

Effect of elevation in temperature on inhibitory action of *Murraya koenigii* leaves on acid corrosion of AA6063

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ABSTRACT

Corrosion inhibition of metals and their alloys is the subject of tremendous technological importance due to their increased industrial applications. As an effective environmentally safe inhibitor, *Murraya koenigii* leaves extract was used to combat acid corrosion of aluminium alloy (AA 6063). The temperature effect on its inhibitory efficacy was investigated employing chemical method. Various corrosion parameters, viz., corrosion rate (ρ_{corr}), percentage inhibition efficiency (IE %) and the kinetic, adsorption and thermodynamic parameters were evaluated. Inhibition efficiency was found to decrease with elevation in temperature. The inhibitor obeyed the Langmuir isotherm and the thermodynamic calculation revealed that adsorption of inhibitor is of physical nature.

Key words: *Murraya koenigii* leaves, Aluminium, Acid corrosion, Kinetic and adsorption parameters, thermodynamic diagrams.

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INTRODUCTION

Aluminium and its alloys have remarkable economic and industrial importance because of its light weight, high thermal, electrical conductivity, and its low cost. The protection of aluminium from corrosive media has attracted the attention of many investigators. One of the most effective methods for the protection of metallic surface is the use of corrosion inhibitors. The inorganic inhibitors act as anodic inhibitors while the organic inhibitors form protective film through the adsorption of their molecules on the metal surface. The organic compounds possess hetero atoms such as N-, S-, or O- and an aromatic ring in their molecules and thus exert a significant influence on extent of adsorption [1-4]. The synthesis of these organic compounds is expensive and they are toxic and hazardous to human beings and environment. Therefore, the

need of non-toxic, ecologically harmless, green corrosion inhibitors is vital. The interest in employing naturally occurring substances and extracts which fulfill the requirements to be used as corrosion inhibitors has become more prominent [5-13]. Under this greener approach, researches has been carried out using *Murraya koenigii* (kadi patta / curry) leaves for corrosion protection for mild steel and its alloys [14-16].

In view of this, an attempt was made employing ethanolic extracts of *Murraya koenigii* leaves (EEMkL) for combating corrosion of aluminium alloy (AA 6063) in 0.5 N HCl, at room temperature, which has produced encouraging results [17]. Literature survey [18-21] reveal that Karipatta (*Murraya koenigii*) leaves are rich in organic compounds like murrayacine (3-formyl-1-methoxycarbazole), carbazole carboxylic acid (mukoeic acid), alkaloids (mahanimbine, koenimbine, koenigicine), pyranocarbazole alkaloid (grinimbine), antioxidant vitamins α -tocopherol, β -carotene, lutein, etc. These organic compounds exert significant effects on extent of adsorption and form a protective film on the metal surface.

Since the temperature is one of the key factors in corrosion phenomenon which can influence the adsorptive pattern of the inhibitor, an attempt has been made to investigate the upshots of temperature variation on adsorptive propensity of *Murraya Koenigii* leaves on aluminium alloy (AA 6063) in 0.5 N HCl. Moreover, the effect on inhibition efficacy of the inhibitor with its increasing concentration at various elevated temperatures has also been studied.

MATERIALS AND METHODS

The effect of temperature on anti-corrosive property of the ethanolic extract of *Murraya Koenigii* Leaves (EEMkL) on acid corrosion of aluminium alloy (AA 6063) was investigated employing chemical method. All the chemicals, acids and reagents were of AnalR grade and bidistilled water was used for the preparation of all the solutions. 0.5N HCl solution was used as corrodent. The experiments were performed in duplicate to check the reproducibility of the results. Average value of weight loss was reported for weight loss measurements. The experimentations was performed at elevated temperatures in the range of 30 to $60 \pm 1^\circ\text{C}$ (during experimentation, it was observed that above 60°C , the metal dissolution was accelerated, hence going beyond and above this temperature was not wise).

Preparation of Coupons:

The industrially used Aluminium (AA 6063) of 98 % purity (Si 0.20-0.60 %; Fe 0.35 %; Cu 0.10 %; Mn 0.10 %; Mg 0.45-0.90 %; Cr 0.10 %; Zn 0.10 %; Ti 0.10 %; the remainder is aluminium) was used as test coupons. Mechanically press-cut rectangular coupons aluminium having dimensions 3 cm x 2 cm x 0.15 cm with a hole of about 0.12mm diameter near the upper edge for the purpose of hanging were made. The coupons were examined carefully to check for rough edges and the surface treatment was carried out immediately before each experiment of corrosion tests as per standard procedures [11, 17].

Preparation of Extract:

Room temperature-dried and finely powdered *Murraya koenigii* leaves were soaked in a ethanol for a desirable period. Thereafter, the ethanolic extraction process was carried out using Soxlet extractor as per standard procedures [11, 17]. The mass of *Murraya koenigii* leaves extract was evaluated as 19.62 g/L of plant compounds.

Preparation of Test Solutions:

For each set of experimentation, test solutions were prepared containing 100 ml of the aggressive solution (0.5 N HCl) in six separate 250 ml beakers numbered as: S-0, S-1, S-2, S-3,

S-4 and S-5. In each beaker EEMkL was added in the order of increasing concentrations so as to have 0.1962, 0.3924, 0.5886, 0.7848 and 0.9810 g/L in S-1, S-2, S-3, S-4 and S-5 beakers respectively. No extract was added to the (S-0), the first beaker.

The corrosion behavior of AA 6063 was investigated at different exposure periods (24 to 312 h) at 30 ± 1 °C. The optimum concentration of EEMkL for its effective inhibition on acid corrosion of AA6063 was assessed from these experimental results. To investigate nature of adsorption isotherm and subsequently to evaluate the adsorption and activation processes, the temperature effect was carried out by exposing test coupons for 24 h at various temperatures (ranging from 30 to 60 ± 1 °C).

The cleaning, drying and weighing of the test coupons was done after fixed period of immersion. Various corrosion, thermodynamic, kinetic, and adsorption parameters were determined. The nature of adsorption was also thereby assessed.

RESULTS AND DISCUSSION

Effect of Immersion Time and Various Concentrations of EEMkL:

The corrosion behavior of AA 6063 for various exposure times (24 h to 312 h) without and with different concentrations of EEMkL was investigated at 30 ± 1 °C. The corresponding corrosion parameters, like corrosion rate (ρ_{corr}) (mmpy), percentage inhibition efficiency (IE %), fractional surface coverage (θ), adsorption equilibrium constant (K_{ad}) etc. were evaluated and tabulated in Table 1. The subsequent graphs of experimental data, viz., the corrosion rate, ρ_{corr} (mmpy^{-1}) vs exposure time, t (h) and inhibition efficiency (IE% vs t) were also drawn (Figs. 1-3).

From table-1, it is clear that the minimum weight loss of AA 6063 was observed at its higher concentration i.e. 0.981 g/L, indicating EEMkL as an effective corrosion inhibitor for AA6063, since a substantial decrease in corrosion rate was observed on its addition to the test solutions (Fig.1).

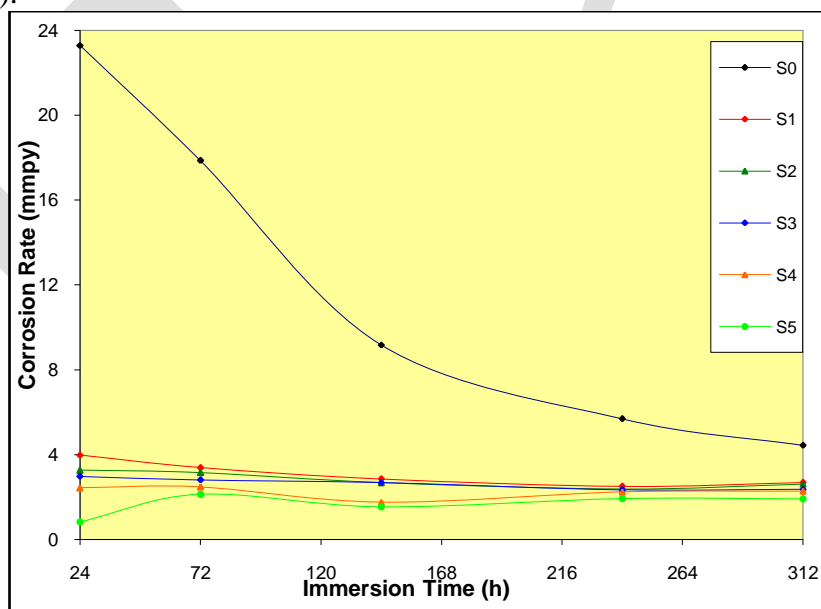


Fig 1:. Corrosion Rate vs Immersion Time without and with Various Concentrations of EEMkL

This sizeable decrease in corrosion rate is may be due to the adsorption of active organic compounds of EEMkL at the reaction sites of AA6063, such as, murrayanine (3-formyl-1-methoxycarbazole), alkaloids (mahanimbine, koenimbine, koenigicine), pyranocarbazole alkaloid (grinimbine), a carbazole carboxylic acid (mukoeic acid), lutein, antioxidant vitamins alpha-tocopherol, etc., thereby by decreasing the available reaction area (geometric blocking effect). Moreover, at higher exposure periods, the corrosion rate becomes almost independent of exposure time and was observed at its minimum value ($1.9 - 2.7 \text{ mmy}^{-1}$).

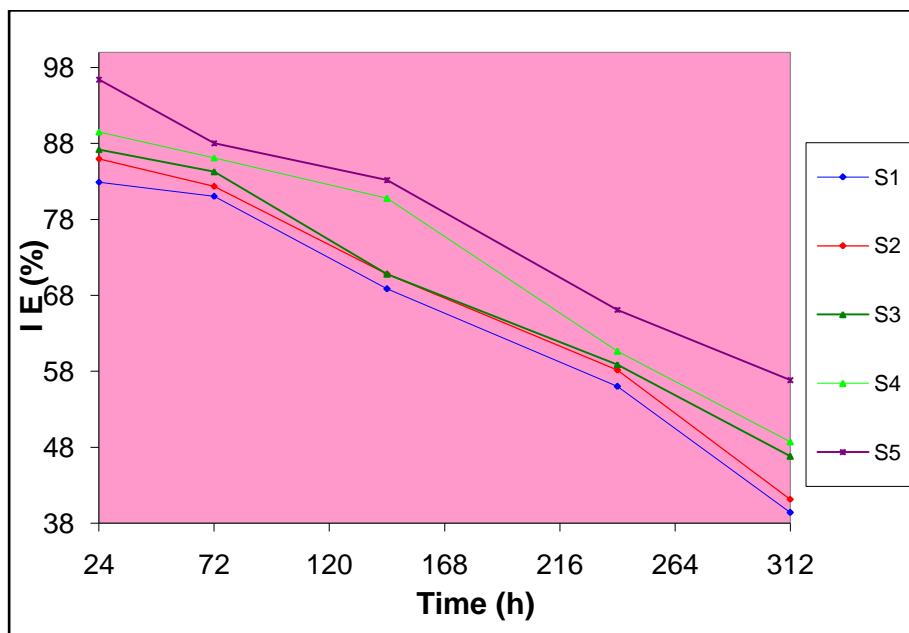


Fig 2: Inhibition Efficiency vs Immersion Time (at $30 \pm 1^\circ\text{C}$)

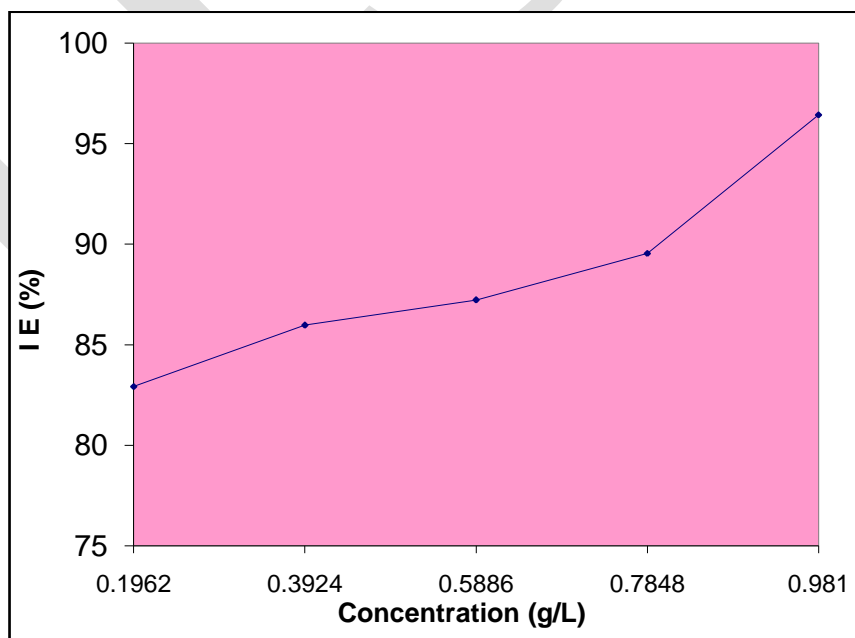


Fig 3: Inhibition Efficiency vs Concentration of EEMkL (at 24 h & $30 \pm 1^\circ\text{C}$)

Time (h)	EEMkL Concentration (g/L)	Corrosion Parameters			
		Corrosion Rate (ρ_{corr}) (mmpy)	Inhibition Efficiency (IE %)	Fractional Surface Coverage (θ)	Adsorption Equilibrium Constant (K_{ad})
24	S-0 0.000	23.2810	-	-	-
	S-1 0.1962	3.9752	82.924	0.8292	24.7441
	S-2 0.3924	3.2643	85.978	0.8597	15.6156
	S-3 0.5886	2.9739	87.225	0.8722	11.5948
	S-4 0.7848	2.4332	89.548	0.8954	10.9075
	S-5 0.9810	0.8311	96.430	0.9643	27.5343
72	S-0 0.000	17.8571	--	-	-
	S-1 0.1962	3.3845	81.046	0.8104	21.7852
	S-2 0.3924	3.1508	82.355	0.8235	11.8902
	S-3 0.5886	2.8037	84.299	0.8429	9.1154
	S-4 0.7848	2.4766	86.130	0.8613	7.9125
	S-5 0.9810	2.1328	88.056	0.8805	7.3765
144	S-0 0.000	9.1638	--	-	-
	S-1 0.1962	2.8538	68.858	0.6885	11.2654
	S-2 0.3924	2.6752	70.806	0.7080	6.1790
	S-3 0.5886	2.6752	70.806	0.7080	4.1193
	S-4 0.7848	1.7590	80.804	0.8080	5.3623
	S-5 0.9810	1.5387	83.208	0.8320	5.0482
240	S-0 0.000	5.6875	--	-	-
	S-1 0.1962	2.5023	56.003	0.5600	6.4868
	S-2 0.3924	2.3791	58.169	0.5816	3.5424
	S-3 0.5886	2.3381	58.890	0.5889	2.4337
	S-4 0.7848	2.2389	60.633	0.6063	1.9622
	S-5 0.9810	1.9275	66.109	0.6610	1.9876
312	S-0 0.000	4.4374	--	-	-
	S-1 0.1962	2.6889	39.402	0.3940	3.3137
	S-2 0.3924	2.6111	41.156	0.4115	1.7819
	S-3 0.5886	2.3600	46.814	0.4681	1.4951
	S-4 0.7848	2.2761	48.706	0.4870	1.2096
	S-5 0.9810	1.9148	56.847	0.5684	1.3169

Table: 1. Corrosion Parameters of Acid Corrosion of AA 6063 without and with different Concentrations of EEMkL at Various Immersion Time (h) at temperature 30 ± 1 °C.

With the increase in exposure time, the IE (%) of EEMkL was found to decrease for all its concentrations (Fig. 2). The IE (%) of EEMkL was also observed to vary linearly as a function of its concentration. Figs. 2, 3 and Table-1 clearly indicate that on increasing the concentration of EEMkL, the percentage inhibition efficiency (IE %) increases and it reaches maximum at the highest concentration of EEMkL (i.e. 0.9810 g/L) for all the immersion time periods. The highest IE (96.43 %) was observed at 0.9810 g/L of EEMkL with a minimum

corrosion rate ($\rho_{\text{corr}}=0.8311\text{mmy}^{-1}$) for 24 h exposure time. It depicts that the molecules of EEMkL cover the AA6063 surface very effectively. This can be explained as the active constituents of EEMkL contain N- (in addition to O-), and as a rule of thumb it holds that N-containing inhibitors exert their best efficiencies in HCl [22].

Effect of Temperature:

The effect of temperature on the inhibited solution-metal reaction is highly complex. Many changes may occur on the metal surface, such as rapid etching and desorption of inhibitor, or the inhibitor itself undergoing decomposition and/or rearrangement etc. In order to understand the nature of the adsorption phenomenon of EEMkL on AA6 063 in 0.5 N HCl, the weight loss measurements were carried out in the temperature range of 30 to 60 ± 1 °C at its various concentrations exposed for a period of 24 h. From the experimental data, various corrosion parameters along with the thermodynamic and kinetic parameters were calculated and tabulated in Tables-2 & 3. The results were graphically depicted as Figures 4, 5 and 6 illustrating plots between weight loss (mg), corrosion rate (ρ_{corr}) (mmy^{-1}), and IE (%) vs various concentrations of EEMkL (g/L) respectively.

From the Table-2 and Figs. 4-6, it is clear that in the concentration range examined (0.1962 to 0.9810 g/L of EEMkL) as well as in free acid; with increasing temperature, there is an increase in weight loss as well as corrosion rate of AA6063, which indicate that the process follows Arrhenius type reactions.

Temperature ($T \pm 1$ °C)	EEMkL Concentration (g/L)	Corrosion Parameters			
		Corrosion Rate (ρ_{corr}) (mmy^{-1})	Inhibition Efficiency (IE %)	Fractional Surface Coverage (θ)	Adsorption equilibrium Constant (K_{ad})
30	S-0 0.000	23.2810	-	-	-
	S-1 0.1962	03.9752	82.924	0.8292	24.7441
	S-2 0.3924	03.2643	85.978	0.8597	15.6156
	S-3 0.5886	02.9739	87.225	0.8722	11.5948
	S-4 0.7848	02.4332	89.548	0.8954	10.9075
	S-5 0.9810	00.8311	96.430	0.9643	27.5343
50	S-0 0.000	31.0310	-	-	-
	S-1 0.1962	28.3283	08.739	0.0871	0.4856
	S-2 0.3924	38.0380	-22.573	-	-
	S-3 0.5886	37.9379	-22.283	-	-
	S-4 0.7848	34.0340	-09.642	-	-
	S-5 0.9810	38.5380	-24.153	-	-
60	S-0 0.000	44.4414	-	-	-
	S-1 0.1962	42.1421	-01.666	-	-
	S-2 0.3924	45.0450	-08.695	-	-
	S-3 0.5886	42.0420	-01.473	-	-
	S-4 0.7848	41.3413	-00.193	-	-
	S-5 0.9810	44.1441	-06.521	-	-

Table: 2. Corrosion Parameters of Acid Corrosion of AA6063 with Different Concentrations of EEMkL at Various Temperatures at 24 h Immersion Time.

This may be attributed to increase in agitation of solution ions due to higher rates of H_2 gas evolution at elevated temperatures, which enhances the corrosion process and also reduces the ability of the inhibitor to be adsorbed on the metal surface. Such behavior suggests physical adsorption of EEMkL on the corroding aluminium surface. The minimum weight loss (8.30 mg) and corrosion rate (0.83 mmy^{-1}) were observed at room temperature ($30 \pm 1^\circ\text{C}$) with 0.981 g/L of EEMkL, indicating the maximum inhibitory action of EEMkL on acid corrosion of AA 6063 (i.e. 96.43 %).

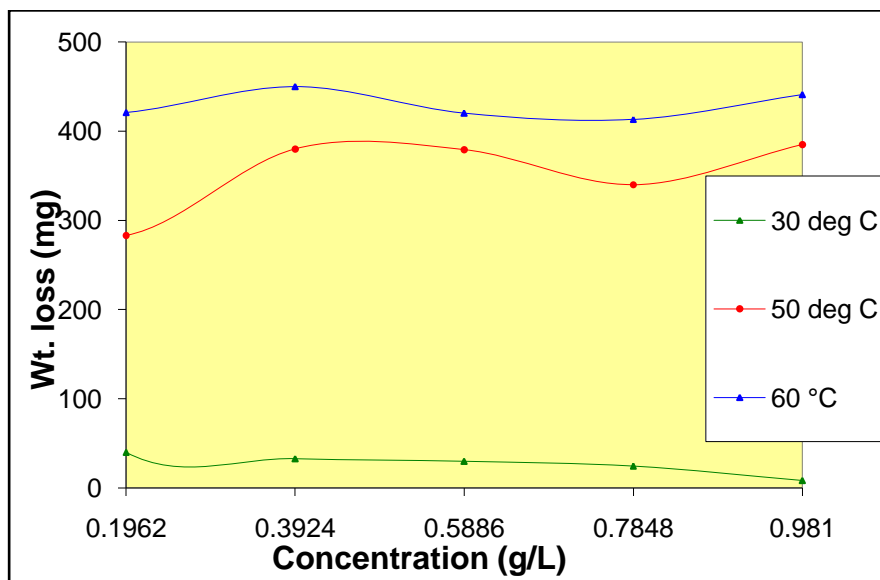


Fig4: Weight loss vs Concentration at different Temperatures

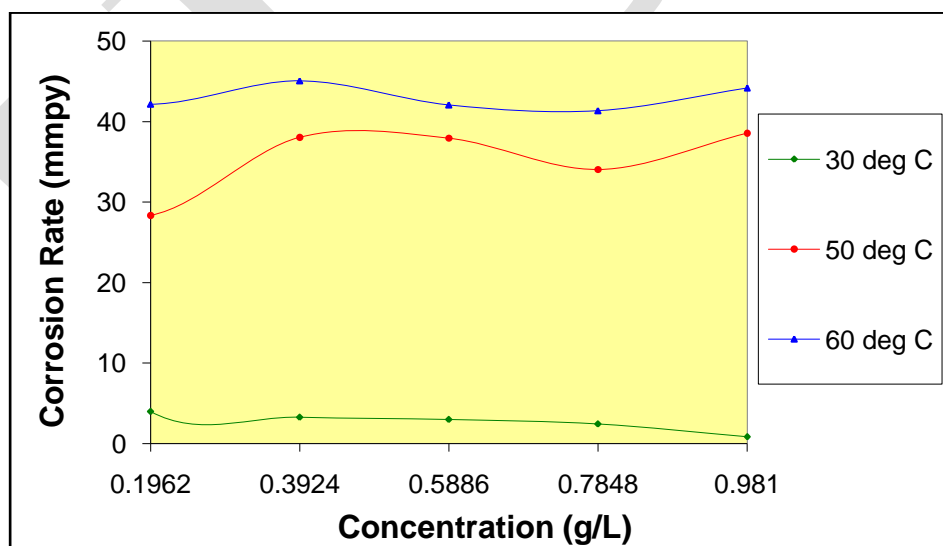


Fig 5: Corrosion Rate vs Concentration at different Temperatures

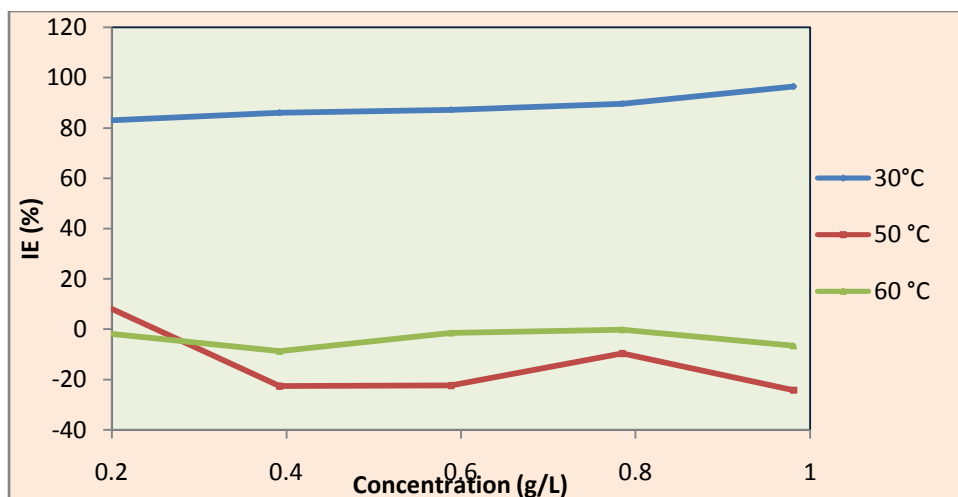


Fig 6.: Inhibition Efficiency vs Concentrations of EEMkL at different Temperatures

The IE (%) EEMkL was observed to decrease drastically at elevated temperatures (as compared to room temperature). This may be due to desorption of the physisorbed molecules of EEMkL, leaving AA6063 surface accessible for corrosive attacks. However, the variation in IE (%) vs concentration of EEMkL seems more complex at moderately high temperature i.e. 50 ± 1 °C (Fig. 6). The IE (%) was first observed to decrease with increase in concentration of EEMkL, but with further increase in concentration of EEMkL, it was observed to increase (though not in the positive scale). But, by and large, the IE (%) at temperature 50 ± 1 °C was observed less as compared to that at higher temperature (i.e. 60 ± 1 °C). The variations in IE (%) with 10 °C temperature elevations may be because of specific interaction between the metal and the inhibitor, or the inhibitor itself may undergo decomposition and/or rearrangement due to thermal agitations.

In the present case, at elevated temperatures, the IE (%) was observed in negative scale, implying no inhibitory action of EEMkL at elevated temperatures (rather inhibitor is enhancing metal dissolution process at elevated temperature); whereas at room temperature, it possess significantly high anti-corrosive property for AA6063 in acid medium (IE= 96.43%) (Table-2).

The apparent activation energy (E_a) for the corrosion process in corrosive and inhibitive environments was evaluated from Arrhenius type plot. The Arrhenius plots for the acid corrosion of AA6063 are illustrated in Fig 7. The slope of the straight lines obtained from plots between $\ln \rho$ vs $1/T$ resulted in E_a values, and the intercept resulted value of A [23]. The thermodynamic and kinetic parameters such as, ΔH^0 , ΔS^0 , ΔG^0 , and E_a were also evaluated from the investigations of the inhibition process carried out at different temperatures and tabulated in Table-3.

On comparing the activation and thermodynamic parameters (E_a , ΔH^0 , ΔS^0 and ΔG^0) of the corrosion of AA6063 in corrodent (0.5 N HCl) and corrodent-EEMkL solutions, these were observed to be higher for inhibitive solutions than those for the corrosive solution alone (blank). The apparent activation energy, E_a , was increased with inhibitor concentration, indicating the change in the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules (signifying physical adsorption). The value of E_a was observed to be much lower than 80 kJ/mol which further supports physisorption mode of adsorbed molecules of EEMkL (Table-3) [23-24]. In addition to this, the average value of the difference between E_a and ΔH^0 is $\cong RT$;

indicating that the corrosion process was a unimolecular reaction in the present case, as it is characterized by the equation [25]: $E_a - \Delta H^0$ is = RT

Concentration (g/L)	E_a (kJmol ⁻¹)	ΔH^0 (kJmol ⁻¹)	ΔS^0 (Jmol ⁻¹ K ⁻¹)	ΔG^0 (kJmol ⁻¹)
S-0 0.0000	02.9537	00.4346	054.1924	-15.99
S-1 0.1962	20.1899	17.6708	118.3877	-18.20
S-2 0.3924	25.2451	22.7260	131.2445	-17.04
S-3 0.5886	26.1765	23.6574	131.8432	-16.29
S-4 0.7848	27.1224	24.6033	134.4570	-16.14
S-5 0.9810	39.4442	36.9251	182.8188	-18.47

Table:3. Activation Parameters of acid corrosion of AA6063 without and with EEMkL.

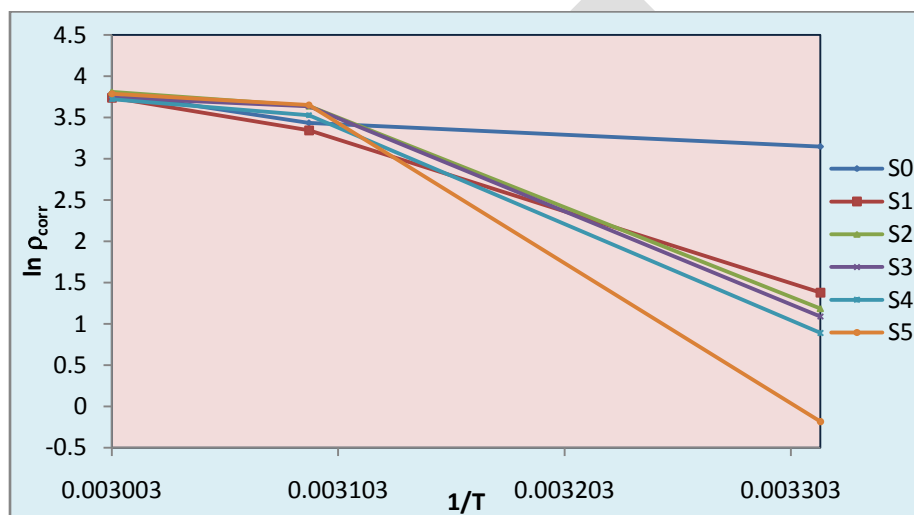


Fig 7: $\ln \rho_{\text{corr}}$ vs $1/T$

Similarly, the entropy of activation (ΔS^0) of solutions containing EEMkL was also found to be more than that of corrosive solution alone. Besides, the positive ΔS^0 values indicate an endothermic adsorption nature. When adsorption is an endothermic process, it must be accompanied by an increase in the entropy energy change and vice versa [23].

As justified earlier, the enthalpy of activation (ΔH^0) is another criterion on the basis of which the mode of adsorption can be explained. The positive values of ΔH^0 show that the adsorption is endothermic with a disordered phenomenon ascribed by the positive values of ΔS^0 . In the present investigations, the values of enthalpy of activation, ΔH^0 , were observed lower than 50 kJ/mol, thereby, indicating physical adsorption of EEMkL over the surface of AA6063 [16]. The ΔG^0 values for the corrodent-EEMkL systems were in the range of -15.99 to -18.47 kJmol⁻¹ (i.e. < -20 kJ/mol), further endorsing the physisorption of the EEMkL over AA6063 surface (Table-3).

It has been suggested that the adsorption of the organic constituents of EEMkL can affect the corrosion rate by either decreasing the available reaction area (geometric blocking effect) or by modifying the activation energy of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process [24].

Kinetic / Thermodynamic Treatment of Weight Loss Results

Assuming that the corrosion rate of aluminium against the concentration of the EEMkL obeys the kinetic relationship as shown [22-24]:

$$\log \rho_{\text{corr}} = \log k + B \log C$$

where, k is the rate constant and equals to ρ_{corr} at inhibitor concentration of unity; B is the reaction constant which, in the present case, is a measure for the inhibitor effectiveness and C is the concentration of EEMkL in g/L. The plot of $\log \rho_{\text{corr}}$ vs $\log C$ resulted in straight lines (Fig. 8), thus verifying that the kinetic parameters (k and B) could be calculated by using the above equation.

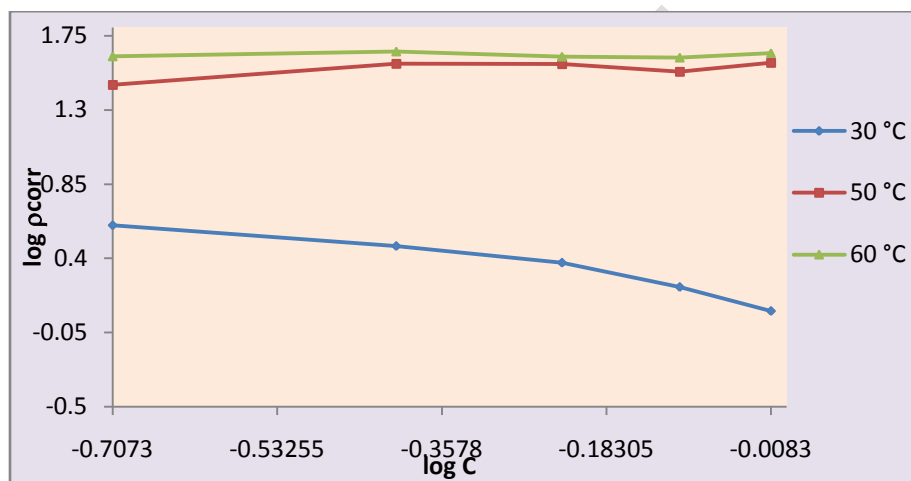


Fig 8: $\log \rho_{\text{corr}}$ vs $\log C$

The slopes of the lines were observed negative (except at higher temperatures (50 ± 1 °C)), depicting that the rate of corrosion process is inversely proportional to EEMkL concentration, indicating EEMkL becomes more effective as its concentration is increased. When the change of ρ_{corr} with the inhibitor concentration becomes steep (high negative value for constant B) it reflects good inhibitive properties for the studied inhibitor [23-25]. The results obtained agree well to it, the minimum corrosion rate (0.8311 mmy^{-1}) was observed at the higher concentration of EEMkL (0.9810 g/L) at 30 ± 1 °C at 24 h exposure period (Tables 1 & 2). Besides, the EEMkL was ineffective at higher temperatures, as clearly illustrated in Fig. 8.

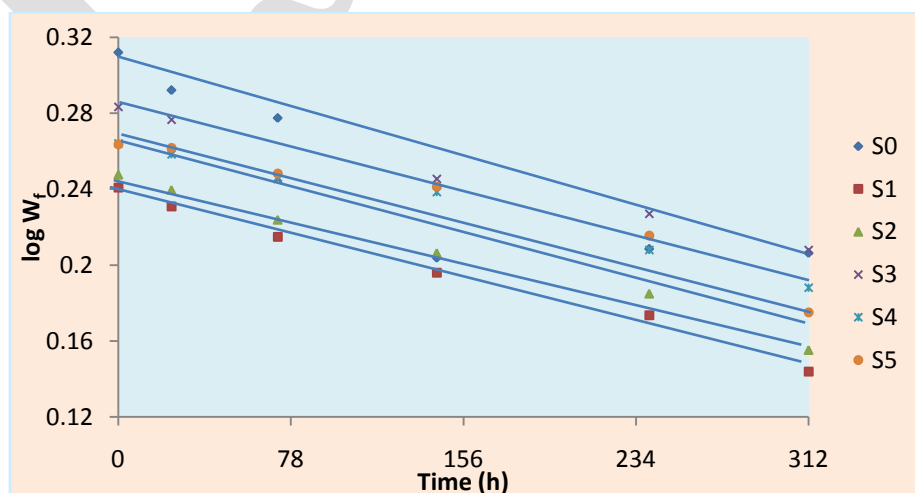


Fig 9: $\log W_f$ vs. Immersion Time

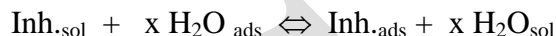
Precisely, the corrosion reaction is an overall reaction in which both solid and liquid phases are consumed, thus, it is difficult to apply most of the principles of the chemical kinetics to corrosion reaction. The log plot of the measured weight of coupons after post treatment ($\log W_f$) against exposure time (t) (Fig. 9) at the room temperature ($30 \pm 1^\circ\text{C}$) helps to explain the kinetics of the corrosion process of AA6063 in 0.5 N HCl in the corrodent and corrodent-EEMkL systems. It is formulated as [18]:

$$\log W_f = \log W_o - Kt$$

where, W_f and W_o are the post treatment and initial weights of the coupons respectively; K is the rate constant for corrosion process; and t is the immersion time (h). A linear variation was observed in corrodent and corrodent- EEMkL systems, thus confirming a first order kinetics.

Adsorption Isotherms

During corrosion inhibition of metals and alloys, the nature of inhibition on metal surface is deduced in terms of adsorption characteristics of the inhibitor [24]. The surface coverage, θ , of inhibitor are very useful while explaining the adsorption characteristics. The adsorption of an inhibitor species, Inh., at a metal/solution interface can be expressed as a place exchanger process between the inhibitor molecules in the aqueous solution (Inh._{sol}) and the water molecule on the metallic surface ($\text{H}_2\text{O}_{\text{ads}}$) [25]:



where x is the size ratio, representing the number of water molecules displaced by one molecule of inhibitor during adsorption process. When the equilibrium of the process described in above equation is reached, it is possible to obtain different expressions of the adsorption isotherm plots, and thus the degree of surface coverage $\{\theta = \text{IE} (\%)/100\}$ can be plotted as a function of the concentration of the inhibitor under test. The fractional surface coverage (θ) was found maximum at the higher concentration (0.9810 g/L) of EEMkL at 24 h immersion period (Table-1). It is assumed that the water molecules dipoles have to be oriented and their orientation depends on the metal charge adapting the suitable adsorption isotherm [24-26].

The adsorption isotherm provides useful insights into the mechanism of corrosion inhibition, thus it is necessary to determine empirically which adsorption isotherm fits best to the surface coverage data in order to use the corrosion rate measurements to calculate the thermodynamic parameters pertaining to inhibitor adsorption.

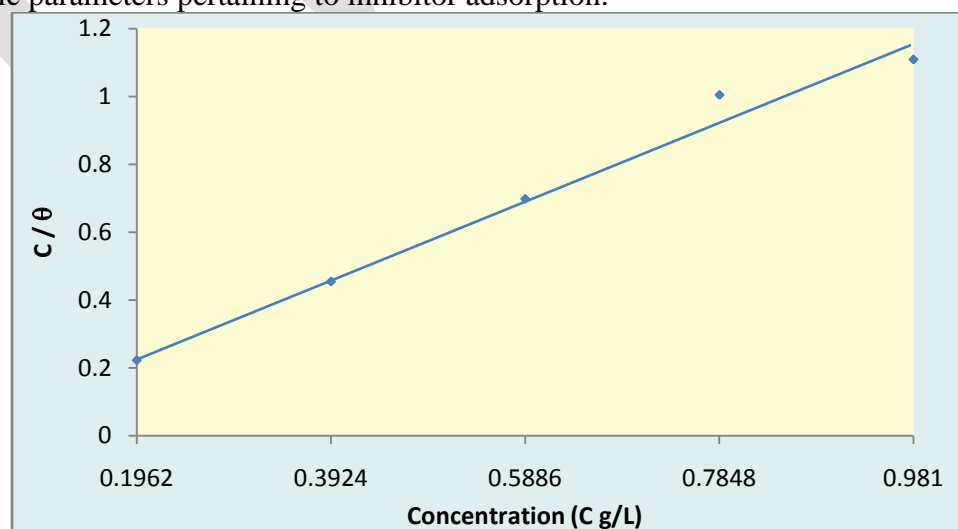


Fig 10: Langmuir Adsorption Isotherm of EEMkL on AA6063

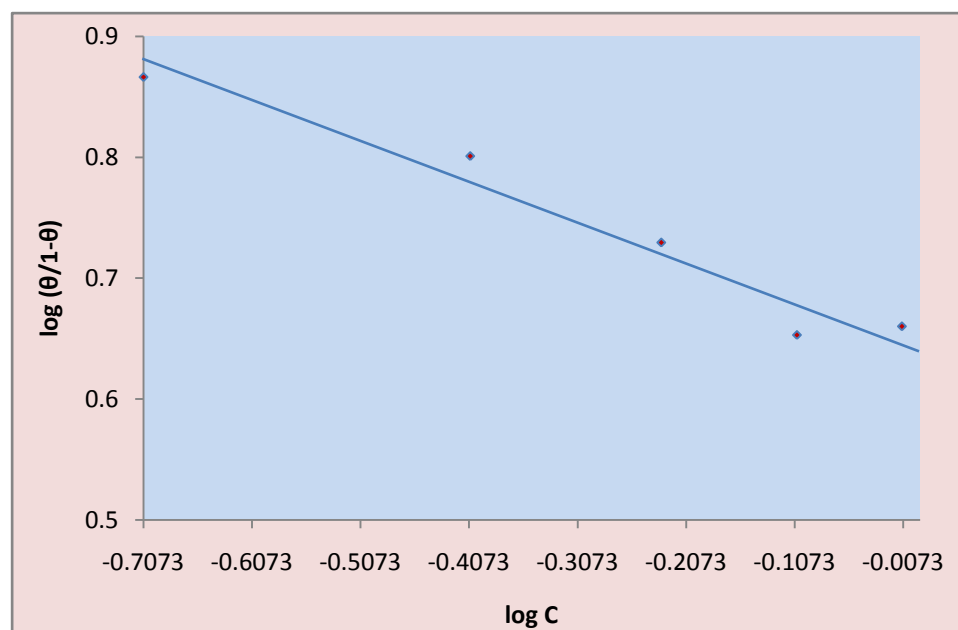


Fig 11: Thermodynamic Kinetic Model

The best fitted straight line was obtained for the plot of C_{inh}/θ versus C_{inh} with slopes around unity (Fig. 10), thus suggesting that the adsorption of EEMkL on AA6063 surface obeyed Langmuir adsorption isotherm. Langmuir adsorption isotherm is mathematically expressed as:

$$(C/\theta) = C + 1/K_{ad}$$

where, C is the concentration of the inhibitor (EEMkL), θ is the fractional surface coverage, and K_{ad} is the adsorption equilibrium constant. It is based on the assumption that the adsorbed molecule decreases the surface area available for the corrosion reactions to occur [27-29]. Curve-fitting of the data to the thermodynamic-kinetic model has been illustrated in Fig. 11, which shows a linear dependence of $\log \theta / (1 - \theta)$ as a function of $\log C$.

The adsorption equilibrium constant (K_{ad}) were high at higher concentrations of EEMkL at 24 h exposure, hence it is understood that higher concentration of EEMkL is needed for maximum adsorption to form unimolecular layer at $30 \pm 1^\circ\text{C}$ (Table-1). The K_{ad} values were found to decrease with the increase in temperature (Tables 1 & 2), depicting poor adsorption or increase in desorption process at elevated temperatures. The K_{ad} is related to the free energy of adsorption ΔG as:

$$K_{ad} = (1 / C_{\text{solvent}}) \exp^{(-\Delta G / RT)}$$

where C_{solvent} represents the molar concentration of the solvent (in case of water it is 55.5 mol/dm^3); R = universal gas constant $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$; & T = temperature (K).

The values of thermodynamic functions are very approximate because the inhibition efficiency is dependent on time, as is the surface coverage (θ).

CONCLUSION

- The results confirm that the EEMkL possess remarkable anti-corrosive property on AA6063 in 0.5 N HCl; the metal dissolution was inhibited to a significant extent at room temperature only.

- Significantly high IE (%) was found (96.43 %) at highest concentration (0.98 g/L) of EEMkL at 30 ± 1 °C.
- At elevated temperature, IE (%) was observed in negative, indicating metal dissolution process. Consequently, use of EEMkL is not advisable at elevated temperatures.
- The Langmuir adsorption isotherm provides a formal description of the adsorption behavior of the EEMkL on AA6063 (at room temperature).
- The values for the activation and thermodynamic parameters (E_a , ΔH^0 , ΔS^0 and ΔG^0) for the inhibitor-metal interactions were observed to be higher for inhibitive solutions than those for the corrosive solution alone (blank).
- The values of enthalpy of activation, ΔH^0 , were observed lower than 50 kJ/mol. Similarly, E_a was observed to be much lower than 80 kJ/mol and ΔG^0 values were in the range of -15.99 to -18.47 kJmol⁻¹, thereby endorsing the physisorption mode of adsorption of the EEMkL over AA6063 surface.
- Since Karipatta (*Murraya koenigii*) is an environmentally friendly, low priced, easily available, abundantly found, natural product with remarkably good inhibition efficiency (96.43 %) at room temperature. Therefore, it is recommended to use Karipatta as a replacement for many toxic inhibitors for Aluminium & its alloys in HCl medium. But its use at higher temperatures is not advisable since metal dissolution was observed at higher temperatures.

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