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Kinetic, Thermodynamic and Adsorption Studies for Corrosion Inhibition of Carbon Steel by Asparagaeus Setaceus L. + Mn^{2+} in Neutral Media

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Abstract: The present study involves the inhibition of corrosion of carbon steel by the plant extract Asparagaeus Setaceus .L(ASLE) with 10 ppm of Mn^{2+} having 180 ppm of Cl^- ion. It is studied by the weight loss method at 303 K-333 K. The energy of activation and the thermodynamic parameters were calculated and evaluated from the results of temperature studies. The result has proved that the extract is a good inhibitor of corrosion of carbon steel in neutral medium and revealed that the inhibition efficiency depends on both the concentration of the inhibitor and the temperature of the system. The effectiveness and characteristics of the adsorption process of the ASLE were studied with Langmuir, El-Awady, Temkin, Frumkin, Flory-Huggins and Freundlich isotherms and were found to be consistent with all isotherms.
Keywords: Corrosion, inhibition, temperature studies, adsorption isotherm, plant extract, Asparagaeus Setaceus L.

I. INTRODUCTION

The use of inhibitor is one of the best methods[1]in preventing the carbon steel against corrosion. Corrosion inhibitors are organic compounds containing oxygen, sulphur and nitrogen atoms containing multiple bonds in their molecules through which they can adsorb on the metal surface.The present study investigates the potential of the extract of *Asparagaeus Setaceus L.* as an inhibitor against corrosion in ethanol extract at different temperatures at different concentrations and studies the consistency of ASLE for different adsorption isotherms.

II. METHODOLOGY

A. Mass-Loss Method

Polished specimens are initially weighed in an electronic balance. Weighed samples are immersed in 100 ml of the DD water with and without the different concentrations of the inhibitor for various temperature (303 K to 333 K) in a thermostat for twelve hours of time. They are then taken out and then washed thoroughly with tap water, rinsed with distilled water, dried, stored in desiccators and reweighed. From the change in weight of the specimens, the corrosion rate is calculated using the following relationship.

Corrosion Rate = W/(A x T)

W = Loss in weight in mg
A = Surface area of the specimen (dm^2)
T = Period of immersion (hours)

Corrosion inhibition efficiency (IE) was then calculated using the equation

$$IE = 100\,[1 - (W_2 / W_1)]\%$$

where W_1 = corrosion rate in the absence of the inhibitor and
W_2 = corrosion rate in the presence of the inhibitor.

III. RESULTS AND DISCUSSION

A. Temperature Studies

The effect of temperature on the corrosion rates of carbon steel in aqueous medium in the absence and presence of various concentrations of ASLE by weight loss method is studied. The corrosion rates for carbon steel at 303 K,313 K,323 K and 333 K in presence and absence of ASLE is given in Table1.

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Table 1 – Corrosion Rate of carbon steel for different temperatures and different concentration of inhibitor ASLE

Temp in K	Corrosion Rate, mdh					Inhibition Efficiency, %				
	0 ppm	50 ppm	100 ppm	150 ppm	200 ppm	0 ppm	50 ppm	100 ppm	150 ppm	200 ppm
303	39	23.83	17.29	10.61	5.39	-	38.89	55.66	72.79	86.17
313	41	26.89	20.93	13.16	8.26	-	31.05	46.33	66.25	78.82
323	43	29.98	24.16	17.8	12.21	-	23.12	38.05	54.35	68.69
333	45	33.86	28.98	24.47	20.63	-	13.17	25.69	37.25	47.1

The presence of inhibitor decreases the corrosion rate and the increases the inhibition efficiency[2]. But as the temperature is increased, the rate of corrosion increases and inhibition efficiency decreases. This clearly tells that the increase in temperature, increases the mass loss of the metal in corrosion medium and is shown in Figure1. Increase in temperature favors the desorption process and inhibition efficiency is decreased as show in Figure2.

Figure 1 – The corrosion rate of carbon steel at different temperatures and at different concentration of inhibitor ASLE

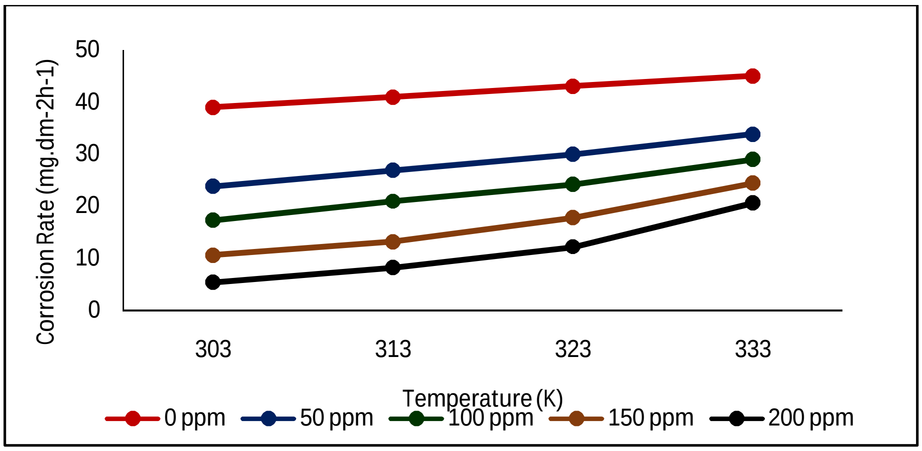
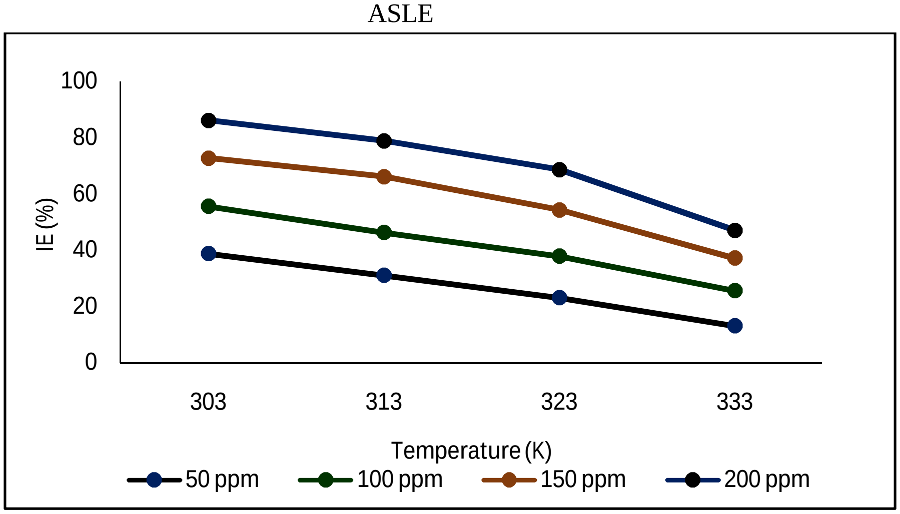


Figure 2 – The inhibition efficiency of carbon steel at different temperatures and at different concentration of inhibitor ASLE



The dependence of corrosion rate (CR) on the temperature is given by the Arrhenius equation: CR=Aexp (-Ea / RT) where A is the pre exponential factor Ea is the activation energy is the gas constant and T is the temperature. A graph is plotted between log CR and 1/T and is shown in Figure3.

Figure 3 – Arrhenius plot for ASLE at different temperatures for different concentrations

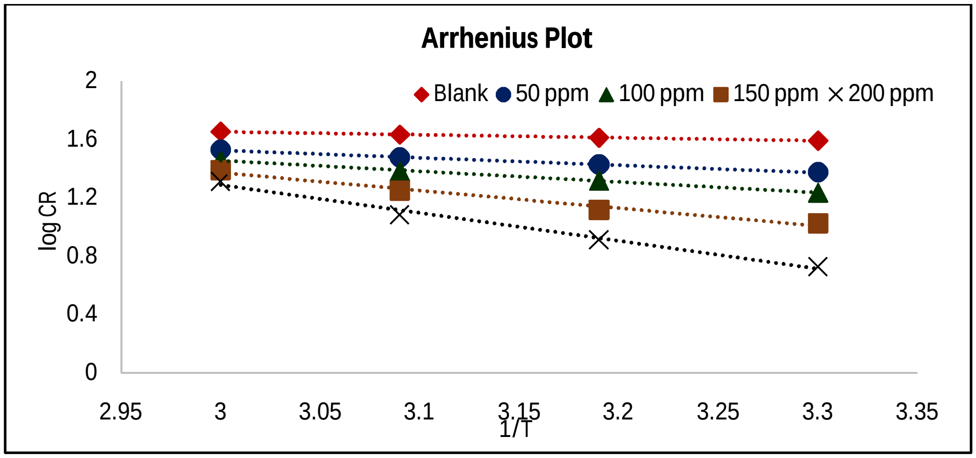
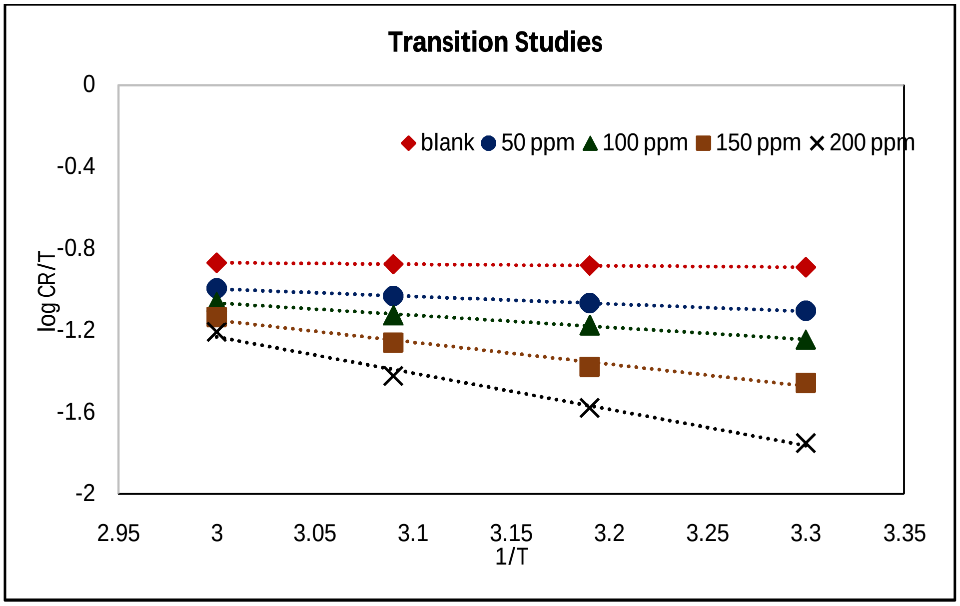


Table 2 – Kineticparameters for the Arrhenius equation for different concentration of the inhibitor

Conc, ppm	E_a, KJ/MOL	R^2
0	3.955	.9991
50	9.57	.9973
100	14.06	.9965
150	23.2	.9832
200	36.57	.9897

The activation energy (E_a)for the system is found out from the slope of the Arrhenius plot of log CR versus 1/T. Here the slope is equal to E_a/2.303R where R is the gas constant and T is the temperature in Kelvin. These values ranges from 3.95 – 36.57 KJ Mol^{-1}.The E_a is higher for the inhibited system than the uninhibited system which is an indication of spontaneous adsorption of the ASLE on the metal surface and is attributed to physical adsorption.

Figure 4 – Kinetic parameters and the transition studies



A graphical representation of log (CR/T) versus 1/T will give straight lines[3] with a slope equal to ΔH/2.303 RT and intercept equal to [log(RT/Nh) +(ΔS^0/2.303R)]. From this ΔH^0 and $\Delta S^0$are calculated and is given in Table 3.

Table 3 – Kineticparameters for the transition state equation for different concentrations of the inhibitor ASLE on carbon steel

Conc,ppm	ΔH^0,KJ/Mol	$-\Delta S^0$ J/Mol/K
0	1.346	-210.16
50	7.009	-195.58
100	11.41	-183.69
150	20.62	-157.68
200	33.91	-119.4

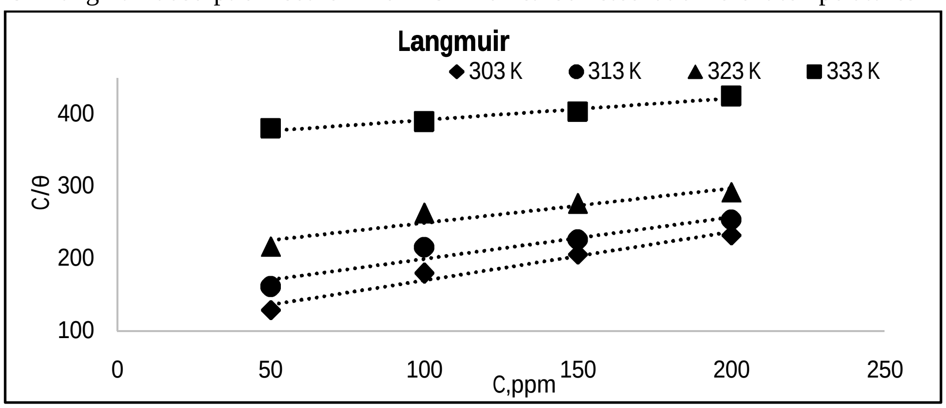
The enthalpy has positive sign which implies the endothermic process and the value of ΔH^0 increases as the concentration of ASLE increases. This tells us that corrosion rate decreases and is controlled by parameters of activation.ΔH^0 value is lower than -40 KJ/Mole, which attributes physisorption. The increase of ΔS^0 with the increase in concentration of ASLE ,implies that there is an increase in disorderliness[4] and adsorption process has happened efficiently.

B. Adsorption Isotherms

Adsorption isotherms values are important in explaining the mechanism of corrosion, and in inhibition of organoelectro chemical reactions. The degree of surface coverage, θ which is calculated gives information about the metal-inhibitor interactions. The observed surface coverage, θ could be due to the adsorption of its molecules on the surface of the steel making a barrier between the metal and the environment. The data obtained from the degree of surface coverage, θ for different temperatures are used for the evaluation of different adsorption isotherms[5] like Langmuir, Frumkin, Frendlich, Temkin, El-Awady and Florry Huggins.

1) *Langmuir adsorption isotherm:* For the testing the Langmuir adsorption isotherm a graph is plotted between the C/θ and C for different temperatures and different concentration of the inhibitor ASLE.

Figure 5 –Langmuir adsorption isotherm for ASLE on carbon steel at different temperatures



It is found that as the concentration of ASLE increases, surface coverage, θ also increases. A straight line is obtained and the linear correlation co efficient values are almost equal to one which indicates that the ASPE on mild steel obeys Langmuir adsorption isotherm[6]. The K_{ads} values decreases as temperature increases states that adsorption process did not favour at high temperatures and is given in Table 4.

Table4 – Langmuiradsorption parameters for the inhibition of the corrosion of carbon steel by ASLE

Temp,K	Conc (ppm)	K_{ads}	ΔG^0_{ads} (KJ/Mol)	R^2
303	50	9.77	-15.862	0.9682
313	100	7.03	-15.529	0.9175
323	150	4.94	-15.077	0.9016
333	200	2.76	-13.932	0.9692

The free energy of adsorption $\Delta G^{\mathbf{0}}_{ads}$ at various concentration of inhibitor at different temperatures is calculated using the following relation: $\Delta G^{\mathbf{0}}_{ads}$ = - RTln(55.55 K) where R is the gas constant, T is the temperature in Kelvin. The value of ΔG^{0}_{ads} is negative and less than – 20 KJ/Mol signifies that the reaction is spontaneous and indicates physisorption.

2) *El-Awady adsorption isotherm:* The experimental data have been used to fit into the modified form of Langmuir adsorption known as El-Awady isotherm which will represent the behaviour of the inhibitor on the adsorbent. It is given by log (θ/1-θ) = log K + y log C, where θ is the surface coverage, y is the number of inhibitor molecules occupying one active site, C is the concentration and K_{ads} is the equilibrium constant of the adsorption process. The values of K, 1/y, R^2 and $\Delta G^{\mathbf{0}}_{ads}$are given in Table5.

Figure 6 – El-Awadyadsorption isotherm for ASLE on carbon steel at different temperatures

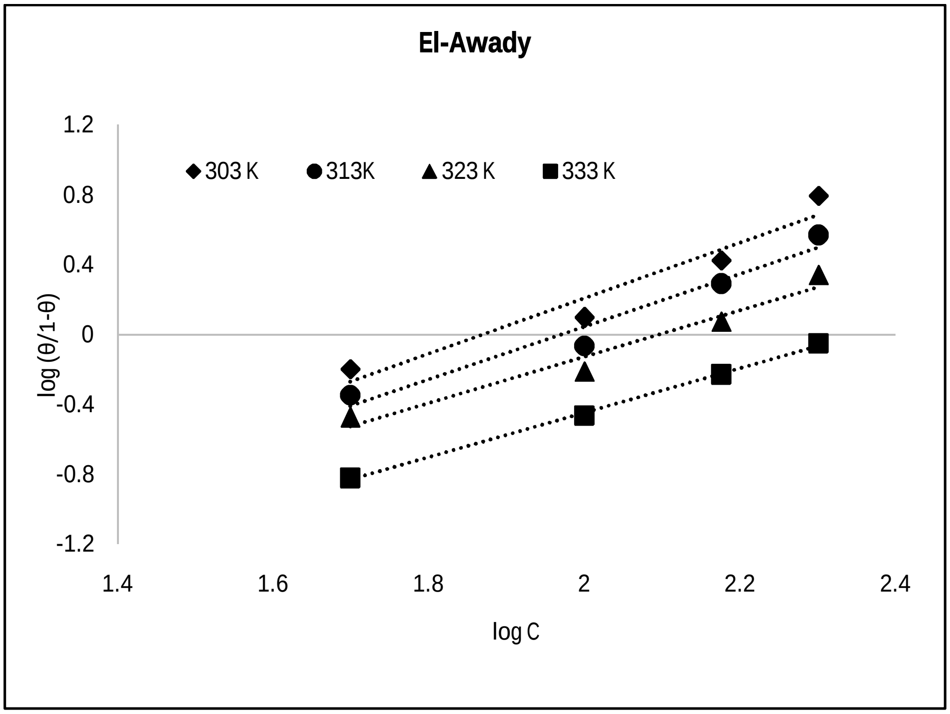


Table 5 – El-Awady adsorption parameters for the inhibition of the corrosion of carbon steel by ASLE

Temp,K	K_{ads}	1/y	ΔG^{0}_{ads}	R^2
303	1.1	0.6311	-10.362	0.9401
313	1.09	0.6646	-10.68	0.9562
323	1.72	0.7549	-12.246	0.9575
333	1.02	0.7864	-11.178	0.9985

The values of 1/y is less than one which implies multilayer adsorption[7]. K_{ads} represents the strength between the inhibitor and the metal surface. The larger the values of K_{ads}, more efficient will be the inhibition. The value of K_{ads} decrease with increase in temperature indicating that the adsorption of indicator was unfavorable at higher temperatures. Free energy of adsorption is found out and the negative values of $\Delta G^{\mathbf{0}}_{ads}$implies the spontaneity of adsorption and the stability of adsorbed layer on the metal surfaces. $\Delta G^{\mathbf{0}}_{ads}$vales are less than – 20 $KJMol^{-1}$ ensures physisorption. The co- efficient values are almost near to one indicates strong adherence to El-Awady adsorption isotherm.

3) *Flory-Huggins adsorption isotherm:* The Flory-Huggins adsorption isotherm is drawn for ASLE for the corrosion inhibition of carbon steelin neutral medium. A plot of log C/θ versus log (1-θ) yields a straight line[8]where slope gives x and intercept gives K.The values of K_{ads}, $\Delta G^{\mathbf{0}}_{ads}$, x, R^2 are given in Table6.

Figure7 – Flory-Huggins adsorption isotherm for ASLE on carbon steel at different temperatures

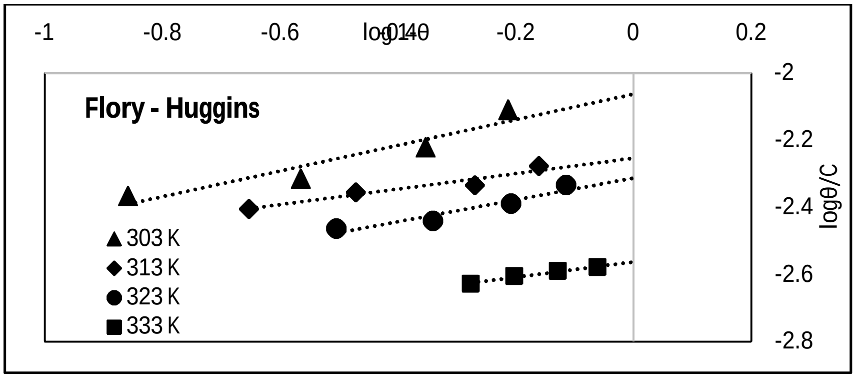


Table 6 – Flory-Huggins adsorption parameters for the inhibition of the corrosion of carbon steel by ASLE

Temp,K	K_{ads}	ΔG^0_{ads}	R^2
303	3.98	-13.602	0.9043
313	2.186	-12.491	0.9307
323	8.743	-16.613	0.9207
333	5.029	-15.596	0.9798

The results indicate that the values of x are less than unity and suggests that the inhibitor molecules occupies less than one active site on the mild steel and the valves of K_{ads} decreases with increase in temperature ensures that the adsorption process slows down at high temperatures. ΔG^0_{ads} values which are negative indicates that the process is spontaneous and tells about the stability of adsorption. The values of ΔG^0_{ads} are lesser than -20KJ/Mol ensures physisorption of adsorbate on adsorbent. R^2 values are approximately equal to one explains the linearity of the adsorption process and the values obeys Flory-Huggins adsorption isotherm.

4) Freundlich adsorption isotherm: Freundlich proposed an empirical relationship between amount of gas adsorbed by unit mass of adsorbent and pressure at a particular temperature. Following equation was proposed for Freundlich adsorption isotherm:**$x/m = k.\ p^{1/n}$ (n > 1)**

It is clear that the degree of surface coverage of an inhibitor is proportional to its adsorption process. The values of n, K_{ads} andΔG^0_{ads} are tabulated in Table7.

Figure8 – Freundlich adsorption isotherm for ASLE on carbon steel at different temperatures

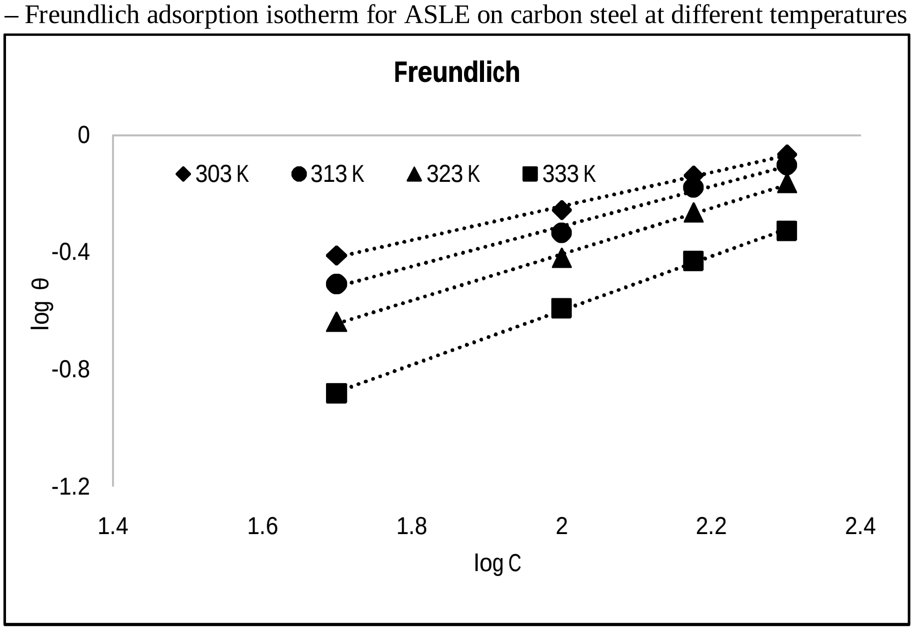


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Table7 – Freundlich adsorption parameters for the inhibition of the corrosion of carbon steel by ASLE

Temp K	K_{ads}	ΔG^0_{ads}	n	R^2
303	40.2	-9.307	0.576	0.997
313	20.9	-7.911	0.683	0.9921
323	10.4	-6.289	0.787	0.9978
333	3.5	-3.468	0.924	0.999

Negative sign of ΔG^0_{ads} indicates that this process is spontaneous and it slows down as the temperature is increased. The K_{ads}[9]values too decreases with increase in temperature ensures adsorption process is unfavorable at higher temperature. Straight lines are obtained and the values of R is nearer to one indicating that the adsorption of the inhibitor onto the mild surface of carbon.

5) *Temkin adsorption isotherm:* In Temkin adsorption isotherm, the degree of surface coverage and inhibitor concentration are related by the following equation, θ= - 2.303 log K/2a – 2.303 log C / 2a where K_{ads} is the adsorption equilibrium constant, and "a" is the attractive parameter. When a graph is plotted between θ and log C, it gives a linear plot, which shows that it obeys Temkin adsorption isotherm. The parameters obtained from the plot are shown in Table 8.

Figure9 – Temkinadsorption isotherm for ASLE on carbon steel at different temperatures

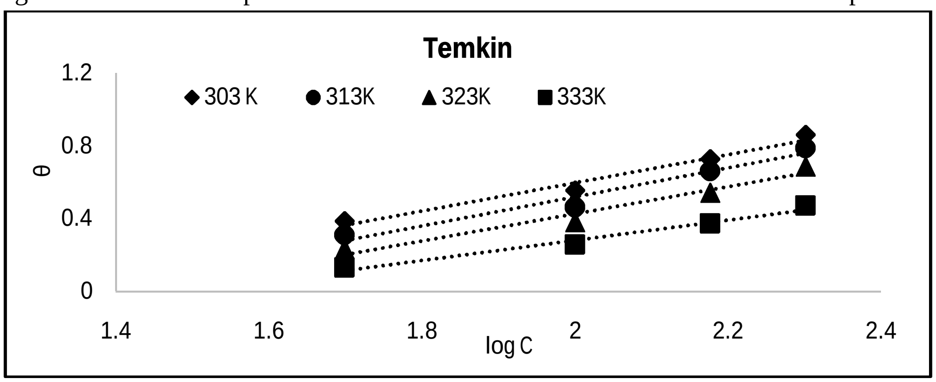

Table8 – Temkinadsorption parameters for the inhibition of the corrosion of carbon steel by ASLE

Temp,K	K_{ads}	ΔG^0_{ads}	R^2	a
303	16.91	-17.247	0.9743	-1.48
313	22.09	-18.511	0.9631	-1.44
323	26.52	-19.594	0.9619	-1.55
333	30.819	-20.616	0.9777	-2.07

The K_{ads} increases with increase in temperature and the negative ΔG^0_{ads} values gives a high efficient spontaneous adsorption and is clearly indicating that there is physisorption happening between the adsorbent and adsorbate and is inefficient at high temperatures. It is seen that the values of 'a' are negative in all cases, indicating that there exists repulsion in adsorbed layer. The fit of experimental data to the above isotherm suggests that the inhibitor inhibits the corrosion reaction by adsorption[10] on metal surface. The decrease in inhibition efficiency with rise in temperature suggests possible desorption of some of the adsorbed inhibitor from the metal surface at higher temperatures. Such behavior implies that the additives were physically adsorbed on the metal surface.

6) *Frumkin adsorption isotherm:* The Frumkin approach applied to the adsorption of corrosion inhibitors on metal surfaces has been explained by the relation log[(θ/1-θ)x C] = log K +2αθ/2.303 where α is the interaction parameter that describes about the interaction between adsorbatean the adsorbent. It can have positive and negative values. When α is less than zero there is repulsion otherwise there will be attraction.

A graph is plotted between log[(C x(θ/1-θ)]and θ , and a straight line[11]is got. From that K_{ads} and α values and $\Delta G^0_{ads}$is calculated which is given in Table 9.

Figure 10 – Frumkinadsorption isotherm for ASLE on carbon steel at different temperatures

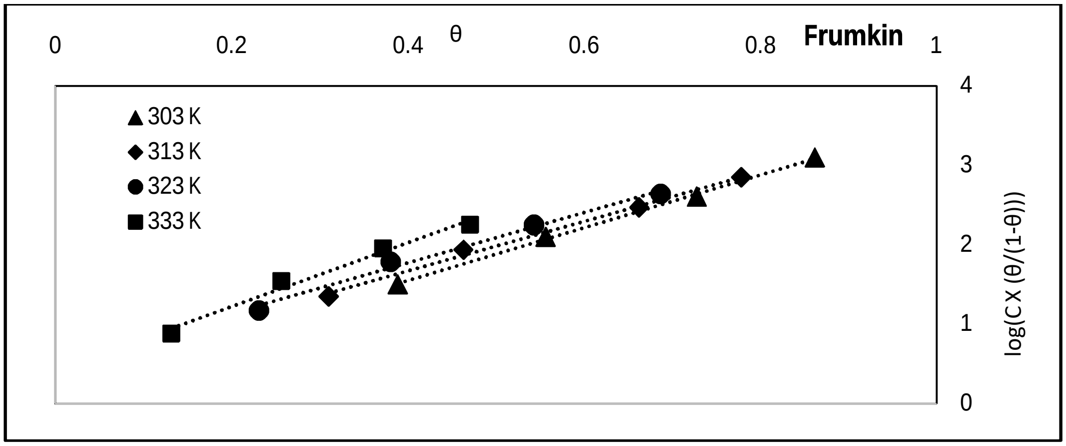

Table 9 – Frumkinadsorption parameters for the inhibition of the corrosion of carbon steel by ASLE

Temp, K	α	K_{ads}	ΔG^0_{ads}	R^2
303	1.65	1.664 x10^3	-28.809	0.9983
313	1.56	2.650x10^3	-30.971	0.9948
323	1.58	3.180x10^3	-32.45	0.9901
333	2	2.617x10^3	-32.916	0.9837

The positive α values explains the increased adsorption energy with increased surface coverage, θ as a result of molecular interactions. α value is greater than 1 and has positive value and it is clear that there is attraction between adsorbent and adsorbate. K_{ads}value implies that it has got adsorbed well and negative $\Delta G^{\mathbf{0}}_{ads}$ values indicates the spontaneity and since the value ranges below -40 $KJMol^{-1}$ physical adsorption has taken place. The coefficient of variation is approximately equal to one which ensures that the values obey Frumkin adsorption isotherm well.

IV. CONCLUSION

The results obtained showed that ASLE is a good corrosion inhibitor for carbon steel under neutral medium. The inhibition efficiency decreases when the temperature is increased and it increases when the concentration of the ASLE is increased. There is an increase in energy of activation as a result of adsorption and the enthalpy has a positive sign and increases which tells that the adsorption process is endothermic. The entropy values indicates that there is disorderliness indicating spontaneity of adsorbate on adsorbent. An excellent agreement between the different adsorption isotherms is obtained. The data from all the isotherms value showed that the inhibiting action is preferably physisorption and the -$\Delta G^{\mathbf{0}}_{ads}$ values indicates a strong and spontaneous adsorption of the ASLE on the metal surface. The adsorption behavior is consistent with these isotherms stating that the inhibitor adsorbs physically on the metal surface and its efficiency decreases when the temperature is raised. Thus ASLE with Mn^{2+}inhibitor system is found to be a good,green[12]corrosion inhibitor for carbon steel in neutral media.

V. ACKNOWLEDGEMENT

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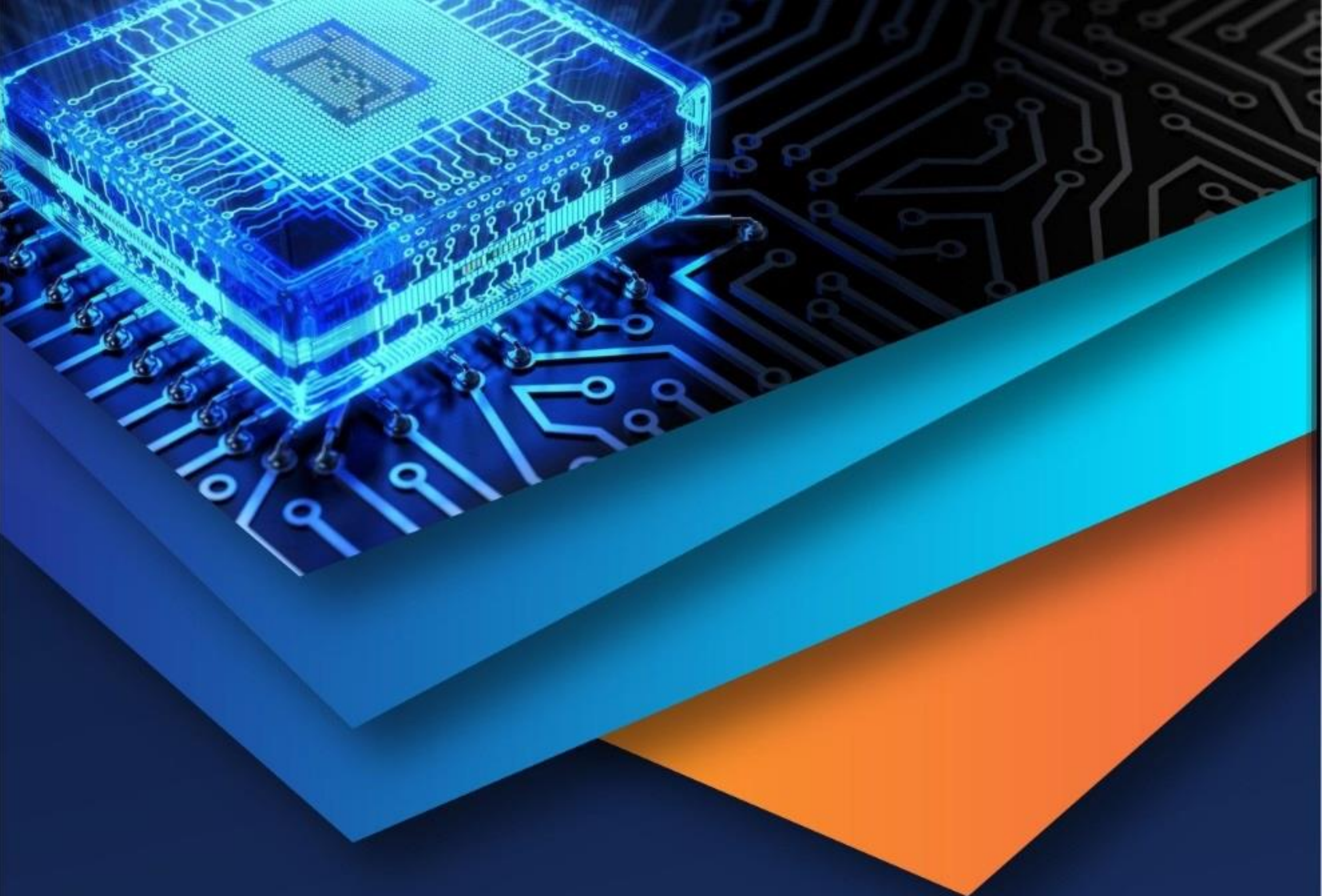

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