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Study of Protic Ionic Liquids as Sustained Corrosion Inhibitors for Mild Steel in Saline Solution with Acidic pH and Temperature Variations

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The industry's principal objective is to comprehend the optimal application of each metal alloy in terms of corrosion resistance. A key focus lies in exploring alternative approaches to address this corrosive process in a manner that is both sustainable and economically feasible. The major strategy to mitigate this contest involves the utilization of inhibitors. However, it is imperative to note that certain inhibitors pose environmental risks. This study explores the effect of the addition of protic ionic liquids (PILs) on the corrosion of carbon steel (A36) in a saline solution (3.5 wt% NaCl), considering variations in pH and temperature. It focuses on understanding the effects of pH and temperature on the PILs' ability to protect the steel surface. Notably, changes in pH do not affect the protective capacity of the inhibitors. Efficiency values exceeding 72% were achieved under both acidic conditions tested. The study reveals two scenarios: At 40 °C, the PILs effectively protect the steel, with an efficiency of approximately 74% at concentrations of 500 and 1000 ppm. However, at 60 °C, efficiency decreases notably, reaching a maximum of 51% at a concentration of 500 ppm. Afterward, to evaluate the protective effectiveness of these compounds, gravimetric and electrochemical impedance spectroscopy (EIS) serve as the main methods, accompanied by optical and atomic force microscopy (AFM) for evaluating the surface. In electrochemical tests, PILs 1 and 2 exhibit superior efficiency, with film formation, while PILs 3 to 6 demonstrate comparatively lower values.

Keywords: *A. Protic Ionic Liquids, B. Corrosion Inhibitor, C. Mild Steel A36, D. Electrochemistry.*

1. Introduction

It is common knowledge that damage caused by corrosion is a universal problem; annually, each country loses 3 - 5% of its GDP (Gross Domestic Product) because of actions to combat this dilemma. Then, the global economic loss due to corrosion was estimated at approximately 2.5 trillion dollars by The National Association of Corrosion Engineers (NACE) in 2016[1]. Consequently, the industry sector opts to apply low-alloy materials in their structures as an alternative solution to reduce corrosion-induced damage costs[2,3].

The application of alloys with less than 0.2% carbon, such as AISI 018, AISI 1020, and ASTM A36, is commonly seen in the petroleum/chemical industry by the reason of their ductility, malleability, and structural resistance. This type of material is normally selected for industrial applications because it combines without difficulty with other alloys such as AISI/SAE 304, ASTM A182 F22, and ASTM A992, which results in an improved final product capable of enduring extreme conditions in industrial plant[4-6].

Intended for low-carbon alloys, this material is applied in regions near the ocean with high and aggressive external salinity. Therefore, evaluating this type of material in a saline environment is justified and is an attractive factor for the investigation of corrosion inhibitors in this type of electrolyte. Thus, with these results, it is feasible to search for new techniques to mitigate corrosion and improve efficiency and sustainability. Another factor that must be taken into consideration is that, generally, in the literature, there are no studies with variations in external factors in saline electrolytes, such as pH and temperature[7-11].

Among the possibilities for preventing corrosion, the industrial field has generally chosen inhibitors as the principal method to protect industrial manufacturing, structures, and distribution pipelines[12]. The motive for this option is because of the practicality and efficiency of this technique, and this kind of method is capable of protecting the material at different pH

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values, temperatures, and pressures proving it to be polyvalent. However, in contrast to the use of these chemical compounds, some are seriously harmful to human health and the environment because they contain heavy metals, such as Cr, Cd, Pb, and Hg[13-17].

Ionic liquids are chemical compounds classified as aprotic (AILs-Aprotic Ionic Li) and protic (PILs) and have emerged as one of the most researched topics in scientific literature. These chemicals are innovative alternatives to address countless issues from the capture of polluting gases (CO_2) to extremally complex reactions that require a thermally stable ionic environment[18-21]. Still on ionic liquids, the most popular class are Aprotics (AILs), mainly because they are particularly versatile due to their high ionic character, originated by cations and anions that are reactive to different electrolytes and can ease transfer electrons in a chemical reaction[22-25].

It is important to note that ionic liquids, such as those discussed by Ardakani et al.[26], are less environmentally damaging. These compounds can be classified as eco-friendly inhibitors since they do not use toxic volatile solvents such as Hexane or Chloroform during synthesis and do not contain heavy metals in their composition[27]. However, due to their high stability, aprotic ionic liquids have certain disadvantages compared with protic ionic liquids. According to the literature, AILs are bio-accumulative in some organisms and soil, making them unviable when evaluating the choice of these compounds as corrosion inhibitors from an ecological perspective[28-30]

Given the current focus on environmental issues, it is essential to consider the efficiency and ecological impact of compounds used as inhibitors. While Aprotic Ionic liquids are plausible from the perspective of efficiency in corrosion protection, they fail when evaluated in the sustainable context. Therefore, it is necessary to investigate new inhibitor options, and in this regard, protic ionic liquids (PILs) emerge as a promising alternative for this application. PILs have several advantages over AILs, including their simplicity in synthesis, low production costs, non-bio accumulative nature, and biodegradability, as observed in the literature[31-34].

Considering the current concern regarding the environment, it is necessary to evaluate the ecological impact of compounds used as inhibitors, in addition to their efficiency, given the potential harm they can cause to the environment if not used responsibly. Therefore, the interest in evaluating these compounds as inhibitors is present in saline environments but with variations in their parameters, such as pH level and temperature[35].

Thus, using protic ionic liquids (PILs) obtained from a simple acid-base reaction between carboxylic acids and primary and secondary amines (ethanolamine and diethanolamine). These compounds are commonly used as thermal fluids in specific applications focused on the field of chemical engineering. However, they present chemical structures that can facilitate adsorption on the surface of ASTM A36 carbon steel. In that way, it was decided to investigate these compounds innovatively and originally with the saline environment in different situations (pH and temperature)[36,37].

As per the literature, research into corrosion inhibitors with protic ionic liquids is relatively new and scarce. Agreeing with Ortega-Vega et al.[38], the use of PILs acted as a mixed-type organic inhibitor as it promoted the decrease of the oxygen reduction reaction rate on the material surface and consequently pit formation through its adsorption on the metal surface of aluminum in a neutral medium with efficiency value above 95%. Interestingly, the utilization of PILs in the corrosive solution reduces the corrosion of AISI 1020 steel.

In agreeing with the discussion defended by Schmitzhaus et al.[20] inhibition properties of protic ionic liquids are most related to the effect of physic-chemical adsorption on the metallic substrate reaching massive values of corrosion efficiency (97%). In succession, Zunita et al.[39] developed an innovative and relevant study with protic ionic liquids as corrosion inhibitors for carbon steel application. This material, the compounds were effective on carbon steel (1% NaCl solution) at a temperature of 25 °C with efficiency of values above 98%.

Utilizing Protic Ionic Liquids (PILs) as sustainable corrosion inhibitors presents an appealing prospect from an ecological standpoint, as it enables the efficient and environmentally protective mitigation of corrosion. This study emphasizes the ecologically favorable characteristics of such compounds, particularly their biodegradability, by selecting one that exhibits low synthesis cost and a straightforward reaction mechanism[40]. Furthermore, there is a crucial factor when evaluating the application of a corrosion inhibitor synthesized in the laboratory. Its accessibility is a subject that must be considered seriously, as when adopting a certain compound combination to contend corrosion, this valuation must be exact[41]. Furthermore, it is known that the industry can merely use a particular formulation as an inhibitor if it has excellent efficacy.

Thus, another factor related to the ability to protect the material is its applicability, which is directly related to its viability. Since large quantities are applied in the industry, these factors should be carefully weighed to utilize the complete capacity of the inhibitor. Because of this, ionic liquids stand out in general, as they present a simplified chemical synthesis with an acid-base reaction, practically, and obtaining the reagents used is considered manageable with an acceptable cost from the point of view of the return on structural protection[42,43].

In the previous study, six distinct protic ionic liquids (PILs) were synthesized and tested for their capability to inhibit corrosion on ASTM A36 carbon steel in a 3.5 wt. % NaCl solution. However, since satisfactory results were achieved previously, this article aims to explore additional/adverse factors and present them for discussion. Specifically, different pH and temperature levels were selected for evaluation, as these aspects are underexplored in inhibitor literature. Additionally, this study introduces an innovative approach to surface characterization by examining samples based on immersion time.

2. Experimental

2.1. Protic ionic liquid synthesis and characterization

The protic ionic liquid synthesis was conducted with a dropping funnel by adding the reagents (bases and acids) in a three-necked glass flask equipped with a thermometer to determine the reaction temperature and a reflux condenser to avoid solvent evaporation, standardized methodology in accordance with literature[44-46]. In summary, 2-hydroxy diethanolamine formate (PIL 1 = 2-HEAF), 2-hydroxy ethanolamine formate (PIL 2 = 2-HDEAF), 2-hydroxy ethanolamine propionate (PIL 3 = 2-HEAP), 2-hydroxy diethanolamine propionate (PIL 4 = 2-HDEAP), 2-hydroxy ethanolamine pentanoate (PIL 5 = 2-HEAPe) and 2-hydroxy diethanolamine pentanoate (PIL 6 = 2-HDEAPe) were used as chemical nomenclature, details in Figure 1[47-50]. The reagents were purchased from Aldrich with mass purity of 0.99 and the carboxylic acids from Sigma (mass purity of 0.996) to ensure the quality and reliability of the final products[47,49-52].

For this examination, an infrared spectrometer (Fourier Transform Cary 630, Agilent Technologies) was used, which allowed the evaluation of liquid and solid samples. Thus, the samples were applied directly to the spectrometer without prior preparation to avoid error. Absorbance spectra were collected at a wavelength in the range of the most significant interest for organic components (400 – 4000 cm^{-1}) and with a spectral resolution of 1 cm^{-1}.

2.2. Sample preparation for general evaluation

The chemical composition of the structural steel spent in the experiments (wt.%) was determined with structural steel A36 (ASTM) using PDA 7000 Optical Emission Spectrometer (Shimadzu/Japan), with average: C = 0.21029%, Si = 0.03306%, Mn = 0.50905%, P = 0.00569%, S = 0.00841%, Ni = 0.02425%, Cr = 0.0233% and Fe = 98.71%, similar composition to the literature data[53,54]. First, the steel samples (ASTM A36) with a size of one cm^2 were ground with 120, 220, 400, 600, and 1200 grit every paper without further polishing. Before electrochemical evaluation, the material was washed with distilled water and ethanol[55].

2.3. Corrosion tests

2.3.1. Weight loss measurements

The ASTM A36 carbon steel coupons (1.0 x 3.5 x 0.5 cm) underwent priming through the following procedure: abrading, rinsing, and drying, resulting in the initial weight (W_1). The immersion test was conducted in a 500 mL solution containing 3.5% wt. sodium chloride (NaCl), the concentration of which was determined based on the total sample area. The tests were performed both with and without the presence of PILs (01-06) (1000 ppm) for a specified duration of 100 hours in triplicate.

Subsequently, after the immersion exposure, the specimens were cleaned to remove corrosion products utilizing Clark solution (admiring the ASTM G1 standard methodology), and the samples were then dried and re-weighed (W_2). Weight loss was determined by gravimetric tests using an analytical balance, Shimadzu (220g) with 0.0001g precision.

This process was systematically repeated for weight loss measurements, encompassing variations in pH (2 and 4) and temperature (40 and 60 °C)[56,57]. Additionally, the same methodology was replicated for mass losses with heat, utilizing two optimized concentrations (500 and 1000 ppm). Each experiment was carried out in triplicate. The weight loss (ΔW) was determined using the following equation, consistent with the literature on mass-loss measurements[12,15,58-60].

$$\Delta W = W_1 - W_2 \tag{1}$$

The corrosion rate, denominated by υcorr (mmy), was calculated by the Equation 2[5,19,57,61-64]:

$$\upsilon corr = \frac{\Delta W * k}{S.t.p} \tag{2}$$

Fundamentally, the symbol (S) is the sample area (cm^2), (t) is the dousing period (h), and (p) is the density (k). The inhibition efficiency, % IE_{WL} was calculated by:

$$\% IE = \frac{\upsilon\text{corr}(\text{b}) - \upsilon\text{corr}(\text{i})}{\upsilon\text{corr}(\text{b})} x100 \tag{3}$$

where $\upsilon_{corr(b)}$ and $\upsilon_{corr(i)}$ are the corrosion rates with inhibitors and without them[5,19,57,61-64].

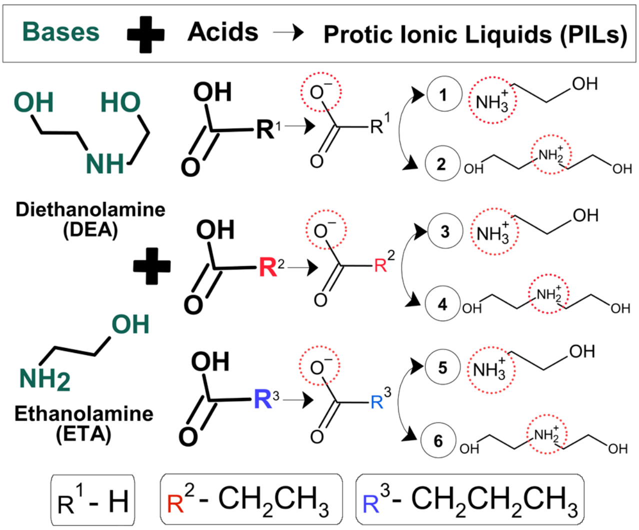

Figure 1. Schematic route for PILs synthesis.

2.3.2. Electrochemical measurements

For the electrochemical measurements, a conventional three-electrode cell arrangement with a working electrode of ASTM A36 carbon steel (0.5 cm x 0.5 cm). An Ag/AgCl wire as a reference electrode saturated with KCL because even with temperature changes and water evaporation the system will remain stable, and a platinum wire as a counter electrode (1.2 cm x 1.2 cm).

This evaluation was possible with the assistance of an Autolab 302N Modular potentiostat / galvanostats widely used in the literature in the study of corrosion[20,65]. The samples were immersed in solutions containing protic ionic liquids optimized concentrations (500 and 1000 ppm) for electrochemical evaluation in saline solution.

In detail, the electrochemical impedance spectroscopy technique was tested in a frequency range from 100 kHz to 0.01 Hz with a sinusoidal perturbation of 20 mV amplitude and 3600s OCP - Open Circuit Potential. The use of this electrochemical potential range can be found in the literature on ionic liquids as inhibitors[66-68].

The corrosion inhibition efficiency (IE%) was calculated using charge transfer resistance (Rct) values, obtained from the EIS tests, according to Equation 4[69-75].

$$\%IE = \frac{\mathrm{Rct} - R^{o}_{ct}}{R^{o}_{ct}} x100 \qquad (4)$$

where R_{ct} and R^{O}_{ct} are the charge transfer resistances for the systems in a 3.5 wt. % NaCl) solution, in the presence and absence (Blank experiment) of the inhibitor, respectively[69-75].

2.4. Surface analysis

At first, the surface evaluation was conducted by applying optical microscopy. The samples were fully immersed in a saline solution containing 500 and 1000 ppm of all evaluated Protic Ionic Liquids (PILs) for a standard period of 24 hours, with both adverse conditions evaluated (pH and temperature).

A Leica DMI3000M optical microscope was employed with a DFC 295 color camera. The methodology outlined in ASTM G1 standard practice for preparing, cleaning, and evaluating corrosion test samples was strictly adhered to. Additionally, to analyze modifications in the surface morphology of A36 carbon steel after 24 hours of immersion, Atomic Force Microscopy (AFM) was employed. AFM measurements were acquired in intermittent contact mode using Asylum MFP-3D BIO equipment, featuring curved radius tips smaller than 10 nm and a resonant frequency of 75 kHz. The scan area for AFM imaging was at least 10 µm x 10 µm.

3. Results and Discussion

3.1. Fourier transform infrared spectroscopy (FTIR)

Significantly, through FTIR analysis, it was possible to investigate the structural differences among the protic ionic liquids evaluated in this study. Figures 2 and 3 exhibit the absorption spectra of PIL 01 to 06. In detail, to facilitate the evaluation of aspects, Table 1 contains the abbreviations and nomenclatures of protic ionic liquids.

A broad band, distinct by sections A and B, in the range of 3600-2250 cm^{-1} presents the elongation bands O-H and N-H (3600-3200 cm^{-1}) and (3000-2800 cm^{-1}) of the C-H elongation band, which are characteristic bands of the ammonium cation structures[76-78]. These results confirm the presence of the polar fractions of the main base (diethanolamine) present in protic ionic liquids synthesis.

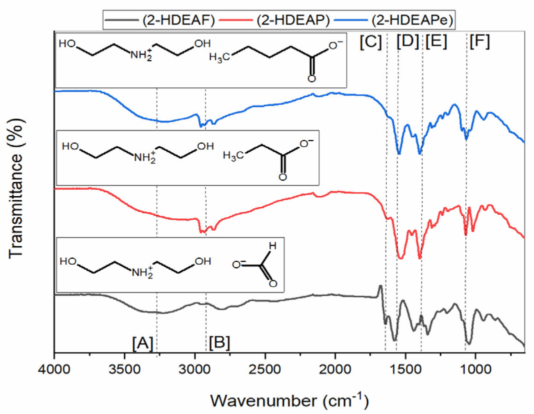

Figure 2. FT-IR spectra of PIL 02, PIL 04, and PIL 06.

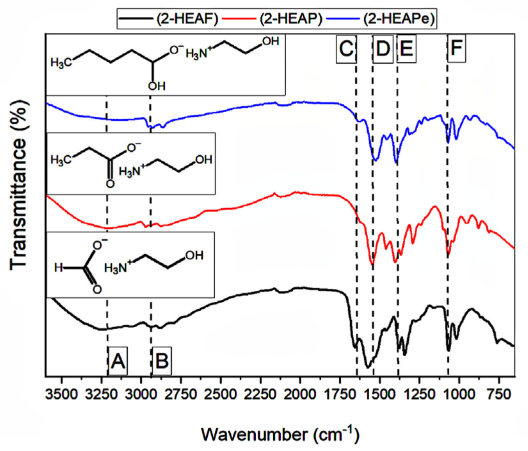

Figure 3. FT-IR spectra of PIL 01, PIL 03, and PIL 05.

Table 1. Classification of protic ionic liquids

Abbreviations	(PILs)	Nomenclature
2-HEAF	PIL 01	2-Hydroxy ethyl ammonium formate
2-HDEAF	PIL 02	2-Hydroxy diethyl ammonium formate
2-HEAP	PIL 03	2-Hydroxy ethyl ammonium propionate
2-HDEAP	PIL 04	2-Hydroxy diethyl ammonium propionate
2-HEAPe	PIL 05	2-Hydroxy ethyl ammonium pentanoate
2-HDEAPe	PIL 06	2-Hydroxy diethyl ammonium pentanoate

Furthermore, in the subsequent sections, C and D, two bands are noted at (1650 cm^{-1}) and (1550 cm^{-1}) respectively (Figure 2). These bands can be attributed to the C=O asymmetric stretches of the anionic carboxylate and neutral carboxylate groups[76-78]. Finally, in the regions marked as E and F, bands with values of (1375 cm^{-1}) are observed, which can be related to the symmetric angular deformation band CH_2 and (1090 cm^{-1}) attributed to the C-N stretch band. In detail, these results reiterate the presence of the main fractions found in carboxylic acids applied in the synthesis of protic ionic liquids evaluated in this study as alternative corrosion inhibitors.

Figure 3 shows the other spectra, in this case PILs 01,03 and 05. These have as a difference a different structure in their basic fraction of protic ionic liquids. The base that was used differently and investigated with variation in pH and temperature was ethanolamine in combination with the same carboxylic acids described previously.

In detail, similarly, to Figure 3, the band marked by sections A and B in the range of 3600-2250 cm^{-1}, displays the O-H and N-H stretching bands (3600-3200 cm^{-1}), as well as the stretching band C-H (3000-2800 cm^{-1})., characteristic of the structures of ammonium cations. However, due to the difference in the size of the carbon chain, it is noted that some bands have a lower intensity, a response justified due to the smaller main chain found in ethanolamine[76-78].

Furthermore, in sections C and D, two bands are observed at (1650 cm^{-1}) and (1550 cm^{-1}), which can be attributed to the asymmetric stretches of C=O in the anionic carboxylate and neutral carboxylate groups[76-78]. In these stretches, a response similar to that found in Figure 3 is observed, confirming the success of the synthesis. Finally, in the regions designated as E and F, bands are noted at (1375 cm^{-1}), probably associated with the symmetric angular deformation band CH2, and (1090 cm^{-1}), attributed to the C-N stretching band.

3.2. Anticorrosive performance of ILs

3.2.1 Weight loss measurements for acid electrolyte and temperature

The mass loss tests were conducted using two distinct methodologies. Initially, a constant inhibitor concentration of 1000 ppm was selected to optimize the results, and it was applied to systems with pH variations of 2 and 4 (Figure 4). Subsequently, two concentrations (500 and 1000 ppm) were employed to evaluate the influence of temperature (40 and 60 °C). These results allow for the assessment of the effective corrosion protection provided by protic ionic liquids within a specific temperature range.

In summary, the results demonstrate a significant reduction in corrosion rate (υcorr) upon the introduction of protic ionic liquids (PILs), irrespective of variations in pH or temperature. This data implies a potentially effective protection for carbon steel in a saline environment, as outlined in Tables 2 to 5. Particularly, PIL 01 exhibited a characteristic corrosion inhibitor behavior, with its concentration reaching the maximum evaluated value of 1000 ppm. The inhibition efficiency continued to improve, validating the preference of this optimized concentration.

Indeed, Table 2 illustrates the variation in weight loss corresponding to the corrosion rate (υcorr in mmy) of ASTM A36 carbon steel throughout immersion period in a 3.5 wt. % NaCl solution. The experiments were conducted both in the absence and presence of 1000 ppm of Protic Ionic Liquids (PILs) under severe conditions of an acidified electrolyte (pH 2). Specifically, the constant impact of pH on the weight loss variation of carbon steel revealed an enhanced material protection efficiency for PIL 01, with efficiency values surpassing 70%. This observed trend may be attributed to the increased adsorption and surface coverage associated with higher concentrations.

In this context, the separation of the surface from the medium is more efficient due to the film formation originating from the adsorption of PILs. Notably, the smaller carbon chain

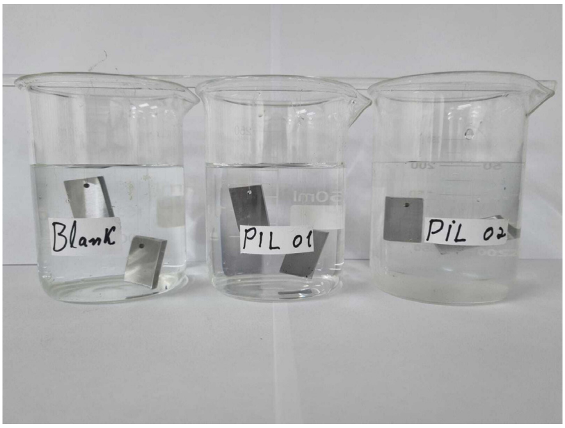

Figure 4. Corrosion test samples immersed in solution (3.5% wt. NaCl) for the weight loss test with pH variation.

Table 2. Corrosion parameters from mass loss of carbon steel (100h) in 3.5 wt. % NaCl solution with pH 2 (1000ppm).

	ΔW(g)	**SD**	υcorr (mmy)	**ε (%)**
Blank	0.114	0.0033	2.09	0
Pil 01	0.031	0.0045	0.58	72.1
Pil 02	0.053	0.005	0.98	53.0
Pil 03	0.072	0.015	1.33	36.1
Pil 04	0.059	0.006	1.08	48.2
Pil 05	0.019	0.011	0.35	64.1
Pil 06	0.035	0.004	0.65	51.1

A-Average / W-Weight (1) and (2), ΔW (W_1-W_2) / υcorr - Corrosion Rate / SD- Standard Deviation / ε - Efficiency.

Table 3. Corrosion parameters from mass loss of carbon steel (100h) in 3.5 wt% NaCl solution with pH 4 (1000ppm).

	ΔW(g)	**SD**	υ corr (mmy)	**ε (%)**
Blank	0.016	0.001	0.30	0
PIL 01	0.004	0.0006	0.07	75.1
PIL 02	0.004	0.0008	0.07	74.3
PIL 03	0.011	0.0145	0.20	30.5
PIL 04	0.008	0.006	0.16	46.2
PIL 05	0.005	0.001	0.10	64.0
PIL 06	0.008	0.0003	0.14	50.9

A-Average / W-Weight (1) and (2), ΔW (W_1-W_2) / υcorr - Corrosion Rate / SD- Standard Deviation / ε - Efficiency.

Table 4. Corrosion parameters from mass loss of carbon steel (100h) in 3.5 wt % NaCl solution at a temperature of 40 °C.

	Concentration (ppm)	ΔW(g) ± SD	υ corr (mmy)	ε (%)
Blank	-----	0.1228 ± 0.0134	2.24	------
PIL 01	500	0.0347 ± 0.0051	0.63	71.7
	1000	0.0501 ± 0.0072	0.91	59.1
PIL 02	500	0.0419 ± 0.0043	0.76	65.8
	1000	0.0344 ±0.0092	0.63	71.9
PIL 03	500	0.0402 ± 0.0039	0.73	67.2
	1000	0.0477 ± 0.0051	0.87	61.1
PIL 04	500	0.0515 ± 0.0007	0.94	58.0
	1000	0.0662 ± 0.0018	1.21	46.1
PIL 05	500	0.0344 ± 0.0074	0.62	71.9
	1000	0.0512 ± 0.0101	0.93	58.3
PIL 06	500	0.0478 ± 0.0041	0.87	61.0
	1000	0.0424 ± 0.0124	0.77	65.4

A-Average / W-Weight (1) and (2), ΔW (W_1-W_2) / υcorr - Corrosion Rate / SD- Standard Deviation / ε - Efficiency.

Table 5. Corrosion parameters due to mass loss of carbon steel (100h) in 3.5 wt % NaCl solution at a temperature of 60 °C.

	Concentration (ppm)	ΔW(g) ± SD	υ corr (mmy)	ε (%)
Blank	-----	0.1541 ± 0.0229	2.81	------
PIL 01	500	0.0790 ± 0.0104	1.44	48.7
	1000	0.1152 ± 0.0058	2.10	25.2
PIL 02	500	0.1051 ± 0.0051	1.92	31.7
	1000	0.1030 ± 0.0033	1.88	33.1
PIL 03	500	0.1264 ± 0.0446	2.31	17.9
	1000	0.1082 ± 0.0121	1.97	29.7
PIL 04	500	0.0921 ± 0.0001	1.68	40.1
	1000	0.0824 ± 0.0011	1.50	46.5
PIL 05	500	0.0818 ± 0.0002	1.49	46.8
	1000	0.0959 ± 0.0059	1.75	37.7
PIL 06	500	0.0761 ± 0.0092	1.39	50.6
	1000	0.0954 ± 0.0067	1.74	38.0

A-Average / W-Weight (1) and (2), ΔW (W_1-W_2) / υcorr - Corrosion Rate / SD- Standard Deviation / ε - Efficiency.

of the acidic fraction of the protic ionic liquid was identified as a crucial factor in the assimilation process observed in PIL 01. These results emphasize the value of evaluating the carbon chain size for corrosion inhibition efficiency.

Because normally the Protic Ionic Liquids (PILs) with intermediate carbon chain sizes, particularly those exceeding 3 carbons in the main chain, did not demonstrate significant efficiency (protection) in a saline environment (3.5 wt. % NaCl) within this specific pH range. In literature, there is an increasing emphasis on investigating external influences on gravimetric and corrosion tests[79,80].

Solely assessing inhibitors in a saline environment with varying concentrations, such as 0.5 M, 1 M, and 2 M or even higher concentrations, without considering potential parameter variations, results in theoretical and limited findings. In practical field applications, parameters such as pH and temperature are often adjusted depending on external environmental conditions. Therefore, it is essential to recognize the need for evaluating these factors in corrosion studies, and publications that concentrate on such investigations should be encouraged more widely.

Furthermore, Table 3 presents analogous information to that identified in Table 2, with the only distinction being the milder pH variation set at 4 to assess a slightly less acidic environment compared to the pH 2 saline solution, with a lower concentration of Cl^- ions in solution. It was observed that, in the presence of Protic Ionic Liquids (PILs), the influence of pH on the weight loss variation of carbon steel demonstrated enhanced material protection efficiency for PILs 01 and 02, exceeding values of 74%. Once again, this highlights the effectiveness of ionic liquids with a shorter carbon chain, combined with ethanolamine and diethanolamine bases[78,81].

This observed tendency is likely attributed to the increased adsorption and surface coverage with rising pH levels. The mass loss tests conducted at pH 4 exhibited relatively better efficiency compared to those at pH 2. Thus, the size of the main carbon chain in the acidic fraction of the ionic liquid remains a crucial factor in the adsorption process observed in PILs 01 and 02.

Considering Table 4, the difference in temperature from 25 °C to 50 °C did not diminish the effectiveness of protic ionic liquids as corrosion inhibitors considerably, proving to be advantageous for protecting the carbon steel surface. However, simultaneous reaching a temperature of 60 °C, the maximum temperature investigated, the protective capacity is not as adequate for all compounds investigated in this study.

In detail, this observation associates with microscopy results, indicating a drastic change in the material's roughness at the maximum temperature. In addition, mass loss tests at 40 °C demonstrated satisfactory anticorrosive protection, with emphasis on PILs 01 and 05, presenting efficiency values above 70%, being plausible to apply in systems that do not have such intense heating. This aligns with previous studies involving these inhibitors in a saline environment at room temperature[10,82].

In summary, this result holds significance in electrolyte studies, especially regarding organic inhibitors. As the temperature increases beyond 30 or 40 °C, many organic inhibitors tend to lose effectiveness due to kinetic changes in the electrolyte system and degradation of their chemical structure, as seen in the case of amino acids[83-85]. Therefore, researching inhibitors capable of withstanding temperature fluctuations is crucial for the future of industry and the ongoing battle against corrosion.

Finally, to conclude the discussion about the weight loss measurements, as per Table 5, it was detected that with the increasing of the solution temperature, a clearly defined limit was reached at 60 °C incorporating protic ionic liquids as corrosion inhibitors in a saline solution (500 and 1000 ppm), satisfactory material protection was not achieved, as implied in Table 5. Notably, protic ionic liquids with the smallest and largest carbon chains, despite PIL 01 and PIL 06, still displayed values close to 50%, achieving maximum efficiency on this condition.

The identified limit of 60 °C manages a significant relevance for corrosion inhibitor research in general. Understanding the coverage and capacity of protective efficacy assists in determining the applicability of a given compound for various industrial uses. In the context of this study, the proposed protic ionic liquids demonstrate potential success in systems operating under milder conditions, ranging from room temperature to a maximum evaluated temperature of 50 °C.

For instance, these inhibitors could be effectively applied in external areas of industrial plants, such as distant distribution pipelines, where operating temperatures do not exceed 60 °C.

3.2.2. EIS - electrochemical impedance spectroscopy measurements

The EIS results are shown in Figures 5 to 9, and the impedance parameters are listed in Tables 6 to 9. Initially, the Nyquist plots exhibit a complete capacitive circle, representing the interaction between the PILs and the saline electrolyte. This result indicated an increase in the intensity of the polarization resistance (Rp) caused by the protic ionic liquids. This information was obtained because of the increase in the capacitive arcs compared to the blank in saline solution.

Furthermore, the results presented in Figure 5 agree with the data obtained by weight loss evaluation, where PIL 01 presents greater inhibition efficiency than the other investigated compounds. Furthermore, Figure 5 shows the inhibition efficiency of protic ionic liquids (PIL 02 to 06) evaluated at 1000 ppm as an optimized concentration was also satisfactory, however PIL 01 presented a notable highlight compared to the others.

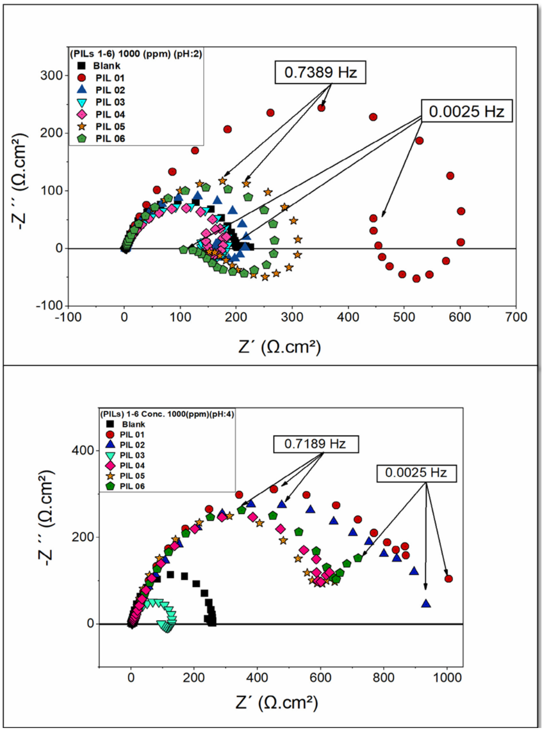

Figure 5. Impedance spectra of carbon steel (ASTM A36) in 3.5% wt. NaCl solution in the absence of PILs, in the presence of PILs at optimized concentration (1000 ppm) for pH 2 and 4.

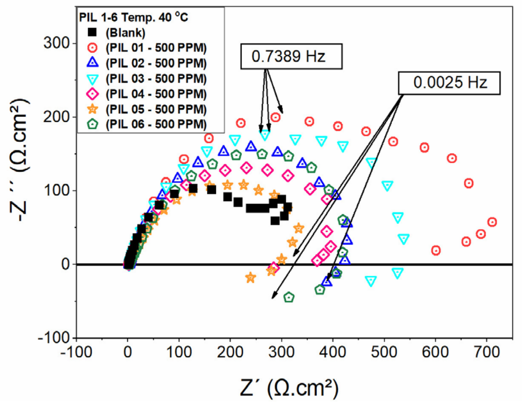

Figure 6. Impedance spectra of carbon steel (ASTM A36) in 3.5% wt. NaCl solution in the absence of PILs, in the presence of PILs at 500 ppm with a temperature of 40 °C.

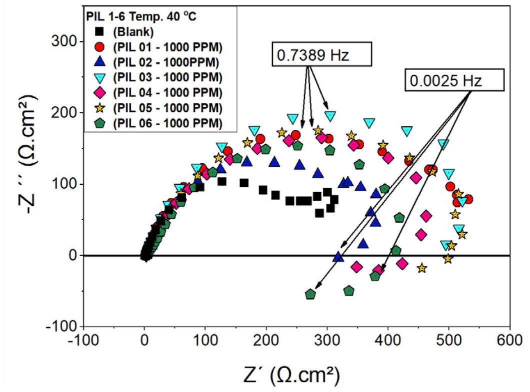

Figure 7. Impedance spectra of carbon steel (ASTM A36) in 3.5% wt. NaCl solution in the absence of PILs, in the presence of PILs at 1000 ppm with a temperature of 40 °C.

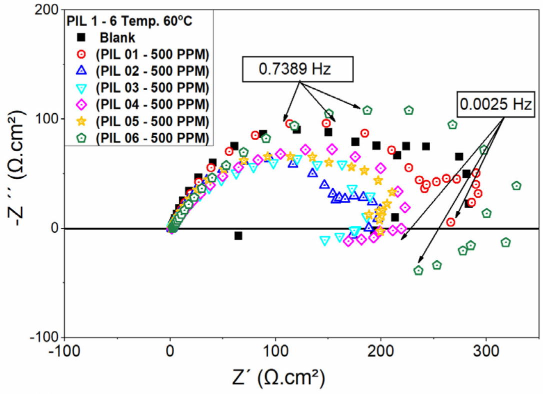

Figure 8. Impedance spectra of carbon steel (ASTM A36) in 3.5% wt. NaCl solution in the absence of PILs, in the presence of PILs at 500 ppm with a temperature of 60 °C.

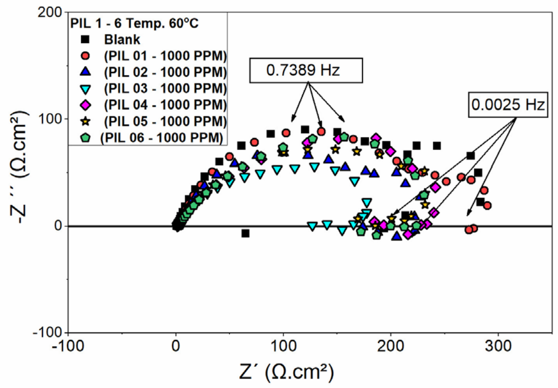

Figure 9. Impedance spectra of carbon steel (ASTM A36) in 3.5% wt. NaCl solution in the absence of PILs, in the presence of PILs at 1000 ppm with a temperature of 60 °C.

The corrosion conducts of carbon steel in saline solution with and without PILs was investigated by electrochemical impedance spectroscopy (EIS) at pH 2 and 4 (Figure 5) and with different temperatures 40 °C (Figure 6 and 7) and 60 °C (Figure 8 and 9).

The electrolyte, a 3.5 wt. % NaCl solution with a concentration of 3.5% by weight, was adjusted to pH 2 and pH 4 to evaluate the inhibitory effect of PIL at an optimized concentration of 1000 ppm, considering that previous studies with lower concentrations and the best efficiencies were with this parameter. As a result, a decrease in pH escorted to reduced RP (Polarization Resistance) values due to the amplified aggressiveness of the electrolyte, starting with 1000 ($\Omega.cm^2$) at pH 4 to values around 600 ($\Omega.cm^2$) at pH 2.

Notably, PIL 01 exhibited an inhibition efficiency exceeding 71% in both pH ranges, while PIL 02 demonstrated a similar outcome only at pH 4. Additional details regarding the impedance of acid evaluation can be found in Tables 6 and 7.

Therefore, Tables 6 and 7 emphasize that increasing protic ionic liquids into acidified saline electrolytes under both pH conditions produces distinct consequences.

The recorded values notably diminution, especially at the extreme pH of 2, because this decreasement would be ascribed to the inherent aggressiveness of the initial solution (NaCl), which, after the acidification process, becomes excessively enriched with chloride ion (Cl^-). Then, the change in the chemical mechanism requires a corrosion inhibitor capable of rapid and efficient adsorption onto the metal surface to counteract the heightened corrosive potential of the medium.

Futhermore, regarding the impedance measurements conducted at pH 4, it is distinct that within a less aggressive acidic medium, protic ionic liquids demonstrate a more favorable behavior in terms of their corrosion inhibition capacity with higher RP values. Probably this behavior would be justified because the amount of aggressive ions in the solution is much less than if we compare pH 2.

In the literature, the use of corrosion inhibitors in acidified saline media is commonly observed, typically with pH values ranging between 2 and 5[86-88]. Thus, the objective of these assessments is to determine if there is an important modification of the inhibition mechanism when the medium is enriched with excess ions, particularly Cl^-.

Furthermore, the impact of temperature is another essential parameter under evaluation. The protic ionic liquids

Table 6. Impedance factors of A36 in 3.5% wt. NaCl with and without inhibitors (PIL) with pH 2.

PILs (ppm)	Rs ($\Omega.cm^2$)	CPE		Cdl ($F.cm^{-2}$).10^{-3}	Rp* ($\Omega.cm^2$)	I.E (%)
		$Y_0(s^n. \Omega^{-1}.cm^{-2})$ .10^{-3}	n. 10^{-2}			
Blank	1.56 ± 0.08	2.31 ± 8.37	76 ± 2	2.87 ± 1.31	785 ± 19	----
PIL 01	4.81 ± 0.14	1.08 ± 1.80	73 ± 1	1.37 ± 2.75	3132 ± 28	71.2 ± 1.39
PIL 02	3.01 ± 0.27	3.43 ± 1.32	75 ± 1	4.41 ± 2.09	1618 ± 16	42.1 ± 3.25
PIL 03	1.87 ± 0.11	5.52 ± 1.36	78 ± 3	5.86 ± 5.51	880 ± 98	10.3 ± 0.86
PIL 04	3.61 ± 0.27	3.01 ± 0.20	75 ± 2	4.17 ± 1.02	901 ± 67	37.8 ± 4.25
PIL 05	4.08 ± 0.11	2.34 ± 0.21	75 ± 2	1.51 ± 3.09	2016 ± 26	60.2 ± 1.31
PIL 06	3.16 ± 0.14	2.68 ± 1.09	75 ± 1	4.02 ± 2.13	1051 ± 78	52.7 ± 3.25

*Normalized value of Rp.

Table 7. Impedance factors of A36 in 3.5% wt. NaCl with and without inhibitors (PIL) with pH 4.

PILs (ppm)	Rs ($\Omega.cm^2$)	CPE		Cdl ($F.cm^{-2}$).10^{-3}	Rp* ($\Omega.cm^2$)	I.E (%)
		$Y_0(s^n. \Omega^{-1}.cm^{-2})$ .10^{-3}	n. 10^{-2}			
Blank	1.66 ± 0.08	2.45 ± 1.37	77 ± 2	2.77 ± 1.31	725 ± 19	----
PIL 01	5.11 ± 0.14	1.28 ± 2.70	71 ± 1	1.31 ± 1.95	2832 ± 28	76.2 ± 1.39
PIL 02	4.91 ± 0.27	1.43 ± 1.32	71 ± 1	1.21 ± 1.21	2718 ± 16	75.1 ± 3.25
PIL 03	1.77 ± 0.81	5.22 ± 1.36	77 ± 3	5.56 ± 5.51	850 ± 98	12.3 ± 0.86
PIL 04	3.81 ± 0.11	2.01 ± 0.70	76 ± 2	2.27 ± 0.02	1381 ± 57	48.8 ± 2.25
PIL 05	4.58 ± 0.11	1.84 ± 0.21	73 ± 2	1.41 ± 3.09	2116 ± 05	62.2 ± 1.01
PIL 06	3.06 ± 0.84	2.58 ± 1.88	76 ± 1	3.02 ± 2.13	1151 ± 78	43.7 ± 1.25

*Normalized value of Rp.

Table 8. Impedance factors of A36 in 3.5% wt. NaCl with and without inhibitors (PIL) with temp. of 40 °C.

PILs (ppm)	Rs ($\Omega.cm^2$)	CPE		Cdl ($F.cm^{-2}$).10^{-3}	Rp ($\Omega.cm^2$)	I.E (%)
		$Y_0(s^n. \Omega^{-1}.cm^{-2})$ .10^{-3}	n. 10^{-2}			
Blank	1.46 ± 0.08	2.21 ± 2.37	78 ± 2	2.87 ± 2.41	342 ± 11	----
01-500	5.36 ± 0.80	1.88 ± 4.51	72 ± 3	1.36 ± 1.01	1336 ± 61	74.1 ± 2.83
01-1000	3.82 ± 0.34	1.71 ± 2.10	75 ± 2	2.37 ± 2.95	780 ± 18	55.2 ± 1.39
02-500	4.17 ± 0.11	1.92 ± 2.36	75 ± 2	1.56 ± 3.51	940 ± 48	63.3 ± 0.86
02-1000	5.01 ± 0.97	1.13 ± 1.32	73 ± 1	1.11 ± 6.09	1200 ± 26	70.5 ± 3.25
03-500	5.21 ± 0.17	1.06 ± 0.20	73 ± 2	1.17 ± 1.02	1144 ± 37	70.8 ± 4.25
03-1000	3.98 ± 0.11	1.94 ± 0.11	75 ± 2	1.68 ± 1.09	861 ± 86	59.2 ± 1.31
04-500	4.06 ± 0.12	2.18 ± 0.09	75 ± 1	1.92 ± 1.13	769 ± 78	55.7 ± 3.25
04-1000	3.13 ± 0.12	3.45 ± 0.42	77 ± 1	4.16 ± 2.21	568 ± 20	39.0 ± 1.13
05-500	3.88 ± 0.22	1.78 ± 1.52	76 ± 1	1.51 ± 0.09	1058 ± 13	67.7 ± 1.12
05-1000	4.18 ± 0.92	3.68 ± 1.22	76 ± 1	4.31 ± 0.09	882 ± 13	37.0 ± 1.12
06-500	4.18 ± 0.02	1.88 ± 0.12	75 ± 1	2.21 ± 0.39	814 ± 55	58.0 ± 1.12
06-1000	4.08 ± 0.01	1.58 ± 0.32	75 ± 1	2.01 ± 0.19	820 ± 10	59.0 ± 1.12

*Normalized value of Rp

have been previously electrochemically assessed at various concentrations (250 to 1000 ppm), the two most significant concentrations were chosen in this study, namely 500 ppm and 1000 ppm. In detail, it was definite to apply optimized concentrations in the electrochemical tests since, according to previously obtained results with ionic liquids, when the

Table 9. Impedance factors of A36 in 3.5% wt. NaCl with and without inhibitors (PIL) with temp. of 60 °C.

PILs (ppm)	Rs ($\Omega.cm^2$)	CPE		Cdl ($F.cm^{-2}$).10^{-3}	Rp ($\Omega.cm^2$)	I.E (%)
		Y_0(s^n. Ω^{-1}.cm^{-2}) .10^{-3}	n. 10^{-2}			
Blank	1.46 ± 0.18	3.81 ± 0.27	77 ± 2	4.87 ± 2.41	160 ± 11	----
01-500	3.16 ± 0.20	3.58 ± 0.51	76 ± 3	4.06 ± 1.01	298 ± 04	45.1 ± 1.83
01-1000	3.82 ± 0.14	4.51 ± 0.10	75 ± 2	5.27 ± 2.95	235 ± 01	30.4 ± 2.39
02-500	1.77 ± 0.21	5.22 ± 0.36	75 ± 2	5.86 ± 0.51	189 ± 10	13.5 ± 0.86
02-1000	2.51 ± 0.17	4.83 ± 0.32	76 ± 1	5.51 ± 0.09	210 ± 01	23.5 ± 1.25
03-500	2.11 ± 0.07	4.66 ± 0.20	75 ± 2	5.47 ± 0.02	206 ± 22	22.8 ± 1.25
03-1000	2.78 ± 0.01	4.74 ± 0.11	77 ± 2	5.38 ± 0.01	219 ± 06	26.1 ± 0.21
04-500	3.56 ± 0.02	4.28 ± 0.09	76 ± 1	5.22 ± 0.53	251 ± 05	36.2 ± 1.15
04-1000	3.23 ± 0.01	4.35 ± 0.42	77 ± 1	5.36 ± 0.61	272 ± 03	38.0 ± 0.13
05-500	3.28 ± 0.20	4.18 ± 0.52	76 ± 1	4.51 ± 0.19	270 ± 11	40.7 ± 0.12
05-1000	3.24 ± 0.92	4.08 ± 0.22	76 ± 1	4.41 ± 0.09	287 ± 09	41.7 ± 0.09
06-500	3.90 ± 0.02	2.68 ± 0.12	75 ± 1	3.81 ± 0.39	345 ± 10	51.5 ± 2.12
06-1000	3.32 ± 0.01	4.08 ± 0.32	76 ± 1	4.09 ± 0.29	297 ± 03	44.8 ± 1.12

*Normalized value of Rp.

amount of inhibitor added to the system exceeded 500 ppm, the efficiency increased significantly.

Therefore, these inhibitors were investigated under different conditions, but after the results were obtained, it was decided to use an optimized condition above 500 ppm. According to the literature[89-91], organic compounds, when evaluated as corrosion inhibitors when increased in temperature have a reduction in their protection efficiency.

Hence, as Protic Ionic Liquids (PILs) were previously evaluated at room temperature, increasing the temperature would be the next stage in this examination of applying alternative inhibitors to adverse conditions. Hence, initially, the temperature utilized was 40 °C where, with a concentration of 500 ppm (Figure 6), PILs 01, 02, and 03 presented satisfactory performance with efficiencies of around 74%.

The values obtained were not that extreme (around 95%) nevertheless considering that these inhibitors are easy to synthesize and biodegradable to the environment, their use is totally justifiable. However, as the concentration increased to 1000 ppm, the polarization resistance (PR) values decreased, leading to lower corrosion protection efficiencies of approximately 50% (Figure 7). This behavior can be justified due to the agglomeration factor of ionic liquid molecules being negatively affected by film formation at a higher temperature.

Seeing both Figures 6 and 7, it is clear that the addition of PILs in 3.5 wt. % NaCl solution is advantageous from the point of view of protection against corrosion, but one detail observed is crucial in this investigation, because some inhibitors benefit from the increase in temperature (PIL 02) and other inhibitors are harmed (PIL 01, 03, 04, 05 and 06). Detailing the RP values obtained in EIS tests at 40 °C, Table 8 is available. As stated previously, several corrosion inhibitors have an adsorption advantage with the growth of temperature, and others are harmed by this factor. This behavior would be justified according to the difference in the size of the carbon chain of the carboxylic acid, (C1 to C5)[92,93].

This inspection was also conducted by Ortega-Vega et al.[94], evaluating the influence of anion chain length of protic ionic liquids on the corrosion resistance of API X70 steel 52. Therefore, evaluating these external factors is crucial for evaluating corrosion inhibitors because, in the reality of application, an electrochemical system does not always remain at the same temperature for a long period. Two studies in parallel highlight the importance of evaluating the size of the carbon chain, highlighting the real importance of this type of study. Falcade et al.[95] Electrochemical Study of AISI 1004 steel in Protic Ionic Liquids: Influence of Carbon Chain and Ortega-Vega et al.[77], Protic ionic liquids used as metal-forming green lubricants for aluminum: Effect of anion chain length.

Next, still discuss electrochemical results in Figures 8 and 9. In this system, the temperature was increased to its maximum limit, 60 °C. Therefore, in view of the evaluation of the Figures shown above, it is clear that with the addition of PILs in 3.5 wt. % (NaCl) solution at this temperature range they do not have the capacity to protect the metallic material by acting as corrosion inhibitors effectively as seen in previous conditions, at 40 °C for example.

During the Electrochemical Impedance Spectroscopy (EIS) tests conducted at 60 °C, the protic ionic liquids did not demonstrate satisfactory inhibition efficiency (Figures 8 and 9). Specifically, the highest efficiency value recorded was for PIL 06, approaching 51%, which represents the maximum experimental threshold of action. In other words, when surpassing this temperature range, the compounds employed as inhibitors lose their inhibition efficiency (Table 9).

Summarizing the discussion on electrochemical impedance testing, it is crucial to underscore the importance of establishing an operational threshold for protic ionic liquids and comparing it with literature findings regarding the use of aprotic ionic liquids[96-99].

The mass loss and impedance results revealed a temperature limit of 60 °C, crucial information for assessing the protective performance of Protic Ionic Liquids (PILs) under challenging conditions. Due to its significant behavior previously observed at room temperature, it was decided to evaluate its effectiveness under different conditions and establish the maximum limit of its effectiveness, thus contributing to new studies and to contribute to the existing literature.

The fitting results are presented in detail in Tables 6 to 9 with all data obtained from the impedance tests. All concentrations of the studied inhibitors (PIL 01 - 06) were tested applying distinct circuits, however revealing a respectable simulation is presented as the Nyquist plots using the equivalent circuit. In particular, in order to calculate the ininhibition efficancy (I.E) and double layer capacitance (Cdl), Equations 5 and 6 were used respectively[61,62,100-104]. Where Rp and Rp($_{\text{inh}}$) are the polarization resistances in the presence and absence of inhibitors[69-75].

$$\text{I.E}(\%) = \frac{\left(\text{Rp}(\text{inh}) - \text{Rp}\right)}{\left(\text{Rp}(\text{inh})\right)} x\ 100 \tag{5}$$

$$Cdl\left(\text{F.cm}^{-2}\right) = \left(Q x\ R_P^{1-n}\right)^{1/n} \tag{6}$$

3.3. Surface analysis

Morphological evaluation is a visual and partial method for assimilating the effectiveness of corrosion inhibition before and after electrochemical testing, which was applied using microscopy techniques to provide an initial overview of a material[105,106]. The micrograph obtained provides crucial information about the compounds assessed in the experiments, such as excessive oxide production, changes in solution color, and the solubility of the inhibitor in the electrolyte. Notably, for surface evaluation, it opted to apply the inhibitors (PIL 01 and 02) that demonstrated the best results in combating corrosion previously. Both optical and atomic force microscopy were employed for this purpose.

3.3.1. Morphology evaluation of steel by optical microscopy

The micrograph in Figure 10 represents ASTM A36 surface with and without inhibitors in a 3.5% wt. NaCl solution after 24 hours. These micrographs facilitated the assessment of surface damage in a saline electrolyte. Specifically, the adsorption of chloride ions (Cl^-) on the outer surface of the oxide film, followed by their incorporation into the film by occupying vacancies alongside oxygen, leads to the formation of cationic vacancies.

These cationic vacancies interact with Cl^- present on the oxide/solution surface, generating more cathodic vacancies. These cationic vacancies diffuse towards the interface between the metal and oxide, where they are ultimately eradicated through the flow of oxidized cations originating from the metal[19,23,107,108]. After 24 hours, the corrosion of the material became more severe, evidenced by the rough surface visible in the Figure 10. This outcome is justified as carbon steel is more susceptible to corrosion in saline atmospheres due to its low Cr and Ni contents.

Then, it is possible to observe as a macroscopic idea that certain areas of the sample (ASTM A36) are characterized by an apparent absence of massive corrosion products, indeed this formation of oxides is also confirmed through the AFM technique, due to the action of the protic ionic liquid on the surface forming a protective film[109]. The tests were performed in 3.5 wt. % NaCl solution under four different conditions: at room temperature (25 °C) and pH 2 or pH 4; and at 40 °C or 60 °C with a neutral pH 7.

Then, immersion tests were performed for 24 h in a solution containing 1000 ppm (optimum condition) of all PILs. The surface of the samples was evaluated using microscopic techniques such as optical and Atomic Force Microscopy (AFM).

3.3.2. AFM - atomic force microscopy

At first, the Figure 11 illustrates the differentiation between the surface of the material (ASTM A36) and the significant improvement in surface protection achieved with the addition of protic ionic liquids, as compared to the acidified (2 and 4) saline solution with an inhibitor (PILs) for 24 hours. The inspection of Figure 11, which is the micrograph of carbon steel surface, clearly reveals the difference between blank (NaCl 3.5% wt. pH 2 and 4) and the surface with the film formation over the material.

Figure 12 presents additional plots generated through the Atomic Force Microscopy (AFM) method, illustrating a two-dimensional analysis of the results. These plots showcase the distinct profiles, evident in variations of peak heights and valley depths across the material. The average root mean square (RMS) roughness, measured in nanometers, was determined using Gwyddion v. 2.63 (2023) software. Then, for pH 2, the values are Blank (B): 230.5 / PIL 1: 35.38 / PIL 2: 80.2. Under pH 4 conditions: Blank (B): 219.2 / PIL 1: 9.46 / PIL 2: 26.78.

The surface image of ASTM A36 steel exposed to the inhibited solution for 24 hours is shown in Figure 12. Therefore, the inhibitory molecules (PILs) end up fully and comprehensively adhering to the surface of the investigated material, except for just a few places that present greater roughness and a clear oxide production.

Furthermore, it is interesting to note that the surface of the material without the addition of the inhibitors starts to obtain a completely excessive roughness of around 150 to 200 nm[110-112]. These values are under the literature on the use of the AFM technique to evaluate corrosion inhibitors. Therefore, it can be concluded that the high inhibition efficiency of PILs after longer immersion, in this case with a period of 24 hours, can be attributed to the adsorption of inhibitory molecules on the active sites of the steel surface, forming a protective film, which means that, after a long period of immersion, adsorption is more chemical and physical on the material.

Figure 13 displays AFM images of both protected and unprotected metallic samples, with the sole variation being the temperature ranges investigated (40 and 60 °C). The unprotected surface exhibits significant corrosion, characterized by a remarkably high surface roughness.

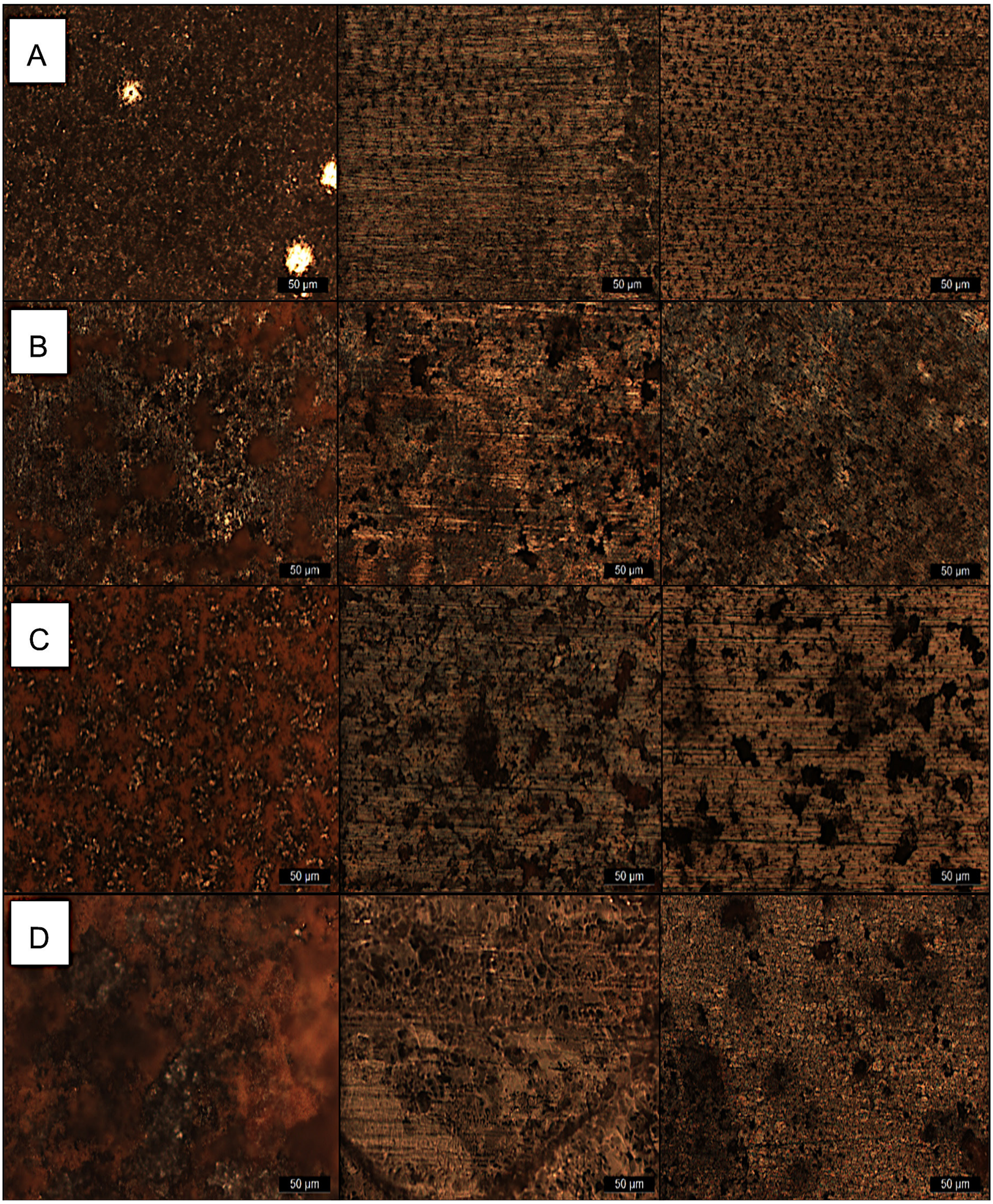

Figure 10. Optical Microscopy (A) pH 2 - Blank, PIL 1 – 1000 PPM, PIL 2 – 1000 PPM / (B) pH 4 - Blank, PIL 1 – 1000 PPM, PIL 2 – 1000 PPM / (C) Temp. 40 °C - Blank, PIL 1 – 1000 PPM, PIL 2 – 1000 PPM / (D) Temp. 60 °C - Blank, PIL 1 – 1000 PPM, PIL 2 – 1000 PPM.

The calculated average surface roughness ranges from 381 to 430 nm. In contrast, surfaces protected by PILs 01 and 02 appear smoother and less damaged, with values below 200 nm. These findings underscore the corrosion inhibition capability of the studied protic ionic liquids, demonstrating effective adsorption on the metal surface at both room temperature and elevated temperatures. Lastly, the surface characterization section was presented by 2D graphics depicted in Figure 14.

In contrast to Figure 11, the Figure 13 reveals a notably more unstable and degraded profile from a roughness perspective, evident in the assessment of peaks and valleys. Specifically, at 40 °C, the recorded roughness values are as follows: White (B): 381.1 / PIL 1: 202.2 / PIL 2: 223.6. Similarly, at 60 °C: White (B): 438.2 / PIL 1: 150.2 / PIL 2: 120. This behavior is attributed to the accelerated kinetic effect induced by the combination of a 3.5% saline solution and elevated temperatures (40 and 60 °C).

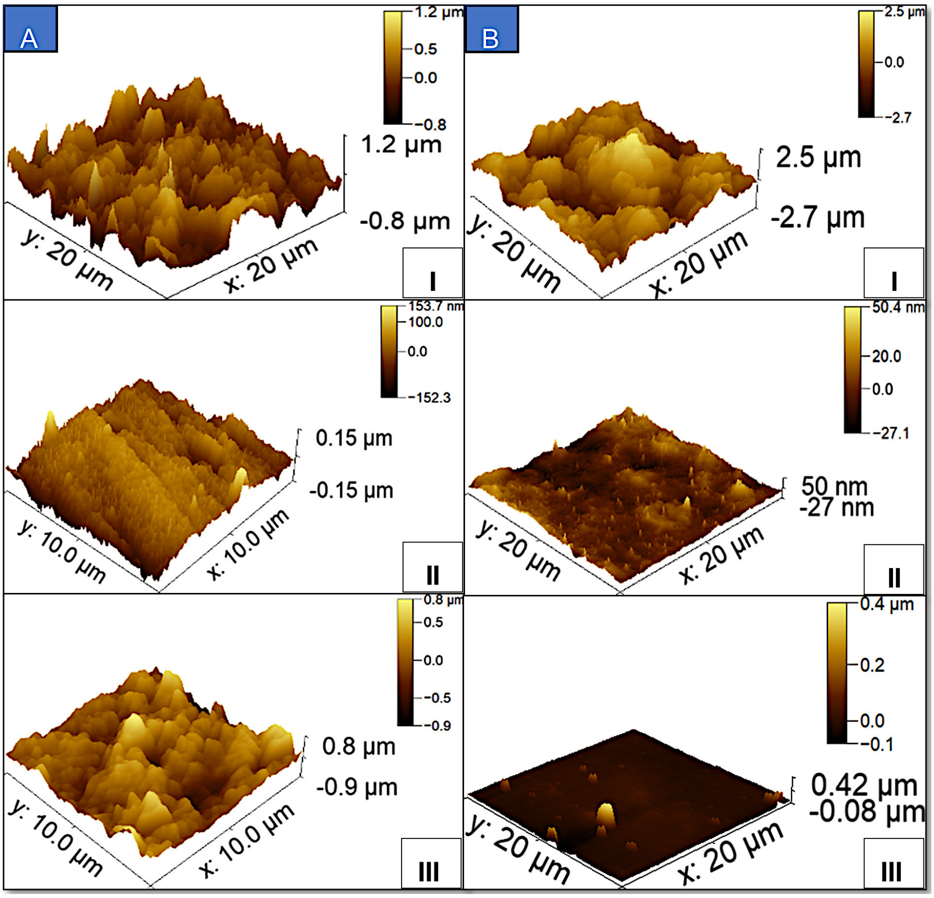

Figure 11. Atomic Force Microscopy – (AFM) 3D images of the ASTM A36 alloy surface after immersion in 3.5% wt. NaCl: A) System with NaCl (3.5%) with adjusted pH (2) Blank (I), PIL 1 (II), PIL 2 (III) / B) System with NaCl (3.5%) with adjusted pH (4) Blank (I), PIL 1 (II), PIL 2 (III).

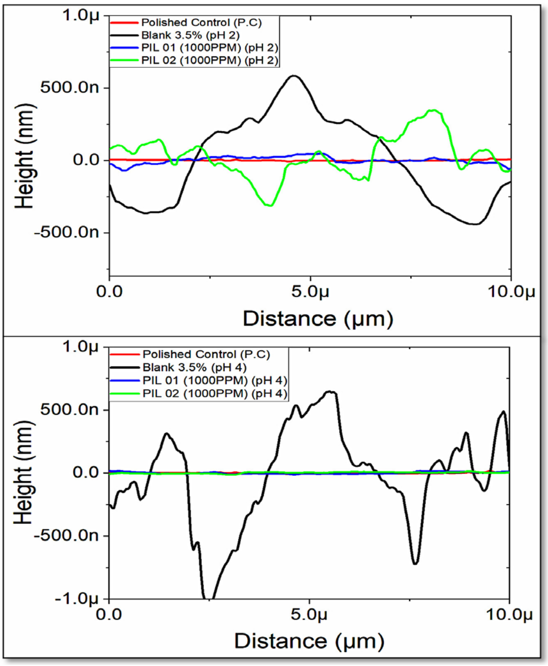

Figure 12. AFM (2D) - Atomic Force Microscopy with different pH (2 and 4).

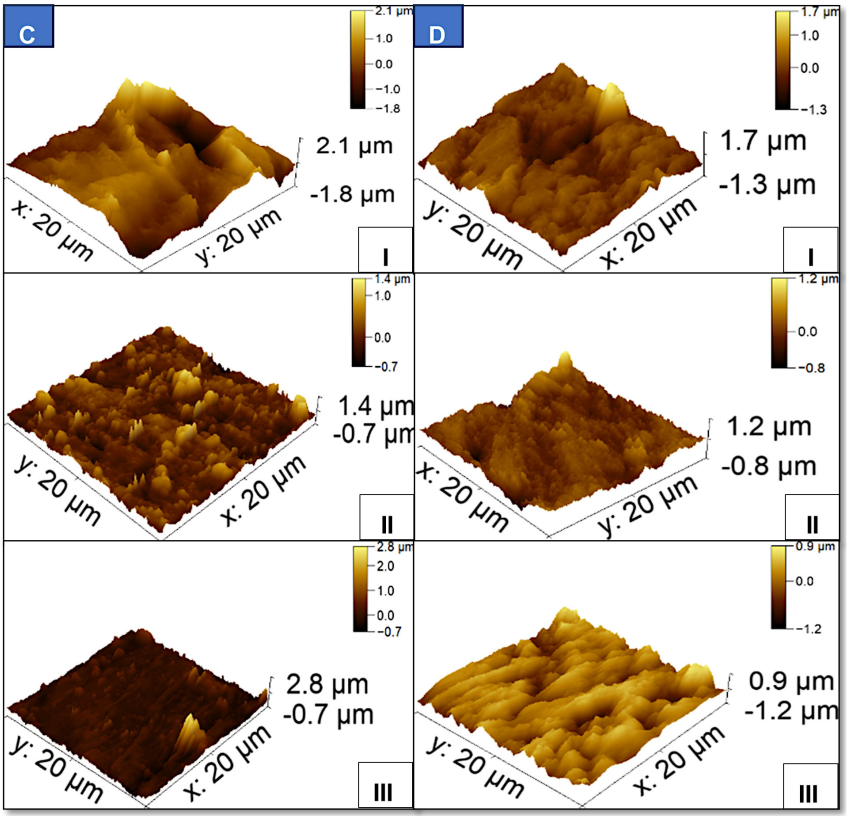

Figure 13. Atomic Force Microscopy – (AFM) 3D images of the ASTM A36 alloy surface after immersion in 3.5% wt. NaCl: C System with NaCl (3.5%) with temperature 60 °C, Blank (I), PIL 1 (II) and PIL 2 (III) / D - System with NaCl (3.5%) with temperature (40 °C) Blank (I), PIL 1 (II), PIL 2 (III).

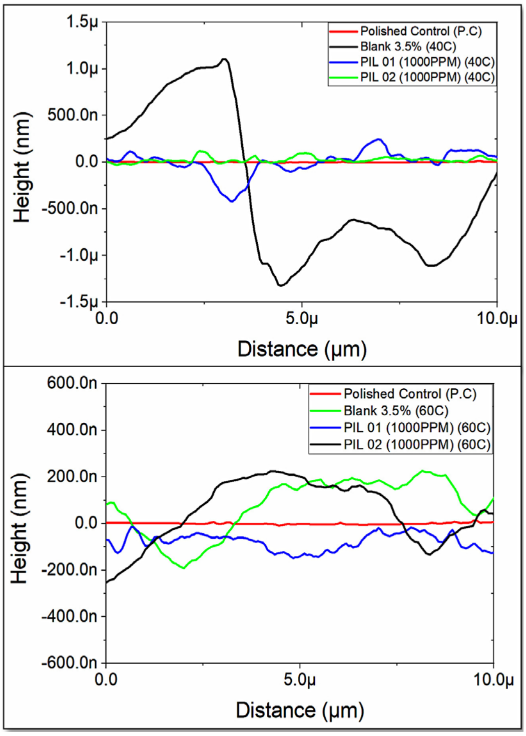

Figure 14. AFM (2D) - Atomic Force Microscopy with different temperatures 40 and 60 °C.

The presence of Cl- in the solution, coupled with heightened heating, results in a two to threefold increase in the oxidative process, as reported in the literature. Therefore, assessing inhibitors capable of effectively protecting the material in such aggressive systems is crucial for advancing corrosion research.

4. Conclusions

The present paper evaluated Protic Ionic Liquids (PILs) as a novel and eco-friendly corrosion inhibitor for carbon steel (ASTM A36) in a 3.5 wt. % NaCl medium. The main conclusions of this work are:

At first, the observed inhibition efficiency was consistently satisfactory and positive; it is noteworthy to acknowledge that their protection capabilities become compromised with alterations in pH levels exceeding 72% and displayed similar values in both acidic conditions. The inhibitor with the best efficiency was the 2-hydroxy diethanolamine formate (PIL 1). The protic ionic liquids could protect the material's surface, especially PIL 01, because of its smaller carbon chain size, which facilitated the adsorption on the substrate.

Then, the experiments were conducted with an increase in temperature. The results indicated two distinct scenarios: at 40 °C, the PILs protected the material successfully (approx. 74%), while at 60 °C, their efficiency decreased significantly (maximum 51%). At 40 °C, the inhibitor PIL1 was the more efficient, while at 60 °C, the inhibitor PIL6 presented the best results.

It was observed at 40 °C to increase the concentration of 1000 ppm; all inhibitors reduced their efficiency, except PIL 02. This behavior can be justified according to the action of the kinetic effect on the surface; as the temperature is higher when more material is added, film formation is complex, thus altering its final efficiency. At 60 °C, it was observed that they could not protect the carbon steel, thus reaching their action threshold.

The mass loss tests yielded results that align with the efficiency values observed in the electrochemical tests. This information validates the effectiveness of protic ionic liquids and identifies their operational tolerance, which, in this instance, was a temperature of up to 60 °C.

Finally, concerning pH variations tests, the inhibitors exhibited a protective behavior similar to that observed in a neutral saline solution. Furthermore, microscopy techniques utilized to assess the effects of pH and temperature highlighted the impact of PILs on metal surface protection against corrosion. 2D and 3D AFM projections and optical micrographs provide additional support for this conclusion.

5. Acknowledgments

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