

Inhibition of Limestone (CaCO_3) Concentrated Rich Water Effects on Zinc Sheets Using Crude Alkaloids and Non Alkaloids Extracts of *Nepeta cataria* (Catnip) Plant

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Abstract

The corrosion inhibition study of crude ethanol extracts of alkaloids and non-alkaloid obtained from *Nepeta cataria* leaves on the corrosion of zinc sheets in limestone concentrated rich solution at the temperature of 303, 318 and 328K was investigated using weight loss, hydrogen evolution and electrochemical impedance spectroscopic techniques respectively. The results indicated that both plant extracts inhibit the corrosion of zinc in the medium by adsorption. However, AENCL exhibited higher maximum inhibition efficiency (99.0%) than NAENCL (78.6%) at 7.5 g/L. Inhibition mechanisms were deduced from the temperature dependence of the inhibition efficiency as well as from activation parameters that govern the process. Adsorption of both plant extracts on the zinc coupon was found to obey the Langmuir adsorption isotherm. The phenomenon of physical adsorption is proposed from the obtained thermodynamic parameters.

Keywords: Calcium carbonate, zinc, adsorption, impedance, charge transfer, weight loss.

1. Introduction

Corrosion is a constant and continuous problem, often difficult to eliminate completely. Prevention will be more practical and achievable than complete elimination. Corrosion process develop fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of both the metal surface and the local environment [1] for example, formation of oxides, diffusion of metal cations into the coating matrix, local PH changes, and electrochemical potential. The use of inhibitors is one of the best options of protecting metals and alloys against corrosion. The environmental toxicity of organic corrosion inhibitors has prompted the search for green corrosion

inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds. As in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable [1, 2].

Organic inhibitors generally have heteroatoms. Oxygen, Nitrogen, Sulphur, Phosphorus, are found to have higher basicity and electron density and thus acts as corrosion inhibitors. They are the active centres for the process of adsorption on the metal surface. They reduce corrosion rate by adsorption of ions/molecules onto metal surface, increase or decrease the anodic and/or cathodic reaction, decrease the diffusion rate for reactants to the surface of the metal, decrease the electrical resistance of the metal surface, etc. [1 – 3]. Most published works have shown that most organic inhibitors adsorb on the metal surface by displacing water molecules on the surface and forming a compact barrier. Presence of non-bonded and p-electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal. Some factors that may contribute to the action of inhibitors are chain length, size of the molecule, bonding, aromatic/conjugate, strength of bonding to the substrate, cross linking ability, solubility in the environment, etc. [1 – 3].

2. Experimentation

2.1 Extraction procedure and preparation of inhibitors

Nepeta cataria leaves were collected from a Kayang forest in Boki local government area of Cross River, Nigeria intended for herbal medicine. These were cut into small chips, dried in a MEMMERY UNB–500 laboratory oven at 50o C and ground into powdered form. Two

hundred grams of the powdered sample was extracted continually with 200 cm³ of ethanol in a Soxhlet extractor for over Five (5) days. The solvents (ethanol) was evaporated using a water bath to afford crude ethanol extract.

Thirty grams of the crude ethanol extract was digested with 150 ml diethyl ether and 0.5 M HCl acids respectively with the aid of a separating funnel and allowed for 2.00 hours. The tailing fraction was collected, evaporated of diethyl ether and used as the non-alkaloid fraction. The HCl solution in the float fraction was diluted with ammonia solution and this was taken well above pH 7. Diethyl ether was immediately added and the layer with the diethyl ether eventually taken away from the funnel and distilled off. A small quantity of moderately pure alkaloids was obtained and used as the alkaloid fraction. Ten grams of each alkaloid and non alkaloid fractions were taken and diluted in 1000 cm³ of 5 M CaCO₃ solution, kept for 24 hours and filtered. The filtrates which were taken as crude alkaloid and nonalkaloid inhibitors were used for the preparation of different concentrations of inhibitor (1.0 g/L, 2.0 g/L, 3.5 g/L, 5.0 g/L and 7.5 g/L) which were now used for the corrosion inhibition investigation.

2.2 Weight loss experiments

Weight loss measurement was performed on resized zinc sheets with a rectangular dimension of 5cm x 0.08cm x 4cm in 5.0 M CaCO₃ solutions with and without different concentrations of AENCL and NAENCL. Every coupon was weighed using ADAM PGW–253e digital analytical balance and then suspended in the inhibition solution using a string for a period of 1 hour. After immersion the surface of the specimen was washed with distilled water using a bristled brush to scrub off the corroded surface followed by degreasing with absolute ethanol, rinsing with acetone and reweighed. This process was repeated progressively for 5 hours for both inhibitors.

2.3 Hydrogen evolution experiments

100 ml of the CaCO₃ solution without the inhibitor (5 M concentration) was introduced into a two-necked flask and the initial volume of the air in the burette was noted. Thereafter, a zinc sheet coupon of dimension 1.2cm x 0.08cm x 4cm initially weighed was dropped into the test solution and the flask quickly closed. The volume of the hydrogen gas evolved from the corrosion reaction was monitored by volume changes in the level of paraffin oil in the graduated burette at fixed time intervals. This volume changes in the level of paraffin oil was recorded every minute for 1 hour. In another experiment, a set of fresh coupons were immersed in the flask containing the alkaline solution plus different concentrations each of AENCL and NAENCL 1.0 g/L, 2.0 g/L, 3.5 g/L, 5.0 g/L and 7.5 g/L).

The study was conducted at 303K, 318K and 328K using a MEMMERT WNB–14 Thermostat water bath. Each experiment was repeated twice to ensure reproducibility, and the average values were recorded.

2.4 Electrochemical measurements

The electrochemical measurements were undertaken in a three-electrode cell using Gamry Instrument with a Gamry framework system based on ESA410. zinc samples, graphite rod and silver/silver chloride (Ag/AgCl) were used as working, counter and reference electrodes, respectively. All the measurements were taken after the working electrode was immersed for 30 minutes in the test solution at room temperature in order to attain a steady-state open-circuit potential (OCP). A frequency range of 100 kHz to 0.01 Hz with amplitude of 10 mV was used in electrochemical impedance experiments.

3. Analysis and result

3.1 Inhibitor effects on corrosion rate

Five different inhibitor concentrations (1.0 g/L, 2.0 g/L, 3.5 g/L, 5.0 g/L and 7.5 g/L) were tested using the weight loss method and the result obtained is presented in Table 1. Corrosion rate of zinc sheet was found to decrease with increase in the concentration of alkaloid and non alkaloid extracts of *Nepeta cataria* (AENCL and NAENCL) in limestone concentrated water. This may be explained on the basis that the extracts reduced the rate of corrosion consequence upon the strong adsorption of the extracts molecules on the zinc surface [1, 4 – 7]. Surface coverage (θ) and inhibition efficiency (IE%) of inhibitors increased with increase in AENCL and NAENCL concentrations, this proved that the corrosion of the metal has been inhibited and a larger fraction of the surface is protected against limestone concentrated water attack [6 – 12].

Table 1:

Calculated values of corrosion rates, surface coverage and inhibition efficiency for mild steel coupons in 5 M CaCO₃ in the absence (blank) and presence of AENCL and NAENCL at 30°C.

Conc. (g/L)	AENCL			NAENCL		
	CR (mg/cm ² /h)	θ	%IE	CR (mg/cm ² /h)	θ	%IE
Blank	0.926	-	-	0.926	-	-
1.0 g/L	0.295	0.681	68.1	0.506	0.454	45.4
2.0 g/L	0.208	0.775	77.5	0.401	0.567	56.7

3.5 g/L	0.163	0.824	82.4	0.320	0.654	65.4
5.0 g/L	0.092	0.901	90.1	0.261	0.718	71.8
7.5 g/L	0.009	0.990	99.0	0.198	0.786	78.6

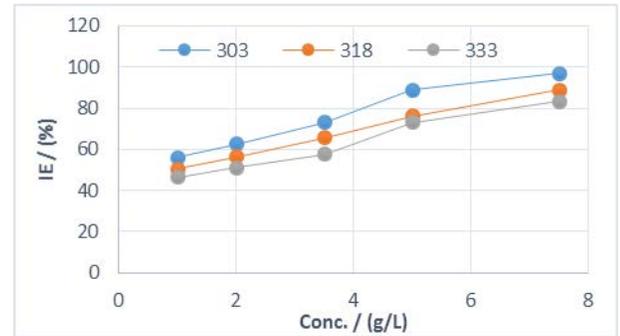
3.2 Temperature effects on inhibitor

Values for the corrosion rate of the metal Inhibition efficiencies and degree of surface coverage of the inhibitors with variation in temperature are presented in Table no. 2. It is observed from the results as presented Table no. 2 that the corrosion rate of the zinc sheets decreases with increase in concentration of AENCL and NAENCL, and increases with increase in temperature. This is indicative of the fact that there is an increase molecular adsorption of the inhibitors on the metal surface hence decreasing the corrosion rates but consequently the inhibitor is affected by increased energy of agitation hence increasing corrosion rate with temperature. These results are in similar with those of Obot et al. [1], Dada et al. [12] and Hui et al. [13]. From Figs 1a – d, we have that the variation of inhibition efficiency (%IE) of inhibitors with concentration for zinc sheets in 5 M CaCO₃ solutions showed increase with extracts concentration and decrease with temperature similar to the works previously reported by Pradeep et al [14]. This suggest that the phytochemical components of *Nepeta cataria* leaves are adsorbed on the zinc -interface, thereby reducing the surface area available for corrosion, thus inhibiting the rate of the metal dissolution process [15].

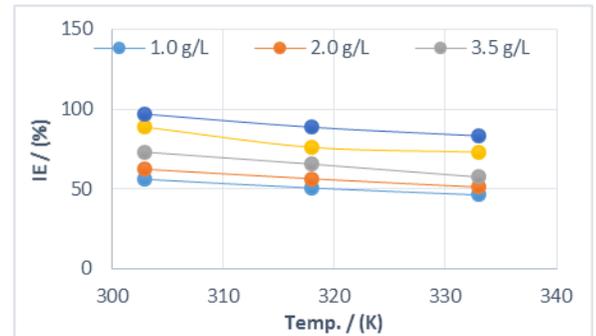
Table 2.

Calculated values of corrosion rate of zinc, surface coverage and inhibition efficiency of inhibitor for corrosion inhibition of zinc in 5 M CaCO₃

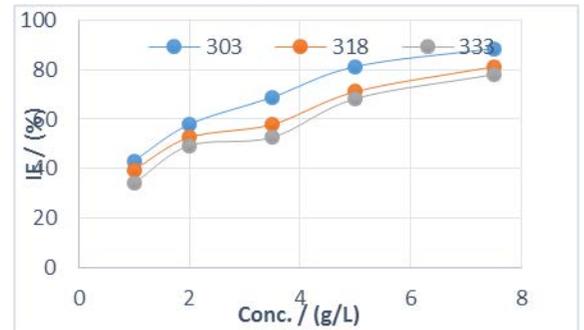
	Conc. (g/L)	CR (mg/cm ² h)			θ			% IE		
		303K	318K	333K	303K	318K	333K	303K	318K	333K
AENCL	(5 M CaCO ₃)	9.145	13.699	23.027	-	-	-	-	-	-
	1.0 g/L	4.011	6.774	12.365	0.561	0.506	0.463	56.1	50.6	46.3
	2.0 g/L	3.441	5.972	11.236	0.624	0.564	0.512	62.4	56.4	51.2
	3.5 g/L	2.461	4.713	9.793	0.731	0.656	0.575	73.1	65.6	57.5
	5.0 g/L	1.024	3.278	6.195	0.888	0.761	0.731	88.8	76.1	73.1
	7.5 g/L	0.286	1.542	3.847	0.969	0.887	0.833	96.9	88.7	83.3
NAENCL	(5 M CaCO ₃)	9.145	13.699	23.027	-	-	-	-	-	-
	1.0 g/L	5.198	8.274	12.840	0.432	0.396	0.442	43.2	39.6	44.2
	2.0 g/L	3.847	6.488	11.682	0.579	0.526	0.493	57.9	52.6	49.3
	3.5 g/L	2.846	5.761	10.888	0.689	0.579	0.527	68.9	57.9	52.7
	5.0 g/L	1.709	3.954	7.291	0.813	0.711	0.683	81.3	71.1	68.3



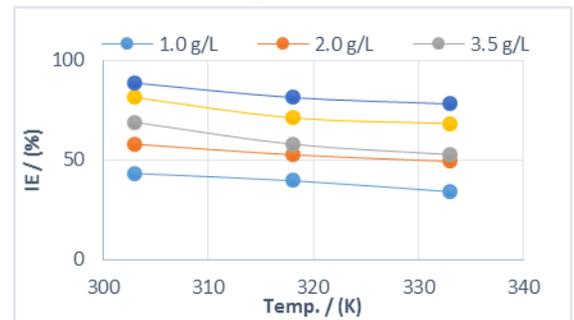
(a)



(b)



(c)



(d)

Fig. 1. Variation of IE (%) with Conc. (a and c) and Temp. (b and d) for AENCL and NAENCL in 5 M CaCO₃

3.3 Electrochemical impedance spectroscopic result

The behavior of Zinc sheet in 5 M concentrated limestone (CaCO₃) rich water with and without the different concentration of AENCL and NAENCL was further investigated using the electrochemical impedance spectroscopic measurements. The Nyquist plots for Zinc sheets in 5 M CaCO₃ without and with various concentrations of the studied extracts are displayed in Figs. 2a – b. There is an observed depressed semicircle in the Nyquist plots as a result of non-ideal behavior of the electrochemical interface of the Zinc sheets in the aggressive electrolytes 1, 10, 16. There was also an increase in the diameter of the Nyquist plots as the concentration of the AENCL and NAENCL was increased. This is explained on the basis that the inhibitors established a protective film on the zinc surface hence leading to an increase in the impedance of the zinc interface to the electrochemical corrosion [9, 17 – 21]. The %IE was determined from the charge transfer resistance data (Table no. 3) as Eq.

$$\%IE = \frac{R_{ct} - R_{ct}^1}{R_{ct}} \times 100$$

Where R_{ct} and R_{ct}^1 are the charge transfer resistance values in the presence and absence of the inhibitors. Meanwhile the values of the double layer capacitance C_{dl} were determined following Eq.

$$f(-Z''_{max}) = \frac{1}{2\pi R_{ct} C_{dl}}$$

Where $f(-Z''_{max})$ is the maximum frequency on the imaginary impedance axis, and its values are also listed in Table 3. It is clear from the results in Table 3 that the increase charge R_{ct} values following increase inhibitor concentration is as a consequence of the formation of protective film of inhibitor molecules on the zinc surface thereby reducing the transfer rate of charge species across the interface [1, 18 – 25]. The double layer capacitance values in the presence of the inhibitors are generally lower than that of the blank alkaline system. This may mean decrease in local dielectric constant or increase in thickness of capacitive layer, which is attributed to the adsorption of inhibitor molecules on the zinc surface [5, 11, 26 – 28].

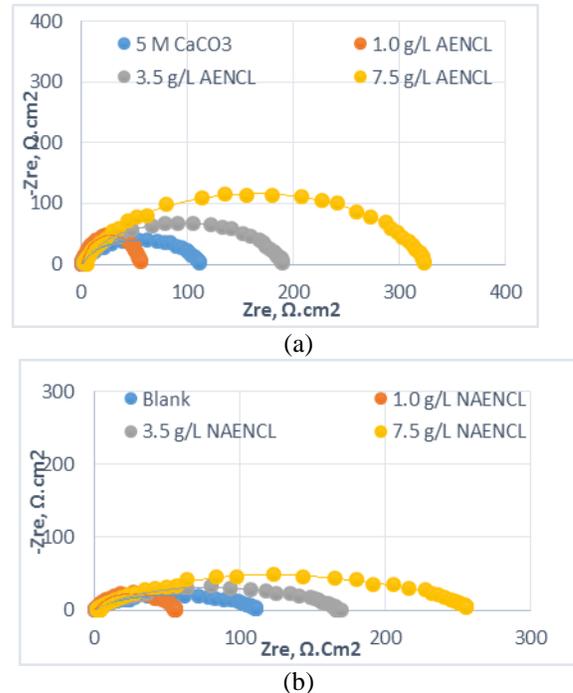


Fig. 2. Electrochemical impedance plots (Nyquist) relating the inhibition of zinc by (a) AENCL and (b) NAENCL in 5 M CaCO₃ solution.

Table 3. Calculated values from the Nyquist plots for the inhibition of zinc by AENCL and NAENCL in 5 M CaCO₃ solution.

	Conc. (g/L)	R_{ct} (Ωcm^{-2})	C_{dl} (μFcm^{-2})	IER %
	Blank (5 M CaCO ₃)	51	7.4×10^{-4}	-
AENCL	1.0 g/L	121	2.6×10^{-4}	57.9
	3.5 g/L	194	1.4×10^{-4}	73.7
	7.5 g/L	333	5.9×10^{-5}	84.7
NAENCL	1.0 g/L	110	5.2×10^{-4}	53.6
	3.5 g/L	165	3.7×10^{-4}	69.1
	7.5 g/L	252	1.7×10^{-4}	79.8

3.4 Adsorption mechanism

Langmuir isotherms for AENCL and NAENCL were tested to determine their fit to experimental data (Figs 3a - b). Their correlation values (R^2) obtained from these isotherms are approximately 1.0 (Table 4). This could be explaining the fact that the data obtained for the inhibitor fits well in Langmuir adsorption isotherm and that the adsorption process is monolayer and mechanism of adsorption is physical. Similar results have been obtained by Abeng et al [20], Okafor and Apebende [27]. It is also observed that although these plots are linear, the gradients are never

unity, contrary to what is expected for an ideal Langmuir adsorption isotherm equation. Literatures have shown that organic molecules having polar atoms or groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slope values from unity [28 – 30]. The adsorption of the inhibitor on the metal surface leads to high degree of surface coverage and hence shows better inhibitive property [7, 19,31].

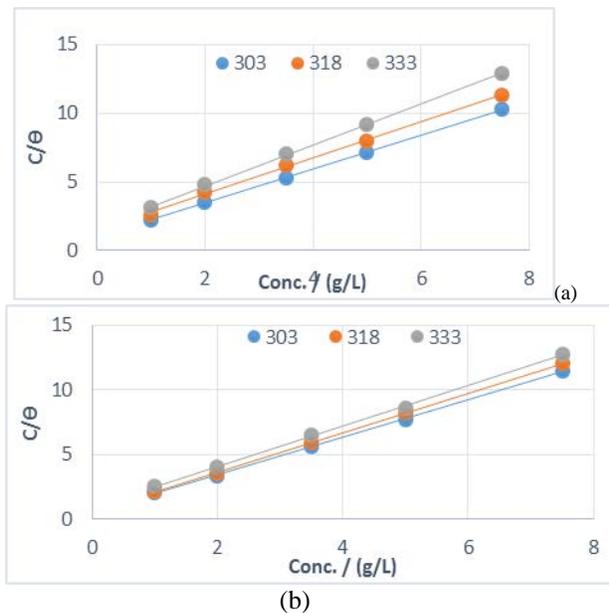


Fig. 3. Adsorption plots drawn from Langmuir isotherm for the inhibition of zinc by (a) AENCL and (b) NAENCL in 5 M CaCO₃ solution.

Table 4. Calculated values of equilibrium constant, correlation coefficient and adsorption free energy for the inhibition of zinc by (a) AENCL and (b) NAENCL in 5 M CaCO₃ solution.

Temp. (K)	AENCL				NAENCL			
	k (g/L)	R ²	Slope	ΔG* _{ads} (kJ/mol)	k (g/L)	R ²	Slope	ΔG* _{ads} (kJ/mol)
303	0.988	0.9997	1.2292	-10.09	1.925	0.9997	1.2292	-12.045
318	0.684	0.9994	1.4891	-9.615	1.715	0.9996	1.5254	-11.247
333	0.573	0.9984	1.3226	-9.578	1.047	0.9994	1.5638	-11.768

3.5 Thermodynamics

The standard adsorption free energy (ΔG^o_{ads}) was obtained from

$$\Delta G_{ads}^{\circ} = -RT \ln(55.5K_{ads})$$

where R is the gas constant (R= 8.314 J K⁻¹), T is the absolute temperature, K_{ads} is the equilibrium constant. The

thermodynamic parameter, ΔG^o_{ads} obtained from equilibrium constant derived from Langmuir isotherm plots is listed in **Table 4**. The large negative values of ΔG^o_{ads} revealed a spontaneous process of adsorption reaction. It also show that the adsorbed layer on the surface of zinc sheet is highly stable and the process is a physical adsorption process. Similar results have been obtained from the works of Ugi and Obeten [8], Hui *et al* [13], Okafor and apebende [27]. The activation energy at different concentration of the inhibitor in 5 M CaCO₃ solution was calculated by plotting log CR vs. 1/T (**Fig. 4a - b**) and presented in **Table 5**). Ea values for the inhibited systems were higher than those for the uninhibited system indicating that both inhibitors inhibited the zinc dissolution [19, 22, 32 – 34]. This can also be attributed to an appreciable decrease in the adsorption of the inhibitor on the zinc sheet surface with increase in temperature [8, 14, 35]. This has been confirmed from the hydrogen evolution result.

From **Figs. 5a - b**, [-ΔH^o_{ads}/2.303R] is the slope of the straight line from plot of log(lnCR/T) vs. 1/T and the intercept log(R/h) + ΔS/2.303R, from which the values of ΔH and ΔS were calculated and given in Table 5 according to the transition state equation,

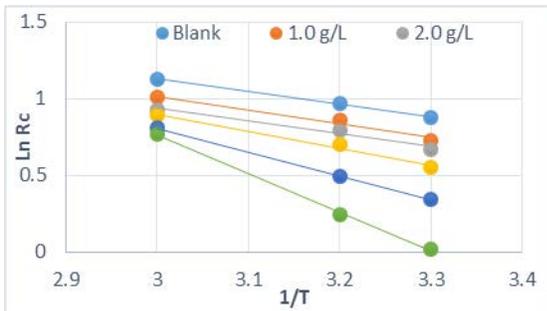
$$\log \frac{CR}{T} = \log \frac{R}{Nh} + \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}$$

Inspection of these data reveals that the positive signs of enthalpy (ΔH) reflect the endothermic nature of dissolution process [29, 33]. In this work, from the average ΔH values calculated, the absolute values of enthalpy are low approaching those of typical physisorption. The shift towards negative value of entropy (ΔS) imply that the activation complex in the rate determining state represents association rather than dissociation, meaning that the disordering decreases on going from reactants to the activation complex [1, 10, 24]. Negative values of ΔS indicates that entropy decreases upon achieving the transition state, which often indicates associative mechanism according to Hui *et al* [13].

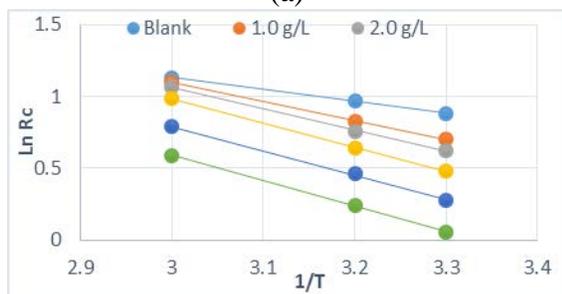
Table 5. Values of activation energy/thermodynamic parameters for zinc sheets corrosion in the absence and presence of the plant extracts in 5 M CaCO₃ solution

Conc. (g/L)	AENCL			NAENCL		
	Ea	ΔH _{ads} (kJ/mol)	ΔS _{ads} (kJ/mol)	Ea	ΔH _{ads} (kJ/mol)	ΔS _{ads} (kJ/mol)
Blank (1 M H ₂ SO ₄)	8.29	11.50	-69.21	8.29	11.50	-69.21
0.5 g/L	8.43	13.14	-91.37	13.36	13.79	-85.67
1.0 g/L	9.07	14.71	-129.84	15.07	14.29	-106.39
2.0 g/L	11.07	15.21	-134.21	16.93	14.36	-117.38

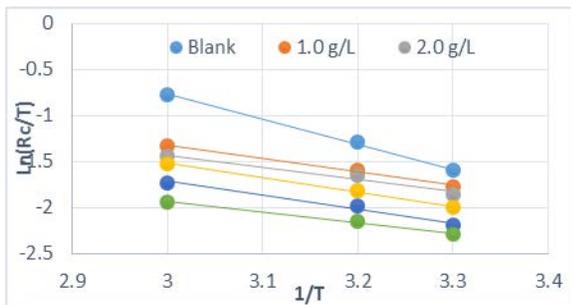
3.5 g/L	15.71	15.50	-176.59	17.07	15.50	-135.28
7.0 g/L	25.21	27.07	-293.28	17.93	19.93	-174.53



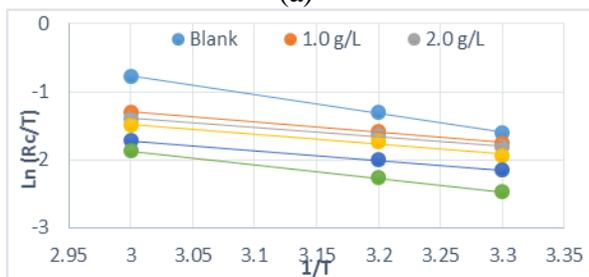
(a)



(b)

 Fig. 4. Arrhenius plots for the inhibition of zinc by (a) AENCL and (b) NAENCL in 5 M CaCO₃ solution.


(a)



(b)

 Fig. 5. Transition state plots for the inhibition of zinc by (a) AENCL and (b) NAENCL in 5 M CaCO₃ solution.

4. Conclusions

From the research so far, it has been deduced that both inhibitors (alkaloid and non alkaloid) extracted from *Nepeta cataria* plant have shown significant inhibition of the zinc sheet from the limestone concentrated rich water effects (%IE – 99.0 and 78.6 for AENCL and NAENCL), respectively. The inhibition process was found to be as a result of strong adsorption of inhibitor molecules on the zinc sheet surface especially those of AENCL. The mechanism of adsorption was seen to be a physical process and monolayer in nature from the obedience of the Langmuir isotherm. The inhibitors were very stable and the reaction was spontaneous. At lower temperatures, both inhibitors exhibited a strong adsorption on the zinc surface leading to a reliable corrosion retardation.

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