

Joint Effect of *Anogessius Leocarpus* Gum (AL Gum) Exudate and Halide Ions on the Corrosion of Mild Steel in 0.1 M HCl

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Abstract

In an attempt to improve the corrosion inhibition potential of *Anogessius leocarpus* gum exudates for mild steel in solutions of HCl, corrosion inhibition efficiencies of the gum, KI, KCl, and KBr were determined experimentally using weight loss and gasometric methods. 0.05 M KI, 0.05 M KBr and 0.05 M KCl were combined with various concentrations of *Anogessius leocarpus* gum and their combined inhibition efficiencies were used in computing synergistic parameters for the respective combinations. The results obtained indicated that combination of 0.4 and 0.5 g/L of AL gum with 0.05 M solutions of KI and KBr, respectively, enhanced inhibition efficiency of the gum. However, for all concentrations of AL gum, combinations with 0.05 M KCl recorded a remarkable increase in inhibition efficiency, but calculated values of the synergistic parameter indicated that the adsorption of AL gum on mild steel surface is antagonized by the presence of Cl⁻. Theory of competitive and co-operative adsorption has been used to explain the co-adsorption of the gum and the halides. From calculated values of activation energy (< 80kJ/mol), free energy of adsorption (< -40 kJ/mol) and the variation of inhibition efficiency with temperature, the adsorption characteristics of the gum, halides and that of gum-halide mixtures were found to be consistent with the mechanism of physical adsorption. The adsorption was also found to be endothermic, spontaneous and favored the Langmuir adsorption model.

Keywords: corrosion, inhibition, adsorption, *Anogessius leocarpus* gum, synergism, potassium halides.

Introduction

Corrosion is the deterioration of materials by chemical interaction with their environment. The consequences of corrosion are many and varied and its effects on the safe, reliable and efficient operation of equipment or structures are severe.

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Most corrosion inhibitors are synthetic chemicals that are expensive and hazardous to the environment [1]. The use of natural products (green corrosion inhibitors) has been given extensive research interest because most of them are easily available, less expensive, less toxic and biodegradable [2-14]. In our research group, we have found that some natural polymers are effective corrosion inhibitors and can compete with green corrosion inhibitors [15]. According to Eddy et al. [15], polymers are effective corrosion inhibitors because through their functional groups they form complexes with metal ions and on the metal surface. These complexes occupy a large surface area that can blanket the metal surface and protect it against corrosion [16-17].

In spite of their numerous advantages as corrosion inhibitors, some natural polymers are found to be characterized with low values of inhibition efficiency. Therefore, it could be beneficial to work out efforts that can be adopted to improve upon their inhibition potentials. One of the ways of achieving this is through synergism [18]. Synergism has become one of the most important effects in inhibition processes and serves as the basis for all modern corrosion inhibitor formulations. It is an effective method to improve the inhibitive performance, to decrease the amount of usage, and to diversify the application of the inhibitor in acidic media [19]. Eddy *et al.* [3,20] stated that addition of Br⁻ and I⁻ ions to *Lasianthera Africana* and *Gnetum African* leaves extract antagonized their inhibition potentials for mild steel in solutions of H₂SO₄, while Cl⁻ exerted synergistic effect in the same media. Synergistic inhibition effect between iodide ion and natural exudate gums of *Raphia hookeri* [20] and *Pachylobus edulis* [21] for mild steel in acidic media has been reported. In view of the high favourable composition of *Anogessius leocarpus* gum exudates and their low corrosion inhibition potential [15], the objective of the present study is to investigate the effect of halide ions (KI, KCl and KBr) on the enhancement of the corrosion inhibition potential of *Anogessius leocarpus* gum exudates.

Materials and methods

Materials

Materials used for this study were mild steel sheets of composition (wt %, as determined by quantimetric method): Mn (0.6), P (0.36), C (0.15), Si (0.03) and Fe (99.01). The sheets were mechanically cut into different coupons, each of dimensions 5 x 4 x 0.11 cm. Each coupon was degreased by washing with ethanol, cleaned with acetone and allowed to dry in the air before preservation in a desiccator. All reagents used for the study were analar grade and double distilled water was used in preparing the required solutions. The *Anogessius leocarpus* gum exudates used for the studies were obtained from the *Anogessius leocarpus* tree, purified and concentrated using the method reported in our last work [15].

Weight loss measurement

In the gravimetric experiment, a previously weighed metal (mild steel) coupon was completely immersed in 250 mL of the test solution in an open beaker. The

beaker was covered with aluminium foil and inserted into a water bath maintained at 303 K. After every 24 hours, in order to remove the corrosion product, each coupon was withdrawn and washed with a solution containing 50 % NaOH and 100 g L⁻¹ of zinc dust. The washed coupon was rinsed in acetone and dried in the air before re-weighing. The experiment was repeated at 333 K. In each case, the difference in weight for a period of 168 hours was taken as the total weight loss. From the average weight loss (mean of three replicate analysis) results, the inhibition efficiency (%I) of the inhibitor, the degree of surface coverage (θ) and the corrosion rate of mild steel (CR) were calculated using equations 1, 2 and 3, respectively,

$$\%I = [1 - (W_1/W_2)] \times 100 \quad (1)$$

$$\theta = (1 - W_1/W_2) \quad (2)$$

$$CR = (W_1 - W_2)/At \quad (3)$$

where CR is the corrosion rate of mild steel in g/cm²/h, W₁ and W₂ are the weight losses (g) for mild steel in the absence and presence of the inhibitor, θ is the degree of surface coverage of the inhibitor, A is the area of the mild steel coupon (in cm²), t is the period of immersion (in hours).

Results and discussion

Effect of AL gum and halides

Fig. 1 shows the variation of weight loss with time for the corrosion of mild steel in various concentrations of HCl at 303 K. The figure indicates that the rate of corrosion of mild steel in HCl increases with increase in concentration. The corrosion rate of mild steel in solutions of HCl was also found to increase with increase in temperature (figure not shown). Fig. 2 shows the variation of weight loss of mild steel in solution of HCl containing various concentrations of AL gum as an additive at 303 K. The figure depicts that weight loss of mild steel in the blank is higher than those measured for solutions of HCl containing various concentrations of AL gum. This indicates that AL gum retarded the rate of corrosion of mild steel in solutions of HCl and that AL gum is an inhibitor for the corrosion of mild steel in solutions of HCl. At higher temperature (333 K), weight loss of mild steel in solution of HCl was found to follow similar pattern. However, at higher temperature (333 K), measured values of weight loss were higher than those obtained at a lower temperature (303 K). From the calculated values of corrosion rate of mild steel and of the inhibition efficiency of AL gum (Table 1), it can be seen that the inhibition efficiency of AL gum for mild steel in solutions of HCl increases with increase in the concentration of the inhibitor, but decreases with increasing temperature, indicating that AL gum is an adsorption inhibitor for the corrosion of mild steel in solutions of HCl and that the adsorption of AL gum favours the mechanism of physical adsorption.

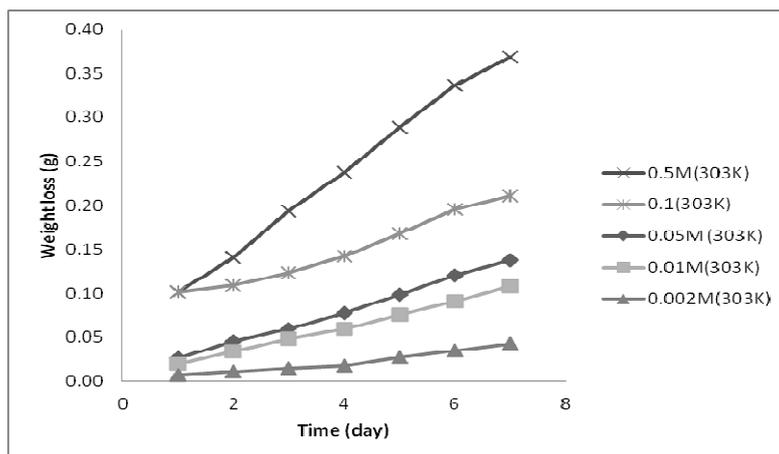


Figure 1. Variation of weight loss with time for the corrosion of mild steel in various concentrations of HCl .

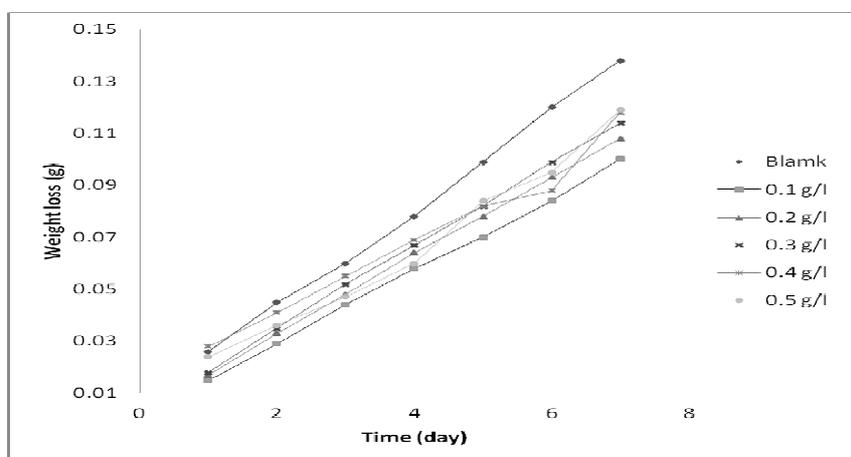


Figure 2. Variation of weight loss with time for the corrosion of mild steel in 0.05 M HCl containing various concentrations of AL gum at 303 K.

Calculated values of inhibition efficiency for AL gum are relatively low when compared to those obtained for some good green corrosion inhibitors. Therefore, in order to enhance the inhibition potential of AL gum for mild steel in solutions of HCl, synergistic effects of AL gum and halides (KI, KBr and KCl) were studied. Fixed concentration of the halides (0.005 M) in combination with various concentrations of Al gum was used for synergistic studies. According to Eddy et al. [19], synergism occurs when the combined inhibition efficiency of two or more inhibitors is greater than the sum of the inhibition efficiencies of the individual inhibitors, and that synergism of the corrosion inhibitor is due to the interaction between the components of the inhibitors, or the inhibitor and one of the ions present in aqueous solution. Table 2 presents values of the corrosion rate of mild steel and of the inhibition efficiency of various concentrations of KI, KBr, KCl, Al gum in combination with halides. From the results obtained, it is evident that there is a significant enhancement of the inhibition efficiency of AL gum by potassium halides. Synergistic combination of AL gum with 0.005 M KCl, 0.005 M KBr and 0.005 M KI is found to increase the inhibition efficiency of AL gum, indicating that these halides have the potential of modifying the adsorption of AL gum on mild steel surface. In Fig. 3, plots showing the

variation of the inhibition efficiencies of AL gum and those of halides and AL-halides mixtures with concentration of AL gum are presented. From the figure, it is significant to note that inhibition efficiencies of the respective AL-halide mixture are higher than those of the corresponding halides and that of AL-gum. From the plots, it is evident that the increase in inhibition efficiency of AL gum as due to interaction with potassium halides is consistent with the following trend, KI > KBr > KCl.

In order to ascertain synergistic, antagonistic and non effect of halides on the adsorption of AL gum, synergistic parameters, S, were calculated for various combinations of the inhibitor and fixed concentrations of the halides (KI, KCl and KBr) using the following equation [19],

$$S = \frac{1 - I_A - I_B + I_A I_B}{1 - I_{AB}} \quad (4)$$

where I_A and I_B are inhibition efficiencies of compound A and B, respectively, and I_{AB} is the inhibition efficiency of a combination of the two inhibitors. Calculated values of S are presented in Table 2.

The results indicate that the synergistic parameters for combinations of various concentrations of AL gum with 0.005 M KI, 0.005 M KBr and 0.005 M KCl tend to increase with increase in the concentration of AL gum, as shown in Fig. 4. Consequently, calculated values of the synergistic parameters were greater than unity at AL concentration of 0.5 g/L when the inhibitor was co-employed with 0.005 M KI and KBr, respectively. Also S values calculated for combination of 0.4 and 0.5 g/L of AL gum inhibitor and 0.005 M KI were greater than unity. Therefore, at these concentrations, adsorption of AL gum on mild steel surface is enhanced by synergistic combination of KI and KBr at concentrations ≥ 0.4 g/L and ≥ 0.5 g/L, respectively. Below these critical concentrations and for all concentrations of Al gum in combination with KCl, calculated values of the synergistic parameter were less than unity, indicating that the adsorption of AL gum on mild steel is antagonized by the presence of KCl. The synergistic effect observed for iodide and bromide ions may be due to co-adsorption of iodide or bromide with the inhibitors' cations. It has been found that co-adsorption can be either competitive (in which the anion and the cation are adsorbed at different sites on the metal) or co-operative adsorption, in which the anion is chemisorbed on the surface of the metal and the cation on the layer of the anion [23]. However, it is possible to have both types of adsorption.

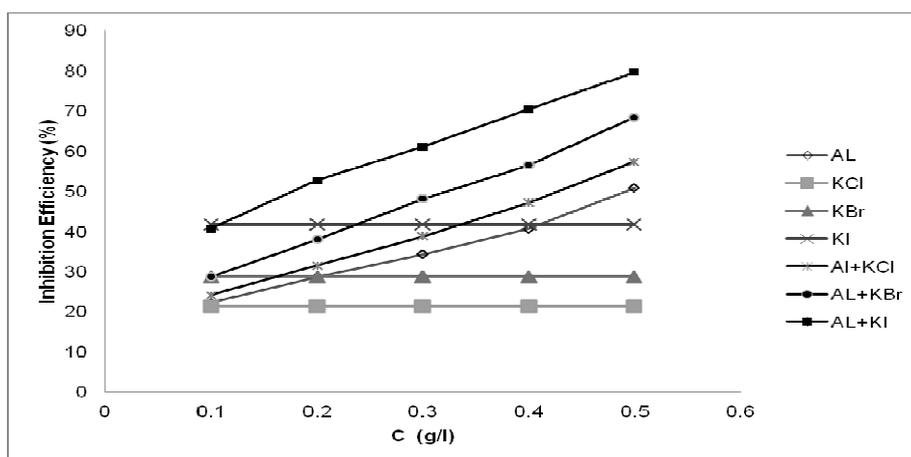


Figure 3. Variation of the inhibition efficiencies of AL gum, AL-halides combinations and halides with concentration at 303 K.

Table 1. Inhibition efficiency of AL gum and corrosion rates of mild steel in various media.

System	%I at 303 K	%I at 333 K	θ_2	θ_1	CR_1 (g/cm ² h)	CR_2 (g/cm ² h)
0.05 M KCl	21.3	18.6	0.21	0.19	7.5×10^{-3}	1.0×10^{-2}
0.05 M KBr	28.7	24.3	0.29	0.24	6.8×10^{-3}	9.4×10^{-3}
0.05 M KI	41.7	36.4	0.42	0.36	5.6×10^{-3}	7.9×10^{-3}
0.5 g/L AL	50.9	40.0	0.51	0.40	4.7×10^{-3}	7.5×10^{-3}
0.4 g/L AL	40.7	32.1	0.41	0.32	5.7×10^{-3}	8.4×10^{-3}
0.3 g/L AL	34.3	28.6	0.34	0.29	6.3×10^{-3}	8.9×10^{-3}
0.2 g/L AL	28.7	22.9	0.29	0.23	6.8×10^{-3}	9.6×10^{-3}
0.1 g/L AL	22.2	18.6	0.22	0.19	7.5×10^{-3}	1.0×10^{-2}
0.5 g/L AL + 0.05 M KCl	57.4	48.6	0.57	0.49	4.1×10^{-3}	6.4×10^{-3}
0.4 g/L AL + 0.05 M KCl	47.2	40.0	0.47	0.40	5.1×10^{-3}	7.5×10^{-3}
0.3 g/L AL + 0.05 M KCl	38.8	32.1	0.39	0.32	5.9×10^{-3}	8.4×10^{-3}
0.2 g/L AL + 0.05 M KCl	31.5	26.4	0.32	0.26	6.6×10^{-3}	9.1×10^{-3}
0.1 g/L AL + 0.05 M KCl	24.1	20.0	0.24	0.20	7.3×10^{-3}	9.9×10^{-3}
0.5 g/L AL + 0.05 M KBr	68.5	60.7	0.69	0.61	3.0×10^{-3}	4.9×10^{-3}
0.4 g/L AL + 0.05 M KBr	56.5	47.1	0.56	0.47	4.2×10^{-3}	6.6×10^{-3}
0.3 g/L AL + 0.05 M KBr	48.1	40.0	0.49	0.40	5.0×10^{-3}	7.5×10^{-3}
0.2 g/L AL + 0.05 M KBr	38.0	31.4	0.38	0.31	5.9×10^{-3}	8.5×10^{-3}
0.1 g/L AL + 0.05 M KBr	28.7	24.3	0.29	0.24	6.8×10^{-3}	9.4×10^{-3}
0.5 g/L AL + 0.05 M KI	79.6	75.7	0.80	0.76	2.0×10^{-3}	3.0×10^{-3}
0.4 g/L AL + 0.05 M KI	70.4	62.8	0.70	0.63	2.9×10^{-3}	4.6×10^{-3}
0.3 g/L AL + 0.05 M KI	61.1	52.9	0.61	0.53	3.7×10^{-3}	5.9×10^{-3}
0.2 g/L AL + 0.05 M KI	52.7	43.6	0.53	0.44	4.5×10^{-3}	7.0×10^{-3}
0.1 g/L AL + 0.05 M KI	40.7	32.9	0.41	0.33	5.7×10^{-3}	8.3×10^{-3}

Table 2. Synergistic parameters for combination of 0.005 M KI, KCl and KBr with various concentrations of AL gum.

C (g/L)	AL + KCl		AL + KBr		AL + KI	
	303 K	333 K	303 K	333 K	303 K	333 K
0.5	0.91	0.95	1.11	1.09	1.40	1.57
0.4	0.88	0.92	0.97	0.92	1.17	1.16
0.3	0.84	0.86	0.90	0.85	0.98	0.96
0.2	0.82	0.85	0.82	0.80	0.88	0.87
0.1	0.81	0.83	0.77	0.77	0.76	0.77

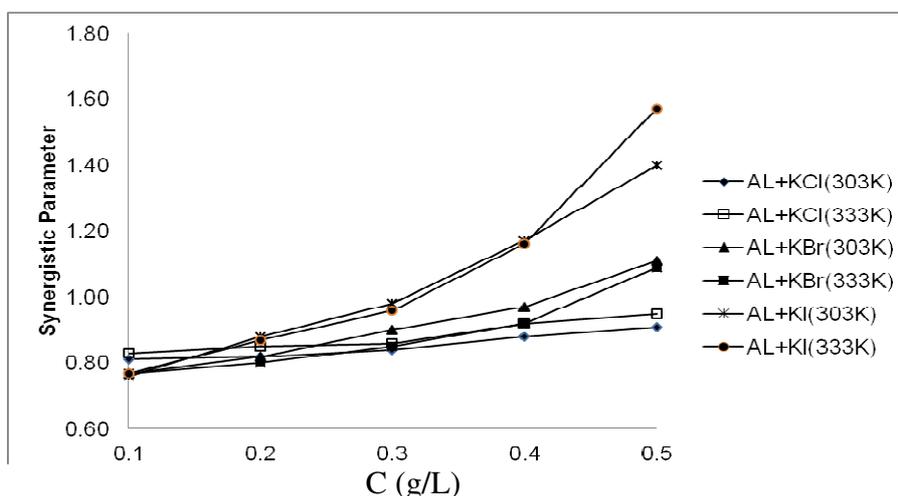


Figure 4. Variation of the synergistic parameter with concentration for joint combinations of AL gum with 0.005 M KI, KBr and KCl, at 303 K.

Effect of temperature

The effect of temperature on the corrosion of mild steel in solutions of HCl containing various concentrations of AL was studied using the Arrhenius equation, which can be written as follows [24]:

$$CR = A \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

where CR is the corrosion rate of mild steel in a given medium, A is the Arrhenius or pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the temperature. If the corrosion rates of mild steel at two temperatures [T_1 (303 K) and T_2 (333 K)] are assumed to be CR_1 and CR_2 , respectively, then equation 5 can be simplified and written as follows,

$$\frac{CR_2}{CR_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (6)$$

The activation energies calculated from equation 6 are presented in Table 3. From the results obtained, it can be seen that the activation energies are less than the threshold value required for chemical adsorption (80 kJ/mol), indicating that the adsorption of AL gum and those of AL gum-halides mixtures are consistent with the mechanism of charge transfer from the charged inhibitor to the charged

metal surface, which indicates physisorption. The results also revealed that there is an improvement in the adsorption of AL gum due to synergism, which was observed for the following systems: 0.5 g/L AL + 0.05 M KI, 0.5 g/L AL + 0.05 M KI and 0.05 M KBr + 0.5 g/L KBr. This also implies that at higher concentration of AL gum, enhancement of inhibition efficiency through synergistic combinations with KI or KBr can be achieved through improved adsorption.

Table 3. Activation energy and heat of adsorption of AL gum and combinations of AL gum with halides on mild steel surface.

System	Ea (kJ/mol)	Qads (kJ/mol)
Blank	10.92	-
0.05 M KCl	8.55	2.67
0.05 M KBr	9.07	5.40
0.05 M KI	9.63	5.30
0.5 g/L AL	13.08	9.34
0.4 g/L AL	10.86	8.18
0.3 g/L AL	9.67	4.87
0.2 g/L AL	9.65	6.56
0.1 g/L AL	8.05	3.87
0.5 g/L AL + 0.05 M KCl	12.47	6.75
0.4 g/L AL + 0.05 M KCl	10.80	5.98
0.3 g/L AL + 0.05 M KCl	9.89	6.43
0.2 g/L AL + 0.05 M KCl	8.99	6.13
0.1 g/L AL + 0.05 M KCl	8.53	4.90
0.5 g/L AL + 0.05 M KBr	13.74	7.40
0.4 g/L AL + 0.05 M KBr	12.65	7.58
0.3 g/L AL + 0.05 M KBr	11.35	7.67
0.2 g/L AL + 0.05 M KBr	10.22	6.51
0.1 g/L AL + 0.05 M KBr	9.36	5.40
0.5 g/L AL + 0.05 M KI	11.35	4.90
0.4 g/L AL + 0.05 M KI	12.92	6.61
0.3 g/L AL + 0.05 M KI	13.06	6.86
0.2 g/L AL + 0.05 M KI	12.37	7.58
0.1 g/L AL + 0.05 M KI	10.52	7.22

Heat of adsorption

The heat of adsorption of AL gum and for various combinations of AL gum with halides were estimated using the following equation [15],

$$Q_{ads} = 2.303R \left(\frac{\log \theta_2}{1 - \theta_2} - \frac{\log \theta_1}{1 - \theta_1} \right) \times \frac{T_2 T_1}{T_2 - T_1} \quad 7$$

where Q_{ads} is the heat of adsorption, R is the gas constant, θ_1 and θ_2 are the degrees of surface coverage for the inhibitor or inhibitor-halide combination at the temperatures T_1 (303 K) and T_2 (333 K), respectively. Values of Q_{ads} calculated from equation 8 are also recorded in Table 3. The results obtained indicate that the adsorption of AL gum, KI, KBr, KI, as well as joint adsorption of AL with halides, is endothermic.

Adsorption/thermodynamic studies

Adsorption characteristics of an inhibitor can be studied using adsorption isotherm. Several adsorption isotherms have been defined for various inhibitors including Temkin, Langmuir, Flory-Huggins, Frumkin and Freundlich adsorption isotherms [25]. Values obtained for the degree of surface coverage of the inhibitor (including combinations of AL gum and halides) at various temperatures and concentrations were used to fit curves for different adsorption isotherms. The test revealed that the best adsorption isotherm that describes the adsorption characteristics of Al gum is the Langmuir adsorption isotherm, which can be expressed as follows [26],

$$bC = \theta/(1-\theta) \tag{8}$$

where b is the equilibrium constant of adsorption and is related to the standard Gibb free energy of adsorption (ΔG_{ads}) according to the following equation,

$$b = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \tag{9}$$

where R is the universal gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution (molL^{-1}). Simplification of equation 9 yields equation 10 and from the logarithm of both side of equation 10, equation 11 was obtained

$$C/\theta = 1/b + C \tag{10}$$

$$\text{Log}(C/\theta) = \text{log}C - \text{log}b \tag{11}$$

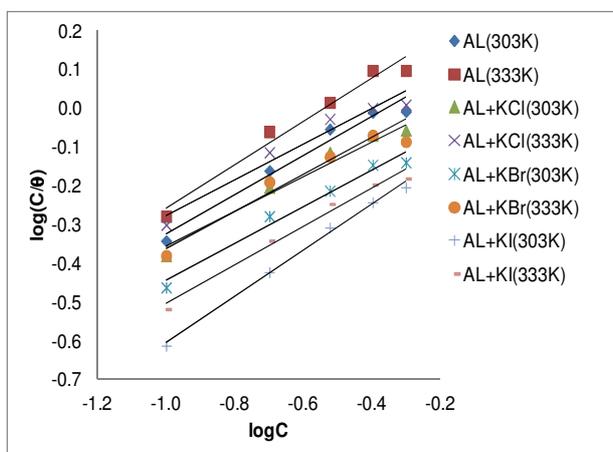


Figure 5. Langmuir adsorption isotherm for of AL gum and for joint adsorption of AL gum with KI, KCl and KBr at 303 and 333 K.

Table 4. Langmuir adsorption parameters for adsorption of AL gum and co-adsorption of AL gum with halides.

System	logb	b	ΔG_{ads} (kJ/mol)	R^2
AL+0.05 M KI at 303 K	-0.0104	0.9897	-10.10	0.9957
AL+0.05 M KI at 333 K	-0.0069	0.9931	-11.11	0.9813
AL+0.05 M KBr at 303 K	0.0288	1.0292	-10.20	0.9749
AL+0.05 M KBr at 333 K	0.0881	1.0921	-11.37	0.9375
AL+0.05 M KCl at 303 K	0.1137	1.1204	-10.41	0.9751
AL+0.05 M KCl at 333 K	0.1797	1.1969	-11.62	0.9503
AL at 303 K	0.1781	1.1949	-10.57	0.9654
AL at 333 K	0.2983	1.3476	-11.95	0.9698

From equation 11, a plot of $\log(C/\theta)$ versus $\log C$ should be expected to give a straight line with intercept equal to $-\log b$. Fig. 5 presents the Langmuir adsorption isotherm for AL gum and for co-adsorption of AL gum-halides mixture. Values of Langmuir parameters obtained from the plots are presented in Table 4. The results reveal that R^2 values are very close to unity, which indicates that the adsorption of AL gum and co-adsorption of AL gum-halide mixtures obeyed the Langmuir adsorption model. 'b' value indicates the strength of adsorption. The higher the value of 'b', the better is the adsorption. Recorded values of 'b' were deduced from the intercepts of the Langmuir plots for the various systems, and by substitution into equation 9, the free energy associated with the adsorption of the inhibitor was also computed (Table 4). The free energies are negatively less than the threshold value of -40 kJ/mol expected for the mechanism of chemical adsorption; therefore, the adsorption of AL gum and co-adsorption of AL gum with KI, KCl and KBr is spontaneous and supports the mechanism of physical adsorption.

Conclusions

The findings of the present study indicate that the inhibition efficiency of AL gum can be improved through co-adsorption with KI and KBr. However, critical concentrations of AL gum that allowed for the synergism with the halides are 0.5 g/L and 0.4 g/L for KBr and KI, respectively. The adsorption of AL gum and co-adsorption of the gum with the halides is consistent with the mechanism of physical adsorption. The adsorption is also spontaneous and can best be described by the Langmuir adsorption model.

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