation (5).

$$CR = A \exp^{-E_a/RT} \quad (5)$$

where CR is the corrosion rate of aluminium, A is Arrhenius constant or Pre-exponential factor, R is the universal gas constant and T is absolute temperature. Linearisation of equation (5) gives equation (6).

$$\ln CR = \ln A - \frac{E_a}{RT} \quad (6)$$

A plot of $\ln CR$ against $\frac{1}{T}$ gives a slope of $-E_a/R$, from where the values of apparent activation energy were evaluated (Table 3). The apparent activation energy value of the blank is higher than the inhibited; however it did not change significantly in the presence of inhibitor, supportive of the earlier proposed chemical adsorption mechanism [4, 23, 24]. The average value of E_a of 76.55 kJ/mol for inhibitor is, indeed, very close to the threshold value of 80 kJ/mol, evidently supporting the fact that the extract was chemically adsorbed onto the aluminium surface. According to reports, E_a due to chemical adsorption (>80 kJ mol⁻¹) is considerably larger than due to physical adsorption (<80 kJ/mol) [25 - 27].

The values of heat of adsorption, Q_{ads} , of *Portulaca oleracea* leaves extract adsorption onto the aluminium surface were obtained using equation (7) [28].

$$\log\left(\frac{\theta}{1-\theta}\right) = \log A + \log K - \frac{Q_{ad}}{2.303R} \left(\frac{1}{T}\right) \quad (7)$$

where, θ is the degree of surface coverage, T is the temperature, and A is temperature independent constant. Values of heat of adsorption were obtained from the slope $\left(\frac{-Q_{ad}}{2.303R}\right)$ of a plot of $\log\left(\frac{\theta}{1-\theta}\right)$ against $1/T$. Obtained values of Q_{ads} are all positive, indicative of endothermal nature of the dissolution process of the metal sample in the acid solution [20].

The apparent enthalpy of activation, ΔH^* , and entropy of activation, ΔS^* , values were obtained through the linearised transition-state theory equation given thus;

$$\ln\left(\frac{CR}{T}\right) = \ln\left(\frac{R}{N^{\frac{1}{h}}}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad (8)$$

where h is Planck's constant and N is Avogadro's number. A plot of $\ln\frac{CR}{T}$ versus $\frac{1}{T}$ will give a straight line and the slope is equal to $-\frac{\Delta H^*}{R}$ and the intercept is $\ln\left(\frac{R}{N^{\frac{1}{h}}}\right) + \frac{\Delta S^*}{R}$, from where values of ΔH^* and ΔS^* were calculated and are presented in Table 3.

Values of ΔH^* are all positive, reflecting endothermic nature of the aluminum dissolution process in the acid solution [4]. Its value in the blank is however greater than the inhibited solution, an indication that inhibition effectiveness increased with increase in temperature.

The negative values of ΔS^* in presence of the inhibitor imply that the activated complex in the rate-determining step was association rather than a dissociation step; a decrease in disorderliness took place on going from reactants to the activated complex [4, 29].

Values of free energy of adsorption of *Portulaca oleracea* onto the aluminium surface were calculated using the equation (9) [7, 14, 30].

$$\Delta G_{ad} = -2.303RT \log(55.5K) \quad (9)$$

where $K = \frac{\theta}{[(1-\theta)C]}$, C is the concentration of the inhibitor. Calculated values of ΔG_{ad} are presented in Table 3. The values are all negative, a clear indication that adsorption of the inhibitor onto the metal surface is spontaneous and the increase in values with rise in temperature shows that the spontaneity of the adsorption increased as temperature was raised. However, the values are below -20 kJ/mol, the threshold value for physical adsorption mechanism. Generally, values of ΔG_{ad} up to -20 kJ/mol are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physical adsorption), while those above -40 kJ/mol involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorption) [33]. The mode of adsorption (physisorption and chemisorption) observed could be attributed to the fact that *Portulaca oleracea* contains many different chemical compounds, which some can adsorb chemically and others adsorb physically [4].

Table 3: Thermodynamic Parameters of the adsorption of *Portulaca oleracea* onto the aluminium metal surface

Conc. E_a + Q_{ads} + $\Delta H^*_{ads}\Delta S^*_{ads}$ - ΔG_{ads} g/dm ³ (kJ/mol)(kJ/mol) (kJ/mol) (J/mol)(kJ/mol)											
		305 K	307 K	309 K	311 K	313 K	315 K				
		Blank	92.60	90.02	+0.4523						
0.1	76.95	83.25	74.37	-0.3039	10.75	11.78	12.28	12.60	13.11	14.21	
0.2	73.96	80.16	71.87	-0.4377	9.73	10.54	11.43	11.54	12.24	12.82	
0.3	77.44	63.36	72.99	-0.3821	9.57	10.25	11.16	11.13	11.54	12.15	
0.4	76.88	63.65	71.33	-0.4670	9.33	9.83	10.77	11.09	11.33	11.72	
0.5	77.54	68.59	74.96	-0.3100	9.07	9.90	10.85	11.03	11.43	11.83	
Aver	76.55	71.80	73.10	-0.3801	9.69	10.46	11.30	11.48	11.93	12.55	

3.4 Adsorption Considerations

The use of thermodynamic parameters to solely characterise the adsorption behaviour of extracts has its limitation, primarily due to the fact that thermodynamic parameters are molar quantities, but extracts are usually mixtures of several compounds of no exact molecular mass (Lebrini et al., 2011b). Due to this fact, therefore, information obtained through adsorption isotherms are of great importance in the characterisation of adsorption process of plant extracts for the protection of metal against corrosion reaction. Most frequently used adsorption isotherms are the Langmuir, Freundlich, Temkin, Frumkin, Hill de Boer, Parsons, Flory-Huggins, Dhār-Flory Huggins, El-Awady and Bockris-Swinkels' isotherms. All these isotherms follow a general expression as given by equation (10) [32, 33] below.

$$f(\theta, x) \exp(-2\alpha\theta) = KC \quad (10)$$

where $f(\theta, x)$ is configuration factor which depends upon the physical model and assumption underlying the derivative of the isotherm [13, 32], θ is the surface coverage, C the inhibitor concentration, x is the size ratio, ' α ' is the molecular interaction parameter and K is the equilibrium constant of adsorption process which is temperature dependent and it is related to the free energy of adsorption by equation (9) above.

The data obtained best fitted the Langmuir, Freundlich, El-Awady and Temkin adsorption isotherm models going by their values of coefficient of determination, R^2 , being close to unity in each case (Table 4). The positive value of K_{ads} for all the isotherms is indicative of favourable adsorption. For the Langmuir isotherm (equation 11), a plot C/θ against C gave a straight line. However, the slopes are not unity, with non-zero intercepts, signifying non-total conformity to the ideal Langmuir isotherm (ILI) [9, 34]. This is an indication of existence of molecular adsorption within the adsorbed layer [35-36].

$$\text{Langmuir} \quad \frac{C}{\theta} = \frac{1}{K} + C \quad (11)$$

$$\text{Freundlich} \quad \log \theta = \log K + n \log C \quad (12)$$

$$\text{El-Awady} \quad \log \frac{\theta}{1-\theta} = \log K + y \log C \quad (13)$$

$$\text{Temkin} \quad \frac{g\theta}{2.303} = \log K + \log C \quad (14)$$

where g is equal to $-2a$.

The Langmuir isotherm, originally derived for the adsorption of gas molecules on solid surfaces has then been modified to fit the adsorption of solutes onto the solid surfaces in solution [38]. Consequently, the adsorption data were fitted to the Modified Langmuir Isotherm (MLI) equation (15) put forward by Villamil and Co-workers [39].

$$C/\theta = n/K_{ads} + nC \quad (15)$$

And n is obtained as the slope of the plot of C/θ against C . The values of ΔG_{ads} obtained through the MLI are -13.51, -14.24, -14.09, 14.18, 15.00 and 16.41 kJ/mol at 305, 307, 309, 311, 313 and 315 K, respectively. These values, which are however still below -20 kJ/mol, are closer to those obtained through equilibrium constant, actually a confirmation of existence of molecular interaction within the adsorbed layer.

Values of Langmuir dimensionless separation factor, R_L , calculated through equation (16) are shown in Table 4, showing favourable adsorption, as they are all below unity [14, 40].

$$R_L = \frac{1}{1+KC} \quad (16)$$

R_L is greater than 1 implies the adsorption is unfavourable, R_L equal to 1 is an indication of linear adsorption, and if R_L equal to 0 it is irreversible. R_L decreases with rise in temperature (Table 5), supportive of the above observation of increase in spontaneity with increase in temperature.

Table 4: Values of parameters of linearised various adsorption isotherms for adsorption of the extract on the aluminum surface

Isotherm	Temp	R^2	Slope	Intercept	K		ΔG_{ad} (kJ/mol)
Langmuir	305	0.9635	2.7136	0.7318	1.3665		-10.98
	307	0.9428	2.4235	0.5090	1.9646		-11.98
	309	0.9681	1.8816	0.4332	2.3084		-12.47
	311	0.9467	1.8286	0.4223	2.3680		-12.62
	313	0.9588	1.8652	0.3250	3.0770		-13.38
	315	0.9656	1.9421	0.2053	4.8709		-14.67
Freundlich	305	0.9610	0.8716	-1.0188	0.0958	n	-4.24
	307	0.9869	0.7307	-0.8795	0.1320	0.8716	-5.08
	309	0.9638	0.8055	-0.8063	0.1562	0.7307	-5.55
	311	0.9920	0.7851	-0.7875	0.1631	0.8055	-5.70
	313	0.9726	0.6755	-0.7094	0.1953	0.7851	-6.20
	315	0.9889	0.4601	-0.5839	0.2607	0.6755	-7.00
El-Awady	305	0.9676	1.0534	-0.9852	0.1035	y	-4.43
	307	0.9761	1.1059	-0.7505	0.1776	1.0534	-5.84
	309	0.9852	1.1857	-0.7622	0.1729	1.1059	-5.81
	311	0.9968	1.0977	-0.7294	0.1865	1.1857	-6.04
	313	0.9839	1.0111	-0.6359	0.2313	1.0977	-6.64
	315	0.9816	0.7262	-0.4666	0.3415	1.0111	-7.71
Temkin	305	0.9849	2.8681	-0.2220	1.6672	a	-11.48
	307	0.9884	2.2772	-0.3020	2.0045	-3.3026	-12.03
	309	0.9891	1.9973	-0.2629	1.8319	-2.6222	-11.88
	311	0.9985	1.9675	-0.2705	1.8642	-2.2999	-12.00
	313	0.9852	2.0432	-0.3518	2.2480	-2.2656	-12.60
	315	0.9748	2.5321	-0.6175	4.1448	-2.3527	-14.24

Table 5. Values of dimensionless separation factor R_L for Langmuir adsorption isotherm.

Conc. (g/dm ³)	0.1	0.2	0.3	0.4	0.5
305K	0.8798	0.7854	0.7092	0.6466	0.5941
307K	0.8358	0.7179	0.6292	0.5600	0.5045
309K	0.8125	0.6841	0.5908	0.5199	0.4642
311K	0.8085	0.6786	0.5847	0.5136	0.4579
313K	0.7647	0.6190	0.5200	0.4483	0.3939
315K	0.6725	0.5065	0.4063	0.3392	0.2911

The results (Table 4) show that the adsorption of *Portulaca oleracea* on aluminum also obeyed the Freundlich isotherm. The average value of n which is 0.7214 is not too far from the typical value of 0.6 [14], implying that the adsorption be reasonably modeled by Freundlich adsorption isotherms supported by good R^2 values. The values of ΔG_{ads} obtained through this isotherm are, however, very low questioning the applicability of the isotherm to the system. The fact that the adsorption also followed the isotherm is an indication of existence of molecular interaction in the adsorbed layer, that non-totally ideal as may be suggested by Langmuir isotherm.

The adsorption process also followed the kinetic-thermodynamic model of El-Awady isotherm as a plot of $\log \frac{\theta}{1-\theta}$ versus $\log C$ (equation 12) gave straight lines with slopes equal to y . The reciprocal of y gives the number of water molecules replaced by one inhibitor molecules and are 0.9493, 0.9043, 0.8434, 0.9110, 0.9890 and 1.3770 at 305, 307, 309, 311, 313 and 315 K, respectively. These values are approximately unity; implying one water molecule was replaced in the course of the inhibition process. However, the ΔG_{ads} values are not close to those obtained through equilibrium constant.

The adherence of this adsorption process to Temkin adsorption isotherm is suggestive of molecular interaction within the adsorption layer species [41]. And the negative values of ' a ' are indication of repulsive interaction in the

adsorbed layer [42, 43]. The increase in the value of ΔG_{ads} with rise is a feature of chemical adsorption process and Temkin isotherm is actually a feature of chemical adsorption.

CONCLUSION

This work has shown that ethanol extract of leaves of *Portulaca oleracea* inhibited the corrosion of aluminium in 2 M H₂SO₄. The corrosion rate decreased with increase in the extract concentration. The inhibition efficiency increase with increase in both concentration of the extract and rise in temperature. The increase in the values of both inhibition efficiency and Gibb's free energy with rise in temperature is suggestive of chemical adsorption process. The data obtained therefrom best fitted the Langmuir, Freundlich, El-Awady and Temkin isotherm. The adherence of the data to Temkin isotherm is a further support of chemical adsorption process.

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