Journal of Materials and Environmental Science
ISSN : 2028-2508
e-ISSN : 2737-890X
CODEN : JMESCN

J. Mater. Environ. Sci., 2022, Volume 13, Issue 05, Page 553-563

http://www.jmaterenvironsci.com

Corrosion of aluminium in hydrochloric acid solution containing thiodiglycolic acid

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Received 03 May 2022,
Revised 28 May 2022,
Accepted 30 May 2022

Keywords
- ✓ Corrosion,
- ✓ thiodiglycolic acid,
- ✓ accelerator,
- ✓ aluminium,
- ✓ adsorption.

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Abstract

The corrosion of aluminium in 0.5M hydrochloric acid solution containing thiodiglycolic acid (TDG) was studied using weight loss technique. The result reveals that thiodiglycolic acid acts as an accelerator of acid corrosion on aluminium by decreasing the activation energy of the corrosion reaction. Generally, the weight loss was found to increase with increase in the additive (thiodiglycolic acid) concentration. Temperature was also observed to aid of corrosion of aluminium as the weight loss increased with increase in temperature. The corrosion process followed first order kinetic reaction. Thermodynamic parameters revealed that the adsorption of thiodiglycol on aluminium surface was spontaneous and exothermic with increase in disorderliness of the system and was best described by the Langmuir adsorption isotherm. Phenomenon of physical adsorption was proposed from kinetic and thermodynamic parameters.

1. Introduction

Corrosion of metals and metallic alloys in harsh acidic, alkaline and /or saline environment results in mechanical failure and reduction in economic values when exposed to these environment [1]. One of the methods used in preventing/reducing corrosion of metals is the addition of inhibitors to the solution in contact with the metal surface in order to reduce the corrosion rate [2]. Some organic compounds, particularly those which contain nitrogen, oxygen, and/or sulphur in conjugated systems, have demonstrated good corrosion inhibiting abilities [3] although several of them are as well toxic and expensive. Corrosion inhibitors characteristics include possession of suitable functional groups, aromatic rings, long alkyl chain, multiples bond and presence of heteroatoms such as nitrogen, oxygen, sulphur, and phosphorus [4]. Some researchers have reported the use of organic acids as corrosion inhibitors for metals and metal alloys. The corrosion inhibitive properties of carboxylic acids like tartaric acid, citric acid, maleic acid, succinic acid, malic and tricarboxylic acid in alkaline environment [5], aromatic carboxylic acids like 4-bromomethyl, 3-bromo and 3-hydroxyl benzoic acid in IM NaOH alkaline solution [6] and an amino acid like glutamic acid and its derivatives as corrosion inhibitors in different aggressive environment [7] have been reported.

2. Methodology

2.1 Preparation of Metal Coupon

The aluminium coupons were press out mechanically into 2cm x 4cm sizes, with perforation at the centre of each of the metal. Each of the aluminium coupons were weighed using electric weighing balance and their initial weight obtained and recorded. The coupons weight ranges from 3.000g – 4.1978g. A thread is then passed through the perforation made in each of the coupon and masking tape was labelled and placed on the thread in other to identify each of the aluminium coupons as well as their initially measured weights. The coupons were used without further polishing, but was degreased in absolute ethanol, rinsed with deionised water, and dried with acetone. The coupons were then wrapped in clean polyethylene bags and stored over silica gel in a desiccator to be used for the experiment when required.

2.2 Thiodiglycolic Acid Additive Concentration

Several concentrations of the thiodiglycolic acid additive were prepared using the 0.5M hydrochloric acid solution. The concentrations of the additive (thiodiglycolic acid) used are: $1x10^{-6}$M, $1x10^{-5}$M, $5x10^{-5}$M, $1x10^{-4}$M, $5x10^{-4}$M and$1x10^{-3}$M.

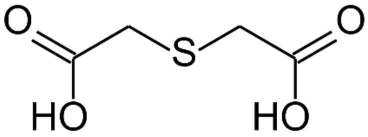

Figure 1: Structure of thiodiglycolic acid (TDG)

2.3. Gravimetric Analysis

The previously weighed aluminium coupons were immersed in 100ml open beakers containing 0.5M hydrochloric acid solution without thiodiglycolic acid (Blank) and thiodiglycolic acid concentrations of $1x10^{-6}$M, $1x10^{-5}$M, $5x10^{-5}$M, $1x10^{-4}$M, $5x10^{-4}$M and$1x10^{-3}$M in hydrochloric acid solution at different temperatures (303, 308, 313, 318, 323 and 328K). The variation of weight loss was followed at 4 hours interval progressively for 28 hours at different temperature variations. In each time, the coupons were properly washed with deionised water, rinsed in acetone to dry properly. The weight loss was calculated in grams as the difference between the initial weight prior to immersion and weight after removal of the corrosion product. The procedure for weight loss determination was like that reported previously [8]. Because TDG acted as an accelerator of aluminium corrosion in HCl solution, corrosion enhancement efficiency (E.E%) was computed using equation 1:

$$\% \text{ Enhancement Efficiency E.E\%} = \frac{Wl_e - Wl_b}{Wl_e} \times 100 \ldots\ldots\ldots\ldots \text{Eqn 1}$$

Where Wl_e and $Wl_b$are the weight loss of aluminium with and without TDG accelerator respectively

The corrosion rate CR was computed using equation 2:

$$\text{Corrosion rate CR } (mg/h^{-1}\,cm^{-2}) = \frac{\Delta W}{At} \ldots\ldots\ldots\ldots \text{Eqn 2}$$

Where A is the area of coupon exposed (in cm^2), t is immersion time in hours while ΔW is the change in weight (weight loss). ΔW is the difference between initial weight of coupon before immersion and the final weight of coupon after immersion.

The degree of surface coverage was computed using equation 3:

$$\text{Surface coverage } \Theta = \frac{E.E\,\%}{100} \ldots\ldots\ldots\ldots \text{Eqn 3}$$

3. Results and Discussion

3.1 Gravimetric Analysis

The weight loss of aluminium increases in the presence of TDG than in its absence (blank). This is because TDG acted as an accelerator (enhancer) of corrosion process unlike inhibitors that retard the corrosion process. Increase of the corrosion process may be due to the liberated H^+ ions from TDG carboxylic acid ends which increases the acid concentration in solution thereby increasing weight loss. The weight loss also increases with time of immersion, temperature, and concentration of TDG.

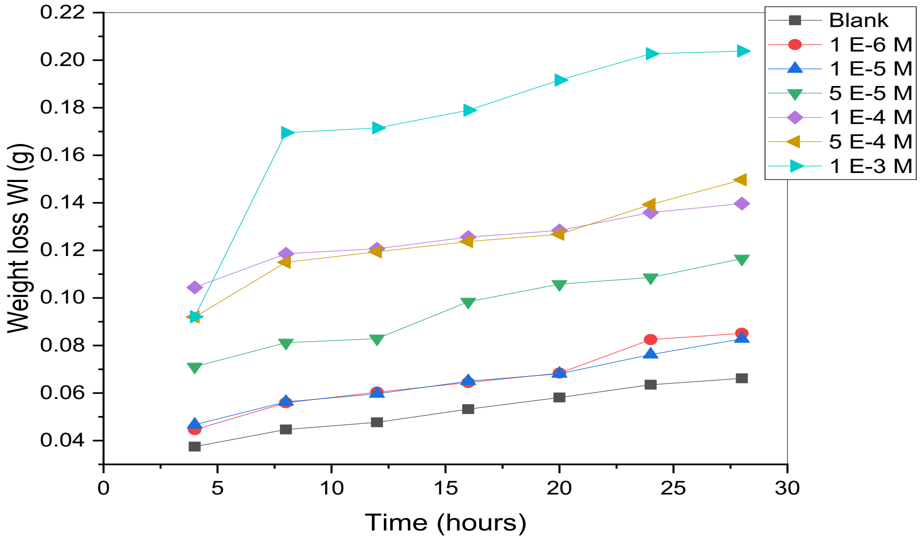

Figure 2: Variation of weight loss with time of aluminium in 0.5 M HCl at 303K in the presence of different concentrations of TDG

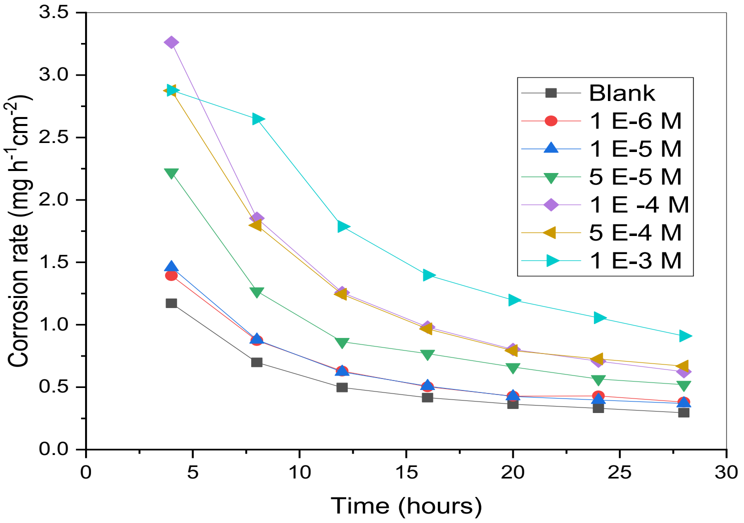

Figure 3: Variation of corrosion rate of aluminium with time in 0.5 M HCl at 303K in the presence of different concentrations of TDG.

As can be seen from Figure 4, enhancement efficiency of TDG for aluminium corrosion increase from 308K to 313K, then falls at 318K and increases again up to 328K.

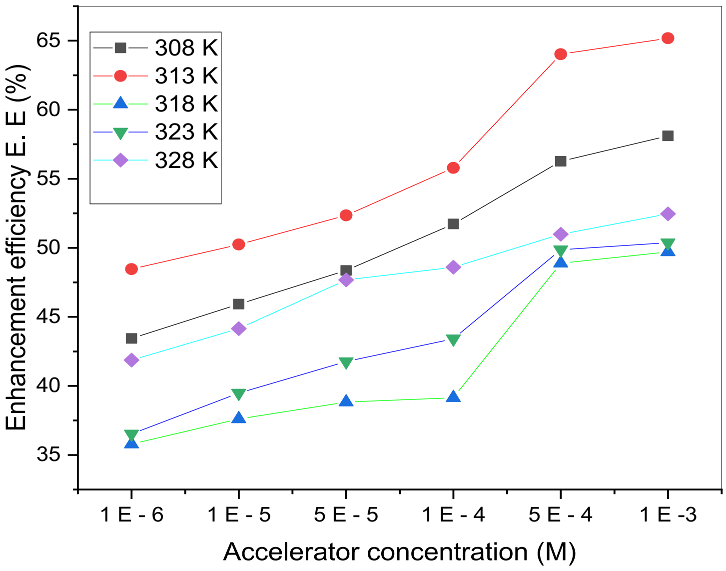

Figure 4: Variation of enhancement efficiency with TDG accelerator concentration in 0.5 M HCl at different temperatures

3.1 Kinetic study

The kinetics of TDG as an accelerator in 0.5 M HCl solution was investigated by fitting the obtained data from weight loss measurements into equation 4 [9]:

$$-\log(\text{Weight loss}) = \frac{k_1\,t}{2.303}$$ ---Eqn 4

Where k_1 is the first order rate constant and t is the time in hours. The plot of variation of - log (weight loss) against time for aluminium corrosion in 0.5 M HCl in the presence of various concentrations of TDG is shown in Figure 5.

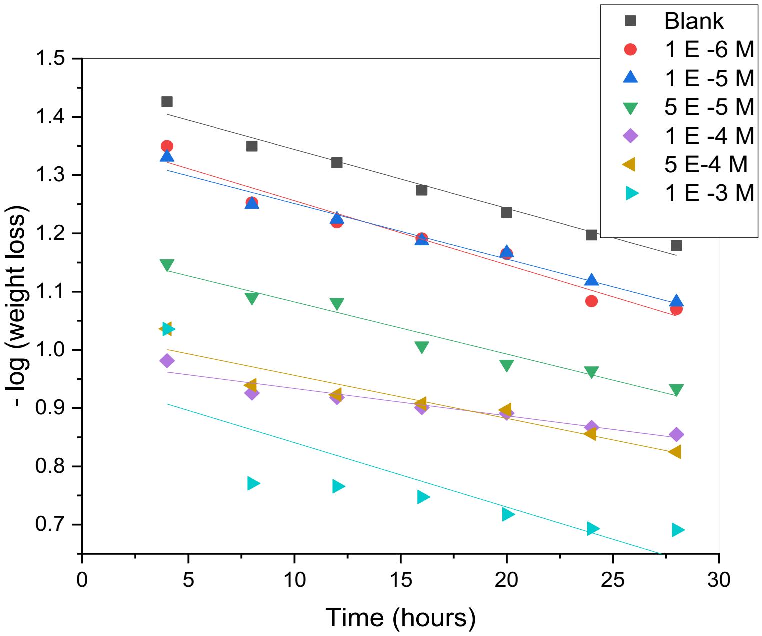

Figure 5: Variation of – log (weight loss) with time for corrosion of aluminium in 0.5 M HCl containing various concentrations of TDG at 303K

Table 1: Kinetic parameters for the corrosion of aluminium in 0.5M HCl in the absence and presence of different concentrations of TDG

Concentration of TDG (M)	Rate Constant k	R^2
Blank	0.0233	0.976
1×10^{-6}	0.0251	0.956
1×10^{-5}	0.0229	0.972
5×10^{-5}	0.0250	0.960
1×10^{-4}	0.0238	0.926
5×10^{-4}	0.0242	0.895
1×10^{-3}	0.0256	0.932

The linear plots with R^2 values close to unity show the fitness of the data to first order kinetics [10] [11]. Moreso, Table 1, shows that the rate constant increases with increased concentration of TDG, thereby confirming that fact that TDG acted as accelerator of the corrosion process.

3.2 Effect of temperature

Arrhenius equation was used in calculating the activation energy Ea of the aluminium corrosion in 0.5 M HCl in the presence of varying concentrations of TDG. The activation energy Ea was calculated using the expression [12] of Arrhenius equation given by:

$$\log \mathrm{CR} = \left(-\frac{\mathrm{Ea}}{2.303\mathrm{RT}}\right) + \log \mathrm{A} \text{ .... Eqn 5}$$

Where T is the temperature in kelvin, R is the universal gas constant (8.314J mol^{-1} K^{-1}) and A is the pre-exponential factor. A plot of log CR against $\frac{1}{\mathrm{T}}$ gives a straight line with slope $\left(-\frac{\mathrm{Ea}}{2.303\mathrm{R}}\right)$ and intercept (log A) as shown in Figure 6. and recorded in Table 2.

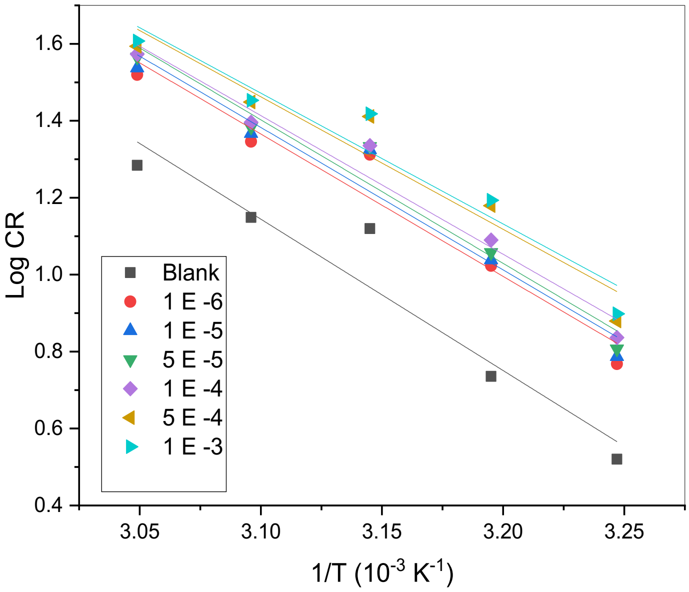

Figure 6: Arrhenius plots in the absence and presence of different concentrations of TDG on aluminium corrosion

As can be seen in Table 2, the values of activation energy in the presence of TDG are all lower than that of the blank. This implies that the presence of TDG enhances the dissolution of aluminium by lowering the energy barrier for the corrosion reaction by the process of adsorption on the aluminium surface [13]. Thus, TDG, is not an inhibitor rather an accelerator of the corrosion process. This result is in reverse order of those obtained for most inhibitors where the Ea increases with concentration of inhibitors [14] [15] [16]. In addition, since the values of Ea are all less than 80 kJ/mol [17] [18], physical adsorption of TDG on aluminium surface was proposed. The values of E_a for the corrosion process, both in the absence and presence of TDG, are greater than 20 kJ mol^{-1} and this suggests that the entire process is controlled by surface reaction [19].

Table 2: Corrosion activation energy for aluminium in 0.5M HCl in the absence and presence of different concentrations of TDG

Concentration of TDG (M)	Slope	Ea (kJ/mol)
Blank	-3.9356	75.36
1×10^{-6}	-3.7006	70.86
1×10^{-5}	-3.7053	70.95
5×10^{-5}	-3.7336	71.49
1×10^{-4}	-3.6043	69.01
5×10^{-4}	-3.4452	65.97
1×10^{-3}	-3.4017	65.13

3.3 Adsorption Isotherm/Thermodynamics

The degree of surface coverage values for TDG on the aluminium surface was obtained using equation 3. The results were fitted into Freundlich, Langmuir and El-Awady isotherm as shown in Figures 7 - 9. Based on the R^2 values obtained (Table 3), the experimental data fitted the Langmuir adsorption isotherm more Freundlich and then El-awady isotherm.

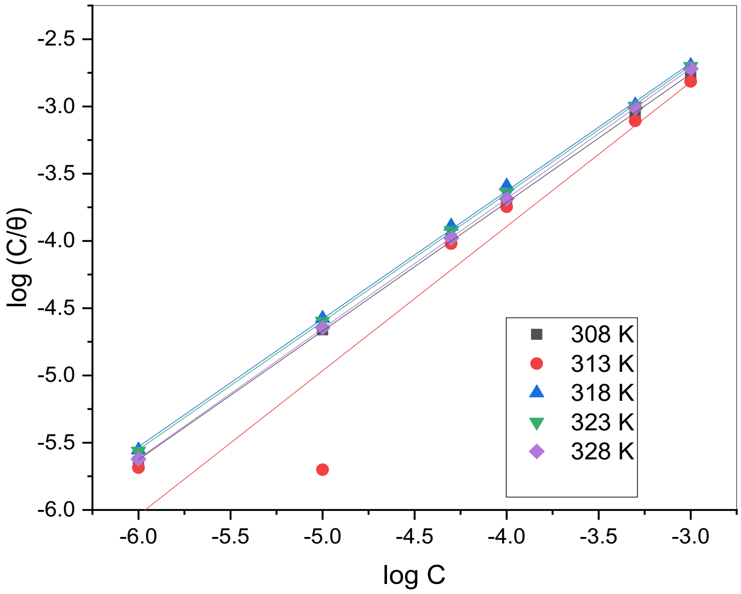

Figure 7: Langmuir adsorption isotherm plot for aluminium corrosion in 0.5 M HCl at 1 hour

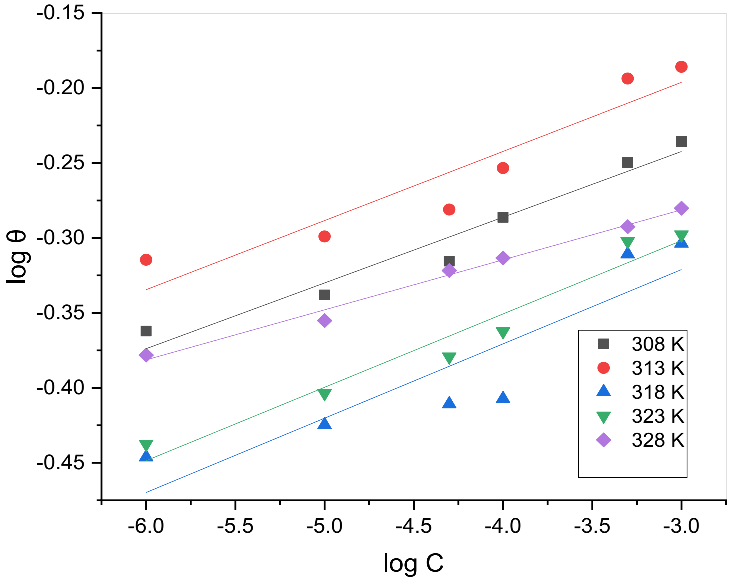

Figure 8: Freundlich adsorption isotherm plot for aluminium corrosion in 0.5 M HCl at 1 hour

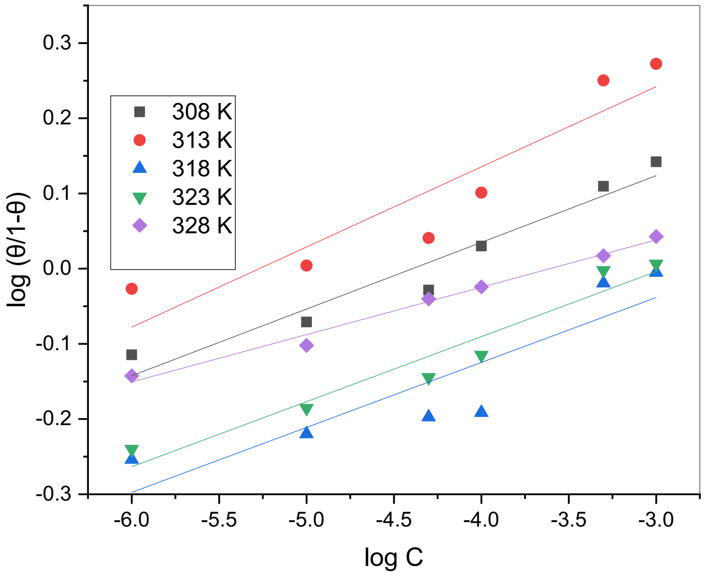

Figure 9: El-Awady adsorption isotherm plot for aluminium corrosion in 0.5 M HCl at 1 hour

The values of K_{ads} decreases with increase temperature. This shows that desorption of aqueous TDG from aluminium surface might have occur, thereby decreasing corrosion [20]. From the equilibrium adsorption constant K_{ads}, Gibb's free energy of adsorption ΔG_{ads}, was calculated using the expression [21]:

$$\Delta G_{ads} = -2.303RT \log K_{ads} \text{ ....Eqn 6}$$

From Table 3, the free energy values are all negatively less than the threshold value of - 40 kJ/mol required for mechanism of chemical adsorption to take place. Therefore, the adsorption of TDG on aluminium surface is spontaneous and consistent with physiosorption [22] [23] [24]. The enthalpy and entropy of adsorption of TDG on aluminium surface can better be explained using different thermodynamics equations - van't Hoff and Gibb's free energy [25]. van't Hoff equation is given by:

$$\ln K_{ads} = \frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} - \ln 55.5 \text{ .... Eqn 7}$$

Table 3: Isotherms for adsorption of TDG on aluminium surface

Isotherm	**Temperature (K)**	**R^2**	**Slope**	**intercept**	**K_{ads}**	**ΔG (kJ/mol)**
Langmuir	308	0.9999	0.9562	0.1108	0.7748	-9.631
	313	0.9070	1.0730	0.1560	0.6982	-9.517
	318	0.9994	0.9505	0.1725	0.6722	-9.418
	323	0.9990	0.9511	0.1552	0.6995	-9.826
	328	1.0	0.9666	0.1812	0.6589	-9.815
Freundlich	308	0.9567	0.0439	-0.1108	0.7748	-9.631
	313	0.8909	0.0461	-0.0579	0.8752	-10.105
	318	0.8127	0.0496	-0.1724	0.6724	-9.569
	323	0.9560	0.0489	-0.1550	0.6998	-9.827
	328	0.9894	0.0334	-0.1811	0.6590	-9.815
El-Awady	308	0.9434	0.0887	0.3896	2.4524	-12.582
	313	0.8662	0.1066	0.4209	2.6357	-12.974
	318	0.7965	0.0864	0.2209	1.6630	-11.963
	323	0.9415	0.0865	0.2557	1.8018	-12.367
	328	0.9874	0.0630	0.2273	1.6877	-12.380

A plot of $\ln K_{ads}$ against $\frac{1}{T}$ (Figure 10) gives a straight line with slope $\frac{\Delta H_{ads}}{R}$ and intercept $\frac{\Delta S_{ads}}{R} - \ln 55.5$. Gibb's free energy equation is given by :

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \text{ .... Eqn 8}$$

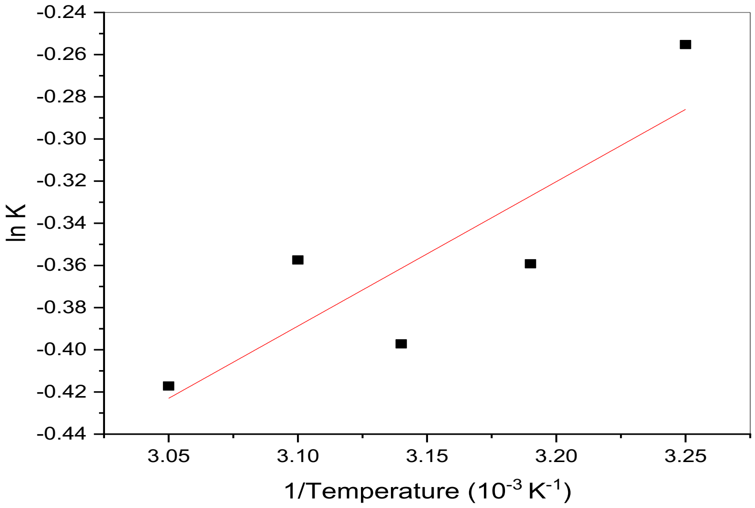

Figure 10: The relationship between $\ln K_{ads}^{\circ}$ and $\frac{1}{T}$

A graph of ΔG_{ads} against T (Figure 11) gives a straight line with slope $-\Delta S_{ads}$ and intercept ΔH_{ads}. The values of enthalpy and entropy of adsorption from the two plots were compared in Table 4. The values of the thermodynamic parameters obtained from the two equations are in good agreement.

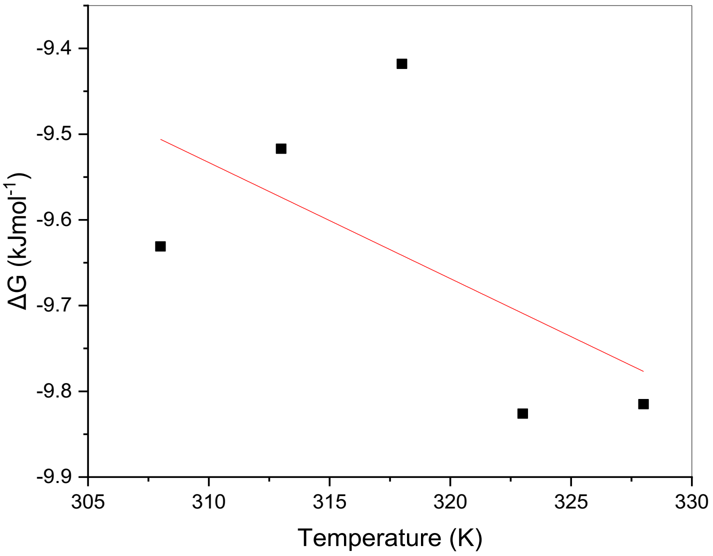

Figure 11: The relationship between ΔG_{ads}° and T

Table 4: Enthalpy and entropy of adsorption values calculated by different thermodynamic equations

Thermodynamic equation	**ΔH_{ads}° (kJ/mol^{-1})**	**ΔS_{ads}° (J mol^{-1} K^{-1})**
van't Hoff (Eqn 7)	-5.698	12.498
Gibb's free energy Change (Eqn 8)	-5.336	13.540

The results from Table 4 shows the negative values enthalpy of adsorption of TDG on the aluminium surface which corresponds to exothermic process while the positive value of entropy of adsorption indicates that the adsorption is accompanied by increase in disorderliness of the system (dissociation).

Conclusion

Thiodiglycolic acid acts as an accelerator of corrosion of aluminium in hydrochloric acid solution and cannot be used as corrosion inhibitor for aluminium in acid solution. This can be attributed to the fact that it is unable to form a passivation layer on the aluminium surface. This can be seen as TDG lowers the activation energy process thereby enhancing the corrosion reaction of aluminium in 0.5 M HCl.

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