ABSTRACT: Ionic liquids have significantly enhanced ecofriendly benefits compared to the traditional inhibitors. In the present work, new four polymeric ionic liquids based on benzimidazole derivatives were synthesized through the reaction of 2-styryl-1H-benzo[d]imidazole with alkyl halide to form PIL1. Then, Cl− anions were exchanged with different anions through the neutralization reaction to form other investigated polymers. Their structures were chemically elucidated using Fourier transform infrared spectroscopy, 1H NMR, and 13C NMR. Their influence on carbon steel (CS) as corrosion inhibitors has been checked with dielectric spectroscopy in addition to potentiodynamic polarization curves. It was found that the percentage of inhibition efficiency increases as inhibitor’s concentrations increase, suggesting a decrease in the rate of CS corrosion. Additionally, the hydrogen evolution rate controlled by the four polymers was monitored. Addition of the prepared polymers lessened the rate of generation of hydrogen as the inhibitor’s concentrations augmented. Scanning electron microscopy in addition to energy-dispersive X-ray diffraction has proved the morphology of the CS surface as well as the formed protective film.

1. INTRODUCTION:

The utilization of carbon steel (CS) is extensively prevalent in the production as well as the transportation of both crude oil and natural gas because of its nominal price, simple production, and significant mechanical merits. Nevertheless, CS shows a high rate of corrosion.1−6

Many of the corrosion inhibitors used in acidic media for CS corrosion control are particularly toxic and harmful to the environment.7−9 As a consequence, in recent years, ionic liquids (ILs) have been designed and synthesized. Ionic liquids’ application has been considered as a novel green approach owing to their numerous interesting properties, for instance, low melting point (lower than 100 °C), high polarization, low toxicity, insignificant vapor pressure (which means they do not evaporate and not pollute the environment), and thermal and chemical stability. Consequently, ILs reduced the harmful impact on the environment, and this makes them a perfect substitute for extremely volatile, traditional, harmful corrosion inhibitors.10,11

Ionic liquids (ILs) are melted salts formed from both organic cations and several inorganic anions with countless functional groups. ILs own a large number of physicochemical properties,12−15 essentially, nonflammability and enhanced ionic conductivity, electrical conductivity, and solvent transport, besides outstanding thermal and chemical steadiness. Generally, ILs have N, S, and P as the essential atoms of cations. Besides, most of these IL salts are established on imidazolium and pyridinium moieties as cations, whereas the characteristic anions are sulfonates, tetrafluoroborates, phosphates, and bis(trifluoromethane-sulfonyl) imide.16−18 Imidazolium compounds are stated to show anticorrosion performance on various metals and alloys such as aluminum, copper, mild steel, etc. Parveen et al. studied the corrosion inhibitive action of imidazolium-based ionic liquids in 1 M H2SO4 on mild steel.19 Likhanova and co-workers studied different imidazolium-type ionic liquids containing hexafluorophosphate as an anion in 1 M H2SO4 which have shown good efficiency as corrosion inhibitors of carbon steel.20 Atta et al. studied the effect of different types of ammonium tosylate ionic liquids as corrosion inhibitors on a carbon steel surface in 1 M HCl, which show good anticorrosion properties.21
The unique characteristics of ILs are the key for applying ILs in innovative and new applications. In general, ILs are considered as effective anticorrosion compounds for different metal surfaces owing to their elevated activity in acidic corrodent media.22−24 The anticorrosion potential of polymeric ionic liquid (PIL) nanoparticles via thiol-ene photo-polymerization within a mini-emulsion was disclosed by Taghavikish et al.25 Atta et al.26 have also investigated the boosted anticorrosion performance of a hyperbranched PIL. Furthermore, in our previous work, PILs based on chitosan derivatives27 and acrylamides28 have also been reported.

The present research was aimed to synthesize four polymeric ionic liquids based on benzimidazole derivatives. Their anticorrosion performance was tested for CS surface with lower concentrations in HCl (hydrochloric acid, 1 M concentration). The polymers under analysis were prepared through the reaction of 2-styryl-1H-benzo[d]imidazole with alkyl halide to form PIL1. Then, the Cl− anion was exchanged with different anions through the neutralization reaction to form other investigated polymers. Their influence on carbon steel (CS) as corrosion inhibitors has been checked with dielectric spectroscopy (EIS), "Nyquist as well as bode plots", in addition to potentiodynamic polarization curves. Furthermore, the hydrogen evolution rate regulated by the prepared polymers was monitored. Scanning electron microscopy [SEM] in addition to energy-dispersive X-ray diffraction (EDX) was used to examine the CS surface morphology to verify the defensive films formed.

2. RESULTS AND DISCUSSION

Polyionic liquid (PIL1) was synthesized through the reaction of 2-styryl-1H-benzo[d]imidazole (Sb1) with alkyl halide to form a monomer (IL1). Thereupon, a radical polymerization reaction transformed this monomer into an ionic liquid polymer (PIL1). The chloride ("Cl−") anion of monomer IL1 was exchanged with different anions to form the monomers IL2, IL3, and IL4. The monomers were transformed to ionic liquid polymers (PIL2, PIL3, and PIL4) by the radical polymerization reaction. As a result, an anticorrosive film protecting carbon steel surfaces was formed. Scheme 1 describes the chemically elucidated structure of the polymeric ionic benzimidazole liquids.

2.1. PILs' Characterization. The Fourier transform infrared (FTIR) spectrum of PIL1 is shown in Figure 1a. The signals at 3057.23 and 3022.47 cm−1 are assigned to the stretching of aromatic hydrogens. The signals at 2922.64 and 2852.58 cm−1 are allocated to asymmetric and symmetric C−H stretching, respectively.

The bands at 1636.55, 1595.61, 1551.11, and 1383.18 cm−1 are assigned to the C≡N stretching band, aromatic ring's C=C stretching, aromatic ring's C-C stretching, and C-N vibrational stretching, respectively. However, the strong peak at 711 cm−1 is assigned to the C-H bending of the (CH2)ₙ skeleton. The polymerization reaction has been ascertained through the disappearing of the characteristic vinyl band (=C-H, out-of-plane bending) at 985 cm−1.

Figure 1b displays the 1H NMR spectrum of PIL1. Lack of C≡CH signals within the range of 5−6.5 ascertains the occurrence of polymerization. Furthermore, signals were displayed at chemical shifts of 0.86 ppm (t, 6H, (CH2)ₙ-CH₃), 1.25 (t, 44H, (CH2)ₙ-CH₃), 1.71 (t, 4H, N-CH₂-CH₂), and 3.2 (1H, N=C-CH₂-CH₂-Ph) of polymerized hydrogens, 3.6 (t, 4H, N-CH₂-CH₂), and 7.23−7.87 (m, 9H, Ar H). Figure 1c displays the 13C NMR spectrum of PIL1. It indicates
Figure 1. Chemical structure characterization of the PIL1 inhibitor: (a) FTIR, (b) 1H NMR, and (c) 13C NMR.

signals at 141.82–127.33 (N-Ph & CH-Ph) and 29.44 ((CH2)n).

The FTIR spectrum of PIL2 is shown in S1(a). The bands at 2921.77 and 2852.72 cm⁻¹ are allocated to asymmetrical and symmetrical C–H stretching, respectively. The bands at 1711, 1639.74, 1596.86, 1547.73, 1391.90, and 1306.31 cm⁻¹ are assigned to the carbonyl C=O ester stretching, C≡N stretching, aromatic ring’s “C≡C” stretching, aromatic ring’s C-C stretching, C-N vibrational stretching, and C-O vibrational stretching, respectively. However, the strong band at 718.63 cm⁻¹ is assigned to the C-H bending of skeletal (CH2)n. The absence of the 985 cm⁻¹ band for the vinyl group (≡CH out-of-plane bending) assigns the occurrence of polymerization. S1(b) illustrates the 1H NMR spectrum of PIL2. Lack of C==CH signals within the range of 5 to 6.5 assigns the occurrence of polymerization. Moreover, chemical shifts’ signals are obvious at 0.86 ppm (t, 6H, (CH2)11-CH3), 1.25 (t, 44H, (CH2)11-(CH3), 1.71 (t, 4H, N-CH3), 3.2 (t, 1H, N==C-CH-Ph) of polymerized hydrogens, 3.60 (t, 4H, N-CH2-CH3), 7.28–7.90 (m, 9H, Ar H), and 8.51 ppm (s, 1H, H-COO⁻). S1(c) displays the 13C NMR spectrum of PIL2. It demonstrates signals at 169.91 (O-C==O), 126.70–140.9 (Ar C), 31.7 (N-CH2-(CH2)n), 29.44 (N-CH2-(CH2)n), and 14.36 (N-(CH2)n-CH3).

S2(a) demonstrates the FTIR spectrum for PIL3. The signals at 3057.22 and 3031.14 cm⁻¹ are assigned to the aromatic hydrogens. Bands at 2807.92 cm⁻¹ are allocated to asymmetrical and symmetrical C–H stretching, respectively. The band at 708.18 cm⁻¹ is assigned to the aldehyde hydrogen. Bands at 1702.54, 1639.88, 1551.36, 1449.99, and 1415.61 cm⁻¹ are allocated to the asymmetric and symmetric C–O vibrational stretching, C-N vibrational stretching, and C-O vibrational stretching, respectively. The strong band at 708.18 cm⁻¹ is assigned to the C–H bending of skeletal (CH2)n. The absence of the 985 cm⁻¹ band for the vinyl group (≡CH out-of-plane bending) assigns the occurrence of polymerization. S2(b) illustrates the 1H NMR spectrum of PIL3. Lack of C==CH signals within the range of 5 to 6.5 assigns the occurrence of polymerization. In addition, chemical shifts’ signals are clear at 0.87 ppm (t, 6H, (CH2)11-CH3), 1.25 (t, 44H, (CH2)11-(CH3), 1.71 (t, 4H, N-CH2-CH3), 3.2 (t, 1H, N==C-CH-Ph) of polymerized hydrogens, 3.60 (t, 4H, N-CH2-CH3), 7.28–7.90 (m, 9H, Ar H), and 8.51 ppm (s, 1H, H-COO⁻). S2(c) displays the 13C NMR spectrum (DMSO-d6, 400 MHZ) of PIL3. It demonstrates signals at 166.5 (H-C==O), 127.6–140.9 (N-Ph & CH-Ph), 31.0 (N-CH2-(CH2)n), 27.00 (N-CH2-(CH2)n), and 14.00 (N-(CH2)n-CH3).

S3(a) displays the FTIR spectrum of PIL4, The bands at 3371.69 and 3043.72 cm⁻¹ are assigned to NH2 and aromatic hydrogens, respectively. The 2922.77 and 2853.00 cm⁻¹ bands are allocated to the asymmetric and symmetric C–H stretching, respectively. The 1639.74, 1545.17, 1449.99, and 1388.89 cm⁻¹ bands are ascribed to the vinyl group (≡CH out-of-plane bending) assigns the occurrence of polymerization. S3(b) illustrates the 1H NMR spectrum of PIL4. Lack of C==CH signals within the range of 5 to 6.5 assigns the occurrence of polymerization. Additionally, chemical shifts’ signals are displayed at 0.87 ppm (t, 6H, (CH2)11-CH3), 1.25 (t, 44H, (CH2)11-(CH3), 1.71 (t, 4H, N-CH3), 3.2 (t, 1H, N==C-CH-Ph) of polymerized hydrogens, 3.60 (t, 4H, N-CH2-CH3), 7.28–7.90 (m, 9H, Ar H), and 8.51 ppm (s, 1H, H-COO⁻). S3(c) illustrates the 13C NMR spectrum of PIL4. It demonstrates signals at 169.41 (O-C==O), 122.96–129.42 (Ar C), 31.0 (N-CH2-(CH2)n), 27.00 (N-CH2-(CH2)n), and 14.00 (N-(CH2)n-CH3).

2.2. Hydrogen Evolution Reaction (HER) Quantification. Figures 2 and S4 illustrate the volume of H2 gas generated from CS corrosion in a 1 M HCl solution with time when PIL inhibitors are absent and also in their presence. A significant increase in H2 was obvious as the immersion period increased. The hydrogen generation rate (H¿) was calculated using eq 1.

In addition, adding several concentrations of PIL1, PIL2, PIL3, and PIL4 disturbs the hydrogen generation rates (H¿) as
can be observed in Figure 3, since as PILs’ concentrations increase, $H_r$ decreases.

Equation 2 was used to assess the efficiency ($I_{HH}$) of PILs for regulating $H_2$ evolution. Figure 4 demonstrates the inhibitors’ efficiency ($I_{HH}$) plotted versus logarithmic PILs’ concentrations. It has been concluded that the effect of PILs on inhibition increases as their concentrations increase. In fact, PIL1 > PIL2 > PIL3 > PIL4 was the order of the inhibitors’ anticorrosion effectiveness.

These PIL inhibitors inhibit the CS dissociation in HCl and, thus, delay and obstruct the cathodic $H_2$ generation reaction through adsorption at the metal/acidic solution interface. The strength of the prepared PILs to inhibit the hydrogen evolution is significantly influenced by the inhibitors’ chemical structures.30 Inhibitors of PIL type are capable of creating a thin film on the CS surface. The heteroatoms (predominantly N and O) transfer their electrons (charges) to the metal’s d-orbitals. Then, they form a strong shielding cover on the metal through forming coordinate bonds (called the chemisorption mechanism). Also, the existence of homoatomic $>\text{C}==\text{C}<$ or heteroatomic $>\text{C}==\text{O}>\text{C}==\text{N}=$ multiple bonds enriches the ability of the inhibitor molecules to be adsorbed by improving the electron donating tendency resulting from extensive conjugation.

Throughout the metal—inhibitor interactions, the negatively charged metallic surface (due to adsorption of counterions of the electrolytes) attracted the positively charged ($^+\text{N}$) PIL inhibitor molecules via electrostatic attractions.3 These electrostatic attractions showed that, in an acidic electrolyte, interaction of inhibitor molecules (having heteroatoms) with metal surfaces includes a physisorption mechanism. Then, it was followed by a chemisorption mechanism in the final interaction stage.

There is a synergistic effect between the cation and the anion of the corrosion inhibitors. PIL1 offers high corrosion resistance as compared to other synthesized PILs because of the presence of chloride ions. The presence of halide ions assists the adsorption of organic inhibitors through forming intermediate bridges between positively charged inhibitor molecules and the carbon steel surface. Consequently, corrosion inhibition synergism results from increasing surface coverage as a result of ion-pair interactions between the organic cation and the anion.31

2.3. Potentiodynamic Polarization (PDP) Measurements. Steel electrochemical polarization curves attained in 1 M HCl solution with and without different PIL inhibitor concentrations are shown in Figures 5 and S5. Dwindling was observed in anodic along with cathodic currents in the case when the inhibitor was present. The decline became more apparent at higher inhibitor concentrations. The arrangement of a protective overlay to protect the steel surface against the corrosion medium may be the logical reason for the apparent decline, since inhibitor’s adsorption on the steel surface minimizes the hydrogen evolution [cathode’s reaction] as well as minimizes iron metal deterioration [the reaction at the anode].

Parameters such as the corrosion potential ($E_{corr}$) and corrosion current density ($I_{corr}$) in addition to Tafel slopes of the cathode ($\beta_c$) and anode ($\beta_a$) have been extracted from the...
polarization curves and then gathered and tabulated in Table 1. The degree of surface coverage ($\theta$) and the inhibition efficacy (IE%) are computed through eqs 1 and 2, respectively.32

$$\theta = [1 - (I_{\text{corr}}(2)/I_{\text{corr}}(1))] \times 100$$

(1)

$$\text{IE}\% = [1 - (I_{\text{corr}}(2)/I_{\text{corr}}(1))] \times 100$$

(2)

in which $I_{\text{corr}}(1)$ and $I_{\text{corr}}(2)$ are the corrosion current densities in the absence and presence of the inhibitor, respectively.

Table 1 lists the IE percentages with increasing inhibitor levels. It has been shown that IE percentages increased as the inhibitor’s concentrations were augmented, due to an increase in the amount of inhibitors’ accumulation along with adsorption on the steel surface. This process thus leads to a high inhibition of corrosion. At 250 ppm concentration of PIL1, the utmost efficient inhibition was approximately 99.3%.

The use of different techniques may be the logical reason for the dissimilar values of the IE% obtained from the potentiodynamic polarization technique and the hydrogen evolution technique. Furthermore, the inhibitor may be named anodic or cathodic if the value of $E_{\text{corr}}$ surpasses 85 mV. Table 1 shows the various values of $E_{\text{corr}}$ with an utmost $E_{\text{corr}}$ value of less than 85 mV indicating the mixed corrosion mode (disrupting both the anodic and the cathodic reactions together). Nonetheless, a slight change in $E_{\text{corr}}$ in cathodic patterns makes the cathodic path more clear. Potentiodynamic results show the effective cutting down of steel’s corrosion when using the formulated PILs even at minifying concentrations in 1 M HCl.

Values of mean and standard deviation (SD) for the corrosion current density for the carbon steel electrode at different concentrations of PIL inhibitors in a 1 M HCl solution are indicated in S6.

2.4. Electrochemical Impedance Spectroscopy (EIS) Evaluation. The inhibitory activity can also be examined utilizing the EIS technique in aggressive 1 M HCl media alone and also while employing diverse concentrations of PIL1, PIL2, PIL3, and PIL4.

The Nyquist plots for different PIL concentrations with fitting curves are shown in Figures 6 and S7. Throughout Figures 6 and S7, the capacitive loop’s diameter in the Nyquist graph increases with the increase in the concentrations of the PIL inhibitors.

Figure 6. Nyquist plots for the carbon steel electrode in a 1 mol L$^{-1}$ HCl solution with and without various concentrations of the PIL1 inhibitor.
inhibitor. This clearly implies that steel deterioration primarily depends on the charge transfer reaction. \(^{36-38}\)

\(R_{\text{ct}}\) [charge transfer resistance] and \(C_{\text{dl}}\) [double layer capacitance] values gained from Nyquist plots are then collected in Table 2. Reduced \(C_{\text{dl}}\) values and increased \(R_{\text{ct}}\) values in the presence of PIL inhibitors affirm their protective efficiency depending on their concentrations. A reduction in \(C_{\text{dl}}\) values may have occurred due to the decrease in the electric double layer thickness, since PIL moieties \([\text{with a minimal dielectric constant}]\) swap water molecules \([\text{with a high dielectric constant}]\). On the whole, corrosion is related to the behavior of the double layer. Therefore, action of inhibitors includes their arrangement as well as adsorption through replacing aquatic molecules from the interface between steel and the corroding medium.\(^{39}\)

As the inhibitor concentrations augmented, both \(R_{\text{ct}}\) and IE \% values increased, as observed in Figures 6 and S7 and also in Table 2. The effectiveness of the inhibition (IE\%) can be computed through utilizing eq 3.\(^{40-42}\)

\[
\text{IE}\% = 1 - \left(\frac{R_{\text{ct}}^1}{R_{\text{ct}}^2}\right) \times 100
\]

in which \(R_{\text{ct}}^1\) and \(R_{\text{ct}}^2\) are the charge transfer resistance in the uninhibited and inhibited solutions, respectively.

In impedances, \(R_{\text{ct}}\) values were determined through variation at lesser and higher frequencies. The use of different techniques may be the logical reason for the dissimilar values of the IE\% obtained from the potentiodynamic impedance technique and the hydrogen evolution technique. At a concentration of 250 ppm of PIL1, extreme efficacy (96.85\%) inhibition was achieved. The utmost inhibition efficacy of 96.85\% was achieved at 250 ppm of the PIL1 inhibitor.

The Bode as well as phase angle graphs for CS in hydrochloric acid whose concentration is 1 M alone as well as in the presence of PILs are shown in Figures 7 and S8. A spectrum of frequency was implemented for the Bode phase

![Figure 7. Bode plots for a carbon steel electrode in 1 mol L\(^{-1}\) HCl solution with and without various concentrations of the PIL1 inhibitor.](https://dx.doi.org/10.1021/acsomega.0c04505)

values in the presence of PIL inhibitors affirm their protective efficiency depending on their concentrations. A reduction in \(C_{\text{dl}}\) values may have occurred due to the decrease in the electric double layer thickness, since PIL moieties \([\text{with a minimal dielectric constant}]\) swap water molecules \([\text{with a high dielectric constant}]\). On the whole, corrosion is related to the behavior of the double layer. Therefore, action of inhibitors includes their arrangement as well as adsorption through replacing aquatic molecules from the interface between steel and the corroding medium.\(^{39}\)

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\]

in which \(R_{\text{ct}}^1\) and \(R_{\text{ct}}^2\) are the charge transfer resistance in the uninhibited and inhibited solutions, respectively.

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The Bode as well as phase angle graphs for CS in hydrochloric acid whose concentration is 1 M alone as well

| inhibitor | concentration (ppm) | \(R_{\text{ct}}\) (Ohm) | \(C_{\text{dl}}\) (\(\mu F/cm^2\)) | \(\theta\) | IE\% |
|-----------|---------------------|------------------------|-------------------------------|------|------|
| blank     | 0.00                | 16.97                  | 680.2                         |      |      |
| PIL1      | 50                  | 399.8                  | 90.26                         | 0.9575 | 95.75 |
|           | 100                 | 430                    | 84.16                         | 0.9605 | 96.05 |
|           | 150                 | 479                    | 74.34                         | 0.9645 | 96.45 |
|           | 200                 | 528.8                  | 120.3                         | 0.9679 | 96.79 |
|           | 250                 | 539.3                  | 62.6                          | 0.9685 | 96.85 |
| PIL2      | 50                  | 211.3                  | 84.76                         | 0.9196 | 91.96 |
|           | 100                 | 322.5                  | 78.80                         | 0.9473 | 94.73 |
|           | 150                 | 371.3                  | 68.40                         | 0.9542 | 95.42 |
|           | 200                 | 408.1                  | 70.11                         | 0.9584 | 95.84 |
|           | 250                 | 489.1                  | 65.49                         | 0.9653 | 96.53 |
| PIL3      | 50                  | 236.8                  | 142.7                         | 0.9283 | 92.83 |
|           | 100                 | 346.9                  | 82.62                         | 0.9510 | 95.1  |
|           | 150                 | 369.7                  | 77.65                         | 0.9540 | 95.4  |
|           | 200                 | 421.8                  | 50.5                          | 0.9597 | 95.97 |
|           | 250                 | 454                    | 42.39                         | 0.9626 | 96.26 |
| PIL4      | 50                  | 99                     | 158.89                        | 0.8285 | 82.85 |
|           | 100                 | 159.8                  | 131.65                        | 0.8938 | 89.38 |
|           | 150                 | 213.5                  | 88.1                          | 0.9205 | 92.05 |
|           | 200                 | 274.6                  | 65.20                         | 0.9382 | 93.82 |
|           | 250                 | 316.3                  | 50.38                         | 0.9463 | 94.63 |

The SEM picture in Figure 8b displays a perfect reduction in the corroded surface has been observed with total destruction on the CS surface. In Figure 8b, on adding 250 ppm PIL1 inhibitor, the EDX spectrum displays additional signals, approving the existence of C and N atoms in the PIL1 inhibitor. Moreover, the signals of Fe are significantly inhibited, compared to those of the samples in Figure 8a, because of formation of a defensive inhibitor film. The SEM picture is also illustrated in Figure 8a. A coarse and heavily corroded surface has been observed with total destruction on the CS surface.

**2.5. Surface Morphology Examination.** To observe the morphology of the CS surface, scanning electron microscopy (SEM) has been performed. Additionally, energy-dispersive X-ray (EDX) spectrometry was carried out to identify the composition of the CS surface elements prior to and after immersion of the inhibitor in the corroding medium. Figure 8a depicts the EDX bands for the adsorbed elements on the CS surface in the case of blank solution. Signals of O and Fe prove that iron oxide is present in the solution, resulting from metal dissolution on the anodic reaction. Additionally, after dipping into HCl solution (1 M) with no inhibitor (blank), the SEM picture also illustrated in Figure 8a. A coarse and heavily corroded surface has been observed with total destruction on the CS surface.
2.6. Corrosion Inhibition Mechanism. The pictorial diagram for the inhibition mechanism on carbon steel surface in 1 M HCl can be seen in Figure 9. The anion improves the adsorption ability of the organic cation by forming a connecting bridge between the negatively charged metal surface and the organic inhibitor and synergistically increases the corrosion inhibition ability of organic compounds significantly. The adsorption of anions makes the CS surface negatively charged, as a result making it easier for organic cations to be adsorbed on the CS surface by electron interactions. This is the physical adsorption.

Chemically, the inhibitor molecule directly reacts with the CS surface to form a coordination bond, and this process is called chemical adsorption. As a result, a defensive film is

Figure 8. EDX and SEM for the (a) sample after immersion in 1 M HCl without the inhibitor (blank) and (b) sample after immersion in 1 M HCl solution containing 250 ppm PIL1 inhibitor.
formed on the CS surface by the physicochemical adsorption of inhibitor molecules for protection against the corrosive ion attack. In addition, the synergism between cations and anions of ionic liquids offers good protection for the CS surface.

3. CONCLUSIONS

Four new polymeric ionic liquids (PILs) have been chemically synthesized based on styryl benzimidazole derivatives and assessed as anticorrosion agents. Spectroscopic techniques such as $^1$H NMR, $^{13}$C NMR, and FTIR spectroscopy chemically elucidated the structures of the new polymers. CS corrosion was measured in HCl (1 M), as a source for generating H$_2$ gas and as an acidic medium. Addition of the PILs diminished the rate of hydrogen production. The H$_2$ generation rate reduced as PILs’ concentrations increased. Electrochemical methods such as polarization and impedance revealed that the PIL inhibitors have improved anticorrosive properties in the corrosive medium for CS surface. The percentage of inhibition efficiency increased as the inhibitor concentrations increased in the solution of 1 M hydrogen chloride, demonstrating a decrease in the CS corrosion rate. Further, the effectiveness order was PIL1 > PIL2 > PIL3 > PIL4. The experimental values achieved from polarization, impedance, and hydrogen evolution methods were in good agreement and showed the same trend. Morphological studies (SEM and also EDX) verified the formation of a defensive overlay of PILs on the surface of CS, hence ensuring the protection of steel surface. In addition, there is a synergistic effect between cations and anions of the corrosion inhibitors. In conclusion, ionic liquids offer a potential opportunity for pioneering applications for green chemistry. Unlimited growth in this field is expected due to the outstandingly superior, ecofriendly, and sustainable benefits of these compounds compared to conventional and known inhibitors.

4. EXPERIMENTAL SECTION

4.1. Materials. O-Phenylenediamine, cinnamic acid, tetradecylchloride, and m-amino sodium benzoate were purchased from Aldrich Chemicals Company and used with no further purification. Benzoyl peroxide was purchased from Merck and used as a radical initiator. Hydrochloric acid was obtained from BDH Company. Distilled water was used for preparing all test solutions. The corrosive acid environment was 1 M HCl. Tests were performed on carbon steel (CS) of type X-65, which was attained from an unutilized oil pipeline and was used as the working electrode in the experiments. It has the following composition: Mn, 1.51; Si, 0.23; C, 0.08; Ni, 0.05; S, 0.04; Al, 0.03; Cu, 0.02; Cr, 0.02; P, 0.02; Mo, 0.005; and V, 0.002, whereas Fe is the remaining part. A saturated calomel electrode (SCE) as a reference electrode and a platinum (Pt) electrode as an auxiliary electrode were utilized.

4.2. Synthesis Procedure. 4.2.1. Synthesis of 2-Styryl-1H-benzo[d]imidazole (Sb1). O-Phenylenediamine (0.01 mol) was dissolved in ethanol, and cinnamic acid (0.01 mol) was added. Then, the mixture was refluxed for 3 h at 80 °C. The reaction mixture was cooled, and sodium carbonate solution was added to basify. The product was precipitated by adding 20 mL of cold water. Then, the product was filtered, washed with cold water, and subsequently recrystallized from the aqueous solution to get the product “2-styryl-1H-benzo[d]imidazole”, labeled as Sb1.

4.2.2. Synthesis of Ionic Liquid of Styrylbenzimidazolide (IL1). Sb1 (0.01 mol) was dissolved in ethanol, and potassium hydroxide (0.02 mol) was added. The mixture was stirred at 70 °C for 30 min. To the reaction mixture under stirring, tetradecylchloride (0.022 mol) was added dropwise. Then, the mixture was heated at 70–80 °C for 24 h. The mixture was then cooled down to ambient temperature. The substance was subsequently extracted with ethanol, washed with ethyl acetate, filtered, and finally dried to give oily products with the IL1 label.

4.2.3. Synthesis of Polymeric Ionic Liquid of Styrylbenzimidazolide (PIL1). The benzoyl peroxide initiator (0.5 wt % monomer) was added to IL1 dissolved in water, and thereafter the temperature was elevated to 70 °C and maintained for about 10 h. The product was precipitated by addition of 250 mL of acetone. Then, the product was filtered, washed with diethyl ether as well as absolute methanol, and finally dried in a vacuum at 20 °C to attain the PILs.

4.2.4. Synthesis of Polymeric Ionic Liquids Labeled as PIL2–4. IL1 (0.001 mol) was dissolved in water, and sodium benzoate (0.001 mol) was introduced. The mixture was refluxed for 6 h to produce IL2. Benzoyl peroxide (0.5 wt % monomer) was then introduced to the refluxed mixture, and subsequently, the temperature was increased to 70 °C and maintained for about 10 h. Afterward, the reaction mixture was cooled and acetone (250 mL) was added. The precipitate thus formed was filtered off, washed with absolute methanol as well as diethyl ether, and finally dried at 20 °C under vacuum. The formed polymer was labeled as PIL2. The same procedure was used to synthesize PIL3 and PIL4 using sodium formate and m-amino sodium benzoate, respectively.

4.3. Spectroscopic Assessments. The molecular structure of the prepared ionic liquid polymers was assessed through analyses like infrared (IR) as well as $^1$H NMR, in addition to $^{13}$C NMR spectra. Infrared (IR) analysis was performed utilizing a Fourier transform infrared spectrophotometer, FTIR, Bruker. The spectrometer [Bruker Advance DRX-400] along with the solvent DMSO-$d_6$ was utilized for $^{13}$C NMR and $^1$H NMR analyses. The spectrometer has a resonance frequency of 400 MHz.

4.4. Hydrogen Evolution Reaction (HER) Quantification. Water replacement is the technique used to estimate the rate of hydrogen evolution. This method aimed to quantify hydrogen evolution is parallel to that described earlier. $^{45,46}$ First, the corroding medium (1 M HCl), 100 mL, was put into a glass container. A CS coupon, having dimensions of 3.5 cm × 2.5 cm × 2 mm, was immersed within the corroding medium. This vessel was immediately locked up to avoid the leakage of H$_2$ gas. Thereupon, the amount of H$_2$ gas produced was
recorded at almost fixed times during the corrosion reaction. The hydrogen gas volume was measured on the basis of the fact that the gas volume (in cm³) replaces the water level in the burette.

The following expression⁶⁷ was used to evaluate the hydrogen generation rate (Hᵢ)

\[ H_i = (v_2 - v_1)/(t_2 - t_1) \]  \hspace{1cm} (4)

where \( v_2 \) and \( v_1 \) are the volumes of \( H_2 \) gas produced at \( t_2 \) and \( t_1 \) time intervals, respectively. Additionally, the efficacy of PILs (\( I_{H2} \%) \) for governing hydrogen gas production was revealed using the following equation

\[ I_{H2}^{\%} = [1 - (H_i/H_{in}))] \times 100 \]  \hspace{1cm} (5)

in which \( H_{in} \) and \( H_i \) are the rates of evolution of hydrogen in the absence and presence of the readily prepared PILs, respectively.

4.5. Electrochemical Measurements. Potentiostat PGZ 402 [Voltalab 80 Tacussel Radiometer] was run to perform the electrochemical measurements. The Voltamaster-4 program was used to perform these measurements. A 100 mL electrochemical glass cell with 3 electrodes’ spaces has been used. The electrochemical cell was filled with the corroding medium (100 mL of 1 M HCl). The carbon steel was the working electrode (WE).

A saturated calomel electrode [SCE] as the reference electrode and a platinum [Pt] electrode as an auxiliary electrode were utilized.

Moreover, the SCE was connected to a Luggin capillary. The capillary slope was made adjacent to the WE surface to lessen the potential drop (IR drop). All potential values were quantified versus SCE. Prior to all tests, the CS electrode’s surface was hand-glazed with various specific emery sheets, subsequently washed with distilled water, and ultimately dried. After keeping for an hour in the test solution, the electrode potential was stabilized to maintain a steady-state “open-circuit potential”. An electrode area of 1 cm² was exposed to the devastating media. The whole steps function at ambient temperature and exposed the electrochemical cell to air.

4.6. Surface Morphology Studies. For this research, a scanning electron microscopy (SEM) instrument of model Quanta 250 FEG and an EDX (energy-dispersive X-ray diffraction) instrument were employed.

The applied accelerating voltage was 30 kV, and the magnification force was \( X = 2000 \). The surface morphological properties were tested through dipping the carbon steel (CS) coupon in the blank solution as well as in the inhibitor solution containing certain concentration of the prepared inhibitor.

ASSOCIATED CONTENT

1. Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04505.

Chemical structure characterization of PIL2–PIL4 inhibitors; volume of hydrogen evolved with time, polarization plots, values of mean and standard deviation for corrosion current density, Nyquist plots, and Bode plots for carbon steel in 1 mol L⁻¹ HCl with and without various concentrations of the inhibitors (PDF)

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Notes
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