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Inhibition Effects of a Quaternary Ammonium-Based Ionic Liquid on Steel in Acid Solution: Electrochemical and Surface Analyses

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The present work reports the performance of N-dimethyl-N-di(cocoalkyl) ammonium methyl sulfate (DCA), as a corrosion inhibitor of API-X52 carbon steel exposed to a 1M HCl solution. The EIS technique was used to assess the inhibition efficiency. Surface analyses were performed by XPS and GIXRD. The addition of DCA to the corrosive solution promoted the formation of an interfacial protective layer, which can include corrosion products such as FeO(OH) and FeCl₂·*n*H₂O. The long term stability of DCA was ascertained by the ICP-OES technique. The inhibition efficiency subsequent to 1 month of solution immersion was 97 %.

Keywords: Ionic-liquid; Acid media; EIS; XPS; Corrosion inhibitor.

1. INTRODUCTION

Acid solutions have been used in different engineering applications such as chemical processing and oil production [1, 2]. For instance, oil well acidification is a process aimed at

improving the well productivity that involves the pumping of hydrochloric acid solutions into wellbores, about 15 %, that increase the oil flow. However, the injection of highly concentrated acids into the wells creates high corrosive media which quickly degrade the properties of other materials used by the oil industry [3-5]. In the early 1930s, this process was limited by the lack of effective acid corrosion inhibitors to protect carbon steel used in wells [6]. In recent decades, the industrial use of corrosion inhibitors to reduce the corrosion rate of metals exposed to corrosive environments has not only been focused on their inhibition performance, but also on extrinsic aspects such as ecological and economic impacts, and availability [7].

On the other hand, the use of ionic liquids (ILs) to inhibit the corrosion of metallic materials has generated a great deal of interest due to the unique characteristics of these materials which have been considered as green compounds, i.e., non-volatility, wide liquid range, high thermal stability, low toxicity and incombustibility [8, 9]. ILs are salts constituted entirely of ions, organic cations and inorganic or organic anions. Hence, the large variety of possible combinations between anions and cations provides them unique physicochemical properties [10]. Some ILs with nitrogen-containing cations such as imidazolium, pyridazinium, pyrrolidinum and pyridinium have been widely evaluated as corrosion inhibitors of different metals and have exhibited good inhibition properties [11-14]. The effectiveness to diminish the corrosion damage displayed by such ILs is due to their adsorption on metallic surfaces, and their performance is dependent on many factors such as the presence of long-chain alkyl groups, molecular size, active centers present in the molecule and electron density around the nitrogen atom, among others [14-16].

Ammonium-based ILs have been the focus of attention in different research fields owing to their ability to modify the properties of interfaces and surfaces; thus, their use has been addressed as demulsifying [17] and CO_2 capturing agents [18], electrolytes for hydrogen production [19, 20], lubricants or lubrication additives [21], antimicrobial agents [22], biocidal agents [23], and most recently, as corrosion inhibitors [24-26]. Additionally, the synthesis chemistry of this kind of ILs involves relatively-low-cost methods, high yields, high purity and easy-to-carry-out synthesis, which according to their acquisition could represent an advantage over other ILs [27, 28]. Some tertiary amines such as dialkyl-ethanol amine, diethylenetriamine, polyethylene polyamine and dicocoalkylamine, used as IL precursors, have corrosion inhibitor properties, and probably, by quaternization of these amines, the enhancement of their inhibitory effect could be possible.

In this context, the present research work studied the inhibition effects of N-methyl-N-alkyl-Ndi(cocoalkyl) ammonium methyl sulfate (DCA) on the corrosion of API-X52 steel in 1 M HCl. Inhibition efficiencies and electrochemical parameters were determined by electrochemical impedance spectroscopy (EIS). Furthermore, surface analysis techniques, including X-ray photoelectron spectroscopy (XPS), grazing incidence X-ray diffraction (GIXRD) and scanning electron microscopy (SEM) were used to ascertain the interfacial chemical composition.

2. EXPERIMENTAL

API-X52 steel was employed as metallic substrate in this study, which possesses a nominal composition (weight %) of C (0.08), Mn (1.06), Si (0.26), P (0.019), S (0.003), Al (0.0039), Nb

(0.041), Cs (0.018), Cr (0.02), Ni (0.019), V (0.054), Ti (0.003), Ca (0.0002), B (0.0003) and Fe (balance). For the electrochemical tests, cylindrical samples were used with an exposed area of 0.1256 cm⁻². Prior to each measurement, the samples were ground with 320 to 600 SiC emery papers washed in absolute ethanol and deionized water and then dried using air flow. The corrosion effects on the surface morphology and chemical composition were characterised by means of X-ray photoelectron spectroscopy (XPS), grazing incidence x-ray diffraction (GIXRD) and scanning electron microscopy (SEM). For these analyses, API-X52 steel was cut into $1 \times 1 \times 1$ cm samples and then ground with 320 to 2000 SiC emery papers and polished using 3-µm alumina. Analytical grade HCl and deionized water were employed to prepare 1M HCl as corrosion solution. N-dimethyl-N-di(cocoalkyl) ammonium methyl sulfate (DCA), used as IL, was investigated as corrosion inhibitor and its molecular structure is depicted in Figure 1. The IL was added to the corrosion solution to reach concentrations of 10, 25, 50, 75 and 100 ppm.



n= mixture of esters and amides of carboxylic (C_{6} - C_{18}) acids Figure 1. Molecular structure of N-dimethyl-N-di(cocoalkyl) ammonium methyl sulfate.

EIS measurements were performed in a conventional three-electrode glass cell using a potentiostat/galvanostat PGSTAT302N controlled by a PC through the Nova 1.10 software. Corrosion tests were performed at 25 °C. API-X52 cylindrical samples, a platinum wire and a saturated calomel electrode (SCE) were used as working, auxiliary and reference electrodes, respectively. The potentials were referred to SCE. Prior to the electrochemical tests, the working electrode was immersed in test solutions for 20 min to attain a steady-state open circuit potential (E_{OCP}). Measurements were performed under naturally aerated and unstirred conditions. EIS measurements were carried out over a frequency range from 100 to 10 mHz at stable open circuit potential.

XPS and GIXRD techniques were used to explore the API-X52 steel surface after being exposed to 1M HCl for 12 h at room temperature with and without 100 ppm DCA. The XPS spectra were acquired with a THERMO Scientific K-alpha spectrometer equipped with an Al K X-ray source (1486.6 eV) and a hemispherical electron analyser. The applied analyser pass energy was 20 eV and the base pressure used during the test was about 4.5×10^{-8} Pa. Due to the organic character of DCA, the C 1s position could have been shifted in the presence of inhibitor. Therefore, it was concluded that the C 1s peak was not a suitable reference peak; instead, the Fe⁰ peak was used as a reference peak employing a binding energy of 706.6 eV. The determination of chemical species was derived from the curve fitting with the CasaXPS software. Gaussian-Lorentzian (GL) line shape functions (30% Lorentzian) were employed to model all photoelectron peaks except the Fe 2p 3/2 level of metallic iron, where a Lorentzian asymmetric (LF) line shape with tail damping was used. X-ray patterns were acquired in a Phillips Xpert-MPD diffractometer equipped with a copper anode X-ray tube; Ka radiation was selected with a diffracted beam monochromator (K α = 1.5406 Å), covering a 2 θ diffraction angle range from 15 to 85 at a scan rate of 0.33° min⁻¹. Grazing incidence angles of 3° were used. Phase ID was carried out using the International Centre for Diffraction Data (ICDD) database [29].

The stability of DCA as a time function was monitored by the quantification of dissolved iron in HCl solutions containing 100 ppm of DCA at 40 °C. Perkin Elmer Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) Optima 8300 was employed in order to quantify iron ions in the test solutions. The surface morphology was recorded by a Scanning Electron Microscope (SEM). Carbon steel samples were immersed in 1 M HCl for 4 and 12 months with and without 100 ppm of DCA at room temperature and dried in nitrogen before the SEM analysis. Images were taken by a SEM model JEOL-JSM-6300.

3. RESULTS

3.1. EIS measurements

EIS measurements were carried out to explore the electrochemical process occurring in the electric double layer formed at the carbon steel-HCl solution interface containing DCA.



Figure 2. Nyquist plots for API-X52 steel in 1 M HCl solution containing different concentrations of DCA.

Figure 2 shows a Nyquist plot of API-X52 steel in a 1M HCl solution in absence and presence of different DCA concentrations. The EIS spectra exhibit a depressed capacitive loop whose center is below the abscissa, which indicates that steel corrosion is mostly controlled by a charge-transfer

processes [30, 31], that is to say that the electrochemical reaction rate becomes limited by the mass transport of electro-active species to the electrode surface. On the other hand, the impedance response of steel was modified with the addition of DCA to the corrosive medium. At low frequencies, Z' was increased with the increasing inhibitor concentration. In a typical Nyquist plot, the total resistance of the metal-solution interface is given by Z' at low frequencies [32]. Therefore, the increasing inhibitor concentration increased the charge transfer resistance due to the adsorption of DCA molecules onto the metallic substrate; thereby, the transfer of chemical species such as H^+ and CI^- is retarded.

Bode plots of API-X52 in the test solution are shown in Figure 3. The addition of 25 to 100 ppm of DCA to the corrosive medium caused the evident appearance of two time constants of about 10^4 and 10^1 Hz. This observation confirms the impedance behaviour at high frequencies as plotted in Figure 2, where two capacity loops appeared.



Figure 3. Bode plots for API-X52 steel in 1 M HCl solution containing different concentrations of DCA.

Equivalent electric circuits (EECs) were used to analyse the impedance results. Figure 4a shows EEC₁, which fitted impedance spectra of carbon steel in the absence and presence of 10 ppm of DCA. This circuit consists of a constant phase element (*CPE*_{dl}) that depicts the double layer capacitance, the solution resistance (R_s) and a resistance (R), which includes a charge-transfer resistance (R_{ct}), a layer resistance (R_d) and all accumulated species at the metal solution interface (R_a) such as iron oxides, iron oxide-hydroxides and iron chlorides [33]. The impedance response at high DCA concentrations allows the incorporation of a *CPE* and *R* associated with the IL adsorption to an EEC. The data fitting was obtained through EEC₂, Figure 4b. EEC₂ takes into account the formation of

a heterogeneous protective film formed by DCA molecules deposited on the steel surface, where CPE_f and R_f represent the capacitance and resistance, respectively.



Figure 4. Equivalent electrical circuits of the steel corrosion process in acid medium with 0 - 10 ppm (a) and 25-100 ppm of DCA (b).

The constant phase elements (*CPEs*) involved a proportionality coefficient (Q) and an exponent (n) with values between -1 and 1. The latter is related to the roughness and heterogeneity of the metallic interface. The *CPE* impedance can be calculated as follows [34, 35]:

$$Z_{CPE} = \frac{1}{\left(Q(i\omega)^n\right)}$$
(1)

where $i^2 = -1$ is a complex number and ω is the angular frequency. The electric double layer can be considered as a capacitor due to its electrical properties. The capacitance associated with the *CPE* was calculated with the following equation [2]:

$$C = \left(Q \cdot R^{1-n}\right)^{\frac{1}{n}}$$

Table 1 reports $C_{\rm f}$ values at different DCA concentrations. The adsorption of DCA onto the steel surface modified the capacitance of the electrode-electrolyte interface, i.e., charging/discharging rate at the interface.

Concentration	Re		R	Ca		Rf	Cf	Rn	IE_{im}
(ppm)	$(\Omega \text{ cm}^2)$	n_1	$(\Omega \text{ cm}^2)$	$(\mu F \text{ cm}^{-2})$	n_2	$(\Omega \text{ cm}^2)$	$(\mu F \text{ cm}^{-2})$	$(\Omega \text{ cm}^2)$	р %
0	0.60	0.87	202	91.9	-	-	-	202	
10	0.56	0.84	298	70.3	-	-	-	298	32
25	0.56	0.71	322	82.0	0.93	11	16.2	333	39
50	0.53	0.75	681	148.0	0.87	13	3.4	694	71
75	0.59	0.77	912	87.5	0.91	18	4.6	931	78
100	0.51	0.71	833	109.0	0.91	16	3.0	849	76

Table 1. Electrochemical parameters of API-X52 steel obtained from EIS data in 1 M HCl with different DCA concentrations.

The $C_{\rm f}$ values decreased with the increasing DCA concentration. The relationship between the capacitive effect and the interface dielectric constant can be described in terms of the following equation [33, 36]:

$$C = \frac{\varepsilon \varepsilon_0 A}{\delta}$$
3)

where, δ is the layer thickness, ε is the medium dielectric constant, ε_0 is the vacuum permittivity and A is the effective electrode area. According to this equation, it is possible to deduce that the increasing IL concentration decreased the interface dielectric effect. The substitution of water molecules by DCA molecules adsorbed onto the steel surface can explained this behaviour, where water has a large dielectric constant in comparison with DCA. These results indicate that the inhibitor stimulated the formation of a heterogeneous protective film, which reduces the number of surface active sites and retards the electrochemical reaction rate. Furthermore, an increase in the film thickness can also be deduced from the C_f values. The surfactant character of the DCA cations encouraged hydrophobic interactions between coco-alkyl chains from the adsorbed molecules; owing to this, the formation of a DCA multilayer can happen. Table 1 reports the n_1 and n_2 data acquired from EIS measurements. It is known that values of n = 1, related to capacitive elements, may be ascribed to homogenous surfaces [32]. In the absence of inhibitor, the n_1 value was 0.87, indicating a heterogeneous surface.



Figure 5. Inhibition efficiency of DCA as corrosion inhibitor of API-X52 steel in 1M HCl obtained by EIS technique.

The presence of impurities, surface roughness, size and irregular distribution of active sites and defects in the crystal lattice can explain this behaviour. On the other hand, in the inhibited system, the n_2 values are higher than n_1 , which suggests that the surface covered by IL is more homogeneous. The coco alkyl chains of DCA cations parallel to the steel surface can give more homogeneity to the protected zones. Furthermore, R_p values, shown in Table 1, were acquired from resistive elements in

Figure 4. In the case of EEC₁, R_p is equal to R, and for EEC₂, $R_p = R + R_f$. The R_p values were increased by the IL concentration, which implies a slower corrosion rate due to the addition of inhibitor to the corrosive medium. The inhibition efficiency (IE_{imp} %) of DCA was calculated from EIS data that obey the following equation [33]:

$$IE_{imp} \% = \left[\frac{R_{p}^{'} - R_{p}}{R_{p}^{'}}\right] \cdot 100$$

$$\tag{4}$$

where R_p ' and R_p are polarization resistances in the absence and presence of DCA, respectively. Figure 5 plots the values of IE_{imp} as a function of concentration of DCA at 25° C, which show the same trend as those obtained by potentiodynamic polarization (PDP) results reported in a previous work [26]. The maximum value of IE_{imp} % was 78 % at 75 ppm, indicating the satisfactory performance of DCA as corrosion inhibitor under these conditions.

3.2. XPS analysis



Figure 6. High resolution Fe 2p spectra of the XPS analysis of API-X52 steel after 12h of immersion in 1 M HCl in absence and presence of 100 ppm of DCA.

X-ray photoelectron spectroscopy (XPS) was carried out to confirm the adsorption of inhibitor onto the steel surface. Figure 6 presents high resolution XPS spectra of the Fe 2p region of the API- X52 steel after 12 h of immersion in the 1M HCl solution in the absence and presence of 100 ppm of DCA.

In both spectra, the Fe⁰ 2p peak for metallic iron at 706.6 eV along with its satellite structure can be seen. It is worth mentioning that the exposure time to the aggressive medium (12 hours) was short, nevertheless, it can be seen that the intensities of the Fe⁰ signals from the sample protected with inhibitor are higher than those displayed by the steel sample exposed to acid medium without DCA.



Figure 7. High resolution C 1s (a) and N 1s (b) spectra of the XPS analysis of the surface film formed on API-X52 steel after 12h of immersion in 1 M HCl containing 100 ppm of DCA.

Great similarity is observed in Figure 6 spectra, where in both cases there is a peak at 709.7 eV, which is attributed to Fe²⁺ compounds such as iron chloride (FeCl₂) or iron oxide; additionally, a peak at 710.9 eV present in both spectra is attributed to iron oxide-hydroxide (FeOOH) [37], however, the intensities of these signals are higher in the unprotected sample. In addition, the high resolution Fe 2p spectrum of the blank material presents a peak at 712.3 eV, which corresponds to ferric (Fe³⁺) compounds such as iron chloride (FeCl₃) or iron oxide (Fe₂O₃) [38].

Figure 7a presents high resolution C 1s spectra of API-X52 steel. In absence of DCA, the signal intensity of C 1s at 284.6 eV is relatively lower than that from the protected surface, and it is due to the environment contamination.

In the presence of 100 ppm of DCA, a predominant peak at 285 eV, corresponding to C-(CH), is associated with DCA coco-alkyl chains. Furthermore, low intensity peaks at 286.2 and 287.0 eV were assigned to C-O and C-N bonds, respectively [39].

A high resolution N 1s spectrum was employed to confirm the DCA adsorption onto the metallic substrate. The XPS deconvolution of N 1s, Figure 7b, exhibits a peak at 402.7 eV that is attributed to $(R)_4$ -N⁺ of the IL cation whose high binding energy is the result of the nitrogen positive charge [40-42]. In addition, low intensity signals at 400.3 and 397.7 eV were attributed to N from the amide groups and sp² hybridization, respectively. The last assignment can be due to iron nitrides coming from the carbon steel matrix and/or environmental contamination [43, 44]. The XPS results demonstrated that the DCA addition to the aggressive medium promoted the formation of a protective film consisting of DCA molecules, iron oxide-hydroxides and iron chlorides. This protective barrier blocked the active sites on the metallic surface and controlled the corrosion reaction rates.

3.3. GIXRD analysis

Grazing incidence x-ray diffraction is a non-destructive method used specially to characterize thin films and nanoscale objects. In the present work, GIXRD was carried out to characterize the film formed on the steel sample subsequent to the acid solution immersion. Figure 8 displays GIXRD patterns of API-X52 steel after 12 h of immersion time in 1M HCl in the absence and presence of 100 ppm of DCA.

In both cases, clearly defined reflections at $2\theta = 44.6$, 65.0 and 82.4° were assigned to Fe. In addition, in the absence of DCA, low intensity reflections attributed to corrosion products deposited on the steel sample are shown: hydrated forms of iron (II) chlorides (i.e. FeCl₂.2H₂O and FeCl₂·4H₂O), which are the result of the reaction between Fe²⁺ and Cl⁻; hydrated iron (III) oxides (i.e. FeO(OH) stemming from the adsorption of water molecules onto the metallic substrate; iron (II/III) oxides (i.e. Fe₂O₃ and Fe₃O₄), resulting from the dehydration of iron oxides. These phases are characteristic of corrosion products formed in HCl solutions. In the absence of inhibitor, the solubility of the FeCl₂·*n*H₂O and FeO(OH) phases is increased in acidic solutions, resulting in the desorption of corrosion products. Consequently, new active sites are produced to continue the adsorption of aggressive species that promote iron dissolution. The GIXRD patterns of API-X52 steel in HCl

containing DCA show slightly discernible reflections attributed to corrosion products. These findings suggest that DCA reduces the amount of corrosion products on the metallic surface.



Figure 8. GIXRD analysis of API-X52 steel after 12 h of immersion in 1 M HCl in absence (red line) and presence of 100 ppm of DCA (black line).

3.4. Protective film stability



Figure 9. Variation of dissolved Fe (a) and IE_{ICP} (b) as functions of the immersion time of API-X52 steel in 1 M HCl containing 100 ppm of DCA.

The stability of DCA as corrosion inhibitor of API-X52 steel in hydrochloric acid was analysed by establishing the corrosion rate using long term immersion tests. The concentration measurement of dissolved metallic ions (M^{x+}) produced in the corrosive solution is a chemical method that gives information about the metallic corrosion rate [45]. ICP-OES was used to quantify dissolved Fe²⁺ ions in the 1M HCl solution and ascertain the DCA long term performance. Figure 9a shows dissolved Fe as a function of time obtained from HCl solutions containing 100 ppm of DCA at 40 °C.

As expected, the amount of dissolved Fe was increased with the increasing immersion time in the absence and presence of inhibitor because corrosion is a natural process under these conditions. However, in the inhibited system, the amount of dissolved Fe is lower, confirming the inhibition corrosion effect of DCA. Additionally, the corrosion rate (CR) in mm year⁻¹ and inhibition efficiencies (IE_{ICP}) in percentage (%) were calculated as follows:

$$CR = \frac{K \cdot W}{A \cdot T \cdot D}$$

$$IE_{ICP} = \left[1 - \frac{CR_i}{CR_0}\right] \cdot 100$$

$$6)$$

where *K* is a constant (8.76 x 10^4), *W* is the weight loss (g) estimated by the concentration of dissolved Fe²⁺ ions in the solution, *T* is the immersion time in the test solution (h), A is the exposed area of API-X52 steel (cm²), *D* is the metal density (g cm⁻³), *CR*_i and *CR*₀ are steel corrosion rates with and without inhibitor (mm year⁻¹).

Figure 9b presents IE_{ICP} and CR data calculated from the ICP-OES analysis. The immersion time increment decreased the CR, thus increasing the IE_{ICP} . The maximum IE_{ICP} was 97 %, which was reached subsequent to a solution immersion for 748 h (~ 1 month). These results suggest that DCA works as a long term corrosion inhibitor. After short immersion times, the addition of DCA to the HCl solution does not promote the formation of a homogenous monolayer on the metallic substrate as confirmed by previous results. However, the long term performance of DCA could suggest the interaction between DCA chemical bonds (chemical adsorption) and the metallic substrate, which give stability to the metal-solution interface. Potentiodynamic polarization results reported in a previous work showed that DCA was adsorbed preferentially onto anodic sites of the metallic substrate when the immersion time was increased [26]. In this respect, studies related to the evaluation of oxyanions as corrosion inhibitors have reported good inhibition properties and identified their behaviour as that of anodic inhibitors on different metallic substrates [46-48]. Therefore, methyl sulfate anions could be adsorbed on the metal interface on anodic sites, acting as an important key factor to improve the performance of DCA at long immersion times.

3.5. Morphologic analysis

SEM was used to explore the steel surface morphology. Figure 10 presents a general view of the sample surface subsequent to exposure times of 4 (a) and 12 months (b) in 1M HCl solutions, respectively. The API-X52 steel sample exhibits a rough and highly damaged surface due to the rapid corrosion attack in the acid solution as shown in Figure 10a. Furthermore, corrosion products, i.e. (FeCl₂·nH₂O and FeO(OH), deposited on the steel surface are observed. The highly porous layer allows the continuous diffusion of aggressive species such as Cl⁻ and H⁺ to the electrode-electrolyte

interface. The steel SEM micrograph after 12 months of immersion in acid solution, Figure 10b, presents a severely corroded surface with clear evidence of mass loss and pits.



Figure 10. SEM analysis of API-X52 steel after 4 (a) and 12 (b) months of immersion in 1 M HCl.

On the other hand, the surface analyses of protected steel samples subsequent to 4 and 12 months of immersion in HCl solution containing DCA are displayed in Figures 11a and 11b, respectively. After 4 months, the surface morphology is remarkably improved, more homogenous and smoother with respect to what is shown in Figure 10a. In addition, corrosion products built up along grain boundaries as observed in Figure 11a. As for the steel sample exposed to the test solution for 12 months, Figure 11b, a more uniform surface without pits or cavities, with respect to the blank, is clearly observed. This result indicates the formation of a compact layer on the steel surface under inhibiting conditions. In this way, DCA attenuates the surface damage and controls the localized corrosion on API-X52 steel.



Figure 11. SEM analysis of API-X52 steel after 4 (a) and 12 (b) months of immersion in 1 M HCl in the presence of 100 ppm of DCA.

3.6. The inhibition mechanism

As follows from EIS and surface analyses, the corrosion rate of API-X52 steel in 1 M HCl is retarded in the presence of DCA. The EIS and XPS results indicate that the inhibition process is due to the adsorption of DCA molecules on the metallic substrate. The adsorption process can be explained as follows: it is well known that in hydrochloric acid, negative charges on the metallic surface can be formed by the adsorption of chloride or hydroxyl ions coming from the HCl solution [49]. Consequently, DCA cations can be adsorbed on the metallic surface by electrostatic forces of attraction between adsorbed chloride ions and DCA cations through $(R)_4$ -N⁺ as illustrated in Figure 12; in addition, DCA was adsorbed chemically on the metal surface through amide groups.



Figure 12. Schematic representation of the molecular adsorption of DCA on API-X52 steel in HCl solution.

The arrangement of coco-alkyl chains can favour the spatial orientation toward the bulk solution; as a consequence, hydrophobic interactions between hydrocarbon chains awarded a hydrophobic character to the metal-solution interface. Accordingly, slow diffusivity of water molecules toward the metallic surface could be obtained, retarding the dissolution of Fe. However, there are some unprotected zones, confirmed by the IE_{imp} % values, where corrosion products such as iron oxide-hydroxides and iron chlorides are likely produced. On the other hand, at long immersion times, the effectiveness of DCA as corrosion inhibitor is improved, as it was confirmed by ICP-OES and SEM results. This behaviour could be explained by the interactions between DCA molecules and corrosion products. Thus, the creation of this compact layer restrains the dissolution of Fe and reduces the corrosion rate of API-X52 steel.

4. CONCLUSION

The results of this study proved that DCA acts as an effective corrosion inhibitor of API-X52 steel in 1M HCl. EIS measurements revealed that the charge transfer resistance was increased with the

increase in the DCA concentration, suggesting that the IL allows the formation of a porous protective film that inhibits the corrosion process. Additionally, the XPS analysis indicated the presence of $(C)_{4}$ -N⁺ on the steel surface and a reduction of Fe^{2+/3+} species in comparison with the blank, confirming that the corrosion inhibition performance of DCA is due to its adsorption on the metal-solution interface through the N atom. The stability of DCA as corrosion inhibitor was determined by ICP-OES, where IE_{ICP} reached 97 % after 1 month in the test solution. The effectiveness of DCA under long term conditions was confirmed by SEM.

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