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Design and synthesis of a novel corrosion inhibitor embedded with quaternary ammonium, amide and amine motifs for protection of carbon steel in 1M HCl

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Abstract

Methyl 11-bromoundecanoate $[Br(CH_2)_{10}CO_2Me]$ (1) on treatment with tripropylamine gave quaternary salt $[Pr_3N^+(CH_2)_{10}CO_2Me]Br^-$ (2) which on treatment with diethylenetriamine afforded $[Pr_3N^+(CH_2)_{10}CONH(CH_2)_2NH(CH_2)_2NH_2]$ Br⁻ (3) containing inhibitive motifs of ammonium, amide and amine motifs embedded in a single frame. The precursor salt 2 and its derivative 3 were successfully synthesized in excellent yields and characterized using different spectroscopic techniques. For the first time, a detailed study on the corrosion inhibition behavior of corrosion inhibitors 2 and 3 for mild steel in 1M HCl was carried out using electrochemical measurements and comprehensive computational analysis. Both the studied inhibitors showed excellent aqueous solubility. The high inhibition efficiency of 91% and 93% at a concentration of 200 mg L^{-1} was obtained for corrosion inhibitors 2 and 3, respectively. The adsorption of the corrosion inhibitors exhibited the Langmuir isotherm with a mixture of physical and chemical modes of adsorption. The impedance studies showed a rise in the polarization resistance with increasing concentration of the inhibitors. Polarization measurements demonstrated that the inhibitors displayed a mixed-mode of inhibition with primarily cathodic nature. Surface analytical studies supported the inhibitor adsorption and a protective film formation on the carbon steel surface, which improved the surface smoothness of the steel surface. The DFT based quantum chemical calculations supported the experimentally obtained results and showed that the inhibitor **3** displays superior inhibition in comparison to the inhibitor **2**. The Monte Carlo simulations revealed higher adsorption energy for the inhibitor **3** compared to **2**.

Keywords: Amidoamine; Quaternary ammonium salt; Corrosion inhibitor; Impedance; DFT study.

1. Introduction

Alloy steels are commonly used in the industrial processes of acidizing, descaling, and acid pickling on account of their low cost and good mechanical properties [1-3]. However, these processes involve the use of concentrated mineral acids, namely hydrochloric and sulfuric acids, which cause severe corrosion of the steel structures [3-5]. To counter the huge losses to the economy and to avoid potential structural failure, which could harm human life, the acidic solutions are mixed with corrosion inhibitors [6-8]. The corrosion inhibitors undergo adsorption on the metallic surfaces and develop a protective film, which reduces the corrosion damage [9]. Most of the corrosion inhibitors are organic molecules containing an abundance of heteroatoms (N, S, O), π bonds, and phenyl rings. The organic compound based corrosion inhibitors are mostly heterocyclic molecules having an abundance of functional groups and phenyl rings [2, 10]. These structures, although they are expected to aid in the capability of adsorption on the metal surfaces and can donate/ accept electrons; however, the poor solubility of these organic compounds, high cost of synthesis, and toxicity limit their applicability in the corrosion inhibitor.

In this context, the quaternary ammonium salt-based corrosion inhibitors present a potent and environment benign category of corrosion inhibitors [11-14]. Nowadays, research and development in the area of quaternary ammonium salt-based corrosion inhibitors are gaining attention due to the attractive structural features of this class of compounds. The quaternary ammonium salts exhibit high solubility, are environmentally benign, and show effective adsorption behavior due to their charged structures [15-17]. These molecules considerably decrease the extent of corrosion damage occurring at both the cathodic as well as the anodic active corrosion sites. It is noteworthy to mention that in the case of heterocyclic corrosion inhibitor compounds, in addition to the active corrosion inhibitor constituent, it is required to add another synergistic agent to improve the inhibition efficiency and surfactant molecules to aid in the dissolution [18, 19]. On the other hand, the quaternary ammonium salts possess a combination of a cation and an anion, which can be expected to provide synergistic improvement in the corrosion inhibition.

Continuing our research work in the area of the organic corrosion inhibitors, we designed and synthesized an inhibitor molecule **3** containing three inhibitor motifs of quaternary ammonium, amide, and amine in a single frame (Scheme 1). The molecule of type **3** synthesized using cheap and readily available commercial precursors and tested for the first time as a corrosion inhibitor. The corrosion evaluation was carried out in 1M HCl solutions by the electrochemical measurements, which were supported by the surface analysis. The experimental results were supplemented with the computational studies carried out using the density functional theory (DFT) based on quantum chemical calculations. The two quaternary ammonium salts appear as potent candidates to be used in the acid pickling industry as corrosion inhibitor formulations.

2. Experimental

2.1 Materials

11-Bromoundecanoic acid (99%), Tripropylamine (\geq 98%), and diethylenetriamine (DETA) (99.5%) were purchased from Sigma Aldrich. Sodium bicarbonate (NaHCO₃), sodium chloride (NaCl)₁ and sodium sulfate (Na₂SO₄) were obtained from BDH chemical Ltd. Methanol, acetonitrile, diethyl ether, and acetone were procured from Fluka Chemie AG. Hydrochloric acid (37%) and sulfuric acid (98%) were purchased from Fisher Scientific. All chemicals used in this study were reagent grade and used without further purifications. Milli-Q system was utilized to produce deionized water. Before use, all glassware was cleaned using de-ionized water and dried.

2.2 Characterization of the corrosion inhibitors

¹H NMR spectra were acquired in CDCl₃ using Bruker 400 MHz (Rheinstetten, Germany) instrument. FT-IR (Perkin Elmer 16F PC FTIR) instrument (spectral resolution, 4 cm⁻²; number of scans: 32) was utilized to acquire the FTIR spectra. Carlo-Erba elemental analyzer (Model: NA-1500) conducted the elemental analysis. Melting points are recorded in a calibrated Electrothermal-IA9100- Digital Melting Point Apparatus using heating rates of 1 °C/min near the melting points. Thermogravimetric analysis (TGA) was performed by a thermogravimetric analyzer from TA instruments (SDT Q600, USA) under N₂ (flow rate 50 mL/min) using

Platinum/Platinum–Rhodium using step-up temperature 10 °C/min at the temperature range 20–400 °C.

2.3 Synthesis of the corrosion inhibitors

The synthetic process of precursors and corrosion inhibitors is illustrated in Scheme 1.

2.3.1 Synthesis of methyl 11-bromoundecanoate (1)

The precursor compound 11-bromoundecanoic acid methyl ester (1) was synthesized following the modified procedure published elsewhere in the literature [20]. Briefly, 11-bromoundecanoic acid (25 g, 94.2 mmol) was dissolved in 250 mL of methanol. 5 mL H₂SO₄ was added slowly to the reaction mixture while stirring. The system was refluxed at 80 °C for 18 h in an oil bath with continuous stirring. After completion of the reaction, the crude reaction mixture was cool, and excess methanol was removed by N₂ purging in a hot water bath at 60 °C. 150 mL of de-ionized water was added to the reaction mixture. The organic layer was extracted by diethyl ether (250 mL), followed by 125 mL of 5% NaHCO₃, 125 mL of water, and 125 mL of 15% NaCl. Finally, the organic layer was dried with Na₂SO₄, and then diethyl ether was evaporated by purging N₂ to obtain 11-bromo- undecanoic acid methyl ester, 23.9 g (91%).

Elemental composition of $C_{12}H_{23}BrO_2$ is as follows: calculated; C, 51.6; H, 8.3; found; C, 51.3; H, 8.5. ¹H NMR: δ_H (CDCl₃) 1.30 (10H), 1.41 (2H), 1.63 (2H), 1.86 (2H), 2.32 (2H), 3.40 (2H), 3.68 (3H), FTIR: ν_{max} (neat): 3460, 2923, 2858, 1741, 1149, 1366, 1171, 1111, 1009, 869, 727, and 645 cm⁻¹.

2.3.2 Synthesis of quaternary salt 2 [11-methoxy-11-oxo-N,N,N tripropylundecan-1-aminium bromide]

The precursor compound **1** (20.2 g, 72.2 mmol) was dissolved in 50 mL of acetonitrile, and then 20.7 g (145 mmol) of tripropylamine was added slowly to the reaction mixture while stirring. The reaction mixture was refluxed at 90 °C for 20 h in an oil bath fitted with a long neck condenser with continuous stirring. After the time elapsed, the reaction mixture was cool, and excess acetonitrile was removed by N₂ purging in a hot water bath at 60 °C. The resultant crude reaction mixture was then diluted with 5 mL of acetone, followed by the addition of diethyl ether

(25 ml) results in the formation of precipitates. The precipitate was separated and was washed twice with acetone and diethyl ether. Then acetone was evaporated by purging N_{2} , and store in a refrigerator to obtain a corrosion inhibitor **2** as crystal solid. Yield is 25.3 g (83%).

Melting point: 62-65 °C. Elemental composition of $C_{21}H_{44}BrNO_2$ is as follows: calculated; C, 59.7; H, 10.5; found; C, 59.9; H, 10.4. ¹H NMR: δ_H (CDCl₃) 0.95 (9H), 1.16- 1.25 (12H), 1.47-1.68 (10H), 2.21 (2H), 3.25 (8H), 3.55 (3H), FTIR: v_{max} (neat): 2942, 2863 (CH₃, CH₂ stretching), 1733 (C=O stretching), 1632, 1471 (O-CH₃ stretching), 1181 (C-O stretching), 974, 856, 757 and 569 cm⁻¹.

2.3.3 Synthesis of inhibitor molecule **3** [11-((2-((2-aminoethyl)amino)ethyl)amino)-11- oxo-N,N,N tripropylundecan-1-aminium bromide]

The new inhibitor compound **3** was synthesized following a modified procedure for amide synthesis [21]. The compound **2** (2.94 g, 6.91 mmol), DETA (3.03 g, 29.4 mmol), and methanol (50 mL) were added into a 200 mL round bottom flask. Then reflux the reaction mixture at 80 °C for 20 h, followed by the evaporation of methanol, the reaction mixture was stirred for an additional 20 h at 90 °C. After completion of the reaction, the reaction mixture was cool to room temperature, and 5 mL methanol was added to dissolve the reaction mixture. The organic compound was then extracted using diethyl ether (3 × 50 mL). The extraction process using methanol and diethyl ether was repeated twice. Finally, methanol was evaporated to obtain **3** and dried under vacuum at 60° C for 4 h. The yield was 3.24 g (95%).

Melting point: 135-139 °C. Elemental composition of $C_{24}H_{53}BrN_4O$ is as follows: calculated; C, 58.4; H, 10.8; found; C, 60.1; H, 10.5. ¹H NMR: δ_H (CDCl₃) 0.99-1.04 (9H), 1.16-1.32 (12H), 1.56-1.77 (12H), 2.10-2.25 (3H), 2.63-2.78 (6H), 3.26-3.44 (10H), 6.98 (NH), FTIR: v_{max} (neat): 3595 (NH₂; amide, NH stretching), 2919, 2858 (aliphatic CH₂ stretching), 1670 (amide, C=O stretching), 1551(amide, N-H stretching), 1465, 1311, 1125, 965, 858, 756, and 579 cm⁻¹.

2.4 Corrosion Studies

2.4.1 Mild steel sample

A carbon steel working electrode having a surface area of 1 cm² was employed for the electrochemical tests. The elemental composition of the carbon steel sample is as follow (wt.%): Fe 99.3; C 0.218; Si 0.0198; Mn 0.188; P 0.0091; S 0.0246; Ni 0.0256; Al 0.0456; Cu 0.0376; Cr 0.0189; Mo 0.0089. Different grades of SiC papers were used to abrade the steel samples for obtaining a smooth surface finish followed by acetone degreasing and washing with distilled water. The electrochemical corrosion evaluation was carried out using a Gamry Reference 600 potentiostat equipped with EChem Analyst 6.33 suite.

2.4.2 Electrochemical corrosion evaluation

The electrochemical measurements were undertaken using a standard three electrochemical assembly employing a saturated calomel reference electrode (SCE) and a cylindrical graphite counter electrode, respectively. The test electrolyte of 1M HCl was freshly prepared before each test using analytical grade HCl, and the measurements were taken in triplicate. The electrochemical testing was carried out in the stagnant and aerated condition. Prior to the electrochemical measurements, the open circuit potential (E_{OCP}) of the cell was recorded to achieve a steady-state value. Based on the stable E_{OCP} , the electrochemical impedance spectroscopy (EIS) testing was undertaken in the frequency window of 100 kHz to 10 mHz at an AC amplitude of 10 mV. The potential of the working electrode at a sweep rate of 1 mVs⁻¹. All the electrochemical measurements were carried out in triplicate to check the reproducibility of the experimental data. Surface studies of the steel samples following immersion in the acid electrolyte without and containing the inhibitors were carried out using scanning electron microscope Quattro ESEM-FEG from ThermoFisherTM Scientific.

2.5 Computational analysis

The analysis of the pKa was performed using the ChemAxon Chemicalize suite in the pH range of 0-14 [22, 23]. Quantum chemical calculations using the density functional theory (DFT) approach were utilized to obtain the reactivity indices of the two corrosion inhibitors for estimating the adsorption capability of the inhibitors on the steel surface. For this purpose, the computations were undertaken using Gaussian 09 software suite [24] employing the 6-31G (d,p) basis set and B3LYP correlation functional. The electron density distributions of the frontier

molecular orbitals (FMO) were computed, and the different reactivity parameters were determined. The inhibitor adsorption on the Fe surface was further investigated computationally by Monte Carlo simulations. For this purpose, the surface of the Fe (110) plane was chosen as described *vide infra*. The surface was cleaved with a thickness of 5 Å and enlarged to 10×10 supercells, which was followed by the creation of a vacuum slab, which had a thickness of 30 Å over it. The calculations were performed using the Adsorption Locator module of Biovia Materials Studio 7.0 [25, 26].

3. Results and discussion

3.1 Synthesis and characterization of corrosion inhibitors

The synthetic steps of the precursor compound 1 and corrosion inhibitors 2 and 3 are portrayed in Scheme 1. Briefly, 11-bromoundecanoic acid was treated with methanol in the presence of H_2SO_4 afforded precursor compound 1 in excellent yield. The methyl ester 1 was refluxed with tripropylamine to give 2, which was then treated with DETA to generate 3 in a 95% yield. The ¹H NMR and FTIR were utilized to confirm the structural composition of the corrosion inhibitors 2 and 3. The ¹H NMR and FTIR spectra are shown in Figs. 1 and 2, respectively. The corrosion inhibitors were synthesized from cheap and commercially available precursors. For an approximation, the cost of the synthesized inhibitor 3, assuming an average yield of 90%, is estimated to be US\$ 13 per kg. Both the molecules, being quaternary ammonium salts, were readily soluble in the aqueous environment. When the corrosion inhibitor dissolved in the 1M HCl solution for the corrosion evaluation, clear solutions were obtained without any suspension or turbidity.

The TGA curves for the corrosion inhibitors **2** and **3** (dried under vacuum at 55 °C for 12 h) were examined at a temperature range 20-400 °C to study the thermal stability of the corrosion inhibitors. The TGA curves are depicted in Fig. 3. There is no weight loss occur up to 200 °C, which suggested that both corrosion inhibitors are thermally stable up to ≈ 200 °C.

3.2 Open circuit potential vs. time

Prior to conducting the electrochemical testing, it is a prerequisite to obtaining a stable open circuit potential (OCP) of the working electrode. The OCP refers to the potential difference

between the working and the reference electrodes in the condition of zero net current flow (in other words: Open circuit condition). The determination of a stable OCP vs. time is significant in understanding the nature of corrosion and corrosion inhibition. The OCP-time curves of the two inhibitors **2** and **3** are displayed in Fig. 4 (a, b) in the absence and the presence of the varying concentrations. From the results, it is seen that the addition of the two corrosion inhibitors to the electrolyte solution, produces a noticeable shift in the OCP towards more negative potentials compared to that of the blank, which indicates that the inhibitor action is cathodic. The shift in the potential can be understood to occur as a result of the development of a protective inhibitor film on the metallic substrate [27, 28].

3.3 Electrochemical impedance measurements

The electrochemical impedance spectroscopy (EIS) affords a non-destructive analytical measure for understanding the electrochemical phenomena taking place at the surface of a metallic sample immersed in the electrolytic solutions [29, 30]. The EIS measurements were performed in the present study for the carbon steel sample immersed in 1M HCl without and containing the different concentrations of the inhibitors **2** and **3**. The results of the EIS analysis as the Nyquist plots are shown in Fig. 5 (a and b). The Nyquist plots represent the characteristic depressed semicircles with their centers lying under the real x-axis suggesting that the electrochemical process is charge-transfer controlled [30-32]. This type of behavior is commonly attributed to the frequency distributed electrochemical response of a metallic sample undergoing corrosive attack under the influence of an acidic electrolyte. The electrochemical data were fitted to the equivalent circuits shown in Fig. 5 (c and d) to obtain the different electrochemical parameters, which are listed in Table 1.

The equivalent circuit is a modified Randel's circuit containing the R_s , which represents the uncompensated resistance of the electrolytic solution, and the R_{ct} , which represents the charge transfer resistance. Herein, we have used a constant phase element (CPE) rather than an ideal double-layer capacitor (C_{dl}), to accurately model the frequency distribution response [33-35]. In the case of the inhibited samples, the Nyquist plots show an additional capacitive semicircular loop suggesting a significant contribution from the R_f (resistance of the film) and the CPE_f (the corresponding constant phase element). Therefore, in this case, we have used an equivalent

circuit model different from that of the blank carbon steel sample. The goodness of fit (χ^2) values was of the order of 10⁻³, supported the accuracy of the fitness of the proposed circuit diagrams. The impedance of the CPE can be represented as [36]:

$$Z_{\rm CPE} = Y_{\rm o}^{-1} (j\omega)^{-n} \tag{1}$$

Where, Z_{CPE} is the impedance of CPE, Y_o is a coefficient of proportionality, ω is the angular frequency, and *n* is a measure of the phase shift. The corrosion inhibition efficiency from the EIS measurements was calculated as follows [37, 38]:

$$\eta_{\rm EIS}\% = \frac{R_{\rm p}^{\rm i} - R_{\rm p}^{\rm b}}{R_{\rm p}^{\rm i}} \times 100$$
⁽²⁾

In the above equation, R_p^b and R_p^i respectively represent the polarization resistance of the blank and the inhibited samples. Wherein, the R_{p} (polarization resistance) is equal to the R_{ct} for the blank steel sample as described previously [39, 40]. In the case of the inhibited samples, the $R_{\rm p}$ is the collective contribution of the resistance from the $R_{\rm ct}$ and $R_{\rm f}$ [39, 40]. From the data in Table 1, it is revealed that administering the increasing dosages of the inhibitors results in a successive rise in the inhibition efficiency. The n values can also act as a gauge of the homogeneity of the metallic surface. These values show an increase with the increase in the inhibitor concentration, which supports and improvement in the homogeneity of steel surface upon the adsorption of the corrosion inhibitor. The corrosion inhibitors adsorb at the metallic surface via the replacement of the pre-adsorbed water molecules. The adsorption of the inhibitor molecules results in a successive rise of the resistance at the electrochemical interface. The increase in the interfacial resistance creates a barrier against the charge and the mass transfer processes proceeding at the metal-solution interface and provides protection from corrosion. Both the inhibitor showed a remarkable inhibition performance with an inhibition efficiency more than 90% at a modest dosage of 200 mg L^{-1} . The corrosion inhibitor compound **3** showed a greater inhibition performance compared to that of the 2. Both the inhibitor molecules are composed of quaternary ammonium ions containing the three-propyl side chains in addition to a large 11-membered hydrocarbon chain terminating in an ester group in case of inhibitor 2 and a diethylenetriamine group in case of inhibitor 3. The presence of extra nitrogen atoms in the form

of amine groups is attributed to provide a superior adsorption and inhibition performance to the inhibitor **3** compared to the inhibitor **2**.

3.4 Potentiodynamic polarization studies

The potentiodynamic polarization experiments (PDP) are carried out in the corrosion testing of inhibitor compounds for estimating the electrochemical kinetic parameters of the inhibitor adsorption at the metal/solution interface [41]. The PDP technique was run for the carbon steel sample without and with the inhibitors **2** and **3** at varying concentrations, and the resulting Tafel plots are displayed in Fig. 6 (a and b). The linear branches of the anodic and the cathode PDP curves were extrapolated to meet at their intersection point from where the various electrochemical parameters including the Tafel slopes for the anodic/ cathodic processes (β_a and β_c) corrosion current density (i_{corr}) and the corrosion potential (E_{corr}) were computed and are given in Table 2. The corrosion current density (i_{corr}) data were used to calculate the inhibition efficiency as follows [42]:

$$\eta_{\rm PDP}\% = \frac{i_{\rm corr}^{0} - i_{\rm corr}^{i}}{i_{\rm corr}^{0}} \times 100$$
(3)

From the data shown in Table 2, it is seen that the i_{corr} values for the carbon steel surface in the presence of the inhibitors are significantly lower compared to that in the blank 1M HCl solution. This supports that the addition of the corrosion inhibitors to the acid medium resulted in the adsorption of the inhibitors on the steel surface and the formation of a protective film. As expected, the inhibition efficiency rose with the introduction of successively higher concentrations of the inhibitor molecules, and the inhibitor **3** showed better inhibition performance compared to that of the **2**. The anodic and the cathodic current curves show almost parallel lines with no significant change in the slope values. This indicates that the inhibitor adsorption on the steel surface does not cause any substantial change in the mechanism of corrosion [43]. Furthermore, beyond a potential value of -300 mV, when the potential is swept towards higher positive values, there is a change in the pattern of current flow, and a significant rise in the rate of metal dissolution could be observed. This can be attributed to the desorption of the inhibitor from the electrode surface and this value can be ascribed as the desorption potential [43]. It can also be observed that the dosage of the inhibitors to the corrosive electrolyte produced a lowering in both the anodic as well as the cathodic currents of the Tafel curves. This suggests that the inhibitors effectively mitigate both the anodic metal electro-dissolution as well as the cathodic evolution of the hydrogen gas. Moreover, with the successive rise in the inhibitor concentration, a noticeable shift in the corrosion potentials was observed towards a negative direction. However, the magnitude of the shift in the E_{corr} is not prominent enough to designate the inhibitors as a purely cathodic type. It suggests a mixed type of inhibition behavior with cathodic predominance [44-46].

3.5 Elucidation of adsorption isotherm

The interaction between an organic corrosion inhibitor with a metallic substrate is strongly dependent upon its capability to adsorb on the metal surface. The structural aspects of the inhibitor molecules, the composition of the corrosive electrolyte, nature, and composition of the metallic substrate and the studied temperature are all crucial factors influencing the inhibitor adsorption. The experimental data were fitted to several adsorption isotherms *viz*. Langmuir, Temkin, and Freundlich as given below [47]:

Temkin:	$\exp(f.\theta) = \mathbf{K}_{ads}.\mathbf{C}$	(4)
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Freundlich:	$\theta = K_{ads}.C$	(5)
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Langmuir:
$$(\theta/1-\theta) = K_{ads}.C$$
 (6)

The most suitable fit of the data was incurred in the case of the Langmuir adsorption isotherm, where K_{ads} denotes the equilibrium constant for adsorption, C is the inhibitor concentration, and *f* is energetic inhomogeneity. Equation (6) can be rearranged in the form of a plot of C *vs*. C/ θ as:

$$C/\theta = 1/K_{ads} + C \tag{7}$$

The plots of Langmuir isotherm for the 2 and 3 inhibitors calculated using the data of EIS and PDP measurements are given in Fig. 7 (a and b). The obtained slope and the correlation coefficients are close to unity, thereby validating the Langmuir isotherm. The obtained data of

the K_{ads} were used to calculate the standard free energy of adsorption ΔG_{ads}^0 as shown below [48, 49]:

$$\Delta G_{ads}^0 = -RTln(1000K_{ads})$$
(8)

The values of K_{ads} and ΔG_{ads}^0 for the inhibitors **2** and **3** were calculated and listed in Table 3. The obtained values of the ΔG_{ads}^0 are in the range of -20 to -40 kJ mol⁻¹, which indicates a mixed-mode of chemical and physical adsorption mechanisms [48, 49]. The negative values of the ΔG_{ads}^0 illustrated that the adsorption of the inhibitor on the carbon steel substrate is a spontaneous process.

3.6 Temperature effect on the inhibitor adsorption

The process of acid treatment carried out in the industries usually require the involvement of high temperatures to achieve effective cleaning of the metallic substrates. Temperature is a significant factor influencing the kinetics of inhibitor adsorption-desorption [8]. An elevation in the temperature of the acidic solution can potentially weaken the adsorption-desorption equilibria of the inhibitors on the metallic substrate. It may weaken the strength of the inhibitor adsorption [8]. Therefore, it becomes necessary to investigate the influence of the effect of temperature on the adsorption-desorption behavior of a corrosion inhibitor on a given metallic substrate in the acidic electrolyte. Accordingly, the impact of the temperature was investigated using the EIS and the PDP measurements at a higher temperature of 333 K [50]. Using the optimum inhibitor dosages of 200 mg L⁻¹, the blank and the inhibited steel samples were subjected to the EIS and PDP measurements, and the results are shown in Fig. 8.

In Fig. 8a, the Nyquist plots for the carbon steel substrate without and containing the 100 mg L^{-1} concentration of the two corrosion inhibitors are displayed. The equivalent circuit diagrams for the blank and the inhibitor-containing samples are the same as those given in Fig. 5 (d). The addition of the inhibitors resulted in a considerable increase in the R_p values suggesting the adsorption and the inhibition behavior of the two corrosion inhibitors. The corresponding data on the electrochemical parameters and the inhibition efficacy are listed in Table 4. In the next step, the corrosion inhibition behavior of the two molecules was investigated using the PDP technique at the elevated temperature, and the results are displayed in Fig. 8(b), and

corresponding electrochemical parameters are given in Table 4 [8]. Similar to the observations at room temperature, the inhibitors primarily affect the cathodic branch of the polarization curves and also shift the E_{corr} more towards the cathodic direction, supporting the cathodic predominance of the inhibition behavior.

It can be noted that the increase in the R_p values is considerably lower compared to that observed in Fig. 8(a) for the identical concentrations of the inhibitors at the room temperature. Similarly, in the PDP analysis, the corrosion current densities, although shown significant lowering in the presence of the inhibitors, however, still the corrosion current densities are quite large. This behavior could be attributed to the desorption of the inhibitors at the elevated temperature. Although the inhibitors still exhibit an appreciable corrosion inhibition efficiency close to 70% at the higher temperature. The corrosion rates (C_R) were obtained from the extrapolation of the linear Tafel segments and then used to determine the energy of activation (E_a) according to the following equation (9) [51]:

$$\log \frac{C_{\rm Rb}}{C_{\rm Ra}} = \frac{E_{\rm a}}{2.303R} \left(\frac{1}{T_{\rm 1}} - \frac{1}{T_{\rm 2}} \right) \tag{9}$$

where the symbols C_{Ra} and C_{Rb} symbolize the corrosion rates obtained at the two different temperatures (T_1 and T_2). The E_a in the presence of inhibitors **2** and **3** were higher (56.1 kJ mol⁻¹ and 60.7 kJ mol⁻¹ respectively) in comparison to the absence (25.2 kJ mol⁻¹) of inhibitors. This supports the formation of a protective inhibitor film on the surface of carbon steel, which acts as a protective barrier and increases the E_a value, which is required to be overcome for the corrosion reaction to take place [37, 50].

3.7 Surface analysis

The morphological investigation of the carbon steel samples was conducted following the immersion in the corrosive electrolyte of 1M HCl without and with 200 mg L⁻¹ of inhibitors **2** and **3** for 24 h at room temperature. The scanning electron microscopy (SEM) images recorded of the metallic substrate are displayed in Fig. 9. The blank steel surface (Fig. 9a) shows a large number of furrows and striations caused by the corrosive attack of the 1M HCl solution. Extensive damage to the surface can be visualized due to the corrosion caused by the acid solution. On the other hand, the steel samples inhibited by the introduction of the corrosion

inhibitors 2 and 3 show a considerably smooth surface (Fig. 9 b and c). This suggests that the adsorption of the inhibitors on the metallic samples protected from the corrosive attack of the acid solution.

3.8 Computational studies

3.8.1 Analysis of pKa

An organic corrosion inhibitor, when added to an acidic corrosive electrolyte, can undergo protonation [31, 42]. Therefore, it becomes necessary to identify the sites present in an organic corrosion inhibitor molecule that are amenable to get protonated. For this purpose, the analysis of pKa was performed in the pH range of 0-14 for both the molecules 2 and 3. The molecule 2 does not undergo any further protonation whereas molecule 3 shows protonation at the two N-atoms of the diethylene-triamine chain, as shown in the protonated form of 3 in Fig. 10. The neutral forms of both the inhibitors and the protonated form of inhibitor 3 were chosen for the DFT study (*vide infra*).

3.8.2 Theoretical estimation of the reactivity indices

A computational appraisal of the capability of organic molecules for the adsorption on the metallic substrates can be achieved using DFT based computational studies. The frontier molecular orbital energy levels can suggest the possibility of interaction between the two reacting species. The high level of the energy of the highest molecular orbital (E_{HOMO}) signifies a greater inclination towards electron donation. On the contrary, a smaller value of the energy of the lowest unoccupied molecular orbital (E_{LUMO}) can signify the greater tendency to accept the electrons in a given molecule. Therefore, a higher E_{HOMO} and a lower E_{LUMO} value in a corrosion inhibitor molecule signify a greater tendency to undergo interaction with a given metallic surface. The difference between the E_{HOMO} and E_{LUMO} of a molecule is termed as the molecular orbital energy gap (ΔE), and it is itself considered as a significant reactivity parameter. A lower energy gap represents a greater tendency of reaction between two reacting species. Further, the electronegativity (χ), and the chemical hardness (η) of a corrosion inhibitor are as follows [52]:

$$\chi = -\frac{1}{2} \left(E_{\text{LUMO}} + E_{\text{HOMO}} \right) \tag{10}$$

$$\eta = -\frac{1}{2} \left(E_{\text{LUMO}} - E_{\text{HOMO}} \right) \tag{11}$$

and,
$$\sigma = \frac{1}{\eta}$$
 (12)

Where σ represents the global softness. Following the Hard and Soft Acids and Bases Principle, a hard molecule is characterized by a large energy gap. On the inverse, a smaller energy gap describes a soft or more reactive molecule [53]. The difference in the electronegativities of two reacting species provides the driving force for the electron transfer to take place between two molecules, which needs to overwhelm the energy difference posed by the global hardness [54]. The electrophilicity ω and its reciprocal, the nucleophilicity index ε are given by [55, 56]:

$$\omega = \frac{\chi^2}{4\eta} = \frac{1}{\epsilon} \tag{13}$$

The electrophilicity index describes the propensity to accept the electrons in a given inhibitor molecule [52, 56]. Therefore, a greater value of the electrophilicity index and hence, a smaller nucleophilicity denote a higher tendency to accept electrons in a given molecule.

Fig. 11 shows the optimized geometries and the frontier molecular electron density distributions of molecules 2 and 3 and the protonated form of 3, and the corresponding data are presented in Table 5. It can be seen that the major sites for the HOMO surface are the Br⁻ ions, which suggests that these are the major sites for electron donation. On the other hand, in both the molecules, the three propyl chains attached to the charged nitrogen together represent the LUMO, signifying that the molecules tend towards electron acceptance at these sites. This is a major observation, which shows that in both the molecules, the inhibitor 2 containing the – COOCH₃ group and the inhibitor 3 containing the diethylenetriamine group, the electron acceptance process is predominating. This is supported further with the values of the E_{LUMO} in the inhibitors, which is negative in both cases. However, in the case of inhibitor 3, the value is more significant negative compared to that of inhibitor 2, suggesting that inhibitor 3 shows a greater propensity to adsorb on the metal surface. Taking a look at the other parameters, it shows that the hardness is lower, and correspondingly, the global softness is higher in the case of 3

compared to 2. Besides, the electrophilicity index is greater and the nucleophilicity is lower in 3 compared to 2, which together represents its greater tendency to accept the electrons from the metallic substrate. A look of the data shown in Table 5 reveals that the protonated form of the inhibitor 3 shows the considerably high negative values of the E_{HOMO} as well as the E_{LUMO} . This is explained based on a decrease in the tendency to donate electrons to the metal surface, however, with a considerable rise in the inclination of the electron acceptance tendency from the metallic substrate. The ΔE value after protonation is also lower, signifying a high reactivity in the protonated form. The inhibitor also shows a lower hardness and a higher value of softness, which support its greater reactivity in the protonated form. The electronegativity index has risen very greatly in the protonated form, and the nucleophilicity index is lowered accordingly, which again supports the tendency of electron acceptance in the protonated form.

3.8.3 Monte Carlo simulations

Monte Carlo simulations are carried out in the corrosion inhibition studies to figure out the most probable orientation of a corrosion inhibitor on a given metal surface. In the present case, the corroding metal surface is the carbon steel substrate [57]. Generally, Fe (110), Fe (111) and Fe (110) planes are most commonly studied. Among the three planes, the Fe (110) surface is most widely used because it covers > 60% of the entire Fe crystal surface area [58]. Thus, in the present study, we selected this surface for modeling the inhibitor adsorption.

Fig. 12 (a, b) displays the adsorption orientations of the inhibitors **2** and **3** on the surface of the Fe (110) plane, and the corresponding energy parameters are provided in Table 6. A noteworthy observation is the alignment of the inhibitors on the Fe plane. Both the inhibitors undergo flat adsorption on the Fe surface. This can allow the coverage of the large surface coverage area of the Fe surface and results in a high inhibition efficiency. The adsorption energy describes the total amount of energy released during the adsorption of the relaxed adsorbate (inhibitor) on the surface of the adsorbent (metal). A higher value of the adsorption energy in the negative direction suggests a strong and stable interaction between the metal and the inhibitor [26]. In the present case, the molecule **3** exhibits higher adsorption energy compared to that of the **2**. This trend supports the trend of the molecular orbital energy gap (ΔE) calculated above in the DFT based quantum chemical calculations. Here it is to be noted that in the case of inhibitor **3**, a diethylenetriamine group is presently attached to the alkyl chain compared to an $-COOCH_3$ in the case of **2**. The presence of the $-COOCH_3$ functionality can provide an effective adsorption behavior to molecule **2**. On the other hand, in the case of molecule **3**, attached to the -C=O group is a diethylenetriamine (DETA) side chain instead. Earlier, we have contributed to the DETA functionalized graphene oxide (GO) as an effective corrosion inhibitor for steel surface in 1M HCl as well as in 15% HCl [36, 59]. In Fig. 12 (d), it is well evident that the inhibitor **3** lies almost in a flat orientation, which allows the three N atoms of the DETA chain to come into contact with the Fe surface. The presence of the DETA group can impart the resulting inhibitor water solubility as well as good inhibition behavior due to the presence of the multiple adsorption centers in the form of the three nitrogen atoms, as observed in our earlier report [36].

3.9 Mechanism of adsorption

The adsorption and corrosion inhibition behavior of two quaternary ammonium salts (QAS) compounds **2** and **3** were studied using electrochemical impedance measurements and potentiodynamic polarization studies. The increase in the inhibition efficiency with inhibitor concentration observed in the EIS studies supports the inhibitor adsorption on the steel surface in the acidic electrolyte. According to this observation, the adsorption of the QAS-based inhibitors on the steel surface in the acid solution can be represented by equation (14):

$$M_{H2O} + QAS \implies M_{QAS} + H_2O$$
(14)

The above equilibrium suggests that the inhibitors can displace the pre-adsorbed water molecules from the steel surface and adsorb at the metal/ solution interface. The polarization measurements reveal that the addition of the inhibitors to the 1M HCl resulted in a drift in corrosion potential towards the cathodic direction with a mixed type of behavior [60, 61]. The inhibitors are quaternary ammonium ions containing a positively charged nitrogen atom connected to four alkyl chains. The positively charged inhibitors can interact with the cathodic corrosion active sites present on the steel surface *via* columbic attractions [8]. The bromide ions can interact with the anodic sites and then also create an electrostatic bridge type of interaction with the positively charged inhibitor molecules [8]. The mixed nature of the adsorption as

revealed in the PDP measurements, suggests that the inhibitor minimizes both the anodic and the cathodic processes of metal dissolution and the hydrogen evolution.

The surface analysis carried out *via* the SEM studies supported the inhibitor adsorption by showing a considerably smooth morphology of the carbon steel in the presence of the corrosion inhibitors. The DFT based calculations revealed that the significant sites of electron donation in the two inhibitors are the bromide ions. This supports the above hypothesis of the bridge-type linkage formation between the inhibitors and the metal surface. The Monte Carlo simulations further illustrated that among the two inhibitors molecule **3**, having a diethylenetriamine group attached to the hydrocarbon chain shows the better capability of adsorption on the metallic surface. Fig. 13 displays the schematic of the mechanism of adsorption and inhibition performance of inhibitor **3** on the steel surface.

4. Conclusions

Two quaternary ammonium salts namely-11-methoxy-11-oxo-N,N,N tripropylundecan-1aminium bromide (**2**), 11-((2-((2-aminoethyl)amino)ethyl)amino)-11- oxo- N,N,Ntripropylundecan-1-aminium bromide (**3**) were synthesized using low-cost and commercially available precursors and characterized using different spectroscopic analysis. The molecules were evaluated as new corrosion inhibitors for carbon steel surface in 1M HCl solution using the electrochemical measurements and surface analysis complemented by computational studies. Following major conclusions could be drawn from the present investigation:

- 1. Both the molecules **2** and **3** exhibited excellent water solubility and were readily soluble in the corrosive electrolyte of 1M HCl.
- The EIS studies supported the inhibitor adsorption on the metal substrate, revealing a rise in the polarization resistance with an increase in the dosage of the inhibitors. The inhibitor 3 showed a better adsorption behavior compared to that of inhibitor 2 with ≈93% inhibition efficiency at a dosage of 200 mg L⁻¹.
- 3. The PDP studies revealed that the corrosion currents successively reduced with the addition of the increased dosages of the inhibitors to the acid solution. Both the inhibitors showed a mixed type of inhibition behavior with a cathodic predominance.

- 4. The inhibitor adsorption on the steel surface followed the Langmuir adsorption isotherm with a mixed physical and chemical adsorption. The addition of the inhibitors to the corrosive solution increased the energy of activation, indicating that the inhibitor adsorption on the metallic surface increased the energy barrier for the corrosion process.
- 5. The adsorption of the inhibitors on the metallic surface resulted in a considerably smooth surface morphology in comparison to the blank steel surface supporting the adsorption of the inhibitors.
- 6. DFT analysis showed that the inhibitor 3 exhibited a smaller energy gap compared to the inhibitor 2 supporting its greater inclination towards the adsorption on the steel surface. The molecule 3 undergoes protonation in the acid solution and the protonated form reveals a greater tendency to accept electrons.
- Monte Carlo simulation studies supported the superior adsorption behavior of molecule 3 compared to molecule 2 with higher adsorption energy.

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Figure Captions:

Scheme 1 Synthesis of and the corrosion inhibitors 2 and 3.

Fig. 1: ¹H NMR spectra of corrosion inhibitors **2** and **3** in CDCl₃.

- Fig. 2: FTIR spectra of synthesized corrosion inhibitors 2 and 3.
- Fig. 3: TGA curves of synthesized corrosion inhibitors 2 and 3.

Fig. 4: OCP-time curves obtained for the corrosion inhibitors (a) **2** and (b) **3** on the carbon steel surface in 1M HCl at room temperature.

- Fig. 5: Nyquist plots obtained for the adsorption of corrosion inhibitors (a) 2 and (b) 3 on the surface of carbon steel in 1M HCl at room temperature. Equivalent circuit diagrams used for fitting the electrochemical impedance data for (c) blank and (d) inhibited mild steel samples.
- Fig. 6: Potentiodynamic polarization curves obtained for the adsorption of corrosion inhibitors (a) 2 and (b) 3 on the surface of carbon steel in 1M HCl at room temperature.
- Fig. 7 Langmuir isotherm plots obtained via (a) EIS and (b) PDP measurements for the adsorption of corrosion inhibitors 2 and 3 on the carbon steel surface in 1M HCl solution at room temperature.
- **Fig. 8:** (a) Nyquist plots and (b) polarization curves obtained for the adsorption of 100 mg L⁻¹ of corrosion inhibitors **2** and **3** on the surface of carbon steel in 1M HCl at 333 K.
- **Fig. 9:** Surface morphology (SEM) of the carbon steel samples recorded after immersion in 1M HCl in (a) blank, and in the presence of 200 mg L⁻¹ corrosion inhibitors (b) **2** and (c) **3**.
- Fig. 10 Analysis of microspecies distribution of molecule 3 at varying pH.
- Fig. 11: Optimized molecular structures of molecules (a) 2, (b) 3, (c) protonated form of 3, and the corresponding HOMO/ LUMO electron density distributions.
- **Fig. 12:** Top (a, c) and side (b, d) views of the most probable configurations for the adsorption of the corrosion inhibitors **2** (a, b) and **3** (c, d) on the surface of Fe (110).
- Fig. 13: Schematic of the mechanism of adsorption and inhibition behavior of corrosion inhibitor 3 on the carbon steel surface.

Sample	Conc. (mgL ⁻¹)	$R_{\rm s}$ (Ω)	<i>CPE</i> _f		$R_{\rm f}$ ($\Omega {\rm cm}^2$)	<i>CPE</i> _{dl}		$R_{\rm ct}$ ($\Omega {\rm cm}^2$)	$\chi^2 \times 10^{-3}$	η _{EIS} (%)
	-		$Y_0 \times 10^{-3}$	n_1	-	$Y_0 \times 10^{-3}$	n_2			
			$\Omega^{-1} s^n cm^{-2}$			$\Omega^{-1} s^n cm^{-2}$				
	Blank	0.663				81.61	0.73	8.96	6.026	
2	25	1 0 2 1	1 014	0.00	10.60	75.52	0.54	15 11	1 226	724.00
2	25 50	1.231	1.214	0.68	18.62	/5.53	0.54	15.11	1.320	/3.4 <u>+</u> 0.9
	100	0.900	0.748	0.09	27.00	00.19	0.55	24.90 46.78	2.010	82.7 ± 0.0
	200	0.000	0.748	0.71 0.74	48 91	37.52	0.58	40.78 60.69	1.131	91.4 ± 0.2
	200	0.717	0.040	0.74	40.71	51.52	0.01	00.07	1.071)1. 1 0. 1
3	25	0.488	1.158	0.73	20.82	66.58	0.51	15.82	0.432	75.5 <u>+</u> 0.3
	50	1.077	0.733	0.74	37.72	53.19	0.53	29.21	0.405	86.1 <u>+</u> 0.7
	100	1.601	0.658	0.75	49.59	45.84	0.55	38.10	0.697	89.7 <u>+</u> 0.8
	200	1.045	0.523	0.77	63.77	33.17	0.63	62.56	1.225	92.9 <u>+</u> 0.6

Table 1: Electrochemical impedance parameters of carbon steel in 1M HCl at various concentrations of corrosion inhibitors **2** and **3**.

Sample	Conc. (mgL ⁻¹)	- <i>E</i> _{corr} (mV/SCE)	$i_{\rm corr}$ ($\mu A {\rm cm}^{-2}$)	$\beta_a \ (\text{mV dec}^{-1})$	$\frac{-\beta_c}{(\mathrm{mV}\mathrm{dec}^{-1})}$	η _{PDP} (%)
	Blank	423	1249	83.0	139.4	
2	25 50 100 200	490 488 489 501	348 312 206 144	87.7 89.2 88.6 92.2	132.2 130.4 130.0 133.8	$72.05 \pm 0.3 \\74.91 \pm 0.2 \\83.44 \pm 0.4 \\88.42 \pm 0.5$
3	25 50 100 200	459 475 489 493	377 297 199 108	79.3 81.6 89.9 87.8	145.4 124.7 123.5 142.2	$\begin{array}{r} 69.69 \pm 0.7 \\ 76.13 \pm 0.6 \\ 84.00 \pm 0.4 \\ 91.31 \pm 0.2 \end{array}$

Table 2: Potentiodynamic polarization parameters of carbon steel in 1M HCl at different concentrations of corrosion inhibitors 2 and 3.

2	FIS		
3	EIS	3.06×10^{-4} 4.43×10^{-4}	-30.98 -31.78
2 3	PDP PDP	$2.75 imes 10^{-4} \ 4.03 imes 10^{-4}$	-30.75 -31.57
		×	

Table 3: Calculated values of K_{ads} and ΔG_{ads}^0 for carbon steel corrosion in 1M HCl containing corrosion inhibitors 2 and 3 using EIS and PDP techniques.

Sample	$R_{ m s}$ (Ω)	$CPE_{\rm f}$		$R_{\rm f}$ ($\Omega {\rm cm}^2$)	CPE _{dl}		$R_{\rm ct}$ ($\Omega {\rm cm}^2$)	$\chi^2 \times 10^{-3}$	$\eta_{ m EIS}$ (%)
		$\frac{Y_0 \times 10^{-3}}{\Omega^{-1} \mathrm{s}^{\mathrm{n}} \mathrm{cm}^{-2}}$	<i>n</i> ₁		$Y_0 imes 10^{-3}$ $\Omega^{-1} s^n cm$	n^{-2} n^{-2}			
Blank 2 3	0.753 0.890 0.746	 1.455 0.764	 0.82 0.69	 9.89 9.73	108.59 58.56 60.19	0.67 0.45 0.55	7.69 13.55 15.29	2.123 1.773 2.639	 66.6 <u>+</u> 0.7 69.3 <u>+</u> 0.8
-	Sample	- <i>E</i> _{corr} (mV/SCE)	i _{corr} (μΑ	cm ⁻²)	β_a (mV dec ⁻¹)	$-\beta_c$ (mV dec	η_{P} $(^{\circ})$	DP 6)	
-	Blank 2 3	444 487 499	3204 1090 966	X	104.0 97.6 94.1	128.6 132.2 123.4	 65.4 <u>-</u> 69.8 <u>-</u>	<u>+</u> 0.3 <u>+</u> 0.4	
-		50		0					

Table 4: Electrochemical EIS and PDP parameters obtained for the addition of 100 mg L^{-1} of corrosion inhibitors **2** and **3** into 1M HCl at 333 K.

Sample	E _{HOMO}	E _{LUMO}	ΔE	χ	η	σ	ω	Е
2	-1.44	-0.70	0.74	1.07	0.37	2.68	0.77	1.29
3	-1.49	-0.76	0.73	1.13	0.36	2.71	0.86	1.15
3*	-7.83	-7.63	0.21	7.72	0.11	9.43	140.67	0.01

Table 5: Calculated quantum chemical parameters for the molecules 2 and 3 in neutral form and 3 in protonated form [all energy values in eV, σ is in eV⁻¹]

*Protonated form of corrosion inhibitor 3

Table 6: Energy parameters calculated from Monte Carlo simulations for the most probable adsorption configurations of molecules **2** and **3** on the Fe (110) surface [all energy values in kcal mol^{-1}]

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Total energy	Adsorption energy	Rigid adsorption energy	Deformation energy
63.1059	-5.5086	-5.5086	0.0173
58.7494	-12.0082	-12.1578	0.1496
	R		
	Total energy 63.1059 58.7494	Total energy Adsorption energy 63.1059 -5.5086 58.7494 -12.0082	Total energy Adsorption energy Rigid adsorption energy 63.1059 -5.5086 -5.5086 58.7494 -12.0082 -12.1578

Author Statement

Attached please find the manuscript entitled "Design and synthesis of a novel corrosion inhibitor embedded with quaternary ammonium, amide and amine motifs for protection of carbon steel in 1M HCl" that describes author original work. All authors also confirms that this paper has not been submitted for consideration elsewhere.

On behalf of all authors

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Conflict of interests

The authors declare no conflict of interest.

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Graphical Abstract



Highlights

- A new amidoamine ammonium salts have been synthesized.
- A molecule embedded with motifs of quaternary ammonium, amide and amine functionalities.
- The efficacy of different functional motifs in the inhibition of mild steel corrosion in 1 M HCl is compared.
- The inhibitor molecules imparted admirable inhibition of mild steel corrosion.

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