

Synergistic Influence of Gum Arabic and Iodide Ion on the Corrosion Inhibition of Aluminium in Alkaline Medium

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Abstract

The effect of iodide ion on the corrosion inhibition of aluminium in NaOH in the presence of Gum Arabic (GA) was studied using weight loss and hydrogen evolution techniques at 303 and 313 K. The results obtained showed that inhibition efficiency increased with increasing GA concentration. The inhibiting action of GA was considerably enhanced by the addition of KI. The adsorption of KI, GA alone and in combination with iodide ion was found to obey Temkin adsorption isotherm. The inhibiting effect of GA and (GA+KI) increased with increase in temperature of the corrosion medium, indicating chemical adsorption mechanism. Synergism parameter evaluated was found to be greater than unity for the different concentrations of GA, which shows that the enhanced inhibition of GA caused by the addition of iodide ion is due to synergistic effect. It could be deduced from the thermodynamic parameters obtained that adsorption of GA alone and in combination with KI onto the metal surface is spontaneous.

Keywords: Gum Arabic, iodide ion, aluminium, corrosion inhibition, synergism, alkaline.

Introduction

Aluminium and its alloys find extensive applications in industries where they are used in a variety of aggressive and corrosive service environments. The passive metal generally corrodes by processes related to the properties of a protective surface oxide film. The unprotected metal surface sites become exposed to the aqueous corrosive medium after the breakdown of the oxide film, which subsequently leads to a sequence of electrochemical reactions. Such processes at the bared metal surface are uniquely dependent on the environment and usually

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result in soluble complex formation that increases the rate of metal dissolution [1, 2].

An important method to protect metal surfaces deployed in service in aqueous corrosive environments involves addition of suitable inhibitors to retard the corrosion reaction and reduce the corrosion rate. Organic compounds containing nitrogen, sulphur or oxygen have been found adequate for this purpose and their inhibiting action is widely attributed to their adsorption onto the metal/solution interface [3, 4]. Most corrosion inhibitors are known for their specificity of action. However, the combination of inhibitors is more likely to provide multiple effects required for effective corrosion inhibition. Interestingly, previous studies [5 -15] have shown that addition of halide ions to acid/ alkaline solution containing any organic compound has been found to result in synergistic effect, thereby inhibiting corrosion. The presence of halide ions in solution has been found to stabilize the adsorption of some organic cations leading to improved inhibition efficiency. It has been shown that inhibiting effect for the halides increases in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$ which seems to indicate that the radii and electronegativity of the halogen atoms may have an important role to play. The iodide ion is more predisposed to adsorption than bromide ion and the chloride ion.

Synergistic effects of iodide ion in combination with some organic compounds have been reported. For instance, Zhang *et al.* [16] have shown that synergistic effect exists when 2-mercapto benzimidazole is combined together with iodide ions in the prevention of corrosion of copper in aerated sulphuric acid. Wu *et al.* [17] and Schweinsberg [18] have also shown that benzotriazole and 1-[11, 21-dicarboxyl ethyl]-benzotriazole had synergistic effect with KI on the dissolution of copper in aerated H_2SO_4 . Also reported is the synergistic influence of poly (4-vinyl pyridine) and potassium iodide on the inhibition of corrosion of mild steel in HCl [19]. A series of reports from our laboratory has also highlighted the synergistic effect of iodide ion on the corrosion inhibition of metals by polyacrylamide [20], polyvinyl pyrrolidone [21, 22], 2, 3- diaamionaphthalene [23] and alizarine yellow GG dye [24]. However, most of these investigations were carried out in acidic environment. Studies involving organic inhibitors and synergistic effect of halide ions generally, and iodide ions in particular in alkaline medium are rather scanty [25, 26]. A recent contribution in this regard in our laboratory involves the investigation of effect of halide ions on the corrosion inhibition of aluminium in NaOH using synthetic polymers, namely polyvinyl alcohol (PVA) and polyethylene glycol (PEG) [27, 28].

However, no reports exist, to the best of our knowledge, on the effect of iodide ion on the corrosion of aluminium in alkaline environment using naturally occurring polymers. Therefore, in the present investigation, the synergistic effect of iodide ion on the performance of gum Arabic (a natural occurring polymer), which is considered as non-toxic, inexpensive, environmentally friendly, biodegradable and a renewable source of material as a corrosion inhibitor of aluminium in alkaline (NaOH) medium, is reported using weight loss and hydrogen evolution methods at 303 and 313 K.

Experimental

Aluminium sheet used in the study was obtained from the System Metal Industries Limited, Calabar, Nigeria. The composition, purity and preparation of the metal are as previously reported [29, 30]. The concentration of the inhibitor (GA) (BDH supplies chemicals, England) prepared and used in the study was 0.1 g/L to 0.5 g/L. The concentration of KI (BDH Laboratory Chemicals, England) prepared and used was 0.01-0.1 M. However, 0.05 M KI was used for the synergistic study. The concentration of NaOH (BDH Laboratory supplies, England) used was 0.1 M. The chemicals used were all AnalaR grades and were used as received without further purification. All solutions were prepared using deionised water. The procedure followed for weight loss and hydrogen evolution measurements was similar to that previously reported [5 - 7, 13, 14]. The corrosion rate (mpy), inhibition efficiency (%I) and degree of surface coverage (θ) from the weight loss data were evaluated using equations previously reported [13,14]. The inhibition efficiency (%I) was calculated for the hydrogen evolution technique using previously reported equation [31, 32].

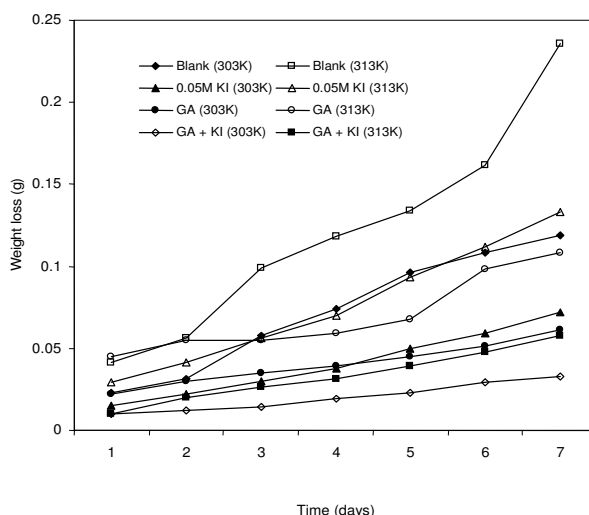


Figure 1. Variation of weight loss (g) with time (days) for aluminium corrosion in 0.1 M NaOH in the absence and presence of KI, GA and GA + KI at 303 and 313 K

Results and discussion

Effect of inhibitor/iodide ion concentration on inhibition efficiency from the two methods

Fig. 1 shows the variation of weight loss (g) with time (days) for the dissolution of aluminium in 0.1 M NaOH devoid of and containing 0.05 M KI, the highest concentration of inhibitor (GA) studied (0.5 g/L) and GA in combination with 0.05 M KI at 303 and 313 K. Inspection of the figure clearly reveals that the weight loss of aluminium in alkaline environment decreased in the presence of KI and GA compared with the blank solution. Further reduction in weight loss was also observed on the addition of KI to GA.

Table 1. Calculated values of corrosion rate (mpy), inhibition efficiency (%I) and surface coverage (θ) for aluminium corrosion in 0.1 M NaOH at 303 and 313 K.

Systems/concentrations	Corrosion rate (mpy) $\times 10^{-3}$		Inhibition efficiency (%I)		Surface coverage (θ)	
	303 K	313 K	303 K	313 K	303 K	313 K
Blank	10.0	20.0	-	-	-	-
0.05 M KI	7.0	13.0	39.5	43.6	0.40	0.44
0.5 g/L GA	5.0	11.5	48.7	54.2	0.49	0.54
0.4 g/L GA	6.0	11.0	43.7	44.9	0.44	0.45
0.3 g/L GA	7.0	13.0	34.5	39.8	0.35	0.40
0.2 g/L GA	8.0	14.0	30.3	34.7	0.30	0.35
0.1 g/L GA	9.0	15.0	15.1	27.1	0.15	0.27
0.5 g/L GA + 0.05 M KI	3.0	5.0	70.6	75.4	0.71	0.75
0.4 g/L GA + 0.05 M KI	3.5	6.0	69.0	72.5	0.69	0.73
0.3 g/L GA + 0.05 M KI	4.0	6.0	62.2	70.8	0.62	0.71
0.2 g/L GA + 0.05 M KI	5.0	7.0	58.0	66.5	0.58	0.67
0.1 g/L GA + 0.05 M KI	5.0	8.0	53.0	62.7	0.53	0.63

Calculated values of corrosion rate (mpy), inhibition efficiency (%I) and degree of surface coverage (θ) from the weight loss measurement are presented in Table 1. Results presented in the table show that corrosion rate decreases in the presence of KI and GA compared to the blank alone. Further decrease in the corrosion rate was recorded when GA was combined with KI, and corrosion rate increased with increase in temperature. The reduction in weight loss and decrease in the corrosion rate of aluminium in the presence of GA alone and in combination with KI is an indication that GA in NaOH solution inhibits the corrosion of aluminium and that the extent of corrosion inhibition is a function of the concentration of GA.

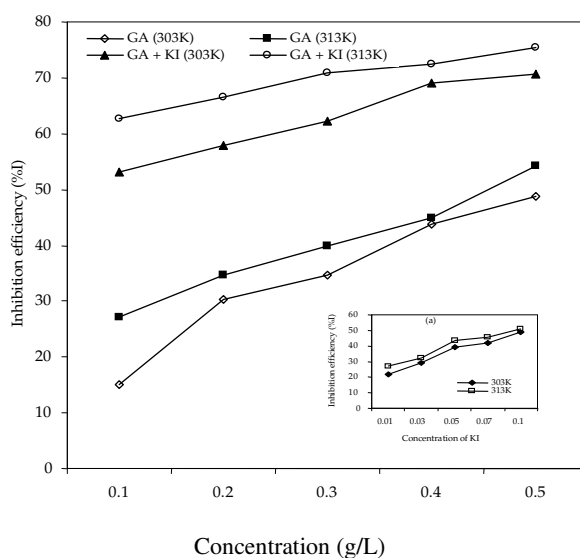
**Figure 2.** Plot of inhibition efficiency (%I) against concentration for GA and GA + KI at 303 and 313 K; (a) inset shows plot of %I against KI concentration at 303 and 313 K.

Fig. 2 shows the plot of inhibition efficiency against different concentrations of GA and different concentrations of GA in combination with 0.05 M KI for aluminium in 0.1 M NaOH at 303 and 313 K. From Table 1 and Fig. 1, it is evident that inhibition efficiency increases with increase in concentration of GA and temperature. The highest inhibition efficiency was obtained with 0.5 g/L GA and at 313 K. This concentration was therefore used to evaluate the effect of KI. Inspection of Table 1 further reveals that inhibition efficiency of GA synergistically increased on addition of KI. Inset of Fig. 2 shows the plot of inhibition efficiency against different concentrations of KI. From this figure, it is seen that inhibition efficiency increases with increase in concentration of KI and temperature.

The volume of hydrogen evolved during the corrosion reaction of aluminium in 1 M NaOH in the presence of GA, KI and GA+ KI at 303 and 313 K as a function of reaction time is shown in Fig. 3. Inspection of this figure reveals that the volume of hydrogen evolved was lower in the presence of GA and KI compared to the blank. A further reduction in the volume of hydrogen evolved was also observed on addition of KI to GA. It was also noticed that the volume of hydrogen evolved increases with time of exposure and temperature rise. The decrease in the volume of hydrogen evolved in the presence of the inhibitors is an indication of an excellent ability of GA to inhibit the corrosion of aluminium in the alkaline solution. The values of inhibition efficiency obtained for 0.05 M KI, different concentrations of GA alone and GA in combination with 0.05 M KI at 313 K are presented in Table 2. The values are comparable to some extent with those obtained using the weight loss method.

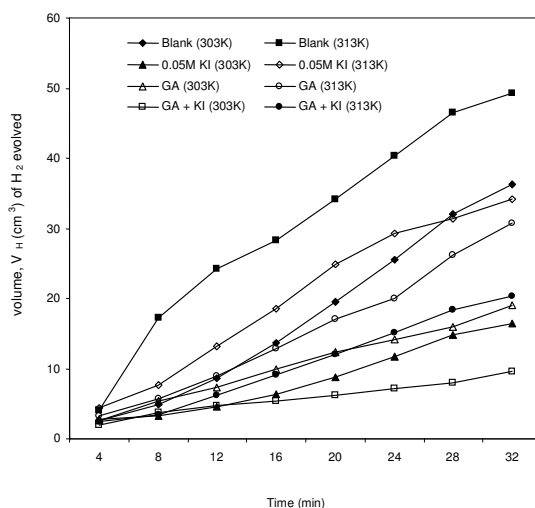


Figure 3. Variation of volume of H_2 (cm^3) evolved with time (min) for aluminium corrosion in 1 M NaOH in the absence and presence of KI, GA and GA + KI at 303 and 313 K.

The two methods used in this study clearly reveal that the inhibition efficiency and degree of surface coverage increased with increasing GA concentration and with increase in temperature. The increase in inhibition efficiency with increase

in temperature is suggestive of chemical adsorption mechanism. Similar observations have been reported elsewhere [33, 34]. GA is a branched, neutral or slightly acidic, complex polysaccharide obtained as a mixed calcium, magnesium and potassium salt. The backbone consists of 1, 3-linked β -D-galactopyranosyl units. The side chains are composed of two to five 1, 3 – linked β - D – galactopyranosyl units joined to the main chain by 1, 6 – linkages. Both the side and main chains contain units of α - L – arabinofuranosyl, α - L – rhamnosyl, β - D – glucuronopyranosyl and 4 – O – methyl - β - D – glucuronopyranosyl [35]. It also contains glucoproteins. The adsorption of these compounds through their oxygen and nitrogen atoms on the aluminium surface creates a barrier for mass and charge transfers. Consequently, the metal is protected from the aggressive anions of the alkali. The corrosion inhibition of aluminium may be attributed to adsorption of GA components through these atoms which are regarded as active centres for adsorption onto the metal surface. Owing to the complex chemical composition of GA, 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.

Table 2. Comparison of inhibition efficiency obtained from weight loss and hydrogen evolution methods at 313 K.

Systems/concentration	Inhibition efficiency (%I)	
	Weight loss method	Hydrogen evolution method
0.05 M KI	43.6	39.9
0.5 g/L GA	54.2	50.0
0.4 g/L GA	44.9	47.0
0.3 g/L GA	39.8	44.0
0.2 g/L GA	34.7	35.0
0.1 g/L GA	27.1	41.0
0.5 g/L GA + 0.05 M KI	75.4	74.0
0.4 g/L GA + 0.05 M KI	72.5	69.0
0.3 g/L GA + 0.05 M KI	70.8	61.0
0.2 g/L GA + 0.05 M KI	66.5	55.0
0.1 g/L GA + 0.05 M KI	62.7	46.9

The addition of KI improved the inhibition efficiency significantly. The synergistic effect between GA and KI may be due to interactions between chemisorbed iodide ions and organic polycations of GA. The stabilization of the adsorbed polycations on the aluminium surface, which may be exhibited by electrostatic interactions with iodide ions, leads to higher coverage and hence greater corrosion inhibition.

Adsorption studies

Results obtained in this study clearly revealed that GA inhibits the corrosion of aluminium in alkaline environment and the inhibition process is greatly enhanced in the presence of iodide ion. One possible mechanism of inhibition of corrosion

of metals by organic compounds that has been widely studied is the adsorption of the inhibitor, which blocks the metal surface thereby preventing the occurrence of the corrosion process. Organic molecules are adsorbed onto metal surface following either chemisorption or physisorption mechanism. For chemisorption, inhibition efficiency increases with increase in temperature, whereas a decrease in inhibition efficiency with rise in temperature is suggestive of physical adsorption mechanism.

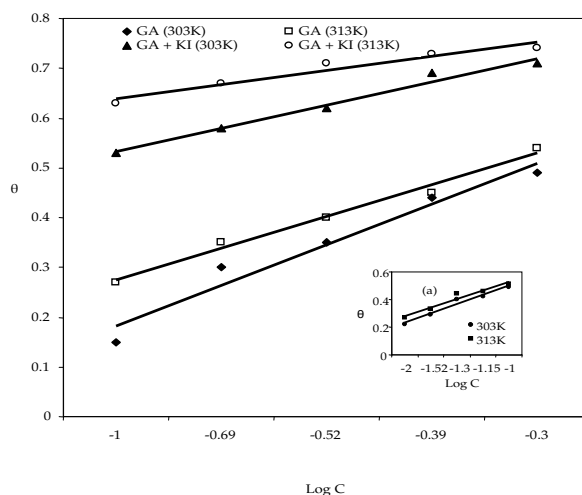


Figure 4. Plot of θ against $\log C$ for GA and GA + KI at 303 and 313 K; (a) inset shows plot of θ against $\log C$ for KI at 303 and 313 K.

In this study, inhibition efficiency is found to increase with increase in temperature for both GA and GA in combination with KI, which is suggestive of chemical adsorption.

The degree of surface coverage (θ) obtained from the weight loss measurements have been applied to different adsorption isotherm equations, and correlation coefficients were used to determine the best fitted isotherm. By far, best result was obtained for Temkin adsorption isotherm. Fig. 4 shows the plot of θ against $\log C$ for GA and GA – KI combination at 303 and 313 K while the inset of Fig. 4 shows the plot of θ against $\log C$ for KI at 303 and 313 K. Linear plots were obtained indicating that the experimental data obtained from the weight loss measurements fit Temkin's adsorption isotherm. Temkin's isotherm characterizes chemisorption of uncharged molecules on a heterogeneous surface and is given by the equation:

$$\exp(-2a\theta) = KC \quad (1)$$

where 'a' is a molecules interaction parameter, θ is the degree of surface coverage, 'C' is the concentration of the inhibitor, and K is the equilibrium constant of adsorption process and is related to the free energy of adsorption, ΔG_{ads}^0 by the equation:

$$k = \frac{1}{55.5} \exp \left[\frac{-\Delta G_{ads}^o}{RT} \right] \quad (2)$$

where 55.5 are the moles of water in mol dm⁻³.

Table 3. Some parameters of the linear regression from Temkin's adsorption isotherms.

Inhibitor	Temperature (K)	ΔG (kJmol ⁻¹)	Temkin		
			a	K	R ²
KI	303	-24.21	-3.24	269	0.97
	313	-31.96	-3.56	3890	0.95
GA	303	-17.10	-2.65	16	0.96
	313	-30.09	-3.39	1901	0.99
GA+KI	303	-69.67	-4.62	2.08 x 10 ¹⁰	0.98
	313	-141.42	-7.75	7.20 x 10 ²¹	0.94

The linear correlation coefficients, molecular interaction parameters 'a', and the adsorption coefficient deduced from Temkin's adsorption isotherm plot (Fig. 4) are listed in Table 3. From this table it is seen that the linear correlation coefficient is quite good and an evidence to show that the experimental data obtained and hence adsorption of KI, GA and GA in combination with KI followed Temkin's adsorption isotherm. In all cases, the values of 'a' are negative, showing that repulsion exists in the adsorption layer [36].

Kinetic/thermodynamic studies

The plot of logarithm of final weight loss (W_f) against time (t) (not shown) with respect to aluminium in NaOH solution in the absence and presence of 0.05 M KI, GA and GA in combination with KI, gave straight lines, which confirms a first order kinetics. The values of rate constant evaluated from the slope of the plots are presented in Table 4. From this table it is seen that the rate constant increases with increase in temperature. It was also found that the rate constant decreased in the presence of GA and GA + KI compared to the blank. Also, an increase in rate constant with decrease in GA concentration (especially at 313 K) was observed. The values of half-life, $t_{1/2}$, were calculated using the equation:

$$t_{1/2} = \frac{0.693}{k} \quad (3)$$

The results are given in Table 4, which revealed that half-life increased in the presence of the inhibitors compared to the blank. It decreases with increase in temperature and decrease with decrease in GA concentration.

Table 4. Calculated values of activation energy E_a (kJmol^{-1}), heat of adsorption Q_{ads} (kJmol^{-1}), rate constant K (hr^{-1}), and Half-life $t_{1/2}$ (hr), for different systems.

Systems/concentration	E_a (kJmol^{-1})	Q_{ads} (kJmol^{-1})	Rate constant (hr^{-1})		Half-life (hr)	
	303-313 K	303-313 K	303 K	313 K	303 K	313 K
Blank	54.9	-	1.09	1.99	0.64	0.35
0.05 M KI	48.8	12.9	0.50	1.11	1.39	0.62
0.5 g/L GA	50.83	15.8	0.41	0.69	1.69	1.00
0.4 g/L GA	47.9	3.2	0.39	0.95	1.78	0.73
0.3 g/L GA	48.8	16.8	0.51	1.05	1.36	0.66
0.2 g/L GA	44.3	18.0	0.49	1.25	1.41	0.55
0.1 g/L GA	40.6	58.4	0.68	1.27	1.02	0.55
0.5 g/L GA + 0.05 M KI	40.6	16.0	0.29	0.51	2.39	1.36
0.4 g/L GA + 0.05 M KI	42.5	15.3	0.31	0.54	2.24	1.28
0.3 g/L GA + 0.05 M KI	32.1	32.0	0.34	0.46	2.04	1.51
0.2 g/L GA + 0.05 M KI	26.6	30.4	0.32	0.45	2.17	1.54
0.1 g/L GA + 0.05 M KI	37.2	32.5	0.35	0.49	1.98	1.41

The activation energy, E_a for aluminium corrosion in 0.1 M NaOH in the absence and present of GA and GA + KI mixtures was calculated from the Arrhenius equation.

$$\log \frac{r_2}{r_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4)$$

where r_1 and r_2 are the corrosion rates at temperatures, T_1 and T_2 , respectively. The values obtained for the blank, inhibited systems containing KI, GA and GA + KI mixtures are presented in Table 4. Results presented in this table show that lower E_a values were obtained in the presence of inhibitors compared to the blank. Also, E_a values decreased with increase in concentration of GA. Lower E_a values in the presence of the additives compared to those in the blank solution indicate that the inhibitor will be less effective at ordinary temperatures, but inhibition efficiency increased considerably at higher temperatures [37, 38]. Such behaviour was observed for the temperature dependence of the inhibition efficiency for GA alone and in combination with KI in this study and further supports the proposed chemisorption mechanism.

The heats of adsorption, Q_{ads} were obtained from the trend of surface coverage with temperature using the expression:

$$Q_{\text{ads}} = 2.303R \left[\log \left(\frac{\theta_2}{1 - \theta_2} \right) - \log \left(\frac{\theta_1}{1 - \theta_1} \right) \right] \left(\frac{T_1 T_2}{T_2 - T_1} \right) \quad (5)$$

where θ_1 and θ_2 are the degrees of surface coverage at temperatures, T_1 and T_2 respectively. The values obtained are shown in Table 4. From the same table it is seen that the Q_{ads} values are positive and range from 3.5 to 58.4 kJmol^{-1} . The positive values are an indication that adsorption and hence inhibition efficiency increase with increase in temperature, which also supports the chemical adsorption mechanism. Free energy of adsorption ΔG_{ads}^0 for aluminium in 0.1 M NaOH in the presence of KI, GA and GA + KI mixtures at the temperatures

studied were obtained from equation (2) and the values obtained are listed in Table 3. It is evident from the result presented in that table that in all cases $\Delta G_{\text{ads}}^{\circ}$ values are negative. The negative values suggest that the inhibitor molecules are spontaneously adsorbed on aluminium surface. Generally, values of $\Delta G_{\text{ads}}^{\circ}$ up to -20 kJmol^{-1} are consistent with electrostatic interaction between the charged metal and charged molecules, which signifies physical adsorption, while values more negative than -40 kJmol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form coordinate type of bond, which signifies chemical adsorption [5]. The values of $\Delta G_{\text{ads}}^{\circ}$ obtained in this study are not up to -40 kJmol^{-1} for GA alone, which is a deviation from the chemical adsorption mechanism proposed. These and other results obtained in the present study are not surprising, judging from the fact that adsorbed organic molecules can influence the behaviour of electrochemical reactions involved in corrosion processes in several ways. The action of organic inhibition also depends on the type of interaction between the substance and the metallic surface. The interaction can bring about change either in electrochemical mechanism or in the surface available for the processes [39, 40]. Furthermore, results of the present study have shown that GA inhibits the alkaline induced corrosion of aluminium by virtue of adsorption of its components onto the metals surface. The inhibition process is a function of the metal, inhibitor concentration, temperature, as well as inhibitor adsorption abilities, which is so much dependent on the number of adsorption sites. The mode of adsorption (physisorption and chemisorption) observed could be attributed to the fact that GA is a complex molecule with components having different functional groups. The presence of more than one functional group in a molecule has been reported to lead to changes in the electron density of a molecule, which could influence its adsorption behaviour [41]. Adsorbed molecules may orient differently on the metal surface, depending on their functionality and other variables. The observed mixed adsorption behaviour displayed by GA may suggest that GA is first physically adsorbed and then slowly react with the metal surface to form chemisorbed layer, thus the possibility of multilayer physisorption on top of chemisorbed monolayer as suggested by Shaw [42], could account for the dual adsorption mechanism.

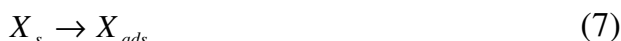
Synergism consideration

The synergism parameter S_1 was evaluated using the relationship below, initially given by Aramaki and Hackermann and reported elsewhere [6, 12]:

$$S_1 = \frac{1 - I_{1+2}}{1 - I_1 - I_2} \quad (6)$$

where $I_{1+2} = I_1 + I_2$, I_1 = inhibition efficiency of iodide ion, I_2 = inhibition efficiency of GA, and I_{1+2} is measured inhibition efficiency for GA in combination with iodide ion. The calculated values of synergism parameters for the various concentrations of GA are presented in Table 5. The calculated values are greater than unity for all the concentrations of GA studied. The value of S_1 greater than unity is an indication that the enhanced inhibition efficiency

resulting from the addition of iodide ion to GA is synergistic in nature. This can be explained on the basis that iodide ion has a greater tendency to be adsorbed on the surface and this may be responsible for the synergistic effect of iodide ion on GA. Halide ions are normally strongly adsorbed on metal surfaces where the chemisorbed ions enter the metallic part of the charged of the metal surface [43]. Thus the inhibitor is not adsorbed directly on the metal surface itself, but rather by coulombic attraction to the adsorbed halide ions on the metal surface. This process is similar to the so-called phenomenon of anion induced adsorption and may be represented by the highly simplified mechanism [12, 44]:



where X_s and M_s designate the halide ion and organic species, respectively, in the bulk state, X_{ads} and MX_{ads} refer to halide and ion pair, respectively, in the adsorbed state. This ion pair interaction consequently increases the surface coverage thereby reducing metal dissolution.

Table 5. Synergistic parameter S_1 values for different concentrations of GA from weight loss method at 313 K.

GA concentrations (g/L)	Synergism parameter (S_1)
0.5	1.30
0.4	1.22
0.3	1.29
0.2	1.18
0.1	1.13

Conclusions

Gum Arabic inhibits the corrosion of aluminium in NaOH. The inhibition efficiency of GA increases with increase in GA concentration and temperature. Synergistic effect between GA and KI was observed. The adsorption of KI, GA and GA+KI on the aluminium surface follows the Temkin's adsorption isotherm. The values of ΔG_{ads}° obtained were negative, which suggests that GA was strongly adsorbed, and indicates spontaneous adsorption of GA unto the aluminium surface. The phenomenon of a mixed adsorption mechanism (chemisorption and physisorption) is proposed from the calculated values of some kinetic and thermodynamic parameters.

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