# Synergistic Effect of Halide Ions on the Corrosion Inhibition of Aluminum in Acidic Medium by Some Polymers

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**ABSTRACT:** The corrosion inhibition of aluminum in $H_2SO_4$ in the presence of polyvinyl alcohol (PVA) and polyethylene glycol (PEG) and the effect of addition of halides (KCl, KBr, KI) was studied using the hydrogen evolution technique at 30 and 40°C. Inhibition efficiency (%I) increases with concentration of PVA and PEG—-but with PEG having higher %I. The %I decrease with increase in temperature from 30 to 40°C in the absence and presence of inhibitor and halides. PVA and PEG were found to obey Freundlish adsorption isotherm. Phenomenon of physical adsorption is proposed from the obtained $E_a$, $\Delta G_{ads}$, and $Q_{ads}$ values obtained. The synergism parameters ($S_I$) obtained were found to be greater than unity for both PVA and PEG, which indicates that the enhanced inhibition efficiency caused by the addition of halides is only due to synergism. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2889–2894, 2006

**Key words:** aluminum; corrosion inhibition; polymers; acid; synergism; halide ions

## INTRODUCTION

The use of polymers as corrosion inhibitors has attracted considerable attention recently. Polymers such as polyvinylpyridine, polyvinylbipyridine, polyvinylpyrrolidine, polyvinylpyrolidone (PVP), polyethylenimine, polyaniline, polyacrylic acid, polyacrylamide, and polyvinylimidazoles has been widely examined.[1–7] The application of water soluble polymers as corrosion inhibitors of metals in aggressive media has been cited as examples by some research groups. The inhibitive power of these polymers is related structurally to the cyclic rings, heteroatoms (oxygen and nitrogen), which are the major active centers of adsorption.

The aim of this work is to study the inhibition effect of the polymers namely polyvinyl alcohol (PVA) and polyethylene glycol (PEG) on the corrosion of aluminum in $H_2SO_4$ solution, using the hydrogen evolution technique at 30 and 40°C. The effect of different halides (KCl, KBr, and KI) on the efficiency of the polymers is also being investigated to determine synergism.

## EXPERIMENTAL

The method of hydrogen evolution (via gasometric assembly) was determined as previously described elsewhere.[8,9] Polyvinyl alcohol (PVA) and polyethylene glycol (PEG) used as inhibitors were obtained from BDH Laboratory Supplies, England, and were used without further purification. The concentrations of PVA and PEG used for this study are $0.0001–0.001M$. The concentrations of $H_2SO_4$ (BDH Laboratory Supplies, England) prepared are $0.001–1.0M$. The halides used (KCl, KBr, and KI) were all BDH Laboratory Supplies Chemicals, England, and the concentrations prepared were $0.01–0.1M$. $0.06M$ KCl, KBr, and KI were used for the synergistic studies. The studies were carried out at 30 and 40°C.

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

$$\%I = \left( 1 - \frac{V_H^i}{V_H^o} \right) \times 100 \tag{1}$$

where $V_H^i$ is the volume of hydrogen evolved at time $t$ for inhibited solution and $V_H^o$ that for uninhibited solution.

## RESULTS AND DISCUSSION

The results are presented in Tables I–IV and Figures 1–6. Figure 1 shows the plot of %I versus concentra-
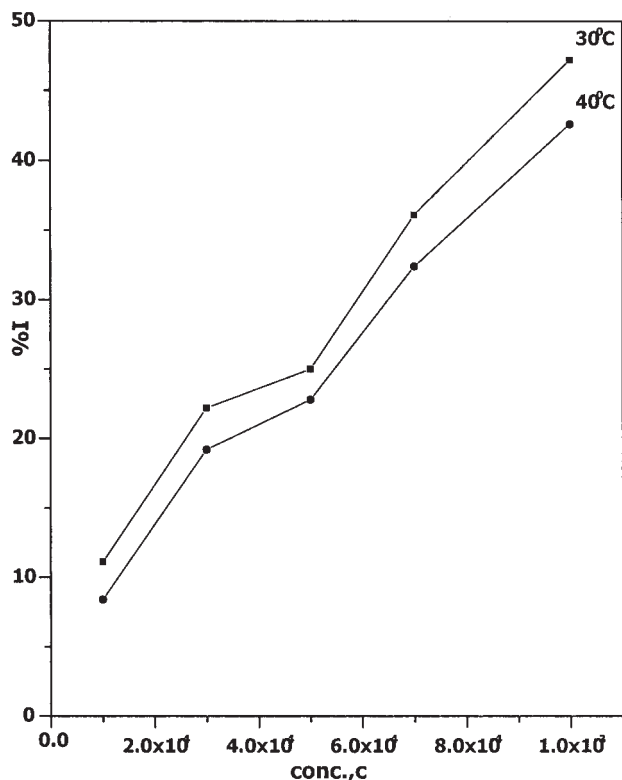
**Figure 1**    Plot of %*I* versus concentration, *c*, for PVA.

tion, *c*, for PVA while Figure 2 shows the plot of log %*I* versus log *c* for PVA. Figures 3 and 4 shows similar plot for PEG. Figure 5 shows the plot of volume of hydrogen evolved, H$_2$ versus time (s) for PVA and
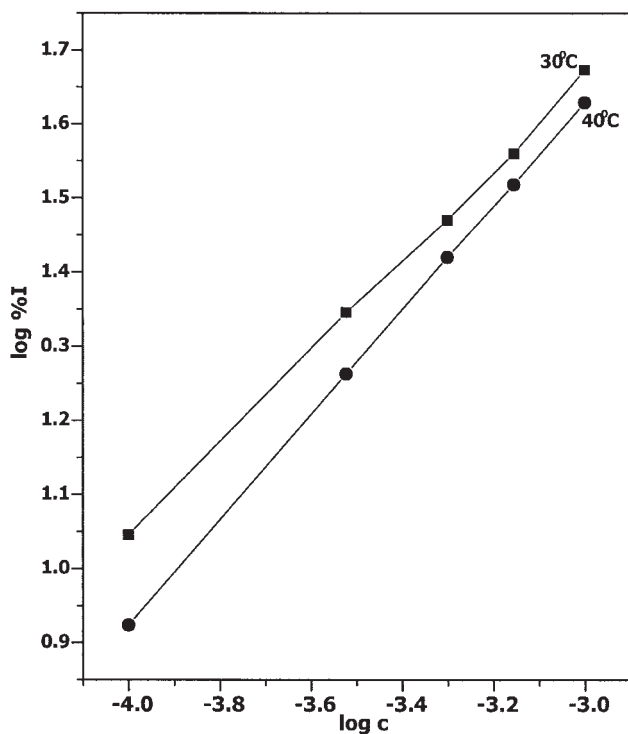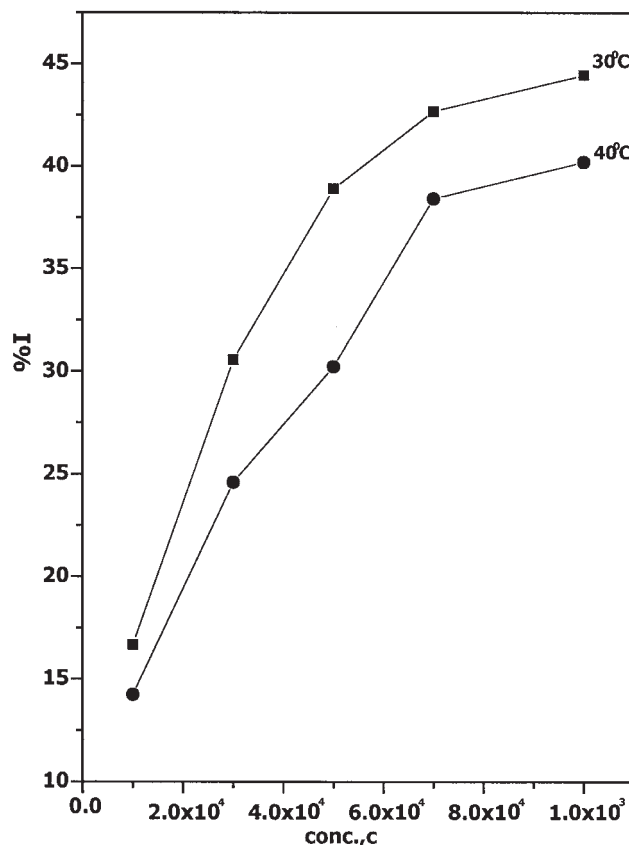


**Figure 3**    Plot of %*I* versus concentration, *c*, for PEG.

halides combination at 30°C while Figure 6 shows plot for PEG and halides.

### Effect of the PVA and PEG concentrations and halides combination on the inhibition efficiency (%*I*)

Tables I and II show the calculated values of corrosion rate (mpy), inhibition efficiency (%*I*), and degree of surface coverage (θ) for aluminum in H$_2$SO$_4$ with halides, inhibitors (PVA and PEG, respectively), inhibitor (PVA and PEG)—halide mixtures and blank for the different systems.

The corrosion rate (mpy) obtained at the highest concentrations of inhibitors (0.001*M* PVA and PEG) was lowest compared with other concentrations, which shows that PVA and PEG inhibited corrosion reaction compared to blank (H$_2$SO$_4$) alone (Tables I and II). With the addition of halides (0.06*M* KCl, 0.06*M* KBr, and 0.06*M* KI), the corrosion rate decreased in the order KCl < KBr < KI at 30°C. Similar trend is also reported at 40°C (see Tables I and II). Addition of the inhibitors (PVA and PEG) to the halides further decreased the corrosion rate values. The most significant change being observed with the
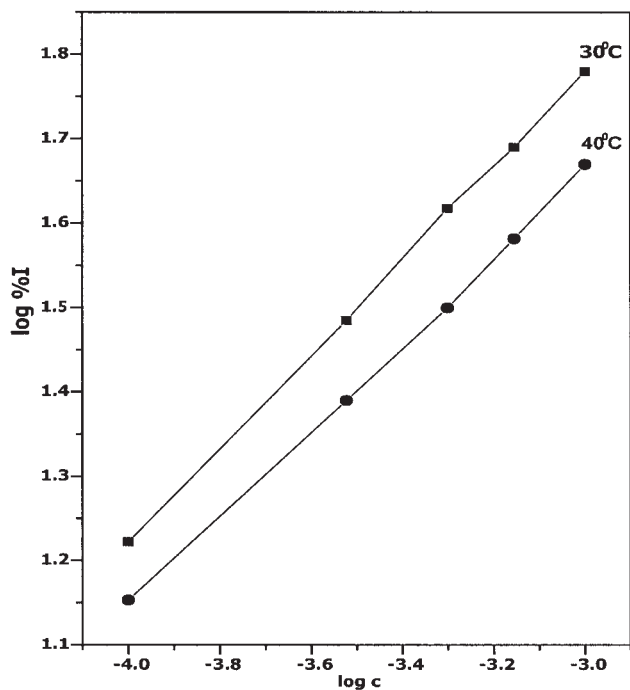


**Figure 2**    Plot of log %*I* versus log *c* for PVA.

Figure 4   Plot of log %$I$ versus log $c$ for PEG.



Figure 6   Plot of volume of $H_2, V_H$ evolved versus time (s) for PEG and halides.

0.06$M$ KI and PVA, and 0.06$M$ KI and PEG. Similar trend is also observed at 40°C.

The inhibition efficiency (%$I$) of the halides decreased with temperature, with the highest value
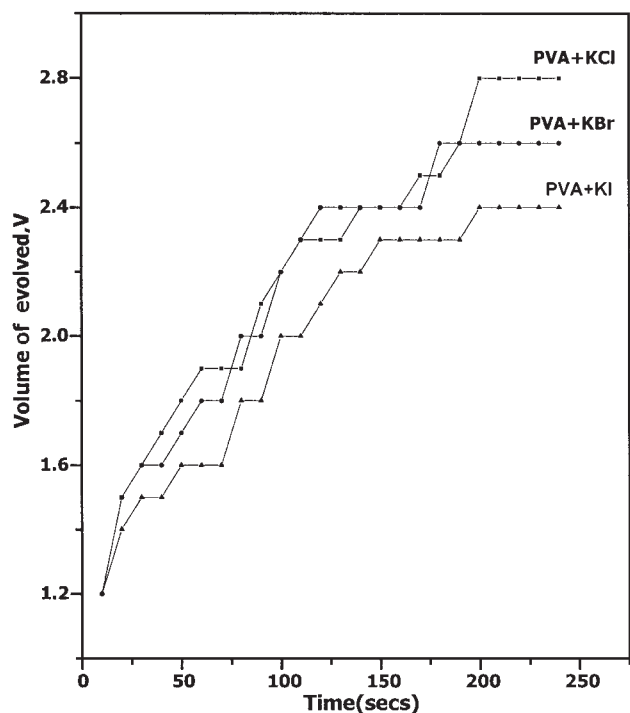


Figure 5   Plot of volume of $H_2, V_H$ evolved versus time (s) for PVA and halides.
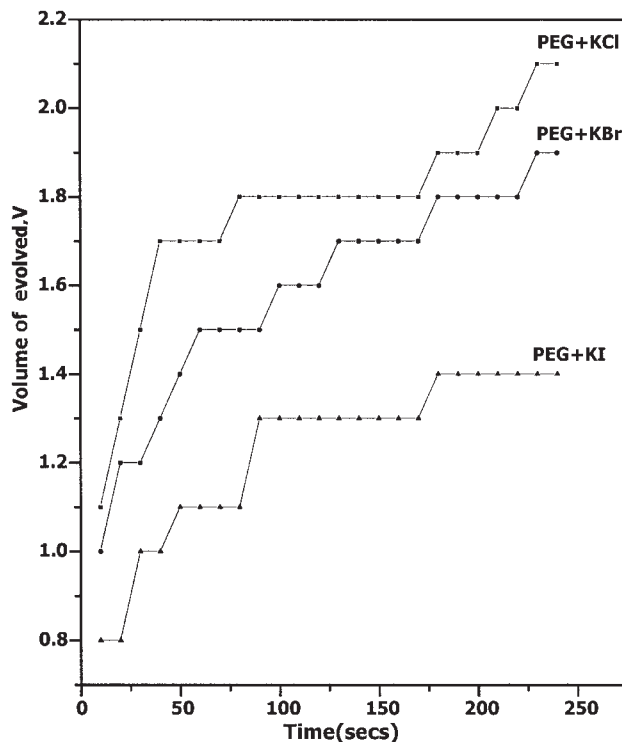
shown for 0.06$M$ KI (Tables I and II). The addition of halide ions further increased the inhibition efficiency values. The inhibition efficiency values are also observed to increase with concentration of PVA and PEG at 30–40°C (Tables I and II, Figs. 1 and 3). The values of the %$I$ decreases with temperature; the highest inhibition efficiency was observed with PVA and PEG combined with iodide ion (0.06$M$ KI) at the temperatures studied (Tables I and II). PEG is a better inhibitor than PVA. The synergistic effect increases with the addition of concentration of halides to the PVA and PEG solution in the order: $Cl^- < Br^- < I^-$. Similar observation has been reported elsewhere[10,11] and that for the addition of halide salt to sulfuric acid solution containing any organic compound, 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 sites, and the nature and concentration of halide ions. Stabilization of adsorbed halide ions by means of interaction with PVA and PEG leads to greater surface coverage, $\theta$ (from $Cl^-$ to I) thereby greater %$I$ (Tables I and II). Halide ions are good ligands because they exhibit low electronegativity (less than 3.5) except fluoride ion.[10] Electronegativity decreases from $Cl^-$ to $I^-$ ($Cl^- = 3.0$, $Br^- = 2.8$, $I^- = 2.5$), while atomic radius increased from $Cl^-$ to $I^-$ ($Cl^- = 90$ pm, $Br^- = 114$ pm; $I^- = 135$

**TABLE I**
**Calculated Values of Corrosion Rate (mpy), Inhibition Efficiency (%*I*) and Degree of Surface Coverage (*θ*) for Aluminum in H$_2$SO$_4$ with Halides, Inhibitor (PVA), Inhibitor (PVA)–Halide Mixtures and Blank for Different Systems**

| System | Corrosion rate (mpy) | | Inhibition efficiency (%*I*) | | Surface coverage (*θ*) | |
|---|---|---|---|---|---|---|
| | 30°C | 40°C | 30°C | 40°C | 30°C | 40°C |
| Blank | 750 | 840 | | | | |
| PVA (inhibitor) | 583.3 | 600 | 25.00 | 18.10 | 0.25 | 0.18 |
| 0.06*M* KCl | 400.4 | 420 | 16.20 | 14.21 | 0.16 | 0.14 |
| 0.06*M* KBr | 348.7 | 401 | 18.24 | 16.88 | 0.18 | 0.17 |
| 0.06*M* KI | 360.0 | 372.2 | 20.16 | 18.14 | 0.20 | 0.18 |
| 0.06*M* KCl + PVA | 543.3 | 560 | 22.22 | 20.11 | 0.22 | 0.20 |
| 0.06*M* KBr + PVA | 531.4 | 551 | 27.78 | 24.20 | 0.28 | 0.24 |
| 0.06*M* KI + PVA | 500 | 524 | 33.33 | 28.42 | 0.33 | 0.28 |
| 0.0001*M* PVA | 720.1 | 780 | 11.11 | 8.4 | 0.11 | 0.08 |
| 0.0003*M* PVA | 708.3 | 720 | 22.2 | 19.2 | 0.22 | 0.19 |
| 0.0005*M* PVA | 666.7 | 684 | 25.0 | 22.8 | 0.25 | 0.23 |
| 0.0007*M* PVA | 625.4 | 642 | 36.1 | 32.4 | 0.36 | 0.32 |
| 0.001*M* PVA | 583.3 | 600 | 47.2 | 42.6 | 0.47 | 0.43 |

pm).[12] Hence, aluminum can form compounds with halide ions. It has been reported[10,11] that the inhibitive effect increases in the order Cl$^-$ < Br$^-$ < I$^-$, which seems to indicate that the radii of halogen atoms may have an important role to play. The iodide ion (radius 135 pm) is more predisposed to adsorption than the bromide ion (radius 114 pm) and the chloride ion (radius 90 pm).

Figures 1 and 3 show that inhibition efficiency (%*I*) increases with inhibitor concentration and decreases with temperature. This suggests physical adsorption mechanism for both PVA and PEG. Figures 2 and 4 show the plot of logarithm inhibition efficiency (%*I*) versus logarithm inhibitor concentration for PVA and PEG at 30 and 40°C. A linear plot is obtained (for PVA

and PEG), which obeys the Freundlish adsorption isotherm.

## Kinetic/thermodynamic considerations

Tables III and IV show the calculated values of activation energy, $E_a$ (kJ mol$^{-1}$) and heat of adsorption, $Q_{ads}$ (kJ mol$^{-1}$) for aluminum corrosion in H$_2$SO$_4$ with halides, inhibitors (PVA and PEG), inhibitor–halide mixtures, and blank for the different systems. The values of $E_a$, $Q_{ads}$, and $\Delta G_{ads}$ were evaluated from expressions used previously.[11] The phenomenon of physical adsorption is proposed from the values of $E_a$ obtained both for PVA and PEG (i.e., 18.30 and 14.20 kJ mol$^{-1}$, respectively). From Tables III and IV also,

**TABLE II**
**Calculated Values of Corrosion Rate (mpy), Inhibition Efficiency (%*I*) and Degree of Surface Coverage (*θ*) for Aluminum in H$_2$SO$_4$ with Halides, Inhibitor (PEG), Inhibitor (PEG)–Halide Mixtures and Blank for Different System**

| System | Corrosion rate (mpy) | | Inhibition efficiency (%*I*) | | Surface coverage (*θ*) | |
|---|---|---|---|---|---|---|
| | 30°C | 40°C | 30°C | 40°C | 30°C | 40°C |
| Blank | 750 | 840 | | | | |
| PEG (inhibitor) | 354.17 | 420 | 38.89 | 30.20 | 0.38 | 0.30 |
| 0.06*M* KCl | 400.4 | 420 | 16.20 | 14.21 | 0.16 | 0.14 |
| 0.06*M* KBr | 398.7 | 401 | 18.24 | 16.88 | 0.18 | 0.17 |
| 0.06*M* KI | 360.0 | 372.2 | 20.16 | 18.14 | 0.20 | 0.18 |
| 0.06*M* KCl + PEG | 437.50 | 480.4 | 41.67 | 37.40 | 0.42 | 0.37 |
| 0.06*M* KBr + PEG | 395.83 | 410.2 | 47.22 | 40.21 | 0.47 | 0.40 |
| 0.06*M* KI + PEG | 291.67 | 340.2 | 59.01 | 52.10 | 0.59 | 0.52 |
| 0.0001*M* PEG | 625.0 | 660.8 | 16.67 | 14.24 | 0.17 | 0.14 |
| 0.0003*M* PEG | 520.83 | 541.4 | 30.56 | 24.60 | 0.31 | 0.25 |
| 0.0005*M* PEG | 458.33 | 501.2 | 38.89 | 30.20 | 0.39 | 0.30 |
| 0.0007*M* PEG | 416.67 | 490.4 | 42.67 | 38.41 | 0.43 | 0.38 |
| 0.001*M* PEG | 354.17 | 420.0 | 44.44 | 40.20 | 0.44 | 0.40 |

**TABLE III**
**Calculated Values of Activation Energy, $E_a$ (kJ mol$^{-1}$), and Heat of Adsorption, $Q_{ads}$ (kJ mol$^{-1}$), for Aluminum Corrosion in $H_2SO_4$ with Halides, Inhibitor (PVA), Inhibitor (PVA)–Halide Mixtures and Blank for the Different System**

| System | Activation energy, $E_a$ (kJ mol$^{-1}$) 30–40°C | Heat of adsorption, $Q_{ads}$ (kJ mol$^{-1}$) 30–40°C |
|---|---|---|
| Blank | 28.12 | |
| PVA (inhibitor) | 18.30 | −30.20 |
| 0.06M KCl | 20.10 | −52.24 |
| 0.06M KBr | 14.33 | −40.81 |
| 0.06M KI | 10.21 | −24.20 |
| 0.06M KCl + PVA | 17.20 | −42.24 |
| 0.06M KBr + PVA | 10.11 | −38.10 |
| 0.06M KI + PVA | 8.20 | −32.66 |
| 0.0001M PVA | 10.14 | −41.44 |
| 0.0003M PVA | 12.28 | −40.10 |
| 0.0005M PVA | 14.10 | −38.41 |
| 0.0007M PVA | 16.24 | −34.28 |
| 0.001M PVA | 18.30 | −30.20 |

the $Q_{ads}$ values are negative and range from −24.20 to −52.24 kJ mol$^{-1}$ for PVA and −30.81 to −61.20 kJ mol$^{-1}$ for PEG. PEG has $Q_{ads}$ values more negative than PVA. These negative $Q_{ads}$ values show that the adsorption and, hence, inhibition efficiency decreases with rise in temperature.[13] $\Delta G_{ads}^{o}$ values obtained for PVA are −17.418 kJ mol$^{-1}$ at 30°C and −18.844 kJ mol$^{-1}$ at 40°C. The mean $\Delta G_{ads}^{o}$ for PVA = 18.131 kJ mol$^{-1}$, whereas those obtained for PEG are −19.118 kJ mol$^{-1}$ at 30°C and −19.585 kJ mol$^{-1}$ at 40°C, with mean value of −19.488 kJ mol$^{-1}$. The $\Delta G_{ads}^{o}$ values for PEG are more negative than those for PVA. The values of $\Delta G_{ads}^{o}$ obtained indicate the spontaneous adsorption of the inhibitors (PVA and PEG), with PEG being more adsorbed. Generally values of $\Delta G_{ads}^{o}$ up to –20 kJ mol$^{-1}$ are consistent with the electrostatic interaction between the charged molecules and the charged metal, which indicates physical adsorption as obtained in

this study, whereas those more negative than −40 kJ mol$^{-1}$ involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (i.e., chemical adsorption).[14–16]

## Synergism considerations

The synergism parameter ($S_I$) was evaluated using the relationship earlier reported.[11,17] The calculated values are presented in Table V for the halides. The $S_I$ values in Table V are greater than unity for both PVA and PEG, which suggests that the enhanced inhibition efficiency caused by the addition of halide ions to PVA and PEG in the order Cl$^-$ < Br$^-$ < I$^-$ is only due to synergistic 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 syner-

**TABLE IV**
**Calculated Values of Activation Energy, $E_a$ (kJ mol$^{-1}$), and Heat of Adsorption, $Q_{ads}$ (kJ mol$^{-1}$), for Aluminum Corrosion in $H_2SO_4$ with Halides, Inhibitor (PEG), Inhibitor (PEG)–Halide Mixtures and Blank for the Different System**

| System | Activation energy, $E_a$ (kJ mol$^{-1}$) 30–40°C | Heat of adsorption, $Q_{ads}$ (kJ mol$^{-1}$) 30–40°C |
|---|---|---|
| Blank | 22.10 | |
| PEG (inhibitor) | 14.20 | −30.81 |
| 0.06M KCl | 17.41 | −61.20 |
| 0.06M KBr | 12.42 | −48.24 |
| 0.06M KI | 9.28 | −32.18 |
| 0.06M KCl + PEG | 15.80 | −54.20 |
| 0.06M KBr + PEG | 10.28 | −46.40 |
| 0.06M KI + PEG | 7.14 | −41.62 |
| 0.0001M PEG | 8.24 | −49.48 |
| 0.0003M PEG | 9.10 | −48.20 |
| 0.0005M PEG | 10.40 | −44.86 |
| 0.0007M PEG | 12.10 | −40.24 |
| 0.001M PEG | 14.20 | −30.81 |

**TABLE V**
**Calculated Values of Synergism Parameter, $S_I$**

| Halides | $S_I$ | |
| | PVA | PEG |
| --- | --- | --- |
| KCl | 1.354 | 1.001 |
| KBr | 1.556 | 1.209 |
| KI | 1.854 | 1.332 |

gistic effect of halide ions on PVA and PEG. The increase in inhibition efficiency (and surface coverage values) found to be in the order $I^- > Br^- > Cl^-$ is also displayed in the synergistic consideration, which clearly indicates that the radii and the electronegativity of halides play a significant role in the adsorption process. The same trend is displayed in Figures 5 and 6 where the volume of $H_2$ evolved for inhibitor (PVA and PEG) and KI is lower than that for KBr and KCl. It can also be concluded that the iodide ion is strongly adsorbable and facilitates the adsorption of organic cations, thus producing an inhibition synergism.

## CONCLUSIONS

- Inhibition efficiency (%$I$) of PVA and PEG and other systems decreases with temperature—-but with PEG having higher %$I$.
- The values of $E_a$ obtained in the presence and absence of PVA and PEG are less than 40 kJ mol$^{-1}$, indicating physical adsorption but with PEG having lower values compared to PVA.
- The mean $\Delta G^{\circ}_{ads}$ values are negative, with that of PEG being more negative, which suggests that they were strongly adsorbed on the aluminum surface. The values obtained support physical adsorption mechanism.

- PVA and PEG were found to obey the Freundlish adsorption isotherm from the fit of the experimental data.
- Surface coverage values ($\theta$) obtained increases in the order $I^- > Br^- > Cl^-$, which indicates that the radii and the electronegativity of the halides play important roles in the adsorption process.
- The $S_I$ values obtained for PVA and PEG are greater than unity, showing that corrosion inhibition brought about by PVA and PEG and the halides is synergistic in nature.

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