Ionic Liquid as an Effective Corrosion Inhibitor on 6061 Al-15 Vol. Pct. SiC\(_{(p)}\) Composite in 0.1 M H\(_2\)SO\(_4\) Medium - an Ecofriendly Approach

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**Abstract:** The inhibition property of the ionic liquid 1,3-bis(2-oxo-2-phenylethyl)-1H-imidazol-3-ium bromide (OPEIB) was studied on the corrosion of 6061 Al-15 vol. pct. SiC\(_{(p)}\) composite in 0.1 M H\(_2\)SO\(_4\) medium at a temperature range of 30-50 °C by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) techniques. The inhibition efficiency increased with the increase in the concentration of the inhibitor and also with the increase in temperature. The surface morphologies of the polished, corroded and inhibited surface were analyzed by recording the scanning electron microscope (SEM) images. The energy dispersive X-ray (EDX) spectroscopy method was used for qualitative assessment of adsorption of the inhibitor on the composite surface. The activation parameter like energy of activation, enthalpy of activation and entropy of activation were calculated and analyzed. Thermodynamic parameters for the adsorption of the inhibitor on the composite surface were calculated and analyzed. The inhibitor acted as a mixed inhibitor, with predominant cathodic control. Adsorption of inhibitor on the composite surface was through both physisorption and chemisorption, with predominant chemisorption, following Temkin adsorption isotherm. The maximum inhibition efficiency was found to be 96.7% and 94% by PDP and EIS studies, respectively at 50 °C. OPEIB acted as a promising, highly efficient, low cost and green corrosion inhibitor for the composite under consideration.

**Keywords:** 6061 Al composite; Electrochemical techniques; Acidic corrosion; Silicon carbide reinforcement; Ionic liquid; Green inhibitor.

1. **INTRODUCTION**

Aluminum is the third most abundant element (8.23% of the Earth’s crust). Lightness in weight, formability into useful shapes, comparatively higher corrosion resistance and high electrical and thermal conductivities are some of the potentially valuable attributes of aluminum [1, 2]. However, particle reinforcement of aluminum matrix composites ameliorates strength, density and stiffness as compared to pure aluminum [3, 4]. Although particle reinforced of aluminum matrix composites (PAMCs) are a boon to the aerospace, military, automobile industries etc., the lowered corrosion resistance due to discontinuity
in the protective oxide film because of the reinforced ceramic particles is a bane [5, 6]. Micro-galvanic corrosion of PAMCs is more likely to occur during acid pickling and descaling procedures used in the surface preparation of such composites as the ceramic particles function as efficient cathodic sites and trigger corrosion in the presence of acid or moisture [7, 8]. Past decades have witnessed the use of cerium, chromate and other inorganic ions to combat corrosion [9, 10]. Although the efficiency of such inhibitors are high, their use is restricted due to the environmental hazards associated with them [11]. Controlling the extent of micro-galvanic corrosion by nitrogen or sulfur containing organic heterocyclic moieties is a widely followed methodology due to their ability to act as efficient corrosion inhibitors for pure aluminum, aluminum alloys and aluminum alloy composites [12-18]. But, most of the organic inhibitors used are not environment friendly by nature. Therefore, in recent years, an impulse to produce green and efficient inhibitors, has been the field of interest by many researchers [19]. One of the approach towards green inhibition is the use of natural products like extracts from plants, leaves, flowers, fruits, etc., [20, 21]. The efficiency of such products are reasonable. However, associated problems like exact assessment of the inhibiting groups, the binding sites and mechanism of inhibition, etc., is difficult and tedious process, due to the isolation procedures of extract into individual compounds. Also, the plant extracts have low stability and are readily biodegradable which make their use at the industrial level limited [22]. It thereby becomes necessary to design and synthesize organic molecules with lesser environmental threats. Majority of the ionic liquids (ILs), also called as quaternary N-heterocyclic compounds are known to be environment friendly due to their extremely low vapor pressure, relatively high thermal stability, water solubility, recyclability, product recovery and moisture-stability [23]. Despite of the wide range of advantages of ILs, their use in corrosion inhibition studies on aluminum alloys/composites in acidic medium are limited [24].

Cost of ILs may be one such reason for limited studies on ILs as corrosion inhibitors on aluminum alloys/composites. The present work aims at low-cost synthesis of 1,3-bis (2-oxo-2-phenylethyl)-1H-imidazol-3-ium bromide (OPEIB) which is otherwise a very expensive molecule to be readily procured (available as custom made chemical MolPort-000-741-356, MCULE-6854945788 and STK018522). OPEIB is a bulky molecule with more number of pi-electrons, N and O atoms, which is a pre-requisite to predict the inhibitors efficiency. Herein we report OPEIB as an effective low cost, green inhibitor for the corrosion of 6061 Al-15 vol. pct. SiC(p) composite in 0.1 M H₂SO₄ medium.

2. EXPERIMENTAL SECTION

2.1. Material

Experiments were carried out using the 6061 Al-15 vol. pct. SiC(p) composite in the extruded rod form whose extrusion ratio is 30:1. Table 1 gives the composition of the 6061 Al alloy. The cylindrical test coupon was obtained from the rod and was mould using epoxy resin which is resistant to most of the aggressive medium. This moulding technique enabled to expose a constant area of 1.102 cm² of the sample to the corrosion medium in the studies. As per the customary metallographic practice, test coupons were subjected to belt grinding, polishing over rough to smooth grades of emery paper and mirror finish on disc polishing wheel containing levigated alumina. The test coupons were thoroughly cleaned with double distilled water and acetone, dried and immediately subjected to analysis.

2.2. Medium

The stock solution of 1 M sulfuric acid was prepared using double distilled water, from which 0.1 M solution was prepared. This solution was titrated against sodium carbonate which is a primary standard to get accurate concentration, using methyl orange as an indicator. The experiments were carried out at
temperatures 30-50 °C (±0.5 °C) with 5 °C increments, in a calibrated thermostat under unstirred and aerated conditions.

**Table 1.** The composition of the base metal Al 6061 alloy

<table>
<thead>
<tr>
<th>Element</th>
<th>Cu</th>
<th>Cr</th>
<th>Si</th>
<th>Mg</th>
<th>Al</th>
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<td>Composition (wt. %)</td>
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<td>0.6</td>
<td>1.0</td>
<td>97.9</td>
</tr>
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</table>

2.3. **Inhibitor**

2.3.1. **Synthesis of inhibitor**

Step 1: Synthesis of 2-(1H-imidazol-1-yl)-1-phenylethanone: A mixture containing imidazole (1 g, 14.6 mM) and excess of phenacyl bromide (6.3 g, 32.1 mM) was dissolved in 50 mL dimethyl formamide (DMF) in the presence of 1.5 equivalents of K₂CO₃/KOH in a round bottom flask and the reaction temperature was maintained at 80 °C for 4 h with slight modification in the reported procedure [25]. The completion of the reaction was checked by thin layer chromatography. The reaction mixture was allowed to attain room temperature and then was poured into a trough containing ice with constant stirring, the orange brown precipitate thus obtained was filtered and washed thoroughly with ice-cold water and dried.

Step 2: Synthesis of OPEIB: The orange brown product obtained from step 1 was refluxed with excess phenacyl bromide (6.3g, 32.1 mM) dissolved in acetonitrile, at 80 °C for 8 h. The product obtained was filtered off and washed thoroughly with hexane and dried. The final product was recrystallized with methanol and was characterized by FT-IR spectra, ¹H-NMR spectra, ¹³C-NMR spectra and LC-MS.

The synthetic route for OPEIB is shown in **scheme 1**.

![Scheme 1. Synthesis of OPEIB](image)

The solutions of 2 mM, 4 mM, 6 mM, 8 mM and 10 mM concentrations of OPEIB were prepared in 0.1 M H₂SO₄ solution.

2.3.2. **Characterization techniques**

FT-IR spectrum was recorded using Jasco-4200, Japan FT-IR spectrophotometer. ¹³C-NMR and ¹H-NMR were recorded using Bruker NMR (400 MHz) with dimethyl sulfoxide (DMSO) as solvent and tetramethyl silane (TMS) as internal reference standard. LC-MS was recorded using Agilent ion-trap 3600 liquid chromatography mass spectrometer.
2.4. Electrochemical measurements

The electrochemical work station, Gill AC having ACM instrument version 5 software was used to carry out the electrochemical measurements. All tests were performed under aerated conditions. A three electrode cell was used, the molded test coupon acted as a working electrode, the platinum electrode served as an auxiliary electrode, and the saturated calomel electrode as the reference electrode. Immediately after the electrochemical impedance studies, test coupon was subjected to potentiodynamic polarization measurements without any further surface treatment.

2.4.1. Potentiodynamic polarization (PDP) measurements

The finely polished test coupon was immersed in 0.1 M sulfuric acid containing different concentrations of inhibitor in the temperature range 30 - 50 °C with 5 °C increment. It was allowed to attain steady state open circuit potential (OCP) for 500 s. The potentiodynamic current-potential curves were recorded by polarizing the specimen to −250 mV cathodically and +250 mV anodically with respect to the OCP at a scan rate of 1 mV s⁻¹.

2.4.2. Electrochemical impedance spectroscopy (EIS)

The EIS measurement was carried out by impressing a 10 mV amplitude of ac signal and a wide frequency spectrum of 100 kHz-0.01 Hz on the OCP. The impedance data was analyzed by using Nyquist and Bode plots to assess the corrosion characteristics. The charge transfer resistance (Rₜ), resistance associated with inductive loop (Rᵢ), and the double layer capacitance (Cᵢ) were deduced from the simulation of impedance behavior with equivalent circuit using Zsimpwin version 3.21 software. All the results reported are average of three similar results.

2.4.3. Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX) spectroscopy

JEOL JSM-6380LA model SEM was used to image the surface morphology of the polished, corroded and inhibited specimen and corresponding EDX was used for the qualitative analysis of adsorption of inhibitor on the composite surface.

3. RESULTS AND DISCUSSION

3.1. Characterization of OPEIB

The OPEIB molecule was characterized using FT-IR spectra, ¹H-NMR spectra, ¹³C-NMR spectra and LC-MS. Nature: White solid, yield: 83%, m.p. 258-260 °C. Characterization data: FT-IR (ATR, cm⁻¹): 3085, 3043 (-C-H aromatic stretching), 2836 (-C-H aliphatic stretching), 1689 (C=O), 1596 (C=N), 1446 (C=C), 1229 (C-N) (Fig. 1). ¹H NMR (400 MHz, DMSO-d₆): δ (ppm), 9.12 (s, 1H), 8.09-8.07 (m, 4H), 7.82-7.76 (m, 4H), 7.67-7.63 (m, 4H), 6.20 (s, 4H) (Fig. 2). ¹³C-NMR (100 MHz, DMSO-d₆) δ (ppm) : 191.80, 139.06, 134.88, 134.23, 129.58, 128.63, 124.22, 56.12 (Fig. 3). LC-MS (+ve mode) m/z Calculated for C₁₉H₁₇N₂O₂: 305.49, Found: 305.5 [M+H]⁺ (Fig. 4) with 100% purity (Fig. 5).
1. FT-IR spectrum of the synthesized OPEIB molecule.

Figure 2. $^1$H-NMR spectrum of the synthesized OPEIB molecule.
Figure 3. $^{13}$C-NMR spectrum of the synthesized OPEIB molecule.

Figure 4. Mass spectrum of the synthesized OPEIB molecule.
Figure 5. Liquid chromatography spectrum of the synthesized OPEIB molecule.

3.2. Potentiodynamic polarization measurements

The potentiodynamic polarization curves for the corrosion of 6061 Al-15 vol. pct. SiC(ρ) composite in 0.1 M sulfuric acid in the presence of different concentrations of OPEIB at 40 °C are shown in Fig. 6.

Figure 6. Potentiodynamic polarization curves for the corrosion of composite in 0.1 M H₂SO₄ in the presence of different concentrations of OPEIB at 40 °C.

The anodic region represents the metal oxidation and the cathodic region corresponds to the evolution of hydrogen in acidic conditions [26-27]. Owing to the ill-defined Tafel region of the anodic
polarization curve, the corrosion current density ($i_{\text{corr}}$) values were determined by extrapolating the linear cathodic regions up to one decade of current density at about 50 mV from the open circuit potential (OCP) to the respective corrosion potentials. The corrosion rate ($v_{\text{corr}}$) and the percentage inhibition efficiency ($\eta\%$) were calculated using the equations 1 and 2.

$$v_{\text{corr}} \text{ (m m y}^{-1}) = \frac{K \times M \times i_{\text{corr}}}{\rho \times n} \quad (1)$$

where, $M$ and $n$ are the molar mass and valence of the metal, $K = 0.00327$ mm g/µA cm y which defines the unit of corrosion rate (mm y$^{-1}$), $\rho$ is the density of the corroding material equal to 2.78 g cm$^{-3}$.

$$\eta(\%) = \frac{i_{\text{corr(blank)}} - i_{\text{corr(inh)}}}{i_{\text{corr(blank)}}} \times 100 \quad (2)$$

where, $i_{\text{corr(blank)}}$ and $i_{\text{corr(inh)}}$ are the corrosion current densities mentioned in identical units in the absence and presence of the inhibitor, respectively.

The electrochemical parameters such as the corrosion potential ($E_{\text{corr}}$), the corrosion current density ($i_{\text{corr}}$), cathodic Tafel slope (-$\beta_c$), the percentage inhibition efficiency ($\eta\%$) in 0.1 M sulfuric acid medium at different temperature are tabulated in Table 2.

From Table 2, it may be observed that the corrosion current density, $i_{\text{corr}}$ value decreases when the concentration of the inhibitor and the temperature increases. The decrease in $i_{\text{corr}}$ may be attributed to the barrier effect of the inhibitor to the corrosive species, thereby preventing the attack on the composite surface. The $E_{\text{corr}}$ value recorded with respect to saturated calomel electrode (SCE) in the presence of inhibitor doesn’t vary beyond the accepted threshold of ±85 mV, as compared to $E_{\text{corr}}$ of the blank and, therefore, OPEIB cannot be exclusively considered as anodic or cathodic inhibitor [28]. But the $E_{\text{corr}}$ values shift to the cathodic side, indicating that inhibitor is of mixed type with predominant control over cathodic reaction [29]. The predominant cathodic control is also evidenced by the relatively larger shift in cathodic polarization curves than that in the anodic polarization curves in Fig. 6. The maximum inhibition was 81.2 to 96.7% in the presence of 10 mM concentration of the inhibitor at all the temperatures studied. Further increase in the concentration of the inhibitor showed negligible change in the inhibition efficiency. The efficiency achieved with OPEIB is much more than the previously reported work from our research group for the same composite in sulfuric acid medium which was about 70% and inhibition was by physical adsorption [30], it also doesn’t take greener approach in corrosion control.

3.3. Electrochemical impedance spectroscopy measurements

The Nyquist plots for the corrosion of the composite in 0.1 M sulfuric acid in the presence of different concentrations of OPEIB at 40 °C are shown in Fig. 7.

From the semi-circles in the plots it can be inferred that the process of corrosion is largely charge-transfer controlled [31]. The Nyquist plots are comprised of a large capacitive loop at high frequency (HF) region and a small inductive loop at lower frequency (LF) region. A search in the literature reveals reporting of similar impedance plots for the corrosion of pure aluminum and aluminum alloys in different electrolytes such as sodium sulfate [32–34], sulfuric acid [33, 34], acetic acid [33], sodium chloride [35, 36] and hydrochloric acid [37–43]. The high frequency capacitive loop could be accounted to the charge transfer of the corrosion process and to the formation of oxide layer [44, 45]. The capacitive loop is attributed by Brett [38, 40] to the interfacial reactions, particularly, the reaction of aluminum oxidation at the
metal/oxide/electrolyte interface. The process includes the formation of Al\(^{+}\) ions at the metal/oxide interface, and their migration through the oxide/solution interface where they are oxidized to Al\(^{3+}\).

**Table 2.** PDP data for the corrosion of 6061 Al- 15 vol. pct. SiC\(_{p}\) composite in 0.1 M H\(_2\)SO\(_4\) solutions containing different concentrations OPEIB at different temperatures

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<th>Inhibitor Conc. (mM)</th>
<th>(-E_{corr}) (mV/SCE)</th>
<th>(-\beta_c) (mV dec(^{-1}))</th>
<th>(i_{corr}) (µA cm(^{-2}))</th>
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Figure 7. Nyquist plots for the corrosion of composite in 0.1 M H$_2$SO$_4$ in the presence of different concentrations of OPEIB at 40 °C.

Figure 8. Simulation plot of Nyquist plot for the corrosion of the composite in 0.1 M H$_2$SO$_4$ in the presence of 6 mM of OPEIB at 40 °C (inset: equivalent circuit).
At the oxide/solution interface, OH\(^{-}\) or O\(^{2-}\) ions are also formed. The fact that all the three processes are represented by only one loop could be attributed either to the overlapping of the loops of processes, or to the assumption that one process dominates and, therefore, excludes the other processes [34]. In the presence of the inhibitor, the inhibitor layer on the alloy surface also influences one or more of the above processes. The LF inductive loop is related to the relaxation process obtained by the adsorption and incorporation of sulfate ions, oxide ion and charged intermediates on and into the oxide film [33]. The capacitive semicircles are enlarged in the presence of the inhibitor, OPEIB, as compared with that in the absence of the inhibitor. This is an indication of improved corrosion resistance of the composite when OPEIB is present in 0.1 M sulfuric acid medium.

The equivalent electrical circuit (EEC) consisting of five elements, depicted in the inset of Fig. 8 was used to fit the impedance data points of the Nyquist plots. The representative simulation plot is shown in Fig. 8.

In the equivalent circuit, \( R_s \) is the solution resistance, \( R_{ct} \) is the charge transfer resistance. \( R_L \) and \( L \) represent the inductive elements. The equivalent circuit also consists of a constant phase element, CPE \( Q \) corresponding to the capacitance of the double layer, in parallel to the parallel resistors \( R_{ct} \) and \( R_L \), and the latter is in series with the inductor \( L \). In simulation analysis, CPE \( Q \) is used as a substitute for ideal capacitive element \( C \) in order to account for the depressed capacitive loops. A porous and non-uniform electrode surface causes frequency dispersion during impedance analysis and results in depressed semicircles in Nyquist plots indicating a deviation from ideal capacitive behavior [46]. The real double layer capacitance after accounting for frequency dispersion was deduced using following expression (Eq. 3)

\[
C_{dl} = Q_{dl} (\omega_{max})^{n-1} \quad (3)
\]

where \( Q_{dl} \) is the CPE constant, \( \omega_{max} \) is the frequency at which the imaginary part of the impedance \(-Z'\) has a maximum and \( n \) is a CPE exponent which provides a measure of the non-uniformity of the electrode surface. The value of \( n \) is given by \((-1 \leq n \leq 1)\), when \( n = 1 \), CPE behaves like an ideal capacitor.

The polarization resistance \( R_P \) was calculated using equation 4.

\[
R_P = \frac{R_{ct} \times R_L}{R_{ct} + R_L} \quad (4)
\]

where, \( R_{ct} \) is the charge-transfer resistance, \( R_L \) is the resistance associated with the inductive loop. As the polarization resistance is inversely proportional to the corrosion rate, the inhibition efficiency \( \eta \) was calculated from the relation:

\[
\eta(\%) = \frac{R_{P(inh)} - R_{P(blank)}}{R_{P(inh)}} \times 100 \quad (5)
\]

where \( R_{P(inh)} \) and \( R_{P(blank)} \) are the polarization resistance in the presence and absence of the inhibitor, respectively.

The EIS data such as \( R_P \), \( C_{dl} \), and \( \eta(\%) \) obtained from the simulation of Nyquist plot for the corrosion of composite in 0.1 M H\(_2\)SO\(_4\) in the presence of different concentrations of OPEIB at different temperatures are listed in Table 3. It can be observed that as the concentration of the inhibitor increases, the value of \( R_P \) increases, which means that the resistance for the process of corrosion is increased there by reducing the rate of corrosion [47]. Also, the values of \( C_{dl} \) decreases as the concentration of the inhibitor is increased, this observation may be ascribed to increase in thickness of the electronic double layer possibly due to the adsorbed inhibitor molecules on the surface of the composite [48]. The percentage inhibition efficiency
increases with the increase in the concentration of the inhibitor. The trend is in line with the results of potentiodynamic polarization measurements.

**Table 3.** EIS data for the corrosion of 6061 Al-15 vol. pct. SiC\(_{(p)}\) composite in 0.1 M H\(_2\)SO\(_4\) solutions containing different concentrations OPEIB at different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Inhibitor Conc. (mM)</th>
<th>(R_p) (Ω cm(^2))</th>
<th>(C_{dl}) (µF cm(^{-2}))</th>
<th>(\eta) (%)</th>
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Figure 9. Bode magnitude plots for the corrosion of composite in 0.1 M H$_2$SO$_4$ in the presence of different concentrations of OPEIB at 40 °C.

Figure 10. Bode phase angle plots for the corrosion of composite in 0.1 M H$_2$SO$_4$ in the presence of different concentrations of OPEIB at 40 °C.
Bode plot defines the frequency specific impedance behavior of the system under consideration. Bode magnitude plots and Bode phase angle plots for the corrosion of the composite in 0.1 M sulfuric acid in the presence of different concentrations of OPEIB at 40 °C are shown in Fig. 9 and Fig. 10, respectively. From Fig. 9, it may be observed that for increasing concentrations of OPEIB, the impedance modulus ($Z_{\text{mod}}$) corresponding to lower frequency increases. Higher value of $Z_{\text{mod}}$ points out better corrosion resistance [49]. Similarly, Fig. 10, displays an increase in medium frequency phase maximum ($\theta_{\text{max}}$) that depicts the barrier effect for corrosive species through surface film, with the increase in OPEIB concentration. It is also observed that $\theta_{\text{max}}$ shifts towards lower frequency with the increase in inhibitor concentration. The shift in $\theta_{\text{max}}$ towards lower frequency suggests higher time constant of the system [47].

3.4. Effect of temperature and evaluation of activation parameters

At the temperature range considered, it may be seen in Tables 2 and 3 that as the temperature increases the percentage inhibition efficiency also increases. This type of a trend is feature of a predominantly chemisorption phenomenon [42]. The apparent activation energy ($E_a$) in the absence and presence of OPEIB can be evaluated from Arrhenius equation 6.

$$\nu_{\text{corr}} = A e^{-E_a/R T} \quad (6)$$

where $A$ is a constant and $R$ is the ideal gas constant in J K$^{-1}$ mol$^{-1}$, $T$ is temperature in Kelvin. The activation energies were calculated using the slopes obtained from linear fitments of the plots of ln$\nu_{\text{corr}}$ vs. 1/$T$, presented in Fig. 11.

![Figure 11](image)

**Figure 11.** Arrhenius plots for corrosion of the composite in 0.1 M H$_2$SO$_4$ in the presence of different concentrations of OPEIB.

The transition state equation 7 was used to calculate the apparent enthalpy of activation ($\Delta H^\theta$) and entropy of activation ($\Delta S^\theta$).

---

**Figure 11.** Arrhenius plots for corrosion of the composite in 0.1 M H$_2$SO$_4$ in the presence of different concentrations of OPEIB.
where \( N \) is the Avogadro number, \( T \) is temperature in Kelvin and \( h \) is Planck's constant. The enthalpy of activation and entropy of activation were calculated from the slope and intercept values, respectively, of the linear plots of \( \ln(v_{\text{corr}}/T) \) vs. \( 1/T \) shown in Fig. 12. The values of activation parameters are listed in Table 4. From the values it may be observed that the activation energy required for the corrosion reaction in the presence of OPEIB is greater than the one required in the absence of the inhibitor. As \( E_a \) is the measure of hindrance for the corrosion process, the higher value of \( E_a \) in the presence of inhibitor implies that the presence of OPEIB energetically hinders the corrosion of the composite in the sulfuric acid medium, most likely by adsorption on the composite surface [51]. The negative values of \( \Delta S^\# \) indicate association process in the formation of activated intermediate complex [52].

![Figure 12. Transition state equation plots for the corrosion of the composite in 0.1 M H\(_2\)SO\(_4\) in the presence of different concentrations of OPEIB.](image)

<table>
<thead>
<tr>
<th>Inhibitor Conc. (mM)</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
<th>( \Delta H^# ) (kJ mol(^{-1}))</th>
<th>( \Delta S^# ) (J K(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
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</tr>
<tr>
<td>10</td>
<td>35.6</td>
<td>36.7</td>
<td>-128.9</td>
</tr>
</tbody>
</table>

**Table 4.** Activation parameters for the corrosion of 6061 Al-15 vol. pct. SiC\(_{ip}\) composite in 0.1 M H\(_2\)SO\(_4\) solutions containing different concentrations of OPEIB.
3.5. Adsorption isotherm

Adsorption isotherm represents the variation in the extent of inhibitor adsorption on the composite surface with pressure or concentration of the inhibitor \(C_{\text{inh}}\) at constant temperature. In order to understand the nature of interactions which may possibly occur between the composite surface and OPEIB molecules, attempts were made to fit the experimental data to get linear relation between the surface coverage \(\theta = \eta / 100\) and \(C_{\text{inh}}\) using various adsorption isotherms like Langmuir, Frumkin, Freundlich and Temkin adsorption isotherms. However, best fit was obtained for Temkin adsorption isotherm with the regression value 0.99, which are shown in Fig. 13. Temkin adsorption isotherm is mathematically expressed as in equation 8.

\[
\theta = - \left[ \frac{1}{f} \right] \ln (KC_{\text{inh}}) \tag{8}
\]

where, \(f\) is the heterogeneity factor, \(K\) is the adsorption equilibrium constant, \(C_{\text{inh}}\) is the concentration of OPEIB in mol dm\(^{-3}\). The value of \(K\) from the adsorption isotherm plot was substituted in equation 9 to get the standard free energy of adsorption \((\Delta G^0)_{\text{ads}}\).

\[
\Delta G^0_{\text{ads}} = -RT \ln 55.5K \tag{9}
\]

where, 55.5 in mol dm\(^{-3}\) is the molar concentration of water in solution, \(R\) is the universal gas constant and \(T\) is absolute temperature.

The standard enthalpy of adsorption \(\Delta H^0_{\text{ads}}\) and standard entropy of adsorption \(\Delta S^0_{\text{ads}}\) were calculated from the plot of \(\Delta G^0_{\text{ads}}\) vs. \(T\), by thermodynamic relation as given in equation 10.

\[
\Delta G^0_{\text{ads}} = \Delta H^0_{\text{ads}} - T \Delta S^0_{\text{ads}} \tag{10}
\]

The calculated thermodynamic parameters are listed in Table 5. The standard free energy \((\Delta G^0_{\text{ads}})\) value ranges between \(-27.95\) kJ mol\(^{-1}\) to \(-28.50\) kJ mol\(^{-1}\) in 0.1 M sulfuric acid. The widely accepted threshold for free energy to indicate physisorption or chemisorption is less negative than \(-20\) kJ mol\(^{-1}\) and more negative than \(-40\) kJ mol\(^{-1}\), respectively [53, 54]. The obtained value therefore, is indicative of both physisorption and chemisorption of the inhibitor on the metal surface. It may be observed that the standard enthalpy \((\Delta H^0_{\text{ads}})\) value for the adsorption of inhibitor on the composite surface in 0.1 M acid concentration is well below the threshold value of \(-100\) kJ mol\(^{-1}\) which is required for the formation of co-ordinate bonds between the metal and OPEIB molecule facilitating the inhibition chemisorption process [55]. But it is evident from the PDP and EIS measurements that as the temperature increases the inhibition efficiency increases, which indicates at the chemical adsorption of inhibitor molecules on the composite surface. Therefore, it can be concluded that OPEIB is adsorbed on the composite surface through both physisorption and chemisorption, but with predominant chemisorption. The \(\Delta S^0_{\text{ads}}\) is positive, indicating an increasing disorderliness in the system during adsorption phenomenon which may be attributed to the replacement of water molecules from composite surface by the OPEIB molecules [56]. The increase in entropy due to the desorption of water molecules from the surface of the composite surface more than compensates to the decrease in entropy due to the adsorption of the inhibitor molecules.

3.6. Mechanism of inhibition

The corrosion inhibition of the composite is the consequence of molecular adsorption of OPEIB on the alloy composite-solution interface. Pure aluminum readily reacts with oxygen in aqueous solution and gets converted into aluminum oxide. The oxide layer thus formed serves as a protective layer preventing corrosion. In dilute solutions of sulfuric acid, the oxide layer may become porous and pervious without complete dissolution, as suggested by anodic passivity in Tafel plot. However, there is increase in \(i_{\text{corr}}\) value,
which indicates the acceleration of corrosion probably due to the adsorption of aggressive anions like $SO_4^{2-}$ ions. The corrosion of aluminum in aqueous solution is dependent on the concentration of corrosive anions present in the electrolyte. The inhibitor molecule has an organic cation and an inorganic anion.

![Figure 13. Temkin adsorption isotherm plots for the adsorption of OPEIB on the composite surface in 0.1 M H$_2$SO$_4$.](image)

**Table 5.** Thermodynamic parameters for the corrosion inhibition of 6061 Al-15 vol. pct. SiC$_{(p)}$ composite in 0.1 M H$_2$SO$_4$ solutions containing different concentrations of OPEIB

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\Delta G^0_{ads}$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^0_{ads}$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^0_{ads}$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>28.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>28.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>27.9</td>
<td>22.9</td>
<td>17.2</td>
</tr>
<tr>
<td>45</td>
<td>28.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>28.5</td>
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</tbody>
</table>

3.6.1. Anodic reactions

In the absence of OPEIB, the protective oxide film undergoes partial dissolution in the presence of 0.1 M sulfuric acid, by interaction of the hydrated film of aluminum oxide with bisulfate anions when the complex $Al_2[(SO_4)_3(H_2O)_n]_{ads}$ is formed (equation 11 and 12) [57]. The complex thus formed is soluble in aqueous conditions, and therefore gets desorbed from the surface leaving behind free active sites for further attack by the anions like HSO$_4^-$ or $SO_4^{2-}$.

$$4Al + nH_2O + 3O_2 \rightarrow 2Al_2O_3(H_2O)_n$$  \[(11)\]
\[
\text{Al}_2 \text{O}_3 (\text{H}_2 \text{O})_n + 3\text{HSO}_4^- + 3\text{H}^+ \rightleftharpoons \text{Al}_2[(\text{SO}_4)_3(\text{H}_2 \text{O})_n]_{\text{ads}} + 3\text{H}_2 \text{O} \quad (12)
\]

In the presence of OPEIB, the anodic reactions are modified. The \(\text{Al}_2[(\text{SO}_4)_3(\text{H}_2 \text{O})_n]_{\text{ads}}\) complex can adsorb \(\text{HSO}_4^-\) ion and interact electrostatically with the organic cation \((\text{OPEI})^+\) of the OPEIB molecule (equation 13). Such interaction between the composite and inhibitor leads to inhibition by physisorption phenomenon. Similarly, the counter ion like \(\text{Br}^-\) present in OPEIB molecule may also interact electrostatically with the organic cation \((\text{OPEI})^+\) of OPEIB (equation 14) \[58\]. However, the concentration of \(\text{Br}^-\) in the solution is very less as compared to \(\text{HSO}_4^-\) ions, and therefore the presence of \(\text{Al}_2\text{H}[\text{SO}_4(\text{H}_2 \text{O})_n \text{OPEI}^+]_{\text{ads}}\) is more likely.

\[
\text{Al}_2[(\text{SO}_4)_3(\text{H}_2 \text{O})_n]_{\text{ads}} + \text{HSO}_4^- + \text{OPEI}^+ \rightleftharpoons \text{Al}_2\text{H}[(\text{SO}_4)_3(\text{H}_2 \text{O})_n \text{OPEI}^+]_{\text{ads}} \quad (13)
\]

\[
\text{Al}_2 \text{O}_3 (\text{H}_2 \text{O})_n + \text{Br}^- \rightleftharpoons [\text{Al}_2 \text{O}_3 (\text{H}_2 \text{O})_n \text{Br}^-]_{\text{ads}} \quad (14)
\]

\[
[\text{Al}_2 \text{O}_3 (\text{H}_2 \text{O})_n \text{Br}^-]_{\text{ads}} + \text{OPEI}^+ \rightleftharpoons \text{Al}[(\text{H}_2 \text{O})_n \text{Br}^- \text{OPEI}^+]_{\text{ads}} \quad (15)
\]

3.6.2. Cathodic reactions

The equation 16 depicts the general cathodic reaction in acidic conditions.

\[
\text{Al}_2 \text{O}_3 + \text{H}_2 \text{O}^+ + e^- \rightleftharpoons \text{Al}_2 \text{O}_3 (\text{H}_2 \text{O}) + \frac{1}{2} \text{H}_2 \quad (16)
\]

In the presence of OPEIB, the macromolecular cations \((\text{OPEI})^+\) compete with protons to occupy active cathodic sites, leading to the formation of \(\text{Al-OPEI}_{\text{ads}}\) (equation 17). The size of protons are very less compared to the macromolecular OPEIB, therefore \(\text{OPEI}^+\) can cover larger area and thereby reduces the kinetics of cathodic reaction and thus helps in controlling the rate of corrosion.

\[
\text{Al} + \text{OPEI}^+ + e^- \rightleftharpoons \text{AlOPEI}_{\text{ads}} \quad (17)
\]

Also, there are pi electrons and lone pairs of electron on the O and N atoms of the organic cation \[58\]. The donation of electrons to the vacant p-orbitals of aluminum atoms may lead to a bond formation between the metal and inhibitor molecule resulting in blocking of metal surface via chemisorption phenomenon \[59\]. As stated earlier, the inhibition of corrosion of alloy composite is of mixed type, with both anodic and cathodic control, however, cathodic reactions were predominantly controlled by both chemisorption and physisorption processes.

3.7. Surface morphology: SEM and EDX analyses

The impact of sulfuric acid in the presence and absence of OPEIB on the surface of the composite was analyzed through SEM images. Figures 14(a), 14(b) and 14(c) show freshly polished sample surface, surface of the sample immersed in 0.1 M \(\text{H}_2 \text{SO}_4\) and surface of the sample immersed in 0.1 M \(\text{H}_2 \text{SO}_4\) containing 10 mM OPEIB, respectively, for three hours at 30 °C. Figure 14(a) shows a smooth and even morphology with reinforced SiC ceramic particles, whereas from Fig. 14(b), micro-galvanic corrosion is evident at the sites between metal and the ceramic particles. Figure 14(c) shows a smooth morphology as compared to Fig. 14(b) which demonstrates the possible corrosion inhibition of the sample by adsorption of OPEIB on the metal surface. Further, EDX was recorded for qualitative analysis of adsorbed OPEIB on composite surface (Fig. 15). The area analysis of the inhibited sample showed peaks corresponding to
nitrogen (N) and oxygen (O) apart from (C) peak and other elements present in the composite. This reflects the possible adsorption of OPEIB on the composite surface.

**Figure 14.** SEM images of (a) freshly polished surface of the composite (b) surface of the composite immersed in 0.1 M H$_2$SO$_4$ for three hours at 30 °C (c) surface of the composite immersed in 0.1 M H$_2$SO$_4$ containing 10 mM OPEIB for three hours at 30 °C.

**Figure 15.** EDX spectrum of composite surface immersed in 0.1 M H$_2$SO$_4$ containing 10 mM OPEIB at 30 °C.

4. CONCLUSIONS
   - The rate of corrosion drastically reduces in the presence of OPEIB in 0.1 M H$_2$SO$_4$ acid medium in the studied temperature range of 30 - 50 °C. Optimum concentration of inhibitor was found to be 10 mM.
The inhibitor acts as a mixed type of inhibitor influencing both anodic and cathodic reactions, with predominant control on cathodic reaction.

The adsorption of OPEIB on the metal is through both physisorption and chemisorption processes, but with predominant chemisorption; and the adsorption process follows Temkin adsorption isotherm.

Owing to the relatively high thermal stability, water solubility, recycling ability, product recovery and moisture-stability of OPEIB, it may be considered as a green, promising and efficient inhibitor on 6061 Al-15 vol. pct. SiC\textsubscript{(p)} composite in 0.1 M H\textsubscript{2}SO\textsubscript{4} medium.

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REFERENCES


The authors declare no conflict of interest

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