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CONTENTS

CORROSION INHIBITION OF ALUMINIUM IN ACID MEDIUM USING CHRYSANTHEMUM FLOWER EXTRACT

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Abstract

Chrysanthemum flower extract as a green inhibitor for the corrosion inhibition of Aluminium in Hydrochloric acid solution was examined using weight loss, Potentiodynamic Polarization and Surface Examination Studies. It was found that the flower extract acts as a good inhibitor. The formation of the protective film on the metal surface may be due to the adsorption of the inhibitor on the metal surface which protects the metal surface from further corrosion. The results obtained showed that the inhibition efficiency increases with the increase in concentration of the inhibitor. The adsorption process was found to be spontaneous and it follows Langmuir adsorption isotherm. The protective film formed on the metal surface due to the adsorption of the inhibitor was confirmed by Scanning Electron Microscopy (SEM). Hence it was found that the Chrysanthemum flower extract acts as an inexpensive, eco-friendly and sustainable corrosion inhibitor.

Key Words: *Weight loss, protective film, inhibitor, adsorption*

1. Introduction

Aluminium which is the second most elements in the earth's crust offers a wide range of properties and applications. The excellent properties include light weight, ductility and conductivity. It is widely used in many industries. When aluminium surfaces are exposed to the atmosphere, a thin invisible oxide skin forms immediately, this protects the metal from further oxidation. This protective film offers high resistance to corrosion. The corrosion can be prevented mechanically by adding suitable substances called as inhibitors. The aim of adding the inhibitor to the corrosive media is to delay the reaction between the metal and the corrosive species in the medium. The organic compounds containing hetero atoms like chromates, sulphates, phosphates, etc., were used as the corrosion inhibitor, but the toxicity of these inhibitors to the environment has stimulated the search for the green inhibitors [1]. The green inhibitors are eco-friendly, cheap and they do not contain any toxic compounds and are found to be safe to the environment.

The purpose of the investigation is to reveal the use of the Chrysanthemum flower extract as a green inhibitor for the corrosion of aluminium in acid medium. The inhibition efficiency of the Chrysanthemum flower extract was determined by weight loss measurement and potentiodynamic polarization. It also follows the Langmuir and Temkin adsorption isotherms.

2. Experimental Methods

2.1 Preparation of the specimen

Aluminium metals of dimensions 1.0 cm x 4.0 cm x 0.1 cm containing 1.5% Pb, 0.1% Ga, 1% In and the remainder Al were mechanically polished to a mirror finish and degreased with acetone and used for the weight loss method and surface examination studies.

2.2 Preparation of the flower extract

An aqueous extract of Chrysanthemum flower was prepared by refluxing 5 g of shade dried Chrysanthemum flowers with double distilled water for 3 hours, cooled, filtering the suspended impurities, and making up to 200 ml. This extract was used as a corrosion inhibitor in the present study.

2.3 Weight loss method

The weight loss techniques are the conventional and simplest of all corrosion techniques. Aluminium metals were completely immersed in 100 ml of the test solution (0.5 N, 0.3 N and 0.1 N HCl) containing various concentrations of the inhibitor Chrysanthemum flower extract (PE) for a period of 3 hours. The weights of the specimen before and after immersion were determined using a digital balance. The corrosion inhibition efficiency (IE) was then calculated using the equation

$$IE = 100[1-(W_2/W_1)]\ \%$$

W_1 and W_2 are the corrosion rate in the absence and in the presence of the inhibitor.

Corrosion rate is calculated assuming uniform corrosion over the entire surface of the coupon. Corrosion rates (CR) are calculated from weight loss method using the formula

$CR = 534\ W / DAT$ Mils per year (mpy)

where, W = weight loss in milligrams, D = density of specimen g/cm^3, A = area of specimen in square inches, T = exposure in hours.

2.4 Potentiodynamic polarization

Polarization studies were carried out in a CHI electrochemical work station with impedance model 608 E. A three-electrode cell assembly was used. The working electrode was Aluminium metal. A SCE was the reference electrode. Platinum as the counter electrode. Both cathodic and anodic polarization curves were recorded in the absence and presence of the flower extract. From polarization studies, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = β_a and cathodic = β_c were calculated and a linear polarization study was done. The scan rate (V/S) was 0.01. Hold time at E_f(s) was zero and quiet time (s) was two.

2.5 AC Impedance Spectra

The same instrument used for polarization study was used to record AC impedance spectra also. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated.

2.6 Scanning Electron Microscope

The nature of the film formed on the surface of the aluminium was examined using SEM. The surface analysis of the aluminium for fresh, inhibited and uninhibited systems was investigated. Aluminium specimens immersed in blank and in the inhibitor solutions for a period of 3 hours was removed, rinsed with double distilled water, dried and observed under scanning electron microscopy to examine the surface morphology.

3. Results and Discussion

3.1. Weight loss method

The weight loss study was carried out with different concentrations of PE ranging from 2 ml to 10 ml. Their corresponding IE and CR are given in Table 1. It was observed that in all the systems the IE increases up to 8 ml and then it gets decreases. The highest IE of 88% was observed at 8 ml in 0.3N HCl when compared with the other systems. Hence this system was chosen as the best system for further studies. When IE increases the corresponding CR decreases. The results obtained also showed that the PE acts as an efficient inhibitor in acid solution [2].

Table 1 Corrosion inhibition efficiency (IE) and the corresponding corrosion rates (CR) in mills per year (mpy) of PE in controlling the corrosion of Aluminium in various acidic solutions

PE in ml	0.5N HCl		0.3N HCl		0.1N HCl	
	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)
0	0	231.5	0	160.67	0	137
2	41	136.58	52	77.12	21	108.23
4	46	125.01	67	53.02	32	93.16
6	52	111.12	77	36.95	39	83.57
8	**64**	**83.34**	**88**	**19.28**	**48**	**71.24**
10	53	108.84	62	61.05	36	87.68

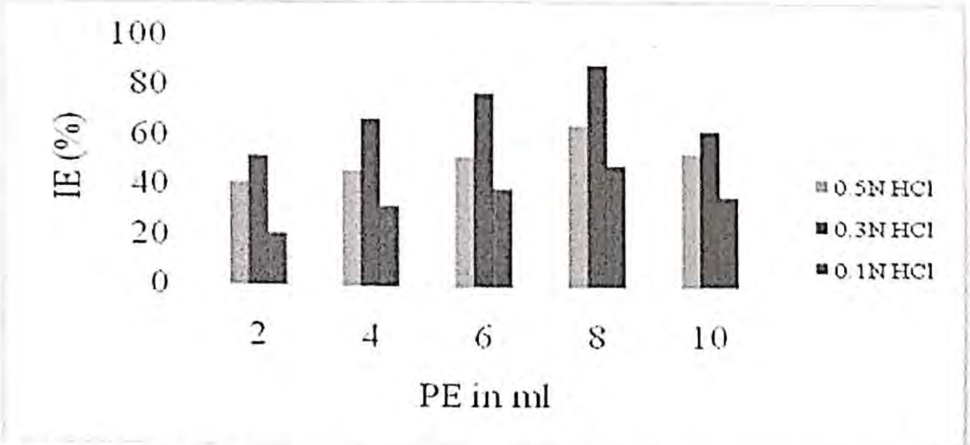

Figure 1 Graph of inhibition efficiency (IE) of PE in controlling the corrosion of Aluminium in various concentrations of acid (HCl)

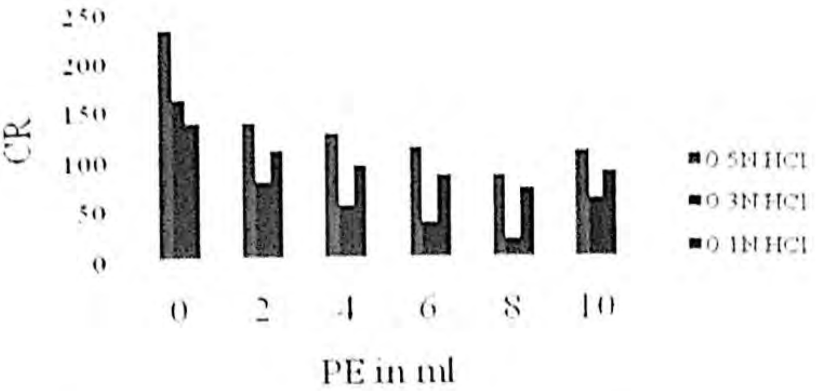

Figure 2 Graph of corrosion rate of PE in controlling the corrosion of Aluminium in various concentrations of HCl

3.2 Effect of influence period

The effect of inhibitor on the corrosion of aluminium in acid medium was studied at various exposure time periods. The variation in the IE has been reported in table 2. It was observed that IE increases up to 3 hours of exposure time, and then it was found to decrease. The decrease in the IE is due to the attack of the protective film by other ions present in the solution. Hence it was found that the protective film was stable up to 3 hours [3].

Table 2 Immersion period on the IE % of PE in 0.3N HCl

Time (h)	Immersion Period				
	1	2	3	4	5
IE (%)	37	70	88	67	42

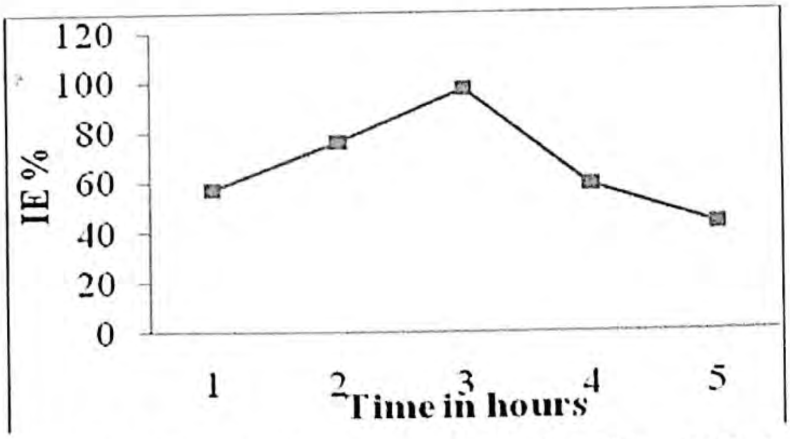

Figure 3 Graph of immersion period on the IE of PE in 0.3N HCl

3.3. Effect of Temperature

The corrosion behaviour of aluminium metal in 0.3N HCl in the absence and presence of various concentrations of PE was studied at different temperatures like 303 K. 313 K and 323 K for 3 hours of immersion period. The value of IE, CR and the surface coverage (θ) are tabulated in table 3. It can be seen from the table that the corrosion rate increases with the rise in temperature. As the temperature was increased from 303 K to 323 K, the IE was found to decrease, this shows that the adsorption of PE on the metal surface may be due to physical adsorption [4]. The high surface coverage data also implies that the adsorption of PE at the aluminium interface may be due to the electrostatic force between the atoms on the metal surface and the adsorbate (inhibitor molecules) [5]. By plotting the values of θ versus log C and C/θ values versus C, straight line graphs were obtained (Figure 4 and 5), which showed that Temkin and Langmuir adsorption isotherms are obeyed [6].

Table 3 Effect of Temperature on the IE of the PE

PE in ml	303 K			313 K			323 K		
	IE (%)	θ	CR (mpy)	IE (%)	Θ	CR (mpy)	IE (%)	Θ	CR (mpy)
0	67	0.67	127.5	57	0.57	193.7	46	0.46	321.3
2	74	0.74	33.15	65	0.65	67.795	53	0.53	151.01
4	77	0.77	29.325	71	0.71	56.173	65	0.65	112.45
6	82	0.82	22.95	79	0.79	40.677	72	0.72	89.964
8	86	0.86	17.85	83	0.83	32.929	80	0.80	64.26

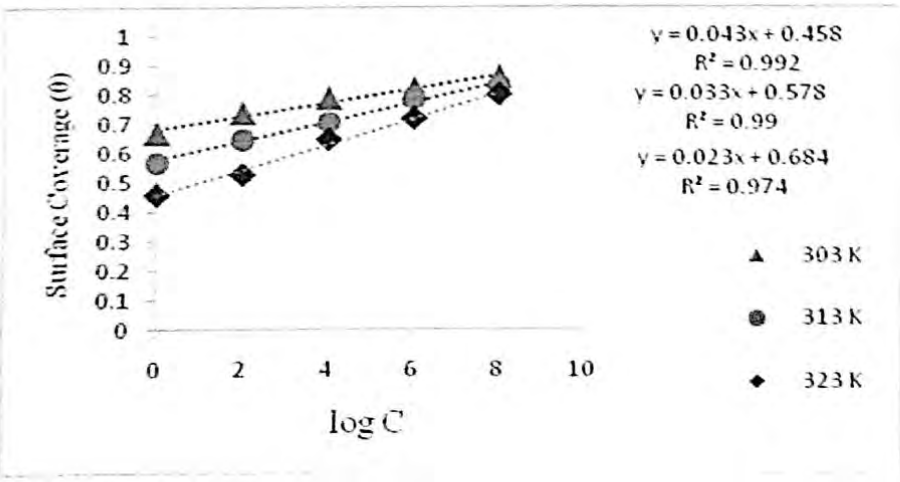

Figure 4 Temkin adsorption isotherm plotted as "θ" versus log "C" for aluminium corrosion in 0.3N HCl containing various concentrations of PE at 303 K to 323 K

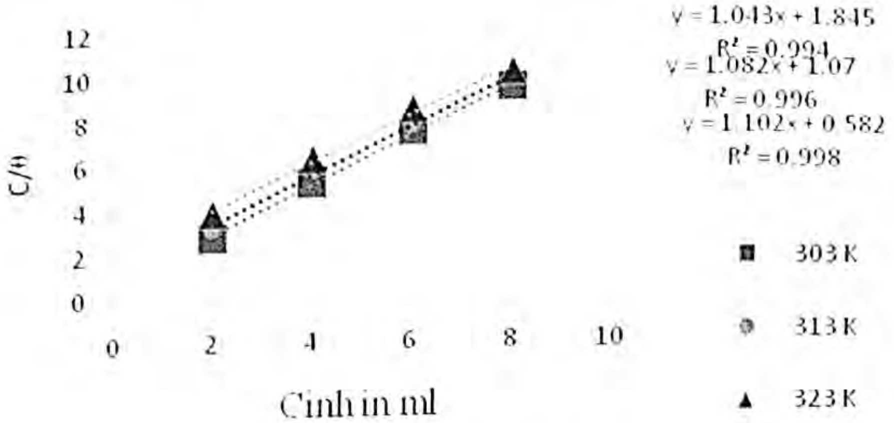

Figure 5 Langmuir adsorption isotherm plotted as "C/θ" versus "C" for aluminium corrosion in 0.3N HCl containing various concentrations of PE at 303 K to 323 K

3.4 Analysis of polarization curves

The cathodic and anodic polarization curves of aluminium in 0.3N HCl solution at various concentrations of PE in the absence and presence of the inhibitor is represented in figure 6. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (βa and βc) and linear polarisation resistance (LPR) are given in table 4. It was observed that both the cathodic and anodic reactions were suppressed with the addition of PE, which suggested that the inhibitor exerted an efficient inhibitory effect both on anodic dissolution of metal and on cathodic reduction reaction.

It is clear from table 4 that values of βc decreases with increasing extract concentration which is due to the adsorption of PE on the metal surface and the acid attack on the aluminium electrode was hindered by the addition of inhibitor. In the anodic branch the value of βa decreases in the presence of the inhibitor. The anodic slope value increases when compared with the cathodic slope. This suggests that the inhibitor predominantly controls the anodic reaction. The shift in the anodic tafel slope implies the modification of the anodic reaction due to the adsorption of inhibitor molecules on the active sites when compared to the free acid solution [7]. Table 4 also reveal that increasing the concentration of the PE give rise to a steady decrease in the anodic and cathodic current densities without much remarkable change in the corrosion potential. The above findings suggest that the PE acts as a mixed inhibitor [8].

Further inspection of table 4 indicates an increase in LPR value in the inhibited system compared with the uninhibited system suggests aluminium corrosion is reduced in the presence of the inhibitor [9]. The highest LPR value (1690.4 ohm cm²) was obtained at 8 ml of the PE indicates the formation of adherent protective film on the metal surface.

Table 4 Corrosion parameters for aluminium in 0.3N HCl solution in the absence and presence of various concentrations of the inhibitor obtained by polarization method

PE in ml	E_{corr} V VS SCE	I_{corr} A/cm²	βa (v/dec^{-1})	βc (v/dec^{-1})	LPR ohm cm²
0	-0.8390	1.099×10^{-5}	13.464	9.929	1015.7
2	-0.8299	2.131×10^{-6}	11.616	8.939	1127.1
4	-0.8292	2.103×10^{-6}	9.491	8.848	1320.5
6	-0.8256	1.856×10^{-6}	9.487	8.687	1488.3
8	-0.8214	1.413×10^{-6}	9.001	8.469	1690.4
10	-0.8225	1.657×10^{-6}	9.057	8.63	1669.6

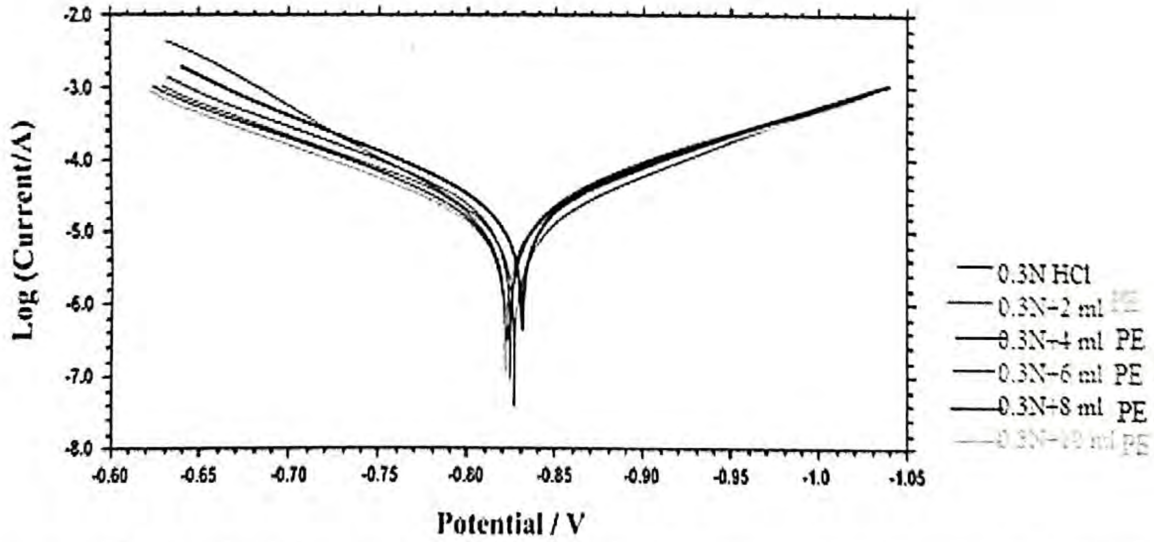

Figure 6 Polarization curves for aluminium in 0.3N HCl solution in the absence and presence of various concentrations of the inhibitor

Figure 6 denotes the potentiodynamic polarisation curves for the influence of Garlic Extract (GE) on the IE of PE. The corrosion parameters are given in the table 5. It was found that E_{corr} value for 0.3N HCl was -0.8390V versus SCE. When 2 ml of PE was added the E_{corr} decreases to -0.8299V versus SCE, on addition of the 8 ml of GE the E_{corr} value rises to -0.8325. i.e., the corrosion potential is shifted to the positive direction. It was also observed that the shift in the anodic slope (from13.464 to 9.931 V/dec) is greater than the cathodic slope (from 9.929 to 8.874 V/dec). Hence it was found that the inhibitor predominantly controls the anodic reaction. It was also observed that in the presence of GE, the I_{corr} was reduced from 2.131×10^{-6} A/cm² to 1.103×10^{-7} A/cm² and the LPR value was also increased from 1127.1 ohm cm² to 2537.2 ohm cm². Therefore mixture of inhibitors shows better IE than the individual inhibitors.

3.5 Analysis of AC impedance spectra

AC impedance spectra can be used to detect the formation of protective film on the metal surface. Figure 7 shows the Nyquist plots for aluminium in 0.3N HCl in the absence and presence of various concentrations of PE and their corresponding impedance parameters are represented in the table 5. It was observed that the Nyquist plots are approximately elliptical in nature. The elliptical nature of the plot was due to the formation of oxide film on Al surface. The increase in size and shape of the loop with the increase in concentration of the inhibitor may be attributed to the formation of protective layer on the metal surface and this further controls corrosion [10].

Table 5 Impedance parameters of aluminium in 0.3N HCl solution in the absence and presence of various concentrations of the PE

System	Nyquist plot	
	R_t ohm cm²	C_{dl} F/cm²
Blank	550	1.6449×10^{-8}
2 ml P.E	840	1.077×10^{-8}
4 ml P.E	1970	7.7328×10^{-9}
6 ml P.E	1170	7.0683×10^{-9}
8 ml P.E	1570	5.7627×10^{-9}
10 ml P.E	1410	6.4166×10^{-9}

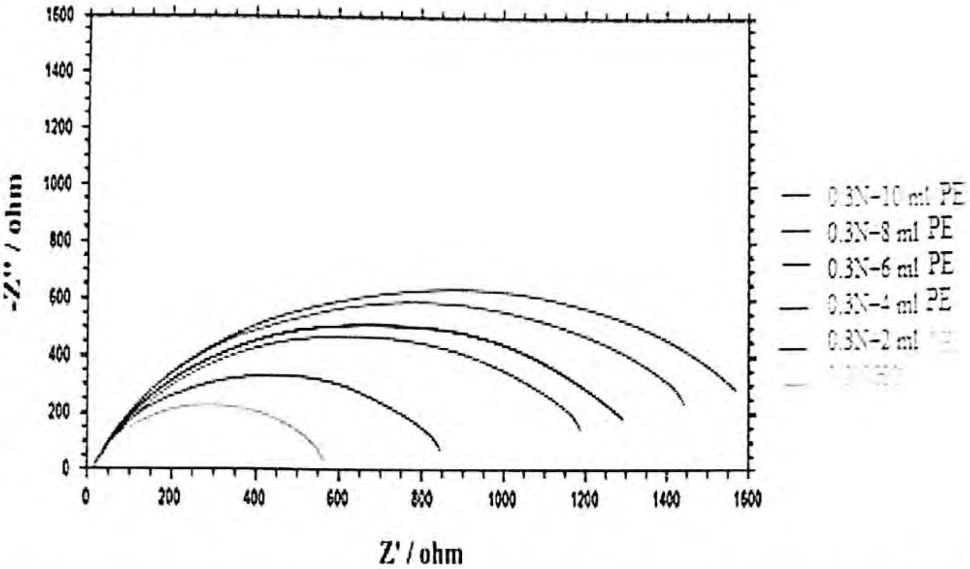

Figure 7 AC impedance spectra of aluminium immersed in 0.3N HCl and various concentrations of the inhibitor

3.6 Thermodynamic Parameters

The apparent activation energy, E_a for corrosion reaction of aluminium in absence and presence of various concentrations of inhibitor was calculated using the Arrhenius equation

$$\text{Log}\ (p_2/p_1) = E_a / 2.303R\ [1/T_1 - 1/T_2] \qquad (1)$$

where p_1 and p_2 are corrosion rates at temperatures T_1 and T_2 respectively, and R is gas constant. The values of free energy of adsorption ΔG_{ads}, of PE inhibitor on aluminium surface were calculated using equation (3) [11].

$$\Delta G_{ads} = -2.303\ RT \log\ (55.5\ K)$$

The calculated values of apparent activation energy (E_a), heat of adsorption (Q_{ads}), and free energy adsorption (ΔG_{ads}) of different concentrations of the PE are shown in table 6. The results show that the apparent activation energy E_a, increases as inhibitor concentration increases. Activation energy of PE ranged between 80.7 and 96.56 KJ/mol. Since corrosion primarily occurs at surface sites free of adsorbed inhibitor, the higher E_a values in inhibited solutions imply that extracts mechanically screen the active sites of aluminium surface thereby decreasing the surface area available for corrosion.

The heat of adsorption, Q_{ads} were all negative and ranged from -33.62 to -18.11 KJ/mol for PE. The negative Q_{ads} value indicate adsorption and hence inhibition efficiency decreases as temperature increases, supporting the earlier proposed physisorption mechanism.

The free energy adsorption ΔG_{ads}, were all negative in the temperatures under study. The negative value of adsorption showed the spontaneity of adsorption of the PE on the metal surface. This adsorption of inhibitor on the surface of aluminium may be physical adsorption ($\Delta G_{ads} < 40$ KJ/mol). Generally, the values of ΔG_{ads} around -20 KJ/mol or less negative are consistent with physisorption while those around -40 KJ/mol or more negative values involve chemisorptions [12]

Table 6 Thermodynamic parameters for the corrosion of aluminium in 0.3N HCl at different temperatures

PE in ml	Activation energy, E_a (KJ/mol)	Heat of adsorption Q_{ads} (KJ/mol)	Free energy change ΔG_{ads} (KJ/mol) of adsorption at 303 K	Free energy change ΔG_{ads} (KJ/mol) of adsorption at 313 K
0	80.7	-33.62	-11.90	-10.82
2	83.87	-33.66	-12.75	-11.67
4	87.62	-33.87	-13.45	-12.37
6	91.3	-15.09	-13.94	-13.45
8	96.56	-18.11	-14.69	-14.11

3.7 Surface Analysis

Surface examination of the aluminium species were made using Scanning Electron Microscope (SEM). The aluminium species before and after immersion in the presence and absence of the inhibitor for a period of 3 hours were taken out, washed carefully with distilled water, dried and kept in desiccators. The SEM micrographs of the examined surfaces are shown in figure 8 (a,b,c). The SEM micrograph of the polished aluminium metal surface was shown in figure 8 (a). It shows the smooth surface of the metal and this is due to the absence of corrosion products on the surface of the metal. The SEM micrograph of the aluminium metal surface 8 (b) immersed in 0.3N HCl was found to be severely corroded due to the aggressive attack by HCl.

Figure 8 (c) represents the surface analysis of the aluminium metal immersed in 0.3N HCl in the presence of 8 ml PE. The analysis showed that the aluminium metal surface was found to be smoother than the uninhibited surface. The improvement in the metal surface was due to the adsorption of the inhibitor over the metal surface. The adsorption of the inhibitor (PE) on the surface of the metal acts as a good protective film on the surface which further reduces the corrosion rate [13-15].

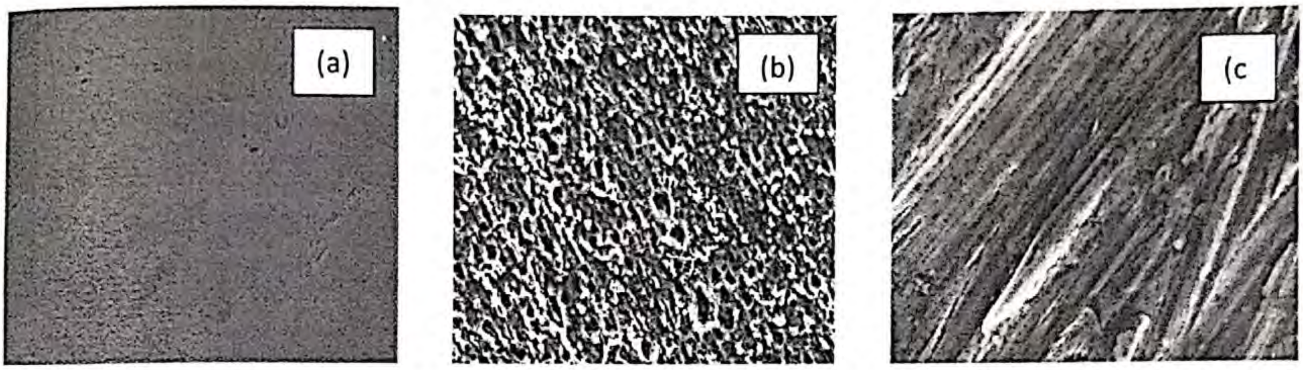

Figure 8 SEM micrographs of

(a) Polished Aluminium metal (control)

(b) Aluminium metal immersed in 0.3N HCl

(c) Aluminium metal immersed in 0.3N HCl containing 8 ml of PE

4. Conclusion

The following are some of the conclusion of the present study:

- The inhibition efficiency increases with the increase in the concentration of the inhibitor
- The protective film formed on the metal surface was able to withstand for a period of 3 hours
- It obeys Langmuir and Temkin adsorption isotherms
- There exist a physical adsorption between the inhibitor and the metal surface
- Potentiodynamic polarization study reveals that the inhibitor predominantly controls the anodic reaction
- The protective film formed on the surface of the metal was confirmed by SEM micrographs.

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