Exploration of synthesized quaternary ammonium ionic liquids as unharmful anti-corrosives for aluminium utilizing hydrochloric acid medium

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1-(benzyloxy)-1-oxopropan-2-aminium 4-methylbenzenesulfonate (BOPAMS) and 4-(benzyloxy)-4-oxobutan-1-aminium 4-methylbenzenesulfonate (BOBAMS) were prepared and confirmed through spectroscopic methods (FT-Infrared, Carbon 13-NMR and Proton-NMR). BOPAMS and BOBAMS were evaluated as unharmful inhibitors for aluminium corrosion. The anti-corrosive properties, inhibition mechanism, inhibitor-metal adsorption behaviour and corrosion inhibition efficiency were evaluated by employing approaches like gravimetric, potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). FT-IR demonstrated functional groups that are responsible for the binding of BOPAMS and BOBAMS with surfaces of aluminium. BOPAMS and BOBAMS resemble a semi-chemisorption/physisorption mechanism, obeying Langmuir binding model. The mechanism of binding adopted by BOPAMS and BOBAMS was proposed.

1. Introduction

Aluminium (Al) is a highly reactive metal that withstands most corrosive environments, although it can undergo corrosion if exposed directly to an aggressive environment. The corrosion resistance of Al is owed to the Al oxide film inert and protective nature, which forms on the metal surface when exposed to moisture (Abdulwahab et al., 2016; Kciuk et al., 2010; Kciuk and Tkaczyk, 2007; Shalabi et al., 2015). Aggressive acid solutions like hydrochloric acid (HCl) are extensively used in industries during the manufacturing of metallic equipments and in other applications such as acid pickling (Verma et al., 2020). During the pickling process, HCl leads to the corrosion of metal vessels and industrial pipelines, thereby reducing the production and resulting in the economic loss (Uhlig and King, 1972; Govindasamy and Ayappan, 2015). To circumvent the corrosion initiated by HCl, corrosion inhibitors are utilized. The utilization of corrosion inhibitors is regarded as an effective method towards the protection of materials from the wrath of corrosion in aggressive environments (Kim et al., 2006; Subasri et al., 2005). Substances that are utilized to protect materials from attack by aggressive species must possess properties that allow them to bind onto the surface of the material and slow down the dissolution of materials. The resultant barrier of chemisorbed substance protects the material by either delaying the electrochemical mechanism or by the role of demarcation between the material and the corrosive medium (Umoren, 2009). Most corrosion inhibitors that are utilized in solvent heating processes are harmful and non-biodegradable, which is a problem because it can lead to the emission of industrial wastewaters with a vast amount of toxic materials finding their path into waterways. Due to their toxicity, most inhibitor compounds do not meet entirely the required environmental protection standards (Antonijevic and Petrovic, 2008). Nowadays, many studies have been devoted to finding eco-friendly organic corrosion inhibitors. Ionic liquids (ILs) have enjoyed more employment as corrosion inhibitors to solve the toxicity problem. ILs resemble the nature of organic salts at atmospheric temperatures and their structures are composed of cations and anions (Zheng et al., 2014a,b). Recently Atta et al. reported on the use of quaternary ammonium salts, namely, Oleylammonium Tosylate and Octadecylammonium Tosylate (Atta et al., 2015). In their report, they concluded that these compounds work as effective semi-chemisorption/physiosorption corrosion inhibitors when steel is exposed to diluted hydrochloric acid. Even though other ILs have demonstrated the ability to act as corrosion inhibitors for Al corrosion, no reports are describing the use of 1-(benzyloxy)-1-oxopropan-2-aminium 4-methylbenzenesulfonate (BOPAMS) and 4-(benzyloxy)-4-oxobutan-1-aminium 4-methylbenzenesulfonate (BOBAMS) as

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anticorrosives of Al utilizing hydrochloric acid medium. This paper reports on the continuation of the work that has been done in our research group in exploring the use of ILs as green inhibitors and adds more data to the literature already available. The most notable improvement or achievements characterizing the current work is the fact that the current ionic liquids were synthesized as opposed to being obtained from the commercially available ones. It is also paramount to note that these compounds are completely novel. The quaternary ammonium salts, namely BOPAMS and BOBAMS utilized as anticorrosives for Al corrosion in 1M hydrochloric acid in this present study are shown in Figure 1. Table 1 puts in comparison the corrosion inhibition abilities by various corrosion inhibitors that are reported in literature and the ones utilized in the current investigation.

2. Experimental

2.1. Materials

Al coupons composed of approximately 99 (wt %), were used as the working electrode for all experimental procedures performed in this study. The coupons had a dimension of 3 cm length x 2 cm breadth and contained a small hole of 2 mm diameter for hanging on a glass rod.

2.2. Preparations of solutions

Approximately 1M HCl aggressive solution was carefully made up through appropriate proportioning of 32% analytical grade HCl utilizing distilled H2O. Parent solutions of 10.0 × 10⁻⁴ M BOPAMS and BOBAMS were thoroughly made up by weighing appropriate amounts of BOPAMS and BOBAMS, followed by the addition of distilled H2O to the mark of 1000 cm³ volumetric flasks. These parent solutions were utilized to make up various concentrations of BOPAMS and BOBAMS as reported in the results section of this paper.

2.3. Synthesis of BOPAMS and BOBAMS

The synthesis of ionic liquids followed reaction Scheme 1 below. The two compounds were synthesized by the suspension of alanine (6.2124 g, 69.7395 mmol) and γ-amino butanoic acid 2 (7.0164 g, 68.0411 mmol) respectively with 10 cm³ benzyl alcohol 3 (10.4 g, 96.1716 mmol) in a mixture of p-toluenesulfonic acid monohydrate (PTSA) (14.5821 g, 84.6812 mmol) and toluene (200 cm³). The mixture was stirred for 10 min and heated to reflux for 10 h with azetropic removal of water. The two products were precipitated by the addition of Et₂O (100 cm³), filtered, dissolved in CH₃OH (60 cm³) and precipitated further by the addition of Et₂O (100 cm³). After the filtration and drying, the products were obtained as white crystals. BOPAMS (C₁₇H₂¹NO₅S, Mol. Wt. 351.42), Yield: 25.3816 g, 91% and BOBAMS (C₁₈H₂₃NO₅S, Mol. Wt. 365.44), Yield: 23.0146 g, 93%. Spectral analysis was carried out to confirm the two ionic liquids.

2.4. Weight loss measurements

Al sheets were first weighed and then totally submerged in 100 cm³ 1M HCl without and with BOPAMS and BOBAMS at various molarities (1.0 × 10⁻⁴ M – 5.0 × 10⁻⁴ M) and temperatures (303–333K) for a period of 8 h. This procedure was performed in a temperature-controlled water bath for purposes of maintaining the heat during the submerging period. This was carefully followed by removing, cleaning with distilled H₂O and finally drying in open air. The overall weight change of the Al sheets was noted.

2.5. Electrochemical techniques

For the electrochemical experiments, a PGSTAT302N Autolab Potentiostat from Metrohm was utilized to carry out potentiodynamic polarization (PDP) as well as electrochemical impedance spectroscopy (EIS). This instrument was equipped with a three-electrode cell consisted of a saturated calomel (Ag/AgCl) reference electrode, Pt counter electrode and the Al sheet was utilized as the working electrode. For EIS, a bridge tube was used to place the working electrode near the reference electrode to minimize IR contribution/Ohmic trop from the electrolyte solution. During the PDP and EIS measurements, Al sheets were allowed to corrode in open circuit potential (OCP) freely for a period of 30 min. PDP studies were performed at −250 to +250 mV (SCE) and 1 mV s⁻¹ potential and scan rate, respectively. EIS curves were done at 100 kHz–0.00001 kHz frequency range at OCP conditions through applying a signal amplitude perturbation of 5 mV by utilizing an AC indicator at corrosion potential. Al sheets that were utilized were of a 1 cm² total area in surface. Nyquist and Tafel curves were obtained from the EIS and PDP measurements, respectively.

3. Results and discussion

3.1. Characterization of BOBAMS and BOPAMS

The ¹H-NMR and ¹³C-NMR spectra of BOBAMS and BOPAMS are represented in Figures 2 and 3, respectively. As expected the aromatic regions of the ¹H-NMR spectra of BOBAMS and BOPAMS are similar. The spectra are characterized by a broad singlet peak accounting for three protons at 8.36 ppm (BOPAMS) and 7.34 ppm (BOBAMS). Also, the two spectra contain two doublets each, which account for two protons each at 7.50 ppm and 7.13 ppm. Lastly, the aromatic region of the two spectra is characterized by a broad singlet peak accounting for three protons at 8.36 ppm (BOPAMS) and 7.34 ppm (BOBAMS). Also, the two spectra are characterized by a broad singlet peak accounting for three protons at 1.41 ppm, a singlet accounting for three protons at 3.41 ppm and another singlet accounting for two protons at 5.34 ppm. The same regions for BOBAMS are characterized by a broad singlet peak accounting for two protons at 1.81 ppm, a triplet accounting for two protons at 2.40 ppm, another triplet accounting for two protons at 2.62 ppm, a singlet accounting for three protons at 3.80 ppm and lastly a singlet accounting for two protons 5.11 ppm. The ¹³C-NMR spectra represent the correct number of carbon atoms at the appropriate chemical shift values. A methyl carbon peak for BOBAMS was observed at around 21.24 ppm (CH₃PTSA). Two methyl carbon peaks were observed at around 16.16 ppm (H₃C(3)Aln) and 21.25 ppm (H₃C(3)PTSA) for BOPAMS. There are four methane carbon peaks at about 22.87 (CH₂(2)GABA), 30.71 (CH₂(2)GABA), 38.67 (CH₂(4) GABA) and 66.07 (CH₂Bn) ppm for BOBAMS. BOPAMS gave a methine carbon at approximately 31.16 ppm (HC(2)Aln) and a methylene carbon peak was observed at around 67.49 ppm (H₂C(Bn). The aromatic protons of the benzene rings were found at around 125–128 ppm (CAr) and four

Figure 1. Molecular structures of BOPAMS and BOBAMS.
**Table 1.** Comparison of the corrosion inhibition abilities by various corrosion inhibitors that are reported in literature and the ones utilized in the current investigation.

| Corrosion Inhibitor | Investigative Techniques | Adsorption mode | Aggressive medium/Metal | IE/% | Reference |
|---------------------|--------------------------|-----------------|-------------------------|------|-----------|
| 2-hydroxyethyl trimethylammonium Chloride | Gravimetric, electrochemical, surface morphology, computational studies | Temkin adsorption isotherm, mixed-type inhibitors | 1 M HCl/mild steel | 92.04 | Verma et al. (2018) |
| 1-allyl-3-ethylimidazolium Bromide | Electrochemical, surface morphology, computational studies | Langmuir adsorption isotherm, chemisorption | 0.5 M H₂SO₄/copper | 92.5 | Qiang et al. (2017) |
| 3,3’-(1,4-phenylenebis(methylene)) bis(1-alkyl-1H-imidazol-3-ium) bromide | Electrochemical | Mixed-type inhibitors | 0.5 M H₂SO₄/Stainless steel | 90.7 | Nessim et al. (2018) |
| 1-butyl-1-methylpyrrolidinium trifluoromethyl sulfonate | Electrochemical, surface Morphology | Langmuir adsorption isotherm | 3.5% NaCl/mild steel | 91.4 | El-Shamy et al. (2015) |
| Current ILs | Gravimetric, electrochemical, spectroscopic | Langmuir adsorption isotherm, mixed-type inhibitors | 1 M HCl/aluminium | 97.8 |

**Scheme 1.** Synthetic scheme of BOPAMS and BOBAMS.

**Figure 2.** ¹H-NMR spectra a), b) BOPAMS and c), d) and BOBAMS.
Figure 3. $^{13}$C-NMR spectra a), b) BOPAMS and c), d) and BOBAMS.

Figure 4. Tafel plots of Al utilizing 1M HCl for the process without and with of various molarities of a) BOPAMS and b) BOBAMS.

Table 2. PDP data of Al corrosion utilizing 1M HCl for the process without and with various molarities of BOPAMS and BOBAMS at 303K.

| Inhibitor | Conc./M | $E_{corr}$/mV | $i_{corr}$/mAcm$^{-2}$ | $\beta_\alpha$/mVdec$^{-1}$ | $\beta_\beta$/mVdec$^{-1}$ | $R_p$ $(10^{-1}/\Omega$ cm$^2$ | IE/% |
|-----------|---------|---------------|--------------------------|-----------------------------|-----------------------------|-----------------------------|-----|
| Blank     | –       | –769          | 0.00491                  | 51                          | 101                         | 30.10                       | –   |
| BOPAMS    | $1.0 \times 10^{-4}$ | –724          | 0.00070                  | 7                           | 16                          | 30.50                       | 85.74 |
|           | $2.0 \times 10^{-4}$ | –730          | 0.00043                  | 6                           | 15                          | 43.76                       | 91.24 |
|           | $3.0 \times 10^{-4}$ | –723          | 0.00027                  | 11                          | 12                          | 43.76                       | 91.24 |
|           | $4.0 \times 10^{-4}$ | –727          | 0.00019                  | 3                           | 4                           | 38.94                       | 96.13 |
|           | $5.0 \times 10^{-4}$ | –729          | 0.00012                  | 2                           | 2                           | 36.44                       | 97.59 |
| BOBAMS    | $1.0 \times 10^{-4}$ | –723          | 0.00083                  | 10                          | 24                          | 36.62                       | 83.10 |
|           | $2.0 \times 10^{-4}$ | –721          | 0.00072                  | 8                           | 1                           | 29.63                       | 85.34 |
|           | $3.0 \times 10^{-4}$ | –727          | 0.00048                  | 6                           | 12                          | 34.15                       | 90.22 |
|           | $4.0 \times 10^{-4}$ | –722          | 0.00034                  | 4                           | 10                          | 38.44                       | 93.08 |
|           | $5.0 \times 10^{-4}$ | –718          | 0.00015                  | 2                           | 2                           | 28.08                       | 96.95 |
quintenary peaks at about 135, 138, 145, and 170 ppm (CO2Bn) for both BOBAMS and BOPAMS.

3.2. Potentiodynamic polarisation (PDP)

Figure 4 shows the characteristic polarization plots found from the corrosion trait of Al in 1M HCl without and with various concentrations of BOPAMS and BOBAMS at 303K. The values of different electrochemical parameters like corrosion current density \(i_{\text{corr}}\), corrosion potential \(E_{\text{corr}}\), anodic and cathodic Tafel slopes \(\beta_a\) and \(\beta_c\) were found by the manipulation of the oxidation and reduction potential up to their intersection, and their values are shown in Table 2. The potentiodynamic efficiencies \(\%\text{IEPDP}\) based on corrosion current density values were obtained utilizing Eq. (1) (Murulana et al., 2015).

\[
\%\text{IEPDP} = \left( \frac{\rho_{\text{corr}} - \rho_{\text{corr},0}}{\rho_{\text{corr},0}} \right) \times 100 \tag{1}
\]

where \(\rho_{\text{corr}}\) and \(\rho_{\text{corr},0}\) represent values of corrosion current density without and with BOPAMS and BOBAMS, respectively.

Tafel extrapolation plots show that the introduction of BOPAMS and BOBAMS altered both the oxidation and reduction sections and caused a decrease in the current densities relative to the ones observed in the blank. The decline is slightly pronounced with increases of BOPAMS and BOBAMS concentrations. The reduction effect, however, is somewhat more noticeable, indicating the process is predominantly of cathodic nature. This kind of behaviour of the BOPAMS and BOBAMS suggests that the acidic attack on the Al surface is hindered. In the reduction region, there is a rise to the parallel effect of the Tafel lines, signifying the activation control of the hydrogen evolution process. This effect indicates that the discharge of hydrogen occurs via the charge transfer process at the metal interface (Musa et al., 2010; Zheng et al., 2014a,b). Literature studies show that if the change in \(E_{\text{corr}}\) is higher than \(\pm 85\) mV relative to that of the blank experiments, then BOPAMS and BOBAMS are said to be either oxidation or reduction inhibitors (Ghames et al., 2017). The highest change in the \(E_{\text{corr}}\) data from the present study were less than 85 mV with BOPAMS and BOBAMS. This kind of change confirms that neither BOPAMS nor BOBAMS are wholly oxidation or reduction but semi-chemisorption/physisorption inhibitors. The data presented in Table 2 shows that there is a change in the shift of both \(\beta_a\) and \(\beta_c\) compared to the blank experiments. The \(E_{\text{corr}}\) values lowered markedly with a rise in the concentration of BOPAMS and BOBAMS and the \(\%\text{IEPDP}\) congruently increased to a maximum at their highest concentrations. This observation by BOPAMS and BOBAMS suggests that they bind on the Al surface and the binding effect increases and become stable due to the availability of more BOPAMS and BOBAMS molecules at higher concentrations.

3.3. Electrochemical impedance spectroscopy (EIS)

The impedence spectra found for Al in 1M HCl solution at various concentrations of BOPAMS and BOBAMS are presented as Nyquist plots as indicated in Figure 5. EIS data found from these data are presented in Table 3. The shape of the curves is the same without or with BOPAMS and BOBAMS. This behaviour signifies that the presence of BOPAMS and BOBAMS does not alter the oxidation and reduction processes of the dissolution of Al. In some cases, there was a shift in Nyquist plots origin as the concentrations of BOPAMS and BOBAMS were raised. This behaviour can be theoretically accounted for by the formation of the binding film layer on the Al surface. Furthermore, as the concentration of BOPAMS and BOBAMS were amplified, more BOPAMS and BOBAMS molecules were able to provide higher coverage of the Al surface. This shift might also be as a consequence of the stabilization of the binding process and the reduction of the passivation of Al. The semicircles obtained are not perfect, and a smaller arch for the blank shows that the corrosion of Al is due mainly to the charge sharing process which also suggests that the Faradaic processes that occur on bare Al surface lower with the introduction of BOPAMS and BOBAMS. As such, BOPAMS and BOBAMS do not change the electrochemical process of corrosion but prevent it by binding on the metal surface (El-Azaly, 2019).

Nyquist diagram presented here consists of a capacitive loop in the high-frequency areas followed by an inductive loop in the low-frequency areas. The high-frequency capacitive loop is said to be a representative of the charge transfer resistance of the corrosion process and the double layer behaviour. The behaviour of the inductive loop may be a consequence of several phenomena. For instance, it can be accounted for as the relaxation of the substances present within the oxide layer covering the electrode surface. Furthermore, through the Ladha and Hachelef’s measurements (Ladha et al., 2015; Hachelef et al., 2016), the inductive loop has been confirmed to be linked with the presence of the film on passivation of Al. Moreover, another cause for the induction loop could be as consequence of the stabilization of the binding intermediate complex on the electrode surface that might involve the reactive products as well as the molecules of the BOPAMS and BOBAMS (Ladha et al., 2015; Yurt et al., 2006). The relevant electrical circuit structure utilized to fit the impedence spectrums has been reported previously (Yurt et al., 2006; Khaled and Al-Qahtani, 2009) and is shown in Figure 6. In this electrical circuit, R1 represents the electrolyte resistance (R_s), Q1 represents constant phase element (CPE), R2 represents the charge transfer resistance (R_{ct}), and R3 and L3 represent the inductive elements. Constant phase element was utilized as opposed to double-layer capacitance (C dl) to reflect a perfect capacitor in order to describe the inhomogeneities within the system. The imperfect semicircle loop at higher frequency section indicates the inhomogeneity of the Al surface due to structural or interfacial origin similar to those existing during the binding processes (Zheng et al., 2014a,b).
charge transfer resistance increases. Additionally, this rise is proportional to the rise in the thickness of the electrical double layer or the fall in local dielectric constant, indicating that the molecules of BOPAMS and BOBAMS work by binding at the interface between the solution and the Al surface through the displacement of water molecules (Alaoui et al., 2020).

3.4. Weight loss measurements

To further understand the mode of binding of BOPAMS and BOBAMS on Al surface and assess the impact of temperature on the corrosion process, weight loss measurements were studied. The consequence of temperature on the binding and calculation of activation parameters for Al corrosion was evaluated from the Arrhenius-type graph according to Eq. (3) (Murulana et al., 2015).

\[
\log C_R = \log A - \frac{E_a}{\gamma_{303K}}
\]

where \( E_a \) represents the apparent activation energy for the corrosion process which signifies the energy necessary for a molecule to react, \( C_R \) represents the corrosion rate in g.cm\(^{-2}\).h\(^{-1} \), \( A \) represents the Arrhenius pre-exponential factor, \( T \) represents the absolute temperature, and \( R \) represents the universal gas constant.

Table 4 shows that the %IE increases with an increase in the concentration of the two inhibitors studied. For instance, at 303K when the concentration of BOPAMS was \( 1.0 \times 10^{-4} \) M the %IE was found to be 87.16 % and increased to a maximum of 93.52 % at \( 5.0 \times 10^{-4} \) M. The same trend was observed in the case of BOBAMS wherein the obtained inhibition efficiency at \( 1.0 \times 10^{-4} \) M was 89.74% and at \( 5.0 \times 10^{-4} \) M was 91.94%. The increase in %IE with an increase in the concentrations of the inhibitors can be attributed to the accumulation of a greater number of molecules on the surface of Al as the inhibitor concentration is increased.
which lead to the separation of the Al surface from the acidic solution and retarding the dissolution of Al (Ezeoke et al., 2012).

From the straight-line type of graph of log $C_R$ against $1/T$ (Figure 7), the numerical data of $E_a$ for various concentrations of BOPAMS and BOBAMS were obtained utilizing the slopes and can be utilized to explain the inhibitive mechanism further. The results obtained from these graphs are shown in Table 4. Figure 7 shows the blank with fatter slope indicating that it has smaller activation energy. When BOPAMS and BOMAMS are introduced into the system, the slope is much steeper with higher activation energy. The similarity in the trend of these figures suggests that the two inhibitors have the same mechanism of action. The data of $E_a$ attained from the figures without the presence of BOPAMS and BOBAMS was 9.9215 kJ mol$^{-1}$. However, evidently the $E_a$ data when $1.0 \times 10^{-4}$ M BOPAMS was added, increased instantly to 41.8773 kJ mol$^{-1}$. BOBAMS also revealed a similar trend of the increase in activation energy which rises immediately when the smallest concentration of the BOBAMS is introduced into the system. This rise signifies that in the availability of BOPAMS and BOMAMS the barrier of energy for the corrosion reaction is induced, and the magnitude of the rise is related to the concentration of BOPAMS and BOBAMS (El-Katori et al., 2020).

Kinetic data like enthalpy ($\Delta H^*$) and entropy ($\Delta S^*$) of activation can be used to provide further details on the dependence of inhibition efficiencies of BOPAMS and BOMAMS on temperature and the concentration of the inhibitor. These data were determined using the equation of transition state (4) (Murulana et al., 2015):

$$\log \left( \frac{C_R}{T} \right) = \left[ \log \left( \frac{R}{Nh} \right) + \left( \frac{\Delta S^*}{2.303R} \right) \right] + \left( \frac{\Delta H^*}{2.303R} \right) \left( \frac{1}{T} \right)$$

where $R$ represents the universal gas constant, $h$ represents the Plank’s constant, $T$ represents the absolute temperature, 2.303 is a numerical value utilized to convert from ln to log and $N$ represents the Avogadro’s number.

The straight-line graph of log ($C_R/T$) against $1/T$ (Figure 8) has a slope equivalent to ($\Delta H^*/2.303R$) and y-intercept equivalent to [log ($R/ Nh$) + $\Delta S^*/2.303R$]. This information enabled the estimation of activation data ($\Delta H^*$ and $\Delta S^*$) which are listed in Table 5. Some insight into a possible type of adsorption mode of BOPAMS and BOBAMS can be gained by relating the corrosion activation data without and with the synthesized compounds. (-) data of $\Delta S^*$ indicate that the damage on the metal surface has decreased and the (+) data indicate that the chaosness of the process has risen. Large (-) data of $\Delta S^*$ are indicative of association of the activated complex in the slowest elementary reaction as opposed to dissociation. This signifies that the destruction on the Al surface has been lessened during the process of migrating from reactants to the activated complex as a result of the binding of BOPAMS and BOBAMS molecules on the Al surface (Verma et al., 2015; El-Katori et al., 2020). (+) sign of $\Delta H^*$ data of the results reflects that the binding of BOPAMS and BOBAMS molecules is of endothermic character. $\Delta H^*$ data for the uninhibited solution was 7.3147 kJ mol$^{-1}$ and increased to 39.2549 and 41.6667 kJ mol$^{-1}$ after the addition of $1.0 \times 10^{-4}$ M BOPAMS and BOBAMS, respectively. This indicates that significant amount of energy was required to form a corrosion product, indicating that the presence of BOPAMS and BOBAMS resulted in the difficulty for the dissolution of the Al surface which increased as the inhibitor concentrations were increased.

### 3.5. Adsorption isotherms and thermodynamic parameters

The binding of BOPAMS and BOBAMS on Al surface is a critical step in the corrosion inhibition mode, which can be explained by adsorption isotherms (Manyt and Al-Rawashdeh, 2004). Therefore, to ascertain the mode of adsorption for BOPAMS and BOBAMS, several well-known adsorption isotherms were adopted and among them, the optimum correlation was obtained through Langmuir adsorption isotherm, which was achieved through a graph of surface coverage ($\theta$) against the concentrations of BOPAMS and BOBAMS. According to Langmuir, $\theta$ is related to the inhibitor concentration ($C_{inh}$) in the bulk of the solution as well as the adsorption constant ($K_{ads}$), according to Eq. (5) (Ekanem et al., 2010).

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

Thermodynamic parameters provide information relating to the strength and inhibitive mechanism of corrosion by the inhibitor. The $\Delta G_{ads}$ values were obtained from $K_{ads}$ using Eq. (6) (Murulana et al., 2015).

$$\Delta G_{ads} = -RT\ln(55.5K_{ads})$$

Figure 7. Arrhenius plots of Al utilizing 1M HCl for the process without and with of various molarities of a) BOPAMS and b) BOBAMS.
where the numeral 55.5 represent the molarity of H₂O in solution, ΔG_{\text{ads}} represents the standard Gibb's free energy of the binding process, R represents the universal gas constant and T is the absolute temperature.

Figure 9 represents the relation between C_{inh}/θ versus C_{inh} which gave straight lines for the two inhibitors with a slope approximately equal to unity and non-zero intercepts at all temperatures investigated. For example, the linear correlation coefficient (R²) for BOPAMS are 0.9966, 0.9974, 0.9957 and 1 at 303K, 313K, 323K and 333K, respectively. This confirms that the adsorption layer formed by the three inhibitors on the Al surface in 1M HCl obeys the Langmuir adsorption

Table 5. Kinetic and activation data of Al corrosion utilizing 1M HCl for the process without and with various molarities of BOPAMS and BOBAMS.

| Inhibitor | Conc./M | E_a/kJ.mol⁻¹ | ΔH*/kJ.mol⁻¹ | ΔS*/J.mol⁻¹ K⁻¹ |
|-----------|---------|--------------|-------------|-----------------|
| Blank     | –       | 9.9215       | 7.3147      | -200.2395       |
| BOPAMS    | 1.0 × 10⁻⁴ | 41.8773     | 39.2549     | -195.5330       |
|           | 2.0 × 10⁻⁴ | 43.5356     | 40.8088     | -195.3432       |
|           | 3.0 × 10⁻⁴ | 48.0641     | 45.4191     | -194.6320       |
|           | 4.0 × 10⁻⁴ | 48.6194     | 45.9999     | -194.5527       |
|           | 5.0 × 10⁻⁴ | 56.7115     | 54.6709     | -193.2145       |
| BOBAMS    | 1.0 × 10⁻⁴ | 43.6773     | 41.6667     | -195.2710       |
|           | 2.0 × 10⁻⁴ | 46.9899     | 44.7879     | -194.7799       |
|           | 3.0 × 10⁻⁴ | 46.3580     | 46.6452     | -194.5330       |
|           | 4.0 × 10⁻⁴ | 48.8856     | 50.3792     | -193.9810       |
|           | 5.0 × 10⁻⁴ | 49.7281     | 51.2025     | -193.8779       |

Figure 9. Langmuir isotherms of Al utilizing 1M HCl for the process without and with of various molarities of a) BOPAMS and b) BOBAMS at various temperatures.
isotherm. The closeness of the slope to unity also indicates that the type of the adsorption layer formed on the Al surface is a monolayer (Ogunleye et al., 2020).

The data of $\Delta G_{ads}$ ranging up to $-20$ kJ mol$^{-1}$ are generally associated with some electrostatic interaction taking place around the charged metal surface and BOPAMS and BOBAMS (physical adsorption) while the data around $-40$ kJ mol$^{-1}$ and beyond are associated with the exchange of electrons between Al and BOPAMS and BOBAMS resulting in the formation of a strong chemical bond (chemical adsorption) (El-Lateef et al., 2019; Lgaz et al., 2016). In this work, the $\Delta G_{ads}$ data for BOPAMS and BOBAMS were all above $-20$ kJ mol$^{-1}$ yet slightly below $-40$ kJ mol$^{-1}$, signifying mixed-type binding process on Al surface, with a dominating chemisorption mechanism as the values are nearing the $-40$ kJ mol$^{-1}$ value. The data of $\Delta G_{ads}$ showed similar behaviour to those for $K_{ads}$ as they seem to increase with a temperature rise. This implies some change in the adsorption mechanism from a physical to a chemical type of adsorption. ($-$) data of $\Delta G_{ads}$ support the spontaneous type of binding process.

Thermodynamic properties like the enthalpy of adsorption $\Delta H_{ads}$ and $\Delta S_{ads}$ can be utilized to further understand the binding process of BOPAMS and BOBAMS on Al surface. $\Delta H_{ads}$ data may be deduced by utilizing the Van’t Hoff expression (7) (Tang et al., 2003).

$$lnK = -\frac{H_{ads}}{RT} + \text{constant}$$

where $K$ represents the adsorption equilibrium constant, $R$ represents the universal gas constant and $T$ represents the absolute temperature.

Gibbs-Helmholtz expression may also be utilized to obtain the enthalpy of adsorption (Noor, 2007).

$$\left[ \frac{\partial (\Delta G_{ads}/T)}{\partial T} \right]_p = -\frac{\Delta H_{ads}}{T^2}$$

(8)

Gibbs-Helmholtz expression (8) may also be rearranged to give expression in Eq. (9).

$$\frac{\Delta G_{ads}}{T} = \frac{H_{ads}}{T} + k$$

(9)

$\Delta S_{ads}$ can be calculated from $\Delta G_{ads}$ and $\Delta H_{ads}$ as shown in Eq. (10).

$$\Delta S_{ads} = \frac{\Delta H_{ads} - \Delta G_{ads}}{T}$$

(10)

Table 6 reports the data of $\Delta H_{ads}$ and $\Delta S_{ads}$ over the temperature range of 303–313K. It has been reported in literature (Amin et al., 2007; Al-Amiery et al., 2013) that if $\Delta H_{ads} > 0$ (endothermic), then the inhibitors adsorb chemically on the metal surface, and if $\Delta H_{ads} < 0$ (exothermic), then the adsorption process can either be taking place through chemisorption or physisorption process. In cases where the $\Delta H_{ads} < 0$, physisorption process can be differentiated from chemisorption based on the magnitude of $\Delta H_{ads}$. To classify the adsorption as physisorption, the $\Delta H_{ads}$ data is normally less than 40 kJ mol$^{-1}$ and it is greater than 100 kJ mol$^{-1}$ for chemisorption (Zarrouk et al., 2011). For BOPAMS, the $\Delta H_{ads}$ values are higher than 40 kJ mol$^{-1}$ yet lower than 100 kJ mol$^{-1}$ showing that the binding process is both of physisorption and chemisorption nature. Additionally, ($+$) values of $\Delta S_{ads}$ with the addition of BOPAMS signifies a rise in the entropy of the solvent. This means that there is a disorder occurring on the metal surface because of the molecules of H$_2$O which gets detached from the Al surface. In the case where the $\Delta S_{ads}$ values are ($+$), literature says that the fall of enthalpy may be the chief motive for the binding of BOPAMS molecules on Al.

![Figure 10. FT-IR spectra comparison of the frequencies for the pure compound and adsorption films resulted on the Al in 1.0 M HCl by a) BOPAMS and b) BOBAMS.](image-url)
negatively charged surface as a result of electrostatic attraction that occurred to the resultant strong Al
possible electron donors. The disappearance of the peaks can be attributed to the higher tendency of Al in forming an oxide film.

3.6. Adsorption film analysis

FT-IR instrument was utilized to analyze the characteristics associated with the protective film that resulted on the surface of Al. FT-IR spectra of Al submerged in aggressive HCl without and with of BOPAMS and BOBAMS (adsorption film formed) were compared to the spectra of the two pure synthesized compounds as shown in Figure 10.

The inspection of the spectra of Al in aggressive HCl without the BOPAMS and BOBAMS shows a broad peak around 3261.62 cm⁻¹ and a weak peak around 1624.44 cm⁻¹ which is indicative of the presence of hydrated aluminium oxide molecule (Al₂O₃·xH₂O) and the presence of water. The stretching frequency of around 849.75 and 502 cm⁻¹ represent the γ-AlO₄ and γ-AlO₃, respectively. Thus, the γ-Al₂O₃ phase contained both octahedral and tetrahedral coordination (Potdar et al., 2007).

The expanded adsorption film formed spectra for BOPAMS and BOBAMS are drawn to highlight the fact that the intensity of the peaks decreased to the point that they look as if they have disappeared due to the smaller scale. This indicates some high strength interaction taking place in the midst the functional groups of the two compounds and Al. These include the ammonium salt (NH₄⁺), O=S=O, S=O, C=C and C=O, which are some possible electron donors. The disappearance of the peaks can be attributed to the resultant strong Al–BOBAMS or Al–BOPAMS and the reason for the high inhibition efficiencies exhibited by BOBAMS and BOPAMS.

3.7. Proposed inhibition mechanism between Al and BOPAMS/BOBAMS

The inhibition capabilities related to inhibitor molecules for Al corrosion are said to be a result of the binding of BOPAMS/BOBAMS molecules on Al, resulting in a protective barrier. The degree of binding offered by the inhibitors is highly dependent on factors such as the condition of the surface of the metal, type of the metal and the mechanism of binding of the inhibitor molecules (Curkovic et al., 2010). During the inhibition process in aggressive HCl solution, the binding of inhibitor molecules at the Al/OH⁻ boundary is assumed to be the initial step. The adsorption may be because of one of three steps, namely; an electrostatic attraction that occurs between charged Al surface and charged BOPAMS/BOBAMS, the formation of coordination bond by the unshared pair of electrons on the BOPAMS/BOBAMS and the empty or half-filled p-orbitals from the Al atoms and the participation of the Ï–electrons of the BOPAMS/BOBAMS (Schweinsberg et al., 1988; El-Rehim et al., 1999).

As such, the prevention of Al corrosion in HCl is accomplished largely as a result of electrostatic interaction; this conclusion is supported by the fall in the %IE with the rise in absolute T. Generally, the inhibitors can be adsorbed on the Al surface either in their neutral or protonated forms. In acidic solution (i.e., HCl), the Al surface is negatively charged and as a result, protonated IL molecules find it easier to attack the negatively charged surface as a result of electrostatic attraction that occurs between them and the Al surface (Desai, 1972). The binding of BOPAMS/BOBAMS is said to involve the replacement of the H₂O molecules on the surface of Al and the exchange of electrons that occurs in the midst of the Al surface and heteroatoms of BOPAMS/BOBAMS.

4. Conclusions

- BOPAMS and BOBAMS are mixed-type anti-corrosive substances for Al in aggressive acid environment solution and obeys Langmuir adsorption isotherm. The highest IE% obtained for BOPAMS and BOBAMS are 97.57% and 97.84%, respectively.
- Polarization study revealed that BOPAMS and BOBAMS act in both oxidation and reduction half-reactions for Al with the reduction half-reaction being polarized more. From the polarization study corrosion parameters Ecorr, icorr, ßa and ßc were obtained. These parameters indicated that BOPAMS and BOBAMS are mixed type corrosion inhibitors and the inhibition of Al was mainly controlled by charge transfer. The increase of the Rp values with an increase in the concentration of the inhibitors indicated that the inhibition of corrosion is primarily due to the formation of the protective film.
- The inhibition efficiencies of BOPAMS and BOBAMS increased with improving their concentrations and fell with the rise of the temperature.
- Al showed Nyquist plots with a more pronounced passive region, and this is attributed to the higher tendency of Al in forming an oxide film. EIS results showed that the charge transfer resistance increased as the concentration of the inhibitors were increased leading to the decrease of the corrosion rate and higher %IE. The constant phase element exponent (n) values were near unity for Al which is indicative of a pseudo-capacitive behaviour of the electrode. Mixed-type adsorption was exhibited for the two inhibitors studied.

Declarations

Author contribution statement

Tshimangadzo Nesane: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
Simon S. Mnyakeni-Moleele: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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