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Corrosion study of API X70 in three different protic ionic liquids

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Abstract

Protic Ionic Liquids (PILs) refer to molecules composed only by ions, obtained by stoichiometric acid-base Brønsted reactions that are able to promote extensive hydrogen bonding. Among the PILs applications, electrolytic cells, heat transfer fluids, separation processes and solvents in catalytic reactions can be mentioned. PILs were synthesized using an amine and carboxylic acids, producing a strongly basic behavior. The cation is constituted by the amine and the anion corresponds to a carboxylic acid whose length chain was varied. Thus, in this work, electrochemical behavior of API X70 steel in contact with three different PILs was evaluated. API X70 steel plates were submersed in the liquids and open circuit potential monitoring and electrochemical impedance spectroscopy tests were carried out. Also, the tests were carried out for an API X70 steel plate in contact with NaCl 0.01 mol.L^{-1} for comparison. Morphology was evaluated by scanning electron microscopy (SEM). Results showed that PILs displace the corrosion potentials towards the anodic region, related to the NaCl 0.01 electrolyte since they are adsorbed on the surface, forming a film that protects the metallic substrate against reactive molecules that cause corrosion. Impedance results show that the film formation through adsorption is accompanied with diffusion and faradic reactions phenomena. PILs electrochemical behavior is corrosion inhibitor-like.

Keywords: Protic ionic liquids, electrochemical impedance spectroscopy, API X70.

Introduction

Protic Ionic Liquids (PILs) are organic salts that are product of a Brønsted neutralization reaction. They are composed by an anion and a cation that form a molecule capable of proton transfer and are liquids at room temperature. Because of their negligible vapor pressure, high thermal stability, high ionic conductivity and low toxicity, they are considered as green solvents and they have entered to play an important role in many applications, such as catalysis, separation processes, energy generation and electrochemical devices. PILs can be prepared with an amine as cation-precursor and a carboxylic acid as anion-precursor, so a wide variety of the substances can be obtained just modifying one part of the molecule (1 – 5). Anyhow, implementation of PILs requires the previous study of the behavior when in

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contact with the materials used in the different processes. In this context, in this work, a corrosion study in API X70 substrate in contact with three different PILs, namely 2-hydroxyethylammonium formiate (2HEAF), 2-hydroxyethylammonium propionate (2HEAPr) and 2-hydroxyethylammonium butanoate (2HEABu), were conducted. The open circuit potential (OCP) monitoring and the electrochemical impedance spectroscopy (EIS) were the techniques employed to carry out the electrochemical characterization. Morphological characterization of the samples was carried out by scanning electron microscopy (SEM).

Methods

API X70 steel plate samples with dimensions of 2 cm x 2 cm were sanded with emery grit paper 120, 400 and 600, without further polishing. Then, samples were washed with water, ethanol and acetone. After each washing step, samples were dried with hot air.

PILs were prepared with monoethanolamine (MEA) and a carboxylic acid, with different carbon chain length, in 1:1 stoichiometric proportion. The carboxylic acids used for each synthesis and the respective PILs are specified in Table 1.

Table 1 – Description of the electrolytes.

PIL	Reactants	pH	Conductivity (mS)
2-hydroxyethylammonium formiate (2HEAF)	MEA + formic acid	9.38	6.25
2-hydroxyethylammonium propionate (2HEAPr)	MEA + propionic acid	8.05	5.25
2-hydroxyethylammonium butanoate (2HEABu)	MEA + butyric acid	8.53	6.35
NaCl 0.01 mol.L^{-1}	-	6.66	1.33

Each carboxylic acid was allowed to drop down onto the MEA inside a flask with stirring in an ice bath. When both reactants were in the flask, the ice bath was removed. The flask was covered with aluminum sheet to protect it from light. Then, the system was submitted to stirring and heating steps.

For the electrochemical tests, the plates were submersed in electrolytic solutions formed by 50 wt% ± 5 wt% PIL aqueous solutions and another one of sodium chloride (NaCl) in a concentration of 0.01 mol.L^{-1}. This concentration is sufficiently high to activate corrosion in a relatively short exposure time. Kozhukharov et al. (6) also used low concentration of NaCl to ensure a sufficiently low concentration to allow for the observation of corrosion inhibitor effects. Then, the samples were analyzed by open circuit potential (OCP) monitoring and electrochemical impedance spectroscopy (EIS) tests for 24 h, 48 h, and 168 h of immersion time. A three-electrode cell was used to carry out the analysis. An Ag/AgCl wire was used as reference electrode, a platinum wire was the counter-electrode and the API X70 plates were the working.

For the EIS measurements, the systems were previously monitored for 168 hours. The amplitude of the EIS perturbation signal was a sinusoidal 10 mV (rms) signal, and the frequency range studied was from 100 kHz to 10 mHz using a AUTOLAB PGSTAT 30 potentiostat.

Morphology was evaluated by scanning electronic microscopy (SEM) with a JEOL JSM 5800 equipment, with an acceleration voltage of 20 kV.

Results and Discussion

Figure 1 shows the OCP monitoring results. The NaCl 0.01 mol.L^{-1} is the most active electrolyte; meanwhile the PILs potentials had very much higher values. It shows that PILs are not as corrosive as NaCl 0.01 mol.L^{-1} and can be considered as non-aggressive electrolytes. Also, PILs show a high stability since their potentials oscillate inside a small difference of approximately 140 mV for 2HEAF, 69 mV for 2HEAPr and 65 mV for 2HEABu; OCP values for NaCl 0.01 mol.L-1 can oscillate with differences close to 232 mV.

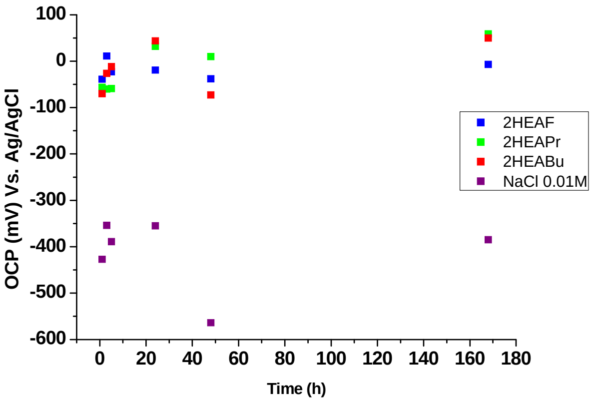

Figure 1 – OCP monitoring for the API X70 samples.

Impedance plots for the first 24 h of immersion appear in Figure 2. Nyquist and Bode plots reveal the existence of a phenomenon at high frequencies for the PIL electrolytes that can be related to the formation of a film on the substrate (7 – 9). It can be related to the adsorption of the PIL on the metallic surface (8 – 10). This phenomenon is stronger for the 2HEABu system, whose film resistance is the highest compared to the other electrolytes (Figure 2-a).
Also, there is a phenomenon at low frequencies that can correspond to the formation of an oxide layer (7, 9). In addition, regarding 2HEAF Nyquist plot and phase angle diagram, it is possible to conclude that there is another phenomenon at medium frequencies (Figure 2-c); since it takes place close to 45 °, it can be attributed to diffusion (11). Meanwhile, for the sample in contact with NaCl 0.01 mol.L^{-1}, there is just the occurrence of a phenomenon in low frequency (Figure 2-a, 2-c), that can be associated to the oxide formation, which is probable given the aggressiveness of this electrolyte that promotes the corrosion process (9).
For 48 h of immersion (Figure 3) system 2HEABu shows stability related to the 24 h, remaining with almost the same resistance and phase angle values. 2HEAPr also presents low variation related to the former measurement, but with an increase in the phase angle for the film formation phenomenon (Figure 3-c). It is related to the fact that the adsorbed PIL formed a film that changed the interfacial structure, as reported by other authors (9). 2HEAF shows a plateau at the low frequency region, with an angle of approximately 35 ° (Figure 3-c), and that appears as a straight line in the Nyquist plot (Figure 3-a). It is associated to two or more than two coupled phenomena. So, it indicates the existence of diffusion as well as the formation of oxide, as found by (9, 11). However, total resistance keeps almost the same value (Figure 3-b).

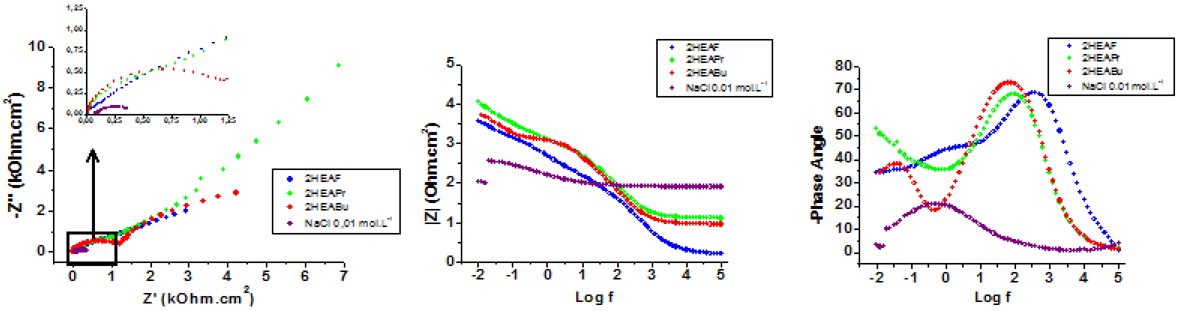

Figure 2 – a) Nyquist diagram and b) impedance modulus and c) phase angle Bode plots for 24 h of immersion.

After 168h of immersion (Figure 4), there is an increase in the total resistance for the 2HEABu system, despite of maintaining the almost the same film resistance. It can be explained by the phenomenon at low frequency that appears in the phase angle plot (Figure 4-c) for this system, since it appears at an angle of about 50° that can be related to diffusion (11).

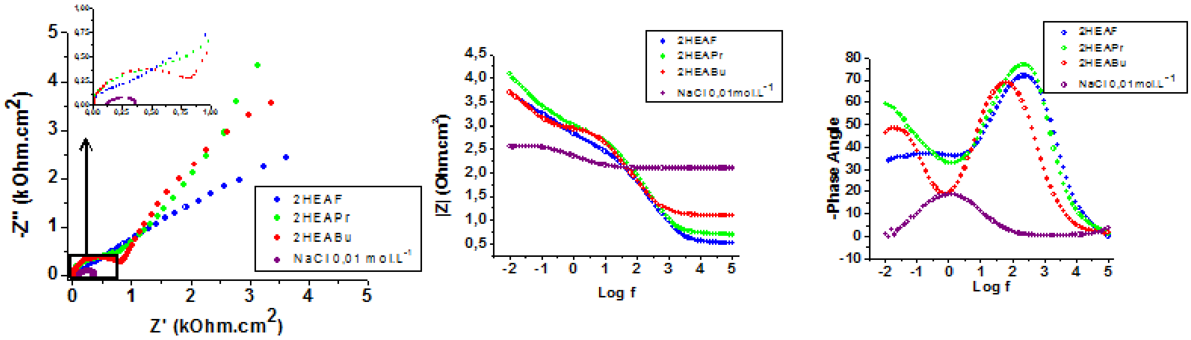

Figure 3 – a) Nyquist diagram and b) impedance modulus and c) phase angle Bode plots for 48 h of immersion.

2HEAPr system is less resistive after 168 h of immersion (Figure 4) and there is the apparition of a phenomenon at low frequency with a phase angle close to 40 ° (Figure 4-c). This phenomenon can be associated to the diffusional effects. 2HEAF do not show coupled phenomena anymore, but there is a phenomenon close to 45 ° (Figure 4-c), maybe associated to diffusion (11). Anyway, in the Nyquist plot for this sample (Figure 4-a), there is the starting of a new semicircle at low frequencies that do not allow discarding the presence of oxide on the surface (9).

None of the studied PILs phase angles approaches to 0 ° at the low frequency region at any of the immersion times, which confirms the presence of diffusional and adsorption phenomena in the samples (11).

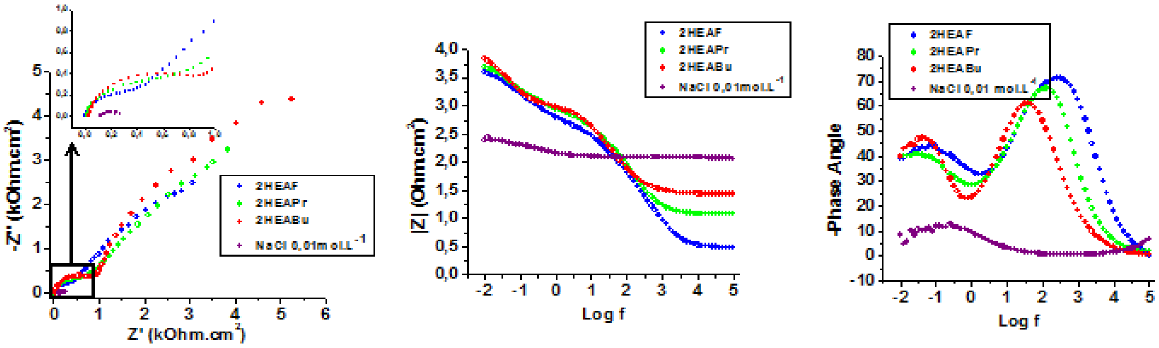

Figure 4 – a) Nyquist diagram and b) impedance modulus and c) phase angle Bode plots for 168 h of immersion.

SEM micrographs (Figure 5) do not show a strong attack produced by the contact of the PILs with the API X70 substrate. SEM micrographs (Figure 5) and EIS plots (Figure 2 to 4) show that the PILs behavior is corrosion inhibitor-like. It seems that, the corrosion inhibition takes place by PIL adsorption on the metallic surface (8, 12), forming a protective film that isolates the metallic surface from the water (13). PILs displace OCP towards more positive values related to the NaCl 0,01 mol.L^{-1} (Figure Z), reflecting a preferential anodic effect of the inhibition. Also, there is only one time constant for the NaCl 0.01 mol.L^{-1} solution, that corresponds to a non-inhibited system; meanwhile PILs presented two time constants, which is a typical phenomenon for inhibited systems (14, 15). Regarding that the centers of the film resistance arcs are located under the real axis, it can be stated that the surface presents heterogeneities and defects (15, 16).

SEM micrographs (Figure 5) show no strong attack onto the metallic surface, explained by the corrosion inhibition phenomena that take place given the interaction of the metal with these organic compounds. However, there are some black spots on the API X70 plate surface that can be attributed to the corrosion, possibly due to the different concentration of oxygen present in the water of the electrolyte. In regions where the PIL is heterogeneously adsorbed there is a differential aeration, created by the difference in oxygen concentration. It generates a bubble with an anodic region inside and a cathodic one outside, to form a galvanic couple that promotes the corrosion process (17). The most attacked surface corresponds to the plate that was in contact with 2HEAF (Figure 5-a), whose molecular size is the smallest. It enhances the molecular mobility, so its trend to desorb in a more spontaneous way, leaving spaces that can expose the substrate to the oxygen and CO_2 molecules dissolved in the water of the electrolyte and promote the oxide formation on localized regions. The less attacked surface is the one for the plate in contact with 2HEABu (Figure 5-c), since it presents a higher molecular size, enhancing the surface coverage. It is in agreement with the electrochemical measurements, in which 2HEABu shows the highest film resistance and a high stability and 2HEAF shows the worst performance, being 2HEAPr (Figure 5-b) the one with an intermediate behavior.

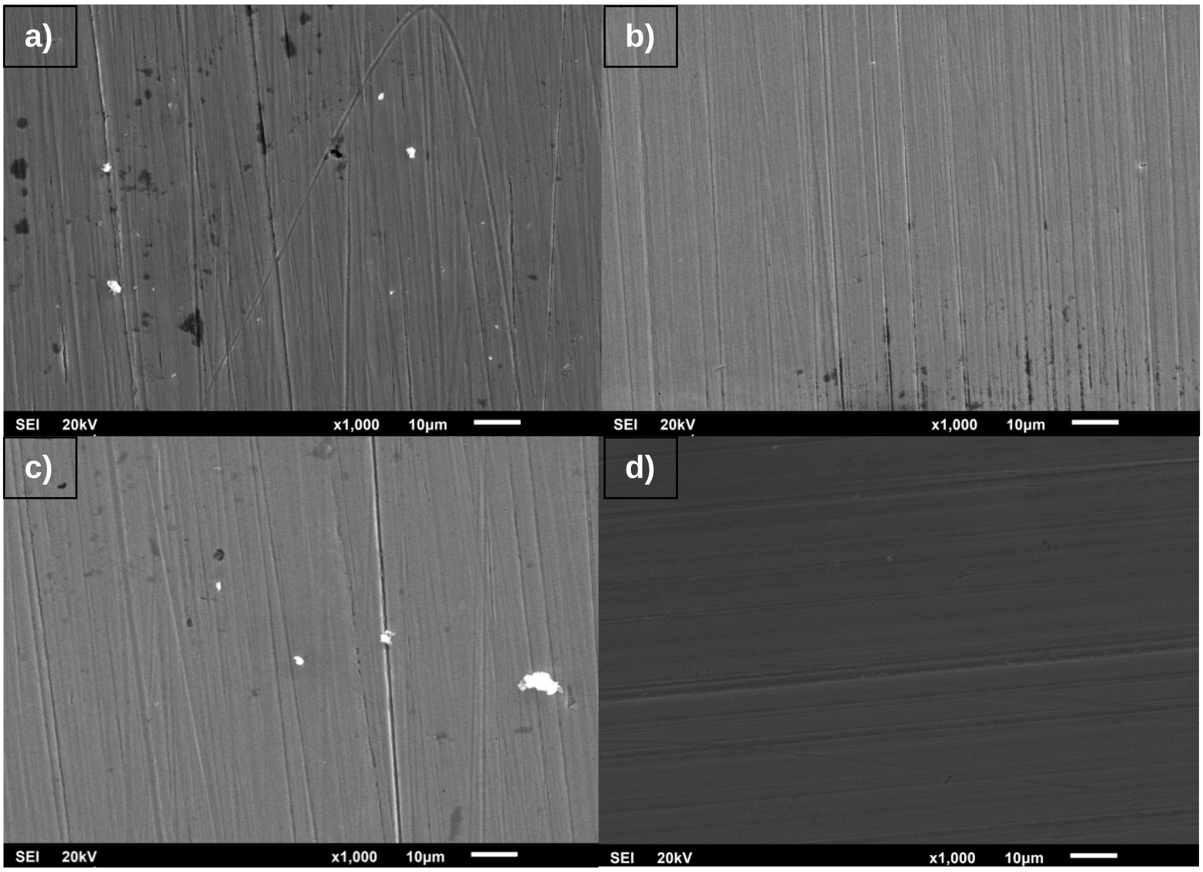

Figure 5 – SEM micrographs for the API X70 plates after being in contact with a) 2HEAF, b) 2HEAPr, c) 2HEABu and d) a plate without contact with any electrolyte.

Conclusion

PILs are very versatile molecules that have found applications in catalysis, separation process and energy generation. However, they have not been widely explored as corrosion inhibitors, a capability found in this work. The EIS results show that PILs form a thin film on the API X70 substrate, due to the adsorption of the molecules on the plate surface. Hence, PILs displace the corrosion potential or open circuit potential towards positive values related to the ones of the NaCl 0.01 mol.L^{-1}, i.e. to the anodic region, exhibiting a preferentially anodic corrosion inhibition. Anyway, diffusion and corrosion reactions phenomena cannot be ignored. The best electrochemical performance in corrosion inhibition corresponds to 2HEABu and the worst electrochemical was observed for the 2HEAF, while the 2HEAPr presents an intermediate behavior, regarding the adsorption-desorption phenomena.

Acknowledgements

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