Kinetic, Thermodynamic and Adsorption Isotherm Analysis for the Corrosion Inhibition of Carbon Steel in Aqueous Media by *Lippia Nodiflora*

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ABSTRACT

The present study involves the inhibition of corrosion of carbon steel by the plant extract *Lippia Nodiflora* with 50 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 LNLE is a good inhibitor of corrosion of carbon steel in aqueous 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 LNLE were studied with Langmuir, El-Awady, Temkin, Frumkin, Flory-Huggins and Freundlich adsorption isotherms and were found to be consistent with all isotherms.

Keywords: corrosion, inhibition, temperature studies, adsorption isotherm, *Lippia Nodiflora*

INTRODUCTION

Mild steel is the most commonly used engineering material. It is exposed to various kinds of attack and aggressive environment during the industrial process which leads to corrosion and deterioration of the steel there by making it important for the usage of inhibitors. 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 are derived from plant extracts. They have become important as an environmentally acceptable, readily available and renewable source of materials for corrosion inhibition. They are biodegradable and do not contain any toxic compounds and are eco –friendly. The present study investigates the potential of the extract of *Lippia Nodiflora* as an inhibitor against corrosion in ethanol extract at different temperatures and at different concentrations and evaluates the consistency of LNLE for different adsorption isotherms.

METHODOLOGY

Mass-loss method

Polished specimens were initially weighed in an electronic balance. Weighed samples were immersed in 100 ml of the DD water with and without the different concentrations of the inhibitor for various temperature in a thermostat for twelve hours of time. They were 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 was 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.

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 LNLE was studied. The corrosion rates for carbon steel at 303 K, 313 K, 323 K and 333 K in presence and absence of LNLE is given in Table 1.

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

Temp in K	Corrosion Rate, mdh							Inhibition Efficiency, %						
	0 ppm	50 ppm	100 ppm	150 ppm	200 ppm	250 ppm	300 ppm	0 ppm	50 ppm	100 ppm	150 ppm	200 ppm	250 ppm	300 ppm
303	39	27.21	24.72	21.36	18.76	13.93	11.88	-	30.23	36.61	45.23	51.89	64.28	69.51
313	41	29.43	26.27	23.46	19.23	15.64	13.93	-	24.53	32.64	39.84	50.69	59.89	64.28
323	43	31.27	28.34	25.89	21.64	19.55	17.03	-	19.82	27.33	33.61	44.51	49.86	56.33
333	45	33.72	30.79	27.98	24.49	22.04	20.14	-	13.53	21.05	28.25	37.20	43.48	48.34

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 Figure 1. Increase in temperature favors the desorption process and inhibition efficiency got decreased as show in Figure 2.

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

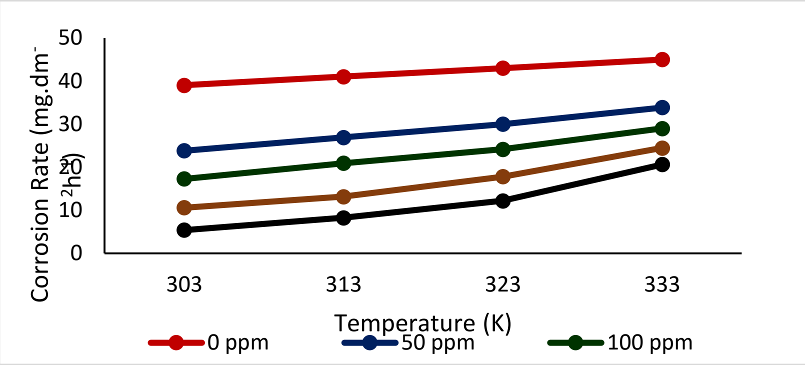
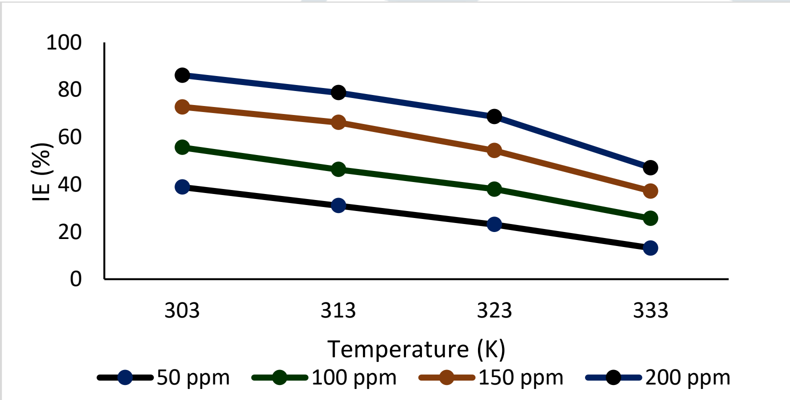


Figure 2 – The inhibition efficiency of carbon steel at different temperatures and at different concentration of inhibitor LNLE



The dependence of corrosion rate (CR) on the temperature is given by the Arrhenius equation: CR=A exp (-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 Figure 3. Energy of activation is calculated from the graph.

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

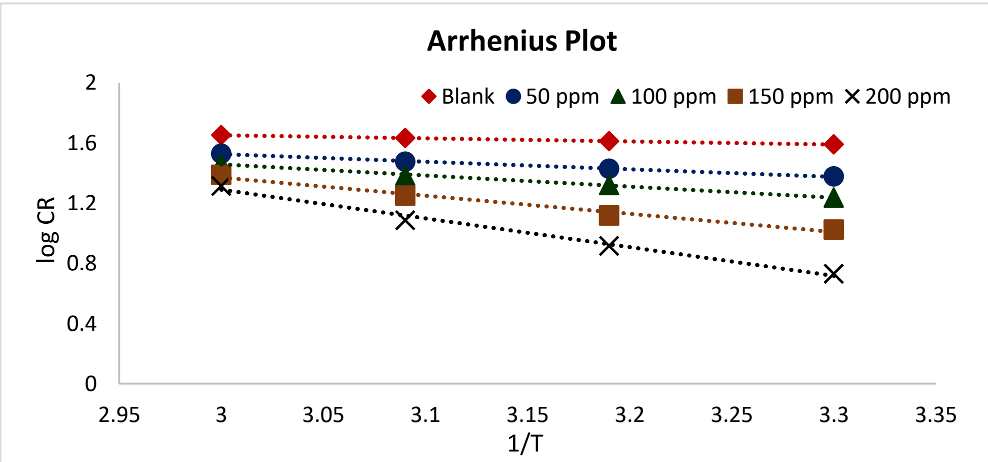
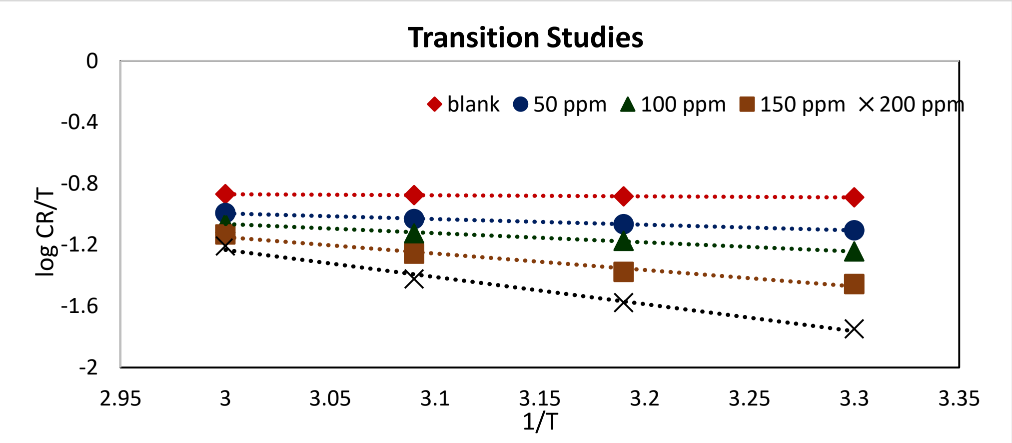


Table 2 – Kinetics parameters for the Arrhenius equation for different concentration of the inhibitor

S.No	Conc, ppm	E_a, KJ/MOL	R^2
1.	0	3.955	0.999
2.	50	5.797	0.9972
3.	100	6.063	0.9871
4.	150	7.509	0.999
5.	200	7.649	0.9157
6.	250	12.24	0.9459
7.	300	17.28	0.9489

The activation energy (E_a) for the system was 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 ranged from 3.95 – 17.28 KJ Mol $^{-1}$. The E_a is higher for the inhibited system than the uninhibited system. This is an indication of spontaneous adsorption of the LNLE on the metal surface and is attributed to physical adsorption. They are lower than the threshold value of -80 KJ Mol $^{-1}$ which is required for the chemical adsorption. This tells us that the adsorption of LNLE on carbon steel is physisorption.

Figure 4 – Transistion state plot for carbon steel in presence and absence of LNLE at different concentrations and temperatures.



The entropy and enthalpy of the corrosion process were calculated from the transition state equation CR=RT/Nh exp ΔS^0/R exp $-\Delta H^0$/RT where h is the Planck's constant, N Avogadro number, R is the gas constant, ΔH^0 is the enthalpy of activation and ΔS^0 is the entropy of activation[3]. A graphical representation of log (CR/T) versus 1/T will give straight lines 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 ΔS^0 were calculated and is given in Table 3.

Table 3 – Kinetics parameters for the transition state equation for different concentrations of the inhibitor LNLE on carbon steel

S.No	**Conc,ppm**	**ΔH^0,KJ/Mol**	**-ΔS^0 J/K/Mol**
1.	0	1.34	-210.15
2.	50	3.18	-207.08
3.	100	3.43	-207.11
4.	150	4.98	-203.18
5.	200	4.58	-205.68
6.	250	10.77	-187.80
7.	300	12.19	-184.35

The enthalpy has positive sign which implies the endothermic process and the value of ΔH^0 increases as the concentration of LNLE 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.

Large and negative values of entropy of activation ΔS^0, shows that the rate determination step is the formation of activated complex and represents an association meaning that a decrease in disordering takes place on going from reactants to the activated complex. ΔS^0 has lower negatives values in the presence of the LNLE compared to blank solution. The increase of ΔS^0 with the increase in concentration of LNLE, implies that there is an increase in disorderliness[4] and adsorption process had happened efficiently.

Adsorption isotherms

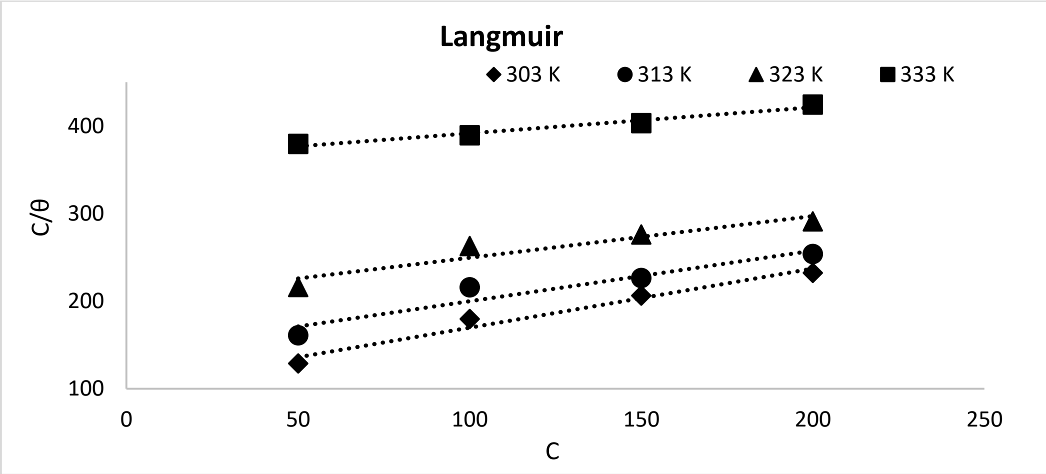
Adsorption isotherms values are important in explaining the mechanism of corrosion, and in inhibition of organo electro chemical reactions. The degree of surface coverage, θ which is calculated gives information about the metal-inhibitor interactions. The observed surface coverage, θ could be due to the adsorption of its molecules on the surface of the carbon steel making a barrier between the metal and the environment.

The data obtained from the degree of surface coverage, θ for different temperatures were used for the evaluation of different adsorption isotherms[5] like Langmuir, Frumkin, Frendlich, Temkin, El-Awady and Florry Huggins.

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 LNLE.

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



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

Table 4 – Langmuir adsorption parameters for the inhibition of the corrosion of carbon steel by LNLE

S.No	Temp, K	K_{ads}	$(\Delta G^0)_{ads}$ (KJ/Mol)	R^2
1.	303	6.404	-14.8	0.9082
2.	313	5.146	-14.719	0.913
3.	323	4.106	-14.583	0.9049
4.	333	2.762	-13.937	0.9118

The free energy of adsorption $(\Delta G^0)_{ads}$ at various concentration of inhibitor at different temperatures is calculated using the following relation: $(\Delta G^0)_{ads}$ = - RTln (55.55 K) where R is the gas constant, T is the temperature in Kelvin. The value of $(\Delta G^0)_{ads}$ is negative and less than – 20 KJ/Mol signifies that the reaction is spontaneous and indicates physisorption and the inhibition is due to the electrostatic interaction between the charged molecules and the charged metal. From the results obtained, it is significant to note that these plots are linear with the co-efficient nearer to unity, which indicates a strong adherence to the Langmuir adsorption isotherm.

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 behavior 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 $(\Delta G^0)_{ads}$ are given in Table 5.

Figure 6 – El-Awady adsorption isotherm for LNLE on carbon steel at different temperatures

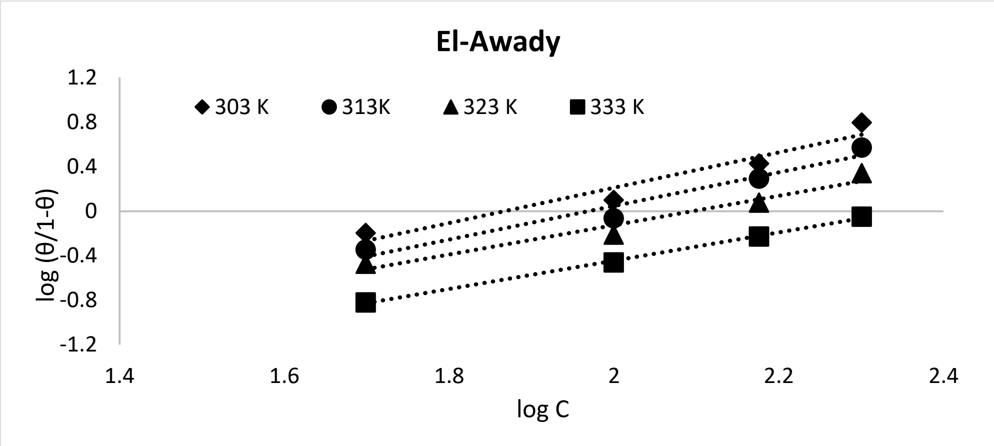


Table 5 – El-Awady adsorption parameters for the inhibition of the corrosion of carbon steel by LNLE

S.No	Temp,K	K_{ads}	1/y	$(\Delta G^0)_{ads}$	R^2
1.	303	9.55	1.08	-15.807	0.9117
2.	313	6.11	1.02	-15.169	0.9501
3.	323	5.83	1.07	-15.525	0.9636
4.	333	2.69	.9839	-13.869	0.9862

The values of 1/y is almost equal to 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 was found out and the negative values of $(\Delta G^0)_{ads}$ implies the spontaneity of adsorption and the stability of adsorbed layer on the metal surfaces. $(\Delta G^0)_{ads}$ vales are less than – 20 $KJMol^{-1}$ ensures physisorption. The co- efficient values are almost nearer to one indicates strong adherence to El-Awady adsorption isotherm.

Flory-Huggins adsorption isotherm

The Flory-Huggins adsorption isotherm is drawn for LNLE for the corrosion inhibition of carbon steel in aqueous medium in figure 7. This model is believed to be a substitutional model because the constant parameter x in the equation describes the substitution of inhibitor molecules[8] for the water molecules. The relationship between surface coverage, θ and the adsorption constant K_{ads} is given by the relation θ= KC/(x-KC). The linearized form has been written as log C/θ=log K +x log (1-θ) where x is a constant associated with the number of molecules of water displaced and the number of molecules of inhibitor adsorbed. A plot of log C/θ versus log (1-θ) yields a straight line where slope gives x and intercept gives K. The values of K_{ads},($\Delta G^0)_{ads}$, x, R^2 are given in Table 6.

Figure 7 – Flory-Huggins adsorption isotherm for LNLE on carbon steel at different temperatures

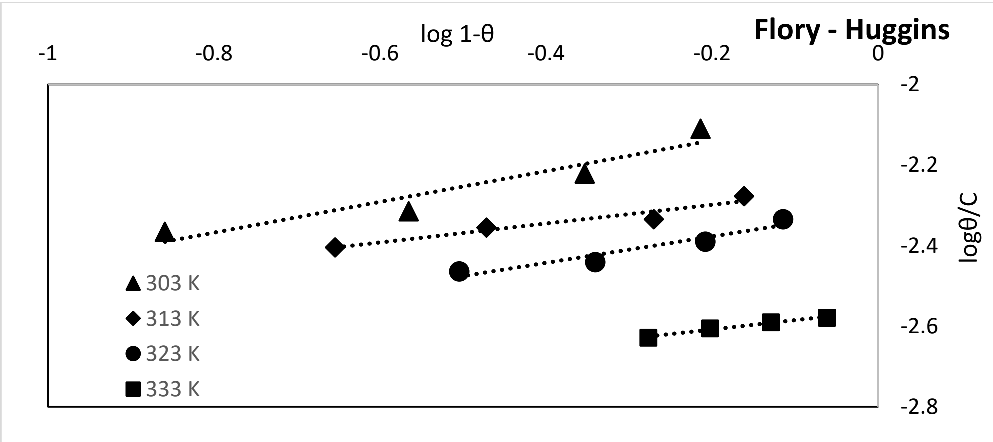


Table 6 – Flory-Huggins adsorption parameters for the inhibition of the corrosion of carbon steel by LNLE

S.No	Temp,K	K_{ads}	ΔG^0_{ads}	R^2	x
1.	303	3.63	-13.370	0.6971	0.9066
2.	313	2.478	-12.817	0.766	0.8818
3.	323	7.78	-16.3	0.801	0.9187
4.	333	.885	-10.78	0.8386	0.8393

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. $(\Delta G^0)_{ads}$ values which are negative indicates that the process is spontaneous and tells about the stability of adsorption. The values of $(\Delta G^0)_{ads}$ are lesser than -20 KJ/Mol ensures physisorption of adsorbate on adsorbent. R^2 values are not equal to one clearly tells it doesn't obey Flory-Huggins adsorption isotherm.

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:

$$x/m = k.\ p^{1/n}\ (n > 1)$$

This model is expressed using the relation logθ = logK + nlogC.

This is obtained by plotting log θ against log C. The value of n is used to describe the ease of adsorption. It is a constant that depends on the characteristics of the adsorbed molecules and has values between 0 and 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} and $(\Delta G^0)_{ads}$ are tabulated in Table 7.

Figure 8 – Freundlich adsorption isotherm for LNLE on carbon steel at different temperatures

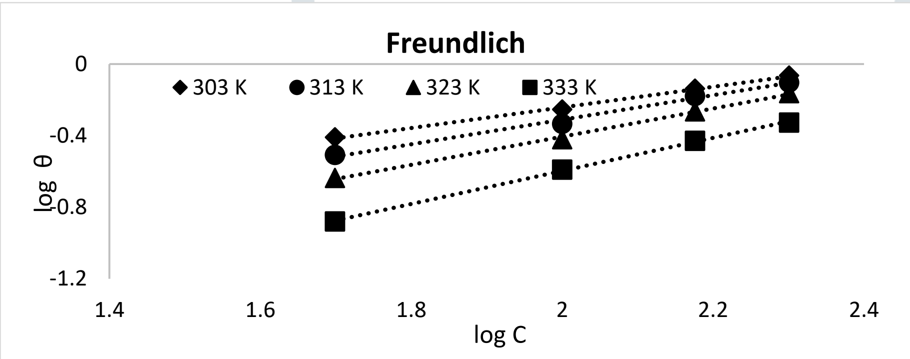


Table 7 – Freundlich adsorption parameters for the inhibition of the corrosion of carbon steel by LNLE

S.No	Temp K	K_{ads}	$(\Delta G^0)_{ads}$	n	R^2
1.	303	43.87	-19.64	0.476	0.9601
2.	313	26.15	-18.95	0.558	0.9796
3.	323	18.51	-18.62	0.594	0.9845
4.	333	7.6	-16.24	0.728	0.9959

From the calculated values of n, it is clear that it indicates a favorable adsorption process. Negative sign of $(\Delta G_0)_{ads}$ indicates that this process is spontaneous and it slows down as the temperature is increased. Since the values of free energy are less than - 20 KJ/Mol the process of adsorption is physisorption. The K_{ads}[9] values decreases with increase in temperature ensures adsorption process is unfavorable at higher temperature.

Straight lines were obtained and the values of R is nearer to one indicating that the adsorption of the inhibitor onto the mild surface of carbon steel can be approximated by Freundlich isotherm.

Temkin adsorption isotherm

In Temkin adsorption isotherm, the characteristics of the isotherm are given by the equation exp (-2aθ)= KC.

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.

Figure 9 – Temkin adsorption isotherm for LNLE on carbon steel at different temperatures

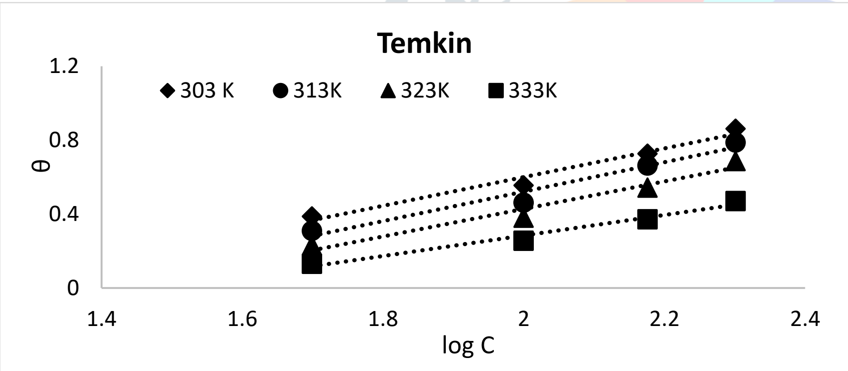


Table 8 – Temkin adsorption parameters for the inhibition of the corrosion of carbon steel by LNLE

S.No	Temp,K	K_{ads}	$(\Delta G^0)_{ads}$	R^2	a
1.	303	15.794	-17.07	0.9074	-2.26
2.	313	20.508	-18.318	0.9341	-2.19
3.	323	22.69	-19.175	0.9377	-2.44
4.	333	29.65	-20.510	0.9526	-2.53

The K_{ads} increases with increase in temperature and it denotes the strength between the adsorbate and adsorbent. Larger values of K_{ads} imply more efficient adsorption and hence better inhibition efficiency. The negative $(\Delta G^0)_{ads}$ values gave a high efficient spontaneous adsorption and is clearly indicating that there was 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.

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

Figure 10 – Frumkin adsorption isotherm for LNLE on carbon steel at different temperatures

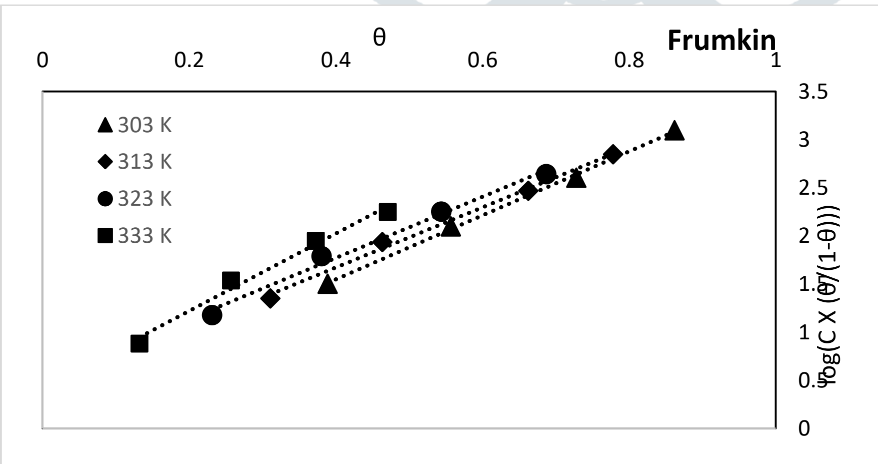


Table 9 – Frumkin adsorption parameters for the inhibition of the corrosion of carbon steel by LNLE

S.No	Temp, K	α	K_{ads}	$(\Delta G^0)_{ads}$	R^2
1.	303	1.801	2.404 x10^3	-29.73	0.9745
2.	313	1.81	2.779 x10^3	-31.09	0.9788
3.	323	1.96	2.758 x10^3	-32.06	0.975
4.	333	2.13	2.809 x10^3	-33.11	0.9744

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. The linearity of graph indicates that there had occurred adsorption process of inhibitor on the metal surface. Larger K_{ads} value implies that it has got adsorbed well and negative $(\Delta G^0)_{ads}$ values indicates the spontaneity and since the value ranges below -40 $KJMol^{-1}$, physical adsorption had taken place. The coefficient of variation is approximately equal to one which ensures that the values obey Frumkin adsorption isotherm well.

CONCLUSION

The results obtained showed that LNLE with Mn^{2+} is a good corrosion inhibitor for carbon steel under aqueous medium. The inhibition efficiency decreases when the temperature is increased and it increases when the concentration of the LNLE 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 indicates that the adsorption process is endothermic. The entropy values indicates that there is disorderliness indicating spontaneity of adsorbate on adsorbent in aqueous media. An excellent agreement between the different adsorption isotherms were obtained except Flory Huggins. The data from all the isotherms value showed that the inhibiting action is preferably physisorption and the $(\Delta G^0)_{ads}$ values indicates a strong and spontaneous adsorption of the LNLE on the metal surface. The adsorption behavior is consistent with these isotherms except Flory Huggins. Thus LNLE with Mn^{2+} inhibitor system was found to be a good, green[12] corrosion inhibitor for carbon steel in aqueous media.

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