

The Inhibition Effect of Cinnamon Extract on Leaching of Aluminum Cook Wares in NaCl Solutions at Quasi-Cooking Condition

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Abstract

The contribution of cinnamon extract on leaching of aluminum (Al) cook wares was investigated using two aluminum alloys (Indian and Egyptian) and pure Al. The cinnamon (Cin) was extracted by heating the Cin sticks at 90°C in distilled water for an hour to make the 10% stock solution. This study was done in aqueous solutions in presence and absence of 1% NaCl using weight loss at 90°C. Moreover surface study (SEM and EDX) and electrochemical methods (Open Circuit Potential and Tafel plot) were applied. The addition of Cin solutions to 1% NaCl decreased the corrosion rates in weight loss and electrochemical method compared to 1% NaCl solutions which showed an inhibitive property of Cin solution. The inhibition was found to obey the modified Langmuir isotherm with a negative Langmuir ΔG_{ads} indicating the spontaneous nature of adsorption even at 90°C. The EDX surface analysis of the Al surface immersed in Cin + NaCl revealed the composition of the pits formed. From Tafel method, it was found that the corrosion current density of pure Al was more than that of the Egyptian alloy. The apparent activation energy values for Cin, Cin + NaCl and NaCl solution were evaluated and discussed.

Keywords

Cinnamon Extract, Aluminum Alloys, Weight Loss Method, Inhibition, Surface Study, Open Circuit Potential, Tafel Plot

1. Introduction

Aluminum (Al) was regarded a neurotoxin agent because it was associated with some diseases like dialysis encephalopathy and bone disorder due to its accumulation in brain, bones, and liver [1]. Sources of Al entering the

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Cinnamon is one of the most popular spices used by mankind. The genus *Cinnamonum* (family: *Lauraceae*) consists of 250 species of trees and shrubs distributed in Southeast Asia, China and Australia [9]. The dried inner bark of cinnamon contains cinammaldehyde, volatile oil, fixed oil, tannin, resin, proteins, cellulose, pentosans, starch, calcium oxalate and mineral elements. The relative abundance of these constituents varies according to location, age of the tree, climatic condition, harvest time and duration of storage [9].

It is well known that Al dissolution is highly dependent on pH, temperature, and the presence of complexing agents. There is a continuous use of Al cook wares in different countries despite its association with serious health problems. Corrosion control of metals is an important activity of technical, economical, and environmental importance. The use of inhibitors is one of the best options of protecting metals and alloys against corrosion. Some inhibitors retard corrosion by adsorption to form a thin invisible film while others form visible precipitates which coat the metal and protect it from aggressive attack. Other inhibitors, when added to an environment, retard corrosion but do not interact directly with metal surface [9].

The toxicity of inorganic corrosion inhibitors to the environment has prompted the search for green corrosion inhibitors for metals as they are biodegradable and do not contain heavy metals or other toxic compounds. Naturally occurring organic substances and plant extract are widely used as corrosion inhibitors [10]-[19]. Moreover, the electrochemical behavior and corrosion of aluminum alloys in chloride media were widely studied [20]-[22].

The purpose of this paper is to study the leaching behavior of two Al alloys used for Al cook wares (Egyptian and Indian alloys) in aqueous solutions containing cinnamon extract in presence and absence of 1% NaCl at concentrations 1 - 5 w/w at 90°C to imitate real cooking conditions. Weight loss method, surface study and electrochemical methods (Open Circuit Potential and Tafel plots) were applied. For the electrochemical methods pure Aluminum (Al) was used for comparison in addition to the Egyptian and Indian alloys.

2. Materials and Methods

2.1. Materials

The cinnamon sticks used in this study were bought from the local market. Pure Al (99.99%) from Good fellow was used in addition to two kinds of Al cook wares chosen from the local market from Egypt (Eg alloy) and from India (In alloy). NaCl (AR) was purchased from BDH.

2.2. Methods

2.2.1. Extraction Method

The best method which was adopted was heating cinnamon sticks at 90° C in distilled water for an hour to make 10% w/v solution. This method is suitable because it resembles real cooking condition. The cinnamon extract stock solution was used to prepare the following concentrations (1%, 2%, 3%, 4%, 5%). These concentrations are close to those used in real cooking.

2.2.2. Weight Loss Method

To study Al leaching of Al alloys weight loss method (WL) was employed in cinnamon solutions w/without NaCl. The mean of two to three replicate experiments was reported. The two Al cook wares were cut into rectangular specimens of dimensions 2×2.2 cm and 2 mm thickness. The average exposed area was 9.0 ± 0.10 cm². The following procedure was done prior to each experiment: wet polishing with emery paper (400 - 1200) grade, washing with distilled water, then ultrasonic cleaning in acetone for 2 minutes, then air drying. The Al samples were weighed in a sensitive balance then immediately immersed in the hot cinnamon solution for 1 hour.

Ultrasonic cleaner from Cole Palmer was used to clean the Al specimens before corrosion experiments. A

sensitive balance (± 0.0001 g from Metler Toledo) was used to weigh the Al specimens before and after corrosion experiments. After the leaching experiments the Al samples were immersed in a cleaning solution of 2% CrO₃ + 5% H₃PO₄ at 80°C for 10 minutes to remove the reaction products. Finally it was washed with distilled water (DW) and acetone then it was weighed again to determine the weight loss. All experiments were performed in aerated solutions and maintained at 90°C ± 1°C.

2.2.3. Surface Study Method

After the leaching experiments some of the Al samples were kept for surface study. The surface morphology of Al samples was studied using a Scanning Electron Microscope (SEM) from (Joel-JSM-6380). Moreover the Al surface after weight loss was analyzed by Energy Diffraction X-Ray (EDX).

2.2.4. Electrochemical Methods

For the electrochemical studies, two cells were used to estimate the small changes of Al leaching using a galvanostat/potentiostat (from ACM). The first one was a three electrode cell and the working electrode was Pure Al (99.99%) with an exposed surface area of 0.20 cm². The second cell was a sample holder from Radiometer and the working electrode was cut into circular disks from Al cook wares with 1.4 cm diameter and an exposed area of 1.13 cm². The reference electrode for both cells was saturated Calomel electrode (SCE) and the auxiliary electrode was Platinum. All electrochemical experiments were performed in aerated solutions and maintained at $60^{\circ}C \pm 1^{\circ}C$ using a circulating water bath (from Haak). After running open circuit potential for 1 hour, Tafel measurements were done to obtain the corrosion current density by scanning the potential, $E_{ss} \pm 250$ mV at a rate of 1 mV/s.

3. Results

3.1. Weight Loss Method

Corrosion rate law (CR) was used to calculate Al leaching using the following equation:

$$CR = \frac{\Delta W}{A \times t} \tag{1}$$

where Δw is the weight loss of Al sample calculated from subtracting the original sample weight minus the sample weight after the immersion experiments (mg); *A* is the exposed surface area of Al sample (cm²) and *t* is the immersion time (hour). The alloying elements of the two Al alloys used for Al cook wares (Egyptian and Indian alloys) was determined as shown in Table 1.

The percentage inhibition efficiency (*IE*%) and surface coverage (θ) is calculated from applying the following equations:

$$IE\% = I \left(1 - \frac{CR}{CR_{\circ}} \right) I \times 100$$
⁽²⁾

$$\theta = \frac{IE\%}{100} \tag{3}$$

where CR_{\circ} and CR are the corrosion rate in the presence and absence of pure Cin.

The weight loss measurements were performed at 90°C to imitate real cooking conditions. The study was performed in tab water (Tab W) and distilled water (DW). The pH of the solutions in the present study was in the range of 5.4 - 5.5 without NaCl and about 6.3 - 6.5 in presence of NaCl. There was no significant change in pH after the leaching experiments. The study was done in cinnamon solutions w/without NaCl prepared from 10% w/v stock solution: 1%, 2%, 3%, 4%, 5% w/v as shown in **Table 2** for the Eg alloy and the In alloy. From gravimetric measurement (**Table 2**), the following observations are noticed:

• The extent of Al leaching in Cin solutions is much less than Al leaching due to distilled water only which reflects the inhibitive effect of Cin solutions.

• For both alloys, the addition of Cin to NaCl in DW and tab W decreased the Al leaching in all concentrations compared to NaCl only. The percentage of surface coverage of the In alloy is smaller than the Eg alloy. The

Fable 1. Percentage of alumium alloying elements (In. $AI = 95.95$, Eg. $AI = 96.55$).										
%	Ti	Sn	Co	Cu	Cr	Ni	Мо	Fe	Mg	Si
In.	0.19	0.99	0.36	0.21	0.19	0.14	0.09	0.65	0.67	0.56
Eg.	0.92	0.59	0.10	0.12	-	0.20	0.06	0.50	0.46	0.60

 Table 2. Effect of concentration of Cin solutions on leaching of Eg and In alloys from WL method at 90°C.

Calastian	%C	Eg	g alloy		In alloy			
Solution	(w/v)	CR*E4 (g/cm ² ·days)	IE%	θ	CR*E4 (g/cm ² ·days)	IE%	θ	
Dis. W only		3.78			3.78			
Tab W only		8.92			10.50			
NaCl, Dis W	1	7.04			8.35			
NaCl, Tab W	1	10.71			11.39			
	1	1.34			1.44			
	2	3.51			2.34			
Cin (DW)	3	2.95			2.79			
	4	2.41			2.80			
	5	3.17			3.62			
	1	3.07	56.4	0.564	6.94	16.89	0.17	
	2	2.76	60.5	0.605	7.07	15.33	0.15	
Cin + NaCl (DW)	3	2.62	62.8	0.628	6.75	19.16	0.19	
(2.11)	4	2.76	60.8	0.608	6.36	23.83	0.24	
	5	2.75	61.1	0.61	6.28	24.79	0.25	
	1	5.00	53.3	0.533	8.55	24.93	0.25	
	2	6.99	34.7	0.347	9.68	15.01	0.15	
Cin + NaCl (Tap W)	3	7.32	31.7	0.317	9.46	16.94	0.17	
(inh)	4	7.80	27.2	0.272	9.44	17.12	0.17	
	5	5.84	45.5	0.455	9.50	16.59	0.17	

highest *IE*% was for 3% w/v where the surface coverage was 62.8. The surface coverage of 1% - 5% w/v using the Eg alloy range between 0.56 - 0.63. On the other hand, the surface coverage of 1% - 5% w/v using the In alloy range between 0.17 - 0.25.

• From the gravimetric measurement, it is shown that using Tab water (which contained many ions Cu^{2+} , F^- , Mg^{2+}) instead of distilled water, increased the CR (Al leaching). This result may be attributed to the aggressive effect of these ions and agrees with other studies [17] [18]. The protective Al_2O_3 oxide layer has amphoteric nature which dissolves in acidic and alkaline solutions. Although this protective film has low solubility in neutral medium, the aggressive effect of Chloride ions is well documented [19]-[22]. Unlike the cardamom solutions which increased the Al leaching in the same concentration range [19]; the Cin solutions decreased the CR compared to 1% NaCl solutions. This shows the large difference between the aggressive constituents of cardamom (twelve times that of cinnamon) and the inhibitive constituents of cinnamon extract.

3.2. Adsorption Mechanism

Different adsorption isotherms were tested in order to find the best one which are:

1) Freundlich and Frumkin isotherms did not fit our data.

2) Langmuir adsorption isotherm gave a good fit to our data ($R^2 = 0.996$). Langmuir isotherm may be formulated as:

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{4}$$

where C is the concentration of inhibitor (ppm), θ is the surface coverage and K is the equilibrium constant of the adsorption process.

From the present study, it was found in **Table 2** that the degree of surface coverage θ increased slightly with increasing concentration of Cin in the concentration range of 1% - 5% w/v. The Al leaching of Cin solutions in DW and Tab W of both alloys at 90°C was less than the Al leaching in DW only. A graph of θ with the change in Cin concentration showed that the curve fits the nonlinear Langmuir adsorption isotherm with a maximum around 62.8% surface coverage at 3% w/v as shown in **Figure 1**. A good fit (R² = 0.994) was obtained for the linear Langmuir plot.

Although there was a good fit to the Langmuir graph as shown in **Figure 1**, it was noticed that the slope was 1.58 which is more than one as suggested by Langmuir Equation (4). Thus another isotherm should be used which is the modified Langmuir equation [23] as shown in Equation (8).

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \tag{5}$$

The value of $K_{ads} = 10.97$ L/g was calculated from the reciprocal of the intercept with the value of n = 1.58. The free-energy of adsorption ($\Delta G_{\circ ads}$) was calculated according to the equation:

$$\Delta G_{\circ_{ads}} = -RT \ln \left(55.5 K_{ads} \right) \tag{6}$$

where 55.5 is the water concentration, R is the universal gas constant, and T is the temperature in Kelvin (363K).

$$\Delta G_{\circ_{ads}} = -8.314 \times 363 \ln (55.5 \times 10.97) = -19.35 \text{ kJ}.$$

From the adsorption isotherm, the negative value of $\Delta G_{\circ_{ads}}$ indicates that the adsorption process of the cinnamon constituent is spontaneous while adherence to the modified Langmuir adsorption isotherm indicates physisorption with mono coverage. The value being of the order less than 20 kJ/mol indicates that cinnamon was physically adsorbed on the Al surface [10]-[16] [23]. It is assumed that the organic inhibitors establish their inhibition action via the adsorption onto the metal surface. The adsorption process is affected by the chemical structures of the inhibitors, the nature of the metal solution, pH and temperature [12]-[14] [23]-[25]. The chemical constituents of Cinnamon are mainly *Cinammaldehyde* (79.8%) [9]. It was reported that *Cinammaldehyde* had an inhibitive effect on iron corrosion of chemisorptive nature [24]. Moreover the presence of Eugenol and some alcohols were reported to play an inhibitive effect as stated by Chaieb *et al.* [12]. We believe that the inhibitive effect of Cin solution is due to the combined effect of all of the constituents of the Cinnamon extract.



Figure 1. Langmuir isotherm for the Eg. Alloy from Weight loss in Dis water for Cin + NaCl. Nonlinear form (left) and linear form (right).

Physisorption involves electrostatic forces between the ionic charges at the metal/interface; this type of adsorption is stable only at relatively low temperatures. On the other hand, chemisorption involves charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type bond which is more stable at higher temperatures. Chemisorption has much stronger adsorption energy than physical adsorption [23]. The present findings and the findings of Zucchi *et al.* [24] about Cin in the temperature range 40°C -90°C made us postulate that the adsorption of Cin aqueous extract on Al surface may include both Physisorption and Chemisorption nature.

From the surface study of the, using 5% Cin and theIn alloy, the presence of the white crystals in **Figure 2** is an indication of the reaction of Cin constituents and Aluminum. The surface showed large dark are as after immersion in 5% Cin + NaCl solution for one hour, as shown in **Figure 3**. This result is compatible with **Table 2**. that when using the In alloy, the CR of 5% Cin equals 3.62×10^{-4} g/cm²·days and the CR of 5% Cin + NaCl equals 6.28×10^{-4} g/cm²·days with 24.7% *IE*%. The difference in CR of the two alloys in **Table 2**, is attributed to the difference in the alloying elements. It is noticed from the alloying elements that the Eg alloy contains 0.19% Chromium while the In alloy contains only 0.02% Chromium. Also the Eg alloy contains more Si and Ti than the In alloy. Copper, Chromium and Titanium are known to increase the corrosion resistance of metals. It is hard to attribute the corrosion resistance of the Eg alloy to these alloying elements because there are other alloying elements in the In alloy which are not present in the Eg alloy and vice versa. It is the total effect of all the alloying elements that make the difference.

3.3. Surface Study

The In alloy was taken as an example to investigate the effect of Cin solution because the CR is higher than the Eg alloy. After WL experiments for 5% Cin solution, the In alloy sample was washed with distilled water only and dried. The surface showed a few white depositions after immersion in 5% Cin solution for 1 hour, as shown in **Figure 2**. The addition of NaCl showed that these depositions turned into dark precipitate which covered the Al surface as shown in **Figure 3**. Analysis of the precipitate by Energy-dispersive X-ray spectroscopy (EDX) showed that this precipitate contained mainly 29.4% Carbon + 23.55% Oxygen or about 53% of the organic Cin constituents in addition to 44.46% Al; the rest are Na and Cl and the alloying elements.

3.4. Electrochemical Methods

3.4.1. Open Circuit Potential (OCP) Method

To detect any small changes in Al leaching, pure Al was used in addition to the two Al alloys. Two methods were applied: Open Circuit Potential Method followed by Tafel. All experiments were performed in aerated solutions at $60^{\circ}C \pm 1^{\circ}C$. As an example, the effect of change of temperature on OCP of pure Al for 5% Cin solutions w/without NaCl is shown in Figure 4 and Figure 5.

The values of E_{ss} decreased with increasing temperatures with and without NaCl. The effect of changing the temperature from 10°C - 60°C on OCP was studied only for pure Al at 5% Cin solutions w/without NaCl as



Figure 2. SEM of In alloy after immersion in 5% Cin for 1 hour.



Figure 3. SEM and EDX of the In alloy after immersion in 5% Cin + NaCl solution for 1 hour.



Figure 4. Effect of change of temperature on OCP of pure Al for 5% Cin solutions (left) without NaCl, and (right) with NaCl.



shown in **Table 3**. The values of E_{ss} decreased after addition of chloride ions and decreased with increasing temperature. The electrochemical behavior of Al in presence of NaCl and the effect of temperature using the following equation was studied [22]:

$$E_{ss} = a - b(T) \tag{7}$$

When applying Equation (5) for pure Al at 5% Cin + NaCl, it gave a linear relation for temperature ($R^2 = 0.992$) with a negative slope indicating thinning of the pre-immersion oxide film with increasing temperature as shown in Figure 5.

From the electrochemical methods, the Eg alloy showed an increase in the values of E_{ss} at 60°C which indicated strengthening of the pre immersion Al oxide layer [25]. The change of the potential with time from OCP method reflected the effect of attack of the constituents of the solution. The resulting E_{ss} is a mixed potential of all the anodic and cathodic reactions. It is known that E_{ss} depends on O₂ concentration, composition of Al, pH and temperature [25]. The values of E_{ss} for 5% - 10% Cin solutions were almost constant at 710 - 715 mV. For the In alloy it showed the same trend as the pure Al. On the contrary, the Eg alloy showed an increase in the values of E_{ss} at 60°C which indicated strengthening of the pre immersion Al oxide layer [25]. The values of E_{ss} decreased after addition of chloride ions and decreased with increasing temperature which indicated thinning of the pre-immersion oxide film. This phenomenon resembled the behaviour found for 8-hydroxy quinoline by Garrigues *et al.* [26]. The pH of the present study was 6.40 ± 0.20 in presence of NaCl solutions which is close to the neutral range. Mazhar *et al.*, explained the competition between OH⁻ and Cl⁻ in neutral solutions which is explained in the following equation [27]:

$$Al^{3+}$$
 (in crystal lattice of the oxide) + $2Cl^{-} + OH^{-} \rightleftharpoons (AlOH)_{2}Cl_{2}^{-}$ (8)

The use of aerated solutions in the present study means that the cathodic reaction of oxygen reduction was applicable (Jones, 1995). Assuming that this was the cathodic reaction with the possible anodic reaction:

$$Al + 3Cl^{-} \rightleftharpoons AlCl_{3} + 3e^{-}$$
(9)

The resulting mixed potential is close to E_{ss} obtained in the present study. The attack of Al₂O₃ may occur through voids and defected sites. A previous model by McCafferty considered that the penetration of Cl⁻ ions can occur by film dissolution or by migration through the oxygen vacancies [21]. These defected sights are more prone to attack at high temperatures. Moreover using labeled chloride ions Kolice had shown that Cl⁻ ions are incorporated to a distance of 10 - 15 Å from the interphase of oxide/solution [20] chloride ions were adsorbed chemically on Al oxide film and reacted as partners in Al dissolution by forming oxy chloride ionic complexes.

3.4.2. Tafel Plots Method

Tafel method was performed to measure the current density (I_{corr}) after OCP measurements reached E_{ss} . To study the effect of concentration, the temperature was kept constant at 60°C. The results are depicted in Figure 6. The following results were obtained as shown in Table 4:

1) For pure Al, the I_{corr} values of Cin solution w/without NaCl are about 1.99 μ A/cm². The constant value of



Figure 6. Tafel graphs of the two Al alloys (Eg left and In right) at 60°C with time at different Cin concentrations, 2 = 2%, 5 = 5%, 7 = 7%, 10 = 10%.

Table 3. Effect of c	hange of temperature o	n OCP of pure	Al for 5% Cin so	lutions w/without NaCL
Lable C. Blicet of c	mange of temperature o	n oor or pure	/ I II IOI 5/0 OIII 50	rations w/ writerout r tuch.

<i>T</i> (°C)	10	25	45	60
E_{ss} (mV) Cin	-674	-687	-779	-728
E_{ss} (mV) Cin + NaCl	-723	-805	-893	-965

Table 4	 Electrochemical 	parameters	of Al	alloys	for Cin	solutions	at different	concentration	from	Tafel 1	me-
thod.											

Alloy	$T(^{\circ}C)$	%C (w/v)	B _a (mV/dec)	$-B_{c}$ (mV/dec)	$I_{\rm corr}$ (μ A/cm ²)
		2	106	73	1.99
Duno A1	60	5	97	79	1.96
Pure Al	00	7	97	79	1.93
		10	91	61	1.99
		2	86	75	0.75
To A1	60	5	84	67	1.04
III AI		7	97	107	1.25
		10	100	88	1.97
		2	93	85	0.73
Ec. 41	60	5	107	65	0.85
Eg Al	60	7	83	88	1.08
		10	128	77	1.31

 I_{corr} regardless of the increase in concentration indicates that the effective parameter in pure Al dissolution is the temperature.

For the Eg Alloy, the values of I_{corr} are less than that of the In alloy. The values of B_a increased slightly with increasing concentration while for B_c values there were no regular trend. For the In alloy the values of I_{corr} increased with increasing concentration. The trend was similar to the trend for E_{ss} . The values of B_a increased but there were no obvious trend for values of B_c .

To study the effect of increasing the temperature on Tafel method, the electrochemical parameters were recorded for 1% NaCl pure Al at 5% Cin solutions w/without NaCl at different temperatures as shown in Table 5. The following observations may be drawn:

• For NaCl solutions the I_{corr} values were larger than their values for Cin w/without NaCl at the same temperature. This result agrees with the aggressive role of Cl⁻ ions in Al dissolution in neutral solutions.

Sol.	T (°C)	B _a (mV/dec)	-B _c (mV/dec)	$I_{\rm corr}$ (μ A/cm ²)	% <i>IE</i>	CR (mm/day)			
	10	19	104	0.22		0.933			
1%	25	22	84	0.64		2.71			
NaCl	45	17	256	0.91		3.86			
	60	21	236	2.94		12.47			
	10	79	72	0.13		0.55			
5%	25	75	62	0.23		0.98			
Cin only	45	77	85	0.39		1.66			
	60	97	79	1.02		4.34			
	10	70	67	0.14	36	0.61			
5%	25	67	52	0.37	42	1.54			
Cin + NaCl	45	67	67	0.40	56	1.68			
	60	67	75	1.14	61	4.81			

 Table 5. Electrochemical parameters of pure Al for 5% Cin solutions w/without NaCl at different temperatures from Tafel method:

• For 5% Cin solution, the values of I_{corr} increased with increasing temperature. There was a slight increase in B_a values but there were no obvious trend for B_c .

• For 5% Cin + NaCl, the values of I_{corr} increased with increasing temperature. There were no obvious trend for the values of B_a and B_c . The values of I_{corr} of Cin + NaCl were comparable to the values of I_{corr} of C in solutions for each degree of temperatures. The *EI*% values range between 36% - 61% which is in accordance with WL results.

To gain more insight about adsorption, the parameters of Tafel method were used to calculate some thermodynamic parameters for 1% NaCl and Cin w/without NaCl using the following Arrhenius equation:

$$k = A e^{-Ea/RT}$$
(10)

Using **Table 5**, and applying Equation (8) to calculate E_a of pure Al in Cin solutions w/without NaCl gave straight lines. The apparent activation energy values were calculated by plotting ln I_{corr} versus 1/T.

From the slopes of the graphs, the value of E_a was calculated and the results are listed in Table 6.

Evaluating the thermodynamic parameters was done using the transition state equation,

$$C_{R} = \frac{RT}{Nh} \exp\left(\frac{\Delta S^{*}}{R}\right) \exp\left(-\frac{\Delta H^{*}}{RT}\right)$$
(11)

where h is Planck's constant, N is Avogadro's number, ΔS is the entropy of the activation, and ΔH is the entropy of activation.

Drawing ln CR/T vs. 1/T gave a straight line with a slope of $-\Delta H_0/R$ and an intercept of $(\ln R/Nh) + \Delta S_0/R)$ as shown in Figure 7 for Cin w/without NaCl solution. The calculated parameters at 5% concentrations of the inhibitor are collected in Table 6.

From Tafel method, the values of apparent activation energy (E_a) , ΔS and ΔH show the following trend:

NaCl > Cin > Cin + NaCl

The values of E_a for Cin solution was 32.45 kJ/mol. The values for E_a were 36.45 and 28.44 kJ/mol for NaCl and Cin + NaCl solutions respectively. The low value of E_a of Cin solution w/without NaCl compared to NaCl indicates the ease of adsorption of Cin constituents on Al surface. The decrease in E_a after adding Cin to NaCl may indicate a competition between Cin constituents to be adsorbed and Chloride ions to dissolve Al as E_a of Cin + NaCl is smaller than E_a of Cin alone. This is in agreement with the trend of CR from WL results that Cin is a good inhibitor of Al dissolution in presence of NaCl.

From **Table 6**, the trend for the thermodynamic values (ΔH , ΔS) and E_a is:

$$NaCl > Cin > Cin + NaCl$$

Table 6. Apparent E_a and thermodynamic parameters of pure Al for Cin solutions w/without NaCl.									
Sol.	рН	E_{ac} (kJ/mol)	ΔH (kJ/mol)	ΔS (J/K.mol)					
Cin	5.00 ± 0.25	32.52	28.03	-151.1					
NaCl	6.40 ± 0.20	36.55	34.00	-124.5					
Cin + NaCl	6.40 ± 0.20	28.44	25.84	-158.0					



The decrease in E_a after adding Cin to NaCl may indicated a competition between Cin constituents to be adsorbed on Al surface as E_a of Cin + NaCl is smaller than E_a of Cin alone. This is in agreement with the trend of CR from WL results that Cin is a good inhibitor of Al dissolution in presence of NaCl. This result agrees with the trend of E_a of Obot *et al.* in 2011 [17] and also with a previous study by Al Juhaiman *et al.* about Polyvinyl Pyrrolidone inhibition of carbon steel in neutral medium containing NaCl [28]. However, some researchers reported a large increase of E_a for the blank + inhibitor compared to the blank although the CR of the metal decreased in presence of the inhibitor [11] [12] [15]. From the present study, the value of E_a for Cin solution shown in Table 6 was 32.45 kJ/mol. The values for E_a were 36.45 and 28.44 kJ/mol for NaCl and Cin + NaCl solutions respectively. The low value of E_a of Cin solution w/without NaCl compared to NaCl indicated the ease of adsorption of Cin constituents on Al surface. It was surprising that the value of E_a of Cin + NaCl is less than the E_a of Cin alone. It is a well-known fact that metal dissolution is pH dependent as shown from Pourbaix diagrams. Thus we think that the pH difference between the two solutions and Kolice et al. findings in 2001 may explain this ambiguity. The oxide film thickness on Al surface is strongly dependent upon the solution pH. Using XRF, Kolice *et al.* found "a slight thickness variation in the passive region of aluminum (4 < Ph < 10) which represented a film thickness of 40 - 45 Å" [20]. The pH of the present study was 6.40 ± 0.20 in presence of NaCl and 5.00 ± 0.25 in presence of Cin solution. From Table 2, Cin solution has inhibitive properties depicted in the lower CR compared to Cin + NaCl and NaCl solutions. Thus we may postulate that due to the aggressive role of chloride ions, the thickness of the Al oxide film was less thicker for Cin + NaCl compared to Cin solutions which needed a lower E_a value as found in Table 6.

The difference in ΔH and ΔS values between Cin and Cin + NaCl solutions may be explained by the difference in pH using the same reasoning discussed for E_a values. It is known that the positive sign of the enthalpies reflect the endothermic nature of the metal dissolution process. It is noticed that ΔH of Cin + NaCl solution is less than ΔH of NaCl. That means that the adsorption process in presence of the inhibitor needs less energy compared to the blank which makes Al dissolution less favored and agrees with the results in WL and Tafel methods.

The elevated temperature had an adverse effect on adsorption process, as the intermolecular and intramolecular forces were weakened [10] [15]. For the change of entropy, **Table 6** shows that ΔS of NaCl solution is larger than that of Cin w/without NaCl which means the increase in disorder in NaCl solutions than in presence of the inhibitor. The decrease in the value of ΔS for Cin w/without NaCl compared to NaCl only is logical as the inhibitor contains many constituents which may be bound to the Al surface by physical bonds as revealed from obeying the modified Langmuir adsorption isotherm which decrease the randomness in the system (increase the order). Although the present trend agree with some studies [17] [28] [29]; but the findings disagree with other

studies as well [11] [12] [15] [30].

4. Conclusions

From WL result, the Al leaching of Cin solutions in DW and Tab W of both the In and Eg alloys at 90°C was less than the Al leaching without Cin solutions. The addition of Cin solutions in DW or Tab W to NaCl decreased the Al leaching in all concentrations for both Al alloys compared to NaCl solution alone. Comparing the Al dissolution in pure NaCl solution with Cin + NaCl showed that Cin solution has inhibitive effect using both alloys but the *IE*% was higher in the Eg alloy. The results of Surface Study are in agreement with WL result.

From Tafel method it was found that current density at 60°C using Al alloys showed the following trend:

Pure Al > In Al > Eg Al

This indicates that some of the alloying elements in the Eg alloy played an inhibitive role in decreasing Al leaching. From Tafel method, the values of E_a , ΔS and ΔH show the following trend:

NaCl > Cin > Cin + NaCl

The solutions of Cin + NaCl were less than those of NaCl only which are in agreement with WL results that Cin is a good inhibitor of Al dissolution. In conclusion using cinnamon in cooking may reduce the extent of Al leaching.

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