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HosseinpourRokni, M., Zeighami, N., Kowsari, E. et al. (4 more authors) (2025) Submolecular insights into the adsorption mechanism of imidazolium-based corrosion inhibitors: A novel quantum parameter for predicting inhibition superiority. Applied Surface Science, 706. 163569. ISSN 0169-4332

https://doi.org/10.1016/j.apsusc.2025.163569

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# Sub-molecular Insights into the Adsorption Mechanism of Imidazolium-based Corrosion Inhibitors: A Novel Quantum Parameter for Predicting Superior Inhibition

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## Abstract

Despite extensive research, there are still debates about distinct aspects of corrosion inhibition by organic inhibitors. In this study, two novel ionic liquids (ILs) were synthesized and investigated as model inhibitors for mild steel in 0.5 M HCl. Electrochemical methods and surface characterization through FTIR, XPS, and FE-SEM, along with thermodynamic and first-principles calculations, were employed to evaluate inhibition efficacy and to unravel the underlying mechanism. Results revealed that, following a one-layer adsorption isotherm, the ILs predominantly exhibited anodic spontaneous physicochemical interactions with the corroding substrate. As a result, according to impedance studies, at least 84% of the acidic corrosion was mitigated using 4 mM of the ILs. Furthermore, chloride-mediated cooperative (indirect) adsorption, apart from direct surface binding, was confirmed experimentally for the first time, providing better justification for the dominant anodic performance. Utilizing quantum calculations, it was demonstrated how the data computed for standalone inhibitors can contribute to estimate the most stable adsorption configurations. In addition, the role of each functional group

and atomic constituent in the adsorptive corrosion inhibition was elaborated, given different possible adsorbate-adsorbent interaction modes. Finally, a novel quantum parameter was introduced, and its potential application as an indicator for identifying superior corrosion inhibition was described.

### **Keywords**

Inhibition mechanism, Acidic corrosion, Ionic liquid, Adsorption, Quantum calculation

## Introduction

At low concentrations, corrosion inhibitors can significantly reduce the corrosivity of the fluids to which metals and alloys are exposed. A wide variety of organic chemicals have been evaluated in order to explore their inhibitory effects. Satisfactory to excellent inhibition efficiencies were copiously reported in the literature [1,2]. However, the inhibition mechanism still remained elusive, requiring further research [3]. It is generally known that the solubility, mobility, and adsorptive behavior of an organic chemical must be compatible with a metal-solution system to have significant corrosion mitigation [4,5]. Ionic liquids (ILs), zwitterions, and betaines are modern organic examples of inhibitors with a particular feature: containing charged components. This characteristic facilitates dissolution and molecular mobility, especially in common corrosive aqueous solutions, thus reducing dependency on the parameters in mechanistic studies.

Among the inhibitor species, ILs with their great qualities—highly soluble in polar and non-polar solvents; negligibly volatile; non-flammable; minimally toxic; thermally, chemically, and electrochemically stable; and considerably tunable—presented prospects for less-toxic anticorrosion applications, which is vital regarding contemporary environmental concerns [6–8]. Multiple studies have scrutinized ILs as corrosion inhibitor in acidic-to-alkaline aggressive media and for different metallic substrates: aluminum [9], copper [10,11], magnesium [12,13], zinc [14],

brass [15] and a broad spectrum of steel alloys [16,17]. Across the wide variety of ILs, those derived from imidazole have received the most attention in light of their easy, low-cost, and high yield synthesis [2]. In the presence of halide counter anions, the resultant imidazolium-based cations are the primary components responsible for inhibitive performance. It is important to note that the cationic moieties essentially undergo protonation during synthesis in strong acids. Hence, their chemical properties are more likely to remain unchanged in corrosive acidic media, particularly with main substituents other than -H. This issue decreases suffering caused by ambiguities usually associated with using (de)protonation-prone organic inhibitors and the dissociative adsorption processes they may come across [18–22]. Moreover, the anion-cation pairs of ILs can present synergistic inhibition performance [23]. The concept of inhibitive synergy between solution anions, acting as intermediate bridge, and organic compounds has been recognized for a long time [24,25]. According to this mechanism,  $I^- > Br^- > Cl^-$  can enhance the adsorption (inhibition efficiency) of organic inhibitors [26]. Nonetheless, most supportive evidence on this subject has been inferred from electrochemical methods [27], and there is no direct published evidence to substantiate bonding either between organic inhibitors and preadsorbed anions or between the anionic and cationic moieties of ILs. It should be also emphasized that, from a mechanistic viewpoint, using ILs with the same anions to the corrosive solution (e.g., Cl<sup>-</sup> as IL anion for corrosion studies in HCl solutions) can reduce the complexity of the system under investigation and aid in unraveling inhibition processes. Given this perspective, even if they may not be the most effective in terms of inhibition efficiency [28], ILs with the specific characteristics discussed can serve as exemplar compounds for enhancing our understanding of corrosion inhibition mechanisms. This is particularly relevant because the anticorrosive performance of the ILs primarily relies on their adsorptive behavior.

Conventional theory frequently proposed in the literature suggests that organic inhibitors adsorb onto metal substrates, making a protective surface film, and prevent corrosion through sharing/donating  $\pi$  and non-bonding electrons to the vacant orbitals of the metal [29,30]. In the majority of cases, this performance is attributed to the presence of constituents capable of doing so, that is, conjugated (double or triple) bonds, heteroatoms (N, P, O, S), and halogens (F, Cl, Br, I) [31–33]. Based on this, inhibition-oriented improvements have been sought either by chemicals containing the constituents or by incorporating the constituents into various core structures – whether as individual elements or functional groups.

Ab initio atomistic simulation as an advanced computational method have enabled us to gain deeper insights into inhibition-bearing adsorption [34,35]. However, even the latest classifications still fail to establish a comprehensive correlation between electronic features and adsorption/inhibition efficacy [33,36-38]. It appears that certain aspects within this field necessitate reevaluation. Kovačević et al. [21] recommended that relevant studies should be devoted to a definite substrate, because the partially or fully occupied d- or sp-orbitals of metals may exhibit different coordination behavior toward organic adsorbates. Despite this, the nature of the metal substrate, at least as long as it belongs to the transition type studied, had no effect on the direction of total electron transfer between the adsorbents and adsorbates [39]. Note that most documented conclusions are drawn without considering the effect of adsorption configuration and that of intermediate species—Inhibitor molecules are assumed to adsorb immediately onto the surface, which may not justify a predominant anodic or cathodic inhibition mechanism [10]. In addition, the traditionally assigned fixed role (electron donation) to organic molecules and their specific constituents (N, O, etc.) has been questionable. The State-of-the-art analysis using the Bader charge concept explicated that electron withdrawal—rather than electron donation—by organic molecules occurs through adsorptive interactions with metallic substrates, contradicting conventional theory [21,37,40–45]. Radilla et al. [41] studied different adsorption sites for 2mercaptoimidazole onto Fe(100) surface. These authors found that the nitrogen atoms of the aromatic imidazole ring can play little to significant roles in electronic exchanges of surface

bonding, depending on the adsorption configuration and relaxation distance from the surface. Kokalj et al. [42] demonstrated that cysteine and penicillamine molecules, during adsorptions onto Fe(110), become negatively charged (taking electrons from the surface) while variable electronic changes for –COOH group and its atoms were observed. In another study, Lgaz et al. [43] made an attempt to compare functional group effects on quinoline derivatives, concluding that oxygen atoms might act as electron donors or acceptors, depending on the functional groups involved. Therefore, it seems that further studies are required to identify up-to-date universal principles and strengthen the link between quantum properties of inhibitors in free and adsorbed states, provided there is sufficient empirical and theoretical validation.

Furthermore, there is still a growing interest in identifying which quantum parameter best discriminates inhibition efficacy. The significance of finding such a parameter lies in its capacity to shed light on the underlying inhibition mechanism and pave the way for the discovery of more sustainable inhibitors without extensive experimental trials. Many studies have used DFTcalculated adsorption energy as a criterion for identifying more effective inhibitors, often focusing on small, planar molecules and in a single parallel configuration to the surface. This approach has limitations for delivering conclusive results, because adsorption energy is not independent; factors such as adsorption configuration, or steric restrictions can crucially influence the final adsorbed configuration and associated quantum values. Some researchers have evaluated 'net electron transfer' for this purpose, yet the correlation with adsorption energy values remained disputable without reasonable explanation. Recently, Fu et al. [37] developed the idea - also briefly proposed by T. Le Minh Pham [44] - that a partial correlation between the d-band center and adsorption energy can be employed as a potential discriminant. It is unfortunate that the authors did not specify which substrate atoms' d-band centers were regarded for establishing the correlation, where the surface atoms revealed different electronic conditions after inhibitor adsorption. More importantly, the d-band center is essentially the first moment of the d-band density of states, which is not intrinsically unique - different distributions can result in the same d-band center.

This study compares mild steel corrosion in 0.5 M HCl without and with two ILs that has not been previously synthesized and investigated as inhibitors. The large, non-planar geometries of the ILs are expected to demonstrate illustrative performance as model inhibitors. Additionally, the presence of heteroatoms (N and O) and halogens (Cl) in the studied structures offers opportunities to observe which elements can have significant effects on adsorptive corrosion inhibition. A systematic examination of inhibition efficacy is conducted using electrochemical methods and surface analysis. Experimental evidence is presented for the first time on cooperative adsorption of  $Cl^-$  and the cationic moieties of the ILs. Adsorption and quantum-based modeling confirm the electrochemical findings and elucidate the factors influencing inhibition mechanism. The study also illustrates how the relative positioning of the frontier orbitals of the adsorbing inhibitors may cause the lowest adsorption energy values and contribute to atomic-level interactions. Last but not least, a new quantum parameter is introduced to find more efficient inhibitors.

## **Experimental and theoretical investigations**

#### Synthesis of ionic liquids

Imidazole (99%), 2-chlorethyl ether (99%), 1,2-bis(2-chloroethoxy)ethane (97%), ethyl acetoacetate (99%), and acetonitrile were purchased from Merck. All reagents were used as received. After synthesis, the chemical structures of the synthesized compounds were verified using <sup>1</sup>H-NMR (500 MHz) spectra obtained by a Bruker Advance 500 instrument, Germany. Additionally, FTIR spectra were recorded and compared to the results of a similar analysis conducted on the mild steel surface, as described in section 0.

Synthesis of 1,3-Bis-[2-(2-chloro-ethoxy)-ethyl]-3H-imidazol-1-ium chloride

To prepare the IL, hereafter denoted as [CE1EI]Cl (Fig. 1), 0.68 g (0.01 M) of imidazole was dissolved in 50 ml of acetonitrile. Then, 2.86 g (0.02 M) of 2-chloroethyl ether was added to the solution. The mixture was heated at 80°C for 24 hours, then cooled to -10°C for 72 hours. The volatile components of the product were removed from the resulting solution under reduced pressure. The residue was recrystallized from ethyl acetate and dried under vacuum, yielding the ionic liquid, [CE1EI]Cl, with approximately 90% yield—<sup>1</sup>H-NMR (500 MHz, Chloroform-*d*)  $\delta$ : 8.35 (1H, s, NC<u>H</u>N), 7.60 (2H, s, N<u>CHCH</u>N), 4,65 (4H, t, =NC<u>H</u><sub>2</sub>CH<sub>2</sub>O), 3.90 (4H, m, =NCH<sub>2</sub>O<u>CH</u><sub>2</sub>), 3.75 (4H, m, =O<u>CH</u><sub>2</sub>CH<sub>2</sub>Cl), 3.60 (4H, m, =OCH<sub>2</sub>CH<sub>2</sub>Cl).

Synthesis of 1,3-Bis-(2-{2-[2-(2-chloro-ethoxy)-ethoxy]-ethyl)-3H-imidazol-1-ium chloride}

To prepare the IL, hereafter denoted as [CE3EI]Cl (Fig. 1), 0.68 g (0.01 M) of imidazole was dissolved in 50 ml of acetonitrile. Then, 4.62 g (0.02 M) of bis[2-(2-chloroethoxy)ethyl] ether was added to the solution. The mixture was heated at 80°C for 24 hours, then cooled to -10°C for 72 hours. The volatile components of the product were removed from the resulting solution under reduced pressure. The residue was recrystallized from ethyl acetate and dried under vacuum, yielding the ionic liquid, [CE3EI]Cl, with approximately 85% yield—<sup>1</sup>H-NMR (500 MHz, Chloroform-*d*)  $\delta$ : 8.40 (1H, s, NC<u>H</u>N), 7.75 (2H, s, N<u>CHCH</u>N), 4,50 (4H, t, NC<u>H</u><sub>2</sub>CH<sub>2</sub>O), 3.80 (4H, m, NCH<sub>2</sub>O<u>CH</u><sub>2</sub>), 3.70 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>Cl), 3.55 (16H, m, O<u>CH<sub>2</sub>CH<sub>2</sub>O), 3.50 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>Cl).</u>

### Fig. 1

#### Preparation of metal substrate and solutions

Mild steel panels ( $10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$ ) used as metal samples in this study were purchased from Foolad Mobarakeh Company. The chemical composition of the steel alloy, determined using

a spark emission spectrometer, is reported in Table 1. The metal samples were mechanically polished with emery papers of grit sizes of 400, 800, 1000, and 1500 in sequence. They were degreased with acetone, rinsed with deionized water, and dried with compressed air before and after polishing to remove organic and inorganic pollutants. Samples used for electrochemical analysis were also soldered to copper wires and mounted in epoxy resin to ensure a consistent electrode surface area (1cm<sup>2</sup>) during immersion. 0.5 M HCl, serving as the blank corrodent, was prepared by diluting analytical-grade hydrochloric acid (37%) purchased from Merck with double-distilled water. Different concentrations of the synthesized inhibitors/ILs, ranging from 0.5 mM to 4 mM, were added into the blank solution to prepare inhibited solutions.

Table 1. Chemical composition of the mild steel substrate, weight percent

С	Si	Mn	Р	S	Cr	Mo	Ni	Al	Со	Cu	Fe
0.058	0.01	0.15	0.007	0.003	0.01	0.003	0.008	0.038	0.007	0.007	Base

# **Electrochemical measurements**

Electrochemical potentiodynamic polarization and impedance spectroscopy (EIS) were performed using an Ivium Compactstat Potentiostat/Galvanostat. The potentiodynamic polarization data were recorded from -150 mV to +150 mV vurses OCP at a scan rate of 1 mV/s. EIS was conducted by applying a 0.01 V AC signal, single sine wave, top-top, over a the frequency range of 10,000–0.1 Hz at OCP. A conventional electrochemical setup comprising a mild steel sample as the working electrode, an Ag/AgCl (3M KCl) reference electrode, and a platinum counter electrode was used for the measurements. The steel samples were immersed in the blank and inhibited solutions for 1 hour to reach a semi-steady state before testing. Approximately 100 ml of test solution was used, kept open to air at 298 K. The data was analyzed using IviumSoft and Zview software. All measurements were repeated at least three times to ensure reproducibility.

**Surface characterization** 

As described for the electrochemical measurements (section 0), sample preparation for the following surface analyses on mild steel samples was performed. FE-SEM images were taken using a TESCAN MIRA3 LMU scanning electron microscope. Fourier transform infrared (FTIR) analysis in the range of 450 – 4000 cm<sup>-1</sup> was <u>conducted</u> using spectroscopic-grade KBr and an FTIR spectrophotometer (PerkinElmer). X-ray photoelectron spectroscopy (XPS) was carried out using a Bes Tek (Germany) spectrometer with an Al K-alpha X-ray source (1486.6 eV) at a vacuum pressure of 10<sup>-10</sup> mbar. The spectral data were then analyzed using CasaXPS software after calibration. Shirley and Gaussians-Lorentzian functions were used for background correction and deconvolution of photoelectron peaks, respectively.

## **Computational methods**

Gaussian 09W software (version 9.5) was used to optimize molecular geometry and calculate quantum chemical parameters of the ILs at the B3LYP/6-311++G(d, p) level. This level of hybrid density functional theory is one of the most commonly used basis sets; it is robust enough to strike a balance between accuracy and computation costs, while considering polarization for all atoms—improving the total energy calculation—and incorporating diffusion functions down to an S orbital for hydrogen atoms.

DFT-based models of the adsorptive behavior of the ILs were studied using the Vienna Ab Initio Simulation Package (VASP) [46]. An Fe(110) slab was selected, as the Miller indices have shown the best coordinating features [47][48]. The model consists of 400 Fe atoms arranged in 4 layers, within a periodically repeated optimized Fe(110) unit cell and a 20 Å vacuum layer perpendicular to the surface, forming the supercells. The top two layers of the Fe slab were set free to interact with the IL molecules placed at a distance of 2.5 Å at the beginning of each calculation. The exchange-correlation energies were computed using frozen-core projector augmented wave (PAW) for pseudopotential and wave functions, and the Perdew Burke Ernzerhof (PBE) of generalized gradient approximation (GGA). The probable effects of long-range van der Waals (vdW) forces in the adsorption process were considered via dispersion correction of the total energy using DFT-D3. To sample the surface Brillouin zone from the slabs, a  $(3\times3\times1)$  Monkhorst–Pack k-point mesh was used. The minimum energy and other properties of the electronic, and ionic structural relaxations were reported when the residual force and energy difference converged to values below 0.03 eV/Å and 10<sup>-5</sup> eV per atom, respectively. Bader charges were calculated using the Bader code [49,50].

## **Results and discussions**

## **Open circuit potential measurements**

The OCP of the steel samples exposed to 0.5 M HCl without and with 0.5, 1, 2, and 4 mM of the ILs were recorded for 3600 s and shown in Fig. 2. In the blank solution, the steel electrochemical potential dramatically declined within the first 250 s, due to surface oxidation by chloride-induced attacks dominating surface reactions during the initial exposure period. After that, the OCP values marginally shifted ( $\approx 5 \text{ mV}$ ) toward more positive values and then followed a continuous drop until around 3500 s. The potential rise can be attributed to the formation and accumulation of the semiprotective oxyhydroxides and hydrogen bubbles created on the surface as a result of the cathodic counter reactions. Corrosion appears to have been more uniform before the second drop in OCP values. During the initial period of immersion ( $t \le 250s$ ), the abraded clean steel electrode was rather free of surface layers, and chloride attacks were uniformly distributed, whereas the presence of the surface barriers that formed because of cathodic corrosion reactions (within  $250 \le t \le 1000$ s) induced non-uniformity and made the surface more susceptible to local dissolution. As time passed (t  $\geq$  1000 s), subsequent chloride incorporation at the steel/solution and oxyhydroxides/solution interfaces led to local corrosion, or meta-stable anode formation. Consequently, the OCP values monotonically decreased after about 1000 s of immersion until around 3500 s when the anodic areas with stable local corrosion probably experienced diffusionrelated limitations. It is worth mentioning that although the low energy level of the transformation of ferrous/ferric oxides to ferrous/ferric chlorides may reduce the likelihood of having surface oxyhydroxides, particularly in concentrated HCl solutions, they have been considered to present a comprehensive OCP interpretation.

## Fig. 2

In the presence of the inhibitors, the mild steel samples followed a different corrosion process during 1-hour immersion in 0.5 M HCl. Both ILs retarded the intense initial effects of the corrosive solution, and almost stabilized the OCP values in a shorter period of immersion. This means that fewer chlorides were allowed to reach the mild steel surfaces to catalyze Fe dissolution. Therefore, steel corrosion was effectively suppressed and remained uniform with the application of the ILs. The process of corrosion inhibition was more evident for [CE3EI]Cl compared to [CE1EI]Cl, since the former acted in a shorter time span, and also limited the otherwise OCP drop more efficiently. The desirable effects of the ILs were enhanced by increasing concentration; despite this, the dependency of the performance on concentration was more noticeable for [CE1EI]Cl. The larger size of [CE3EI]Cl probably facilitated steel surface coverage, but it was also likely to reduce the IL mobility in the adsorption-desorption process of corrosion inhibition.

Inhibitor tendency to control anodic or cathodic corrosion reactions can be correlated with the electrochemical potential shifts that a metallic substrate exhibits in a solution containing the inhibitor compared to a similar but inhibitor-free solution. From this perspective, positive potential shifts are indicators of predominantly anodic inhibition and vice versa [51,52]. Not to mention that the larger the potential shift, the more pronounced the biased corrosion inhibition. Despite general positive potential shifts measured for the steel samples in the presence of both [CE1EI]Cl and [CE3EI]Cl that confirmed a predominantly anodic inhibition mechanism for the ILs evaluated in this study, interestingly, increasing the inhibitor concentration led to distinct effects on

electrochemical performance. The increases in [CE1EI]Cl molarity shifted the ultimate steel OCP values toward higher positive values, while the same increases for [CE3EI]Cl shifted the ultimate steel OCP values toward more negative values. Accordingly, although both ILs revealed mixed-type inhibition with predominant control on the anodic dissolution of mild steel, the anodic inhibition of [CE1EI]Cl and the cathodic inhibition of [CE3EI]Cl were improved at higher concentrations. More specifically, with increasing concentration, [CE1EI]Cl was more effective at blocking anodic sites, while [CE3EI]Cl with its larger chloro-ethoxy wings was better at repelling the otherwise reduced protons of the acidic media.

#### Potentiodynamic polarization measurements

The potentiodynamic polarization (PDP) curves of steel samples immersed in 0.5 M HCl, both with and without different concentrations of the ILs, are shown in Fig. 3. As can be seen, the curves exhibited Tafel behavior, confirming that 'activation polarization' governed the underlying anodic and cathodic reactions. There was no significant difference between the data of the blank and inhibited solutions in this respect, implying that the corrosion mechanism of steel in 0.5 M HCl remained unchanged even with IL addition. On account of this, the kinetic parameters—corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), anodic as well as cathodic Tafel slopes ( $\beta_a$ ,  $\beta_c$ )—were derived through Tafel extrapolation and given in Table 2. Polarization resistance ( $R_p$ ) was also calculated by Eq. 1 [24], as shown in the table.

$$R_p = \frac{1}{2.303i_{corr}(\frac{1}{\beta_a} + \frac{1}{|\beta_c|})}$$
Eq. 1

Fig. 3

Table 2. Electrochemical parameters of mild steel in 0.5 M HCl, derived from potentiodynamic polarization measurements in the absence and presence of different concentrations of [CE1EI]Cl and [CE3EI]Cl. Solutions were kept open to air at 298 K before and during testing.

	IL Conc. mM	$E_{corr} \ { m mV}_{ m Ag/AgCl}$	i <sub>corr</sub> μA.cm <sup>-2</sup>	$R_p$ $\Omega.cm^2$	$egin{aligned} eta_a \  ext{V.dec}^{-1} \end{aligned}$	$-\beta_c$ V.dec <sup>-1</sup>	$\eta_i \ \%$
Blank	0	-460.2±2.72	104.20±10.3	77.51	$0.030 \pm 0.0080$	0.050±0.0053	-
	0.5	-450.1±0.77	39.37±2.24	235.80	0.037±0.0037	0.050±0.0073	62.22
	1	-449.8±0.22	36.48±0.14	250.90	0.039±0.0012	0.046±0.0014	64.99
	2	-449.8±0.01	33.40±0.15	276.50	0.037±0.0050	0.050±0.0017	67.95
	4	-442.4±0.57	19.97±0.67	434.50	0.035±0.0011	0.005±0.0011	80.83
	0.5	-434.4±0.61	22.25±0.11	367.50	0.030±0.0028	0.051±0.0016	78.65
[CE3EI]Cl	1	-441.0±0.50	22.00±0.01	367.70	0.033±0.0026	0.051±0.0041	78.89
	2	-440.9±0.01	21.60±0.02	396.00	0.033±0.0019	0.048±0.0002	79.27
	4	-432.1±0.67	15.65±0.29	486.90	0.029±0.0013	0.045±0.0007	84.98

Based on the polarization results, the  $E_{corr}$  of steel in the inhibited solutions followed a trend similar to OCP measurements (generally more positive values in comparison with the  $E_{corr}$  of steel in the blank solution). This demonstrated that the effect of anodic inhibition was the dominant mechanism when the ILs were applied [5,53]. However, the positive potential shifts was modest (10 – 28 mV), indicating that the anodic performance of the ILs was not significantly more considerable than their cathodic performance. Regarding the results obtained for corrosion current density, the use of ILs clearly decreased the steel corrosion rate:  $i_{corr}$  decreased from 104.20  $\mu$ A.cm<sup>-2</sup> in the blank solution to 19.97  $\mu$ A.cm<sup>-2</sup> and 15.65  $\mu$ A.cm<sup>-2</sup> at 4 mM concentration of [CE1EI]Cl and [CE3EI]Cl, respectively. The corresponding inhibition efficiencies were calculated as follows, Eq. 2 [54]:

$$\eta_i = (1 - \frac{i_{inh}}{i_b}) \times 100$$
 Eq. 2

where i is corrosion current density and the subscripts b and *inh* relate to the blank and inhibitor solutions, respectively. The inhibition efficiency of the ILs enhanced as a result of each increase in IL concentration, implying that further IL molecules were adsorbed on corrosion-prone areas of

the steel surface with higher concentrations. The maximum inhibition efficiency measured in this study for the ILs was different. [CE1EI]Cl hindered steel corrosion less than [CE3EI]Cl, which can be related to the structural differences or electron donating-accepting abilities of the ILs. Notably, although the maximum protection by the ILs was achieved at 4 mM, significant corrosion mitigation was recorded just by using 0.5 mM of the inhibitors.

Table 2 also disclosed that  $\beta_a$  and  $\beta_c$  are almost unchanged across different inhibitor concentrations. The stability confirms that the inhibitory effects of the ILs on the mechanism of steel dissolution and reduction processes such as oxygen or hydrogen were minimal [55]. Alternatively, the inhibitor molecules affected steel corrosion in HCl by non-chemical adsorption mode—only by creating surface protective layers hindering corrosive attacks [56].

## **Electrochemical impedance spectroscopy**

Electrochemical impedance spectroscopy (EIS) was applied to inspect steel/HCl interface in the absence and presence of [CE1EI]Cl and [CE3EI]Cl. Fig. 4 presents the results of the impedance studies as Nyquist and Bode diagrams. Recognizably, the addition of ILs to 0.5 M HCl increased the diameter of the capacitive loops in the Nyquist plots as well as the low-frequency impedance modules (|Z| at 0.1 Hz) in the Bode-phase curves. The enhancements were in great tune with IL concentration; therefore, it appears that protective layers of the ILs were created on steel surface and improved corrosion resistance.

Corrosion normally causes a conspicuous reduction in the absolute phase angle of EIS, since the dissolution of surface atoms and resulting unevenness facilitate corrosion reactions by increasing the reactive surface area. A phase angle value of 0° indicates purely resistive electrochemical phenomenon, while 90 indicates ideal capacitive behavior at the metal/solution interface [57]. Fig. 4 (a, d) illustrates that the phase angles measured for [CE1EI]Cl and [CE3EI]Cl reached lower values compared to those obtained for the blank solution, particularly at medium to low

frequencies and at higher IL concentrations; seemingly, molecular adsorption by the ILs helped the steel surface remain smoother by controlling the corrosion rate and mechanism [58,59].

To obtain electrochemical information from the EIS spectra, two different electrical equivalent circuits (EEC)—see Fig. 4, part b— were selected according to the underlying physicochemical phenomena governing steel corrosion in the blank and inhibitor-containing solutions [60,61]. Instead of pure capacitors (Cs), constant phase elements (CPEs) were used in the EECs, for the sake of various physical-chemical phenomena such as surface roughness, inhibitor adsorption, metal impurities, atomic dislocations, and porous layer formation, deviating the capacitive behavior of the interface/film from an ideal state (capacitance dispersion) [62,63]. The impedance of a CPE is defined by Eq. 3 where  $Y_0$  and n are respectively the magnitude and deviation factor of the CPE,  $\omega$  is the angular frequency, and j is the imaginary unit ( $j = \sqrt{-1}$ ) [64].

$$z_{\text{CPE}} = \frac{1}{Y_0(j,\omega)^n}$$
Eq. 3

As shown in Fig. 4 (b), in addition to solution resistance  $(R_s)$ , the EECs mainly comprise an element for charge transfer resistance  $(R_{ct})$ , and a constant phase element (CPE<sub>dl</sub>) that represents the capacitive behavior of the electrical double layer (EDL) at the steel/electrolyte interfaces. For steel in the inhibited solutions, an additional time constant (a parallel R/CPE) was included to capture the film-forming properties of the ILs. These supplementary elements compensated for the effect of inhibitor film resistance  $(R_f)$  and capacitance  $(CPE_f)$  on the impedance response, leading to better fit results as well. The extracted parameters obtained from fitting the EIS data with these circuits are listed in Table 3. The fit lines in Fig. 4 and the low chi-square values reported in Table 3 confirmed the appropriateness of the EECs employed, albeit the figures showed indistinguishable overlapped time constants in the case of IL-containing solutions. The equivalent values of the ideal

capacitors (*C*) corresponding to the CPEs were calculated using Eq. 4, considering horizontal distribution for the EDL and film time-constants [65]:

$$C = Y_0^{\frac{1}{n}} \frac{R_s R_{ct}}{R_s + R_{ct}}^{\frac{1-n}{n}}$$
 Eq. 4

#### Fig. 4

Table 3. Electrochemical parameters of mild steel in 0.5 M HCl, derived from EIS in the absence and presence of different concentrations of [CE1EI]Cl and [CE3EI]Cl. Solutions were kept open to air at 298 K before and during testing.

	II Conc	R	Re	CPE <sub>f</sub>		R	CPE <sub>dl</sub>		R	n	Chi-
	(mM)	$(\Omega.cm^2)$	$(\Omega.cm^2)$	$n_f$	$C_f$ (µF.cm <sup>-2</sup> )	$(\Omega.cm^2)$	n <sub>dl</sub>	$C_{dl}$ (µF.cm <sup>-2</sup> )	$(\Omega.cm^2)$	(%)	square ×10 <sup>5</sup>
Blank	0	2.34±0.97	-	-	-	73.11±11.31	0.87±0.08	34.042±6.90	73.11	-	12.07±2.82
[CE1EI]Cl	0.5	3.68±0.33	96.08±10.30	0.85±0.01	24.377±1.60	184.00±9.51	0.62±0.00	1.8373±0.05	280.08	73.90	8.91±3.55
	1	3.37±0.12	75.62±6.43	0.86±0.01	20.248±0.11	236.70±6.99	0.62±0.01	1.5040±0.03	312.32	76.59	8.24±2.20
	2	3.10±0.02	91.37±6.31	0.85±0.00	20.491±0.89	272.40±25.3	0.62±0.03	1.5843±0.11	363.77	79.90	8.23±0.91
	4	2.87±0.22	97.23±1.10	0.87±0.01	17.858±0.50	385.70±0.46	0.63±0.03	1.7757±0.09	482.93	84.86	14.4±0.04
	0.5	3.40±0.66	178.10±16.01	0.86±0.00	23.048±1.10	243.40±15.62	0.74±0.02	6.2307±0.73	421.50	82.65	8.65±5.92
	1	2.57±0.53	165.30±11.08	0.86±0.01	18.058±1.73	279.20±30.2	0.72±0.00	3.4202±0.38	444.50	83.55	6.53±0.66
[CE3EI]CI	2	2.83±0.62	180.20±10.77	0.86±0.01	18.097±3.03	311.70±3.75	0.74±0.05	4.0485±0.44	491.90	85.14	8.63±1.11
	4	2.84±0.53	200.30±8.84	0.87±0.01	15.385±1.55	437.10±3.75	0.72±0.03	2.8403±0.11	637.40	88.53	17.4±2.68

The parameter n in the above equations indicates whether the CPEs behaved similarly to a resistance (n = 0), capacitor (n = 1), or diffusion element (n = 0.5) [10,66]. Reported in Table 3, the estimated values for  $n_f$  indicated that the surface films formed by the ILs functioned as nonideal capacitors, with no significant difference in their performance; meanwhile, the nature of the electrode/electrolyte interfaces regarding the  $n_{dl}$  values shifted from capacitive performance for steel in the blank solution toward diffusion-based performance for the inhibitor-containing solutions. This implies that the IL adsorption restricted the movement of chemical species toward or away from the metal-electrolyte interfaces. Furthermore, the reformation of the EDL was dependent on IL type. For [CE1EI]Cl, the  $n_{dl}$  values were closer to 0.5, showing that the IL probably due to its smaller size were adsorbed more homogeneously and made superior diffusion barriers against corrosive species. The decrease in  $C_{dl}$  further support this, because ,according to Helmholtz's equation, a reduction in dielectric constant at the EDL formed on a corroding metal surface is pertinent to the thickening of protective surface layers, reducing reactive surface areas, or adsorbing species that lower the local dielectric constants (as organic inhibitors) [5,67].

The value of total resistance  $(R_t)$  was calculated by summing  $R_f$  and  $R_{ct}$ . The observed improvements in  $R_t$  with the addition of the ILs into 0.5 M HCl also suggested that the active sites of the steel electrodes decreased effectively by the protective films of the adsorbed IL molecules, and such performance isolated the steel surfaces from surrounding corrosive environments [61,68]. In inhibited solutions,  $R_{ct}$  values were higher than corresponding  $R_f$ , implying that steel corrosion in the acid-IL systems were under the control of charge transfers [69].

The inhibition efficiency of the ILs was calculated by the following equation, Eq. 5 [7,10]:

$$\eta_i = (1 - \frac{R_t^0}{R_t}) \times 100$$
Eq. 5

where  $R_t^0$  and  $R_t$  refer to the total AC resistance of the steel electrodes in 0.5 M HCl in the absence and presence of the inhibitors, respectively. The value of the calculated efficiencies revealed that the protection of [CE3EI]Cl was more pronounced in each investigated concentration, likely as a result of better electronic exchanges. The EIS results showed good coordination with the polarization results in a general sense.

#### **Adsorption analysis**

The effectiveness of organic inhibitors substantially relies on their adsorptive behavior on metal surfaces. Adsorption isotherms serve as convenient useful models to describe inhibitor adsorption modes: physical, chemical, or physicochemical, albeit some concerns about proxies by which they are calculated [70]. Langmuir, Frumkin, Frendlich, Temkin, Flory-Huggins, and Villamil isotherms have been frequently used to evaluate the adsorptive characteristics of inhibitors. These isotherms were applied to assess the adsorption mode of [CE1EI]Cl and [CE3EI]Cl, among which Langmuir isotherm, Eq. 6, and Villamil isotherm, Eq. 7, showed the best fit.

$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}}$$
Eq. 6

$$\frac{C_{inh}}{\theta} = mC_{inh} + \frac{m}{K_{ads}}$$
 Eq. 7

In above equations [10],  $C_{inh}$  is inhibitor concentration and  $\theta$  the amount of surface coverage by inhibitor adsorption; *m* stands for the number of active sites blocked by an inhibitor molecule or protective layers created on the surface by adsorbed inhibitor molecules;  $K_{ads}$  is equal to adsorption equilibrium constant. Parameter  $\theta$  was approximated by Eq. 8, assuming that the change in  $i_{corr}$  and  $R_{ct}$  in the presence of the inhibitors, determined from PDP and EIS tests, was correlated with the surface coverage of the active points of the substrate [71].

$$\theta = \frac{\eta_i}{100}$$
 or  $\theta = \frac{\eta_{EIS}}{100}$  Eq. 8

#### Fig. 5

Given the slope values obtained from the linear regressions in Fig. 5, Villamil's isotherm proved to be marginally more appropriate than the Langmuir isotherm, as the latter is typically used when

the slope is precisely equal to one; however,  $K_{ads}$  and standard free energy ( $\Delta G_{ads}^o$ ) were estimated for both isotherms, the results of which are presented in Table 4. Eq. 9 was used to calculate the  $\Delta G_{ads}^o$  values [10]:

$$\frac{\Delta G_{ads}^o}{RT} = \ln \left(55.5 \times K_{ads}\right)$$
 Eq. 9

where *R* is the universal gas constant (8.314  $JK^{-1}mol^{-1}$ ), *T* absolute temperature in Kelvin, and 55.5 the molarity of pure water.

Considering the results of adsorption modeling in Table 4, the obtained negative  $\Delta G_{ads}^o$  values implied spontaneous adsorption of the ILs. Furthermore, all the values were around -30 KJ/mol, indicating that the adsorption of the ILs on mild steel was less likely to involve chemical interactions. Probably, physicochemical phenomena (electrostatic interaction as well as electronsharing) was the dominant mechanism that provided the inhibition [10,72]. In addition, the comparatively lower values found for [CE3EI]Cl reflected the formation of more stable IL-surface complexes for this inhibitor, which may explain its better anticorrosion performance.

Adsorption isotherm	IL	proxy to calculate $\theta$	$K_{ads} \ (\mathrm{mol}^{-1})$	$\Delta G_{ads}^{\circ}$ (KJ/mol)
		i <sub>corr</sub>	2787.14	-29.60
Lonomuin		R <sub>ct</sub>	6856.32	-31.84
Langmuir		i <sub>corr</sub>	9163.93	-32.55
		R <sub>ct</sub>	13121.25	-33.44
		i <sub>corr</sub>	3269.92	-30.00
Willowil		R <sub>ct</sub>	7876.19	-32.18
Villamil		i <sub>corr</sub>	10626.29	-32.92
		R <sub>ct</sub>	14633.36	-33.71

Table 4. Adsorption parameters calculated using PDP and EIS results for the ILs

**FTIR** analysis

The chemistry of the synthesized ILs and their adsorptive behavior toward mild steel immersed in 0.5 M HCl were experimentally investigated using FTIR spectroscopy. Fig. 6 shows the IR spectra of the ILs. The imidazolium substituent of the ILs became detectable with the strong stretching vibrations of N-C=C which appeared at 1637 cm<sup>-1</sup> in both spectra [73]. Multiple peaks and shoulders revealed the nature of the lateral structures connected to the imidazolium rings. The -CH<sub>2</sub>- deformation vibrations at 1455 cm<sup>-1</sup> and the C-C skeletal vibrations at around 755 cm<sup>-1</sup> were associated with alkene carbons in the side chains [73]. The peaks measured at  $1082 \text{ cm}^{-1}$  for [CE1EI]Cl and 1079 cm<sup>-1</sup> for [CE3EI]Cl were likely to result from asymmetric stretching of CH<sub>2</sub>-O-CH<sub>2</sub>, suggesting that the side chains contained ether groups as well [73]. The C-Cl at the end of the side chains was also distinguished regarding the peaks observed at 864 and 824  $cm^{-1}$  and the shoulders found at 1020 and 1039 cm<sup>-1</sup> in the [CE1EI]Cl and [CE3EI]Cl spectrum, respectively [73,74]. Several peaks were, in addition, found at the range of 2840-3080 cm<sup>-1</sup>. The peaks located at 2840–2950 cm<sup>-1</sup> were more referable to the symmetric and asymmetric stretching and in-plane bending vibrations of C–H, and the peaks within the range of 2950–3080 were more likely to arise from CH–Cl stretching vibrations [73,75,76].

The FTIR spectra of mild steel treated with the inhibited solutions are also shown in Fig. 6 (pink lines). The peaks representing imidazolium ring, 1626 cm<sup>-1</sup> in the presence of [CE1EI]Cl and 1630 cm<sup>-1</sup> in the presence of [CE3EI]Cl, were detected on the surface; additionally, the –CH<sub>2</sub>– deformation vibrations of the aliphatic-like components at 1462 cm<sup>-1</sup> ([CE1EI]Cl) and at 1461 cm<sup>-1</sup> ([CE3EI]Cl) proved the carbon-based side chains. The asymmetric ether vibrations at 1168 cm<sup>-1</sup> ([CE1EI]Cl) and 1163 cm<sup>-1</sup> ([CE3EI]Cl) were also implied the presence of C–O–C bonds in the side chains. Moreover, pronounced peaks at 1021 cm<sup>-1</sup> disclosed the C–Cl (the chloro-ethoxy wings) adsorbed. As seen, the obtained IR spectra exhibited similar peaks to those found for the synthesized ILs, which generally indicates that the IL adsorption led to corrosion inhibition.

Other than the above-mentioned characteristic features, two series of FTIR bands were measured in all cases studied. The O–H peaks at around 3500 cm<sup>-1</sup>—resulted from adsorbed water molecules, hydrated iron oxyhydroxides, or H-bonded species [73,77]—and the conspicuous IR absorption bands at the wavenumber range of 2000–2100 cm<sup>-1</sup>. The latter was probably related to the anion-cation interaction of the ILs [78]. The IR absorption features were evident in the IL spectra both separately and as adsorbates on the substrate, suggesting that the IL or solution anion (Cl<sup>-</sup>) and the imidazolium-based cations not only were simultaneously present at the metalsolution interface, but also linked to each other. The performance could indicate cooperative inhibition mechanisms, and as it is normal, the mutual adsorption caused minor shifts toward lower frequencies (energies) from around 2100 to 2000 cm<sup>-1</sup>.

### Fig. 6

#### **FE-SEM observations**

FE-SEM analysis of steel surface after 1 hour of exposure to 0.5 M HCl solution in the absence and presence of the inhibitors was carried out to demonstrate corrosion morphology and to confirm the electrochemical inhibition results. As shown in Fig. 7 (a, d), the steel surface in contact with the blank solution experienced severe corrosion through local and general dissolution, visible in the form of pits and accumulated covering oxides on the surface. The addition of inhibitors at a 4 mM concentration significantly decreased the level of corrosion. Fig. 7 (b, c, e, f) show that the steel corrosion resistance was more enhanced by [CE3EI]Cl. However, both ILs beneficially prevented pit nucleation and growth.

#### Fig. 7

# X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was employed to further investigate the bonding nature of the formed inhibitive films on the mild steel surface. Fig. 8 displays the full-spectrum photo-electron

data of mild steel exposed for 1 hour to 0.5 M HCl in the presence of [CE1EI]Cl and [CE3EI]Cl. As the XPS investigations were carried out without maintaining oxygen-free conditions and after rinsing the samples with water to remove solution residues, the O peaks were the most salient among the detected chemicals; in addition, the physically-adsorbed adsorbates were less likely to remain on the surface, which could bring about some intensity reductions. Therefore, the spectral data mostly represented the species precipitated or adsorbed through strong interplays with the surface.

# Fig. 8

The high-resolution XPS data along with the deconvoluted curves for each chemical species (C 1s, O 1s, Cl 2p, N 1s, and Fe 2p) are shown in Fig. 9. The C 1s spectra consisted of four photoelectron peaks associated with the ILs, all confirming the presence of the inhibitors on the mild steel surface, as previously observed by IR spectroscopy. The peaks seen at 284.5 and 284.6 eV were attributable to C–C and C–H bonds of the cationic moieties of the ILs [79], and the peaks at 287.5 eV and 286.9 eV indicated C-O binding energies for [CE1EI]Cl and [CE3EI]Cl, respectively [80]. The intensity of the IL-related peaks was correlated to the IL chemical structures—that is, the larger chloro-ethoxy chain of [CE3EI]Cl exhibited increased signal strength for C-C, C-H, and C-O. The C=N<sup>+</sup> binding energy arising from imidazolium ring, and representing the number of IL cations on the surface appeared almost with the same height and area for both ILs at 288.5 eV [81]. This observation did not reinforce the idea that the larger IL ([CE3EI]Cl) retarded the corrosion by fewer adsorbed molecules. The detected peaks of C–N and C-Cl overlapped each other and emerged at 285.75±0.05 eV [81,82], which limited drawing conclusive results about the mechanism of protecting the surface. Other than chloro- constituents of the IL cations, potential interactions between Cl<sup>-</sup> and the surface carbon of mild steel, and cooperative inhibition mechanism of pre-adsorbed Cl<sup>-</sup> and the IL cations (see the ab initio results) developed the C-Cl XPS count rates plausibly. In the same way, even though Fe...C photoelectrons

(at 282.7 for [CE1EI]Cl and at 283.3 for [CE3EI]Cl) had possibilities to result from (direct) interactions among the IL cations and surface Fe atoms, because their intensities accorded with the inhibition efficiencies obtained from the electrochemical measurements, they were attributable to the iron carbides of the mild steel substrate as well [83,84].

The XPS spectra of O 1s mostly represented surface oxyhydroxides, any mixed of oxides and hydroxides. The peaks deconvoluted at 532 eV were related to the compounds containing OH<sup>-</sup> as FeOOH, and the peaks deconvoluted at 530.7 eV the compounds containing  $O^{2-}$ , mainly Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> [85,86]. Although the formation of Fe (hydr)oxides substantially occurred during the rinsing and transfer process of the samples from test solutions to XPS chamber, their overall intensity were consistent with the corrosion inhibition order obtained using electrochemical methods: [CE3EI]Cl, with higher surface blockage, had better inhibitory effects on the formation of the rust species compared to [CE1EI]Cl. The bonds found at 534 eV for [CE1EI]Cl and at 533.5 eV for [CE3EI]Cl were taken into consideration to have a comprehensive analysis of the O 1s spectra. There was only a minor difference between the two samples in this case. C–O from the ILs and H–O–H from water molecules or complex compounds of Fe oxyhydroxides likely contributed to create the same peaks [87,88].

#### Fig. 9

The deconvolution of Cl 2p spectra revealed the presence of different types of Cl on the corroded metallic surfaces. The peak at 200.5 eV (Cl 2p3/2) in the [CE1EI]Cl spectrum, and similarly, the peak at 200.6 eV in the [CE3EI]Cl spectrum indicated the existence of organic chloride, or C–Cl bonds [89]; nonetheless, as previously mentioned, the carbon-chlorine peaks were likely to be received from different compounds or interactions, limiting presenting definitive results. The other deconvoluted Cl curves in the 2p1/2 region suggested two states for adsorbed Cl<sup>-</sup> anions. The one found at the higher binding energies (198.55±0.05 eV) demonstrated Cl<sup>-</sup> in a local more positive

environment like N<sup>+</sup>...Cl<sup>-</sup> [89], which presumably was pertinent to cooperative adsorption mechanisms involving Cl<sup>-</sup> and the imidazolium components of the IL cations, and the peaks calculated at 197.3 eV in the [CE1EI]Cl spectrum and at 197.1 eV in the [CE3EI]Cl spectrum corresponded to the physically adsorbed Cl<sup>-</sup> on the metal surface [90], which illuminates a decorated surface by chloride ions as found previously in ref. [18].

The N 1s XPS spectra also verified the presence of the inhibitors on and their interactions with the steel surface. The peaks found at 397.4 eV and 400.1 eV for [CE1EI]Cl, and at 396.5 eV and 400.6 eV for [CE3EI]Cl revealed C–N and C=N<sup>+</sup> binding energies, respectively [91,92]. Of greater importance, the XPS peaks distinguished at 398.6 eV for [CE1EI]Cl, and 399.2 eV for [CE3EI]Cl were related to N and Fe interactions (N...Fe) [91,92], which not only evidences the protective layers of the IL cations through direct interactions with the metal surface, but also suggested that the IL cationic moieties were more likely to have adsorption orientations leading to imidazolium-Fe Coordinations. Additionally, it was observed from the figures that there were indispensable peaks at around 402 eV which were associated with N<sup>+</sup>...Cl<sup>-</sup> [89]. As mentioned in the interpretation of Cl 2p spectra, these peaks could be indicative of indirect interactions between the IL cations with corroding surfaces, mediated by Cl<sup>-</sup>, further justifying the anodic predominance of the inhibition performance of the ILs.

The given XPS spectra of Fe 2p for [CE1EI]Cl and [CE3EI]Cl demonstrated several peaks and consisted of two doublets approximately at 709 eV (Fe 2p3/2) and 723 eV (Fe 2p1/2); in addition, two satellite Fe peaks were assigned at 718.2 eV in the [CE1EI]Cl spectrum and at 717.7 eV in the [CE3EI]Cl spectrum to have better fit results [93,94]. The deconvoluted peaks revealed metallic Fe peaks for the ILs at 705.9 eV and 706.1 eV [95], albeit with a meaningful difference. The lower intensity and area of the Fe<sup>0</sup> peaks for [CE3EI]Cl proved that the larger IL covered mild steel surface more efficiently, thus protecting it from corrosion and the electrochemical measurements showed the higher efficiencies. Two peaks were found for each species of ionic forms of Fe,

substantially related to the type of corrosion products accumulated on the surfaces. The peaks at 709.1 and 722.1 eV in the [CE1EI]Cl spectrum and at 709.27 and 722.6 in the [CE3EI]Cl spectrum were attributed to compounds with Fe<sup>2+</sup>, and those located at 711.5 and 724.3 eV in the [CE1EI]Cl spectrum and at 711 and 724.5 eV in the [CE3EI]Cl spectrum were attributed to the compound containing Fe<sup>3+</sup> [80,85,96]. Considering, FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and FeOOH, the commonest composition of iron rust, it seems that FeO and marginally Fe<sub>3</sub>O<sub>4</sub> formed the main portion of the surface iron (hydr)oxides – since Fe in Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and FeOOH has higher oxidation state than FeO. Despite this, the amount of such (hydr)oxides according to corresponding peaks were generally lower for [CE3EI]Cl in comparison with [CE1EI]Cl, which is in great agreement with the inhibition obtained.

#### **Ab-initio results**

Ab initio calculations were conducted to reveal the electronic properties of the isolated cations of [CE1EI]Cl and [CE3EI]Cl, and also to find correlations between the adsorptive behavior of the IL moieties and the inhibition efficiencies measured by the experimental investigations.

# DFT parameters of isolated IL cations

The electron density distribution of the frontier orbitals of isolated [CE1EI]<sup>+</sup> and [CE3EI]<sup>+</sup> after structural optimization is shown in Fig. 10 and Fig. S. 1. The most electronically active points of inhibitor molecules are typically attributed to the lowest unoccupied molecular orbitals (LUMO) and the highest occupied molecular orbitals (HOMO). For the cationic moieties studied, LUMO is mainly distributed on the positively charged imidazolium rings, as anticipated. However, the location of HOMO depends on the length (chemistry) of the lateral chloro-ethoxy chains. The HOMO of [CE1EI]<sup>+</sup> is mostly concentrated at the chloro– components at the end of the wings, while it is mostly located around the farthest oxygen for [CE3EI]<sup>+</sup>. These DFT-provided results

indicate that the ILs had different potential adsorption centers when interacting with the steel substrate as electron-donating adsorbates.

Fig. 10 and Fig. S. 1 also show the results of condensed Fukui functions, quantitative local equivalents to the HOMO and LUMO described above. The functions were computed using finite difference approximation as follows using Eq. 10-11 [97]:

$$f_k^+ = q_k(N+1) - q_k(N)$$
 Eq. 10

$$f_k^- = q_k(N) - q_k(N-1)$$
 Eq. 11

where  $f_k^+$  and  $f_k^-$  represent electrophilic and nucleophilic tendencies of the inhibitor cationic moieties to a reagent, here the metal surface.  $q_k(N + 1)$ ,  $q_k(N)$ , and  $q_k(N - 1)$  are the atomic charge of the  $k^{th}$  atom of the IL cations at their so-called anionic (with N + 1 electrons), neutral (with N electrons), and cationic (with N - 1 electrons) forms, respectively. It should be noted that the geometry of each chemical structure after optimization with N electrons was constrained to calculate the atomic charges of the other two species with N + 1 or N - 1 electrons.

The obtained  $f_k^+$  indices elucidate that there is almost no difference between the reactivity of the imidazolium substituents of [CE1EI]<sup>+</sup> and [CE3EI]<sup>+</sup>. The carbon located between two nitrogen atoms of imidazolium can have maximum reaction chance for receiving electrons in a nucleophilic interaction by vacant metal orbitals. Interestingly, even the hydrogens of the aromatic rings appear reactive enough to participate in taking electrons. The  $f_k^-$  indices differ from the HOMO spatial analysis to some extent, probably because of the approximations needed to equate the electron density and atomic charge. While the HOMO distributions in both molecular cases show the

neighboring carbons (adjacent to the HOMO center) as likely candidates for electron sharing following the initial involvement of the central constituents, the  $f_k^-$  reactivity indices suggest the neighboring oxygen and chlorine atoms may participate in such interactions. Noteworthily, in the case of [CE3EI]<sup>+</sup>, only two of the oxygens demonstrated capabilities for electronic interactions in an electrophilic attack, or more specifically, most of the atoms between imidazolium and the middle oxygen of the long chloro-ethoxy wings may have little, if any, impacts on electron-donating interactions.

 $E_{HOMO}$  and  $E_{LUMO}$  (the energy values of HOMO and LUMO), and  $\mu$  (dipole moment) were obtained from the DFT-based optimizations of the standalone cationic moieties. Subsequently,  $\Delta E$ (band-gap energy), h (chemical hardness), s (chemical softness),  $\tilde{\chi}$  (the electronegativity index approximated using HOMO–LUMO eigenvalues), and  $\Delta N$  (electron transfer estimation) were calculated using Eq. 12–16 [98]:

$$h \approx \frac{\Delta E}{2}$$
 Eq. 13

$$s = \frac{1}{h}$$
 Eq. 14

$$\tilde{\chi} = \frac{-E_{\rm HOMO} + E_{\rm LUMO}}{2}$$
 Eq. 15

$$\Delta N = \frac{\tilde{\chi}_{\rm Fe} - \tilde{\chi}_{inh}}{\Delta E_{\rm Fe} - \Delta E_{inh}}$$
Eq. 16

where  $\tilde{\chi}_{Fe}$  (Fe electronegativity estimation) was assumed equal to the work function of polycrystalline Fe film (4.5 eV) [99], and  $\Delta E_{Fe}$  (Fe energy gap) was set to 0 on account of the fact that metals have no band-gap; that is, the energy values of HOMO and LUMO for metallic materials are assumed the same as the Fermi energy. Molecular parameters calculated by the first principles method are listed in Table 5. In accordance with frontier molecular orbital theory, the exchange of electrons through interactions between the HOMO and LUMO of reacting chemical agents controls the stability of possible transition states [55].  $E_{\rm HOMO}$  corresponds to the electron-donation ability, and  $E_{\rm LUMO}$  to the electron-acceptance ability of a chemical [100]. Larger values of  $|E_{\rm HOMO}|$  and smaller values of  $|E_{\rm LUMO}|$  for an inhibitor indicate its enhanced capacity for electron transfer to or sharing with a metal substrate (through donation and backdonation), provided that the energy value of the anti-bonding orbitals of HOMO (the energy values of bonding orbitals of LUMO) of the inhibitor is not lower (higher) than the Fermi energy of the metal substrate [34]. Regarding the eigenvalues reported in Table 5, [CE3EI]<sup>+</sup> had more capability for sharing valence electrons with the vacant d orbital of the Fe substrate, which is in agreement with the electronic capacity of the larger molecule. However, the comparable  $E_{\rm LUMO}$  values of the cationic moieties are comparable suggest that feedback-coordinating bonds were equally feasible for both cations.

Table 5. Quantum chemical parameters calculated for [CE1EI] <sup>+</sup> and [CE3EI] <sup>+</sup> in vacuum	solvent
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IL cation	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)	ΔE (eV)	μ (Debye)	h (eV)	s (eV)	$\widetilde{\chi}_{(eV)}$	ΔN
[CE1EI] <sup>+</sup>	-10.38	-5.34	5.04	7.68	2.52	0.40	7.86	-0.67
[CE3EI]+	-9.02	-5.20	3.82	15.55	1.91	0.52	7.11	-0.68

 $\Delta E$  (band-gap energy) is the most reliable measure of chemical reactivity where its lower values hint potentially stronger physicochemical interactions, and as a result better adsorption/protection performance [101]. In this study, the  $\Delta E$  value of [CE3EI]<sup>+</sup> was 1.22 eV (117 KJ.mol<sup>-1</sup>) lower than that of [CE1EI]<sup>+</sup>, predicting superior inhibitor-steel interactions for the larger cationic moiety.

Dipole moment  $\mu$  represents the polarity of a molecule, which can demonstrate the probability of inhibitor adsorption through electrostatic interactions [5]. The value calculated for [CE3EI]<sup>+</sup> is approximately twice that for [CE1EI]<sup>+</sup>. This means that the larger inhibitor cation is a more polar

molecule, consistent with the nature of the longer chloro-ethoxy wings it has. In addition, as  $\mu$  is an indicator for molecular hydrophobicity-hydrophilicity, [CE3EI]<sup>+</sup> compared to [CE1EI]<sup>+</sup> (irrespective of its size negative effects) had more capability for being present at the metalelectrolyte interface.

Defined as the second derivative of energy to the electron number, h (chemical hardness) is a theoretical concept closely related to molecular polarizability and can be estimated by Eq. 13. The lower the value of h, the easier it is for the molecule to be polarized [102]. By contrast, higher values of s (chemical softness defined as the reciprocal of hardness) indicate easier interactions at inhibitor-metal interfaces. Respecting these parameters, [CE3EI]<sup>+</sup> were more probable to act desirably as an inhibitor into the bargain.

The interpretation of the electronegativity index  $(\tilde{\chi})$  should be made regarding the nature of inhibitors. With this, organic molecules with higher electronegativity can be superior inhibitors if they take electrons from metal substrates to moderate corrosion, and inferior ones if they give electron to metal substrates to prevent corrosion. The cationic nature of [CE1EI]<sup>+</sup> and [CE3EI]<sup>+</sup> might suggest that their corrosion inhibition may be more likely to occur through electron-backdonation. Based on this aspect, the smaller  $\tilde{\chi}$  value obtained for [CE3EI]<sup>+</sup> implies weaker inhibitory effects for [CE3EI]Cl. This is likely due to the larger chloro-ethoxy chains of [CE3EI]<sup>+</sup> which may better compensate for the election deficiency of the imidazolium ring. Therefore, global parameters like  $\tilde{\chi}$  should be considered more carefully, because they do not consider the electronic capacity of inhibitor molecules where components could potentially counteract each other's effects.

The results obtained for  $\Delta N$  (electron transfer estimation) indicate that both cations were capable of accepting electrons from the steel substrate. Notably,  $\Delta N$  estimations heavily rely on the considered value of  $\tilde{\chi}_{Fe}$ ; consequently, the calculated values could serve as qualitative estimations of real electron transfers. However, withdrawing electrons by the IL cations was very similar and less than one, meaning that chemical reactions were less probable through adsorption on Fe.

On the basis of the DFT parameters evaluated for the isolated forms of the cationic moieties, [CE3EI]<sup>+</sup> exhibited higher reactivity and had a greater potential for constructive interactions with the substrate, which is in harmony with the PDP and EIS experimental results.

# Competitive adsorption-inhibition

There is always a competition between dissolved corrosive and inhibitive species for interaction with metal substrates. Hence, to gain insight into the adsorptive behavior of the cationic moieties and corrosive agents on the surface, the ab-initio method was employed. Experimental evidence has shown that inhibitor molecules can adsorb on a metal surface in different configurations, regarding the coordination modes they can adopt with the surface [21,103–106]. In light of this probability, five adsorption configurations (C1, C2, ..., C5) for each IL cation were considered as shown in Fig. 11, and corresponding adsorption energies were estimated using the following equation:

$$E_{ads} = E_{mol/Fe(110)} - E_{Fe(110)} - E_{mol}$$
 Eq. 17

where the subscripts mol/Fe(110), Fe(110), and mol represent the energy values obtained for the  $\frac{molecule}{Fe(110)}$  system, the clean Fe(110) surface, and the adsorbed species, respectively. Table 6 shows the resulting  $E_{ads}$  values. The negativity of the obtained values confirms that corrosion was controlled by the exothermic (spontaneous) adsorption when the cationic moieties adsorbed directly on mild steel. The most thermodynamically stable adsorption (the lowest  $E_{ads}$ ) was found for [CE3EI]<sup>+</sup> at C4 configuration. It is incontrovertible that the longer side chains of ethoxy groups enabled the molecule to make further hybridized orbitals with the surface, thereby creating superior protective coverage on the substrate. However, assessing the other possible adsorption configurations elaborated that such long chloro-ethoxy wings were also likely to create limitations depending on the orientation in which the cations approached the metal surface.

#### Fig. 11

Table 6. Adsorption energy of the IL cations on Fe (110) surface

	$E_{ads}$ (eV)									
IL cation/configuration	C1	C2	C3	C4	C5					
[CE1EI] <sup>+</sup>	-4.109	- 3.814	- 4.673	- 5.172	-4.854					
[CE3EI] <sup>+</sup>	- 3.871	-4.377	-4.046	-6.352	-5.847					

Based on the calculated  $E_{ads}$  values , both [CE1EI]<sup>+</sup> and [CE3EI]<sup>+</sup> at C4 and C5 configurations bind the strongest to the Fe surface. The mutual feature of these configurations is that the frontier orbitals of the cations in isolated form (HOMO and LUMO before adsorption, refer to Fig. 10 and Fig. S. 1) had the most proper position (nearest distance) to donate/accept electrons to/from the surface. To validate, consider the C3 configurations. During the relaxation, the adsorbing cations changed their initial geometries toward the surface to have maximum interactions with it. [CE1EI]+ underwent considerable bending and [CE3EI]<sup>+</sup> adjusted its molecular angles within the chloroethoxy chains to bring the distant frontier orbitals as close as possible to the Fe surface atoms. According to Table 6, C5 configuration was the second most favorable situation, with subtle orientational differences from C4. In a comparison between the initial position of C4 and C5 configurations (Fig. S. 2), the chloro-ethoxy substituents were positioned at similar distances from the surface, even though in C4 configuration, chlorine and oxygen atoms were slightly farther due to molecular asymmetry. Within the quantum relaxation periods, however, side chains and especially Cl atoms approached themselves to the surface, and finally, the size effects (electronic capacity) of the wings had more noticeable effects than the distance from the surface, which led to the stronger adsorption in C4 configuration. It should be pointed that the imidazolium rings

exhibited restricted deformations in C4 and C5 configurations. The central imidazolium constituents disposed their bonds with side chains to reach a flat configuration maximizing orbital sharing with the surface, but due to some limitations in deformation, at the end of the relaxation process, C4 configuration showed the lowest  $E_{ads}$ . This was probably because the most active elements of the imidazolium rings - that is, the carbon between two nitrogen, as confirmed by Fukui indices in Fig. 10 and Fig. S. 1- was relaxed closer to the metal surface, leading to the minimum  $E_{ads}$  values for both [CE1EI]<sup>+</sup> and [CE3EI]<sup>+</sup>. With these marginal differences between C4 and C5 configurations,  $|E_{ads}|$  decreased by 30–50 KJ.mol<sup>-1</sup>, which not only demonstrates the influence of the frontier orbital availability to the surface for better adsorption/coordination, but also verifies the significance of N atoms in the inhibition functionality of the cationic moieties.

Long substituents such as alkyl chains can boost inhibition performance thanks to their modification on solubility, the numerical and spatial aspects of the hybrid orbitals inhibitors created through interacting with vacant orbitals of metal surfaces, or the thickness of surface films formed by inhibitors at metal/solution interface [107]; at the same time, enlarging inhibitor molecules may limit corrosion protection by declining mobility and aggravating intermolecular repulsion in adsorption-desorption processes. The evaluation of C3 configuration herein clarified that the long chains of chloro-ethoxy in the case of [CE3EI]<sup>+</sup> had adverse effects on its adsorptive behavior. The longer lateral chains hindered optimal molecular deposition, which is essential for reducing molecule-surface bonding length and increasing desirable inhibitor-substrate interactions. Consequently, a reduction in the corresponding  $E_{ads}$  value for [CE3EI]<sup>+</sup> was observed. This issue can be another reason why long substituents increase the sensitivity of inhibition performance of inhibitor molecules to overconcentration [108].

The  $E_{ads}$  obtained for C1 configuration showed that half of the maximum possible energy release through the adsorption of the cations was achievable solely with the parallel orientation of imidazolium to the surface and without side chain contribution. This emphasizes on the essential role of covalent  $\pi$ -bonds in corrosion inhibition as mentioned by Hamidi et al. [109]. In the case of [CE3EI]<sup>+</sup>, however, the longer wings of chloro-ethoxy provided the adsorbing imidazolium ring with more electronic capacity, which make the adsorption less favored.

Similar simulations and  $E_{ads}$  calculations were performed for the corrosive species of the solution (water and Cl<sup>-</sup>), yielding results that align well with reference [42]:  $E_{ads_{water}} = -0.625$  eV and  $E_{ads_{Cl}} = -1.926$  eV. These results verified that the IL moieties were adsorbed stronger than the corrosive agents, even under the least favorable conditions of C1 and C2 configurations with the minimum adsorption energies.

To illustrate charge redistribution as a result of adsorption either within the cationic inhibitor molecules or between the adsorbates and Fe atoms, differential charge density,  $\rho_{ads}$ , was calculated by subtracting the charge densities of the adsorbed species,  $\rho_{mol}$ , and the clean adsorbent,  $\rho_{Fe(110)}$ , from the charge density of the adsorbate-adsorbent system,  $\rho_{mol/Fe(110)}$ , as follows:

$$\rho_{ads} = \rho_{mol/Fe(110)} - \rho_{Fe(110)} - \rho_{mol}$$
 Eq. 18

The detailed pictures of the analysis are presented in Fig. 11. Without regard to the difference in initial or relaxed configurations, the gap between the adsorbates and adsorbent filled with backdonated electrons. The adsorbates showed greater electronic variations compared to the underlying Fe atoms, primarily owing to the nature of the critical orbitals of the substrate atoms. Clearly, electron transfer is more pronounced wherever larger parts of the IL moieties were relaxed near to the Fe surface. Indeed, the atoms of the IL cations located far from the surface Fe atoms demonstrated little, if any, charge density changes. Concerning the C3 configuration of [CE3EI]<sup>+</sup>, the furthest ethoxy from the Fe slab showed the minimum possible charge density change, which means that the constituent did not effectively take part in the electronic exchange process—a

similar weak contribution for this section of the molecule was predicted by the Fukui functions in the isolated form in Fig. 10 and Fig. S. 1.

For a quantitative elucidation of the electron transfers, Bader charge analysis was conducted. Table 7 lists electron donation and backdonation by the IL cations and their constituents: the imidazolium ring and chloro-ethoxy wings. The negative values of the net molecular electron transfer values indicated that the direction of electron transfer was from metal to [CE1EI]<sup>+</sup> and [CE3EI]<sup>+</sup>, which is compatible with the positively charged (cationic) nature of the adsorbates, as well as previous studies [21,37,40–45]. It can be seen that the electron transfer values for [CE3EI]<sup>+</sup> are not always larger than those calculated for [CE1EI]<sup>+</sup>. However, the electron exchange (donation+backdonation) values of the larger cations ([CE3EI]<sup>+</sup>) are independently higher than those of the smaller cation, [CE1EI]<sup>+</sup>. It is certainly because of the higher amounts of electronic capabilities that the longer chloro-ethoxy chains can provide. Remarkably, despite being electrondeficient in their isolated forms, the imidazolium rings acted as electron donators when they were not initially perpendicular to the surface. Sharing the  $\pi$ -electrons was the main cause of such performance, as this type of orbitals of the cyclic components had more opportunity to engage with the Fe atoms in non-perpendicular orientations [21]. As a result, the assumption that molecular positive cores, even located at IL cationic moieties, consistently play a predictable constant role in interacting with d-orbital of Fe atoms may not always be accurate. Concerning the chloro-ethoxy chains, the constituents were electron acceptors in any case examined, contrary to the conclusions widely accepted in the pertinent papers traditionally claiming electron-donation for long C-based chains.

			[CE1EI] <sup>+</sup>		[CE3EI] <sup>+</sup>			
Configuration	electron transfer type	Total	imidazolium	Chloro- ethoxy chain	Total	imidazolium	Chloro- ethoxy chain	
C1	donation	+0.734	+0.501	+0.233	+2.696	+1.172	+1.524	
	backdonation	-0.985	-0.216	-0.769	-2.902	-0.112	-2.790	

Table 7. Bader charge difference with adsorption

	net	-0.251	+0.285	-0.536	-0.205	+1.060	-1.265
	donation	+0.751	+0.458	+0.292	+2.610	+1.209	+1.401
C2	backdonation	-0.940	-0.124	-0.815	-2.874	-0.116	-2.763
	net	-0.189	+0.334	-0.523	-0.264	+1.093	-1.357
	donation	+0.766	+0.434	+0.332	+2.792	+1.298	+1.495
C3	backdonation	-1.179	-0.085	-1.095	-2.904	-0.142	-2.762
	net	-0.413	+0.349	-0.763	-0.111	+1.156	-1.267
	donation	+0.260	+0.078	+0.182	+0.496	+0.084	+0.412
C4	backdonation	-0.608	-0.150	-0.458	-1.033	-0.197	-0.836
	net	-0.348	-0.072	-0.276	-0.537	-0.113	-0.425
C5	donation	+0.525	+0.201	+0.324	+0.601	+0.085	+0.515
	backdonation	-0.831	-0.262	-0.569	-0.965	-0.143	-0.822
	net	-0.306	-0.062	-0.244	-0.365	-0.058	-0.307

On an atomic scale, Bader charge analysis clarified that the IL cations should be considered as integrated electronic adsorbates. There was no distinct function for the N and O atoms in contrast to what has been repeatedly mentioned in the literature introducing them as inhibitor elements containing free electrons to share with corroding metal surfaces. More specifically, even though the oxygen atoms of the cations generally demonstrated an electron-donating character, the extent of their electron donation was not significant in the majority of the evaluated quantum conditions. Only Cl showed specific features: when Cl atoms were located far from the Fe surface, they released electrons to the surrounding atoms. Otherwise, Cl performed as an electron acceptor from the substrate Fe atoms. The spin-polarized (up and down) projected density of states (PDOS) was also calculated for the chloro- constituents before and after adsorption for different configurations (shown in Fig. 12). This analysis revealed that when the Cl atoms were near Fe surface (C3, C4, and C5 configurations), their orbitals shifted toward lower energy values (occupied orbitals moved further away from Fermi level and non-occupied ones toward Fermi level) and had many more broaden densities of p-states, and conversely when they had no close interaction with the Fe substrates, their orbitals shifted toward higher energy and did not undergo considerable change in electron density. In addition, further in-depth analysis suggested that, for the occupied orbitals, there was no preference between the orientation of the p-orbitals in space, but for the non-occupied
orbitals, the effect of the py orbital of the Cl components were more influential to a limited extent (Fig. 13).

# Fig. 12 Fig. 13

Cooperative adsorption-inhibition

Effect of anionic species upon corrosion protection by organic inhibitors seems undeniable [18,110]. If the negatively charged ions are corrosive, in addition, they primarily form anodic zones on a corroding metallic surface, with which inhibitors with (dominant) anodic performance can have a higher likelihood to interact. Taking this into account, the adsorptive behavior of [CE1EI]<sup>+</sup> and [CE3EI]<sup>+</sup> were evaluated considering a pre-adsorbed Cl<sup>-</sup> anion on the Fe supercell. The Cl<sup>-</sup> may originate from the corrosive solution such as HCl or the anionic moieties of the ILs in the cases studied here; thus, the results of this section describe quantum behavior of either cooperative adsorption of the IL cations and solution anions (the bridge mechanism of inhibition) or a synergistic inhibition mechanism resulted from the IL cationic-anionic moieties—both hereafter called indirect adsorption.

Eq. 17 and Eq. 18 were similarly utilized in the evaluation of indirect adsorption. The Fe(110)related data replaced by the data of a complex of Fe slab and a pre-adsorbed Cl<sup>-</sup>. Table 8, Table 9, and Fig. 14 present the results of molecular relaxation, charge density difference, and Bader charge analysis of two critical configurations of indirect adsorption. These configurations, denoted by C1\* and C4\*, were analogous to C1 and C4 of the previous section analyzing the direct adsorption of the IL cations. They were selected, for the inhibitor cations in C1 and C4 configurations exhibited the highest adsorption energy per unit area and the highest adsorption energy per molecule, respectively.

Table 8. Adsorption energy of the IL cations on Fe (110) surface in the presence of Cl<sup>-</sup>

		$-E_{ads}$ (eV)		
Adsorbed species/configuration		C1*	C4*	
[CE1EI]Cl	[CE1EI] <sup>+</sup>	6.793	8.403	
	Cl-	1.937	1.918	
[CE3EI]Cl	[CE3EI] <sup>+</sup>	6.739	9.489	
	Cl-	1.932	1.931	

Table 9. Bader charge change difference as a result of cooperative adsorption

		[CE1EI] <sup>+</sup>			[CE3EI] <sup>+</sup>		
configuration	electron transfer type	Total	imidazolium	Chloro-ethoxy chain	Total	imidazoliu m	Chloro -ethoxy chain
	donation	+1.878	+0.937	+0.941	+1.89 2	+0.527	+1.365
C1*	backdonatio n	-1.861	-0.600	-1.261	-1.94 0	-0.051	-1.889
	net	+0.017	+0.337	-0.320	-0.04 8	+0.476	-0.536
	donation	+1.816	+0.965	+0.851	+2.49 9	+1.040	+1.458
C4*	backdonatio n	-2.050	-0.633	-1.417	-2.94 8	-0.133	-2.811
	net	-0.234	+0.332	-0.566	-0.44 9	+0.907	-1.356

## Fig. 14

The calculations performed for C1\* and C4\* in Fig. 14 showed perceptible alterations in charge density compared to C1 and C2 counterparts. Evident electron depletion was seen at the interval of the cations and Fe surface where the pre-absorbed chloride anion was present. Reduction in the electron accumulation occurred throughout the adsorbate-adsorbent gaps. In addition, the affected depth at the focal point in the presence of Cl<sup>-</sup> exceeded to the third layer of Fe atoms. Table 8 explains that the adsorption energy of the IL cations increased in the presence of Cl<sup>-</sup>, and the cooperation/synergism led to the adsorption energy values that could not be achieved in direct interaction of IL cations with the surface. The results also revealed that the indirect adsorptive

performance of the IL cations had almost neutral effects on Cl<sup>-</sup> adsorption energies (NB: the adsorption energy of a single Cl<sup>-</sup> equals  $E_{ads_{Cl}-} = -1.926$  eV, as previously mentioned). Bader charge analysis of indirect adsorption yielded the same outcomes as the direct adsorption of the species suggested previously for molecular and elemental (N, O, and Cl) constituents. However, the analysis of net molecular electron transfer showed that [CE1EI]<sup>+</sup> donates mere electrons to the Fe-Cl<sup>-</sup> system and Cl atoms (chloro–) has a consistent electron-donator role only at close distances from the Fe substrates.

#### **Inhibition mechanisms**

Electrochemical degradation of steel in HCl mainly consists of partial electron-regulated reactions, Fe dissolution in anodic areas, Eq. 19–23, and hydrogen evaluation in cathodic areas, Eq. 24–26 [57]:

$Fe + Cl^- \rightleftharpoons [FeCl]_{ads}^-$	Eq	. 19

 $[\text{FeCl}]_{\text{ads}}^- \rightarrow [\text{FeCl}]_{\text{ads}} + e^-$  Eq. 20

$[\text{FeCl}]_{\text{ads}} + \text{Cl}^- \rightleftharpoons [\text{FeCl}_2]_{\text{ads}}^-$	Eq. 21

$$[\text{FeCl}_2]_{\text{ads}}^- \rightarrow [\text{FeCl}_2]_{\text{ads}} + e^-$$
 Eq. 22

$$[\text{FeCl}_2]_{ads} \rightarrow \text{Fe}^{++} + 2\text{Cl}^-$$
 Eq. 23

$$Fe + H^+ \rightleftharpoons [FeH]^+_{ads}$$
 Eq. 24

$$[FeH]_{ads}^+ + e^- \rightarrow [FeH]_{ads}$$
 Eq. 25

$$[FeH]_{ads} + H^+ + e^- \rightarrow Fe + H_2 \uparrow Eq. 26$$

Hydrochloric acid can destabilize metal oxyhydroxides by transforming them into corresponding chlorides, and the considerable solubility of  $Fe(Cl)_n$  complexes (where  $n \ge 2$ ) in aqueous solutions helps maintain the surface free of surface deposits. Under such circumstances, A competition between  $Cl^-$  and inhibitor species, herein [CE1EI]<sup>+</sup> and [CE3EI]<sup>+</sup>, to react with the surface controls

corrosion intensity and inhibition mechanism. The quantum-based illustrations, see section 0, revealed that even if Cl<sup>-</sup> anions may reach the surface first and make anodic sites, subsequent adsorption of the inhibitor cations cannot lead to Cl<sup>-</sup> desorption from the surface. Rather, the adsorption strength improves through stronger inhibitor-surface interactions (cooperation/synergism); Consequently, the anodic sites become effectively blocked, as experimental results suggested. It should be to noted that Chen et al. [111] simulated another adsorption mode: concurrent surface bonding of imidazolium-based IL cations and Cl<sup>-</sup>, but not on the same surface points. One should notice that such performance is not protective. Indeed, although the adsorbed IL cations restrict primary chloride attacks, Eq. 19, similar to what is expected in direct inhibitor adsorption, the separately adsorbed chlorides make the metal surface positively charged, susceptible to further electrostatic (columbic) interactions with other chlorides originating from solvents, Eq. 21, which ultimately leads to Fe dissolution (corrosion), Eq. 22–23 [112]. Moreover, theoretical results necessitate validation through experimental endorsements [41,113]. The type of adsorption that Chen and coworkers considered can give rise to cathodic inhibition, whereas almost all imidazolium-based ILs, like the ones studied in the present study, when come into contact with carbon steels have revealed otherwise, anodic predominance in inhibition.

Adsorption energy versus electron transfer (eT, the net value of electron donation andbackdonation<sup>1</sup>) and electron exchange (eE, the sum of absolute values of electron donation and backdonation<sup>2</sup>) calculated for [CE1EI]Cl and [CE3EI]Cl using the first-principles method are depicted in Fig. 15. It is possible to understand from the figures that the quantum-derived items are interdependent; none unconditionally can be a definitive indicator for superior corrosion protection on their own, due to the influence of adsorption configuration effects. The eT values

 $<sup>{}^{1}</sup> eT = e_{donation} - e_{backdonation}$   ${}^{2} eE = |e_{donation}| + |e_{backdonation}|$ 

always show a positive relationship with adsorption energy, independent of adsorption mode. However, corresponding eE values decrease when the inhibitor-surface interactions are stronger and increase when Cl<sup>-</sup> acts as an intermediate species. This could be attributed to the fact that fewer electronic balance processes are required to reach the most stable state when critical orbitals are located in the vicinity of the surface, or in the absence of Cl<sup>-</sup>. In addition, Fig. 15 (a) clarifies that the amount of the eT values is always lower than one, which aligns with the physicochemical nature of interaction/inhibition by the organic inhibitors.

#### Fig. 15

In contrast to the inhibition efficiencies determined experimentally, the quantum analysis reveals that [CE1EI]Cl adsorption in some cases may result in more favorable magnitudes compared to [CE3EI]Cl, depending on adsorption orientation. One strategy for addressing the discrepancies is to consider a distribution of inhibitor adsorption modes. However, in the cases studied using high-tech instruments thus far, adsorbed inhibitor molecules have exhibited nearly regular and repetitive adsorption/bonding patterns [103,104]. Therefore, it is more sensible to consider those DFT-based factors reliable for screening inhibitors when their predictions accord with experimental findings yet under the same adsorption configuration. With this assumption, eE is the only parameter – among those considered – that is able to successfully predict the superior inhibition function of [CE3EI]Cl, regardless of adsorption mode. It is noteworthy that the parameter can strike a balance between adsorption capability and potential steric limitations that may arise in configurations such as C3, thereby offering an acceptable discrimination between inhibition performance of the ILs, [CE1EI]Cl and [CE3EI]Cl.

The predictive performance of eE can be reasonably justified. To be protective, organic inhibitors generally do not necessarily need to engage in charge transfer interactions. Instead, their participation at the metal-electrolyte interface necessities electronic exchanges that hold them adsorbed onto the surface. Additionally, eE's quantum equivalent in the isolated form of inhibitors

(in the absence of the effects of the metal substrate) i.e. the Band-gap energy, which consider both the electron donation and acceptance capabilities of an organic inhibitor, has hitherto known as the most reliable criterion to compare inhibitory effects.  $\Delta E$  has consistently showed strong correlations with theoretical and experimental adsorption indices in organic inhibitor studies [37]. However, as it does not account for the effects of metal substrates and the deformations as well as orientational differences that occur during adsorption, eE can serve as a more comprehensive alternative. Furthermore, there might be a meaningful correlation between the difference in the eE values calculated theoretically and the difference in the corrosion efficiencies obtained experimentally for the ILs, particularly when the indirect adsorption results are regarded. Note that it is more likely to have molecular adsorption parallel to the surface (the highest adsorption energy per unit area, like C4 and C4\*) in lower concentrations and up-right adsorption configuration (the highest adsorption energy per molecule like C1 and C1\*) in higher concentrations. This may explain why the ILs exhibited more different inhibition efficiencies in lower concentrations like 0.5 mM, where the deference decreased by increasing concentration (see Table 2–3). The ability of the ILs to solely donate or accept electrons is also investigated (data available in Table 6–9), and the results suggest that electron backdonation, when considered individually, is comparable to *eE* in elucidating the adsorption/inhibition behavior, albeit the specific nature of the IL cations.

#### Conclusion

As corroborated by the experimental and theoretical results, it can be appreciated that the synthesized imidazolium-based ILs, designated by [CE1EI]Cl and [CE3EI]Cl herein, showed considerable potential to effectively protect mild steel against corrosion in 0.5 M HCl. The ILs exhibited mixed-type performance with more pronounced inhibition on the anodic regions where chlorides were pre-adsorbed. The larger chloro-ethoxy wings contributed to higher inhibition efficiency to some extent. Maximum corrosion inhibition at the concentration of 4 mM was

80.83% and 84.98% according to Potentiodynamic Polarization (PDP), and 84.86% and 88.53% according to Electrochemical Impedance Spectroscopy (EIS) for [CE1EI]Cl and [CE3EI]Cl, respectively. The spontaneous formation of a protecting one-layer film on the substrate, with releasing around 30 KJ/mol, hindered corrosion and its localization.

The ab-initio method disclosed that Fukui indices, calculated without considering metal effects, can help predict more stable adsorption states. Cooperative adsorption of the IL cations with Clwas so effective that it reduced the adsorption energy by approximately 300 kJ/mol compared to competitive adsorption values. The cationic moieties primarily acted as electron-withdrawing groups to inhibit corrosion; the net electron transfer did not exceed 0.54 e<sup>-</sup>, which confirms the physicochemical nature of the inhibitive interactions. The performance of chloro-ethoxy wings contradicted expectations, and this performance was independent of distance from the metal surface. More importantly, it was found that nitrogen and oxygen in the cationic moieties of the inhibitor chemicals did not have fixed characteristics in terms of electron donation/backdonation. Among the evaluated elements, chloride consistently showed capabilities of invariable interacting with Fe atoms as an electron-donor agent when it was located close to surface. The Py orbitals of the chloro- substituents seem to be the primary contributor to this function. Ultimately, 'electron exchange' derived from quantum calculation demonstrated the best features for differentiating the protective performance of the ILs, and it is recommend that the role of functional groups and atomic components of organic corrosion inhibitors should not be taken for granted.

## Acknowledgement

The authors would like to express their gratitude to AmirKabir University of Technology (AUT) for providing both financial and moral support (Grant No. 1243). SST thanks the UK Royal Society for an International Exchanges grant (IES\R3\223184).

This research utilized the ARCHER2 UK National Supercomputing Service (http://archer2.ac.uk) through our membership of the HEC Materials Chemistry Consortium, funded by EPSRC (grant EP/R029431) in the UK. The computational resources of the Advanced Research Computing at Cardiff (ARCCA) Division, Cardiff University, and HPC Wales were also employed for this study.

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# **Figure captions**

Fig 1. The chemical structures of synthesized ILs

**Fig 2.** OCP-time curves of mild steel in 0.5 M HCl, open to air at 298 K, in the absence and presence of different concentrations of [CE1EI]Cl (a) and [CE3EI]Cl (b)

**Fig 3.** Potentiodynamic polarization curves of mild steel in 0.5 M HCl, open to air at 298 K, in the absence and presence of different concentrations of [CE1EI]Cl (a) and [CE3EI]Cl (b)

**Fig 4.** Nyquist and Bode diagrams of mild steel in 0.5 M HCl, open to air at 298 K, in the absence and presence of different concentrations of [CE1EI]Cl (a, b) and [CE3EI]Cl (c, d)), the EEC used to fit the EIS data is also shown in b.

**Fig 5.** Langmuir/Villamil adsorption isotherm plots based on the data obtained from PDP(a) and EIS (b)

Fig 6. FT-IR spectra of the synthesized ILs, pure and adsorbed on mild steel

**Fig 7.** FE-SEM micrographs of mild steel surface exposed for 1 h to 0.5 M HCl, open to air at 298 K, without (a, d) and with 4 mM of [CE1EI]Cl (b, e) and [CE3EI]Cl (c, f)

**Fig 8.** Full-spectrum XPS data of mild steel surface exposed for 1 h to 0.5 M HCl, open to air at 298 K, containing 4 mM of [CE1EI]Cl and [CE3EI]Cl

**Fig 9.** High-energy resolution XPS spectra of mild steel surface exposed for 1 h to 0.5 M HCl, open to air at 298 K, containing 4 mM of [CE1EI]Cl (a-e) and [CE3EI]Cl (f-j)

**Fig 10.** Distribution of LUMO (a) and HOMO (b) and corresponding Fukui indices of [CE1EI]<sup>+</sup>. Green, gray, white, red, and orange circles are Cl, C, H, O, and N atoms, respectively.

**Fig 11.** Side view of [CE1EI]<sup>+</sup> and [CE3EI]<sup>+</sup> adsorbed directly on Fe (110) surface, with corresponding charge density difference in different configurations. Regions with electron accumulation/depletion are indicated in purple/yellow. Green, brown, white, red, orange, and blue spheres are Cl, C, H, O, N, and Fe atoms, respectively. The amount of net electron transfer of each elemental components—N, O, and Cl—were presented with positive (for electron donation) and negative (for electron backdonation) values. The initial configurations and corresponding top views of the adsorbed states are shown in Figs. S. 2 and S. 3, respectively.

**Fig 12.** Projected density of states (PDOS) of the chloro– constituents of [CE1EI]<sup>+</sup> (a) and [CE3EI]<sup>+</sup> (b) before and after adsorption in different configurations

**Fig 13.** Spin-polarized (up and down) PDOS of  $p_x$ ,  $p_y$ , and  $p_z$  orbitals of the chloro– constituents of [CE1EI]<sup>+</sup> (a, b, c) and [CE3EI]<sup>+</sup> (d, e, f) before and after adsorption in different configurations

**Fig 14.** Side view of [CE1EI]<sup>+</sup> and [CE3EI]<sup>+</sup> adsorbed indirectly (in the presence of a pre-adsorbed chloride) on Fe (110) surface, with corresponding charge density difference in different configurations. Regions with electron accumulation/depletion are indicated in purple/yellow. Green, brown, white, red, orange, and blue spheres are Cl, C, H, O, N, and Fe atoms, respectively. The amount of net electron transfer of each elemental components—N, O, and Cl—were presented with positive (for electron donation) and negative (for electron backdonation) values. The initial configurations are in Fig S. 2.

**Fig 15.** Probable correlation between adsorption energy and electron transfer/exchange. [CE1EI]Cl- and [CE3EI]Cl-related data are shown with pink and purple, respectively. Triangles

represent competitive adsorption data and diamonds represent cooperative adsorption. The trendlines were calculated after excluding the data of C3 configuration. To find the exact numerical values see Table 7–10.







Fig. 17



Fig. 19



Fig. 20



Fig. 21



Fig. 22



Fig. 23



Fig. 24







Fig. 25



Fig. 26



Fig. 27



Fig. 28



Fig. 29


Fig. 30

## **Supplementary material**

## Submolecular Insights into the Adsorption Mechanism of Imidazolium-based Corrosion Inhibitors: A Novel Quantum Parameter for Predicting Inhibition Superiority

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**Fig. S. 1.** Distribution of LUMO (a) and HOMO (b) and corresponding Fukui indices of [CE3EI]<sup>+</sup>. Green, gray, white, red, and orange circles are Cl, C, H, O, and N atoms, respectively.

0.00

-0.00



**Fig. S. 2.** Side view of the initial configurations considered for [CE1EI]<sup>+</sup> and [CE3EI]<sup>+</sup> to investigate adsorption on Fe (110). Green, brown, white, red, orange, and blue spheres are Cl, C, H, O, N, and Fe atoms, respectively.



**Fig. S. 3.** Top view of [CE1EI]+ and [CE3EI]+ adsorbed directly on Fe (110) surface, with corresponding charge density difference in different configurations. Regions with electron accumulation/depletion are indicated in purple/yellow. Green, brown, white, red, orange, and blue spheres are Cl, C, H, O, N, and Fe atoms, respectively.