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Ginseng Root: A new Efficient and Effective Eco-Friendly Corrosion Inhibitor for Aluminium Alloy of type AA 1060 in Hydrochloric Acid Solution

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We report for the first time the inhibitive action of the root of ginseng on aluminium corrosion in HCl solution using weight loss method at 30-60 °C. Results obtained showed that ginseng root functioned as an effective and excellent inhibitor in the acid medium. Corrosion rate increased both in the absence and presence of inhibitor with increase in temperature. Corrosion rate was also found to decrease in the presence of inhibitor compared to the free acid solution. Inhibition efficiency increases with increase in concentration of the inhibitor but decreases with increase in temperature reaching a maximum of 93.1% at 30 °C at 50 % v/v concentration of ginseng. Addition of iodide ions to the root extracts of ginseng enhances the inhibition efficiency considerably and the effect is more pronounced at higher temperatures. The adsorption of extract components onto the aluminium surface was found to be a spontaneous process and to follow the Freundlich adsorption isotherm. The free energies, enthalpy and entropy for the adsorption process as well as the energy of activation, enthalpy of activation and entropy of activation for the dissolution process were determined and discussed. A mechanism of physical adsorption of the root components on the surface of the metal is proposed for the inhibition behaviour.

Keywords: Ginseng, aluminium, corrosion inhibition, adsorption isotherm, thermodynamics

1. INTRODUCTION

Acid solutions are commonly used in the chemical industry to remove the scales from the metallic surfaces. The addition of inhibitors secures the metal against an acid attack effectively. The applicability of organic compounds as corrosion inhibitors for metals in acidic media has been recognized for a long time [1-5]. The existing data show that most organic inhibitors act by adsorption on the metal surface. The adsorption of inhibitors occurs through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, triple bonds or aromatic rings. These compounds which are adsorbed on the metallic surface block the active corrosion sites.

Though many synthetic organic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and the environment. The safety and environmental issues of corrosion inhibitors arisen in industries has always been a global concern. These inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system viz, kidney, liver, or disturb a biochemical process and enzyme system at some site in the body [6]. The toxicity may manifest either during the synthesis of the compound or during its application.

Recent awareness of the corrosion inhibiting abilities of tannins, alkaloids, organic and amino acids as well as organic dyes [7-11] has resulted in sustained interest on the corrosion inhibiting properties of natural products of plant origin. Such investigation is of much importance because in addition to being environmentally friendly and ecologically acceptable, plants products are inexpensive, readily available and renewable sources of materials. The use of natural products as corrosion inhibitors have been widely reported by several authors [12-20]. Among plant materials tested in our laboratory include *Dacroydes edulis* [21], *Pachylobus edulis* [22], *Vigna unguiculata* [23], *Gum Arabic* [24-26], *and Raphia hookeri* [27].

Ginseng refers to species within *Panax*, a genus of 11 species of slow-growing perennial plants with fleshy roots. Ginseng; the root and rhizome of *Panax ginseng* C.A. Meyer (*Araliaceae*) have been used as a medicinal herb for more than 2000 years in oriental countries including China, Korea, and Japan [28]. *Panax ginseng* has been known to have pharmacological activities over a wide spectrum of effectiveness such as anti-fatigue and anti-stress and promotion of longevity [29]. The herb has been shown to contain glycoside, saponin, phenolic acids, alkaloids and lignin [30]. Other components include large amounts of starch and gum, some resin, a very small amount of volatile oil, and panacon but the most active ingredient of *Panax ginseng* is ginsenosides with backbone structure similar to that of sterol, especially cholesterol. Recently more than 25 dammarane-type tetracyclic triterpernoid saponins have been isolated from ginseng, the root and rhizome of *Panax ginseng* [28]. As a continuation of our current interest on eco-friendly corrosion inhibitors, we report for the first time the inhibition action of ginseng root on the acid corrosion of aluminium using the weight loss method at 30-60 ^{o}C. The effect of iodide addition is also reported.

2. EXPERIMENTAL PART

2.1. Materials

The aluminium sheets of the type AA 1060 and purity 98.8% were obtained from Sky Aluminium Ltd, Uyo, Nigeria and of the same composition as those reported previously [22-24]. Each sheet was 0.14 cm in thickness and was mechanically press-cut into coupons of dimension 5cm x 4cm. These coupons were used as cut without further polishing. They were however degreased in absolute ethanol, dried in acetone, and stored in moisture-free desiccators prior to use [23]. All reagents used were BDH analytical grade.

2.2. Preparation of the root extracts of ginseng

The procedure for the preparation of the root extracts is similar to that reported recently by Okafor et al. [19]. Ginseng roots were collected from Yaoundé, Cameroon. They were dried in an N53C-Genlab Laboratory oven at 50 ^{o}C, and ground to powder form. Ten gram of the powder was digested in 1 L of 1 M HCl solution. The resultant solution was kept for 24 h, filtered and stored. From the stock solution, the root extracts test solutions were prepared at concentrations of 50, 40 and 10 %v/v. The effect of iodide additive was studied by combining 5.0 mM of KI salt with different concentrations of the root extracts.

2.3. Weight loss method

In the weight loss measurements, aluminium coupons in triplicate were totally immersed in 200 mL of 1 M HCl solutions devoid of and containing various concentrations of the studied inhibitor (Ginseng root extracts). The metal specimens were withdrawn from the test solutions after 4 h at 30-60 ^{o}C and the weight loss determined [31, 32]. The weight loss was taken as the difference in weight of the specimens before and after immersion determined using LP 120 digital balance with sensitivity of ± 1 mg. The tests were performed in duplicate to guarantee the reliability of the results and the mean value of the weight loss is reported. Weight loss values obtained allowed calculation of the mean corrosion rate in mg cm^{-2} h^{-1}.

The corrosion rate (W) was computed using the expression [26]:

$$W = \frac{m_1 - m_2}{At} \qquad (1)$$

Where m_1 and m_2 are the weight losses (mg) before and after immersion in the test solutions, A is the area of the specimens (cm^2) and t is the exposure time (h).

The inhibition efficiency (% I) was computed using the equation [26]:

$$\%I = \frac{W_{blank} - W_{inh}}{W_{blank}} x100 \qquad (2)$$

where W_{blank} and W_{inh} are the corrosion rates in the absence and presence of the inhibitor respectively.

3. RESULTS AND DISCUSSION

3.1. Corrosion rates and inhibition efficiency

A general mechanism for the dissolution of Al metal would be similar to that earlier reported [33]:

$$Al_{(s)} + H_2O \leftrightarrow AlOH_{ads} + H^+ + e \quad (3)$$
$$AlOH_{ads} + 5H_2O + H^+ \leftrightarrow Al^{3+} . 6H_2O + 2e \quad (4)$$
$$Al^{3+} + H_2O \leftrightarrow [AlOH]^{2+} + H^+ \quad (5)$$
$$[AlOH]^{2+} + X^- \leftrightarrow [AlOHX]^+ \quad (6)$$

The controlling step in the metal dissolution is the complexation reaction between the hydrated cation and the anion present Eq. (5). In the presence of chloride ions the reaction will correspond to:

$$[AlOH]^{2+} + Cl^- \rightarrow [AlOHCl]^+ \quad (7)$$

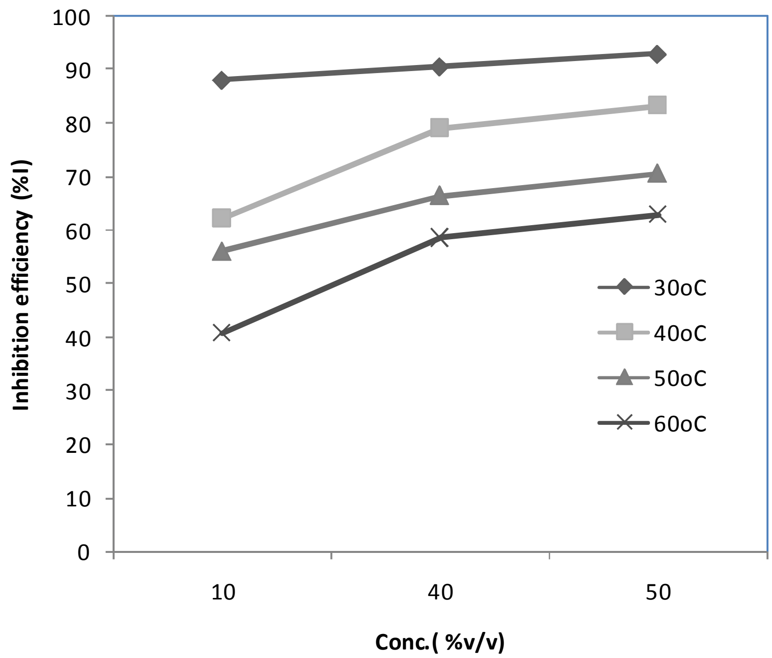
The soluble complex ion formed increases the metal dissolution rate which depends on the chloride concentration.

Table 1. Calculated values of corrosion rate (mg cm^{-2} h^{-1}) and inhibition efficiency (%I) for aluminium corrosion in 1M HCl in the absence and presence of various concentrations of ginseng extracts, 5.0 mM KI and ginseng extracts + 5.0 mM KI at different temperatures using weight loss.

System / Concentrations	Corrosion rate (mg cm^{-2} h^{-1})				Inhibition efficiency (%I)			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
Blank	7.35	29.60	31.80	33.90	-	-	-	-
5.0 mM KI	3.01	17.00	20.10	20.40	59.0	42.6	36.8	39.8
10% v/v	0.87	11.10	13.90	20.00	88.2	62.5	56.3	41.0
40% v/v	0.68	6.10	10.60	14.00	90.7	79.4	66.7	58.7
50% v/v	0.51	4.90	9.30	12.50	93.1	83.4	70.8	63.1
10% v/v + KI	0.60	10.00	12.30	18.10	91.8	66.2	61.3	46.6
40% v/v + KI	0.36	4.90	9.40	11.90	95.1	83.4	70.4	64.9
50% v/v + KI	0.30	3.40	7.90	10.90	96.0	88.5	75.2	67.8

The values of percentage inhibition efficiency and corrosion rate obtained from weight loss method at different concentrations of the ginseng extracts and ginseng extracts in combination with KI at 30 - 60 °C are summarized in Table 1, and the variation of inhibition efficiency with concentrations of ginseng extracts and ginseng extracts in combination with KI are shown in Fig.1. Inspection of the data in the table reveals that the addition of ginseng extract decreases the corrosion rate of aluminium. This result indicates the inhibitive effect of the added extract on aluminium corrosion in the acidic solution. From Fig. 1, it is observed that the inhibition efficiency increases as the concentration of added extract is increased. The observed inhibition action of the ginseng extract could be attributed to the adsorption of its components on aluminium surface. The formed layer, of the adsorbed molecules, isolates the metal surface from the aggressive medium leading to decreasing the corrosion rate. The chemical components of the extract of ginseng roots was identified and determined as reported in literature [28-30]. As earlier stated in the introductory remarks, ginseng root is a complex mixture of glycoside, saponin, phenolic acids, alkaloids and lignin. Other components include large amounts of starch and gum, some resin, a very small amount of volatile oil, panacon, dammarane-type tetracyclic triterpernoid saponins and ginsenosides (or panaxosides), which implies that it contains heteroatom such as oxygen and nitrogen in its molecules. The corrosion inhibition of aluminium may be attributed to adsorption of ginseng extract components through these atoms, which are regarded as centers of adsorption onto the metals surface. Owing to the complex chemical composition of the extract, it is quite difficult to assign the inhibitive effect to a particular constituent. Further investigation using surface analytical techniques will enable the characterization of the active materials in the adsorbed layer and assist in identifying the most active ingredients.

(a)



(b)

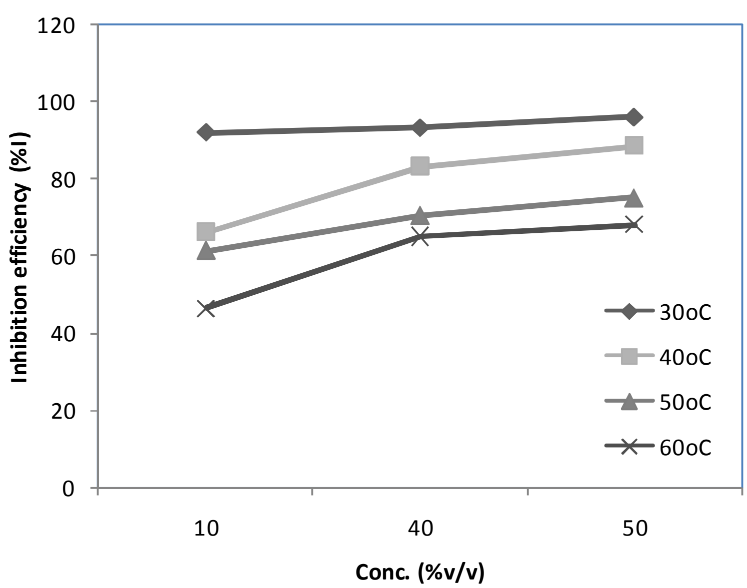


Figure 1. Plots of inhibition efficiency against concentration for (a) Ginseng extracts and (b) Ginseng extracts + KI mixtures at 30-60 ^{o}C .

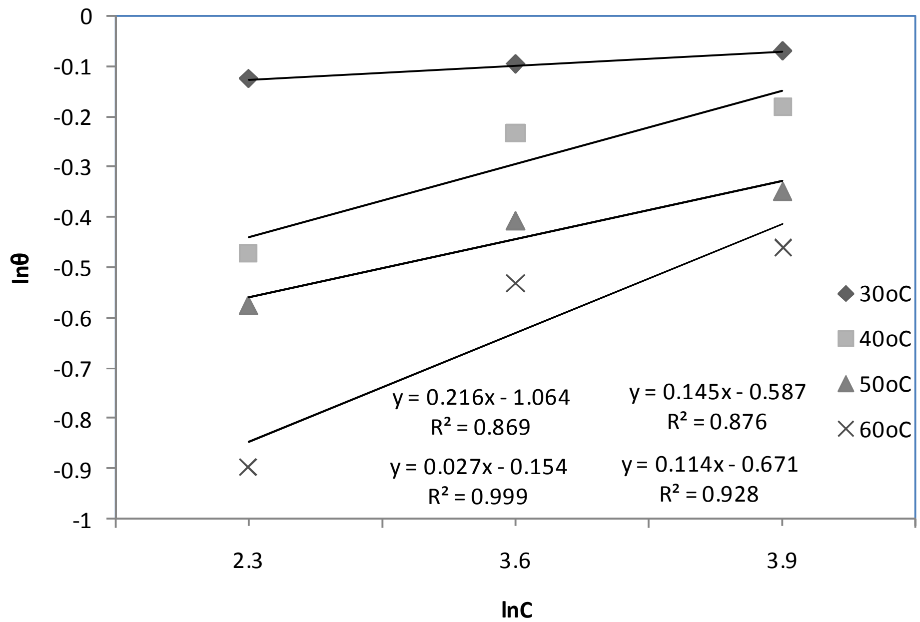


Figure 2. Freundlich adsorption isotherm for aluminium corrosion in 1M HCl at 30 -60°C

Table 2. Adsorption parameters for the adsorption of ginseng extracts in 1M HCl on aluminium at different temperatures.

Temperature (°C)	K_{ads}	n	R^2	ΔG^o_{ads} (kJ/mol)
30	0.86	0.027	0.999	-9.73
40	0.56	0.145	0.876	-8.92
50	0.51	0.114	0.928	-8.98
60	0.35	0.216	0.869	-8.17

3.2. Adsorption isotherm and thermodynamic studies

The efficacy of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface, which consists of the replacement of water molecules at the corroding interface [26]. The adsorption of the inhibitor is influenced by the nature and the charge of the metal, the chemical nature of the inhibitor, distribution of the charge in the molecule, and the type of electrolyte [34]. Basic information dealing with the interaction between the inhibitor molecule and metal surface can be provided by adsorption isotherm. The degree of surface coverage values for different concentrations of ginseng extracts from the weight loss measurements obtained from (θ = % I/100), assuming a direct relationship between surface coverage and inhibition efficiency has been adapted to determine the adsorption characteristics of ginseng extracts in 1 M HCl solution. To ascertain the nature of adsorption, the surface coverage values for ginseng extracts for 30 – 60 °C were fitted into different adsorption isotherm models and correlation coefficients (R^2) were used to determine best fit which was obtained with the Freundlich adsorption isotherm. The observed changes in θ are shown in Fig. 2 as a function of concentration of ginseng extracts in 1M HCl at 30 - 60 ^oC. The linear plots obtained (R^2 > 0.86) suggest that the experimental data fit the Freundlich adsorption isotherm which is given by [34]:

$$\theta = KC^n \quad (8)$$

Where θ < n< 1, or

$$\ln\theta = \ln K + n\ln C \quad (9)$$

C is the concentration of ginseng extracts and K the equilibrium constant for adsorption is related to the thermodynamic parameters for adsorption shown in Table 2 according to the following equations [35]:

$$K = \frac{1}{55.5}\exp\left[\frac{-\Delta G^o_{ads}}{RT}\right] \quad (10)$$

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \quad (11)$$

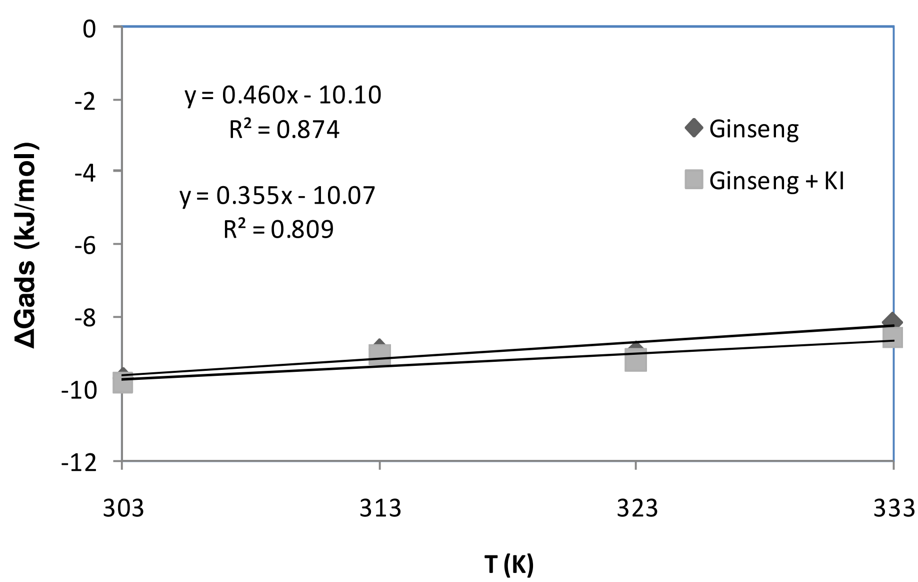


Figure 3. Plot of free energy of adsorption versus temperature

The negative values of ΔG^o_{ads} suggest that the adsorption of ginseng extracts onto aluminium surface is a spontaneous process and the adsorbed layer is stable. Usually the adsorption free energy involved in a physisorption process is less than -25 kJ/mol [33]. The plot of ΔG^o_{ads} versus T was used to determine the enthalpy ΔH^o_{ads}, and the entropy ΔS^o_{ads} for the adsorption process using the basic thermodynamic equation (Eq. 11) (Fig. 3). The values of ΔH^o_{ads} obtained were -10.10 kJ/mol and -10.07 kJ/mol for the ginseng extracts and ginseng extracts + KI respectively. Whereas the values of ΔS^o_{ads} were -0.46 J/mol/K and -0.36 J/mol/K for the ginseng extracts and ginseng extracts + KI respectively. The negative values of ΔH^o_{ads} and ΔS^o_{ads} obtained show that the adsorption is exothermic with an ordered phenomenon. Similar report has been documented [35].

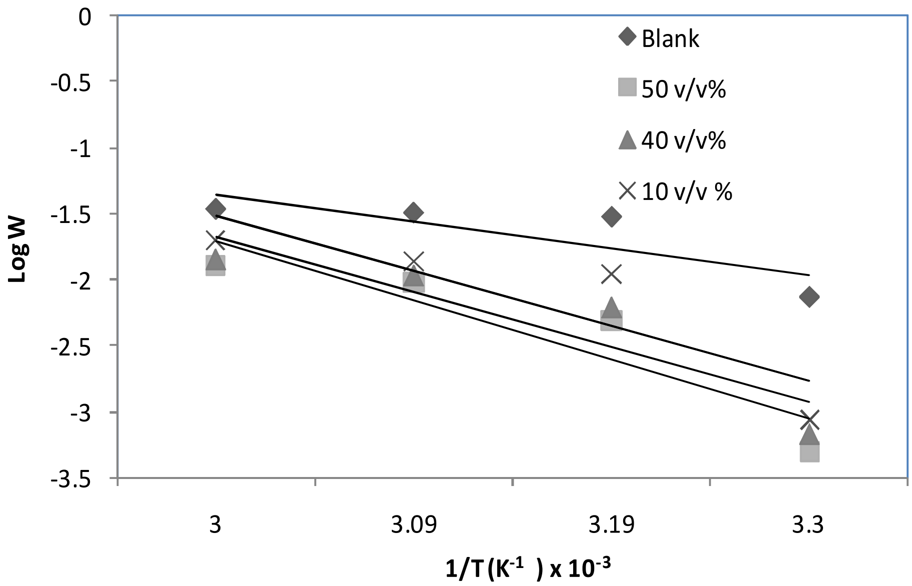


Figure 4. Arrhenius plot for aluminium corrosion in 1M HCl in the absence and presence of various concentrations of ginseng extracts

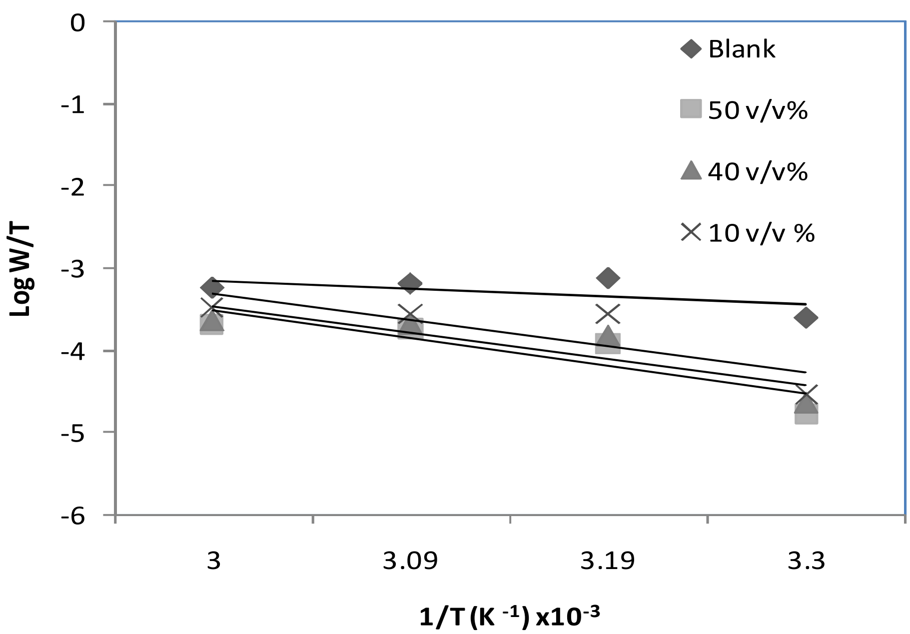


Figure 5. Transition State plot for aluminium corrosion in 1M HCl in the absence and presence of various concentrations of ginseng extracts

Table 3. Activation parameters of aluminium dissolution in 1M HCl in the absence and presence of different concentrations of ginseng extracts.

Systems/Concentrations (g/l)	E_a (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (J/mol/K)
Blank	3.80	1.95	-58.20
10% v/v	8.00	6.08	-57.17
40% v/v	8.00	6.06	-60.23
50% v/v	8.50	6.58	-60.52

3.3. Effect of Temperature

Temperature study was carried out to get more information about the performance of ginseng extract and the nature of adsorption and thereafter to evaluate the activation processes. For this purpose, weight-loss measurements are determined in the range of temperature 30-60 ^{o}C, in the absence and presence of inhibitor at various concentrations during 4 h of immersion. The corresponding data are shown in Table 1. It is clearly seen from the table that increase in temperature leads to an increase in the corrosion rate with or without inhibitor

To calculate activation thermodynamic parameters of the corrosion reaction such as the activation energy E_a, the enthalpy ΔH^o_{ads} and the entropy ΔS^o_{ads} of activation, Arrhenius Eq. (12) and its alternative formulation called transition state Eq. (13) were employed:

$$\log W = \frac{-E_a}{2.303RT} + \log A \quad (12)$$

$$W = \left(\frac{RT}{Nh}\right)\exp\left(\frac{\Delta S^o}{R}\right)\exp\left(\frac{-\Delta H^o}{RT}\right) \quad (13)$$

where W is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature, A is the frequency factor, h is the Planck's constant and N is the Avogadro's number.

The activation energy E_a is calculated from the slope of the plots of Log W versus 1/T (Fig.4). Plots of Log (W/T) as a function of 1/T (Fig. 5) give a straight line with a slope of ($-\Delta H^o$/ 2.303R) and an intercept of (logR/Nh + ΔS^o/2.303R) from which the values of ΔH^o and ΔS^o were calculated, and listed in Table 3. Inspection of Table 3 reveals that the presence of ginseng root extracts increases the values of E_a as compared to the blank (without ginseng extracts) indicating physical adsorption of the extracts on the metal surface [21-23]. The positive values of ΔH^o reflect the endothermic nature of the aluminium dissolution process in the 1 M HCl. The values of ΔS^o in the presence and absence of the extracts are large and negative implying that the activation complex in the rate determining step represents association rather than dissociation. This is an indication that a decrease in disorder takes place on going from reactants to the activated complex [36].

3.4. Synergism considerations

The upgrading of inhibition efficiency of organic compounds in the presence of some anions, particularly halide ions, have been reported by some authors and was ascribed to a synergistic effect [37-39]. It is thought that the anions are able to improve adsorption of the organic cations in solution by forming intermediate bridges between the metal surface and the positive end of the organic inhibitor. Corrosion inhibition synergism thus results from increased surface coverage arising from ion-pair interactions between the organic cations and the anions.

The synergistic parameters were calculated using the relationship initially given by Aramaki and Hackerman and reported elsewhere [40]:

$$S_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \qquad (14)$$

where I_{1+2}= (I_1 + I_2); I_1 = inhibition efficiency of the iodide; I_2 = inhibition efficiency of ginseng exteacts; I'= measured inhibition efficiency for the ginseng extracts in combination with iodide ions. S_1 approaches 1 when no interaction between the inhibitor compounds exists, while $S_1 > 1$ points to a synergistic effect. In the case $S_1 < 1$, the antagonistic interaction prevails, which may be attributed to competitive adsorption. Values of S_1 for different concentrations of ginseng extracts in combination with iodide ion are given in Table 4. S_1 values given in Table 4 are more than unity, thereby suggesting that the enhanced inhibition efficiency caused by the addition of iodide ions to ginseng extract is only due to synergistic effect and the effect is more pronounced at higher temperatures (Table 1). Thus, it can be suggested that iodide ion (I^-) is initially adsorbed on the metal surface, ginseng components in the form of cation are then adsorbed by the coulombic attraction on the metal surface, where the iodide ions are already chemisorbed and thus suppresses the self-corrosion rate by the stabilization of the adsorbed anion and by the increase in surface coverage [33].

Table 4. Synergism parameters (S_1) for the different concentrations of ginseng extracts.

Concentrations of Ginseng extracts (% v/v)	S_1
10	1.61
40	1.53
50	1.50

4. CONCLUSIONS

The following conclusions can be drawn from this study:

1. Extracts from the root of ginseng acts as an effective and efficient inhibitor for aluminium corrosion in 1 M HCl.

2. Corrosion rate increases with increase in temperature both in the absence and presence of the inhibitor and decreases in the presence of the extracts.

3. Inhibition efficiency of the ginseng extracts increases with increase in concentration of the inhibitor but decreases with increase in temperature studied. In addition, there was an enhancement of the inhibition efficiency of the ginseng extracts especially at higher temperatures on the addition of KI.

4. The adsorption of the extracts onto Al surface was found to obey Freundlich isotherm from the fit of the experimental data at all the concentrations and temperatures studied.

5. Phenomenon of physical adsorption is proposed from the kinetic and thermodynamic parameters evaluated.

References

1. A. El-Sayed, *J. Appl. Electrochem.* 27 (1997) 193.
2. A.Y. El-Etre, *Corros.Sci*. 40 (1998) 1845.
3. A. Chetouani, B. Hammouti, T. Benhadda, M. Daoudi, *Appl. Surf. Sci*. 249 (2005) 375.
4. M. Bouklah, B. Hammouti, M. Lagrenee, F. Bentiss, *Corros Sci*. 48 (2006) 2831.
5. S.A. Umoren, I.B. Obot, I.O. Igwe, *The open Corrosion .J.* 2 (2009) 1.
6. P.B. Raja, M.G. Sethuraman, *Matt. Lett*. 62 (2008) 113.
7. A.A. El-Hosary, R.M. Saleh, *Progress in the Understanding and Prevention of Corrosion*, Institute of Materials, London, 2 (1993) 911.
8. S. Martinez, I. Stern, *J. Appl. Electrochem*. 31 (2001) 973.
9. E.E. Oguzie, *Mater. Chem. Phys*. 87 (2004) 212.
10. K. Barouni, L. Bazzi, R. Salghi, M. Mihit, B. hammouti, A. Albourine, S. El Issami, *Matt. Lett*. 62 (2008) 3325.
11. E.E. Ebenso, H. Alemu, S.A. Umoren, I.B. Obot, *Int. J. Electrochem. Sci.* 3(2008) 1325.
12. R.M. Saleh, A.A. Ismail, A.H. El Hosary, *Br. Corros, J*. 17 (1982) 131.
13. A.Y. El-Etre, M. Abdallah, *Corros Sci*. 42 (2000) 731.
14. K.S. Parikh, K.J. Joshi, *Trans. SAEST* 39 (2004) 29.
15. Chetouani, B. Hammouti, *Bull. Electrochem*. 19 (2003) 23.
16. O. Avwiri, F.O. Igho, *Matt. Lett*. 57 (2003) 3705.
17. A.Y. El-Etre, *J. Colloid & Interface Sci*. 314 (2007) 578.
18. E.E. Oguzie, *Portugaliae Electrochimica Acta* 26 (2008) 303.
19. P.C Okafor, M.E. Ikpi, I.E. Uwah, E.E. Ebenso, U, J. Ekpe, S.A. Umoren, *Corros. Sci.* 50 (2008) 2310.
20. P.C. Okafor, E.E. Ebenso, *Pigm. Res. Technol*. 35 (2007) 134.
21. S.A. Umoren, I.B. Obot, E.E. Ebenso, N.O. Obi-Egbedi, *Portugaliae Electrochimica Acta* 26 (2008) 199.
22. S.A. Umoren, I.B. Obot, E.E. Ebenso, *E-J Chem*. 5(2) (2008) 355.
23. S.A. Umoren, I.B.Obot, L.E. Akpabio, S.E. Etuk, *Pigment & Resin Technol*. 37(2) (2008) 98.
24. S.A Umoren, I.B. Obot, E.E. Ebenso, P.C. Okafor, O. Ogbobe, E.E. Oguzie, *Anti-Corros. Methods and Mater.* 53(5) (2006) 277.
25. S.A Umoren, O. Ogbobe, E.E. Ebenso, *Trans. SAEST* 41 (2006) 74.
26. S.A. Umoren, *Cellulose* 15 (2008) 751.
27. S.A. Umoren, I.B.Obot, N.O. Obi-Egbedi, *Mater. Sci.* 44(1) (2009) 274.
28. S. Shibata, *J. Korean Med. Sci.* 16 (2001) 28.
29. W.I. Hwang, *Korean J. Ginseng Sci*. 17 (1993) 52.
30. I.I. Brekman, I.V. Dardymov, *Ann. Rev. Pharmacol.* 9 (1967) 419.

31. S.A. Umoren, E.E. Ebenso, *Mater. Chem & Phys.* 106 (2007) 393.
32. L.R. Chauhan, G. Gunasekaran, *Corros. Sci*. 49 (2007) 1143.
33. I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, *Corros. Sci.* 51 (2009) 276.
34. E.E. Oguzie, *Corros. Sci*, 49 (2007) 1527.
35. M. Bouklah, N. Benchat, B. Hammouti, A. Aouniti, S. Kertit, *Matt. Lett*. 60 (2006) 1901.
36. M. Abdallah, E.A. Helal, A.S. Founda, *Corros. Sci.* 48 (2006) 1639.
37. S.A. Umoren, O. Ogbobe, E.E. Ebenso, *Bull. Electrochem.* 22(4) (2006) 155.
38. S.A. Umoren, O. Ogbobe, E.E. Ebenso, U.J. Ekpe, *Pigment Resin Technol.* 35 (3) (2006) 284.
39. E.E. Oguzie, E.E. Ebenso, *Pigment Resin Technol*. 35 (1). (2006) 30.
40. M. Bouklah, B. Hammouti, A Aouniti, M. Benkaddour, A. Bouyanzer, *Appl. Surf. Sci*. 252 (2006) 6236.