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Stem Extract of Brahmi (*Bacopa monnieri*) as Green Corrosion Inhibitor for Aluminum in NaOH Solution

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The stem extract of *Bacopa monnieri* was investigated as corrosion inhibitor of aluminium in 0.5 M NaOH solution using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) methods, and weight loss measurements. The results revealed that *Bacopa monnieri* stem extract was an effective inhibitor, and the inhibition efficiencies obtained from polarization and weight loss experiments were in good agreement. Using the potentiodynamic polarization technique, the extract proved to be a mixed-type inhibitor for aluminium in alkaline solution by suppressing both anodic and cathodic reactions on the metal surface. The Langmuir adsorption isotherm model fitted results obtained from the weight loss. Thermodynamic parameters such as activation energy, free energy of adsorption were calculated.

Keywords: Aluminium, Corrosion inhibition, Plant extract, Alkaline solution, Weight loss method

1. INTRODUCTION

Aluminium is the second most used metal after iron; it is used in a large number of applications by itself and in a wide range of alloys. Because of its low atomic mass and the negative value of the standard electrode potential, aluminium potentially can be used as an anode material for power sources with high energy densities [1]. The corrosion behaviour of pure aluminium and its alloys in aqueous alkaline solutions have been extensively studied in the development of the aluminium anode for the aluminium/air battery [2-5]. Corrosion of aluminium causes many problems viz., (a) passivation of the cathode active material, (b) its solid products increase the electrical resistance, (c) its soluble products contaminate the electrolyte and increase the self-discharge rate, and (d) the dissolved Al^{3+} ions migrate to the counter anode and reductively deposit. Despite the fact that aluminium/air battery is an eco-friendly system and the energy density of this system is excellent, it is not greatly used in practice due to severe hydrogen evolution problems resulting from corrosion of the aluminium electrode. Thus, commercial application of Al and its alloys requires control of the hydrogen gas evolution must necessarily be achieved without compromising the eco-friendly nature of the system.

In efforts to mitigate aluminium corrosion, the main tactic is to separate the metal from corrosive environments. This can be achieved using corrosion inhibitors. Recently, the use of chemical inhibitors has been limited due to environmental regulations. Plant extracts have again become important because they are environmentally friendly and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. A lot of natural products have been previously used as corrosion inhibitors for different metals in various environments [6-14] and their optimum concentrations were reported. The obtained data showed that plant extracts could serve as effective corrosion inhibitors. It is well established that corrosion inhibition occurs via adsorption of their molecules on the corroding metal surface and efficiency of inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers formed under particular conditions.

As a contribution to the current interest on environmentally friendly, green, corrosion inhibitors [15-20], the present study investigates the inhibiting effect of seed extracts of Brahmi *(Bacopa monnieri)* stem extract on the aluminium corrosion in 0.5 M NaOH solution using the weight loss and polarization techniques.

2. EXPERIMENTAL SECTION

Aluminium (Al-1060) strips were used for weight loss as well as electrochemical studies. The aluminium specimens were machined into test electrodes of dimension 8 cm × 1 cm and embedded in PVC holder by epoxy resin (araldite) leaving a surface area of 1 cm^2 for electrochemical measurements. The exposed surface was abraded with silicon carbide abrasive paper (400 to 1200 grade), degreased with acetone, rinsed in distilled water, and dried in the air. The corrosive medium was 0.5 M NaOH solution prepared from analytical-reagent-grade NaOH (MERCK) and bidistilled water. Stock solution of *Bacopa monnieri* was extracted by reflux of 100 g of the dried material in 500 mL bidistilled water for 5 h. The refluxed solution was filtered to remove any contamination. The concentration of the stock solution was calculated in mg L^{-1}.

Electrochemical experiments were carried out in a conventional three-electrode glass cell of capacity 100 mL, using a GAMRY POTENTIOSTAT/ GALVANOSTAT PCI 4 electrochemical workstation. Saturated calomel electrode (SCE) equipped with a Luggin capillary and a platinum foil of 1 cm × 1 cm were used as reference and counter electrode, respectively. All the potentials reported are with reference to SCE. Before measurement, the working electrode was immersed in test solution for approximately 30 min until a steady open-circuit potential (OCP) was reached. EIS measurement was carried out in the 100 kHz - 10 mHz frequency range at OCP. The sinusoidal potential perturbation was 10 mV in amplitude and the cell temperature was maintained at 308 ± 1 K using a thermostatic water-bath. The electrochemical experiments data were collected and analyzed by electrochemical software Echem Analyst ver. 5.5. The polarization curves were carried out from cathodic potential of -0.25 V to anodic potential of +0.25 V with respect to the open circuit potential at a sweep rate of 1 mV s^{-1}. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential (E_{corr}) to obtain the corrosion current densities (I_{corr}). In each measurement, a fresh working electrode was used. Several runs were performed for each measurement to obtain reproducible data.

The aluminium specimens of 2.5 cm × 2 cm × 0.05 cm sizes were used for weight loss measurements and were abraded with a series of silicon carbide abrasive paper (grade 600-1200) and degreased with acetone, rinsed in distilled water, and dried in the air, and weighed accurately. Aluminium specimens were immersed in 100 mL of 0.5 M NaOH with and without addition of different concentrations of *Bacopa monnieri* stem extract. The temperature of the corrosive system was controlled by an air thermostat. After 1 h immersion, the aluminium specimens were carefully washed in double-distilled water, dried, and then weighed. The weight loss data were obtained from the average value of three parallel samples in 0.5 M NaOH with *Bacopa monnieri* stem extract at different concentrations.

3. RESULTS AND DISCUSSION

3.1 Electrochemical measurements

3.1.1. Polarization measurements

Polarization curves of Al in 0.5 M NaOH solution without and with different concentrations of *Bacopa monnieri* stem extract are shown in Figure 1. It could be observed that both the cathodic and anodic reactions were suppressed with the addition of *Bacopa monnieri*, which suggested that the inhibitor exerted an efficient inhibitory effect both on anodic dissolution of metal and on cathodic hydrogen reduction reaction. Electrochemical parameters such as E_{corr}, I_{corr}, and anodic and cathodic Tafel slopes (β_a, β_c) obtained from the polarization measurements are listed in Table 1. The inhibition efficiency (IE_P%) was calculated by following equation [21]:

$$IE_P\% = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100 \tag{1}$$

I_{corr} and $I_{corr(i)}$ signify the corrosion current density in the absence and presence of inhibitors, respectively.

It is evident from Table 1 that the values of β_c had small changes with increasing extract concentration, which indicated that the *Bacopa monnieri* stem extract was adsorbed on the metal surface and the addition of the inhibitor hindered the alkali attack on the aluminium electrode. Therefore, the inhibitor molecules did not change the hydrogen evolution reaction mechanism. In anodic domain, the value of β_a decreases with the presence of *Bacopa monnieri*. The shift in the anodic Tafel slope β_a might be attributed to the modification of anodic dissolution process due to the inhibitor modules adsorption on the active sites.

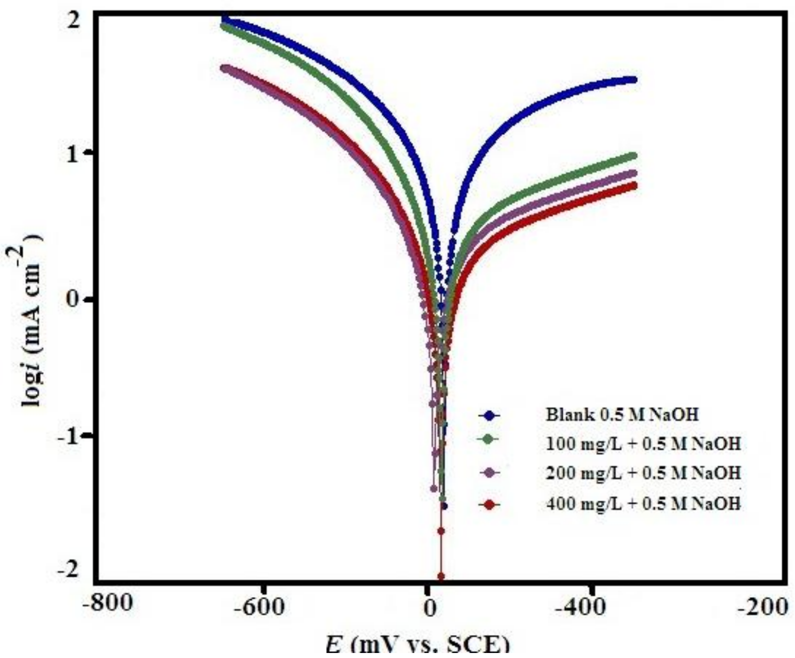

Figure 1. Polarization curves for Al in 0.5 M NaOH in presence of different concentrations of *Bacopa monnieri* stem extract.

Table 1. Electrochemical polarization parameters and the corresponding inhibition efficiencies for Al in 0.5 M NaOH solution in the absence and presence of different concentrations of *Bacopa monnieri* stem extract

Inhibitor (mg L^{-1})	E_{corr} (V/SCE)	I_{corr} (mA cm^{-2})	β_a (V dec^{-1})	β_c (V dec^{-1})	IE_p (%)
0.5 M NaOH	–1.54	270	1.186	0.61	–
30	–1.53	103	1.251	0.70	61
70	–1.51	86	0.516	0.73	68
100	–1.52	36	0.334	0.77	86
200	–1.51	20	0.844	0.78	87
400	–1.50	12	0.632	0.85	96

Compared to the free NaOH solution, the cathodic and anodic curves of the working electrode in the alkaline solution containing the *Bacopa monnieri* shifted obviously to the direction of current reduction, as it could be seen from these polarization results; the inhibition efficiency (IE_P%) increased with extract concentration reaching a maximum value of 90% at 400 mg L^{-1}. In literature [22], it is reported that only when the open circuit potential (OCP) displacement is at least 85 mV in relation to the one measured for the blank solution, can a compound be recognized as an anodic or cathodic inhibitor. From Figure 1 it can be seen that the displacement was at most 40 mV with respect to $E_{corr(0)}$ (the open circuit potential of blank solution). Therefore, *Bacopa monnieri* stem extract might act as a mixed-type inhibitor.

3.1.2. Electrochemical impedance spectroscopy (EIS) measurements

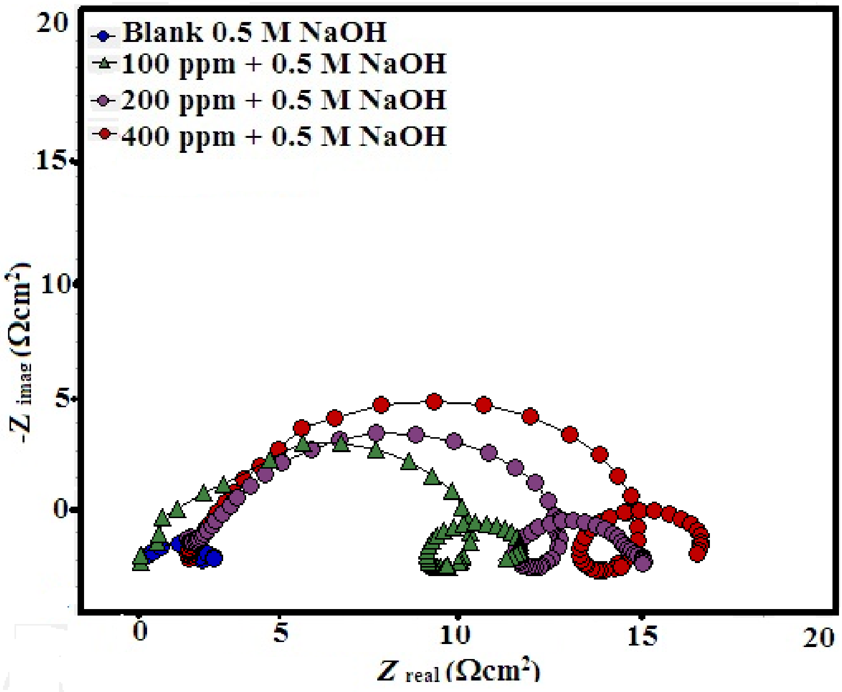

Figure 2. Nyquist plots for aluminium in 0.5 M NaOH with various concentrations of *Bacopa monnieri* stem extract.

Nyquist plots of aluminium in 0.5 M NaOH solution in the absence and presence of different concentrations of *Bacopa monnieri* stem extract are given in Figure 2, where it can be observed that the diameter of the semicircle increases with increasing *Bacopa monnieri* stem extract concentration. This increase in capacitive semicircles suggests that the inhibition action of the inhibitor is due to its adsorption on the metal surface without altering the corrosion mechanism. Furthermore, figure 2 manifested depressed capacitive semicircles, at higher and lower frequencies regions, separated by an inductive loop at intermediate frequencies. Inductive loops can be explained by the occurrence of adsorbed intermediate on the surface. Therefore, adsorbed intermediate species such as Al^{+}_{ads} and $Al^{3+}_{(ads)}$ might be involved in Al dissolution process [23]. The capacitive semicircle at higher frequencies is attributed to the redox Al–Al^{+} reaction since it was assumed to be the rate determining step in the charge transfer process [24]. Therefore, the resistance value obtained from intercepts of the first capacitive semicircle with real axis corresponds to the Al–Al^{+} charge transfer resistance. On the other hand, the second capacitive semicircle could be attributed to the fast complementary redox Al^{+}–Al^{3+} reaction. The curve manifested that addition of extract to alkaline NaOH solution leads to increase in the size of the capacitive semicircles, indicating increase in the resistances and decreasing corrosion rate.

3.2. Weight loss measurements and adsorption isotherm

The values of the inhibition efficiency (IE_w%) obtained from weight loss measurements for different concentrations of *Bacopa monnieri* stem extract in 0.5 M NaOH are given in Table 2. The inhibition efficiencies, IE_w%, were calculated by the following equation:

$$IE_w\% = \frac{W_0 - w}{W_0} \times 100 \quad (2)$$

W_0 and W are the corrosion rates in the absence and presence of the extract, respectively.

Table 2. Corrosion parameters for aluminium in aqueous solution of 0.5 M NaOH in the absence and presence of different concentrations of *Bacopa monnieri* stem extract from weight loss measurements at 308 K for 1 hour

Inhibitor concentration	Weight loss	IE_w	C_R
(mg L^{-1})	(mg cm^{-2} h^{-1})	(%)	(mm y^{-1})
0.5 M NaoH	15.1	-	56
30	5.1	64	19
70	3.7	76	14
100	2.5	83	8
200	1.2	92	5
400	0.8	94	3

The results obtained (Table 2) suggest that the inhibition efficiency increases with increasing concentration of extract. As the concentration reached 400 mg L^{-1}, the inhibition efficiency of extract obtained is 94%, which represented excellent inhibitive property. Adsorption of *Bacopa monnieri* stem extract can be explained on the basis that adsorption of the inhibitor was mainly via hetero atoms (viz., N) present in different constituents of extract in addition to the availability of π electrons in the aromatic system [25]. The phytoconstituents of *Bacopa monnieri* stem includes Saponins, Monnierin, Hersaponin, bacoside -A, bacoside –B, Brahmine [26].

The establishment of isotherms that describe the adsorptive behavior of a corrosion inhibitor is an important part of its study, as they can provide important clues to the nature of the metal–inhibitor interaction. The values of surface coverage (θ) are defined as IE_w%/100 and obtained from weight loss measurements at 308 K. Several adsorption isotherms were assessed to fit θ values, but the best fit was found to obey Langmuir adsorption isotherm [27] which may be expressed by:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \tag{3}$$

where C_{inh} is inhibitor concentration and K_{ads} is equilibrium constant of adsorption. It is well known that the standard adsorption free energy ($\Delta G°_{\text{ads}}$) is related to equilibrium constant of adsorption (K_{ads}) and can be calculated using the following equation [28]:

$$K_{\text{ads}} = \left(\frac{1}{55.5}\right)\exp\left(\frac{-\Delta G^{\circ}_{\text{ads}}}{RT}\right) \tag{4}$$

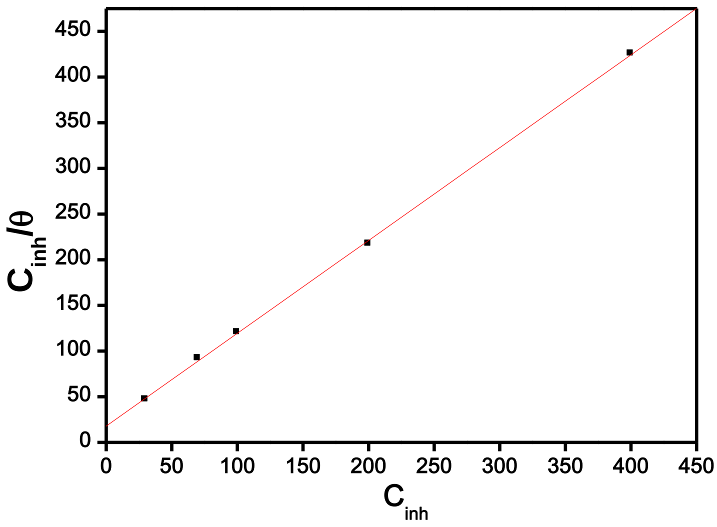

Figure 3. Langmuir adsorption isotherm plot for corrosion of aluminium in 0.5 M NaOH containing different concentration of *Bacopa monnieri* stem extract at 308 K.

Figure 3 represents the plot of (C_{inh}/θ) against C_{inh} for investigated *Bacopa monnieri* stem extract. Also, it is found that the kinetic–thermodynamic model of El-Awady et al. [29], i.e.,

$$\log\left(\frac{\theta}{1-\theta}\right) = \log k' + y \log C_{\text{inh}} \tag{5}$$

is valid to operate the present adsorption data. $K_{\text{ads}} = K'^{(1/y)}_{\text{ads}}$, K'_{ads} is binding constant, and $1/y$ is the number of the surface active sites occupied by one inhibitor molecule and C_{inh} is the bulk concentration of the inhibitor. The plot of $\log(\theta/1\text{-}\theta)$ against log C_{inh} for the extract is presented in Figure 4, where a straight line relationship was obtained suggesting the validity of this model for the present case. A plot of $\log(\theta/1\text{-}\theta)$ versus $1/T$ at the extract concentration of 400 mg L^{-1} (Figure 5) gave straight line according to the following equation:

$$\log\left(\frac{\theta}{1-\theta}\right) = \log A + \log C_{inh} - \left(\frac{Q}{2.303RT}\right) \quad (6)$$

The Q value was obtained from the slope of this line. The values of $\Delta G°_{ads}$ calculated by Langmuir isotherm and $1/y$, and $\Delta G°_{ads}$ calculated by the kinetic model, and the values of Q are given in Table 3.

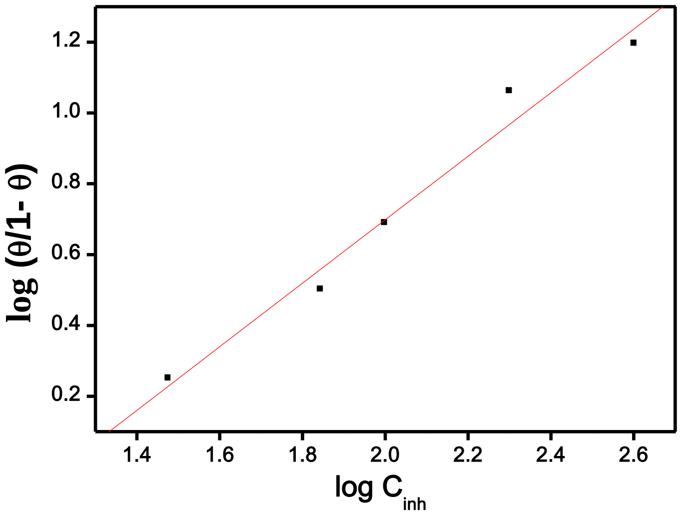

Figure 4. El-Awady et al. [26] model plot for corrosion of aluminium in 0.5 M NaOH containing different concentration of *Bacopa monnieri* stem extract at 308 K.

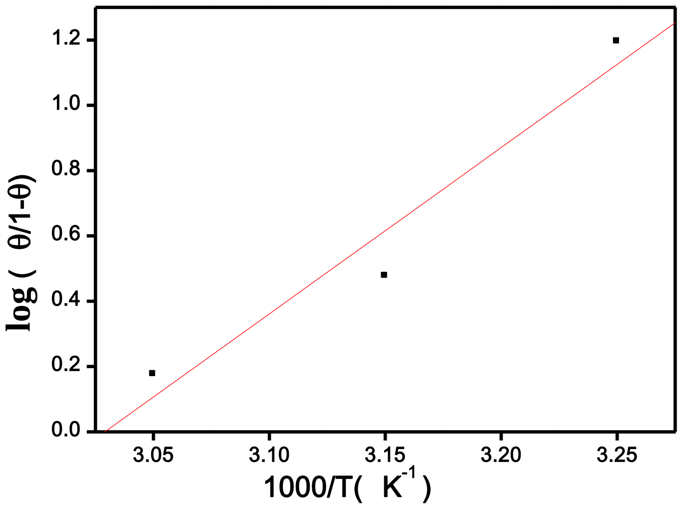

Figure 5. Plot of log (θ/1-θ) versus 1/T for corrosion of aluminium in 0.5 M NaOH solution containing 400 mg L^{-1} *Bacopa monnieri* stem extract.

The negative values of $\Delta G°_{ads}$ suggest that the adsorption of inhibitor molecules onto steel surface is a spontaneous process. The magnitude of heat of adsorption reaches the magnitude of heat of chemical reaction, which is the result of the transference of electron from donating atoms in the phytochemical constituent of the molecules present in the extract to the d-orbital of the iron atom. The negative values of Q show that the process of adsorption is exothermic. It is noted that the value of $1/y$ is more than unity. This suggests that the studied plant extract will form monolayer on the aluminium/solution interface.

Table 3. The values of adsorption constant (K_{ads}), free energy of adsorption ($\Delta G°_{ads}$), number of active sites ($1/y$) and heat of adsorption (Q) for adsorption of compounds present in *Bacopa monnieri* stem extract on aluminium in 0.5 M NaOH in the presence of 400 mg L^{-1} concentrations of the extract

Langmuir isotherm			kinetic model		Q
K_{ads}	$\Delta G°_{ads}$	$1/y$	K'	$\Delta G°_{ads}$	
(mg L^{-1})$^{-1}$	(kJ mg^{-1})		(mg L^{-1})$^{-1}$	(kJ mg^{-1})	(kJ mg^{-1})
0.91	-10.05	4.27	0.064	-3.278	-97.5

3.3. Effect of temperature

The effect of temperature on the rate of dissolution of aluminium in 0.5 M NaOH containing 400 mg L^{-1} of the *Bacopa monnieri* stem extract was tested using weight loss method over a temperature range from 308 to 328 K.

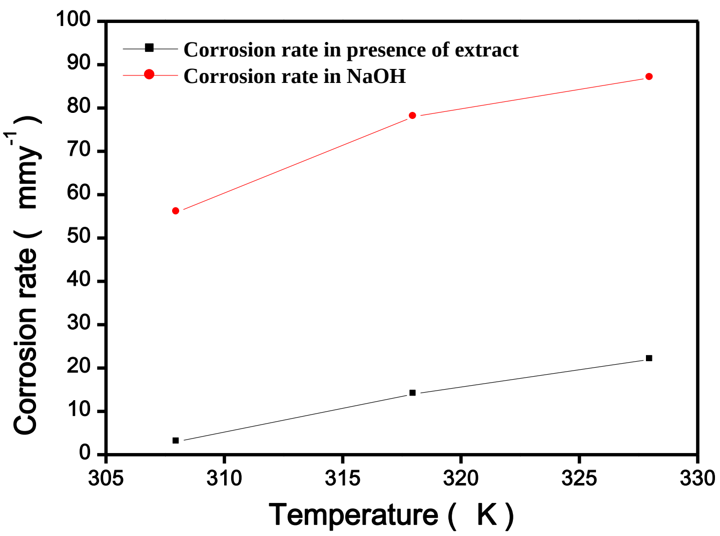

Figure 6. Effect of temperature on dissolution of aluminium in 0.5 M NaOH.

The effect of increasing temperature on the corrosion rate values is given in Figure 6. The results revealed that on increasing temperature there is an increase of corrosion rate in the absence and presence of extract. The increase in corrosion rate in the absence of extract is higher at all temperatures studied, suggests more aggressiveness of free alkaline solution. The increase in corrosion rate with increase in temperature may be probably due to decreasing strength of adsorption (shifting the adsorption-desorption equilibrium toward desorption) and roughening of the electrode surface which results from enhanced corrosion.

The activation energy of the corrosion process was calculated using the Arrhenius equation [30]:

$$C_R = \lambda \exp\left(\frac{-E_a}{RT}\right) \quad (7)$$

where C_R is the corrosion rate, λ is the pre-exponential factor, E_a is the apparent activation energy, R is the universal gas constant, and T is the absolute temperature. The apparent activation energy was calculated by linear regression between ln C_R and $1/T$ (Figure 7).

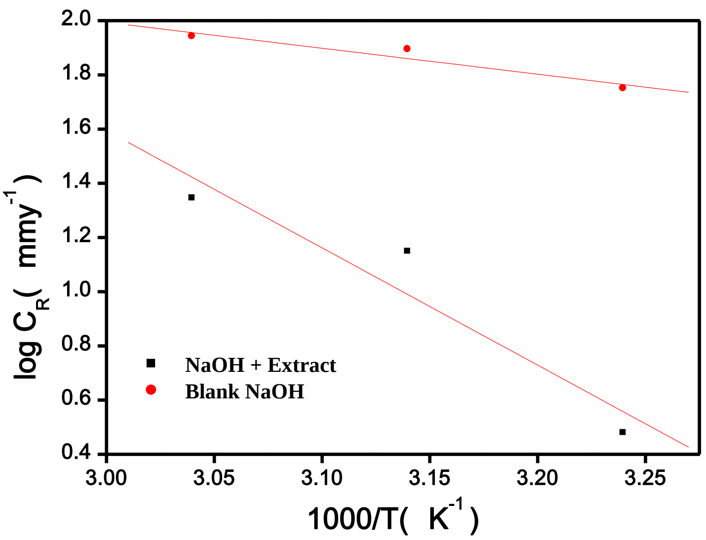

Figure 7. Arrhenius plots of log C_R versus $1/T$ for aluminium in 0.5 M NaOH in the absence and presence of 400 mg L^{-1} *Bacopa monnieri* stem extract.

The value of E_a obtained from the slope of the straight line was found to be 15.9 kJ mg^{-1} and 81.8 kJ mg^{-1} in the absence and presence of 400 mg L^{-1} *Bacopa monnieri* stem extract, respectively. The higher value of E_a in the presence of extract than its absence indicates a strong inhibitive action of the extract by increasing the energy barrier for the corrosion process.

4. CONCLUSION

Bacopa monnieri stem extract was found to inhibit the corrosion of aluminium in 0.5 M NaOH solution and inhibition efficiency increases with increasing extract concentration. At the highest extract concentration of 400 mg L^{-1}, the inhibition efficiency increased markedly to a maximum value of 94%. Potentiodynamic polarization curves proved that the *Bacopa monnieri* stem extract was a mixed-type inhibitor. EIS plots indicated that the charge transfer resistances increase with increasing concentration of the extract. The adsorption model obeys the Langmuir adsorption isotherms.

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