

Effect of Halide Ions on the Corrosion Inhibition of Aluminium in Alkaline Medium Using Polyvinyl Alcohol

S. A. Umoren,¹ E. E. Ebenso,² P. C. Okafor,² U. J. Ekpe,² O. Ogbobe³

¹Department of Chemistry, University of Uyo, Uyo, Nigeria

²Physical Chemistry Unit, Department of Pure and Applied Chemistry, University of Calabar, Calabar, Nigeria

³Department of Polymer and Textile Engineering, Federal University of Technology, Owerri, Nigeria

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ABSTRACT: The corrosion inhibition of aluminum in NaOH in the presence of polyvinyl alcohol (PVA) at 30 and 40°C and the effect of addition of halides (KCl, KBr, KI) were studied using weight loss and hydrogen evolution methods. Results obtained showed that PVA acts as a corrosion inhibitor in the alkaline environment. The inhibition efficiency increased with increase in concentration of PVA and synergistically increased on the addition of the halides but however decreased with rise in temperature. The phenomenon of physical adsorption is proposed from the obtained E_a and

Q_{ads} values. PVA was found to obey Freundlich and Frumkin adsorption isotherms. The increase in inhibition efficiency I (%), surface coverage θ values as well as synergistic parameter, S_I were found to be in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$, which clearly indicates that the radii and electronegativity of the halides play a significant role in the adsorption process. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2810–2816, 2007

Key words: polyvinyl alcohol; synergism; adsorption isotherms; halide ions; alkaline; corrosion inhibition

INTRODUCTION

Aluminum enjoys enhanced commercial usage due to its numerous desirable properties such as lightness, high thermal conductivity, resistance to attack, reflecting surface to mention but a few. The greatly expanded industrial applications of this metal with respect to its properties have received a great deal of considerable attention. However, despite the aforementioned importance, the problem of corrosion of aluminum especially pitting corrosion still remains a cause of concern to all and sundry. Corrosion is indeed one of the major problems affecting performance, safety, and appearance of this metal. Several methods have been devised for preventing or reducing corrosion, which include coating, painting, as well as the use of chemical inhibitors. The use of some organic and inorganic compounds as inhibitors for corrosion inhibition of aluminum in acid environment has been reported.^{1–16} The use of polymers as corrosion inhibitors has attracted considerable attention recently. Polymers such as polyvinylpyridine, polyvinyl bipyridine, polyvinylpyrrolidone, polyvinylpyrrolidone (PVP), polyethylenimine, polyaniline, polyacrylic acid, polyacrylamide, and polyvinylimidazoles have been studied.^{7–13}

However, these investigations were conducted in acidic medium. Corrosion inhibition of aluminum using polymers in alkaline environment has not been reported at all. Furthermore, synergistic effect of halide ions has been studied using different compounds as inhibitors on different materials by different research groups,^{14–23} but report on effects on polymers is scanty.^{24,25} Therefore, in this present work, we have examined the inhibition of corrosion of aluminum in NaOH by polyvinyl alcohol (PVA) and the effect of addition of halides (KCl, KBr, and KI) on the efficiency of PVA as potential corrosion inhibitor, as well as proposing a suitable mechanism for the inhibition using the weight loss and hydrogen evolution methods at 30 and 40°C.

EXPERIMENTAL

Materials preparation

Aluminum metal with purity 98.5% of the type AA 1060 obtained from System Metal Industries Limited Calabar, Nigeria was used in the present study. Each sheet was 0.4 mm in thickness and was mechanically press cut into 5 cm × 4 cm coupons. These coupons were used as cut without further polishing. However, they were degreased in absolute ethanol, dried in acetone, and stored in moisture-free desiccator before their use in corrosion studies. Polyvinyl alcohol (PVA) used as inhibitor (molecular weight of 65,000 g mol⁻¹ and 100% hydrolyzed) was obtained from BDH Laboratory Supplies Chemicals, England, and

Correspondence to: S. A. Umoren (saviourumoren@yahoo.com) or E. E. Ebenso (ebenso@unical.anpa.net.ng) or (eno_ebenso@yahoo.com).

TABLE I
Calculated Values of Weight Loss (g), Corrosion Rate (mpy), Inhibition Efficiency, *I* (%), and Degree of Surface Coverage (θ) for Aluminium in 0.1M NaOH, PVA(Inhibitor), and PVA–Halide Combination for Different Systems at 30°C and 40°C from Weight Loss Data

	Weight loss (g)		Corrosion rate (10^{-1} mpy)		Inhibition efficiency, <i>I</i> (%)		Surface coverage (θ)	
	30°C	40°C	30°C	40°C	30°C	40°C	30°C	40°C
0.1M NaOH (Blank)	0.784	0.984	0.53	0.665	–	–	–	–
1.0×10^{-4} PVA	0.514	0.689	0.347	0.407	34.4	30	0.344	0.3
7.0×10^{-5} PVA	0.532	0.782	0.36	0.529	32.1	20.5	0.321	0.205
5.0×10^{-5} PVA	0.581	0.854	0.393	0.577	25.9	13.2	0.259	0.132
3.0×10^{-5} PVA	0.61	0.887	0.412	0.6	22.2	9.9	0.222	0.099
1.0×10^{-5} PVA	0.665	0.904	0.444	0.611	16.5	8.1	0.165	0.081
0.05KCl + 1×10^{-4} M PVA	0.41	0.603	0.277	0.408	47.7	38.7	0.477	0.387
0.05KCl + 7×10^{-5} M PVA	0.443	0.765	0.299	0.517	43.5	22.3	0.435	0.223
0.05KCl + 5×10^{-5} M PVA	0.462	0.82	0.312	0.554	41.1	16.7	0.411	0.167
0.05KCl + 3×10^{-5} M PVA	0.484	0.867	0.327	0.886	38.3	11.9	0.383	0.119
0.05KCl + 1×10^{-5} M PVA	0.526	0.882	0.356	0.596	32.9	10.4	0.329	0.104
0.05KBr + 1×10^{-4} M PVA	0.381	0.552	0.258	0.373	51.4	43.9	0.514	0.439
0.05KBr + 7×10^{-5} M PVA	0.418	0.624	0.283	0.422	46.7	36.6	0.467	0.366
0.05KBr + 5×10^{-5} M PVA	0.432	0.726	0.292	0.491	44.9	26.2	0.449	0.262
0.05KBr + 3×10^{-5} M PVA	0.451	0.762	0.305	0.515	42.5	22.6	0.425	0.226
0.05KBr + 1×10^{-5} M PVA	0.493	0.805	0.333	0.544	37.1	18.2	0.371	0.182
0.05KI + 1×10^{-4} M PVA	0.311	0.488	0.21	0.33	60.3	50.4	0.603	0.504
0.05KI + 7×10^{-5} M PVA	0.325	0.493	0.22	0.333	58.5	49.9	0.585	0.499
0.05KI + 5×10^{-5} M PVA	0.345	0.682	0.233	0.461	56	44.3	0.56	0.443
0.05KI + 3×10^{-5} M PVA	0.364	0.692	0.246	0.468	53.6	29.7	0.536	0.297
0.05KI + 1×10^{-5} M PVA	0.412	0.702	0.279	0.475	47.4	28.7	0.474	0.287

was used without further purification. The concentrations of inhibitor, PVA prepared and used in the study was 1×10^{-4} to 1×10^{-5} M. The concentration of NaOH (BDH laboratory supplies, England) (corroduct) used was 0.1M. The halides used (KCl, KBr, and KI) were all BDH laboratory supplies chemicals and the concentrations prepared were in the range 0.01M–0.1M. 0.05M KCl, KBr, and KI were used for the synergistic studies.

Weight loss determination

In the weight loss experiment, 250-mL beaker containing 0.1M NaOH solution was placed in a thermostated bath maintained at 30 and 40°C. The weighed aluminum coupons were suspended in the beaker with the aid of glass rods and hooks. These coupons were retrieved at 24-h interval progressively for 168 h (7 days), immersed in concentrated nitric acid (S.G. 1.42) at room temperature, scrubbed with bristle brush under running water, dried in acetone, and weighed.²⁶ The weight losses of the coupons were evaluated in grams as the difference in the weight of the coupons.

Further measurements were carried out after introduction of the inhibitor (PVA) in two sets of 10 beakers maintained at 30 and 40°C. After that, 0.05M KCl, KBr, and KI was now used for the PVA–halide mixtures after the halides had been studied separately.

Each previously weighed aluminum coupons were introduced into all the beakers containing different concentrations of PVA, in combination with 0.05M

KCl, KBr, and KI. Each coupon was retrieved from the corroduct-inhibitor halide system at 24 h intervals for a period of 168 h, washed, and reweighed. The difference in weight recorded for a period of 168 h (7 days) was again taken as the weight loss. Each reading reported is an average of three experimental readings, recorded on a Mettler H35AR digital analytical balance.

The inhibition efficiency, *I* (%) of PVA, halides, and PVA–halide mixtures acting as inhibitor was calculated using the following expression,²⁷

$$I(\%) = \left(1 - \frac{W_0}{W_1}\right) \times 100 \quad (1)$$

where W_0 and W_1 are the corrosion rates for aluminum in the presence and absence of inhibitor, respectively, in NaOH solution at the same temperature. The degree of surface coverage, θ , is given by the equation:

$$\theta = 1 - \frac{W_0}{W_1} \quad (2)$$

The corrosion rates of aluminum in different concentrations of NaOH, PVA, and halides have been determined for a 7 days (168 h) immersion period from weight loss, using the formula

$$\text{Corrosion rate (mpy)} = \frac{534W}{\rho At} \quad (3)$$

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

Hydrogen evolution technique (gasometric assembly)

The volume of hydrogen evolved was determined following the procedure previously described elsewhere.^{28–30} A 100 mL solution of 0.1M–2M solution of NaOH was introduced into the reaction vessel connected to a burette through delivery tube. The initial volume of air in the burette was recorded. An aluminum coupon weighing 2 g was dropped into the solution of NaOH and the reaction vessel quickly closed to prevent any escape of H₂ gas. However, the volume of H₂ evolved from the corrosion reaction was monitored by the depression (in cm³) in the paraffin oil level. The depression in paraffin oil level was monitored every 10 s for about 300 s. The same experiment was repeated in the presence of inhibitor (PVA) having the concentration range of 1×10^{-4} M to 1×10^{-5} M, 0.05M KCl, KBr, and KI and PVA–halides mixtures but with a corrodent (NaOH) concentration of 1M NaOH.

The inhibition efficiency, I (%) was calculated using the equation:

$$I(\%) = \left(1 - \frac{V_{Ht}^1}{V_{Ht}^0}\right) \times 100 \quad (4)$$

where V_{Ht}^1 is the volume of H₂ gas evolved at time t for inhibited solution and V_{Ht}^0 for uninhibited solution.

RESULTS AND DISCUSSION

Effect of inhibitor/halide concentration on inhibition efficiency

The dissolution of aluminum in NaOH starts from the moment the metal is introduced into the corrodent. The mechanism of the process considers the influence of the passivating surface oxide film. When aluminum is introduced into the alkaline solution, the OH⁻ ions are primarily adsorbed on the surface oxide film. Because of the acidic property of the oxide film, it is chemically attacked and this leads to subsequent dissolution of the oxide film. The heat evolved from the above-mentioned reaction accelerates further dissolution of the oxide and activates the dissolution of aluminum exposed to the aggressive medium.

The dissolution of aluminum in NaOH in the absence and presence of various concentrations of PVA and PVA in combination with KCl, KBr, and KI was investigated using weight loss method. Variation of weight loss with time for the different systems is shown in Table I. Figure 1 shows the plot of weight loss against time for the dissolution of aluminum in 0.1M NaOH (blank), PVA, and PVA–halide at 30 and 40°C, respectively. Inspection of the figures reveals that PVA actually inhibited the corrosion of aluminum in the alkaline environment as evident in the

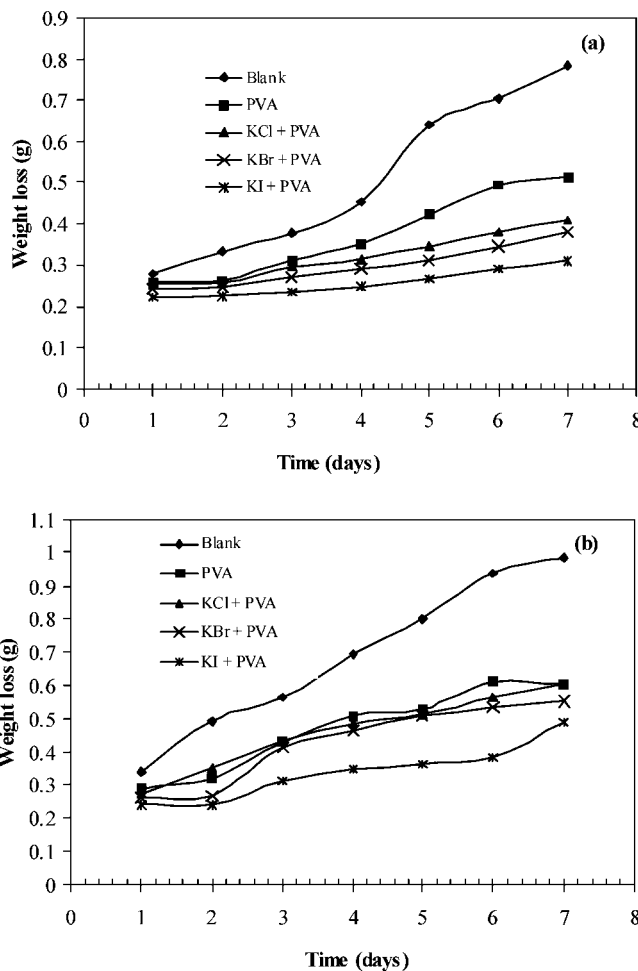


Figure 1 Variation of weight loss (g) with time (days) for aluminum dissolution in 0.1M NaOH (blank), 1×10^{-4} M PVA and 1×10^{-4} M PVA–0.05M halide combination at (a) 30°C and (b) 40°C.

reduction in weight loss of aluminum when compared to the blank. The result obtained also clearly indicates that there was a further reduction in weight loss on the addition of the halides with the lowest weight loss recorded with PVA–KI mixture. From Table I, it could be seen that weight loss increases with decrease in inhibitor (PVA) concentration and increases with increase in temperature. Also, corrosion rate decreases with increase in inhibitor concentration and increases with increase in temperature (Table I). At 30°C and at the highest concentration of PVA (1.0×10^{-4} M), the corrosion rate (mpy) was found to be 0.0347 and 0.0407 at 40°C. On addition of 0.05M KCl, 0.05M KBr and 0.05M KI to the highest concentration of PVA, the corrosion rate was found to reduce to 0.0277, 0.0258, and 0.0210, respectively at 30°C, while at 40°C, the corrosion rate obtained were 0.0408, 0.0373, and 0.0330, respectively. These values are lower when compared with those of the blank, which were 0.0530 at 30°C and 0.0665 at 40°C. Table I shows the calculated values of inhibition efficiency I

TABLE II
Comparison of Inhibition Efficiency, I (%) Obtained from Weight Loss and Hydrogen Evolution Measurements at 30°C

Systems/concentration	Inhibition efficiency, I (%)	
	Weight loss	Hydrogen evolution
Blank	–	–
0.05M KCl	33.2	22.1
0.05M KBr	36.3	22.7
0.05M KI	38.5	37.9
1×10^{-4} M PVA	34.4	30
7×10^{-5} M PVA	32.1	25
5×10^{-5} M PVA	25.9	20.7
3×10^{-5} M PVA	22.2	16.5
1×10^{-5} M PVA	16.5	12.1
0.05M KCl + 1×10^{-4} M PVA	47.7	37.9
0.05M KCl + 7×10^{-5} M PVA	43.5	30.8
0.05M KCl + 5×10^{-5} M PVA	41.1	28.8
0.05M KCl + 3×10^{-5} M PVA	38.3	28.3
0.05M KCl + 1×10^{-5} M PVA	32.9	25.4
0.05M KBr + 1×10^{-4} M PVA	51.4	51.3
0.05M KBr + 7×10^{-5} M PVA	46.7	50
0.05M KBr + 5×10^{-5} M PVA	44.9	47.5
0.05M KBr + 3×10^{-5} M PVA	42.5	42.5
0.05M KBr + 1×10^{-5} M PVA	37.1	36.3
0.05M KI + 1×10^{-4} M PVA	60.3	62.9
0.05M KI + 7×10^{-5} M PVA	58.5	61.7
0.05M KI + 5×10^{-5} M PVA	56	50.4
0.05M KI + 3×10^{-5} M PVA	53.6	37.9
0.05M KI + 1×10^{-5} M PVA	47.4	34.2

(%) and degrees of surface coverage, θ , for aluminum dissolution in 0.1M NaOH with inhibitor (PVA) and inhibitor-halide mixtures at the temperatures studied. Table II shows a comparison of the inhibition efficiency, I (%), values obtained from the two methods used for the study. To a certain extent, there is reasonable agreement in the values.

The volume of hydrogen evolved, V_{H_2} , during the dissolution of aluminum in 1M NaOH solutions in the absence and presence of PVA and PVA-halides (KCl, KBr, and KI) mixtures at 30 and 40°C was measured as a function of the reaction time. The results obtained are shown in Figure 2. The presence of PVA decreases markedly the volume of H_2 evolved compared to the blank. Further reduction in the volume of H_2 was also observed on the addition of the halides at 30°C. Similar trend was observed at 40°C, but with higher values. The least volume of H_2 was evolved with PVA-KI mixture.

Figure 3 shows the plot of inhibition efficiency against inhibitor concentration for aluminum in 0.1M NaOH solution containing different concentrations of PVA at 30 and 40°C. From the figure, it could be seen that with increasing inhibitor (PVA) concentration, there is corresponding increase in percent inhibition efficiency at both temperatures. The addition of halide ions further increases the inhibition efficiency values

(Table I). The inhibition efficiency is also found to increase with increasing concentration of PVA (Table I) at both temperatures. The values of the inhibition efficiency decreases with temperature and the highest inhibition efficiency was obtained with PVA combined with iodide ion (0.05M KI) at the temperatures studied (Table I). The synergistic effect increases with the addition of halides to the PVA in the order $I^- > Br^- > Cl^-$. Similar observation has been reported elsewhere,^{20–23} showing that a cooperative effect results, which inhibits corrosion. Halides have been reported to inhibit the corrosion of some metals in strong acids and this effect depends on the ionic size and charge, the electrostatic field set up by the negative charge of the anion on adsorption site, and nature and concentration of halide ions. Similar trend is observed in alkaline medium. Stabilization of adsorbed halide ions by means of interaction with PVA leads to greater surface coverage θ

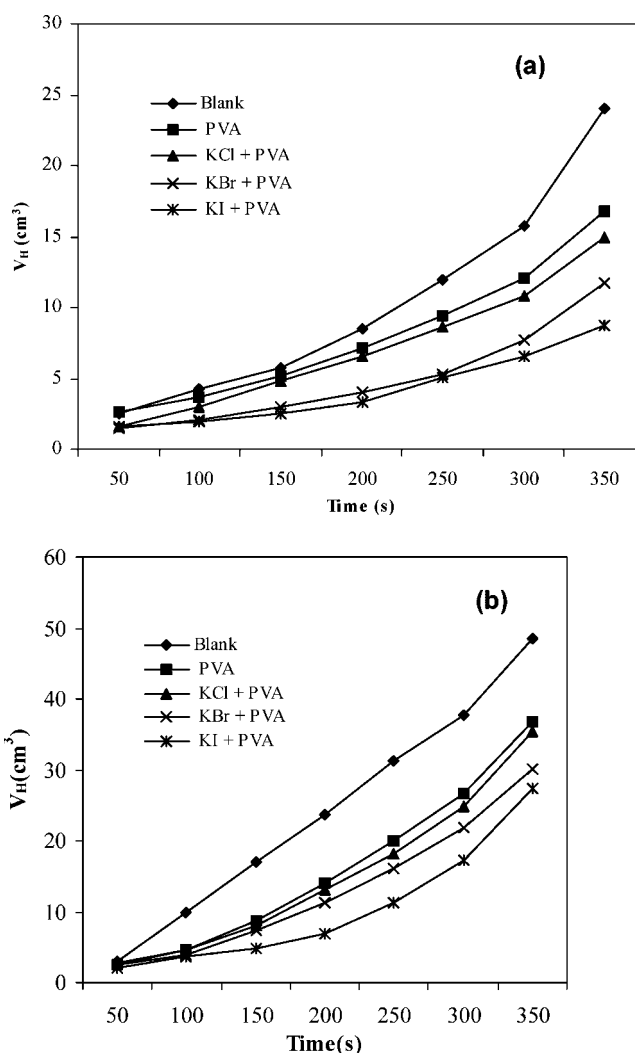


Figure 2 Variation of volume of hydrogen, V_{H_2} (cm^3) evolved with time (s) for aluminum dissolution in 1M NaOH (blank), 1×10^{-4} M PVA and 1×10^{-4} M PVA–0.05M halide combination at (a) 30°C and (b) 40°C.

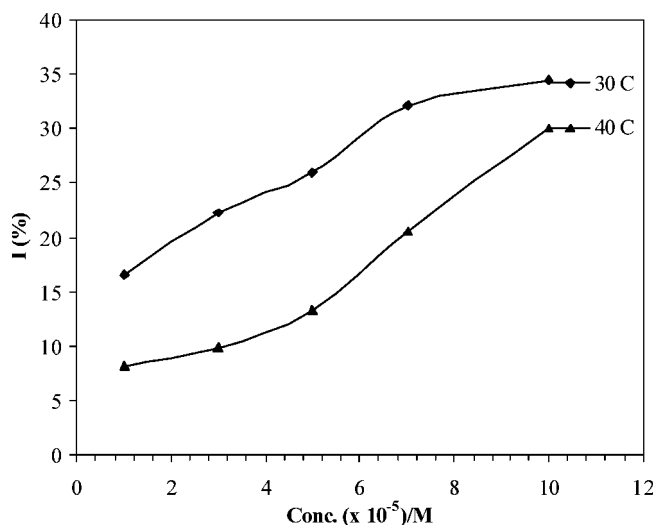


Figure 3 Plot of inhibition efficiency, I (%) against inhibitor (PVA) concentration (M) at 30°C and 40°C.

(from Cl^- to I^-), and hence greater inhibition efficiency (Table I). Halides ions are good ligands because they exhibit low electronegativity (< 3.5) except fluoride ion.²³ Electronegativity decreases from Cl^- to I^- . ($\text{Cl}^- = 3.0$, $\text{Br}^- = 2.8$, $\text{I}^- = 2.5$) while atomic radius increased from Cl^- to I^- ($\text{Cl}^- = 90$ pm, $\text{Br}^- = 114$ pm; $\text{I}^- = 135$ pm).³¹ Hence, aluminum can form compounds with halide ions. It has been shown that inhibitive effect increases in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$, which seems to indicate that the radii of the halogen atoms may have an important role to play. The iodide ion is more predisposed to adsorption than the bromide ion and the chloride ion.

Adsorption considerations

Figure 3 shows the plot of inhibition efficiency, I (%) against inhibitor concentration, C , at 30 and 40°C. The figure reveals that inhibition efficiency increases with

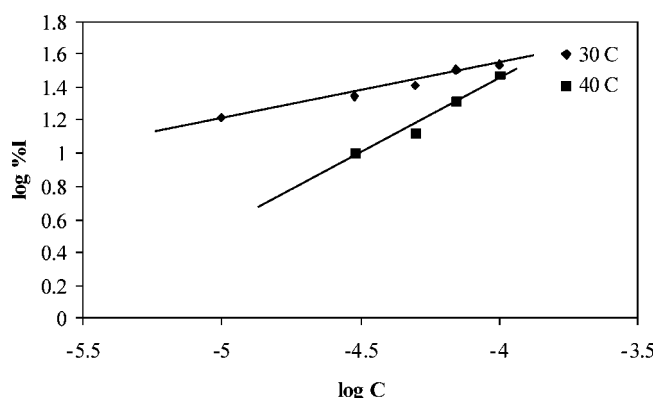


Figure 4 Plot of log of inhibition efficiency, $\%I$ against log of inhibitor concentration, C , at 30°C and 40°C (Freundlich isotherm).

increase in inhibitor concentration and decreases with increase in temperature. This can be attributed to the decrease in the protective nature of the inhibitive film formed on the metal surface (or desorption of the inhibitor molecules from the metal surface) at higher temperatures. This suggests physical adsorption mechanism (see also Table I). Physical (electrostatic) adsorption takes place when inhibition efficiency decreases with increase in temperature (whereas chemical adsorption takes place when inhibition efficiency increases with increase in temperature) and isotherms of high temperature are below isotherms of low temperature (Figs. 3 and 4). Figure 4 shows the plot of logarithm inhibition efficiency (%) against logarithm of inhibitor concentration at 30 and 40°C. A linear plot is obtained, which obeys Freundlich adsorption isotherm. Figure 5 shows the plot of surface coverage, θ , against logarithm of inhibitor concentration, C , which is a representation of a typical Frumkin isotherm given by

$$\frac{\theta}{1 - \theta} = BC e^{2a\theta} \quad (5)$$

where θ is the coverage degree, C the concentration of the adsorbate, B the adsorption coefficient, which represents the adsorption–desorption equilibrium constant, and a is an interaction parameter. It is clear that from what is known about dependence of adsorption as temperatures rises that the quantity of equilibrium adsorption decreases,² and as a result, the isotherms of high temperature are below the isotherms for low ones. This is clearly demonstrated in Figures 4 and 5. PVA obeys physical adsorption because the plot of 40°C is below that of 30°C.

Kinetic/thermodynamics considerations

The apparent activation energy, E_a , for aluminum dissolution in 0.1M NaOH solution in the absence and

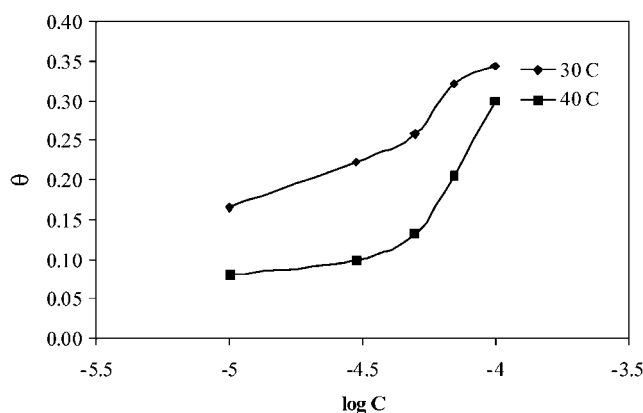


Figure 5 Plot of surface coverage, θ against log of inhibitor concentration, C , at 30°C and 40°C (Frumkin isotherm).

TABLE III
Calculated Values of Activation Energy, E_a (kJ mol⁻¹), Q_{ads} (kJ mol⁻¹), Rate Constants, k (day⁻¹) and Half Life, $t_{1/2}$ (day⁻¹) for Different Systems

Systems/concentration	E_a (kJ mol ⁻¹) 30–40°C	Q_{ads} (kJ mol ⁻¹) 30–40°C	Rate constant (10 ⁻¹ day ⁻¹)		Half life (10 ⁻¹ day ⁻¹)	
			30°C	40°C	30°C	40°C
Blank	5.429	–	–	–	–	–
1 × 10 ⁻⁴ M PVA	3.817	-1.801	1.373	4.360	50.489	15.896
7 × 10 ⁻⁵ M PVA	9.21	-4.78	2.713	6.269	25.540	11.055
5 × 10 ⁻⁵ M PVA	9.189	-6.563	4.074	7.280	17.010	9.520
3 × 10 ⁻⁵ M PVA	8.995	-7.526	4.530	8.489	15.298	8.164
1 × 10 ⁻⁵ M PVA	7.64	-6.367	6.435	11.054	10.770	6.269
0.05M KCl + 1 × 10 ⁻⁴ M PVA	9.267	-7.781	1.607	3.781	43.111	18.326
0.05M KCl + 7 × 10 ⁻⁵ M PVA	13.104	-9.836	2.236	5.398	30.990	12.838
0.05M KCl + 5 × 10 ⁻⁵ M PVA	13.739	-12.027	2.268	6.112	30.550	11.338
0.05M KCl + 3 × 10 ⁻⁵ M PVA	23.852	-11.376	2.586	7.146	26.760	9.697
0.05M KCl + 1 × 10 ⁻⁵ M PVA	12.331	-2.376	3.306	7.173	20.962	9.661
0.05M KBr + 1 × 10 ⁻⁴ M PVA	9.007	-3.29	1.607	3.625	43.111	18.973
0.05M KBr + 7 × 10 ⁻⁵ M PVA	9.561	-6.39	1.948	4.463	35.569	15.527
0.05M KBr + 5 × 10 ⁻⁵ M PVA	12.436	-7.324	2.080	5.234	33.324	13.240
0.05M KBr + 3 × 10 ⁻⁵ M PVA	12.536	-7.689	2.331	6.029	29.734	11.494
0.05M KBr + 1 × 10 ⁻⁵ M PVA	11.745	-3.17	2.619	6.142	26.465	11.283
0.05M KI + 1 × 10 ⁻⁴ M PVA	10.816	-2.739	1.048	3.618	66.134	19.154
0.05M KI + 7 × 10 ⁻⁵ M PVA	9.919	-3.708	1.268	3.623	54.639	21.326
0.05M KI + 5 × 10 ⁻⁵ M PVA	16.329	-5.604	1.396	4.277	49.655	16.203
0.05M KI + 3 × 10 ⁻⁵ M PVA	15.39	-8.132	1.465	4.512	47.313	15.360
0.05M KI + 1 × 10 ⁻⁵ M PVA	12.733	-6.356	1.994	5.159	34.747	13.434

presence of inhibitor (PVA) and PVA–halide mixtures was calculated from Arrhenius equation³²

$$\log \frac{r_2}{r_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (6)$$

where r_1 and r_2 are the corrosion rates at temperatures, T_1 and T_2 respectively. The values obtained for the blank, inhibited systems containing PVA and PVA–halide mixtures are presented in Table III. Higher E_a values in the presence of inhibitor compared to the blank solution indicates that the inhibitor will be effective at low temperatures, but efficiency will be considerably diminished at higher temperature.^{33,34} In this study, such behavior was observed for the dependence of inhibition efficiency on temperature and further supports the proposed mechanism of physical adsorption. The heat of adsorption, Q_{ads} were obtained using the expression,

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

where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2 , respectively. The values obtained are shown in Table III. From the table, it is evident that in all cases, the Q_{ads} values are negative and ranged from -1.801 to -12.027 kJ mol⁻¹. The negative Q_{ads} values show that the adsorption and

hence inhibition efficiency decreases with rise in temperature.³⁵

The values of rate constant, k , were evaluated from the plot of $\log W_f$ (W_f means final weight loss) against time (days). Linear plots were obtained (not shown in this work), which reveal first-order kinetics. The values of half-life, $t_{1/2}$, were calculated using the expression,

$$t_{1/2} = \frac{0.693}{k} \quad (8)$$

The results are presented in Table III which reveal that the rate constant, k , decreases with increase in inhibitor (PVA) concentration, whereas the half-life increases with increase in concentration of PVA. Both parameters increase with rise in temperature.

Synergism considerations

The synergism parameter (S_1) was calculated using the relationship reported elsewhere^{20,21} and given by

$$S_1 = \frac{I - I_{1+2}}{I - I'_{1+2}} \quad (9)$$

TABLE IV
Calculated Values of Synergism Parameter, S_1

Halides	S_1
KCl	1.10
KBr	1.28
KI	1.30

where $I_{1+2} = I_1 + I_2$; I_1 is inhibition efficiency of the halides, I_2 is the inhibition efficiency of inhibitor (PVA), and I_{1+2} is measured inhibition efficiency for the inhibitor in combination with the halides. The calculated values are presented in Table IV. The S_1 values as shown in Table IV are greater than unity, which suggests that the enhanced inhibition efficiency caused by the addition of halide ions to PVA in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$ is only due to synergistic of cooperative effect. This can be explained on the basis that halides have a great tendency to be adsorbed on the surface and this may be responsible for the synergistic effect of halides ions in PVA.

CONCLUSIONS

1. PVA was found to be an inhibitor for aluminum corrosion in alkaline medium.
2. Inhibition efficiency increases with increasing inhibitor concentration, but performed better at 30°C than at 40°C.
3. The experimental data obtained in this study fits into Freundlich and Frumkin adsorption isotherm.
4. Synergistic effect occurred on addition of halides (KCl, KBr, and KI) to the alkaline medium containing PVA, which inhibits aluminum corrosion.
5. Surface coverage values decreases in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$, which indicates that the radii and electronegativity of the halides play important role in the adsorption process.
6. Physical adsorption mechanism is proposed from the obtained E_a and Q_{ads} values.
7. The synergistic parameter (S_j) values obtained for PVA are greater than unity, showing that the corrosion inhibition brought about by PVA and the halides is synergistic in nature.

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