The Use of Glutamic Acid as Corrosion Inhibitor for Aluminium in Hcl Solution

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Abstract: *The adsorptive and inhibitive action of glutamic acid towards general and pitting corrosion of aluminium in HCl solution was investigated using weight loss, gasometric and thermometric methods. Glutamic acid was found to inhibit the corrosion of aluminium in HCl solution. The inhibition efficiency of glutamic acid decreased with increase in temperature, period of immersion and HCl concentration, but increased with increasing glutamic acid concentration. Adsorption characteristics of glutamic acid have also been studied and it was found that the process obeys physical adsorption. Thermodynamic parameters including; E_a, Q_{ads}, ΔS_{ads}, ΔH_{ads} and ΔG_{ads} for the adsorption process signifies a spontaneous process. While Langmuir, Frumkin, Flory-Huggins and El-Awardy isotherm adsorption models can be used to explain the mechanism of glutamic acid adsorption onto aluminium surface in HCl solution.*
Key words: *Aluminium, Corrosion, Glutamic Acid, Physical adsorption, Spontaneous*

I.   Introduction

Aluminium and its alloys exhibit corrosion resistance in varied environments and have many important applications. The manifestation of its corrosion resistance in different aggressive media has continued to generate lots of interest. In aqueous solution, aluminium generally exhibits passive behaviour which influences its corrosion susceptibility. The adhesive passivating surface oxide film is amphoteric and consequently the metal dissolves readily in acidic and basic solutions [1]. Corrosion of aluminium and its alloys has been a subject of numerous studies due to their high technological value and wide range of industrial applications especially in aerospace and household industries. Aluminium and its alloys, however, are reactive materials and are prone to corrosion [2]. The most frequently applied protection of aluminium and its alloys involves the use of chromates either in various organic coatings or for the production of chemical conversion coatings. The environmental and health risks however associated with the use of chromates have imposed pressure towards finding effective alternative solutions. Encouraging results have been obtained by using rare earth metals and organic compounds containing carboxylic groups. The organic compounds act in a different manner than the metal ions which are believed to be incorporated into the protective oxide layer on the aluminium surface. The organic compounds possessing ionisable groups as is the case with the carboxylic acids may interact electrostatically with the metal, alloy and/or the oxide surface possibly through formation of surface complexes which may in turn affect the rate and the extent of the oxide formation [3]. Adsorption characteristics of these inhibitors depend on several factors including the nature and number of potential adsorption sites present in the inhibitor molecule. Numerous attempts are made to link the corrosion inhibitor efficiency with a number of structural parameters of these molecules [3].

In many cases the parameters connected with the electronic and the chemical structure of the molecule act simultaneously on the inhibitor efficiency and it is difficult to decide which parameter plays the most important role in increasing the inhibitor efficiency [2]. Many researchers have used such organic compounds to inhibit the corrosion of aluminium or its alloys [1, 2, 3, 4, 5]. It is within the scope of this research to use and establish the adsorptive and inhibitive properties of Glutamic acid on the corrosion of aluminium in HCl media using various methods.
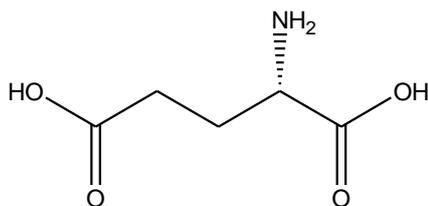

Fig 1: Structure of Glutamic Acid

II. Materials and Methods

2.1 Materials

The material used for the study is aluminium sheet of composition (wt%): Al(98.70), Si(0.48), Cl(0.014), K(0.04), Ca(0.01), Ti(0.005), V(0.016), Mn(0.012), Fe(0.50), Ni(0.013), Cu(0.048), Ga(0.013), In(0.10), Te(0.010), Ba(0.009), Os(0.032), Ir(0.03). The sheet was mechanically pressed-cut into different coupons, each of dimension 5 x 4 x 0.11 cm. Each coupon was degreased by washing with ethanol, dipped in acetone and allowed to dry in air before they were preserved in a desiccator. All reagents used for the study were Analar grade and double distilled water was used for their preparation.

The inhibitor (Glutamic acid) was supplied by CEMAN Pharmaceutical Company, Kano State, Nigeria, and was used without further purification. The range for the concentrations of the inhibitor used for the study was 4.0×10^{-4} to 20×10^{-4} M. Each of these concentrations was dissolved in 0.2, 0.4, 0.6, 0.8 and 1.0M HCl for use in weight loss, gasometric and thermometric methods respectively.

2.2 Methods

2.2.1 Weight Loss method

In the weight loss experiment, a previously weighed metal (aluminium) coupon was completely immersed in 250 cm^3 of the test solution in an open beaker. The beaker was covered and inserted into a water bath maintained at 303 K. After every 24 hours, each coupon was withdrawn from the test solution, washed in a solution containing 50% NaOH and 100 gL^{-1} of zinc dust (in order to remove the corrosion product). The washed aluminium coupon was rinsed in acetone and dried in air and the weight difference recorded. The difference in weight for a period of 168 hours was taken as total weight loss. The experiments were repeated at 313 and 323 K respectively. From the weight loss results, the degree of surface coverage (θ), inhibition efficiency (%I) of the inhibitor and corrosion rates (CR in gh^{-1}cm^{-2}) were calculated using Equations (1), (2) and (3) below:

$$\vartheta = 1 - \frac{W_1}{W_2} \qquad (1)$$

$$\% I = \left(1 - \frac{W_1}{W_2}\right) x\ 100 \qquad (2)$$

$$CR\ (gh^{-1}cm^{-2}) = \frac{\Delta W}{At} \qquad (3)$$

where W_1 and W_2 are the weight losses (g) for aluminium in the presence and absence of the inhibitor in HCl solution, θ is the degree of surface coverage of the inhibitor, A is the area of the aluminium coupon (in cm^2), t is the period of immersion (in hours) and ΔW is the weight loss of mild steel after time, t [6, 7, 8, 9].

2.2.2 Gasometric method

Gasometric methods were carried out at 303, 313 and 323 K as described in the literature [6, 7, 8, 9]. From the volume of hydrogen gas evolved per minute, surface coverage (θ), inhibition efficiencies (%I) and corrosion rate were calculated using Equations (4), (5) and (6):

$$\% I = \left(1 - \frac{V_{Ht}'}{V_{Ht}^o}\right) x\ 100 \qquad (4)$$

$$\vartheta = \frac{\% I}{100} = 1 - \frac{V_{Ht}'}{V_{Ht}^o} \qquad (5)$$

$$CR\ (cm^3 min^{-1}) = \frac{V_{Ht}'}{t} \qquad (6)$$

where V_{Ht}^1 and V_{Ht}^0 are the volumes of H$_2$ gas evolved at time t for inhibited and uninhibited solutions, respectively.

2.2.3 Thermometric method

The reaction vessel is a three-necked round bottom flask and the procedure for determining the corrosion behaviour by this method was described elsewhere by other authors [10, 11, 12]. The flask was well lagged to prevent heat losses. In this technique the corrodent (HCl) concentration was also varied at 0.2, 0.4, 0.6, 0.8 and 1.0 M respectively. The volume of the test solution used was 100cm^3. The initial temperature in all the experiments was kept at room temperature. The progress of the corrosion reaction was monitored by determining the changes in temperature with time (each minute for the first five minutes, each five minutes for the next 25 minutes and each ten minutes for the last thirty minutes) using a calibrated thermometer (0 - 100°C) to the nearest ± 0.05°C. The data was generated for a period of one hour. This method enabled the computation of the reaction number (RN). From the rise in temperature of the system per minute, the reaction number (RN) was calculated using equation (7):

$$RN(\ ^oC min^{-1}) = \frac{T_m - T_i}{t} \qquad (7)$$

Where T_m is the maximum temperature attained by the system, T_i is the initial temperature and t is the time required to reach the maximum temperature. From the above, the inhibition efficiency (%I) of the used inhibitor was computed using equation (8):

$$\% I = \frac{RN_{aq} - RN_{wi}}{RN_{aq}} \ x \ 100 \qquad\qquad (8)$$

where RN_{aq} is the reaction number of aqueous acid in the absence of the inhibitor, and RN_{wi} is the reaction number of aqueous acid in the presence of inhibitor.

III. Results and Discussion

The study on the corrosion inhibition of aluminium in HCl solution using glutamic acid as inhibitor was conducted using weight loss, gasometric and thermometric methods. The results of this study was either presented in graphical or tabular format as the case may be or discussed herewith.

3.1 Weight Loss Results

Weight loss experiments were conducted by varying the temperatures (303, 313, 323K), corrodent (HCl) concentration (0.2, 0.4, 0.6, 0.8 and 1.0M) and inhibitor (glutamic acid) concentrations (0.0004, 0.0008, 0.0012, 0.0016 and 0.0020M) to obtain the results presented below.

A plot of weight loss variation with time for the corrosion of aluminium in varying HCl concentrations without the inhibitor at 303K temperature is as presented in Fig. 2. It was observed that the longer the time of aluminium coupon immersion in the test solution the higher the weight loss through corrosion. Secondly, higher corrodent concentrations resulted into higher weight loss resulting into a higher corrosion rate. The same experiment was conducted at 313 and 323K temperatures with similar results obtained. Similar results were earlier reported by other authors [2, 13].

The effect of temperature on the corrosion system was tested at three different temperatures (303, 313 and 323K) respectively. It can be observed from Fig. 3, the highest weight loss of aluminium was observed at 323K for 0.20M HCl. The results obtained for 0.40, 0.60, 0.80 and 1.0M HCl solutions were similar to that of 0.20M HCl (Figures not shown). Similarly as in the effect of corrodent concentration, higher temperatures produced higher weight loss with time, thus higher rate of reaction. Comparing the results at the five HCl concentrations, it is also evident that a combination of higher temperatures and corrodent concentrations produced respectively higher weight loss resulting into a higher corrosion rate. Therefore, the higher the temperature, the higher the rate of corrosion, suggesting a physical adsorption mechanism [2, 13].

To test and establish whether the inhibitor has an effect on the rate of aluminium corrosion in varying HCl solution, varying concentrations of the inhibitor was used. Fig. 4 presents the results of the effect of glutamic acid on the corrosion of aluminium in 0.20M HCl solution at 303K. Similar results were obtained for 0.40, 0.60, 0.80 and 1.0M HCl and therefore were not presented even though with higher rate of reactions obtained. It reveals that the weight loss of aluminium in HCl increased with increase in the period of immersion but decreased with increase in the concentration of glutamic acid. This suggests that the rate of corrosion of aluminium in HCl increases with increase in the period of contact and decreases with increase in concentration of the inhibitor thereby decreasing the rate of corrosion reaction. At higher temperatures of 313 and 323K (graphs not shown) weight loss were found to increase with increase in temperature even as the glutamic acid concentrations got higher, indicating that the rate of corrosion of aluminium in all HCl concentrations increases with increase in temperature and that glutamic acid is adsorbed on the surface of aluminium according to the mechanism of physical adsorption [13, 14, 15].

To further establish whether corrodent (HCl) concentration has an effect on the corrosion of aluminium in solution containing glutamic acid as inhibitor at varying temperatures, Fig. 5 revealed that the higher the concentration of the corrodent the higher the aluminium coupon weight loss resulting into a higher rate of reaction even in the presence of the inhibitor. But when such results were compared at different HCl concentrations it was observed that the rate of reaction decreases in the presence of the inhibitor when two systems were conducted at the same temperature and HCl concentrations. Similar results were also reported [1, 16, 17].
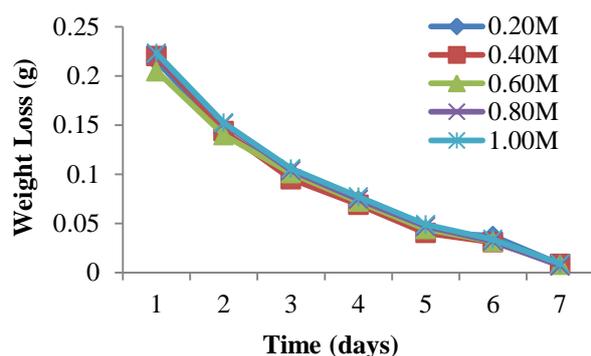
**Fig 2: variation of weight loss with time for the corrosion of aluminium in varying HCl concentrations at 303K**
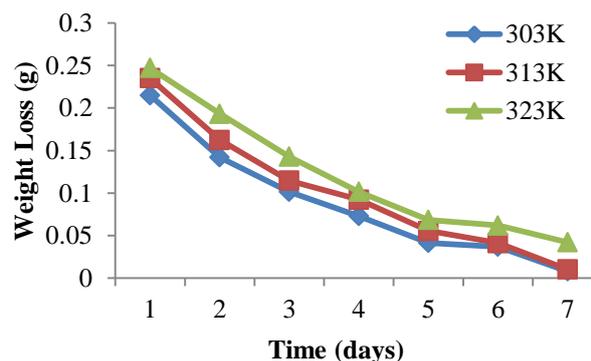
Fig 3: variation of weight loss with time for the corrosion of aluminium in 0.20M HCl solutions at varying temperatures
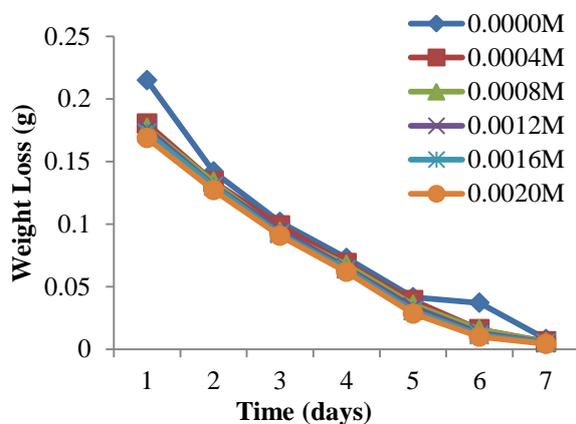

Fig 4: variation of weight loss with time for the corrosion of aluminium in 0.20M HCl containing varying concentrations of glutamic acid at 303K
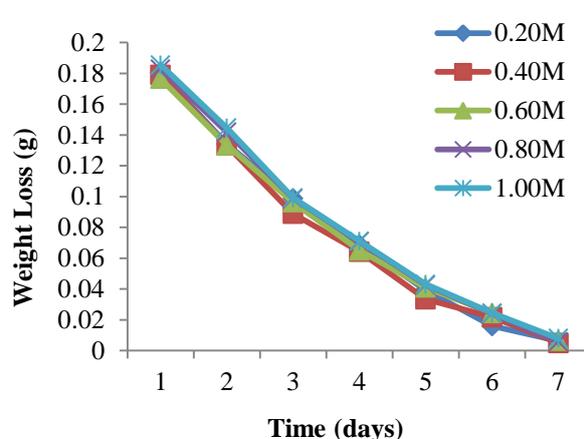

Fig 5: variation of weight loss with time for the corrosion inhibition of aluminium using 0.0004M glutamic acid in various HCl solutions at 303K

3. 2 Gasometric Results

The acidic corrosion of aluminium is characterised by evolution of hydrogen and the rate of corrosion is proportional to the amount of hydrogen gas evolved [18]. Gasometric experiments were carried out at 303, 313 323K respectively by varying the corrodent (0.20, 0.40, 0.60. 0.80 and 1.0M) and inhibitor concentrations (4 to 20 x 10^{-4}M) respectively. From the volume of hydrogen gas evolved per minute, Figs. 6, 7, 8 and 9 resulted by plotting the volume of gas evolved against time in order to establish its corrosion rate.

It can be observed from Fig. 6 that the higher the corrodent concentration the higher the volume of gas evolved per minute at 303K. Similar results were obtained at higher temperatures of 313 and 323K respectively. Fig. 7 presents the results of the effect of temperature variation in the absence of glutamic acid in 0.20M HCl solution. It is evident that higher temperature of 323K provided higher volume of hydrogen gas per minutes resulting into a higher rate of reaction. The same method was applied to 0.40, 0.60, 0.80 and 1.0M HCl concentrations with similar results obtained. Fig. 8 tried to establish the effect of glutamic acid in inhibiting aluminium corrosion in 0.20M HCl at 303K. As the concentration of the inhibitor increases lower volume of hydrogen gas was evolved per minute. Similar results were obtained when 0.40, 0.60, 0.80 and 1.0M HCl at 313 and 323K in the presence of glutamic acid systems were tested. To establish, regardless of temperature or corrodent concentration, the higher the volume of gas evolved per minutes the higher the rate of reaction (Fig. 9). Similar results were obtained from the weight loss experiments. It is also evident from the plots that there is an abrupt increase in the volume of hydrogen gas evolved after the first five minutes. This may be attributed to the reaction of the oxide layer with the HCl solution [19].
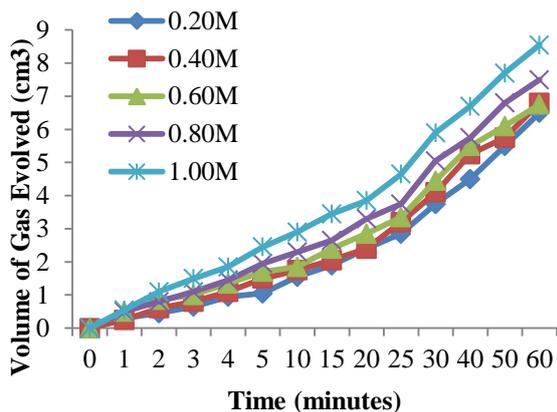
Fig 6: variation of the volume of hydrogen gas evolved with time for the corrosion of aluminium in varying HCl concentrations at 303K
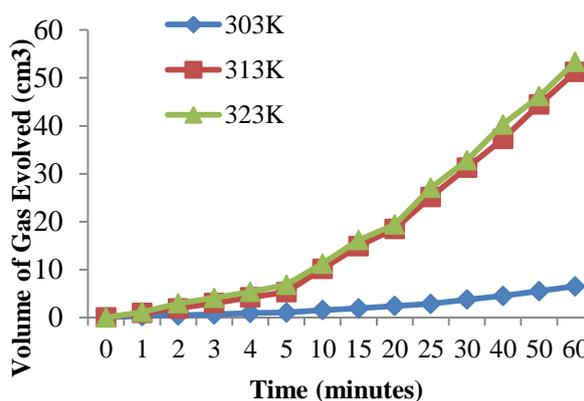
Fig 7: variation of the volume of hydrogen gas evolved with time for the corrosion of aluminium in 0.20M HCl solutions at varying temperatures
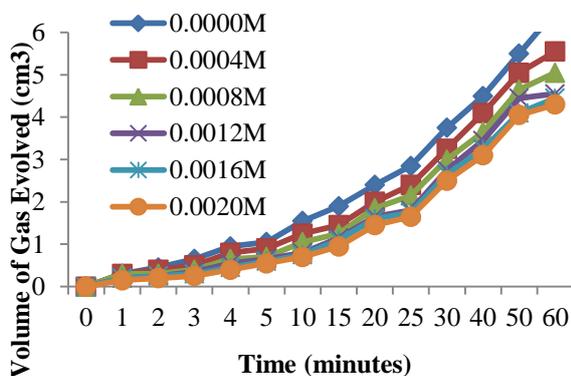
Fig 8: variation of the volume of hydrogen gas evolved with time for the corrosion of aluminium in 0.20M HCl containing varying concentrations of glutamic acid at 303K
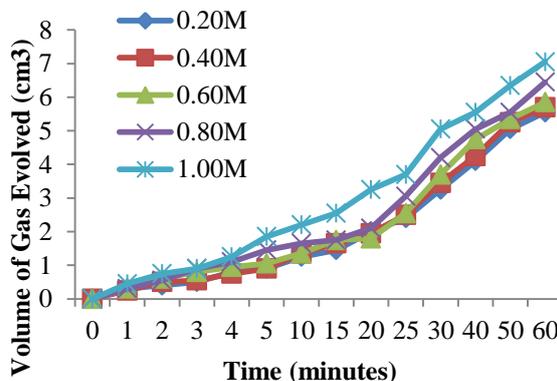
Fig 9: variation of the volume of hydrogen gas evolved with time for the corrosion inhibition of aluminium using 0.0004M glutamic acid in various HCl solutions at 303K

3.3 Thermometric Results

Thermometric methods were conducted by studying the effects of corrodent and inhibitor variation on the corrosion of aluminium at room temperature. Fig. 10 shows the variation of temperature with time for the corrosion of aluminium in varying HCl solutions. From the figure it can be seen that higher reaction temperatures were obtained as the concentration of HCl increases, suggesting an increase in corrosion rate. While in the presence of glutamic acid, the same trend of increase in reaction rate was observed as the concentration of HCl increases but the rate was comparably lower (Fig. 11). Thirdly, in trying to establish the inhibitive effect of varying concentration of glutamic acid in HCl, it was observed from Fig. 12 that an increase in glutamic acid concentration decreases the reaction temperature and hence decreases the rate of reaction [8].
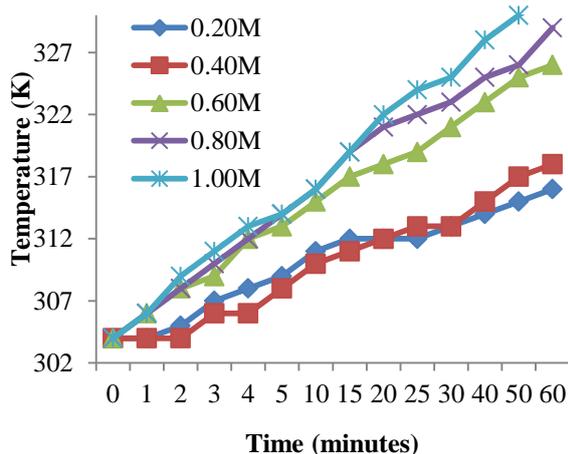
Fig 10: variation of temperature with time for the corrosion of aluminium in different HCl solutions
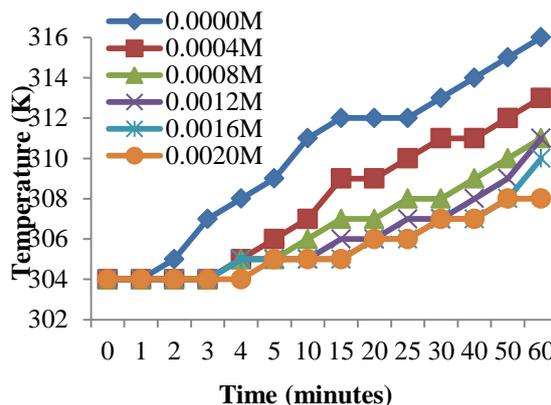
**Fig 11: variation of temperature with time for the corrosion of aluminium in 0.20M HCl containing varying concentration of glutamic acid as inhibitor**
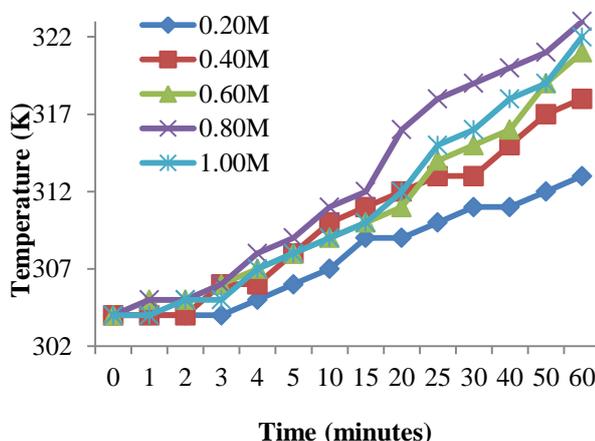
**Fig 12: variation of temperature with time for the corrosion inhibition of aluminium using 0.0004M glutamic acid in various HCl solutions**

3.4 Kinetic Consideration

It has been established by many researchers [6, 8, 9, 19] reported that most corrosion reactions obey the first order kinetic model. To further establish that with respect to the current study, equation (9) was used where k_1 is the first order reaction rate constant and t is the time in days:

$$-\log(weight\ loss) = \frac{k_1 t}{2.303} \qquad (9)$$

The plots of –log(weight loss) versus time (in the presence and absence of glutamic acid) were linear (with almost unity values for R^2) confirming that a first order kinetic is applicable to the corrosion of aluminium in the presence and absence of glutamic acid. Also the half life of a first order reaction is related to the rate constant according to equation (10):

$$t_{1/2} = \frac{0.693}{K_1} \qquad (10)$$

Values of the half life and rate constants obtained from the slopes of the kinetic plots are presented in the TABLE 1. The results revealed that the half lives of aluminium in the presence of glutamic acid were higher than those without glutamic acid indicating that the inhibitors increased the half life of aluminium in HCl solution. Secondly, it was also observed that the higher the glutamic acid concentration the higher the half life values. Thirdly, both temperature and HCl concentrations were found to affect the half life values, as can be seen from the TABLE 1, decrease in half lives were recorded as the concentration of HCl and temperatures were higher.

Table 1: Kinetic parameters for the corrosion inhibition of aluminium in HCl solution using glutamic acid as inhibitor

INHIBITOR CONC.		0.0000M		0.0004M		0.0008M		0.0012M		0.0016M		0.0020M	
KINETIC PARAMETER		k_1	$t_{1/2}$	k_1	$t_{1/2}$	k_1	$t_{1/2}$	k_1	$t_{1/2}$	k_1	$t_{1/2}$	k_1	$t_{1/2}$
	0.20M HCl	0.49	1.41	0.48	1.43	0.48	1.45	0.47	1.46	0.47	1.48	0.45	1.54
	0.40M HCl	0.52	1.34	0.51	1.36	0.50	1.38	0.50	1.40	0.49	1.42	0.47	1.47
323K	0.60M HCl	0.54	1.29	0.53	1.30	0.52	1.33	0.51	1.35	0.51	1.36	0.48	1.43
	0.80M HCl	0.55	1.26	0.54	1.28	0.54	1.29	0.53	1.32	0.52	1.33	0.51	1.35
	1.00M HCl	0.57	1.21	0.56	1.24	0.55	1.26	0.55	1.27	0.53	1.30	0.51	1.35
	0.20M HCl	0.63	1.10	0.62	1.12	0.61	1.13	0.60	1.15	0.59	1.17	0.57	1.22
	0.40M HCl	0.64	1.09	0.63	1.10	0.62	1.12	0.61	1.14	0.60	1.16	0.57	1.21
313K	0.60M HCl	0.65	1.07	0.64	1.09	0.62	1.11	0.61	1.13	0.60	1.15	0.59	1.18
	0.80M HCl	0.65	1.06	0.64	1.08	0.64	1.09	0.62	1.11	0.61	1.13	0.60	1.15
	1.00M HCl	0.67	1.03	0.67	1.04	0.66	1.05	0.64	1.09	0.64	1.09	0.62	1.12
	0.20M HCl	0.72	0.96	0.71	0.98	0.70	0.99	0.69	1.01	0.68	1.02	0.65	1.07
	0.40M HCl	0.74	0.94	0.73	0.95	0.71	0.97	0.70	0.99	0.69	1.00	0.67	1.04
303K	0.60M HCl	0.76	0.91	0.75	0.93	0.74	0.94	0.71	0.97	0.69	1.00	0.67	1.04
	0.80M HCl	0.78	0.89	0.75	0.92	0.75	0.93	0.74	0.94	0.71	0.97	0.67	1.04
	1.00M HCl	0.77	0.90	0.75	0.92	0.74	0.94	0.74	0.94	0.72	0.96	0.67	1.03

3.5 Corrosion rate and inhibition efficiencies

To further establish the results of this study, values of corrosion rate and percentage inhibition efficiencies of aluminium in HCl solution with or without glutamic acid as inhibitor using weight loss, gasometric and thermometric methods was conducted. The results are as presented in TABLES 2 and 3 respectively. From the results obtained it is evident that the corrosion rates increases with increase in HCl concentration, increases with increase in temperature but decreases with increasing glutamic acid concentrations in all methods tested. The results also indicate that values of corrosion rate for weight loss is higher than those of gasometric and thermometric in all tested systems implying that the instantaneous corrosion rate of glutamic acid is better than the average corrosion rate [8]. This finding arises from the fact that gasometric and thermometric methods measure instantaneous corrosion rate while weight loss measure average corrosion rate. The inhibition efficiency (which is inversely proportional to corrosion rate) for the use of glutamic acid on aluminium surface in HCl was also calculated for all three methods (weight loss, gasometric and thermometric). From the results obtained it is evident that the inhibition efficiency decreases with increase in HCl concentration, decreases with increase in temperature but increases with increasing glutamic acid concentrations in all methods tested. These results signify that the inhibitor is an adsorption and that the adsorption of the inhibitor on aluminium surface favours the mechanism of physical adsorption [16, 17].

Table 2: Corrosion rates ($gh^{-1}cm^{-2}$) of aluminium in HCl solution containing various concentrations of glutamic acid at varying temperature

INC		0.0000M			0.0004M			0.0008M			0.0012M			0.0016M			0.0020M		
CRC		WTL	GSM	TMM	WTL	GSM	TMM	WTL	GSM	TMM	WTL	GSM	TMM	WTL	GSM	TMM	WTL	GSM	TMM
	0.20M	31	0.11	0.20	2.1	0.09	0.15	2.0	0.08	0.12	1.9	0.08	0.12	1.8	0.07	0.10	1.6	0.07	0.07
	0.40M	30	0.11	0.23	2.7	0.10	0.23	2.2	0.09	0.20	2.0	0.08	0.12	2.0	0.08	0.13	1.7	0.07	0.10
303K	0.60M	30	0.11	0.37	2.9	0.10	0.28	2.3	0.09	0.25	2.4	0.09	0.20	2.3	0.09	0.13	1.9	0.08	0.12
	0.80M	32	0.13	0.42	3.4	0.11	0.32	2.4	0.10	0.27	2.4	0.09	0.20	2.3	0.08	0.13	2.4	0.08	0.12
	1.00M	32	0.14	0.47	3.8	0.12	0.33	3.5	0.10	0.29	2.9	0.10	0.20	2.6	0.09	0.15	2.4	0.09	0.12
	0.20M	35	0.85	-	3.2	0.78	-	2.7	0.75	-	2.4	0.73	-	2.8	0.70	-	2.5	0.66	-
	0.40M	36	0.89	-	3.6	0.79	-	2.9	0.76	-	2.6	0.74	-	3.0	0.70	-	2.8	0.68	-
313K	0.60M	37	0.90	-	4.2	0.82	-	2.9	0.78	-	2.6	0.75	-	3.1	0.72	-	2.9	0.68	-
	0.80M	37	0.92	-	4.4	0.85	-	3.8	0.78	-	2.7	0.76	-	3.2	0.71	-	3.1	0.68	-
	1.00M	39	0.94	-	4.6	0.87	-	4.1	0.84	-	2.8	0.82	-	3.6	0.80	-	3.5	0.75	-
	0.20M	43	0.89	-	3.4	0.83	-	3.3	0.80	-	4.0	0.76	-	3.7	0.71	-	3.6	0.69	-
	0.40M	43	0.91	-	5.1	0.84	-	3.4	0.81	-	4.2	0.78	-	3.9	0.75	-	3.8	0.72	-
3323K	0.60M	47	0.91	-	6.5	0.85	-	3.7	0.81	-	4.5	0.78	-	3.9	0.75	-	3.8	0.74	-
	0.80M	48	0.93	-	7.4	0.85	-	4.3	0.83	-	4.5	0.81	-	4.9	0.77	-	4.2	0.74	-
	1.00M	51	0.94	-	7.8	0.88	-	4.6	0.86	-	4.5	0.83	-	5.5	0.79	-	4.8	0.75	-

The corrosion rate values for weight loss is multiplied by 10^{-5}

Key: INC (Inhibitor Concentration), CRC (Corrodent Concentration), WTL (Weight Loss), GSM (Gasometric), TMM (Thermometric)

Table 3: Percentage Inhibition Efficiencies of aluminium in HCl solution containing various concentrations of glutamic acid at varying temperature

INC		0.0004M			0.0008M			0.0012M			0.0016M			0.0020M		
	CRC	WTL	GSM	TMM	WTL	GSM	TMM	WTL	GSM	TMM	WTL	GSM	TMM	WTL	GSM	TMM
303K	0.20M	12.16	14.62	25.00	16.86	22.31	41.67	18.30	30.00	51.67	20.05	31.54	52.00	20.54	33.85	66.67
	0.40M	10.63	16.18	24.00	16.28	21.32	34.29	18.10	28.68	50.00	20.01	33.09	42.86	22.09	36.03	65.14
	0.60M	9.78	13.33	22.73	12.53	16.30	36.82	15.27	20.00	45.45	18.02	23.70	49.09	20.05	26.67	58.18
	0.80M	9.60	14.00	23.00	12.55	24.00	31.00	14.64	27.33	42.00	16.96	34.00	48.00	18.54	35.33	56.00
	1.00M	8.77	17.06	22.71	13.80	28.24	30.43	13.90	30.00	41.14	16.46	33.53	47.86	17.88	39.41	55.00
313K	0.20M	4.75	7.19	-	7.74	11.71	-	9.32	14.93	-	11.06	22.85	-	13.14	26.68	-
	0.40M	4.63	7.10	-	7.57	14.46	-	8.81	16.90	-	11.06	21.13	-	12.78	25.92	-
	0.60M	3.98	6.94	-	6.67	14.01	-	7.50	17.05	-	10.10	20.55	-	12.78	24.98	-
	0.80M	3.97	6.00	-	5.95	14.53	-	7.49	17.44	-	9.86	22.43	-	11.86	28.25	-
	1.00M	3.46	5.78	-	5.05	10.22	-	6.76	12.44	-	9.68	14.76	-	11.18	19.64	-
323K	0.20M	3.48	4.29	-	4.93	10.50	-	6.73	14.90	-	9.02	19.87	-	10.78	22.77	-
	0.40M	3.27	11.08	-	4.26	10.48	-	6.21	13.51	-	8.84	17.83	-	10.66	20.77	-
	0.60M	3.24	9.59	-	4.22	10.17	-	5.97	12.61	-	8.49	17.44	-	10.53	22.30	-
	0.80M	2.97	7.54	-	3.90	10.06	-	5.42	12.31	-	7.98	16.71	-	10.40	20.22	-
	1.00M	2.63	6.84	-	3.50	8.27	-	5.25	11.03	-	7.35	15.66	-	9.94	19.57	-

Key: INC (Inhibitor Concentration), CRC (Corrodent Concentration), WTL (Weight Loss), GSM (Gasometric), TMM (Thermometric)

3.6 Thermodynamic considerations
3.6.1 Effect of temperature
In order to study the effect of temperature on the corrosion of aluminium in varying concentrations of HCl containing various concentrations of glutamic acid, the Arrhenius equation (10) was used:

$$CR = Aexp^{(\frac{-E_a}{RT})} \qquad (10)$$

Taking logarithm of both sides at a particular temperature gives equation (11), while at two different temperatures gives equation (12):

$$\log(CR) = logA - \frac{E_a}{2.303}RT \qquad (11)$$

$$\log\left(\frac{CR_2}{CR_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (12)$$

Where CR_1 and CR_2 are the corrosion rates of aluminium at temperatures T_1 (303K) and T_2 (323K) respectively, E_a is the activation energy and R is the g constant. Calculated values of activation energy using equation (12) are presented in TABLE 4. Effect of corrodent concentration and inhibitor concentrations were taken into consideration. It was observed that the values obtained in the presence of the inhibitor were all greater than those without inhibitor at all systems tested, indicating that the inhibitor increases the activation energy and thereby decreasing the rate of reaction. It was also observed that, as the concentration of the inhibitor increases there is an increase in activation energy, also as the concentration of HCl increases the activation energy decreases thereby increasing the rate of corrosion. It can also be observed from TABLE 4 that the activation energies are less than the threshold value of 80KJ/mol which is required for the mechanism of chemical adsorption. Therefore the adsorption of glutamic acid on the surface of aluminium is consistent with the mechanism of physical adsorption [19].

The heat of adsorption Q_{ads} of glutamic acid on the surface of aluminium in HCl solution was calculated using equation (13):

$$Q_{ads} = 2.303R\left[\log\left(\frac{\vartheta_2}{1-\vartheta_2}\right) - \log\left(\frac{\vartheta_1}{1-\vartheta_1}\right)\right] x \frac{T_1 \, x \, T_2}{T_2 - T_1}\frac{KJ}{mols} \qquad (13)$$

Where Q_{ads} is the heat of adsorption of the glutamic acid on the surface of aluminium, R is the gas constant, θ_1 and θ_2 are the degrees of surface coverage of glutamic acid at 303K (T_1) and 323K (T_2) respectively. Calculated values of Q_{ads} are also presented in TABLE 4. These values were all negative and tend to decrease with HCl concentration and increase with glutamic acid concentration indicating that the adsorption of glutamic acid on the surface of aluminium in HCl is in all cases tested exothermic.

Table 4: Some adsorption parameters for the inhibition of the corrosion of aluminium in varying HCl solution by glutamic acid

Inhibitor Conc.	0.0000M		0.0004M		0.0008M		0.0012M		0.0016M		0.0020M	
Corrodent Conc.	E_a	Q_{ads}	E_a	Q_{ads}	E_a	Q_{ads}	E_a	Q_{ads}	E_a	Q_{ads}	E_a	Q_{ads}
0.20M	-55.30	0.00	-54.98	-41.58	-47.02	-46.57	-28.68	-48.10	-26.64	-48.27	-24.86	-49.79
0.40M	-52.51	0.00	-52.48	-36.87	-37.14	-36.98	-25.28	-42.05	-22.57	-42.78	-20.63	-49.11
0.60M	-42.13	0.00	-32.66	-36.47	-27.25	-39.61	-23.66	-36.61	-20.51	-40.93	-19.59	-41.83
0.80M	-22.08	0.00	-14.86	-34.56	-16.99	-36.60	-15.12	-36.03	-13.34	-33.57	-11.12	-31.41
1.00M	-16.78	0.00	-12.49	-34.08	-8.52	-34.36	-5.45	-33.54	-11.23	-33.22	-10.18	-30.69

3.6.2 Entropy and enthalpy of adsorption

In order to calculate some other thermodynamic parameters for the adsorption (ΔS_{ads} and ΔH_{ads}) of glutamic acid on aluminium surface, the transition state equation (13) was used:

$$\log\left(\frac{CR}{T}\right) = \log\left(\frac{R}{Nh}\right) + \frac{\Delta S_{ads}}{2.303R} - \frac{\Delta H_{ads}}{2.303RT} \qquad (13)$$

Where CR is the corrosion rate, T is absolute temperature, R is gas constant, N is Avogadros constant, h is planks constant, ΔS_{ads} and ΔH_{ads} are entropy and enthalpy of adsorption. From this equation (13), a plot of $\log(CR/T)$ versus $1/T$ gave a straight line with a slope and intercept equal to $-\Delta H_{ads}/2.303R$ and $[\log(R/Nh) + \Delta S_{ads}/2.303R]$. Values of ΔS_{ads} and ΔH_{ads} calculated from equation (13) are recorded in Table 5. The negative values of ΔH_{ads} indicated that the corrosion of aluminium inhibited by glutamic acid is exothermic and decrease with increase in glutamic acid concentration but increases with HCl concentration increase, both suggesting a feasible reaction. It was also observed that Q_{ads}, E_a and ΔH_{ads} strongly correlated (R^2 value of 0.9988). This can be explained with the fact that the enthalpy change of a reaction can be represented as in equation (14):

$$\Delta H_{ads} = E_a + PdV \qquad (14)$$

For reactions involving liquids, dV is negligible implying that values of ΔH_{ads} should be equivalent to those of E_a [6].

Table 5: Enthalpy and entropy of adsorption of glutamic acid on the surface of aluminium in HCl solution

INHIB CONC	0.0000M		0.0004M		0.0008M		0.0012M		0.0016M		0.0020M	
CORR CONC	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS
0.20M	-10.68	0.28	-46.35	0.29	-44.21	0.30	-42.90	0.33	-28.69	0.33	-28.00	0.34
0.40M	-11.91	0.27	-59.82	0.27	-48.32	0.28	-41.31	0.30	-25.34	0.31	-24.51	0.32
0.60M	-12.52	0.26	-57.56	0.26	-42.76	0.27	-31.45	0.28	-25.20	0.30	-23.65	0.31
0.80M	-14.44	0.26	-47.39	0.24	-32.73	0.25	-28.06	0.26	-25.16	0.28	-22.86	0.29
1.00M	-16.12	0.26	-42.20	0.24	-31.75	0.25	-26.27	0.25	-24.44	0.25	-22.58	0.25

3.6.3 Free energy of Adsorption

The Gibb's free energy of adsorption of glutamic acid onto the surface of aluminium in HCl solution was calculated at three different temperatures using the Gibbs-Helmholtz equation (15):

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (15)$$

where ΔG_{ads} is the free energy of glutamic acid adsorption onto aluminium surface, ΔH_{ads} is the enthalpy of its adsorption and ΔS_{ads} is the entropy of adsorption and T is the temperature (K). The calculated values of the free energy are as presented in table (6). From the results obtained the free energies were found to increase with temperature, decrease with inhibitor concentration and increase with corrodent concentration. However all these values are lower in actual value than the threshold of -40KJ/mol required for chemical adsorption. This indicates that the adsorption of glutamic acid onto the surface of aluminium is spontaneous and also supports the mechanism of physical adsorption [8].

Table 6: Gibb's free energy of adsorption of glutamic acid onto aluminium surface in HCl solution at varying temperatures

CORRODENT CONC	INHIBITOR CONC	TEMPERATURE		
		303K	313K	323K
	0.0000M	-94.67	-97.44	-100.21
	0.0004M	-102.93	-104.80	-106.66
0.20M	0.0008M	-102.02	-103.60	-105.78
	0.0012M	-101.10	-103.41	-105.73
	0.0016M	-100.64	-103.01	-105.39
	0.0020M	-100.13	-102.58	-105.03
	0.0000M	-94.69	-97.42	-100.16
	0.0004M	-103.96	-105.42	-106.88
0.40M	0.0008M	-102.60	-104.39	-106.18
	0.0012M	-101.20	-103.51	-105.81
	0.0016M	-100.58	-103.06	-105.54
	0.0020M	-100.16	-102.69	-105.22
	0.0000M	-94.72	-97.34	-99.95
	0.0004M	-102.84	-104.00	-105.17
0.60M	0.0008M	-101.67	-103.29	-104.90
	0.0012M	-100.94	-102.77	-104.60
	0.0016M	-100.42	-102.38	-104.34
	0.0020M	-99.91	-102.04	-104.16
	0.0000M	-94.61	-97.26	-99.90
	0.0004M	-102.98	-104.81	-106.65
0.80M	0.0008M	-101.70	-103.97	-106.25
	0.0012M	-101.03	-103.44	-105.84
	0.0016M	-100.47	-102.96	-105.44
	0.0020M	-100.04	-102.61	-105.18
	0.0000M	-94.56	-97.15	-99.74
	0.0004M	-102.40	-104.39	-106.37
1.00M	0.0008M	-101.38	-103.67	-105.97
	0.0012M	-100.67	-103.13	-105.58
	0.0016M	-100.25	-102.75	-105.26
	0.0020M	-99.83	-102.38	-104.93

3.6.4 Adsorption isotherm models

Generally, four types of adsorptions may take place, involving organic molecules at the metal solution interface, namely; the electrolytic attraction between charged molecules and the charged metal, interaction of unshared electron pairs in the molecules with the metal, interaction of s electrons with metal and combination of the above [6]. These mechanisms are usually described by adsorption isotherms. The adsorption behaviour of glutamic acid was studied by fitting data obtained from degree of surface coverage to different adsorption isotherms including Langmuir, Temkin, Frumkin, Flory-Huggins and El-Awardy adsorption isotherms. The tests reveal that the adsorption of glutamic acid on aluminium surface is best described by Langmuir, El-Awardy, Frumkin and Flory-huggins adsorption isotherms in decreasing order based on plot correlation coefficient (R^2) values.

The adsorption behaviour of glutamic acid was studied by fitting the data obtained on the expression of Langmuir adsorption isotherm model as in equation (15):

$$\frac{C}{\vartheta} = \frac{1}{K_{ads}} + C \tag{15}$$

Taking logarithm of both sides yielded equation (16)

$$\log\left(\frac{C}{\vartheta}\right) = logC - logK_{ads} \tag{16}$$

where C is the concentration of the inhibitor in the sollution, θ is the degree of surface coverage of the inhibitor, and K_{ads} is the equilibrium constant of adsorption. Using equation (16), a plot of log(C/θ) versus logC was found to be linear, indicating the application of the Langmuir model to the adsorption of glutamic acid on aluminium surface. Values of Langmuir adsorption parameters deduced from the slopes and intercept of the plots are presented in Table 7. From the results obtained, the slopes and values of R^2 are very close to unity indicating that there is a strong adherence of the inhibitor adsorption to the assumption of Langmuir isotherm; mono layer adsorption and non interaction of adsorbed molecules [8].

According to Temkin adsorption isotherm, the degree of surface coverage (θ) is related to the concentration of the inhibitor (C) in the bulk electrolyte according to equation (17):

$$exp(-2a\vartheta) = KC \qquad (17)$$

Upon taking the logarithm of both sides and re-arranging, equation (18) and (19) resulted:

$$\vartheta = \frac{-2.303 log K}{2a} - \frac{2.303 log C}{2a} \qquad (18)$$

$$\vartheta = \frac{-ln K}{2a} - \frac{ln C}{2a} \qquad (19)$$

Where K and a are the equilibrium constant of adsorption and Temkin interaction parameter. The plots of θ versus logC were not linear and have a very low R^2 values indicating that the adsorption of the inhibitor was not consistent with the assumptions of temkin all conditions tested. Values of the adsorption parameters deduced from Temkin plots are recorded in Table 7.

The adsorption of glutamic acid on aluminium surface was also tested using Frumkin adsorption isotherm which can be expressed as in equation (20)

$$log \left(C \; x \; \frac{\vartheta}{1-\vartheta} \right) = 2.303 log K + 2\alpha\vartheta \qquad (20)$$

Where K is the adsorption-desorption equilibrium constant and α is the lateral interaction term describing the molecular interaction in the adsorbed layer. A plot of log(C x θ/1-θ) versus θ was made, where K and α values where obtained from the slope and intercept respectively. Values of Frumkin adsorption isotherm are also presented in Table 7. From the results, values of α where found to be positive which also indicate the attractive behaviour of the inhibitor on the surface of aluminium which was found to decrease with increase in HCl concentration and increase with inhibitor concentration [19].

The values of θ/C in the plots (not shown) were evaluated directly from equation (21) determined from the weight loss data. It was found that the experimental data obtained within the temperature range (303, 313 and 323K) fits Flory–Huggins adsorption isotherm which is given by equation (21):

$$log \left(\frac{\vartheta}{C} \right) = log K + x log(1 - \vartheta) \qquad (21)$$

where θ is the degree of surface coverage, x the number of inhibitor molecules occupying an active site (or the number of water molecules replaced by one molecule of glutamic acid), K the equilibrium constant of adsorption and C is the different concentrations of the systems studied. The plot of log (θ/C) versus log$(1−\theta)$ for Flory–Huggins' isotherm at 303K gave straight lines for aluminium in all concentrations of HCl in the presence of glutamic acid (inhibitor). Similar trend was observed at 313 and 323K respectively. Results from Table 7 shows that values of x decreases with increase in HCl concentration and also temperature. This clearly indicates that the rate of glutamic acid adsorption on the surface of the aluminium metal decreases with increase in temperature and HCl concentrations [10].

The plot of log(θ/1 − θ) against logC was made and straight lines were obtained which showed that the results obtained from the study also fitted into the El-Awady et al. thermodynamic-kinetic model which is given by equation (22):

$$log \left(\frac{\vartheta}{1-\vartheta} \right) = log K + y log C \qquad (22)$$

Where θ is the degree of surface coverage of the inhibitor, K is the equilibrium constant of adsorption, 1/y represents the active sites on metal surface covered by inhibitor molecules [10]. The values of y is increasing or 1/y dcreasing as temperature and HCl concentration decreases. This also reveals that the number of active sites replaced by the inhibitor molecules decreases with increase in temperature and HCl concentrations. From the results obtained it is seen that K values increase with increase in temperature. Generally larger K values imply more efficient adsorption and hence a better inhibitor. Therefore the adsorption of glutamic acid on the surface of aluminium is retarded by increase in temperature supporting the mechanism of physical adsorption [19].

Table 7: Adsorption isotherm model parameters for the adsorption of glutamic acid on aluminium surface in HCl solution at varying temperatures

	Corrodent (HCl)	303K			313K			323K		
		R^2	Slope	K	R^2	Slope	K	R^2	Slope	K
Langmuir	0.20M	0.91	0.75	0.73	0.97	0.36	0.20	0.99	0.39	1.07
	0.40M	1.00	0.71	0.75	0.97	0.10	0.30	0.94	0.18	1.08
	0.60M	0.99	0.55	0.81	0.99	0.28	0.41	1.00	0.76	1.09
	0.80M	0.99	0.67	0.90	1.00	0.29	0.43	1.00	0.63	1.09
	1.00M	0.99	0.68	0.93	1.00	0.38	0.52	1.00	0.64	1.17
Temkin		R^2	a	K	R^2	A	K	R^2	a	K
	0.20M	0.47	12.97	0.90	0.40	-64.69	0.25	0.44	-45.88	0.27
	0.40M	0.77	9.84	0.33	0.28	-66.56	0.16	0.32	-69.79	0.19

0.60M	0.55	-26.84	0.35	0.36	-63.27	0.22	0.75	-22.02	0.51
0.80M	0.05	-26.72	0.43	0.37	-68.54	0.22	0.48	-48.79	0.30
1.00M	0.67	-24.82	0.45	0.43	-60.93	0.27	0.50	-46.62	0.32

Frumkin		R^2	α	K	R^2	A	K	R^2	α	K
	0.20M	0.68	4.22	0.01	0.96	9.16	0.00	0.98	7.12	0.00
	0.40M	0.98	5.64	0.00	0.96	8.94	0.01	0.97	8.99	0.00
	0.60M	0.98	5.05	0.01	0.96	8.47	0.00	0.97	8.53	0.00
	0.80M	0.96	5.04	0.00	0.97	8.46	0.00	0.97	7.95	0.00
	1.00M	0.96	4.91	0.00	0.98	8.22	0.00	0.96	7.77	0.00

Flory-Huggins		R^2	x	K	R^2	X	K	R^2	x	K
	0.20M	0.17	10.81	418.12	0.83	8.01	102.73	0.95	6.84	162.07
	0.40M	0.94	10.30	1509.38	0.29	7.43	64.24	0.91	5.72	70.96
	0.60M	0.92	9.93	440.86	0.88	6.53	90.89	0.92	5.16	2496.32
	0.80M	0.87	9.86	785.60	0.96	6.15	87.30	0.91	4.59	183.82
	1.00M	0.89	9.01	989.46	0.95	5.97	120.01	0.86	4.02	206.25

El-Awardy		R^2	y	K	R^2	Y	K	R^2	y	K
	0.20M	0.51	0.30	1.61	0.99	0.68	7.01	0.99	0.47	9.46
	0.40M	0.99	0.36	2.48	0.98	0.69	45.07	1.00	0.57	23.83
	0.60M	0.99	0.52	6.34	1.00	0.75	13.30	0.97	0.69	1.57
	0.80M	0.96	0.59	2.47	1.00	0.77	11.13	0.99	0.72	4.79
	1.00M	0.97	0.67	2.39	1.00	0.86	6.56	0.98	0.85	3.96

IV. Conclusion

The adsorptive and inhibitive properties of Glutamic acid was studied on aluminium surface corrosion in HCl solution at varying temperature, inhibitor and corrodent concentrations using weight loss, gasometric and thermometric methods. From the findings of this work, the following conclusions can be drawn;

1. Glutamic acid was found to inhibit aluminium corrosion in HCl solution.

2. Increase in the concentration of glutamic acid decreases the rate of aluminium corrosion in HCl and therefore increases the inhibition efficiency.

3. Higher concentration and temperatures reduced the inhibitive effect of glutamic acid on the corrosion of aluminium in HCl solution.

4. The corrosion reaction in the presence and absence of glutamic acid was found to follow first order kinetics and its half lives increases with glutamic acid concentration, but decreases with increase in temperature and HCl concentration.

5. The thermodynamic parameters (E_a, Q_{ads}, ΔS_{ads}, ΔH_{ads}, ΔG_{ads}) for the adsorption of glutamic acid to the surface of aluminium in HCl was found to obey the mechanism of physical adsorption.

6. The adsorption of glutamic acid onto the surface of aluminium in HCl solution was found to follow the models of Langmuir, Frumkin, Flory-Huggins and kinetic and thermodynamic El-Awardy adsorption isotherms.

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