Synthesis, characterization and application of acrylate-based poly ionic liquid for corrosion protection of C1020 steel in hydrochloric acid solution

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Abstract
Poly ionic liquids (PIL) are eco-friendly in addition to being sustainable compounds that can be easily prepared and tailored according to the application. In this study, a novel PIL polymer based on acrylate was chemically synthesised via free radical polymerization method controlled by quenching the reversible reaction. The prepared 1-Butyl-3 Methylimidazolium Acrylate polymer (PAL) was characterised using FTIR as well as NMR to confirm the chemical structure. GPC was employed to determine the average molecular weight of the new polymer. PAL was applied as an effective corrosion inhibitor for C1020 steel in 1M HCl aqueous solution. Weight loss and electrochemical techniques, PDP and EIS, were applied to evaluate the corrosion inhibition performance. The electrochemical results showed that PAL acts as a mixed-type inhibitor reaches 91.8% at room temperature. The thermodynamic calculations showed that the adsorption process is exothermic. Furthermore, PAL molecules were adsorbed on the metal surface by both chemisorption and physisorption processes. SEM analysis was carried out to confirm the corrosion evaluation results. Also, quantum chemical calculations, at the B3LYP/DND level of theory, were carried out to correlate the electronic structure parameters of PAL inhibitor to its adsorption behaviour which in turn is relevant to the inhibition efficiency. Additionally, Monte Carlo simulation (MC) was conducted to investigate the adsorption modes and the interaction energies of the inhibitor on iron surface.

1. Introduction
Carbon steel is an important industrial alloy that has been widely used in many industries such as pipelines as well as vessels due to its cost, effectiveness and ease of fabrication [1]. Generally, Hydrochloric acid is used in acid pickling and industrial cleaning processes to get rid of the undesirable rust along with scales from the surface of equipment and heat exchangers. This process usually leads to severe corrosion attack on the surfaces of steel alloys [2, 3]. This corrosion attack has negative effects that comprises the loss of material strength, overdesign, damage of equipment as well as safety issues [4–6]. Therefore, corrosion inhibitors are usually added to such acidic solution to protect the metal surface form corrosion attack. A great deal of research has been made to develop organic along with inorganic compounds as industrial inhibitors. Organic corrosion inhibitors include extracts from plants such as henna, bamboo, coffee, cinnamon, Hammada, lemon, Mango and also papaya [7–15]. Although these compounds possess the privilege of being non-toxic and naturally available [16, 17]. However, the extraction process is extremely expensive, laborious, and in addition require considerable amounts of organic solvents which have adverse impacts on humans.

Also, none natural chemicals have been applied as effective inhibitors. For example; Schiff bases [12–14], pyrimidine, thiazole, and imidazole [18–26]. Most of these compounds contain O, S, and N atoms in their molecular structure. These atoms contain lone pairs of electrons that can be donated to the unoccupied d-orbitals of metal through the adsorption process offering corrosion prevention. The inhibition efficiency
improved in the following order: O > N > S > P. Yet, applying an effective suitable corrosion inhibitor to acidic corrosion media needs many considerations such as the environmental impact, cost, toxicity together with the compatibility to the industrial application [27]. Additionally, current global legislations emphasize on the usage of eco-friendly chemicals as corrosion inhibitors [28, 29].

Ionic liquids (ILs) are promising candidates for the green chemistry applications. They have several attractive properties such as low toxicity, low melting point (lower than 100 °C), high polarity, high chemical and thermal stability and reduced hazardous effect on humans and the environment [30, 31]. In a like manner, the low vapour pressure of ILs limits the environmental contamination which makes them suitable corrosion inhibitor candidates. The ILs are oily liquids that suffer from leakage as well as high viscosity issues. These weaknesses can be reduced by polymerization of these ionic liquids [32]. Poly ionic liquids (PILs) can be easily synthesized by the free radical polymerization method of IL monomers [33, 34]. Although PILs have the same characteristics of ILs monomer, they can be adapted to provide specific properties as they can be tailored for a specific application by carefully selecting the cations, anions, functional groups, polymer backbone, and chain length [35]. Nowadays, these substances attract much attention in corrosion engineering because of their excellent wetting properties in addition to their effective adsorption over several substrates of metals in which the π-electrons in conjugation with active polar heteroatoms constitute as chelating centres [36, 37].

To the best of our knowledge, no report on 1-butyl-3-methylimidazolium acrylate polymer as a corrosion inhibitor for steel is available in the literature. The present work is required to contribute to the developing research of using polymeric ionic liquids as eco-friendly corrosion inhibitors.

In this study, PAL inhibitor was chemically synthesised through a two-step reaction. The prepared compound was then characterised using FTIR, NMR, and GPC to confirm its structure and to measure the average molecular weight of the prepared compound. Furthermore, the corrosion inhibition performance of PAL on C2010 carbon steel in one molar concentration of hydrochloric acid was investigated. Electrochemical (PDP and EIS) and gravimetric techniques were applied to study the corrosion performance. In this context, the adsorption isotherm was studied and the corresponding thermodynamic parameters were calculated. Moreover, SEM equipped with EDX was applied to study the surface morphology of the steel samples after the immersion test.

2. Experimental work

2.1. Chemicals and materials

Alloy C2010 carbon steel panels (0.17% C, 0.3% Mn, 0.04%P, 0.05% S, and Fe balance) were used as working electrodes in this study. The steel samples were first mechanically abraded with 400 and 1000 grits using silicon carbide papers abrasive paper. The polished surface was then degreased with acetone before cleaning with de-ionized water, and afterwards dried with warm air. Finally, the samples were left to cool at room temperature before applying the corrosion tests. All samples coupons were prepared in a rectangular shape with the following dimensions: 50 mm × 30 mm × 1 mm. Before the corrosion testing, the sample edges were covered by waxing using a melted mixture of colophony and bees wax (1:1 wt%) leaving an exposed surface area of 10 cm². The blank corrosive electrolyte was 1 M HCl which had been prepared by diluting an analytical grade acid purchased from Sigma Aldrich. The prepared PAL inhibitor was added to the blank corrosive electrolyte (1M HCl) to form the following inhibitor concentrations; 10, 25, 50, 75, 100, 150 and 200 ppm.

2.2. Synthesis of PAL polymer

1-Butyl-3 Methylimidazolium chloride (>98.0%), Acrylic acid monomer (>99.0%), Potassium persulfate as water soluble initiator (>99.0%), Diethyl ether solvent (HPLC grade), acetone (99.6%) Plus hydrochloric acid (37%) were obtained from Sigma-Aldrich and used without further purification. The IL monomer was synthesized as follows: 1-butyl-3-methylimidazolium chloride was dissolved in equimolar amount of the acrylic acid (AA) monomer by continuous stirring overnight at ambient temperature until the pH of the mixture becomes neutral. The dissociation of carboxylic group has pKa value 4.2 [38] which decreased at low pH value due to strong hydrogen bond formation between carboxylic groups [39]. To overcome this, a continuous stripping of formed HCl gas, formed as bi-product, was applied to prevent the reversible reaction. The formed ionic liquid (IL) monomer was extracted with diethyl ether. Soon after, the IL monomer was dissolved in 90 ml water and purged by nitrogen under a reflux condenser with continuous stirring at 75 °C. Potassium persulfate (KPS) free radical initiator (0.5 wt% of monomer) was dissolved in 10 ml of distilled water and was dropwise transferred into the mixture at 75 °C for 10 h. Finally, the PAL precipitated by addition 350 ml acetone, dried under vacuum at room temperature producing transparent viscous oily polymer which was stored away from light for further analysis. The proposed two-step reaction mechanism of PAL synthesis is shown in Scheme (figure 1).
2.3. Characterization of PAL polymer

Fourier transformation infrared (FTIR) spectra of AA, IL, and PAL oil was scanned in the range 4000–400 cm\(^{-1}\) using (Model 4100, JASCO, Japan) with automatic signal gain that was collected in 512 scans at 4 cm\(^{-1}\) resolution. For spectra analysis, the PIL was dropped on a prepared KBr tablet before mounting in the FTIR sample holder. The background spectrum was collected from the clean empty holder at room temperature and was subtracted during the analysis of the samples.

NMR spectra were recorded on a Varian-400 MHz spectrometer at 400 MHz and 101 MHz for \(^1\)H and \(^{13}\)C respectively. Dimethyl sulfoxide (DMSO-d6) was used as solvent, tetramethylsilane (TMS) as internal reference and the coupling constants (J) are reported in Hz.

Gel permeation chromatography (GPC) was applied to determine the molecular weight distribution of the prepared polymer, PAL. The GPC sample was prepared by dissolving 30 mg of PAL in 50 ml of Tetrahydrofuran (HPLC grade) followed by filtration through a 0.2 \(\mu\)m filter. Then, 200 \(\mu\)l of the THF solution was automatically injected in the GPC (Agilent 1100 system, Germany) which was maintained at 40 °C. The molecular weight distribution, number average molecular weight, weight average molecular weight and the polydispersity index were determined.

2.4. Corrosion measurements

Gamry™ Potentiostat/galvanostat, model reference 600 was employed in all electrochemical measurements with a three-electrode type cell where; the carbon steel sample, platinum electrode and saturated calomel electrode (SCE) were served as the working, auxiliary and reference electrodes respectively. For all experiments, the ratio of the corrosive electrolyte volume to sample surface area was minimum 40 ml cm\(^{-2}\). Prior to each corrosion measurement, the steady state condition was established by determining the open circuit potential (OCP) for 30 min, free corrosion in the corrosive solution with different inhibitor concentrations.

The potentiodynamic polarization (PDP) technique was carried out within ±250 mV versus the OCP at a scan rate of 0.166 mV.s\(^{-1}\) and the potential sweeps from the cathodic to anodic in an aerated solution. All polarization kinetic parameters of Tafel extrapolation technique (\(E_{corr}\), \(I_{corr}\), \(\beta_a\) and \(\beta_c\)) were calculated via DC105 Gamry™ software, where at least one of the polarization curves (anodic or cathodic) demonstrates Tafel
region for the minimum of one decade of current density. Moreover, the extrapolation started at least 50 mV away from $E_{corr}$. In this software, a nonlinear least square method of fitting is applied to fit the polarization curve.

EIS tests were conducted at OCP values with 10 mV sinusoidal voltages and the applied frequency ranging from $0.3 \times 10^2$ to $10^3$ Hz. All EIS measurements were performed separately at room temperature and in aerated 1 M HCl solution. The impedance experimental results were fitted to an equivalent electrical circuit using the nonlinear least square fitting technique provided by the Gamry™ software.

The weight loss measurements were performed using C2010 coupons with the following dimension $50 \times 30 \times 1$ mm$^3$ without waxing. The coupons were polished and degreased as stated above. For each concentration, three samples were separately immersed in the corrosive solution for 72 h. The average weight loss was calculated through weighing ($\pm 0.1$ mg) the cleaned coupon before and after the immersion period. For thermodynamic analysis, the adsorption equilibrium was studied at temperatures of 10, 25, 35 and 50 °C.

2.5. DFT and MC calculations details

The quantum chemical calculations were performed to study the correlation between the inhibitor electronic structure and its inhibition efficiency. Quantum chemical calculations were performed in the aqueous phase based on the COSMO model (Conductor like Screening Model) using the DMOl$^3$ module implemented in Materials Studio package v 8.0 (Biovia, USA) [40]. Due to the highly expensive time cost of quantum chemical calculation, the study was limited to two repeating units of poly(1-methyl 3-butyl imidazolium acrylate) and the cation as well as the anion of the inhibitor were optimized separately. The geometry of the studied species was optimized using B3LYP functional [41, 42] and DND numeric basis set. Some quantum chemical descriptors, such as energy of the highest occupied molecular orbital ($E_{HOMO}$), energy of the lowest unoccupied molecular orbital ($E_{LUMO}$), energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) and dipole moment ($\mu$) were obtained directly. Whereas, some other descriptors, such as absolute electronegativity ($\chi$), global hardness ($\eta$), global electrophilicity ($\omega$) and the fraction of electrons transferred ($\Delta N$) were computed from the following equations [43–46]:

$$\chi = \frac{(I + A)}{2}$$

$$\eta = \frac{I - A}{2}$$

$$\omega = \frac{\chi^2}{2 \eta}$$

$$\Delta N = \frac{(\chi_{Fe} - \chi_{inh})}{2(\eta_{Fe} + \eta_{inh})}$$

where $I$ is the ionization potential ($= - E_{HOMO}$), $A$ is the electron affinity ($= - E_{LUMO}$), $\chi_{Fe}$ ($= 7$ eV), $\chi_{inh}$, $\eta_{Fe}$ ($= 0$ eV), $\eta_{inh}$ are the absolute electronegativity and hardness values of iron and the inhibitor, respectively. Moreover, molecular electrostatic potential surface (MPE) and Fukui indices (based on Mulliken’s population analysis) were computed to explore the local sites on the inhibitor molecule susceptible to nucleophilic and electrophilic attacks.

Monte Carlo simulation (MC) was conducted using Adsorption Locator module implemented in material studio to investigate the adsorption modes of the inhibitor ionic species and to compute the interaction energies between the inhibitor and iron surface in the gas phase [47, 48]. This module searches for the possible adsorption sites and the inhibitor’s most favoured adsorption configurations on the metal surface as the temperature is slowly lowered in the simulation box. The simulation was carried out in a simulation box of dimensions $29.8 \text{ Å} \times 29.8 \text{ Å} \times 60.1 \text{ Å}$ with a periodic boundary condition and including six layers of Fe (110) plane. For energy calculations, COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field was used in combination with Ewald and atom based summation methods for calculating electrostatic and Van der Waals interactions respectively.

3. Results and discussion

3.1. Characterization of PAL polymer

The FTIR analysis of AA, IL and PAL is shown in figure 2. The characteristic absorption peaks of AA were observed as the stretching peak of carbonyl group C=O at 1705 cm$^{-1}$, vinylic −C−C− group at 980 cm$^{-1}$ and broad absorption peak at 3440 cm$^{-1}$ assigned to −OH stretching of the carboxylic group. For IL characteristic peaks, the observed peaks at 2961 and 2870 cm$^{-1}$ are attributed to the asymmetric and symmetric stretching of aliphatic (C−H) bond respectively. Also, the in-plan bending vibration of methyl groups is shown at 1168 and 1116 cm$^{-1}$. The quaternary amine salt showed a broad peak in the range of 3200-3500 cm$^{-1}$ in addition two characteristic peaks at 1634 and 1570 cm$^{-1}$ relevant to the stretching of C=O and C=N bonds respectively. The peak at 845 cm$^{-1}$ is due to the stretching of C−N bond [49]. Finally, The appearance of IL and AA characteristic peaks in PAL spectra besides the absence of out of plan bending vinylic −C−C− peak at 980 cm$^{-1}$ strongly confirms the polymerization process of IL monomer into PAL.
1H NMR and 13C NMR spectra are presented in figure 3 and the values of δ are assigned as follows; 1H NMR δ = 0.78 (t, 3H, CH3-butyl), 1.19 (m, 3H, CH2-butyl), 1.71 (m, 3H, CH2-butyl), 2.299 (t, 3H, CH2-butyl), 3.75 (s, 3H, CH3-imidazole), 4.06 (t, 1H, CH-polymer), 4.65 (d, 2H, CH2-polymer), 7.29 (d, 1H, H-imidazole), 7.34 (d, 1H, H-imidazole), 8.57 (s, 1H, H-imidazole).

13C NMR δ = 12.54, 18.66, 31.17, 35.54 (4C-Butyl), 41.40, (CH3-imidazole), 49.19, 60.81 (2C-polymer), 122.1, 123.3, 135.7 (3C-imidazole), 178.5 (C=O).

Also, the average molecular weight of the prepared compound was determined using GPC and the results are summarized in table 1. The weight average molecular weight of the prepared poly ionic liquid polymer (PAL) is 34332 g/mole. This value will be used in the thermodynamic calculation of the adsorption process of PAL inhibitor on the metal surface. Also, the polydispersity index of the polymer is found to be approximately 1.4, which is consistent with the values of polymers that are produced by free radical method (1.2–1.5).

3.2. Corrosion behaviour
3.2.1. Potentiodynamic polarization results
The potentiodynamic polarization technique (PDP) was applied to measure the corrosion resistance of C2010 carbon steel in a naturally aerated 1M HCl solution at room temperature. PDP technique evaluates the rate of electron transfer at anodic and cathodic sites by applying an external potential to polarize the metal from its steady state potential. The cathodic and anodic polarization curves of C2010 for different inhibitor concentrations are displayed in figure 4.

The figure clearly shows that PAL effectively decreased the corrosion rate of C2010 in this acidic corrosive solution. The corrosion current density of the metal substrate steadily reduces by increasing the inhibitor concentration. In addition, the corrosion potential shows slight shift to anodic direction which may be due to an increase in the adsorption process of the PAL molecules on the metal surface with increasing the inhibitor concentration [50, 51].

It may also be noticed from the figure that anodic and cathodic reactions slightly change i.e. the slope of both branches insignificantly altered due to the increase in PAL concentration. The parallel cathodic slopes indicate that the mechanism of the cathodic reaction, the hydrogen reduction reaction, is unaffected by the presence of PAL molecules.

\[
2H^+ + 2e^- \rightarrow H_2
\]  

Moreover, the anodic branch demonstrations an active dissolution of the metal substrate without showing any passivating region. Also, the cathodic reactions are relatively more influenced by adding PAL inhibitor than anodic reactions without significant change in the corrosion potential, \(E_{corr}\) (≤69 mV). This behaviour of unaffected \(E_{corr}\) with sharp decrease of \(I_{corr}\) suggests that PAL could be used as a pickling inhibitor [52].

The above discussion strongly suggests that PAL was adsorbed on the surface of C2010 in 1M HCl solution retarding the redox reactions. Also, PAL is a mixed type inhibitor but predominantly a cathodic inhibitor [53–55].

All the polarization parameters including \(E_{corr}\), \(I_{corr}\), \(\beta_a\), \(\beta_c\), and the inhibition efficiency (IE\%) are summarized in table 2, where the IE\% was calculated according to the following equation:
where: $I_{\text{corr}}^{\text{p}}$ is the corrosion current density of blank sample and $I_{\text{corr}}$ is the corrosion current density of the inhibited sample. Moreover, the table displays the polarization resistance ($R_p$) and its efficiency ($\eta$%) in both the presence and absence of the PAL in the corrosive electrolyte.

$$\eta = \frac{R - R_o}{R} \times 100$$

(7)

where: $R$ and $R_o$ are the polarization resistances of metal substrate in the electrolyte with and without the inhibitor respectively.
The table clearly shows that the inhibition efficiency increased with increasing the inhibitor concentration for both PDP and LP techniques. Also, $\beta_c > \beta_a$ which signifies that the cathodic reaction is more suppressed than the anodic one.

### 3.2.2. Electrochemical Impedance results

An electric double layer is established at the metal/solution interface in the course of a metal corrosion. This double layer comprises of a capacitance and resistance of the charge transfer. The rate of charge transfer between the metal surface and the electrolyte is affected by the characteristics of this double layer. Electrochemical impedance spectroscopy, a semi-quantitative technique, is suitable to investigate the properties of the interface as well as studying the effect of adding a corrosion inhibitor.

Corrosion performance of C1020 steel samples in a molar concentration of HCl solution with different concentrations of PAL inhibitor was assessed using EIS at room temperature after one hour of immersion. Figure 5 shows the Nyquist plots of the working electrode at different concentrations of the PAL inhibitor. The figure shows non-ideal semicircles in addition to depressed loops as anticipated from the EIS theory. These depressed semicircles can be assigned to the inhomogeneity of the surface, the frequency dispersion and/or the adsorbed species [56, 57]. The shape of the Nyquist plots, a single capacitive loop, indicates that this corrosion process is mainly governed by the charge transfer process [58, 59]. In the same context, the presence of a capacitive loop implies that the dissolution process of the working electrode takes place under activation polarization process [32] which is in an agreement with the PDP results. It can be also noticed that both the capacitive and resistive behaviour increases with the increase of PAL concentration implying an overall increase.
in the total impedance of the samples. This increase in the loop size illustrates a gradual formation of a barrier on the metal surface. The Nyquist plots of the inhibited electrodes are not significantly different from that of the blank electrode i.e. the inhibitor decreases the rate of the corrosion process without altering it. Furthermore, the presence of the PAL increases the charge transfer impedance which suggests that the corrosion process is controlled by the inhibitor concentration.

With the purpose of determining the EIS parameters, the experimental results were fitted to an equivalent electrical circuit. In this case, the Randal circuit, figure 6, is used to fit the experimental data. The circuit comprises; a solution electrical resistance \( R_s \), a charge transfer resistance \( R_{ct} \) and a double layer capacitance \( C_{PE_{dl}} \). A constant phase element (CPE) is used instead of pure capacitance due to the porous corrosion products and surface roughness [60, 61]. The capacitance and the inhibition percent can be calculated according to the following equations respectively [62]:

\[
C_{dl} = Y^{1/\alpha} R_{t}^{1-\alpha} \quad (8)
\]

\[
\%IE = \left(1 - \frac{R_{t}}{R_{ct}}\right) \times 100 \quad (9)
\]

where \( Y \) and \( \alpha \) represent the CPE magnitude and exponent respectively. \( R_t \) is the extracted total resistance and \( C \) is the calculated capacitance.

The parametrical Fitting of this circuit with experimental impedance data enables determining the double layer capacitance, charge transfer resistance, value of \( \alpha \) and the total resistance as summarized in table 3. The value of \( \alpha \) characterises the electrode surface roughness and its value ranges from 0 to 1.0. When \( \alpha \) value equal to
1, the electrode surface is homogeneous and the electrode can be assumed as an ideal capacitance. There is a
negative correlation between $\alpha$ and the roughness of the surface $^{[63]}$.

It can be noticed that the value of charge transfer resistance, $R_{ct}$, gradually rises with increasing the inhibitor
concentration. On the other hand, the value of $C_{dl}$ steadily decreases by adding the inhibitor. A possible
explanation for this behaviour might be the desorption of water molecules followed by adsorption of PAL
molecules onto the metal surface $^{[64]}$. At the same time, the value of $\alpha$ slightly increases from 0.72 to 0.89. This
change of $\alpha$ may be because the surface of working electrode becomes smoother as a consequence of coverage
with the inhibitor molecules.

3.3. Adsorption isotherm and thermodynamic parameters
During the adsorption process of an inhibitor on a metal surface in an aqueous electrolyte, numerous
interactions take place between the inhibitor molecules, water (solvent), and metal surface. Studying the
mechanism of these interactions is the appropriate way to understand the corrosion inhibition mechanism
$^{[16, 33, 65]}$. In the traditional approach, adsorption isotherm is used to characterize the adsorption mechanism
for a corrosion inhibitor. Many parameters influence the adsorption process of inhibitor molecules including;
molecular weight, functional groups, steric factor of the inhibitor, molecule electronic configuration and
electron density at the donor site $^{[17, 31]}$.

Adsorption could be classified into two types: (a) chemisorption in which the inhibitor molecules donate a
charge(s) to the metal substrate forming a coordination bond, and (b) physisorption in which the electrostatic
forces govern the adhesion of ionic charges at the metal/solution interface. In fact, chemisorption is
characterized by higher adsorption energy than that of physisorption and consequently chemisorption is more
stable at higher temperatures. On the other hand, physisorption is stable only at relatively low
temperatures $^{[33, 34]}$.

Numerous studies have been conducted to fit the experimental data to different isotherms with the general
mathematical form $^{[36]}$:

$$f(\theta, x) \exp(-2\alpha x) = K_{ads}C_{inh} \tag{10}$$

Where $\theta$ is the degree of surface coverage, $C_{inh}$ is the concentration of inhibitor, $x$ is the size factor ratio, $\alpha$ is the
molecular interaction parameter and $K_{ads}$ is the adsorption equilibrium constant.

In this study, two adsorption isotherms models are applied: Langmuir and El-Awady. The Langmuir
isotherm proposes a monolayer coverage of inhibitor molecules on the metal surface, while the El-Awady model
proposes that the active site is covered with a multilayer $^{[1, 66–68]}$. The Langmuir isotherm has the following
expression $^{[37]}$:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{11}$$

where $C_{inh}$ is the molar concentration of the inhibitor, $\theta$ is the degree of surface coverage and $K_{ads}$ is the
equilibrium constant of adsorption process.

The second model is El-Awady isotherm which has the following linear expression $^{[49, 69]}$:

$$\log\left(\frac{\theta}{1 - \theta}\right) = \log K + y \log C_{inh} \tag{12}$$

where $y$ represents the number of water molecules replaced by one inhibitor molecule. For multilayer
occupation adsorption process, $y$ value should have a value greater than unity $^{[69]}$. Also, $K_{ads}$ can be calculated
from K according to the following:
The surface coverage ($\theta$) of the metal through adsorption of inhibitor molecules is a demanding factor for corrosion inhibition. The values of $\theta$ are determined from the weight loss data for the different inhibitor concentrations using the following expression [38, 39]:

$$q = \theta - \theta_w$$

where $W_o$ and $W$ are the sample weight loss ($\pm 0.1$ mg) before and after immersion in the corrosive electrolyte, respectively. Weight loss technique cannot be applied when the metal substrate is susceptible to severe localized corrosion and also when the penetration rate or surface area change during immersion time [54, 69].

Figures 7 and 8 show the plots fitting the weight loss experimental data to the Langmuir and El-Awady isotherm models, respectively. All the corresponding parameters of both models, in addition to the correlation factor, $R^2$, were calculated from the corresponding plots and are shown in table 4.

Figure 7. Langmuir adsorption isotherm of PAL on mild steel in 1 M HCl.

Figure 8. El-Awady adsorption isotherm of PAL on mild steel in 1M HCl.

$$K_{ads} = K_l^\frac{1}{2}$$

(13)

The surface coverage ($\theta$) of the metal through adsorption of inhibitor molecules is a demanding factor for corrosion inhibition. The values of $\theta$ are determined from the weight loss data for the different inhibitor concentrations using the following expression [38, 39]:

$$\theta = \frac{W_o - W}{W_o}$$

(14)

where $W_o$ and $W$ are the sample weight loss ($\pm 0.1$ mg) before and after immersion in the corrosive electrolyte, respectively. Weight loss technique cannot be applied when the metal substrate is susceptible to severe localized corrosion and also when the penetration rate or surface area change during immersion time [54, 69].

Figures 7 and 8 show the plots fitting the weight loss experimental data to the Langmuir and El-Awady isotherm models, respectively. All the corresponding parameters of both models, in addition to the correlation factor, $R^2$, were calculated from the corresponding plots and are shown in table 4.

For the selected temperatures and according to the degree of linearity of the plots ($R^2$ values close to unity), it could be concluded that the Langmuir model better represents the adsorption process of PAL on the C1020 steel in 1M HCl electrolyte. Also, all $y$ values of El-Awady equation are not greater than unity. Consequently, the metal surface is covered by a mono-layer of PAL inhibitor with no interactions between the adsorbing molecules [70]. However, in the actual condition, the adsorbed molecules interact with each other through common repulsion or attraction mechanisms. These interactions are reflected on the slope of the Langmuir linear plots.
where CR is the corrosion rate indicates the decrease in randomness during the adsorption process. This negative value of Figure 9 shows the relation between concentration in the aqueous solution. The values of free energy of adsorption were calculated and are listed in Table 5. The negative value of increasing temperature increases the rate of C1020 dissolution and deviate it from unity [71] as presented in Table 4. It can be observed that the $K_{ads}$ value decreases with increasing temperature indicating the exothermic nature of PAL adsorption process on the surface of C1020.

The adsorption equilibrium constant, $K_{ads}$, of Langmuir is used to determine the standard free energy of adsorption ($\Delta G_{ads}^{°}$) according to the thermodynamic equation [72–74]:

$$\Delta G_{ads}^{°} = -2.303RT \log (55.5K_{ads}) \tag{15}$$

where $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is the temperature in Kelvin and 55.5 is water molar concentration in the aqueous solution. The values of free energy of adsorption were calculated and are listed in Table 5.

All $\Delta G_{ads}^{°}$ values are negative indicating that the adsorption process is spontaneous and the inhibitor molecules are naturally adsorbed on the metal surface. Generally, $\Delta G_{ads}^{°}$ values around $-20$ kJ mol$^{-1}$ or higher are assumed to be physisorption process and the values around $-40$ kJ mol$^{-1}$ or more negative are assumed to be chemisorption process. As shown from Table 5, all $\Delta G_{ads}^{°}$ values are close to $-40$ kJ mol$^{-1}$ implying that the adsorption mechanism of PAL on C1020 carbon steel comprises both physisorption and chemisorption with more affinity towards chemisorption mechanism. The proposed steps could be as follows: (i) as starting condition the water molecules are adsorbed on the surface of carbon steel, (ii) by the addition of inhibitor, its molecules are continually adsorbed on the metal surface by electrostatic forces at the expense of water molecules, (iii) finally, inhibitor molecules chemically interact with the metal-atoms of the surface through coordination [35].

To determine the enthalpy of the adsorption process ($\Delta H_{ads}$) and the corresponding entropy $\Delta S_{ads}$, $\Delta G_{ads}^{°}$ values were plotted versus the absolute temperature according to the following thermodynamic relation [75, 76]:

$$\Delta G_{ads}^{°} = \Delta H_{ads} - T\Delta S_{ads} \tag{16}$$

Figure 9 shows the relation between $\Delta G_{ads}$ and $T$ where both $\Delta H_{ads}$ and $\Delta S_{ads}$ can be determined from the intercept and slope, respectively, and are summarized in Table 5. The negative value of $\Delta H_{ads}$ reflects the exothermic nature of the adsorption process of PAL on the surface of C1020 steel as indicated earlier. Also, the negative value of $\Delta S_{ads}$ indicates the decrease in randomness during the adsorption process. This negative value of $\Delta S_{ads}$ may be related to the adsorption of PAL large molecules to replace the smaller water molecules on the metal surface.

Temperature has a great impact on the corrosion rate of metal in acidic medium under hydrogen polarization. The increase in temperature rises the rate of corrosion exponentially due to the decrease of hydrogen evolution overpotential [69]. In acidic media, the change of steel corrosion rate with temperature can be expressed in terms of Arrhenius equation [72] from which the activation energy ($E_a$) can be calculated according to the following equation:

$$\log (CR) = \frac{-E_a}{TR} + A \tag{17}$$

where CR is the corrosion rate (mg cm$^{-2}$ h$^{-1}$), $E_a$ is the activation energy (kJ mol$^{-1}$) for the corrosion of mild steel in 1 M HCl solution, $R$ is the universal gas constant, $A$ is the Arrhenius pre-exponential factor, and $T$ is the absolute temperature. Figure 10 demonstrates the change of CR of C1020 obtained from weight loss measurements versus 1/$T$. The figure shows that the effect of corrosion inhibitor is more significant at a low temperature range. Besides, for each inhibitor concentration, the corrosion rate increases with temperature increase which may be due to two factors: (a) increasing temperature increases the rate of C1020 dissolution.
according to Arrhenius theory, and (b) increasing temperature would decrease the exothermic adsorption process of PA on the steel surface, i.e. decrease the inhibition process. For each concentration, the value of $E_a$ can be determined from the slope of the straight line and summarized in table 6. The activation energy can give an indication about the inhibition performance of C1020 in the presence of PAL. Table 6 clearly shows that the values of $E_a$ of the corrosion of C1020 in a molar concentration of HCl solution in the presence of the PAL are greater than that in the blank solution. Also, the activation energy gradually increases as PAL concentration increases. This gradual increase in $E_a$ with PAL concentration reflects the increase of energy barrier for the corrosion reaction. In the same context, the increase of PAL concentration would shift the equilibrium towards more adsorption of inhibitor molecules and enhances the surface coverage of C1020 [66].

### Table 6. Activation energy at different concentrations of PAL.

| Concentration [ppm] | 0   | 10  | 25  | 50  | 75  | 100 | 150 | 200 |
|---------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Activation energy [kJ.mol$^{-1}$] | 1.65 | 3.56 | 4.37 | 5.44 | 7.23 | 7.10 | 8.85 | 16.43 |

3.4. SEM results
Figure 11 demonstrates the SEM images of C1020 surface after 48 h. of immersion in a molar concentration of HCl solution in absence and presence of 200 ppm PAL. The SEM image of the blank sample, figure 11(a),
clarifies that the substrate surface is severely damaged and covered with the corrosion products (arrows). On the other hand, sample with 200 ppm PAL (figure 11(b)) shows few corrosion products and the corrosion reactions seem to be suppressed. These results are in an agreement with the electrochemical results.

3.5. Quantum chemical calculations and MC simulation results
Quantum chemical calculations were conducted as inhibition efficiency is governed by inhibitor’s structural factors such as $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, $\Delta E$, $\mu$, $\chi$, $\eta$, $\sigma$, $\omega$, $\mu$ and $\Delta N$[71]. Figure 12 shows the optimized structure and the frontier molecular orbitals of the inhibitor ionic species. It is clear that both HOMO and LUMO orbitals of 1-methyl 3-butyl imidazolium cation are located on the heterocyclic ring where there exists $\pi$-electrons, lone

| Property         | Inhibitor ionic species |
|------------------|-------------------------|
|                  | Poly(acrylate) anion    | 1-butyl 3-methyl imidazolium cation |
| Optimized Geometry | ![Optimized Molecular Structure](image) | ![Optimized Molecular Structure](image) |
| HOMO             | ![HOMO](image) | ![HOMO](image) |
| LUMO             | ![LUMO](image) | ![LUMO](image) |

Figure 12. Optimized molecular structure and frontier molecular orbital of studies species.
attacks, both Fukui electrophilic (Imidazolium cation is characterized by a positive potential distributed over the heterocyclic ring, but the polyacrylate anion is characterized by negative potential. It can be noticed that the 1-butyl 3-methyl density distribution over the inhibitor ionic species. The red colour represents regions with negative potential, while the blue colour represents regions with positive potential. It can be noticed that the 1-butyl 3-methyl density distribution over the inhibitor ionic species. The red colour represents regions with negative potential, while the blue colour represents regions with positive potential.

The descriptors of the electronic structure of the inhibitor ionic species are listed in Table 7. From the table, it turns out that the ability of the polyacrylate anion to donate electrons to the unoccupied orbitals of the metal is higher than that of 1-butyl 3-methyl imidazolium cation as it has greater value of $E_{\text{HOMO}}$. On the contrary, the ability of accepting electrons from the metal surface is higher in the case of 1-butyl 3-methyl imidazolium cation due to the lower value of its $E_{\text{LUMO}}$. The substituted imidazolium cation has higher energy gap ($\Delta E$) than that of its counter anion meaning better donation of electrons to the metal surface. The dipole moment ($\mu$) values of the species, which is a measure of the intermolecular attraction and ease of adsorption of the species, follows the same trend as the energy gap.

Also, it is obvious that the global hardness ($\eta$) values of both ionic species are almost the same. While the absolute electronegativity ($\chi$) of the substituted imidazolium cation is larger than that of the poly(acrylate) anion. As a result, the global electrophilicity ($\omega$), which is a measure of the electrophilic capacity, is higher for the substituted imidazolium cation. This implies that the substituted imidazolium cation can accept electrons easier while the polyacrylate anion (which has higher nucleophilicity $\sigma = 1/\omega$) can donate electrons better than the cation. Last but not least, the values of $\Delta N$ are greater than zero indicating the ability of donating electrons from the inhibitor species to the metal surface. In addition, the values of $\Delta N < 3.6$ suggests that the inhibition efficiency increases as the electron donating ability of the ionic species increases [77]. The value of $\Delta N$ for poly (acrylate) anion is higher which again emphasizes the higher donation ability of the inhibitor anion.

Molecular electrostatic potential surface (MEP) presented in Figure 13 is a visualization of the electron density distribution over the inhibitor ionic species. The red colour represents regions with negative potential, while blue colour represent regions with positive potential. It can be noticed that the 1-butyl 3-methyl imidazolium cation is characterized by a positive potential distributed over the heterocyclic ring, but the poly(acrylate) anion is characterized by negative potential predominated over the two terminal carboxylate groups.

To further investigate the local sites on the inhibitor ionic species prone to nucleophilic and electrophilic attacks, both Fukui electrophilic ($f^+$) and nucleophilic ($f^−$) fields were mapped on the electron density surface as shown in Figure 14. The red and yellow colours represent the most probable sites susceptible to attack (nucleophilic/electrophilic) depending on the mapped field ($f^+/f^−$). The figure shows that the local nucleophilic site for the poly(acrylate) anion is located on the carbon atom attached to the two oxygen of the carboxylate group, while the nucleophilic site is mainly located on the carbon atom between the two nitrogen atoms and to a lesser extent over the remaining atoms of the heterocyclic ring in the case of 1-butyl 3-methyl imidazolium cation. The electrophilic sites are located over the two terminal carboxylate groups for the poly(acrylate) anion, whereas these sites are found on the (N–C–N) and (C–C) regions for the heterocyclic ring of 1-butyl 3-methyl imidazolium cation. The electrophilic sites are located over the two terminal carboxylate groups for the poly(acrylate) anion, whereas these sites are found on the (N–C–N) and (C–C) regions for the heterocyclic ring of poly(acrylate) anion.

### Table 7. Calculated quantum chemical descriptors of studied species.

| Inhibitor species          | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $\Delta E$ (eV) | $\chi$ | $\eta$ | $\omega$ | $\Delta N$ | $\mu$ (D) |
|----------------------------|------------------------|------------------------|-----------------|--------|--------|----------|------------|-----------|
| Substituted imidazolium cation | −6.74                  | −1.58                  | 5.16            | 4.16   | 2.58   | 3.35     | 0.55       | 5.50      |
| Poly(acrylate) anion        | −4.86                  | 0.14                   | 5.00            | 2.36   | 2.50   | 1.12     | 0.93       | 3.20      |

![Figure 13](image.png)  
Figure 13. MEP of: (a) 1-butyl 3-methyl imidazolium cation and (b) poly(acrylate) anion.

Also, it is obvious that the global hardness ($\eta$) values of both ionic species are almost the same. While the absolute electronegativity ($\chi$) of the substituted imidazolium cation is larger than that of the poly(acrylate) anion. As a result, the global electrophilicity ($\omega$), which is a measure of the electrophilic capacity, is higher for the substituted imidazolium cation. This implies that the substituted imidazolium cation can accept electrons easier while the polyacrylate anion (which has higher nucleophilicity $\sigma = 1/\omega$) can donate electrons better than the cation. Last but not least, the values of $\Delta N$ are greater than zero indicating the ability of donating electrons from the inhibitor species to the metal surface. In addition, the values of $\Delta N < 3.6$ suggests that the inhibition efficiency increases as the electron donating ability of the ionic species increases [77]. The value of $\Delta N$ for poly(acrylate) anion is higher which again emphasizes the higher donation ability of the inhibitor anion.

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1-butyl 3-methyl imidazolium cation. These locations of nucleophilic and electrophilic sites match those of HOMO and LUMO orbitals discussed before.

The interaction energies and the adsorption modes of the inhibitor ionic species on the iron surface were investigated by conducting MC simulation using Adsorption Locator module (Material Studio software v 8.0). In this algorithm, the best adsorption configurations of certain species were obtained using an iterative process, where the species are rotated and translated iteratively under certain criterion until the total energy reaches to its minimum value. Figure 15 shows the fluctuation of interaction energies during MC simulation.
Table 8 lists the interaction energies results computed by MC simulation for the adsorption of inhibitor ionic species on metal surface. The total energy is the sum of the adsorption energy and the internal energy of adsorbed ionic species. The adsorption energy consists of two terms; the rigid adsorption energy which is the energy released (or required) when the adsorbed ionic species are adsorbed onto the metal surface before geometrical optimization and the deformation energy which is the energy resulting from the relaxation of the adsorbed ionic species after being adsorbed onto the metal surface. The term \( \frac{dE_{ads}}{dN_i} \) represents the energy required for specific species to be removed from the metal surface.

Figure 16 depicts the adsorption modes of the inhibitor ionic species on the metal surface. It is clear that 1-butyl 3-methyl imidazolium cation is adsorbed in such orientation that the heterocyclic rings, which bear the HOMO and LUMO orbitals, are parallel to the metal surface. Furthermore, the counter poly(acrylate) anion is extended over the surface with the two terminal carboxylate groups, which bear the HOMO and LUMO orbitals, directed towards the metal surface. Such configurations increase the coverage area of the inhibitor and hence improve the inhibition efficiency.

### 3.6. Proposed inhibition mechanism for PAL

Based on experimental and theoretical results, we can portray a probable mechanism based on the adsorption process as follows; the inhibitive ability of species is relevant to its dipole moment [51]. Higher value of \( \mu \) increases the adsorption process. Since the dipole moment values of both polyacrylate anion and 1-butyl 3-methyl imidazolium cation (3.20 and 5.50 Debye respectively) are higher than that of water (2.62 Debye), it can be assumed that the adsorption process of inhibitor’s ionic species on the metal surface take place through a quasi-substitution process between the inhibitor’s ionic species and water molecules already adsorbed on the metal surface [70]. The negatively charged chloride ions are adsorbed on the steel surface, which is usually positively charged in a strong acidic solution [74], within the inner Helmholtz plane making the surface negatively charged. Hence, the positively charged imidazolium ring is attracted to the metal surface allowing it to donate electrons to the 3d-orbital of iron atoms through the (NCN) and (C=C) regions [73]. Similarly, the polyacrylate anion is attracted to the metal surface by the two positively charged carbon atoms of the carboxylate groups allowing it to donate electrons through (O=C=O) region. This behaviour would explain both physisorption and chemisorption processes that take place during the interaction between PAL molecules and steel surface in HCl electrolyte.

### 4. Conclusions

A novel polyionic liquid based on acrylic acid and 1-butyl-3-methylimidazolium acrylate (PAL) was chemically prepared and both FTIR and NMR prove the polymerization of the ionic liquid monomers. The prepared polymer has an average molecular weight of 34.3 kg.mol\(^{-1}\). Potentiodynamic polarization measurements
showed that PAL acts as a mixed-type but predominantly a cathodic inhibitor. EIS results indicated that the corrosion reaction of C1020 is governed by the charge transfer process and the presence of the inhibitor increases the charge transfer impedance. The corrosion inhibition efficiency reaches 91.8% at room temperature. Weight loss measurements were used in the calculation of the thermodynamic parameters. These calculations conclude that the adsorption of PAL molecules is an exothermic process that formed a mono-layer over the metal surface. Also, the adsorption process follows the Langmuir isotherm and the activation energy value increases with increasing the inhibitor concentration. SEM showed that PAL can effectively improve the corrosion protection of C1020 in a molar solution of HCl. Finally, structural electronic parameters extracted from quantum chemical calculations revealed the ability of the inhibitor’s ionic species to interact with metal surface via both physisorption and chemisorption processes, which is in good agreement with the experimental data. Also, Monte Carlo simulation showed that inhibitor’s ionic species are adsorbed in a way in which they are parallel to the metal surface. This adsorption mode increases the surface coverage, that in turn as well increases the inhibition efficiency this being in a good agreement with the electrochemical results.

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