Polyethylene Glycol and Polyvinyl Alcohol as Corrosion Inhibitors for Aluminium in Acidic Medium

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ABSTRACT: The corrosion inhibition of aluminum in H_2SO_4 in the presence of polyethylene glycol (PEG) and polyvinyl alcohol (PVA) as inhibitors at 30–60 °C was studied using gravimetric, gasometric, and thermometric techniques. The inhibition efficiency (%I) increased with increase in concentration of the inhibitors. Increase in temperature increased the corrosion rate in the absence and presence of inhibitors but decreased the inhibition efficiency. Both PEG and PVA were found to obey Temkin adsorption isotherm at all concentrations and temperatures studied. Phenomenon of physical adsorption is proposed from the activation parameters obtained. Thermodynamic parameters reveal that the adsorption process is spontaneous. PEG was found to be a better inhibitor than PVA. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3363–3370, 2007

Key words: corrosion inhibition; polyethylene glycol-polyvinyl alcohol; adsorption isotherms; aluminum

INTRODUCTION

Corrosion of aluminum and its alloys has been the subject of numerous studies due to their importance and use in many industries, such as machinery, pipes, and reaction vessels, because of their advantages such as lightness and thermal conductivity. However, despite its importance, it is therefore imperative to add corrosion inhibitors to decrease the corrosion rate of aluminum in aqueous solutions. Numerous organic and inorganic compounds including natural occurring substances have been effectively applied to inhibit corrosion of aluminum in acidic environment. Generally, it has been shown that inhibitors established inhibition characteristics due to the presence of heteroatoms such as oxygen, nitrogen, sulfur, phosphorus, triple bonds, and aromatic rings in their molecules. Also it has been reported that the extent of adsorption of an inhibitor is greatly influenced by the nature and surface charge of the metal, the mode of adsorption, chemical structure of the inhibitor, and the type of aggressive electrolyte.[1–5] Physical (electrostatic) and chemical adsorption are the two main modes of adsorption that occur as a result of interaction between organic inhibitors and the metal surface.

In recent times, the use of polymers as corrosion inhibitors has attracted considerable attention. The successful use of homopolymers such as polyacrylamide, polyvinyl pyrollidone, polyacrylic acid, polyethyleneimine, polyaniline, polyvinylpyridine, polyvinylbipyridine, poly(4-vinylpyridine), and polyvinyl imidazoles as corrosion inhibitors have been widely examined.[6–15] The use of copolymers such as styrene-maleic acid and maleic acid-styrene-acrylic ester terpolymer as inhibitors has also been reported.[16–18] We have also reported the use of polyvinyl alcohol and polyethylene glycol as inhibitors of mild steel in H_2SO_4 in our research group.[19] Polymers are used as 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, thereby blanketing the surface and protecting the metals from corrosive agents present in solution.[20]

The present investigation is therefore aimed at studying the corrosion inhibition of aluminum using polyvinyl alcohol (PVA) and polyethylene glycol (PEG) in acidic medium at 30–60°C using gravimetric (weight loss), gasometric (hydrogen evolution), and thermometric methods.

EXPERIMENTAL

Materials

The purity, composition, and preparation of aluminum sheet used in this study were as previously reported

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elsewhere.[21,22] The aluminum coupons were used as cut without further polishing. However, they were degreased in absolute ethanol, dried in acetone, and stored in moisture-free desiccators before use in the corrosion studies. Polyvinyl alcohol (PVA) and polyethylene glycol (PEG) used as inhibitor were obtained from BDH Laboratory Supplies, England, and were used without further purification. The concentration of PEG and PVA used in this study are 10^{-4}–$10^{-5}M$. The concentration of corrodent (H_2SO_4) (BDH Laboratory Supplies Chemicals, England) prepared and used in the study was in the range 0.002–0.1M. All preparations were made using doubly distilled water. The study was carried out at 30–60°C. The temperatures were maintained using a thermo-stated water bath.

Gravimetric measurements

In gravimetric measurements, a clean and weighed aluminum coupon was completely immersed in a beaker with the aid of a glass rod and hook. After 24 h of immersion in different concentrations of H_2SO_4 without inhibitors and in 0.1M H_2SO_4 containing different concentrations of PVA and PEG, they were removed progressively for 168 h (7 days), immersed in concentrated (70%) nitric acid (S.G. 1.42) at room temperature for 2 min, scrubbed with a bristle brush under running water, dried in acetone, and weighed.[23] The weight loss of the coupons was evaluated in grams as the difference in the weight of the coupons. The weight loss was used to calculate the corrosion rate using the formula:

$$\text{Corrosion rate (mpy)} = \frac{534W}{\rho At} \qquad (1)$$

where W is the weight loss (g), ρ is the density of the specimen (g/cm^3), A is the area of specimen (cm^2), and t is the exposure time (h).

The inhibition efficiency of PVA and PEG acting as inhibitor in 0.1M H_2SO_4 was calculated using the following expression:

$$I(\%) = \left(1 - \frac{W_i}{W_o}\right) \times 100 \qquad (2)$$

where W_0 and W_1 are the corrosion rates of aluminum in the absence and presence of inhibitors, respectively, in H_2SO_4 at the same temperature.

The degree of surface coverage (θ) is given by:

$$\theta = 1 - \frac{W_i}{W_o} \qquad (3)$$

Gasometric technique

The apparatus and procedure for corrosion monitoring using this technique has been described else-

where.[24–27] The volume of the test solution was kept at 100 mL. The progress of the corrosion reaction was monitored by careful measurement of the volume of hydrogen gas evolved at fixed time intervals. Experiments were conducted at 30–60°C but with a corrodent concentration of 2M H_2S0_4.

The inhibition efficiency was evaluated using the equation:

$$I(\%) = \left(1 - \frac{V^1_{Ht}}{V^o_{Ht}}\right) \times 100 \qquad (4)$$

where V^1_{Ht} is the volume of H_2 gas evolved at time 't' for inhibited solution and V^o_{Ht} for uninhibited solution.

Thermometric method

The apparatus and procedure for corrosion monitoring using this technique has been described elsewhere by other authors.[28–30] The volume of the test solution was kept at 50 mL. The initial temperature in all experiments was kept at 30°C. The variation of temperature with time was monitored per minute for 60 min in a calibrated thermometer (0–100°C) to the nearest ±0.05°C. This technique allowed for evaluation of reaction number (RN) defined as:

$$\text{RN}(^{\circ}\text{C min}^{-1}) = \frac{T_m - T_i}{t} \qquad (5)$$

where T_m and T_i are the maximum and initial temperatures respectively, and 't' is the time (min) taken to reach the maximum temperature. The inhibition efficiency (%I) was evaluated from percentage reduction in the reaction number namely:

$$\%I = \frac{\text{RN}_{aq} - \text{RN}_{wi}}{\text{RN}_{aq}} \times 100 \qquad (6)$$

where RN_{aq} is the reaction number in the absence of inhibitors (that is, 2M H_2SO_4) and RN_{wi} is the reaction number of 2M H_2SO_4 containing PEG and PVA.[24,31]

RESULTS AND DISCUSSION

Effect of corrodent concentration and temperature on corrosion rate

The corrosion of aluminum in different concentrations of H_2SO_4 at 30–60°C in the absence of the inhibitors was investigated. Figure 1 shows the variation of corrosion rate against acid concentration at all the temperatures studied. From the figure, it is clearly seen that the corrosion rate of aluminum varies with concentration of acid, that is, corrosion
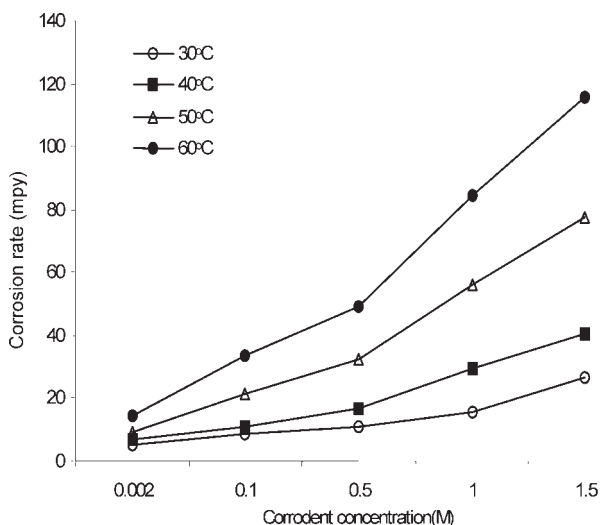
Figure 1 Plot of corrosion rate against acid concentration for aluminum in $0.1M$ H_2S0_4 at different concentrations.

rate increases with increase in acid concentration. The figure also reveals that corrosion rate increased with increase in temperature. The highest corrosion rate for aluminum was observed with acid concentration of $1.5M$ at $60°C$. This observation is attributed to the fact that the rate of chemical reaction increases with increasing acid concentration.

Effect of inhibitors concentration and temperature on the inhibition efficiency

The corrosion of aluminum in H_2SO_4 at $30–60°C$ in the presence of different concentrations of PEG and PVA as inhibitors was also investigated using an

acid concentration of $0.1M$. Figure 2 shows the plot of corrosion rate against inhibitor concentration for PEG [Fig. 2(a)] and PVA [Fig. 2(b)] at different temperatures. The figure shows that both PVA and PEG actually inhibited the H_2SO_4 induced corrosion of aluminum to an appreciable extent. In comparison with Figure 1, the corrosion rate of aluminum in $0.1M$ H_2SO_4 containing PEG and PVA [Fig. 2(a,b)] were greatly reduced. Figures 1 and 2 reveal that aluminum corrosion by H_2SO_4 occurs not by simple homogenous process but by a heterogeneous one consisting of different or same rates. This assertion is made from the nonuniformity or nonlinearity of the plots obtained.

Figure 3 shows the plot of inhibition efficiency against inhibitor concentration for aluminum in $0.1M$ H_2SO_4 containing PEG [Fig. 3(a)] and PVA [Fig. 3(b)] at $30–60°C$. Inspection of the figure reveals that inhibition efficiency increases with increase in concentration of the inhibitor at all the temperatures studied. Also inhibition efficiency decreases with increasing temperature. A decrease in inhibition efficiency with increasing temperature suggests physical adsorption mechanism. It is also quite clear that from what is known about dependence of adsorption as temperature rises, that the quantity of equilibrium of adsorption decreases[32] and as a result, the plot of higher temperatures is below the lower ones. This is clearly demonstrated in Figure 3; panels a (PEG) and b (PVA) show that both PEG and PVA were physically adsorbed on aluminum surface since the plot of $60°C$ is under that of $30°C$. The decrease in inhibition efficiency with increase in temperature may be due to the fact that most effects at elevated tempera-
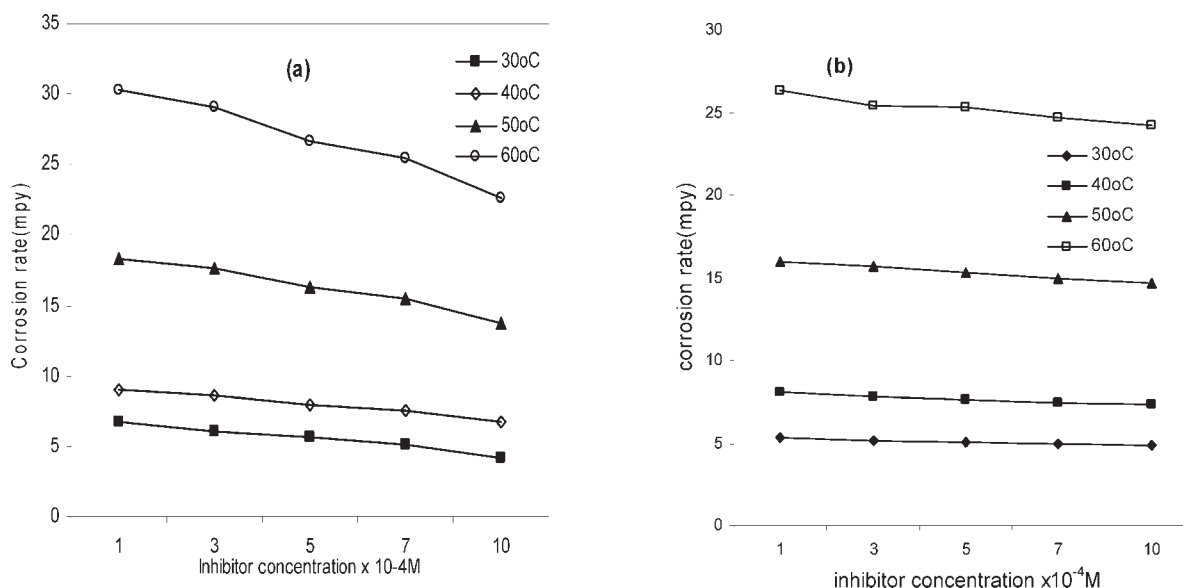

Figure 2 Plot of corrosion rate against inhibitor concentration for aluminum in $0.1M$ H_2S0_4 solution containing (a) PEG and (b) PVA at different temperatures.
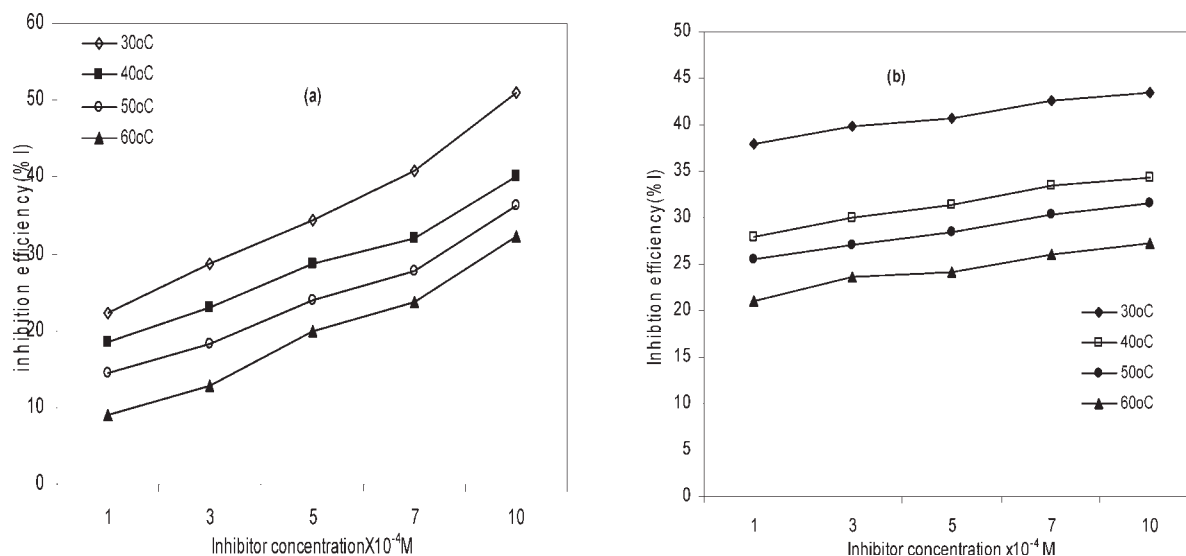
Figure 3 Plot of inhibition efficiency (%I) against inhibitor concentration for aluminum in $0.1M$ H_2SO_4 solution containing (a) PEG and (b) PVA at different temperatures.

tures are adverse to corrosion inhibition by increasing the corrosion rate and decreasing the tendency of the inhibitor to be adsorbed on the metal surface.

Table I shows the values of the inhibition efficiencies (%I) for aluminum in $0.1M$ H_2SO_4 with PEG and PVA, from weight loss, hydrogen evolution at $30°C$, and thermometric methods. The table shows that inhibition efficiency values increases with increase in the inhibitors concentration. It could be deduced from the table that PEG is a better inhibitor than PVA (it has higher values of inhibition efficiency from the three methods employed in the study). Results presented in the table also revealed that the inhibition efficiencies obtained from gasometric and thermometric methods are somehow higher than that from gravimetric technique. This may be attributed to the fact that the weight loss methods gives average corrosion rates, whereas the other two methods give more or less instantaneous corrosion rates.

Adsorption studies

Results obtained from this study have clearly shown that inhibition efficiency increases with increase in inhibitors concentration and decreases with temperature rise. Increase in inhibition efficiency with increase in concentration indicates that inhibition is due to adsorption of inhibitor molecules on the aluminum surface, whereas the decrease in inhibition with temperature may be attributed to desorption of molecules from the metal surface at higher temperature.[33] It is generally assumed that the adsorption of inhibitor molecules at the metal/solution interface is the first step in the mechanism of inhibition in acidic

medium. The adsorption process may occur at the metal/solution interface by:

i. Electrostatic attraction between the charged molecules and charged metal.
ii. Interaction of uncharged electrons pairs in the molecule with the metal.
iii. Interaction of π electrons with the metal.
iv. Combination of (i) and (ii).

The relationship between the amount of inhibitor adsorbed on the unit area of the metal surface and the concentration of the inhibitor molecules in the solution at a given temperature is given by the adsorption isotherm. The values of degree of surface coverage (θ) for different concentration of the compound studied at $30–60°C$ have been employed and

TABLE I
Inhibition Efficiency Values Obtained from the Gravimetric, Gasometric at $30°C$ and Thermometric Methods

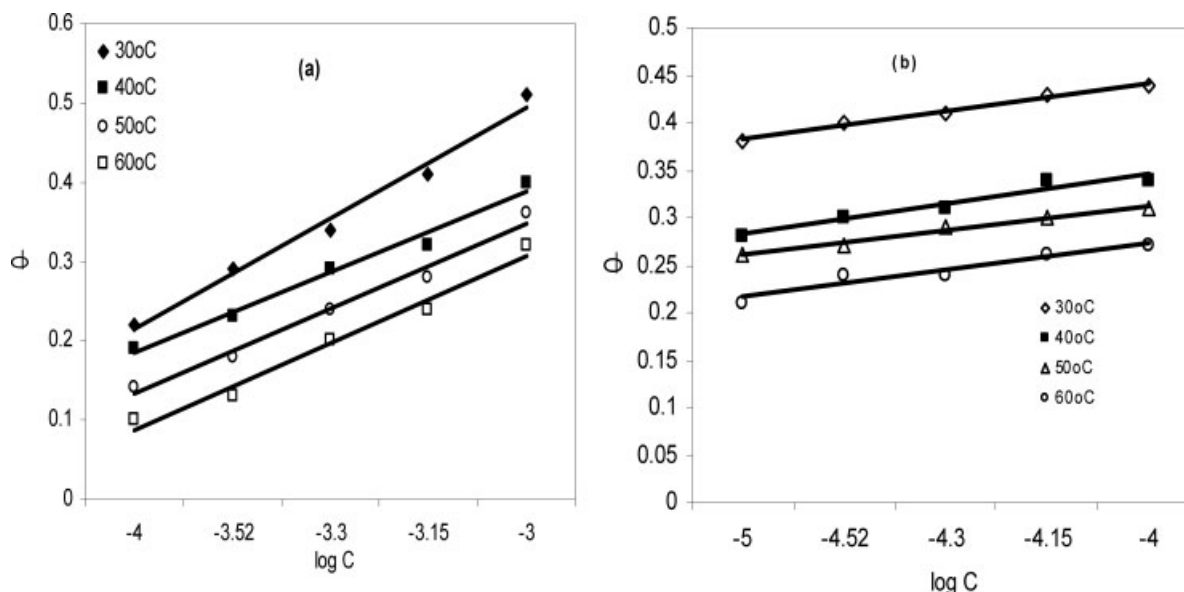| Inhibitor/ concentration (M)	Gravimetric method	Gasometric method	Thermometric method
PEG			
1×10^{-4}	50.93	45.07	54.69
7.0×10^{-5}	40.71	43.66	45.50
5.0×10^{-5}	34.33	36.62	35.48
3.01×10^{-5}	28.72	32.39	24.86
1.0×10^{-5}	22.23	29.58	14.93
PVA			
1×10^{-4}	43.52	42.25	51.01
7.0×10^{-5}	42.59	40.85	48.68
5.0×10^{-5}	40.74	39.43	36.59
3.01×10^{-5}	39.81	38.03	24.42
1.0×10^{-5}	37.96	33.80	17.59

Figure 4 Temkin adsorption isotherm plot as θ against log C for aluminum in $0.1M$ H_2SO_4 solution containing (a) PEG and (b) PVA at different temperatures.

are useful in explaining the best isotherm to determine the adsorption process. The values of degree of surface coverage were applied to various adsorption isotherms. By far, the best result was obtained for the Temkin adsorption isotherm. Figure 4 shows the plot of surface coverage (θ) as a function of logarithm of inhibitor concentration. From the plot, straight lines were obtained for PEG [Fig. 4(a)] and PVA [Fig. 4(b)] indicating that the experimental data fits well into Temkin adsorption isotherm given by the equation:

$$\exp(-2a\theta) = KC \qquad (7)$$

where a is molecules interaction parameter, θ is the degree of surface coverage, K is the equilibrium constant of adsorption process and C is the concentration of the inhibitors.

The linear correlation coefficients, molecular interaction parameters a and the adsorption coefficient deduced from Temkin adsorption isotherm plot (θ versus log c) are listed in Table II. From the table, it is clear that the experimental data obtained and hence the adsorption of PEG and PVA followed Temkin adsorption isotherm. At all the temperatures studied, all values of a are negative, indicating that repulsion exits in the adsorption layer.[34] The linear correlation coefficients are quite good. It is a known fact that K denotes the strength between adsorbate and adsorbent. The values of K as presented in Table II reveals that the adsorption coefficient decreases as the temperature increases. This is a clear indication that adsorption and hence inhibition efficiency decreases with rise in temperature.

Thermodynamic studies

The thermodynamic parameters for the dissolution of aluminum in $0.1M$ H_2SO_4 in the absence and presence of various concentrations of PEG and PVA were obtained by applying Arrhenius equation [eq. (8)] and transition state equation [eq. (9)], respectively.

$$\log CR = -E_a/2.303RT + \log A \qquad (8)$$

$$CR = RT/Nh \, \exp\,(\Delta S^o/R)\exp\,(-\Delta H/RT) \qquad (9)$$

where CR is the corrosion rate, E_a is the apparent activation energy, ΔS^o is the entropy of adsorption, ΔH^o is the enthalpy of adsorption, h is the Planck's constant, and N is the Avogadros number.

Figure 5 represents Arrhenius plot as log CR versus $1/T$ for $0.1M$ H_2SO_4 in the absence and presence of various concentration of PEG [Fig. 5(a)] and PVA [Fig. 5(b)]. Linear plots were obtained. The values of

TABLE II
Some Parameters of the Linear Regression from Temkin Isotherm Plot

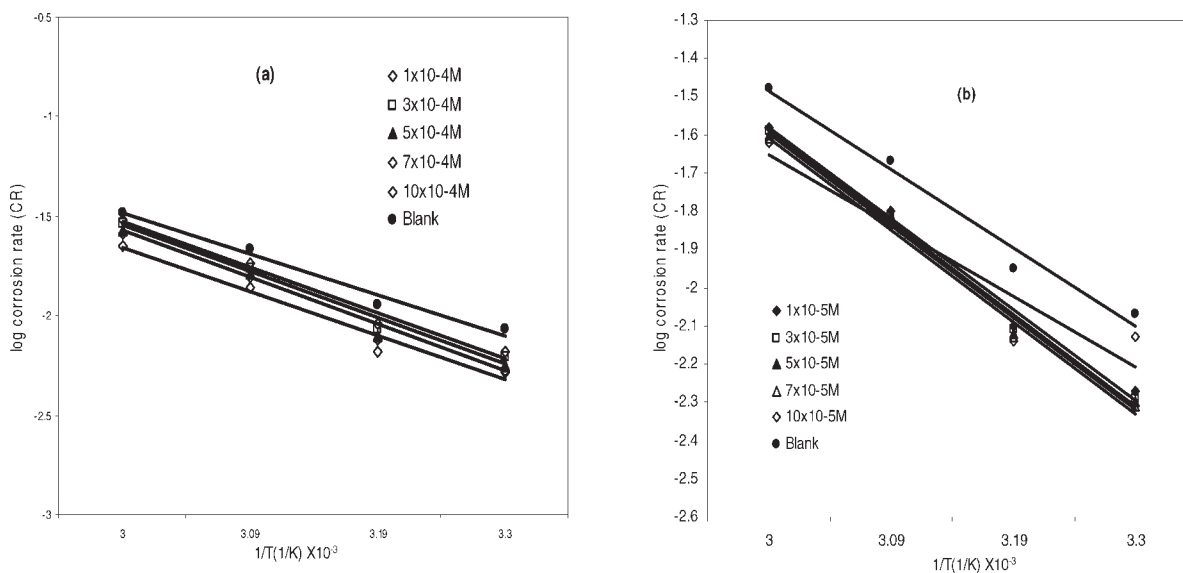| Inhibitor	Temperature (°C)	a	K (M^{-1})	Linear correlation coefficient
PVA	30	-14.47	2.88×10^{24}	0.9868
	40	-13.57	4.27×10^{16}	0.9412
	50	-16.70	9.77×10^{18}	0.9826
	60	-15.51	2.69×10^{14}	0.9245
PEG	30	-3.10	406.44	0.9855
	40	-4.26	113.76	0.9808
	50	-4.02	27.80	0.9851
	60	-3.95	3.98	0.9796

Figure 5 Arrhenius plot as log corrosion rate (CR) against $1/T$ for aluminum in 0.1M H$_2$SO$_4$ solution containing (a) PEG and (b) PVA.

E_a were obtained from the slope of the Arrhenius plot and are presented in Table III.

The enthalpy of adsorption, ΔH^o for dissolution of aluminum in 0.1M H$_2$SO$_4$ in the absence and presence of various concentrations of PEG and PVA was obtained from eq. (10). A plot of log (CR/T) against $1/T$ was made for PEG [Fig. 6(a)] and PVA [Fig. 6(b)]. Straight lines were obtained with a slope of ($-\Delta H^o/2.303R$). The values of ΔH^o obtained from the slope of Figure 6 for PEG and PVA are presented in Table III.

The entropy of adsorption ΔS^o was obtained using the equation:

$$\Delta G^o_{ads} = \Delta H^o - T\Delta S^o \qquad (10)$$

The calculated values of ΔS^o at 30°C are presented in Table III. The values of ΔS^o as shown in the table are

TABLE III
Activation Parameters for Aluminium Corrosion in the Presence of PEG and PVA in 0.1M H$_2$SO$_4$

Inhibitor/ Concentration	E_a (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol)
Blank	3.93	−4.67	
PEG			
1×10^{-4} M	4.23	4.53	0.073
7.0×10^{-5} M	4.47	4.37	0.072
5.0×10^{-5} M	4.50	4.193	0.071
3.01×10^{-5} M	4.42	4.21	0.071
1.0×10^{-5} M	4.37	4.12	0.071
PVA			
1×10^{-4} M	3.52	4.35	0.078
7.0×10^{-5} M	4.50	4.32	0.077
5.0×10^{-5} M	5.85	4.35	0.078
3.01×10^{-5} M	5.18	4.29	0.077
1.0×10^{-5} M	4.54	4.26	0.077

positive and indicates a decrease in the systems order in the presence of the inhibitors.[35]

From Table III, it is seen that activation energy increases in the presence of the inhibitors (PEG and PVA) compared to the blank. This can be attributed to an appreciable decrease in the adsorption process of the inhibitors on the metal surface with increase in temperature and a corresponding increase in reaction rate of greater area of the metal that is exposed to the acid.[28,33]

The free energy of adsorption, ΔG^o_{ads} were obtained from the intercept of the plot of logarithm of inhibition efficiency against the logarithm of inhibitor concentration for PEG [Fig. 7(a)] and PVA [Fig. 7(b)] and calculated using the expression:

$$\log C = \log \theta/(1 - \theta) - \log B \qquad (11)$$

Where log $B = -1.74 - (\Delta G^o_{ads}/2.303RT)$ and C is the inhibitor concentration. The calculated values of ΔG^o_{ads} within the range of temperature (30–60°C) studied reveals that ΔG^o_{ads} values for PEG ranged from -16.45 kJ mol^{-1} to -17.48 kJ mol^{-1} with an average value of -17.208 kJ mol^{-1}, while for PVA the values range from -19.40 kJ mol^{-1} to -19.19 kJ mol^{-1} with an average value of -19.22 kJ mol^{-1} The values of ΔG^o_{ads} are negative which reveals the spontaneity of the adsorption process and the stability of the adsorbed layer on the aluminum surface. Since the values of ΔG^o_{ads} of -40 kJ mol^{-1} is usually accepted as a threshold value between chemisorption and physiosorption, the obtained values of ΔG^o_{ads} for both PVA and PEG are below -40 kJ mol^{-1} which is consistent with electrostatic interactions between charged molecules and charged metal which are indicative of physiosorption.
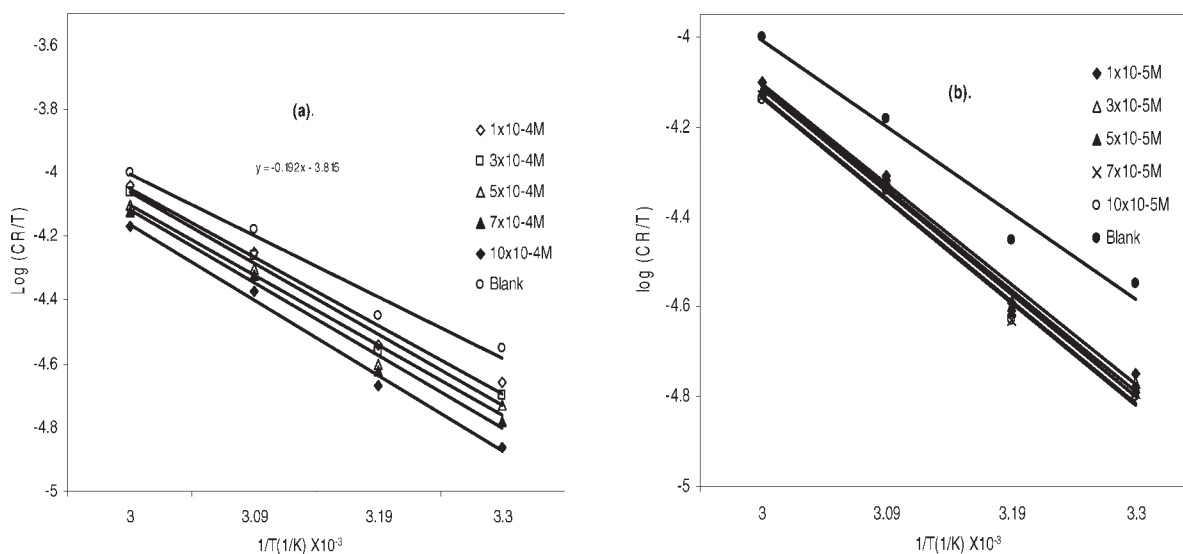
Figure 6 Transition state plot as log (CR/T) versus $1/T$ for aluminum in 0.1M H$_2$SO$_4$ containing (a) PEG and (b) PVA.
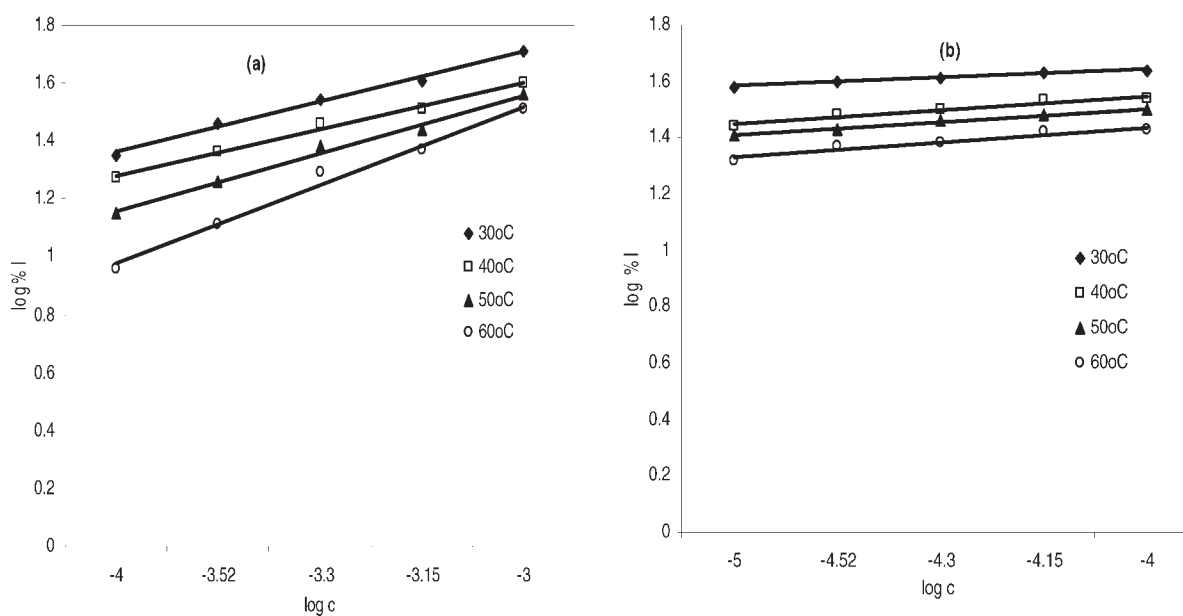

Figure 7 Plot of log inhibition efficiency (%I) against log of inhibitor concentration (a) PEG and (b) PVA at different temperatures.

CONCLUSIONS

1. PEG and PVA act as inhibitor for aluminum corrosion in acidic medium.
2. Inhibition efficiency of PEG and PVA increases with increase in concentration of the inhibitors but decreases with increase in temperature.
3. The values of ΔG^o_{ads} are negative which suggest that the inhibitors were strongly adsorbed on the aluminum surface. The values obtained support the physical adsorption mechanism.
4. PEG and PVA were found to obey Temkin adsorption isotherm from the fit of experimental data.

5. Thermodynamic parameters reveal that the adsorption process is spontaneous.

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