



# Article Investigating the Corrosion Inhibition Mechanisms of Alkanolammonium Salts: A Case Study with Ethylethanolammonium 4-Nitrobenzoate on Carbon Steel in Saline Solution

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Abstract: This study explores the potential corrosion inhibition mechanisms of alkanolammonium salts, exemplified by ethylethanolammonium 4-nitrobenzoate (EEA4NB), for carbon steel, utilizing experimental and theoretical methods. The interactions between metal and inhibitor, focusing on adsorption behavior in saline solutions, will be thoroughly investigated. Analysis of potentiodynamic polarization curves and electrochemical impedance spectroscopy reveals that the inhibition efficiency (IE) increases with the rising concentration of EEA4NB, reaching 96% at  $5 \times 10^{-3}$  M. Negative adsorption free energy and a high adsorption equilibrium constant suggest the spontaneous formation of a protective inhibitor layer on the metal surface, effectively blocking reaction sites and reducing the corrosion rate, according to the Langmuir isotherms model. As confirmed by scanning electron microscopy, physical and chemical interactions contribute to the adsorption mechanisms. Quantum chemical calculations explore the relationship between EEA4NB molecular configuration and inhibition efficiencies. The study emphasizes the potential efficacy of alkanolammonium salts, exemplified by EEA4NB, as effective corrosion inhibitors for carbon steel in aggressive environments.

**Keywords:** corrosion inhibition; ethylethanolammonium 4-nitrobenzoate; carbon steel; 3% NaCl solution; electrochemical methods; computational methods

# 1. Introduction

Iron-based materials, renowned for their versatile mechanical and physical properties and cost-effectiveness, have found extensive applications across diverse industries, ranging from construction and naval sectors to industrial components for oil/gas extraction [1]. Despite their widespread use, a significant drawback lies in their susceptibility to corrosion when exposed to varied environments. Notably, the high salinity and humidity prevalent in marine atmospheres pose a substantial risk, leading to severe corrosion of iron-based structures. This issue is particularly pertinent given the concentration of a major percentage of worldwide industrialization in coastal regions, resulting in considerable economic losses due to corrosion [2–4].

Among the various methods of metal passivation, the application of corrosion inhibitors (CIs) remains the most economical and practical approach. These inhibitors function by controlling cathodic or anodic reactions, thereby influencing the electrochemical corrosion process. Ongoing research is focused on developing corrosion inhibitors that are not only effective but also exhibit low toxicity and cost-effectiveness, providing alternatives to conventional toxic inorganic inhibitors [5]. Another crucial consideration in this context is the inhibitor's solubility in corrosive mediums.



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). While the mechanism of corrosion inhibition is not fully elucidated, it is generally attributed to a physical/chemical adsorption process or a combination thereof. The strength of the interaction formed between the substrate and organic CI plays a pivotal role in this process [6]. In essence, organic inhibitors safeguard the metal substrate by forming an adsorbed layer—a departure from inorganic compounds that passivate the metal by creating an oxide film on its surface [7]. The adsorption of organic inhibitor molecules notably enhances the mechanical and physical properties of the metal when subjected to aggressive attacks, resulting in the formation of a hydrophobic film on the metal surface [8].

Within the extensive range of organic CIs, amines/alkanolamines, and carboxylic acids have emerged as notably active compounds for passivating various metals in aqueous solutions [9,10]. Alkanolamines (e.g., ehtylethanolamine, N,N'-dimethylaminoethanol) function as dual-role mixed corrosion inhibitors, impeding both anodic and cathodic reactions, while diminishing chloride ion migration within the concrete matrix [11–14] The research highlights that the presence of a hydrogen atom on the nitrogen atom enhances hydrogen bond formation, promoting increased inhibition in surface-chelated molecules [11].

To enhance the performance of alkanolamine-based inhibitors, a strategy involves utilizing various formulations by combining two or more types of inhibitors for improved corrosion protection efficiency [15]. Recently, carboxylic acids and their salts have demonstrated effectiveness in preventing corrosion in alkaline media, despite differing perspectives on their interactions with metal surfaces. Studies suggest that carboxylates form chelates with iron ions on the surface, hindering the migration of chloride ions to the reinforcing steel [16,17]. Contradictory opinions still persist regarding the nature of interactions with metal surfaces. The inhibitory effectiveness is significantly influenced by factors such as chemical structure, steric considerations,  $\pi$ -orbital character of donating electrons, aromaticity, and electron density at the donor atoms of the corrosion inhibitors [18–22].

This paper aims to explore the potential mechanisms of a mixed corrosion inhibitor through a comprehensive approach, combining both experimental and theoretical methods. Specifically, our focus is on unraveling the intricate metal-inhibitor interactions and adsorption behavior in saline solutions. In line with our research group's dedication to investigating the structural properties of alkanolamine-substituted benzoic acid systems [23–25], recent findings predict the corrosion-inhibiting potential of ethylethanolammonium 4-nitrobenzoate (EEA4NB) on iron in a NaCl solution, shedding light on its thermal and kinetic behavior under non-isothermal and isothermal conditions [26]. The synthesized EEA4NB is now presented with a focus on its dual functionality, intervening in the control of both anodic and cathodic reactions while concurrently mitigating the aggressive impact of chloride on metal surfaces. In addition to their effectiveness in inhibiting corrosion, alkanolamine-benzoic acid systems are obtained from cost-effective reactants and demonstrate promising plant growth regulator activity [25], with minimal negative environmental impact [24].

To achieve this objective, a combination of different electrochemical techniques and computational calculations has been employed. Experimental methods, including electrochemical impedance and potentiodynamic approaches, have been utilized to assess the material's electrochemical behavior and determine corrosion rates. Complementing these experimental techniques, scanning electron microscopy has been employed to gain a comprehensive understanding of the inhibitor adsorption mechanism.

Employing computational techniques, particularly quantum chemical calculations, enables the electronic-level calculation of inhibitor molecules' adsorption energy. This approach facilitates the comprehensive evaluation of metal-inhibitor interactions and the adsorption behavior of inhibitors in corrosive aqueous solutions. The prediction of anticorrosion potentials is supported by various quantum chemical parameters, including energy gap, energy of the highest occupied molecular orbital, energy of the lowest unoccupied molecular orbital, ionization potential, electron affinity, polarizability, hardness, global softness, and electronegativity [27–33]. This integrative use of computational methods provides valuable insights into the mechanisms underlying mixed-corrosion inhibitors.

# 2. Materials and Methods

# 2.1. Corrosion Inhibitor Solutions

EEA4NB was synthesized according to our previous method [26], using ehtylethanolamine and 4-nitrobenzoic acid as reagents supplied from Sigma-Aldrich (St. Louis, MO, USA). Corrosion inhibitor solutions were prepared by dissolving the required EEA4NB weight in a 3% NaCl solution. Six different EEA4NB concentrations were used, ranging from  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  mol/L. The carbon steel specimen contains the following chemical composition (wt%): C 0.21%, Mn 0.44%, P 0.04%, S 0.05%, and Fe balance. The specimen was made from an iron bar purchased from EPI Sistem (Brasov, Romania).

## 2.2. Electrochemical Analysis

# Open Circuit Potential (OCP)

The potential vs. time analyses were carried out with a potentiostat/galvanostat (Autolab 302N, EcoChemie, Utrecht, The Netherland). All electrochemical measurements were performed in a conventional one-compartment three-electrode cell with carbon steel as the working electrode (surface area of 0.785 cm<sup>2</sup>), inox counter electrodes, and an SCE reference electrode.

# 2.3. Potentiodynamic Polarization (PDP) Testing

The measurements were conducted on carbon steel immersed in a blank solution (3% NaCl) and after immersion in a test solution containing EEA4NB with concentrations ranging from  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  mol/L. The measurements were performed by scanning the potential from -1.2 V to 0.2 V vs. SCE at a rate of 1 mV/s at room temperature. The blank and test solutions were ultrasonicated for 5 min. The experiments were conducted in an aerated electrolyte and repeated in triplicate. Corrosion parameters were extracted from the polarization curves using the AUTOLAB 302N (software NOVA 2.14).

## 2.4. Electrochemical Impedance (EIS) Experiments

EIS experiments were conducted using a potentiostat/galvanostat (Autolab 302N equipped with the FRA2 impedance module). Electrochemical impedance spectra were recorded at open circuit potentials in both blank solution and EEA4NB testing solutions. The experiments were performed at room temperature in a frequency range of 0.01 Hz to 100 kHz, with a sinusoidal potential amplitude of 10 mV. The experimental data were fitted to the equivalent electrical circuit (EEC) using a complex non-linear least squares procedure with the ZView-Scribner Associated Inc. software 3.0 (Southern Pines, NC, USA). The experiments were conducted in aerated electrolyte conditions and were repeated in triplicate.

#### 2.5. Electrode Surface Morphology Analysis

The surface morphology of carbon steel electrodes before and after immersion in blank solution and testing solutions was carried out by scanning electron microscopy (SEM) using the FEI QUANTA FEG 250. The elemental composition of the electrode surface was analyzed using energy dispersive X-ray (EDX).

## 2.6. Computational Methods

The quantum chemical calculations were performed using the density functional theory (DFT) method at the wb97xd level of theory with a 6-31++g(d,p) basis set, implemented in the Gaussian 09 series of programs [31]. The self-consistent reaction field (SCRF) theory, along with Tomasi's polarized continuum model (PCM), was employed for a better understanding of the experimental results [32]. Fukui functions and the dual descriptors [30] were calculated using the Multiwfn package [33]. Quantum chemical parameters such as  $E_{HOMO}$  (highest occupied molecular orbital energy),  $E_{LUMO}$  (lowest unoccupied molecular orbital energy), energy gap ( $E_g$ ), hardness ( $\eta$ ), electronegativity ( $\chi$ ), polarizability (p), dipole moment ( $\mu$ ), and fraction of the transferred electrons  $\Delta N$  [27,28] were calculated and discussed. The local reactivity has been studied through the Fukui indices [29,30].

## 3. Results and Discussions

# 3.1. Electrochemical Analysis

Electrochemical changes occurring during the immersion of carbon steel in a 3% NaCl solution, with and without EEA4NB, were explored by interpreting an electrical signal arising from the metal interface. This signal provides essential information regarding metal corrosion. The evaluation of metal corrosion in saline solution can be performed through OCP, EIS, and PDP measurements.

From the OCP curves, it was observed that for carbon steel immersed in the blank solution, there was a decrease in potential. The potential decreased from approximately -0.55 V at the beginning of immersion to approximately -0.68 V after 1 h of immersion. This potential decrease is attributed to the penetration of Cl<sup>-</sup> ions through the protective oxide layer present on the metal surface. The oxide layer offers only partial protection, and its dissolution is not entirely prevented. It is reported that iron oxides dissolve under the attack of chloride ions, with an increased applied potential in the positive direction [34].

In the case of carbon steel immersed in the testing solutions, the initial potential of carbon steel shifted to a higher potential due to the formation of a protective film on the carbon steel (electrode) surface. After 505 s, the OCP value tended to stabilize, indicating a stable layer deposited on the metal surface. As the concentration of EEA4NB increased, the potential value after 1 h of immersion shifted to more positive values, suggesting the formation of a protective layer on the metal surface.

The EIS technique was employed to study the nature of the electrochemical processes occurring at the carbon steel (electrode)/3% NaCl interface and to understand the influence of EEA4NB on the iron dissolution process. The impedance curves for the Fe electrode recorded in the 3% NaCl solution with different concentrations of EEA4NB are presented as Nyquist plots in Figure 1a and as Bode plots in Figure 1b. The electrochemical equivalent circuit (EEC) considered for modeling the EIS data is shown in Figure 1c.



**Figure 1.** Impedance curves: (a) Nyquist plots, (b) Bode plots, and (c) the electrochemical equivalent circuit (EEC) used for fitting experimental data for carbon steel electrodes immersed in a saline solution with varying EEA4NB concentrations.

The Nyquist plots display a single depressed semicircle that changes with the addition of inhibitor molecules, with the diameter of the semicircle increasing alongside the EEA4NB concentration. These results suggest surface roughness and heterogeneity. Similar conclusions are drawn from the Bode plots in Figure 1b, where only one peak is observed at the middle frequency range both in the absence and presence of EEA4NB. The magnitude of the capacitive loop in Figure 1a, as well as the impedance modulus in the low-frequency domain (Figure 1b), increases with the inhibitor concentration. The impedance data are fitted using the circuit in Figure 1c. The EEC used for the interpretation of EIS data includes a resistance ( $R_s$ ) representing the solution resistance between the reference electrode and working electrode. This is placed in series with a parallel connection between a capacitor ( $C_{dl}$ ), signifying double-layer capacitance, and a resistance ( $R_{ct}$ ), representing charge transfer resistance.

The electrochemical parameters determined with EEC are listed in Table 1.

C <sub>inh</sub> , mM/SD *	$R_s$ , $\Omega \cdot \mathrm{cm}^2$	$R_{ct}, \Omega \cdot \mathrm{cm}^2$	$C_{dl}$ -T, F · cm <sup>-2</sup> /s $\varphi^{-1}$	$CPE_{dl}$ -P, ( $\varphi$ )	IE, %
0	$11.92\pm0.21$	$36\pm12$	$7.93 \times 10^{-3} \pm 0.19 \times 10^{-4}$	$0.80\pm0.03$	
0.5	$12.3\pm0.82$	$430\pm9$	$1.05\times 10^{-4}\pm 1.03\times 10^{-4}$	$0.76\pm0.11$	$86.73\pm2.01$
1	$12.3\pm0.11$	$440\pm9$	$9.05\times 10^{-4}\pm 8.01\times 10^{-6}$	$0.81\pm0.07$	$88.60\pm0.24$
2	$11.69\pm0.41$	$872\pm 6$	$5.80 \times 10^{-4} \pm 0.39 \times 10^{-5}$	$0.82\pm0.05$	$92.70 \pm 1.27$
3	$11.62\pm1.12$	$967\pm11$	$3.80 \times 10^{-4} \pm 0.72 \times 10^{-5}$	$0.85\pm0.04$	$95.22 \pm 1.56$
4	$11.6\pm0.98$	$993\pm12$	$2.80 \times 10^{-4} \pm 0.03 \times 10^{-4}$	$0.87\pm0.05$	$96.48 \pm 2.11$
5	$11.53\pm0.91$	$1130\pm26$	$2.70 imes 10^{-4}\pm 0.08 imes 10^{-4}$	$0.88\pm0.05$	$96.60\pm5.03$

**Table 1.** Corrosion parameters obtained from EIS measurements for carbon steel in 3% NaCl without and with the inhibitor EEA4NB.

\*: Standard deviation.

In the saline solution, the increase in EEA4NB concentration points to a significant improvement in the charge-transfer resistance ( $R_{ct}$ ) and a decrease in  $C_{dl}$  values. A high  $R_{ct}$  value usually indicates a slower corrosion process due to the adsorption of inhibitor molecules on the electrode surface. The decreasing trend observed for  $C_{dl}$  values could be associated with the decrease in the local dielectric constant or the reduction in the electrode exposure area as a result of the protective layer developed on the electrode surface.

Therefore, through the adsorption of corrosion inhibitors on the metal surface, an organic inhibitor layer gradually forms and is capable of replacing the water molecules present at the surface electrode. As the concentration of inhibitors increases, the protective layer becomes denser and, consequently, becomes an effective barrier for the metal surface against the aggressive attack of corrosive species. The inhibitor efficiency (IE) was calculated from EIS data using Equation (1) and is listed in Table 1 [1,20]:

IE (%) = 
$$(1 - C_{dl}/C_{dl0}) \times 100$$
 (1)

where  $C_{dl}$  and  $C_{dl0}$  represent the double layer capacitance (from EIS) in the presence and absence of the inhibitor, respectively, or alternatively, the corrosion current density (from polarization curves) in the presence and absence of the inhibitor, respectively.

The IE values exceed 86% in the presence of EEA4NB and increase with the inhibitor concentration. The highest value is obtained in a 3% NaCl solution with 5 mM EEA4NB, indicating the formation of a protective layer on the metal surface. A concentration of 5 mM is sufficient to form a protective inhibitor layer that can block the penetration of aggressive Cl ions. This concentration ensures the formation of a compact and less porous protective layer. For EEA4NB concentrations lower than 4 mM, the coverage of the metallic surface is incomplete and may not fully protect the steel surface. In such cases, Cl ions can reach the carbon steel surface and promote corrosion.

The number of binding sites on the metal surface/degree of surface coverage affect  $C_{dl}$ .  $C_{dl}$  decreases when the ion species present in the solution are adsorbed on the metal surface, and the available number of binding sites decreases with an increase in immersion time. Consequently, the rate of adsorption decreases over time.

In Figure 2a, the presence of two regions in the decay of  $C_{dl}$  with immersion time was observed. The first stage of adsorption reveals the presence of numerous available binding sites for ionic species, while the second stage exposes the presence of an irreversible organic layer on the metal surface. This second stage corresponds to the prolonged time of adsorption, where the available binding sites decrease and the ionic species in the solution no longer have sufficient space to adsorb directly on the surface (observed as a plateau in Figure 2a).



**Figure 2.** Variation of: (a)  $C_{dl}$  parameter, (b) surface cover  $\theta$  during the adsorption process of EEA4NB over time at different concentrations, and (c) Langmuir isotherm.

Further adsorption results in the formation of a reversible layer, as the ionic species in the solution tend to stay close to the layer formed in the first stage and no longer attach directly to the surface but rather near the formed layer. This corresponds to a weak binding, and as a result, the ionic species can be easily desorbed.

The adsorption of species onto metallic surfaces was found to well describe the experimental data for this work. Complete saturation appears at ~60 min. Using EIS, the fractional surface coverage ( $\theta$ ) can be calculated (according to Equation (2)) because the saturation capacitance represents the capacitance of the fully covered electrode surface.

$$\theta = (C_{dlo} - C_{dl}) / C_{dlo} \tag{2}$$

The IE is associated with the degree of inhibitor coverage at the metal surface. The adsorption isotherm needs to be determined to understand how the inhibitors interact with the metal surface. The adsorption isotherms calculated at different concentrations were found to best fit the Langmuir isotherm (Equations (3) (Langmuir Isotherm) and (4)) [1,20]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{3}$$

$$R_{Langmuir} = \frac{1}{1 + K_{ads}C} \tag{4}$$

where  $\theta$  is the surface coverage, *C* is the EEA4NB concentration,  $K_{ads}$  is the adsorption equilibrium constant, and  $R_{Langmuir}$  is the separation factor.

Experiments related to the adsorption kinetics of EEA4NB on carbon steel were welldescribed by the Langmuir model, as indicated by the high linear regression coefficient ( $R^2$ ). The results indicate that adsorption is a time-dependent process and serves as the rate-limiting mechanism. The experimental data fit well with the  $\theta$  values of the Langmuir isotherm, with an  $R^2$  value closest to unity ( $R^2 = 0.9997$ ). Figure 2c displays the linear plots for the considered isotherm obtained using Equation (3).

The  $K_{ads}$  determined for the Langmuir isotherm is 3460.514 mol<sup>-1</sup> and represents the strength between the adsorbate and adsorbent R<sub>Langmuir</sub> is less than one, indicating the existence of interactions between the adsorbed EEA4NB molecules and metal surface.

The free energy of adsorption ( $\Delta G^{\circ}_{ads}$ ) is  $-30.141 \text{ kJ} \cdot \text{mol}^{-1}$  and was calculated using Equation (5) [1,20]:

$$\Delta G^{\circ}_{ads} = -RTLn(55.5K_{ads}) \tag{5}$$

where *R* is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), *T* is the absolute temperature in Kelvin,  $\Delta G^{\circ}_{ads}$  is the standard free energy of adsorption, and 55.5 is the concentration of water in the solution in mol dm<sup>-3</sup>.

The negative  $\Delta G^{\circ}_{ads}$  value, falling within the range of [-20, -40] kJ/mol, and the high value of  $K_{ads}$  indicate that the adsorption process occurs spontaneously, leading to the formation of a stable layer on the metal surface. This process takes place through a mixed process of physical and chemical adsorption [35]. Potentiodynamic polarization curves were obtained for carbon steel after a 60-min immersion in 3% NaCl solutions, both with and without EEA4NB, as shown in Figure 3.

-2 Fe 5×10<sup>-3</sup> mol·L<sup>-</sup> log I,A.cm<sup>-2</sup> -3 4x10<sup>-3</sup> mol·L<sup>-7</sup> 3x10<sup>-3</sup> mol·L<sup>-1</sup> 2x10<sup>-3</sup> mol·L<sup>-1</sup> 1x10<sup>-3</sup> mol·L<sup>-7</sup> 5x10<sup>-4</sup> mol·L<sup>-1</sup> -5 -6 -0.2 -1.2 -1.0 -0.8 -0.6 -0.4 0.0 0.2 0.4 *E*, V

**Figure 3.** Potentiodynamic polarization curves for carbon steel in a 3% NaCl solution, both with and without EEA4NB, at a scan rate of 1 mV/s.

The values of cathodic ( $\beta$ c) and anodic ( $\beta$ a) Tafel slopes, corrosion potential (E<sub>corr</sub>), corrosion current density (*J*<sub>corr</sub>), polarization resistance (*R*<sub>p</sub>), and corrosion rate (*CR*) for carbon steel in six different solutions are presented in Table 2.

C <sub>inh</sub> , mM/SD *	E <sub>corr</sub> , V	$J_{corr}$ , A·cm <sup>-2</sup>	- $eta c$ , V·decade $^{-1}$	$eta a, {f V} \cdot {f decade^{-1}}$	$R_p$ , ohm·cm <sup>-2</sup>	$CR \text{ mm} \cdot \text{Year}^{-1}$
0	$-0.930 \pm -0.06$	$\begin{array}{c} 8.54 \times 10^{-4} \pm \\ 1.33 \times 10^{-6} \end{array}$	$0.320\pm0.025$	$0.162\pm0.012$	$38\pm2$	$0.942\pm0.042$
0.5	$-0.612 \pm -0.011$	$\begin{array}{c} 6.81 \times 10^{-4} \pm \\ 0.82 \times 10^{-6} \end{array}$	$0.225\pm0.003$	$0.280\pm0.007$	$380\pm7$	$0.812\pm0.007$
1	$-0.524 \pm -0.013$	$\begin{array}{c} 6.10\times 10^{-5}\pm\\ 0.41\times 10^{-6}\end{array}$	$0.122\pm0.073$	$0.095\pm0.016$	$439\pm 6$	$0.750\pm0.021$
2	$-0.532 \pm -0.009$	$\begin{array}{c} 5.84 \times 10^{-5} \pm \\ 1.87 \times 10^{-7} \end{array}$	$0.114\pm0.009$	$0.088\pm0.014$	$866\pm 6$	$0.421\pm0.003$
3	$-0.514 \pm -0.021$	$\begin{array}{c} 5.21\times 10^{-5}\pm\\ 0.92\times 10^{-7}\end{array}$	$0.114\pm0.014$	$0.031\pm0.002$	977 ± 11	$0.408\pm0.004$
4	$-0.520 \pm -0.019$	$\begin{array}{c} 3.83 \times 10^{-5} \pm \\ 1.05 \times 10^{-7} \end{array}$	$0.105\pm0.023$	$0.042\pm0.010$	$988\pm7$	$0.402\pm0.008$
5	$-0.518 \pm -0.013$	$\begin{array}{c} 1.45\times 10^{-5}\pm\\ 1.16\times 10^{-7}\end{array}$	$0.114\pm0.017$	$0.031\pm0.004$	$1062\pm17$	$0.215\pm0.011$

**Table 2.** Electrochemical parameters for carbon steel in a 3% NaCl solution with different concentrations of EEA4NB at 25 °C.

\*: Standard deviation.

The presence of EEA4NB significantly decreases current densities and increases  $R_p$ . The lowest  $J_{corr}$  (1.45 × 10<sup>-5</sup> A·cm<sup>-2</sup>) and the highest  $R_p$  value (1062 Ohm·cm<sup>2</sup>) were recorded at a concentration of 5 × 10<sup>-3</sup> mol·L<sup>-1</sup> EEA4NB in solution. This indicates the formation of a stable organic layer on the carbon steel surface. At higher inhibitor concentrations, an increase in adsorption and surface coverage generates a better protective layer capable of blocking the reaction sites and reducing the rate of the corrosion reaction. The E<sub>corr</sub> values are shifted slightly in the presence of EEA4NB. The *J<sub>corr</sub>* value decreases with the addition of the inhibitor. Tafel slopes  $\beta a$  and  $\beta c$  are affected by the inhibitor, indicating that the inhibitor acts as a mixed-type one. The surface of carbon steel specimens immersed in saline solution in the presence and absence of the inhibitor was examined using SEM. In the absence of the inhibitor, the metal's surface was corroded, but in the presence of the inhibitor, the micrograph reveals a decrease in the corrosion sites due to the formation of a smooth, fusiform, dense protective layer in the presence of the inhibitor (Figure 4b), compared to the uncoated bare carbon steel (Figure 4a).

Based on the approximate quantitative analysis provided by EDX (Figure 4c,d), it is observed that in the carbon steel sample, Fe constitutes approximately 61%, while in the coated sample, it has decreased to around 18% due to the presence of the electrode's protective film. Nitrogen is present in the regions corresponding to C, O, and Fe peaks below 2 KeV, but the peaks generated by N are not visible in the spectrum due to their lower intensity compared to those generated by other elements.

It is observed that the results of surface coverage are in good agreement with those given by the EIS method.

The quantitative measure of the protective effect was calculated by comparing the values of the charge transfer resistance in the absence ( $R_p$ ) and presence of an inhibitor ( $R_{p0}$ ), as given by Equation (6) [1,20]:

IE (%) = 
$$(1 - R_p / R_{p0}) \times 100$$
 (6)

where  $R_p$  and  $R_{p0}$  represent the polarization resistance for inhibited and uninhibited systems, respectively.



**Figure 4.** (a) SEM photograph of the bare carbon steel surface, (b) SEM photograph covered with an EEA4NB film, (c) EDX image of the carbon steel electrode, and (d) EDX image of the carbon steel electrode in the presence of EEA4NB.

This means that the IE values calculated from potentiodynamic polarization curves are nearly equal to the values obtained by the EIS method. The experimental results obtained reveal a higher surface coverage of the electrode and a decrease in corrosion currents in the presence of EEA4NB in saline media.

In the literature, *p*-nitrobenzoic acid is reported as a compound capable of providing low surface coverage of a carbon steel electrode, and consequently, it exhibits low inhibition of corrosion [36]. Additionally, a surface coverage of 49% for aluminum immersed in NaOH with a content of 100 ppm *p*-nitro carboxylic acid was reported [37]. The poor inhibition indicates that the anchoring group during adsorption is only the aromatic ring ( $\pi$  electrons). Amino or hydroxyl groups favor delocalization and offer more inhibition.

A possible explanation for the higher surface coverage of carbon steel in saline media in the presence of EEA4NB results from the coexistence of both *p*-nitrobenzoic anions and ethyletanolamonium cations in the solution. The electrode surface is likely to be covered by both carboxylate anions and ethyletanolammonium cations. These assumptions are based on the amine's ability to provide corrosion inhibition, form hydrogen bonds with oxide or hydroxide species on the metal surface, or engage in van der Waals interactions between the surface and anions.

When the electrode is exposed to a saline solution containing EEA4NB, there is a potential shift from positive to negative on the surface. This change in charge, resulting from the adsorption of  $Cl^-$  at the electrode surface, facilitates the physical adsorption of the salt cations.

Thus, the adsorbed  $Cl^-$  ions on the metal surface will favor the electrostatic adsorption of protonated ethyletanolamonium molecules, promoting the physical adsorption of ethyletanolamonium on the Fe surface. Similar results are reported by Ebenso [38]. One possible mechanism refers to an inhibitor adsorbed on metal with a positively charged surface (Figure 5a).



**Figure 5.** A schematic representation of the inhibiting mechanism proposed for EEA4NB on the carbon steel surface (**a**) without Cl<sup>-</sup> adsorption and (**b**) with Cl<sup>-</sup> adsorption on Fe surface.

In this case, the inhibitor molecules are not only physisorbed (represented by a dotted line) but also chemisorbed, owing to the coulombic forces between the negatively charged oxygen groups of the inhibitor and the positively charged metallic surface (represented by a solid line) [39]. It is possible that inhibitor molecules may first be physically adsorbed and then form electron bonds, ultimately resulting in chemisorption. In the case of EEA4NB, the mixed-type adsorption (physisorption + chemisorption) is in accordance with the negative  $\Delta G^{\circ}_{ads}$  value and a high value of  $K_{ads}$ , indicating spontaneous adsorption and the formation of a stable layer on the metal surface through a combination of physical and chemical adsorption.

In an environment where chloride ions are present, another mechanism can be taken into account. The chloride ions are adsorbed on the surface of carbon and favor the adsorption of inhibitors through  $NH_2^+$  (Figure 5b, left). These adsorbed chloride ions further act as a passage that provides conditions for the chemical adsorption of the  $NH_2^+$ group and/or the O<sup>-</sup> group (Figure 5b, right) [40]. The presence of chloride ions allows the formation of bridges between the inhibitor molecules and the metallic surface. In this manner, the adsorption of organic inhibitors is facilitated. This is supported by EDX images showing the presence of Cl<sup>-</sup> on the surface of the electrode (Figure 4c).

Quantum chemical parameters such as energy gap, energy of the highest occupied molecular orbital, energy of the lowest unoccupied molecular orbital, ionization potential, electron affinity, polarizability, hardness, global softness, and electronegativity were calculated to investigate which mechanism is more likely in the corrosive protection offered by EEA4NB to carbon steel in saline.

#### 3.2. Computational Methods

The experimental results indicate a enhanced surface coverage of the electrode and a reduction in corrosion currents in the presence of EEA4NB. Therefore, from a computational standpoint, it becomes imperative to assess the corrosion inhibition potential of EEA4NB, including its anions and cations. Theoretical methods, particularly quantum chemical calculations, have consistently demonstrated their utility in unraveling the intricate mechanisms underlying the inhibition of materials.

The calculated values for  $E_{HOMO}$  (highest occupied molecular orbital energy),  $E_{LUMO}$  (lowest unoccupied molecular orbital energy), energy gap ( $E_{gap}$ ), hardness ( $\eta$ ), electronegativity ( $\chi$ ), polarizability (p), dipole moment ( $\mu$ ), and fraction of the transferred electrons ( $\Delta N$ ) are presented in Table 3.

Inhibitor	E <sub>HOMO</sub> , eV	E <sub>LUMO</sub> , eV	E <sub>gap</sub> , eV	p, Bohr <sup>3</sup>	μ, Debye	χ, eV	η, eV	ΔN
EEA4NB	-9.41	-1.2	8.21	221.57	16.715	6.033	2.9449	0.164
anion	-8.591	-1.093	7.498	148.04	11.753	4.794	1.798	0.613
cation	-10.695	0.992	11.687	69.9	4.225	5.039	3.801	0.258

Table 3. The calculated quantum chemical parameters of the studied inhibitors.

The highest  $E_{HOMO}$  value was observed for the anion, indicating superior inhibition efficiency. This can be attributed to its ability to accept electrons from the *d*-orbital of the metal, form a feedback bond. The reduction in separation energy ( $E_{gap}$ ) corresponds to an increase in the molecule's inhibition efficiency. Notably, the anion exhibits the lowest  $E_{gap}$  value, signifying higher reactivity compared to EEA4NB and the cation.

The electron density distributions of the frontier orbitals play a crucial role in determining the adsorption preference of inhibitors. The HOMO identifies regions of the molecule prone to donating electrons to electrophilic species, while the LUMO predicts regions with a high tendency to accept electrons from nucleophilic species. The calculated HOMO-LUMO electron density distributions for EEA4NB, the anion, and the cation are illustrated in Figure 6. In EEA4NB and the anion, the HOMO is strongly localized on O4 and O5 atoms (Figure 7), while the LUMO is distributed throughout the aromatic cycles and NO<sub>2</sub>-groups. In the cation, both HOMO and LUMO are predominantly located on the O20 and C22 atoms.

Polarizability plays a significant role in the corrosion inhibition process [27]. Higher values of polarizability, defined as the ratio of the induced dipole moment to the intensity of the electric field, facilitate the adsorption process of inhibitors on a metal surface. The calculated values of polarizability exhibit the following trend: EEA4NB > anion > cation. This same trend is observed in the calculated dipole moments of the potential inhibitors under study (Table 3). Dipole moment is another frequently employed parameter in corrosion inhibition studies, and a high dipole moment likely enhances adsorption on the metal surface [27].

Absolute hardness and softness are important properties for assessing molecular stability and reactivity. Chemical hardness ( $\eta$ ) essentially indicates the resistance to the deformation or polarization of the electron cloud of atoms, ions, or molecules under a small perturbation of a chemical reaction [28]. In the context of material corrosion, the softest base inhibitors prove to be the most effective, and the portions of the inhibitor with the highest softness and lowest hardness are particularly useful [27]. The results presented in Table 4 show that the anion exhibits the lowest hardness among the various potential inhibitors.

Electronegativity ( $\chi$ ) measures the ability of a group of atoms to attract electrons towards itself when chemically combined with another atom. In the context of corrosion inhibition, effective inhibitors are those that donate electrons to the metallic surface. Therefore, it is anticipated that electronegativity values will decrease with the improvement of inhibitive efficiencies [27]. The anion with the lowest electronegativity value demonstrates



increased adsorption on the metal surface. Consequently, it enhances corrosion inhibition efficiency when compared to EEA4NB and the cation, respectively.

Figure 6. HOMO and LUMO for the studied inhibitors.



Figure 7. Labelling of atoms in the EEA4NB; grey—carbon, red—oxygen, blue—nitrogen.

Literature reports indicate that the fraction of electrons transferred from the inhibitor to the metallic surface ( $\Delta$ N, Table 4) reflects the inhibition effect resulting from electron donation [27,28]. A positive  $\Delta$ N value indicates that the molecules function as electron donors, and the inhibition efficiency increases with higher  $\Delta$ N values. It was observed that the anion has the highest fraction of electrons transferred compared to EEA4NB and the cation.

The active sites of the inhibitor molecule can also be described by Fukui functions and dual descriptors, which are associated with sites of nucleophilic and electrophilic attacks [29,30]. The condensed dual descriptors ( $\Delta f$ ), combining two Fukui functions, were calculated for each atom using Hirshfeld population analysis [33]. The obtained results are presented in Table 4:

$$\Delta f = 2q^{N} - q^{N+1} - q^{N-1}$$
(7)

where  $q^N$ ,  $q^{N+1}$ , and  $q^{N-1}$  represent the atomic charges for three electronic states with N, N + 1, and N - 1 electrons, respectively.

Table 4. The calculated condensed dual descriptors of the studied inhibitors.

Atoms	EEA4NB	Anion
N1	0.0502	0.1435
O2	-0.1393	0.2014
O3	-0.1396	0.2013
O4	-0.4833	-0.3275
O5	-0.3895	-0.3013
C6	-0.2217	0.0051
C7	-0.0601	0.0384
C9	-0.0952	0.0051
C11	-0.2104	0.0551
C12	-0.0939	0.0057
C14	-0.0603	0.0386
C16	-0.0843	-0.1018
		cation
N17	-0.0062	0.0563
O20	-0.0217	-0.4216
C22	-0.0031	-0.0581
C25	-0.0010	-0.0322
C28	-0.0005	0.0215
C31	-0.0006	0.0083

The condensed dual descriptor has a positive value where it is electrophilic and a negative value where it is nucleophilic. However, it is sufficient to determine only which sites have more positive or more negative  $\Delta f$ . If the distribution of  $\Delta f$  around a site A is more positive than another site B, then one can infer that A is a more favorable site for nucleophilic attack than B, while B is a more preferential site for electrophilic attack than A. Each inhibitor molecule was allowed to interact with the metal surface at the atom that has the highest  $\Delta f$ . For both EEA4NB and the anion, all oxygen atoms were identified as such sites, and for the cation, it was atom O20. However, it is noteworthy that the anion contains both electrophilic and nucleophilic attacking sites.

The molecular electrostatic potential (MEP) plot illustrates the molecular size, shape, and regions of positive, negative, and neutral electrostatic potential for EEA4NB, anion, and cation, with color grading (Figure 8). In the MEP, the maximum negative region, signifying the preferred site for electrophilic attack, is depicted in red, while the maximum positive region, indicating the preferred site for nucleophilic attack, is represented in blue. The potential increases in the order: red < orange < yellow < green < blue. Examining the MEP of the title inhibitors, it is observed that the most negative potential is located over the oxygen atoms of the anion, while the most positive potential is over the cation.



**Figure 8.** Molecular electrostatic potential maps for study inhibitors, with the values mapped on the isodensity surface ranging from  $-1 \times 10^2$  (red) to  $1 \times 10^2$  (blue).

It is known that atoms with fractional charges, which are typically involved in most hydrogen bonds, tend to generate significant "local" potentials. Therefore, an examination of the potential maps indicates that the oxygen atoms of the anion are most likely to participate in the formation of hydrogen bonds, particularly in the case of hydroxide species (FeOH<sup>+</sup>) on the metal surface.

Therefore, a theoretical estimation of the inhibition efficiency of EEA4NB, the anion, and the cation was conducted at the density functional theory calculation level. The anion exhibits the highest inhibition efficiency compared to EEA4NB and the cation, primarily due to its highest HOMO and lowest energy gap. Quantum chemical parameters, including hardness ( $\eta$ ), electronegativity ( $\chi$ ), and the fractions of electrons transferred ( $\Delta$ N), suggest the following order of inhibition efficiencies: anion > EEA4NB > cation. The presented MEP surface, an overlay of the electrostatic potential (indicating the attraction or repulsion of a molecule), is valuable for describing the overall molecular charge distribution. The most negative potential is identified over the anion's oxygen atoms, while the most positive potential is observed over the cation. The condensed Fukui functions predict the electrophilic and nucleophilic attacking sites of the inhibitors, providing information about the reactivity of the molecules.

Additionally, our study proposed a mechanism for acid-base multicomponent systems as corrosion inhibitors, illustrated in Figure 5a. The positively charged carbon steel surface facilitates the adsorption of EEA4NB through negatively charged oxygen, resulting in a mixed-type adsorption (physisorption + chemisorption), as supported by Langmuir isotherms. The high values of condensed dual descriptors for all oxygen atoms in EEA4NB and the anion suggest effective inhibition. Notably, the anion contains both electrophilic and nucleophilic attacking sites. Consequently, EEA4NB in solution can be adsorbed on the carbon steel surface in three forms: the anion form, the cation form, and as undissociated molecules. The observed high inhibition effect for this alkanolammonium salt results from the anion's more powerful electron-donating ability (higher  $E_{HOMO}$  value) and the lower value of  $E_{LUMO}$ , suggesting that undissociated molecules can accept electrons from the

*d*-orbital of iron to form a feedback bond, thereby increasing the adsorption of EEA4NB on the carbon steel surface. We assume that the mechanism presented in Figure 5b is less likely and is not supported by the low quantity of  $Cl^-$  in the organic surface-layer inhibitor. This is probably due to the strong repulsive action towards chloride ions, resulting from both steric hindrance and the electronic properties of the phenyl group. A similar observation was reported for aryl aminoalcohol inhibitors [41].

For comparison, Table 5 summarizes the corrosion currents, inhibition efficiencies, and adsorption isotherms of various compounds reported in the literature as corrosion inhibitors for iron, along with our results.

**Table 5.** Corrosion currents, inhibition efficiencies, and adsorption isotherms of different compounds on iron in various solutions.

Inhibitor/Inhibitor Concentration	Medium	J <sub>corr</sub> µA/cm <sup>2</sup>	IE, %	Adsoption Isotherm	Ref.
Ammonium salt of the sulfated fatty acid diethanolamine amide (AS)/50 ppm	1% NaCl	31	92.0	Langmuir	[42]
Aminomethylene- phosphonate/4.9 mM	3.5% NaCl, pH = ~3	4.03	87.99	Langmuir	[20]
Amino-alcohol-based mixed inhibitor (Ferrogard 903)/1 mL/50 mL water	0.5 M NaCl, pH = 12.1	12,000	-	-	[43]
Phyllanthus muellerianus leaf extract (2 g) and triethanolamine (6 g)/(C6H15NO3: TEA)	3.5 wt% NaCl	-	98	-	[44]
Aryl aminoalcohol/5 ppm	0.3 M NaCl	1.74	89.9	Langmuir	[41]
N-methyl-2-hydroxyethylamine (M-2HEAOL) and bis-2-hidroxyethylamine (B-HEAOL)oleate/5 mmol/L	0.01 M NaCl	0.12	97	Langmuir	[40]
Polyethyleneimine (PEI)/100 $\mu$ mol L <sup>-1</sup>	3.5 % NaCl	10.9	86.54	Langmuir	[45]
EEA4NB	3% NaCl	0.145	96.6	Langmuir	Present work

The results indicate that alkanolammonium salts can be regarded as promising candidates for the corrosion inhibition of iron and iron alloys.

# 4. Conclusions

Our study provides a comprehensive exploration into the corrosion inhibitor properties of alkanolammonium salts, with a particular focus on EEA4NB, utilizing a combined electrochemical and computational approach on carbon steel in a 3% NaCl solution. Our experimental findings highlight the notable corrosion inhibition capabilities of EEA4NB on carbon steel electrode surfaces in saline solutions, especially at a concentration of  $5 \times 10^{-3}$  mol·L<sup>-1</sup>, achieving an inhibition efficiency of up to 96%. The use of potentiodynamic polarization curves and electrochemical impedance spectroscopy has offered valuable insights, unraveling the intricate dynamics at the interface during the inhibition process. Quantum chemical calculations further strengthen our conclusions, affirming the anion's superiority in inhibition efficiency due to its highest HOMO and lowest energy gap when compared to EEA4NB and cations. This integrated approach enhances our understanding of the inhibitory mechanisms and underscores the potential applications of alkanolammonium salts as effective corrosion inhibitors for carbon steel in aggressive environments. **Author Contributions:** Conceptualization N.P. and M.C.; investigation N.P., C.M. and Y.C.; writing—original draft N.P., M.C. and Y.C.; writing—review and editing N.P. and M.C. All authors have read and agreed to the published version of the manuscript.

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