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Design and synthesis of a novel class of inhibitors for mild steel corrosion in acidic and carbon dioxide-saturated saline media

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p-(9-(2-Methylisoxazolidin-5-yl)nonyloxy)benzaldehyde **I**, prepared using a cycloaddition protocol, was elaborated into its cinnamaldehyde derivative **II** which upon quarternization with propargyl chloride afforded **III** bearing an interesting blend of structural traits suitable for imparting inhibition of mild steel corrosion. Novel compounds **I–III** showed efficient inhibition against mild steel corrosion in CO_2–0.5 M NaCl (40 °C, 1 atm; 120 °C, 10 bar), 1, 4, 7.7 M HCl, and 0.5 M H_2SO_4 at 60 °C as determined by gravimetry and electrochemical methods. The presence of carbonaceous surface and nitrogen, as revealed by XPS study, indicated the formation of a film covering the metal surface, which imparted corrosion inhibition.

1. Introduction

A molecular framework as depicted in Fig. 1, has structural motifs of propargyl, cinnamaldehyde, isoxazolidine as well as a hydrophobe, all known for their excellent efficacies in arresting mild steel corrosion (*vide infra*). It would indeed be an intriguing experience to embed such a multitude of structural traits in a single molecule, which could then be studied for inhibition efficacy with great anticipation. To alleviate the enormous economic losses incurred because of corrosion, there would always be room for better designing of novel inhibitor molecules that could withstand the rigor of corrosive environments in protecting metal such as mild steel. A significant portion (≈30%) of the economic losses in the oil and gas industry is due to failures of mild steel pipelines, which encounter several corrosive environments [1–3]. Crude oil itself is corrosive; carbon dioxide, present in gas or injected into oil wells to increase its production [4], is also corrosive. Mild steel also undergoes severe corrosive attack during industrial acid cleaning.

The corrosive attack in the HCl medium is explained using the following reactions 1–5 in anode and 6–8 in cathode [5,6]:

Anodic dissolution of Fe:

$$\mathrm{Fe} + \mathrm{Cl}^- \rightleftharpoons (\mathrm{FeCl}^-)_{\mathrm{ads}} \tag{1}$$

$$(\mathrm{FeCl}^-)_{\mathrm{ads}} \rightleftharpoons (\mathrm{FeCl})_{\mathrm{ads}} + \mathrm{e}^- \tag{2}$$

$$(\mathrm{FeCl})_{\mathrm{ads}} \rightarrow \mathrm{FeCl}^+ + \mathrm{e}^- \tag{3}$$

$$\mathrm{FeCl}^+ \rightleftharpoons \mathrm{Fe}^{2+} + \mathrm{Cl}^- \tag{4}$$

$$(\mathrm{FeCl}^-)_{\mathrm{ads}} + \mathrm{Inh}^+ \rightleftharpoons (\mathrm{FeCl}^- \cdots \mathrm{Inh}^+)_{\mathrm{ads}} \tag{5}$$

Cathodic evolution of H_2:

$$\mathrm{Fe} + \mathrm{H}^+ \rightleftharpoons (\mathrm{FeH}^+)_{\mathrm{ads}} \tag{6}$$

$$(\mathrm{FeH}^+)_{\mathrm{ads}} + \mathrm{e}^- \rightarrow (\mathrm{FeH})_{\mathrm{ads}} \tag{7}$$

$$(\mathrm{FeH})_{\mathrm{ads}} + \mathrm{H}^+ + \mathrm{e}^- \rightarrow \mathrm{Fe} + \mathrm{H}_2 \tag{8}$$

$$\mathrm{Fe} + \mathrm{Inh}^+ \rightleftharpoons (\mathrm{FeInh}^+)_{\mathrm{ads}} \tag{9}$$

The detrimental reactions are retarded by consecutive adsorption of a chloride ion and a cationic inhibitor (Inh^+) as described in step (5) which restricts the steps (2)–(4) from happening. The corrosion by cathodic evolution of hydrogen, on the other hand, can be minimized by effective competition of the Inh^+ with H^+ (step 6 vs. step 9).

The nature of anions is known to influence the efficiency of corrosion inhibition by ammonium salts [7]; while they are excellent inhibitors in HCl but poor inhibitors in H_2SO_4 [8]. The positive surface charge of iron in both the acidic media, because of the

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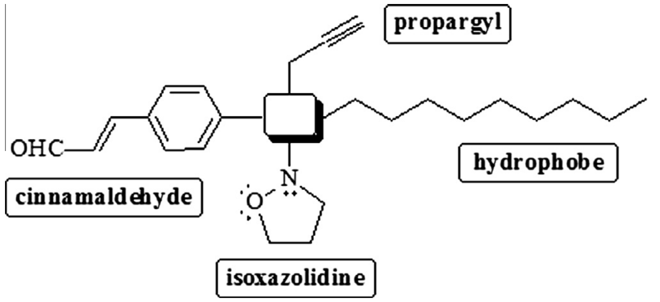

Fig. 1. Design of corrosion inhibitor bearing several structural motifs in a single molecular framework.

corrosion potential E_{corr} being more positive than the potential for zero charge (PZC) $E_{q=0}$, discourages the adsorption of organic cations [9]. However, the stronger adsorbability of the Cl^- in compare to SO_4^{2-} [10,11], shifts the PZC ($E_{q=0}$) towards more positive values than the E_{corr}, thereby allowing the electrostatic adsorption of inhibitor ions Inh^+ [12]. The film of $(FeCl^- \cdots Inh^+)_{ads}$ imparts protection against corrosive HCl media. Note that the inhibitive efficiencies of organic cationic inhibitors in H_2SO_4 media increases significantly in the presence of halide ions [13]. Since the first introduction of isoxazolidines to the corrosion literature [14], our continued efforts have established that these compounds bearing long chain hydrophobic substituents are effective inhibitors both in H_2SO_4 and HCl media [15–17]. Diallylamines bearing long chain hydrophobe and alkyne substituents also imparted very good protection in both the acidic media [18]. The mechanisms through which the corrosion inhibitors function have been ascribed to adsorption processes on either or both the anode or cathode. The formation of a good protective film (coating) on the metal surface essentially requires an inhibitor molecule to have a (1) hydrophilic polar end (e.g. cationic group), (2) a long alkyl chain to form a hydrophobic barrier, and (3) functional group like alkyne or a cinnamyl moiety which can undergo H atom-initiated polymerization between the adsorbed inhibitor molecules [19–21]. Many inhibitors undergo physisorption on the metal surface [22], while inhibitors having nonbonded- and π-electrons may undergo chemisorption [23].

The CO_2 corrosion is explained using the reactions described in steps (10)–(16). It is the carbonic acid (not the dry CO_2) which, at the same pH, has been found to be more aggressive than hydrochloric acid [24] for attacks to mild steel pipelines [25] as a result of the reaction steps (12)–(16) [26]:

$$CO_2(g) \rightleftharpoons CO_2(aq) \tag{10}$$

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq) \tag{11}$$

$$Fe(s) + 2H_2CO_3(aq) \rightleftharpoons Fe(HCO_3)_2(aq) + H_2(g) \tag{12}$$

$$Fe(s) + 2H^+(aq) \rightleftharpoons Fe^{2+}(aq) + H_2(g) \tag{13}$$

$$Fe^{2+}(aq) + 2H_2O \rightleftharpoons Fe(OH)_2(s) + 2H^+(aq) \tag{14}$$

$$Fe(OH)_2(s) \rightleftharpoons FeO(s) + H_2O \tag{15}$$

$$Fe(HCO_3)_2(aq) \rightleftharpoons FeCO_3(s) + H_2CO_3(aq) \tag{16}$$

Corrosion inhibitors bearing hetero-atoms of N, O, P, or S having non-bonded electrons and long chain hydrophobes are used when the formation of a protective ($FeCO_3$) layer [27,28], which helps reduce the corrosive attack, is not favorable [29–31]. $FeCO_3$ is less soluble at high temperatures and pH values; as such higher temperatures usually decrease the corrosion rate because of formation of the more stable surface films [32–34]. Electron-rich imidazolines are extensively used to minimize corrosion in the oil and gas industry [30,35–40].

Inadequate unraveling of the complex mechanism of CO_2 corrosion has become the impediment in designing new inhibitors [41,42]. The effective commercial formulations used in the corrosion inhibition of oil field steel are mixtures of surface-active compounds: *N*-containing compounds, acetylenic compounds, surfactants, and aldehydes. It is our objective to put together cationic charges, hydrophobic environment, alkyne, and cinnamyl motifs in a novel class of inhibitor molecules (Fig. 2) and evaluate their effectiveness in arresting corrosion attack on mild steel in various corrosive media.

2. Experimental

2.1. Materials

Paraformaldehyde, 10-undecenyl bromide, propargyl chloride, p-hydroxybenzaldehyde, and *N*-methylhydroxyamine hydrochloride, malonic acid, manganese dioxide, piperidine, silica gel 100, obtained from Fluka Chemie AG, were used as received. Sodium chloride of >99.5 purity from Baker Chemical Company was used for the inhibition study.

2.2. Physical methods

The chemical composition of the inhibitor compounds were measured by ^1H NMR spectra (500 MHz, JEOL, Japan) in $CDCl_3$, and tetramethylsilane was used as an internal reference. All chemical shifts were reported in parts per million (ppm). The structural composition of all inhibitor molecules were determined by Fourier Transform Infrared (FT-IR) spectrometer (Nicolet Avatar-380). Potentiostat (Model 283, EG&G PARC) was used for the electrochemical measurements. R&D Autoclave Bolted Closure System (Model # 401C-0679 from Autoclave Engineers), Control System interfaced with Computer, and PC with monitor (High Tech Engineering, India) has been installed for the study of corrosion inhibition under higher temperature and pressure.

2.3. Synthesis

2.3.1. Synthesis of p-undec-10-enyloxybenzaldehyde (3)

The following reaction was carried out in the presence of N_2. To a stirring solution of sodium ethoxide (0.065 mol; prepared by adding 1.5 g sodium in 30 cm^3 ethanol) was added *p*-hydroxybenzaldehyde **(1)** (7.95 g, 0.065 mmol) at 20 °C. After the mixture became homogeneous (*ca.* 5 min), 11-bromo-1-undecene **(2)** (15.2 g, 0.065 mol) was added and the mixture was heated at 65 °C for 12 h and at 90 °C for a further period of 12 h. The concentrated residue in ether (50 cm^3) was washed with water (2×100 cm^3), 5% NaOH solution (2×50 cm^3), followed again by water (2×50 cm^3). The organic layer was dried and concentrated to give *p*-undec-10-enyloxybenzaldehyde **(3)** (18.7 g, 88.7%) as a brown liquid. ^1H NMR spectrum revealed the product as very pure, and as such used without further purification.

2.3.2. Reaction N-methyl nitrone **4** with alkene **3**: Synthesis of adduct p-(9-(2-methylisoxazolidin-5-yl)nonyloxy)benzaldehyde (**5**)

To a mixture of *N*-methylhydroxylamine hydrochloride (5.00 g, 60 mmol) in ethanol (45 cm^3) was added sodium acetate-trihydrate (8.84 g, 65 mmol) followed by paraformaldehyde (2.7 g, 90 mmol). After stirring under N_2 at 65 °C for 40 min to generate nitrone **4**, alkene **3** (17.3 g, 63 mmol) was added, and the reaction mixture in a pressure-vessel was then heated at 100 °C for 8 h.