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Synthesis, structural characterization and corrosion inhibition performance of propargyl- and allyl-containing aryloxy alcohol derivatives in H₂S medium

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Abstract

Two novel aryloxy alcohol derivatives, one containing a terminal C≡C bond (RH-1) and an allyl ether containing a C=C bond (RH-2), were synthesized and evaluated as corrosion inhibitors for St-3 carbon steel in a hydrogen sulphide (H₂S)-containing medium. Their molecular structures were characterized by Fourier-transform infrared (FTIR) spectroscopy and nuclear magnetic resonance - ¹H NMR and ¹³C NMR. Corrosion inhibition performance was investigated using gravimetric measurements, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, surface characterization and density functional theory (DFT) calculations. Gravimetric experiments were conducted over the temperature range of 25 to 50 °C using inhibitor concentrations of 10 to 30 ppm. Both compounds effectively reduced the corrosion rate, with inhibition efficiency increasing with inhibitor concentration. At 25 °C and 30 ppm, EIS showed maximum inhibition efficiencies of 97.0 % for RH-1 and 94.0 % for RH-2. EIS measurements showed a substantial increase in charge-transfer resistance and a decrease in double-layer capacitance, consistent with progressive inhibitor adsorption and formation of a protective interfacial layer. Surface analyses further supported the formation of protective inhibitor-containing films on the steel surface. DFT calculations indicated greater electron-donating ability and a stronger adsorption tendency for RH-1, consistent with its superior experimental inhibition performance. The higher efficiency of RH-1 was associated with its propargyl (C≡C) functionality, which promotes stronger interaction with the steel surface than the allyl (C=C) functionality of RH-2. The combined experimental and theoretical results demonstrate that these aryloxy alcohol derivatives provide effective corrosion inhibition of carbon steel in H₂S-containing environments.

Keywords

Organic corrosion inhibitors; hydrogen sulphide; structural characterization; weight-loss method; electrochemical techniques; DFT calculations

Introduction

Corrosion of carbon steel remains one of the most critical challenges in the oil and gas industry, causing severe economic losses, equipment failure, environmental pollution, and safety risks during hydrocarbon production, transportation, and storage. Pipelines, separators, storage tanks, heat exchangers, and downhole equipment are continuously exposed to aggressive production fluids containing hydrogen sulphide (H_2S), carbon dioxide (CO_2), chlorides, dissolved oxygen, and organic acids, which significantly accelerate electrochemical degradation of steel surfaces. The worldwide economic impact of corrosion is estimated to exceed several trillion US dollars annually, underscoring the need for effective, economically viable corrosion protection strategies [1-4].

Among the various corrosive environments encountered in the petroleum industry, sour media containing H_2S are considered particularly aggressive because they simultaneously promote electrochemical corrosion and hydrogen-related degradation mechanisms. Dissociation of H_2S facilitates the formation of iron sulphide corrosion products while increasing hydrogen permeation into the steel matrix, thereby enhancing susceptibility to sulphide stress cracking (SSC), hydrogen-induced cracking (HIC), and hydrogen embrittlement. These degradation processes considerably reduce the mechanical integrity and service life of carbon steel equipment used in oil and gas production systems [5-9].

Several corrosion mitigation strategies have been developed, including metallic and polymeric coatings, cathodic protection, corrosion-resistant alloys, chemical treatment, and optimization of operating conditions. Although these methods have shown varying degrees of effectiveness, organic corrosion inhibitors remain the most practical and economically attractive approach because of their simplicity, adaptability to existing industrial systems, and relatively low operating cost. Organic inhibitors can be continuously injected into production fluids, providing effective protection without major modifications to processing facilities [10-14].

The inhibition efficiency of organic compounds is governed primarily by their adsorption behaviour at the metal/electrolyte interface. Adsorbed inhibitor molecules form compact protective films that isolate the steel surface from aggressive species, suppressing both anodic iron dissolution and cathodic hydrogen evolution reactions. The adsorption process is strongly influenced by the electronic structure of the inhibitor molecules, particularly the presence of heteroatoms such as nitrogen, oxygen, sulphur, phosphorus, and selenium, aromatic rings, multiple bonds, and delocalized π -electron systems capable of donating electrons to vacant iron d-orbitals or accepting electrons through back-donation mechanisms [15-17].

Recent years have witnessed remarkable progress in the development of environmentally acceptable and highly efficient corrosion inhibitors based on Schiff bases, ionic liquids, surfactants, heterocyclic compounds, quinoline derivatives, pyridines, triazoles, oxadiazoles, barbiturates, coumarins, thiosemicarbazones, and organoselenium compounds [18-24]. Numerous experimental and theoretical investigations combining electrochemical measurements with density functional theory (DFT), molecular dynamics (MD) and Monte Carlo simulations have considerably improved understanding of adsorption mechanisms and structure-activity relationships [25-28].

Recent attention has focused on molecules containing unsaturated C-C bonds because these functionalities can provide additional interaction sites during adsorption on metallic surfaces [29].

Propargyl derivatives containing $C\equiv C$ may establish strong surface interactions through their π -electron system, whereas allyl derivatives containing carbon-carbon double bonds can also contribute to inhibitor adsorption through π -electron interactions [30]. However, direct and systematic comparisons between structurally analogous propargyl- and allyl-containing corrosion inhibitors remain limited, particularly under H_2S -containing conditions.

Alongside the search for highly efficient inhibitors, attention has increasingly shifted toward environmentally benign compounds and inhibitors with simplified synthesis routes. A substantial proportion has focused on nitrogen- and sulphur-containing heterocycles, whereas oxygen-containing aryloxy alcohol derivatives remain comparatively unexplored despite their potential adsorption capability through hydroxyl, ether oxygen, aromatic π -electrons, and unsaturated functional groups. Consequently, understanding how different unsaturated substituents influence the adsorption and corrosion inhibition behaviour of aryloxy alcohol molecules represents an important scientific challenge with direct industrial relevance [31].

Therefore, the development of novel oxygen-containing corrosion inhibitors with high inhibition efficiency, low dosage requirements, and straightforward synthesis remains an important objective for corrosion protection in sour oilfield environments. A comparative investigation of structurally related molecules that differ only in the nature of their unsaturated substituent provides valuable insight into the relationship between molecular structure and inhibition performance while minimizing interference from other structural factors.

Despite the extensive investigation of organic corrosion inhibitors, the specific influence of closely related unsaturated functionalities on the adsorption and protective behaviour of aryloxy alcohols in H_2S -containing environments remains insufficiently understood. In particular, systematic comparisons that maintain the molecular framework while varying the unsaturated functionality from an allyl ($C=C$) to a propargyl ($C\equiv C$) group are scarce. Addressing this gap provides an opportunity to distinguish the contribution of the unsaturated moiety to inhibitor-metal interactions rather than attributing differences in inhibition performance to major changes in molecular structure.

In the present study, two structurally related aryloxy alcohol derivatives, RH-1 and RH-2, containing propargyl and allyl functionalities, respectively, were comparatively evaluated as corrosion inhibitors for St-3 carbon steel in an H_2S -containing medium. Their inhibition performance and adsorption behaviour were investigated using gravimetric measurements, electrochemical impedance spectroscopy, potentiodynamic polarization, surface characterization, and density functional theory calculations. By correlating experimental inhibition efficiencies with surface characteristics and calculated electronic descriptors, the study establishes a direct structure-performance relationship between the nature of the unsaturated functionality and corrosion protection. The results demonstrate that the propargyl-containing RH-1 provides stronger inhibitor-metal interactions and superior surface protection than its allyl-containing analogue RH-2. This comparative molecular-level insight advances the understanding of how targeted structural modification controls adsorption and protective-film formation and provides a rational basis for designing more efficient oxygen-containing organic inhibitors for carbon-steel protection under H_2S -containing corrosive conditions.

Experimental

Materials

Corrosion experiments were carried out using St-3 carbon steel, a structural steel widely employed in pipelines, storage tanks, and processing equipment in the oil and gas industry because

of its favourable mechanical properties and economic advantages. Prior to each experiment, the steel specimens were mechanically polished using successive grades of silicon carbide abrasive papers to obtain a smooth and reproducible surface. The polished specimens were rinsed with distilled water, degreased with acetone, dried at room temperature, and weighed using an analytical balance with an accuracy of ± 0.1 mg.

The chemical composition of the steel was determined by spark optical emission spectroscopy (OES) using a SPECTROMAXx optical emission spectrometer (SPECTRO Analytical Instruments, Germany). Prior to analysis, the specimen surface was mechanically ground to expose a clean metallic surface. Measurements were performed at three different positions on the steel specimen, and the mean elemental concentrations were expressed (Table 1).

Table 1. Chemical composition of the St-3 carbon steel used in the corrosion experiments

Element	C	Mn	Si	P	S	Cr	Ni	Cu	Fe
Content, wt.%	0.17	0.48	0.22	0.021	0.018	0.08	0.06	0.10	Balance

The corrosive medium consisted of an H_2S -containing solution simulating sour oilfield conditions. Two synthesized inhibitors, RH-1 and RH-2, were added separately to the corrosive medium at concentrations of 10, 20, and 30 ppm. Blank solutions without inhibitor were also investigated under identical experimental conditions. Corrosion tests were performed at temperatures of 25, 30, 35, 40, 45 and 50 °C.

Synthesis of propargyl ether and allyl ether inhibitors

The aryloxy alcohol derivatives RH-1 and RH-2 were synthesized through the reaction of 2,6-dimethylbenzaldehyde with chloromethyl propargyl ether or chloromethyl allyl ether, respectively, in the presence of activated zinc under a nitrogen atmosphere. The reaction was carried out in anhydrous benzene and ethyl acetate using hexamethylphosphorotriamide (HMPTA) as a promoter. The three-dimensional molecular structures of the synthesized inhibitors were constructed to visualize their geometric configurations and the spatial arrangement of the functional groups responsible for adsorption on the steel surface. Particular attention was given to the orientation of the oxygen atom, hydroxyl group, aromatic ring, and unsaturated allyl/propargyl fragments, as these structural features are expected to influence the adsorption behaviour and corrosion inhibition performance (Figure 1).

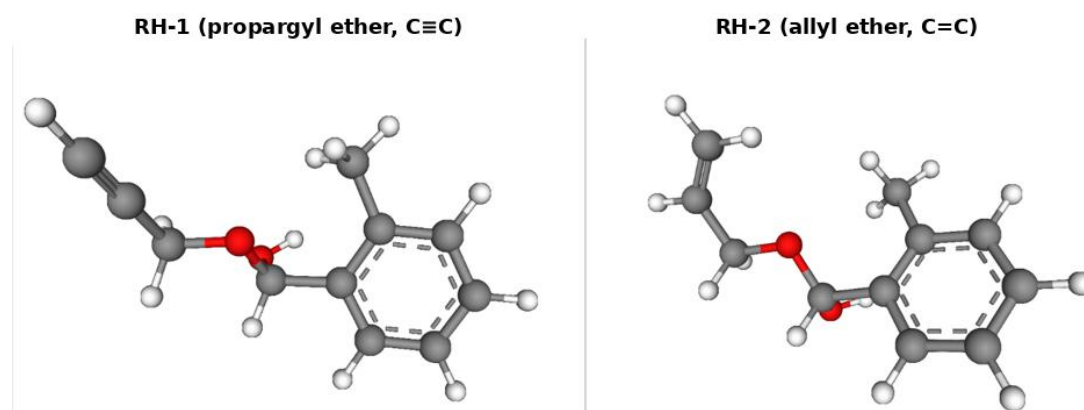
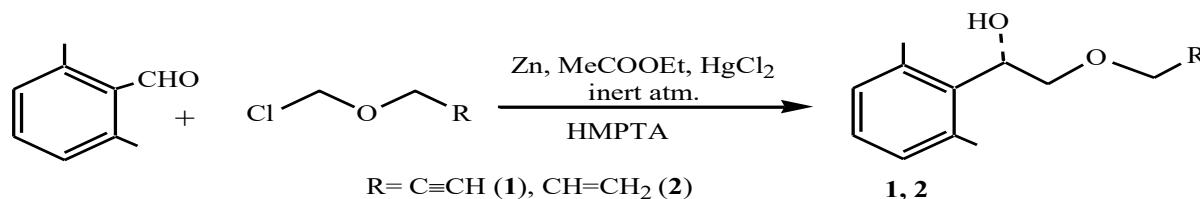


Figure 1. Three-dimensional molecular models of the synthesized corrosion inhibitors RH-1 and RH-

After refluxing for 4 h, the reaction mixture was cooled, hydrolysed with 5 % hydrochloric acid, extracted with ethyl acetate, dried over anhydrous sodium sulphate, and purified by vacuum distillation. The synthetic route of RH-1 and RH-2 is illustrated in Scheme 1.

The obtained products were isolated in good yields (63.9 % for RH-1 and 69.4 % for RH-2). The purity of both compounds was verified by thin-layer chromatography (Silufol UV-254, acetone/hexane 1:1), and elemental analysis confirmed good agreement between the calculated and experimental compositions [32,33].



Scheme 1. Synthetic route for the preparation of aryloxy alcohol derivatives 1 ($R = \text{C}\equiv\text{CH}$) and 2 ($R = \text{CH}=\text{CH}_2$) via the reaction of 2,6-dimethylbenzaldehyde with propargyl or allyl 2-chloroethyl ether in the presence of Zn, methyl acetate (MeCOOEt), HgCl_2 and HMPTA

Structural characterization

The molecular structures of RH-1 and RH-2 were confirmed using spectroscopic techniques. FTIR spectra were recorded on a Specord 75 IR spectrometer. Nuclear magnetic resonance (NMR) - ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker SF-300 spectrometer operating at 300.13 MHz (^1H) and 75 MHz (^{13}C) using CDCl_3 as solvent and HMDS as the internal reference. Elemental analysis was performed using a EURO EA 3000 elemental analyser (EuroVector, UK) [34]. High-resolution mass spectra (HRMS) were recorded using an Agilent 6545 Q-TOF LC/MS system (Agilent Technologies, USA) equipped with an electrospray ionization source operating in positive-ion mode (ESI^+). The molecular compositions of RH-1 and RH-2 were verified by comparison of the experimentally observed protonated molecular ions $[\text{M}+\text{H}]^+$ with their calculated exact masses.

Gravimetric corrosion measurements

Corrosion performance was evaluated using the conventional weight-loss method.

The rectangular St-3 steel specimens (20×20×2 mm) were immersed in blank and inhibitor-containing H_2S solutions for 6 h under controlled temperature conditions. After exposure, corrosion products were removed, the specimens were rinsed with distilled water, dried, and reweighed [35].

The corrosion rate (CR) was calculated according to Equation (1) [35,36]:

$$\text{CR} = \frac{\Delta m}{St} \quad (1)$$

where Δm / g is the mass loss, S / m^2 is the exposed surface area, and t / h is the immersion time. Corrosion rates were also converted into mm year^{-1} for comparison.

The inhibition efficiency (η / %) was calculated using Equation (2) [37-39]:

$$\eta = \frac{\text{CR}_0 - \text{CR}_{\text{inh}}}{\text{CR}_0} 100 \quad (2)$$

where CR_0 and CR_{inh} represent the corrosion rates in the absence and presence of inhibitor, respectively.

Electrochemical measurements

Electrochemical measurements were performed using a conventional three-electrode electrochemical cell connected to a Corrtest CS350M electrochemical workstation. The working electrode was prepared from St-3 carbon steel with an exposed surface area of 1.0 cm^2 . Before each experiment, the steel surface was polished sequentially with silicon carbide abrasive papers (600 to 2000 grit), rinsed thoroughly with distilled water, degreased with acetone, and dried in air. A

platinum wire served as the counter electrode, while an Ag/AgCl (saturated KCl) electrode was used as the reference electrode.

The corrosive electrolyte consisted of an H₂S-containing medium, either without inhibitor or containing RH-1 or RH-2 at concentrations of 10, 20 and 30 ppm. Before each electrochemical measurement, the working electrode was immersed in the test solution and allowed to stabilize at the open-circuit potential (OCP) for approximately 40 min until a steady-state potential was achieved. All experiments were performed at 25 ± 1 °C [40,41].

Electrochemical impedance spectroscopy (EIS) measurements were performed at OCP using a sinusoidal perturbation amplitude of 10 mV over a frequency range from 100 kHz to 0.05 Hz. The AC perturbation amplitude of 10 mV was selected to maintain the electrode response within the approximately linear regime while minimizing disturbance of the steel/electrolyte interface, consistent with established EIS practice and ASTM G106. The broad frequency range was selected to resolve electrochemical processes over different characteristic time scales, including the solution response at high frequencies and interfacial charge-transfer and double-layer processes at lower frequencies, in accordance with the general recommendations for EIS data acquisition given in ISO 16773-2. The impedance spectra were analysed using an appropriate equivalent electrical circuit, and the charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}) were determined [42].

Potentiodynamic polarization measurements were performed after stabilization of the OCP. Polarization curves were recorded at a scan rate of 1 mV s⁻¹ within a potential range of ±350 mV versus OCP. The potentiodynamic polarization procedure was conducted in accordance with the general recommendations of ISO 17475 for electrochemical polarization measurements. A scan rate of 1 mV s⁻¹ was selected to balance acquisition time with the need for a sufficiently stable electrochemical response during potential scanning. The potential interval of ±350 mV relative to OCP was employed to obtain sufficiently developed anodic and cathodic branches for reliable Tafel extrapolation and determination of the corrosion kinetic parameters. The corrosion potential (E_{corr}) and corrosion current density (j_{corr}) were determined by Tafel extrapolation of the anodic and cathodic polarization branches. The inhibition efficiency was calculated from the decrease in corrosion current density after the addition of RH-1 and RH-2 to the H₂S-containing solution [43].

All electrochemical measurements, including EIS and potentiodynamic polarization tests, were independently repeated three times using freshly prepared St-3 steel specimens under identical experimental conditions to ensure reproducibility. The electrochemical parameters reported in the corresponding tables represent the mean ± standard deviation (SD) of three independent measurements ($n = 3$).

Surface morphology, elemental composition and X-ray diffraction analysis

Following the corrosion experiments, the surface morphology and composition of St-3 carbon steel specimens exposed to the H₂S-containing medium in the absence of inhibitor and in the presence of 30 ppm RH-1 or RH-2 were investigated by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). After removal from the corrosive medium, the specimens were gently rinsed with deionized water to remove residual electrolyte and dried under a nitrogen stream. No mechanical polishing or aggressive chemical cleaning was performed after exposure to preserve the corrosion products and adsorbed inhibitor films.

SEM observations were performed using a JSM-6610LV scanning electron microscope (JEOL Ltd., Tokyo, Japan) equipped with an energy-dispersive X-ray spectroscopy system. The surface micrographs were acquired in secondary-electron imaging mode at an accelerating voltage of 20 kV,

a working distance of approximately 10 mm, and a magnification of $\times 50,000$. Elemental analysis was performed by EDS at selected positions on the investigated surfaces. The exact EDS acquisition positions were marked directly on the corresponding SEM micrographs to establish a direct relationship between the observed surface morphology and local elemental composition [44,45].

Density functional theory calculations

Density functional theory (DFT) calculations were performed to investigate the electronic properties of RH-1 and RH-2 and to support the experimental corrosion inhibition results. The molecular geometries of both inhibitors were fully optimized without symmetry constraints using the B3LYP exchange-correlation functional with the 6-31G(d,p) basis set. Frequency calculations confirmed that the optimized structures corresponded to true energy minima with no imaginary frequencies. The frontier molecular orbitals, including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), were obtained from the optimized structures. Quantum chemical parameters, including the HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}), energy gap (ΔE), ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η), global softness (σ), electrophilicity index (ω), fraction of electrons transferred (ΔN) and back-donation energy ($\Delta E_{\text{back-donation}}$), were calculated using the standard Koopmans-based relationships. The optimized molecular structures and frontier molecular orbital distributions were visualized using GaussView 6.0 [46,47].

Statistical analysis

All corrosion experiments were performed in triplicate to ensure the reproducibility of the experimental results. The obtained data are presented as mean $\pm$ standard deviation [48].

The arithmetic mean was calculated according to Equation (4) [49]:

$$\bar{x} = \frac{\sum x_i}{n} \quad (3)$$

while the standard deviation (SD) was determined using Equation (4) [50]:

$$\text{SD} = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} \quad (4)$$

All calculations were carried out using Microsoft Excel and OriginPro software [51]. The relative experimental error did not exceed $\pm 3\%$, indicating good repeatability and reliability of the results.

Post-corrosion Fourier-transform infrared analysis

The chemical characteristics of the surface films remaining on the steel specimens after corrosion exposure were further investigated by attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR). Separate St-3 specimens exposed to the H_2S -containing medium without inhibitor and in the presence of 30 ppm RH-1 or RH-2 were gently rinsed with deionized water and dried under a nitrogen stream. No mechanical or chemical cleaning was performed before spectroscopic examination to preserve the adsorbed inhibitor/corrosion-product layers.

ATR-FTIR spectra were recorded using a Bruker ALPHA II FTIR spectrometer (Bruker Optics GmbH, Ettlingen, Germany) equipped with a diamond ATR accessory. Spectra were collected over the range of 4000 to 500 cm^{-1} at a spectral resolution of 4 cm^{-1} , accumulating 32 scans for each specimen. A background spectrum was recorded before each measurement under identical conditions. The spectra obtained for the blank, RH-1-treated, and RH-2-treated specimens were compared to identify inhibitor-related functional groups and changes in the chemical characteristics of the post-corrosion surface films [52].

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was employed to determine the surface elemental composition and chemical states of species present on St-3 carbon steel after corrosion exposure. The blank specimen and specimens exposed to the H₂S-containing medium (30 ppm RH-1 or RH-2) were gently rinsed with deionized water and dried under a nitrogen stream. The surfaces were not polished or chemically cleaned after exposure to preserve the corrosion-product/inhibitor interfacial layers.

XPS measurements were performed using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer (Thermo Fisher Scientific, East Grinstead, UK) equipped with a monochromate Al K α X-ray source ($h\nu = 1486.6$ eV) and a hemispherical electron-energy analyser. Survey spectra were acquired over a binding-energy range of 0–1200 eV, followed by high-resolution measurements of the Fe 2p, O 1s, C 1s, and S 2p regions. The analysis area was approximately 400 μm in diameter. Survey spectra were recorded at a pass energy of 200 eV, while high-resolution spectra were acquired at 50 eV.

The binding-energy scale was referenced to the hydrocarbon C 1s peak at 284.8 eV. High-resolution spectra were background-corrected and deconvoluted into individual chemical-state components using Thermo Scientific Avantage software [53]. Surface atomic concentrations of Fe, O, C and S were determined from the integrated peak areas using the appropriate relative sensitivity factors. The resulting survey spectra, high-resolution Fe 2p, O 1s, C 1s and S 2p spectra, and surface atomic compositions were used to compare the blank and inhibitor-treated steel surfaces [54].

Results and discussion

Synthesis and structural characterization of propargyl ether and allyl ether

Two novel aryloxy alcohol derivatives, designated RH-1 and RH-2, were synthesized by reacting 2,6-dimethylbenzaldehyde with chloromethyl propargyl ether and chloromethyl allyl ether, respectively, under zinc-mediated conditions (Scheme 1). The synthesized compounds were obtained in satisfactory yields of 63.9 % (RH-1) and 69.4 % (RH-2) after purification by vacuum distillation. Elemental analysis showed excellent agreement between the calculated and experimental elemental compositions, confirming the high purity of the obtained products.

The molecular structures of both inhibitors were verified using FTIR, ¹H NMR and ¹³C NMR spectroscopy. The combination of these analytical techniques confirmed the successful formation of the targeted aryloxy alcohol derivatives containing either a propargyl or an allyl substituent.

Figure 2 presents the FTIR spectrum of the synthesized RH-1 inhibitor. The broad absorption band observed at 3603 cm⁻¹ corresponds to the stretching vibration of the hydroxyl (O-H) group. The absorption at 3301 cm⁻¹ is assigned to the terminal alkyne ($\equiv\text{C-H}$) stretching vibration, while the strong characteristic band at 2200 cm⁻¹ confirms the presence of the carbon-carbon triple bond ($\text{C}\equiv\text{C}$) within the propargyl fragment. Absorption bands appearing at 3081 and 3010 cm⁻¹ are attributed to aromatic and aliphatic C-H stretching vibrations. The peaks at 1270 and 1102 cm⁻¹ correspond to the asymmetric and symmetric stretching vibrations of the ether C-O-C linkage, whereas the bands located between 985 and 700 cm⁻¹ originate from out-of-plane aromatic C-H bending vibrations.

The FTIR spectrum confirms the presence of the hydroxyl, ether, aromatic, and propargyl functional groups expected for the proposed molecular structure of RH-1.

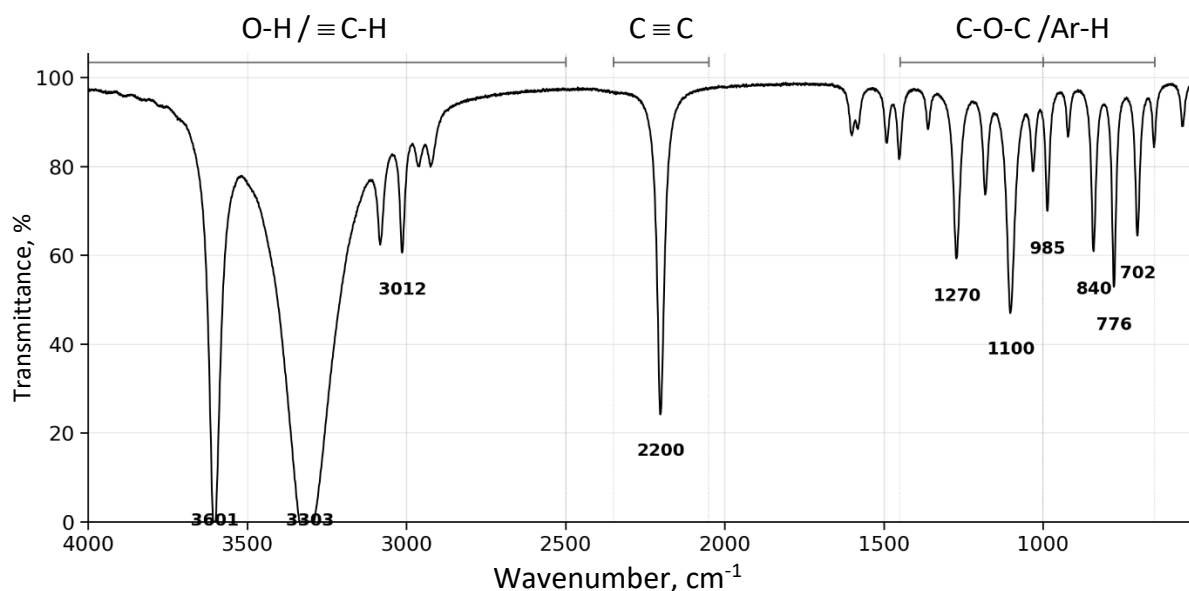


Figure 2. FTIR spectrum of the synthesized RH-1 inhibitor

The FTIR spectrum of RH-2 is shown in Figure 3. Similar to RH-1, a broad absorption band at 3603 cm^{-1} is assigned to O-H stretching vibrations. The absorption bands observed at 3080 and 3010 cm^{-1} are attributed to aromatic and olefinic C-H stretching vibrations. In contrast to RH-1, RH-2 exhibits a strong absorption band at 1640 cm^{-1} , characteristic of the carbon-carbon double bond ($\text{C}=\text{C}$) within the allyl fragment.

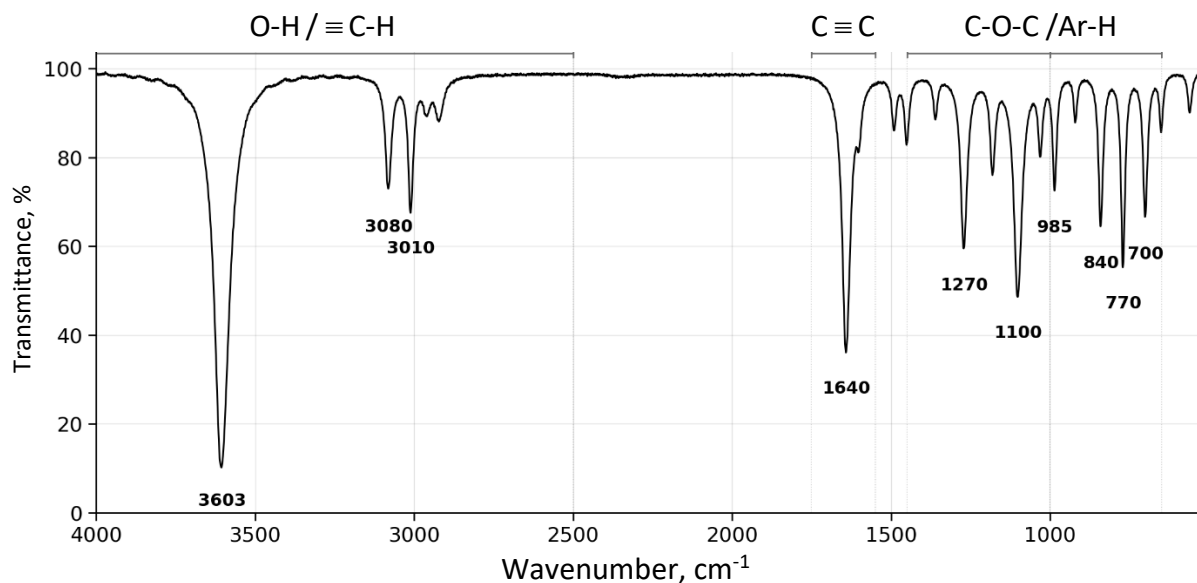


Figure 3. FTIR spectrum of the synthesized RH-2 inhibitor

Notably, the characteristic 2200 cm^{-1} absorption assigned to the $\text{C}\equiv\text{C}$ bond is absent, confirming that no alkyne functionality is present in RH-2.

The ether linkage is confirmed by characteristic C-O-C stretching vibrations at 1270 and 1100 cm^{-1} , while bands in the 985 to 700 cm^{-1} region correspond to aromatic ring deformation vibrations.

These spectral features are fully consistent with the proposed molecular structure of RH-2.

^1H and ^{13}C nuclear magnetic resonance characterization of propargyl ether and allyl ether

^1H and ^{13}C NMR spectroscopy further confirmed the molecular structures of the synthesized inhibitors (Figure 4). The observed chemical shifts were in excellent agreement with the proposed

structures of the propargyl-substituted RH-1 and allyl-substituted RH-2 derivatives, confirming the successful synthesis of both aryloxy alcohol compounds.

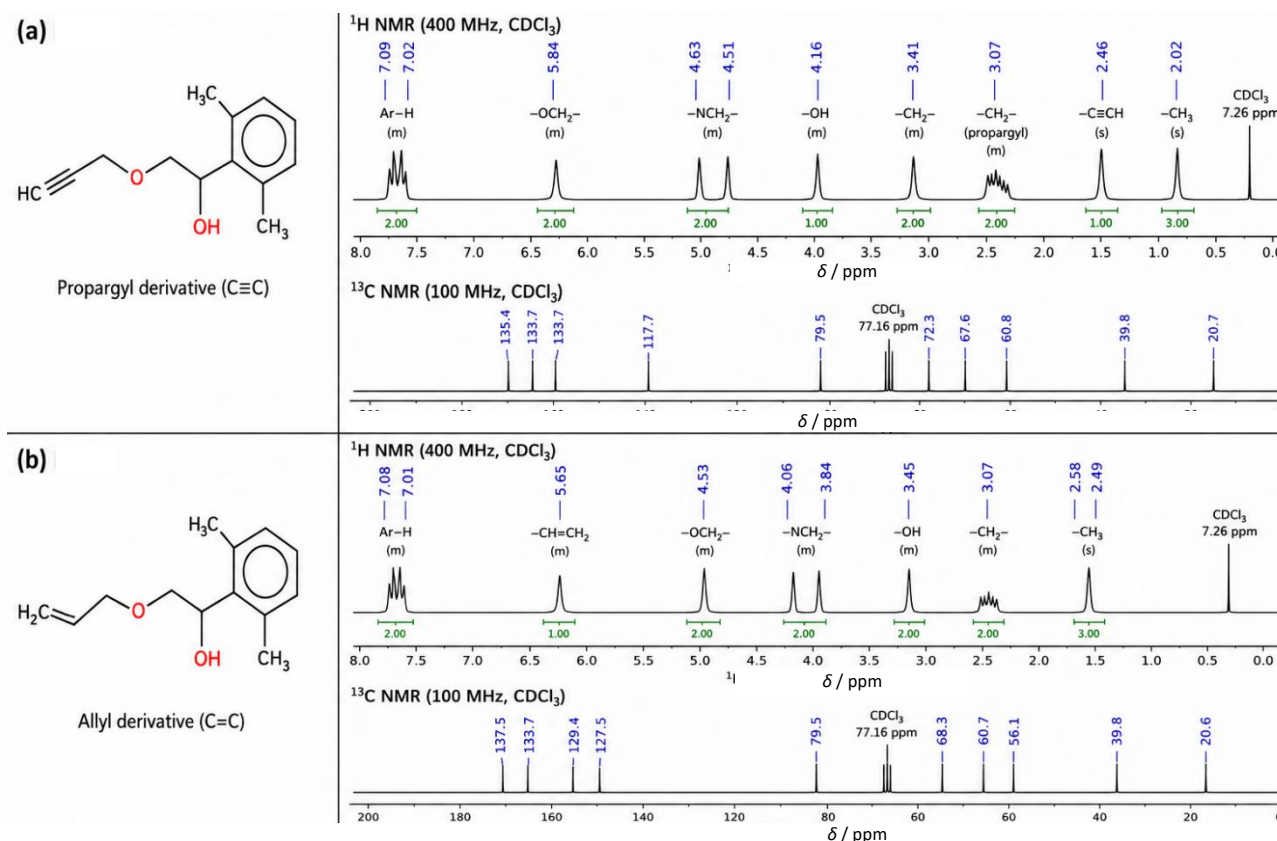


Figure 4. ¹H NMR and ¹³C NMR spectra of the synthesized (a) RH-1 and (b) RH-2 inhibitors. *m* -multiplet; *s* - singlet; δ relative to tetramethylsilane (0.00 ppm)

The ¹H NMR spectrum of RH-1 (Figure 4a) exhibited characteristic aromatic proton resonances at $\delta = 7.01$ to 7.08 ppm, confirming the presence of the 2,6-dimethylphenyl ring. The methylene protons adjacent to the ether oxygen (-OCH₂-) appeared at $\delta = 4.53$ ppm, while the methylene group adjacent to the hydroxyl-bearing carbon resonated at $\delta = 3.84$ to 4.06 ppm. The hydroxyl proton was observed as a broad resonance at approximately $\delta = 3.45$ ppm. A characteristic signal corresponding to the terminal acetylenic proton ($\equiv\text{C-H}$) appeared at $\delta = 2.49$ to 2.58 ppm, providing clear evidence for incorporation of the propargyl fragment. In the ¹³C NMR spectrum (Figure 4a), the two acetylenic carbon atoms of the C $\equiv$ C group gave characteristic resonances at $\delta = 68.3$ and 79.5 ppm, whereas the oxygen-bearing aliphatic carbon atoms resonated at $\delta = 56.1$ to 60.7 ppm. The aromatic carbon atoms appeared in the expected δ 127-138 ppm region, confirming the proposed carbon skeleton of RH-1. HRMS (ESI⁺) *m/z*: [M+H]⁺ calculated for C₁₃H₁₇O₂⁺, 205.1223; found, 205.1220.

The ¹H NMR spectrum of RH-2 (Figure 4b) likewise showed aromatic proton resonances at $\delta = 7.02$ to 7.09 ppm, along with the characteristic vinyl proton signals of the allyl group. The terminal olefinic methylene protons (=CH₂) resonated at $\delta = 5.16$ to 5.33 ppm, whereas the internal vinyl proton (-CH=) appeared at $\delta = 5.84$ to 5.65 ppm, confirming the presence of the allyl substituent. The methylene protons adjacent to the ether oxygen were detected at $\delta = 4.51$ to 4.63 ppm, while the hydroxyl proton produced a broad resonance at approximately $\delta = 4.16$ to 3.41 ppm. Additional methylene resonances of the allyl side chain appeared near $\delta = 3.07$ ppm, and the methyl substituent on the aromatic ring was observed as a singlet at $\delta = 2.46$ ppm. In the corresponding ¹³C NMR spectrum (Figure 4b), the allyl fragment exhibited characteristic olefinic carbon resonances at approximately $\delta = 117.7$ ppm and within the $\delta = 133$ to 135 ppm region, replacing the acetylenic

carbon signals observed for RH-1. The oxygen-containing aliphatic carbon atoms resonated at $\delta = 60.8$ to 72.3 ppm, whereas the aromatic carbon signals remained within the expected chemical shift range, further supporting the proposed aryloxy alcohol structure. HRMS (ESI⁺) m/z : $[M+H]^+$ calculated for $C_{13}H_{19}O_2^+$, 207.1380; found, 207.1376.

Comparison of the NMR spectra clearly distinguishes the structural difference between the two synthesized inhibitors. RH-1 is characterized by diagnostic acetylenic proton and carbon resonances associated with the propargyl fragment, whereas RH-2 exhibits characteristic olefinic proton and carbon signals of the allyl group. The close agreement between the experimental chemical shifts and the expected structural assignments, together with the FTIR results, unequivocally confirms the successful synthesis and structural integrity of both RH-1 and RH-2 inhibitors.

Corrosion inhibition performance of propargyl ether and allyl ether

The weight-loss measurements provide an initial assessment of the corrosion inhibition performance of the synthesized RH-1 and RH-2 inhibitors in an H_2S -containing medium. Table 2 summarizes the corrosion rates and inhibition efficiencies obtained at different temperatures (25 to 50 °C) and inhibitor concentrations (10 to 30 ppm). Both inhibitors reduced the corrosion rate considerably, although their performance depended on both temperature and inhibitor concentration.

Table 2. Corrosion rates and inhibition efficiency of RH-1 and RH-2 inhibitors in H_2S -containing medium at different temperatures

Temperature, °C	C_{inh} / ppm	CR, g m ⁻² h ⁻¹		Effectiveness of inhibitor, %		CR, mm year ⁻¹	
	RH-1 or RH-2	RH-1	RH-2	RH-1	RH-2	RH-1	RH-2
25	0	0.434	0.434	-	-	0.484	0.484
	10	0.130	0.148	70	66	0.145	0.165
	20	0.052	0.065	88	85	0.058	0.073
	30	0.013	0.026	97	94	0.015	0.029
30	0	0.538	0.538	-	-	0.600	0.600
	10	0.194	0.215	64	60	0.216	0.240
	20	0.097	0.113	82	79	0.108	0.126
	30	0.027	0.054	95	90	0.030	0.060
35	0	0.702	0.702	-	-	0.783	0.783
	10	0.274	0.302	61	57	0.306	0.337
	20	0.147	0.175	79	75	0.165	0.196
	30	0.056	0.084	92	88	0.063	0.094
40	0	0.952	0.952	-	-	1.062	1.062
	10	0.390	0.419	59	56	0.436	0.467
	20	0.228	0.267	76	72	0.255	0.297
	30	0.105	0.133	89	86	0.117	0.149
45	0	1.412	1.412	-	-	1.576	1.576
	10	0.635	0.692	55	51	0.709	0.772
	20	0.381	0.438	73	69	0.425	0.488
	30	0.198	0.254	86	82	0.221	0.284
50	0	1.926	1.926	-	-	2.149	2.149
	10	0.905	0.982	53	49	1.010	1.096
	20	0.616	0.674	68	65	0.688	0.752
	30	0.308	0.385	84	80	0.344	0.430

The gravimetric results demonstrate a clear dependence of corrosion inhibition on both inhibitor concentration and temperature. For both RH-1 and RH-2, inhibition efficiency increased with increasing concentration and decreased progressively with increasing temperature. RH-1 consistently exhibited higher inhibition efficiency and lower corrosion rates than RH-2 over the entire investigated range. At 25 °C and 30 ppm, inhibition efficiencies reached 97 % for RH-1 and 94 % for RH-2, whereas at 50 °C they were 84 and 80 %, respectively. The decrease in inhibition efficiency at elevated

temperature is consistent with partial desorption of inhibitor molecules from the steel surface, while the improvement observed with increasing concentration reflects progressive surface coverage. The smaller increment in inhibition efficiency above 20 ppm suggests that adsorption approaches saturation at higher inhibitor concentrations. Overall, the gravimetric results indicate stronger and more persistent adsorption of propargyl-containing RH-1 than allyl-containing RH-2.

To compare the performance of the two inhibitors more clearly, the difference in inhibition efficiency ($\Delta IE = IE(RH-1) - IE(RH-2)$), where IE denotes inhibition efficiency, is plotted in Figure 5. Positive ΔIE values were obtained under all experimental conditions, showing that RH-1 provided higher inhibition efficiency than RH-2 throughout the investigated temperature range. The difference remained between 3 and 5 %, with the highest value observed at 30 ppm and 30 °C. This improvement is attributed to the propargyl ($C\equiv C$) group in RH-1, which favours stronger adsorption than the allyl ($C=C$) group in RH-2.

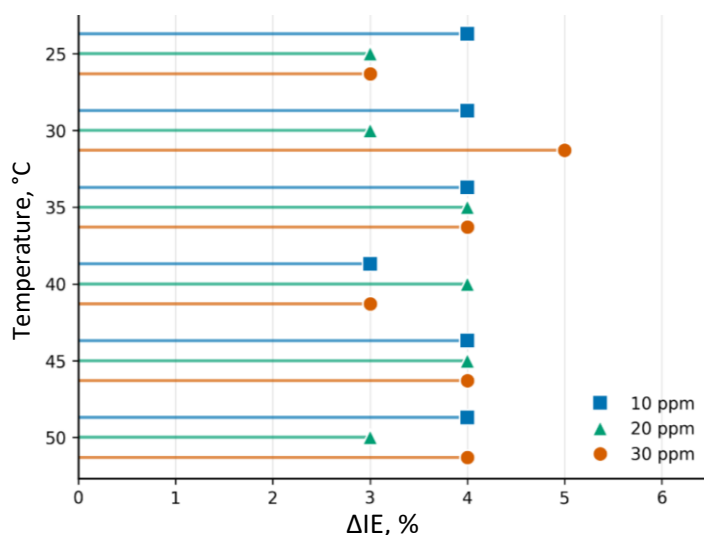


Figure 5. Difference in inhibition efficiency ($\Delta IE = IE(RH-1) - IE(RH-2)$) between RH-1 and RH-2 at different temperatures and inhibitor concentrations of 10, 20 and 30 ppm in H_2S -containing medium

The better performance of RH-1 can be attributed to the propargyl ($C\equiv C$) group, which provides higher π -electron density than the allyl ($C=C$) group in RH-2. This favours stronger interactions between the inhibitor molecules and the Fe surface, leading to a more compact adsorbed layer. As a result, RH-1 produced lower corrosion rates and higher inhibition efficiencies over the entire temperature range.

Electrochemical impedance spectroscopy analysis

Electrochemical impedance spectroscopy (EIS) was carried out to evaluate the effect of RH-1 and RH-2 on the corrosion behaviour of St-3 carbon steel in H_2S -containing medium. The experimental spectra were interpreted using the equivalent electrical circuit shown in Figure 6, comprising the solution resistance (R_s), charge-transfer resistance (R_{ct}), and a constant phase element (CPE) representing the double-layer capacitance (C_{dl}).

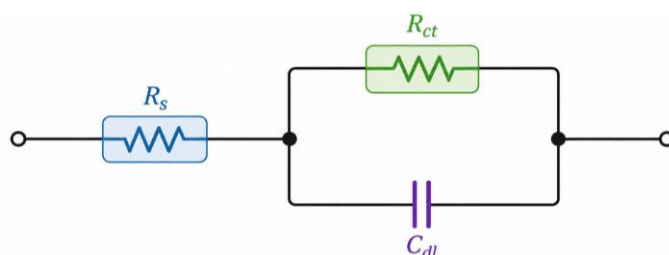


Figure 6. Equivalent electrical circuit used for fitting the EIS spectra of carbon steel in H_2S -containing medium

Figure 7 shows the Nyquist plots obtained in the absence and presence of RH-1 and RH-2. In all cases, the impedance spectra exhibited a single depressed capacitive semicircle, suggesting that the corrosion process was mainly controlled by charge-transfer reactions at the steel/electrolyte interface. For both inhibitors, the semicircle diameter increased with increasing inhibitor concentration, reflecting increased charge-transfer resistance due to inhibitor adsorption on the steel surface.

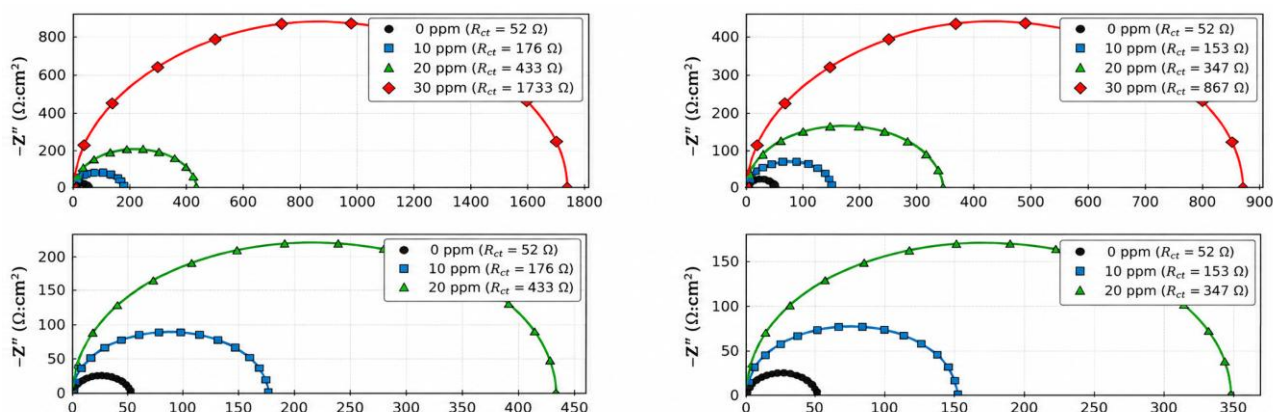


Figure 7. Nyquist plots of St-3 carbon steel in H_2S -containing medium at 25 °C in the absence and presence of RH-1 and RH-2 at different inhibitor concentrations: (a) RH-1, full range, (b) RH-2, full range, (c) enlarged view of the 0 to 20 ppm RH-1 spectra and (d) enlarged view of the 0 to 20 ppm RH-2 spectra

The concentration-dependent increase in impedance is more pronounced for RH-1 than RH-2, particularly at higher inhibitor concentrations, indicating a stronger barrier effect of the RH-1 adsorption layer against interfacial charge transfer.

The electrochemical parameters obtained from equivalent-circuit fitting are summarized in Table 3.

Table 3. Electrochemical impedance parameters of carbon steel in H_2S -containing medium in the absence and presence of RH-1 and RH-2

C / ppm	$R_{ct} / \Omega \text{ cm}^2$		$C_{dl} / \mu\text{F cm}^{-2}$		χ^2		IE, %	
	RH-1	RH-2	RH-1	RH-2	RH-1	RH-2	RH-1	RH-2
0	52 ± 2	52 ± 2	148 ± 5	148 ± 5	1.8×10 ⁻³	1.8×10 ⁻³	0.0	0.0
10	176 ± 6	153 ± 5	102 ± 4	108 ± 4	1.5×10 ⁻³	1.7×10 ⁻³	70.5 ± 1.0	66.0 ± 1.1
20	433 ± 13	347 ± 11	63 ± 2	69 ± 3	1.3×10 ⁻³	1.5×10 ⁻³	88.0 ± 0.7	85.0 ± 0.8
30	1733 ± 45	867 ± 25	28 ± 1	37 ± 2	1.1×10 ⁻³	1.3×10 ⁻³	97.0 ± 0.3	94.0 ± 0.5

The quantitative EIS parameters confirm the concentration-dependent improvement in corrosion protection. At 30 ppm, R_{ct} increased from 52±2 $\Omega \cdot \text{cm}^2$ for the uninhibited system to 1733±45 $\Omega \cdot \text{cm}^2$ for RH-1 and 867±25 $\Omega \cdot \text{cm}^2$ for RH-2, while C_{dl} decreased from 148±5 $\mu\text{F} \cdot \text{cm}^{-2}$ to 28±1 and 37±2 $\mu\text{F} \cdot \text{cm}^{-2}$, respectively. The corresponding inhibition efficiencies reached 97.0±0.3 % for RH-1 and 94.0±0.5 % for RH-2. The χ^2 values remained low (1.1×10⁻³ to 1.8×10⁻³), indicating satisfactory agreement between the experimental impedance data and the fitted equivalent-circuit model.

The simultaneous increase in R_{ct} and decrease in C_{dl} with increasing inhibitor concentration is consistent with progressive adsorption of the inhibitor molecules and the formation of a protective interfacial layer that restricts charge transfer. The reduction in C_{dl} may be associated with displacement of adsorbed water molecules and corrosive species and with changes in the dielectric properties and effective thickness of the electrical double layer. The consistently higher R_{ct} and lower C_{dl} values for RH-1 indicate more effective interfacial protection than for RH-2. This trend agrees with the gravimetric and polarization results and is consistent with the proposed stronger interaction of the propargyl ($C \equiv C$) functionality of RH-1 with the steel surface compared with the allyl ($C = C$) functionality of RH-2.

To further examine the electrochemical response of the inhibitor films, the impedance spectra were also analysed in the Bode representation. The corresponding plots obtained at 25 °C are presented in Figure 8.

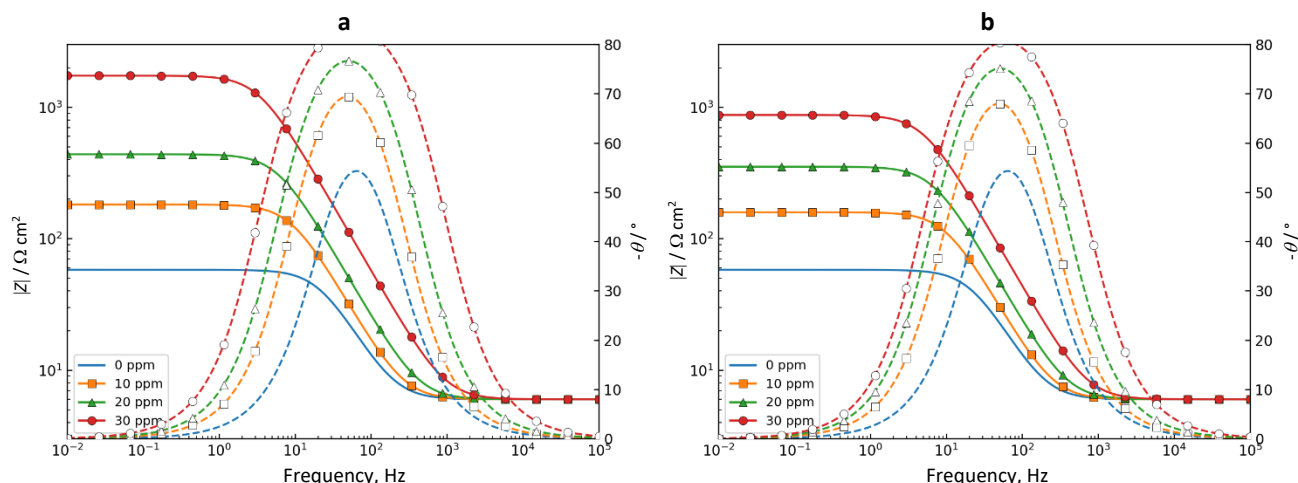


Figure 8. Bode plots showing the impedance modulus ($|Z|$) and phase angle ($-\theta$) of St-3 carbon steel in H_2S -containing medium at 25 °C with different concentrations (0, 10, 20 and 30 ppm) of a - RH-1 and b - RH-2 inhibitors. The solid curves (—) represent the impedance modulus ($|Z|$), whereas the dashed curves (---) correspond to the phase angle ($-\theta$)

For both inhibitors, the impedance modulus increased with inhibitor concentration over the entire frequency range. The highest $|Z|$ values were observed at 30 ppm, indicating improved corrosion resistance as the inhibitor concentration increased. The phase angle curves also changed with inhibitor concentration. Both the maximum phase angle and the width of the capacitive region increased, indicating the formation of an adsorbed inhibitor layer and a more capacitive steel/electrolyte interface.

A comparison of the two inhibitors shows that RH-1 produced higher impedance modulus values and slightly higher phase angles than RH-2 at the same concentrations. This behaviour is consistent with the higher R_{ct} values obtained from the Nyquist analysis and indicates stronger adsorption of RH-1 on the steel surface. The improved performance of RH-1 is attributed to the propargyl ($C\equiv C$) group, whereas RH-2, containing an allyl ($C=C$) group, showed slightly lower impedance values across the investigated concentration range. The Bode results agree well with the Nyquist spectra, polarization measurements, and gravimetric data, confirming that both inhibitors reduce the corrosion rate through adsorption on the steel surface.

Potentiodynamic polarization analysis

The effect of RH-1 and RH-2 on the electrochemical behaviour of St-3 carbon steel was further examined by potentiodynamic polarization measurements. The polarization curves recorded at different inhibitor concentrations are presented in Figure 9.

As shown in Figure 9, both RH-1 and RH-2 decreased the anodic and cathodic current densities relative to the blank solution. This behaviour indicates that the inhibitors influence both anodic and cathodic reactions and therefore act as mixed-type corrosion inhibitors. Increasing inhibitor concentration resulted in a gradual shift of the polarization curves toward lower current densities, reflecting improved surface protection. The electrochemical parameters obtained by Tafel extrapolation are summarized in Table 4.

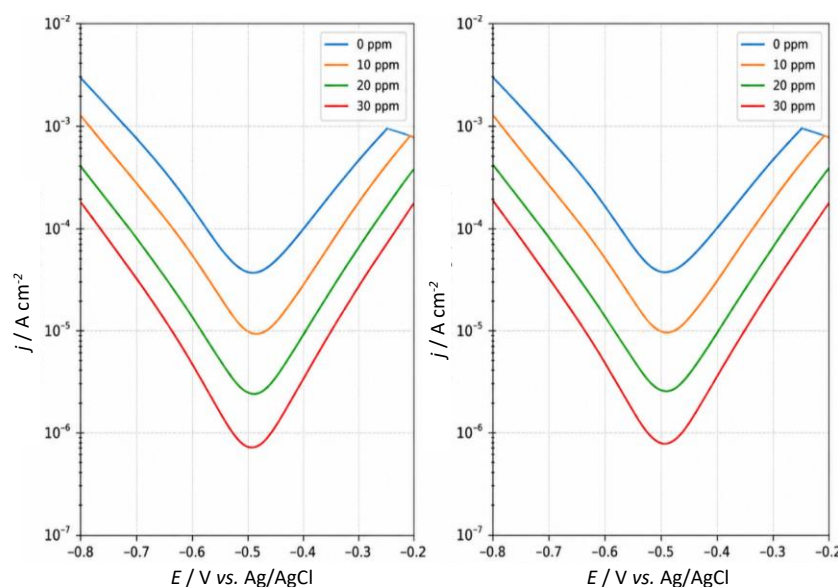


Figure 9. Potentiodynamic polarization curves of carbon steel in H_2S -containing medium in the absence and presence of RH-1 (left) and RH-2 (right) inhibitors at concentrations of 0, 10, 20 and 30 ppm (25 °C)

Table 4. Potentiodynamic polarization parameters of St-3 carbon steel in H_2S -containing medium in the absence and presence of RH-1 and RH-2 inhibitors

C / ppm	E_{corr} / V vs. Ag/AgCl, sat. KCl	j_{corr} / $\mu A\ cm^{-2}$	β_a / mV dec $^{-1}$	β_c / mV dec $^{-1}$	IE, %
RH-1					
0	-0.612 ± 0.004	120 ± 4	86 ± 3	121 ± 4	0
10	-0.598 ± 0.003	36.0 ± 1.1	82 ± 3	116 ± 4	70.0 ± 0.9
20	-0.585 ± 0.003	14.4 ± 0.5	78 ± 2	110 ± 3	88.0 ± 0.6
30	-0.573 ± 0.002	36.0 ± 0.12	74 ± 2	104 ± 3	97.0 ± 0.3
RH-2					
0	-0.612 ± 0.004	120 ± 4	86 ± 3	121 ± 4	0
10	-0.602 ± 0.003	40.8 ± 1.3	84 ± 3	118 ± 4	66.0 ± 1.0
20	-0.590 ± 0.003	18.0 ± 0.6	81 ± 3	113 ± 3	85.0 ± 0.7
30	-0.579 ± 0.002	7.20 ± 0.22	77 ± 2	108 ± 3	94.0 ± 0.4

The corrosion current density (j_{corr}) decreased progressively with increasing inhibitor concentration for both RH-1 and RH-2, while only relatively small changes were observed in the corrosion potential (E_{corr}). At 30 ppm, the maximum shifts in E_{corr} relative to the blank were approximately 39 mV for RH-1 and 33 mV for RH-2. Since these shifts remain below the commonly used threshold of 85 mV, both compounds can be classified as mixed-type corrosion inhibitors.

This interpretation is also supported by changes in both the anodic and cathodic Tafel slopes (β_a and β_b), indicating that the inhibitors affect both the anodic iron-dissolution and cathodic reduction processes.

At each investigated concentration, RH-1 produced a lower j_{corr} than RH-2, demonstrating its consistently higher inhibition performance. At 30 ppm, j_{corr} decreased from $120 \pm 4\ \mu A\ cm^{-2}$ for the blank to $3.60 \pm 0.12\ \mu A\ cm^{-2}$ in the presence of RH-1, corresponding to an inhibition efficiency of $97.0 \pm 0.3\%$. Under the same conditions, RH-2 reduced j_{corr} to $7.20 \pm 0.22\ \mu A\ cm^{-2}$, giving an inhibition efficiency of $94.0 \pm 0.4\%$. The approximately twofold lower corrosion current density obtained with RH-1 at 30 ppm confirms its stronger suppression of electrochemical corrosion.

The superior performance of RH-1 is consistent with the proposed stronger interaction of its propargyl ($C \equiv C$) functionality with the steel surface compared with the allyl ($C = C$) functionality of RH-2. The polarization results therefore agree well with the gravimetric and EIS measurements, which likewise show higher inhibition efficiency for RH-1.

Surface morphology and composition analysis

To provide a direct comparison of the surface condition after corrosion, SEM observations were performed for the uninhibited St-3 steel specimen and specimens exposed to the H_2S -containing medium in the presence of 30 ppm RH-1 and RH-2. The corresponding EDS spectra were acquired at the positions marked directly on the SEM micrographs, allowing the local elemental composition of the examined surface regions to be correlated with their morphology. XRD analysis was additionally performed to identify the crystalline corrosion products and assess changes in the surface layer. The comparative SEM, EDS and XRD results are presented in Figure 10.

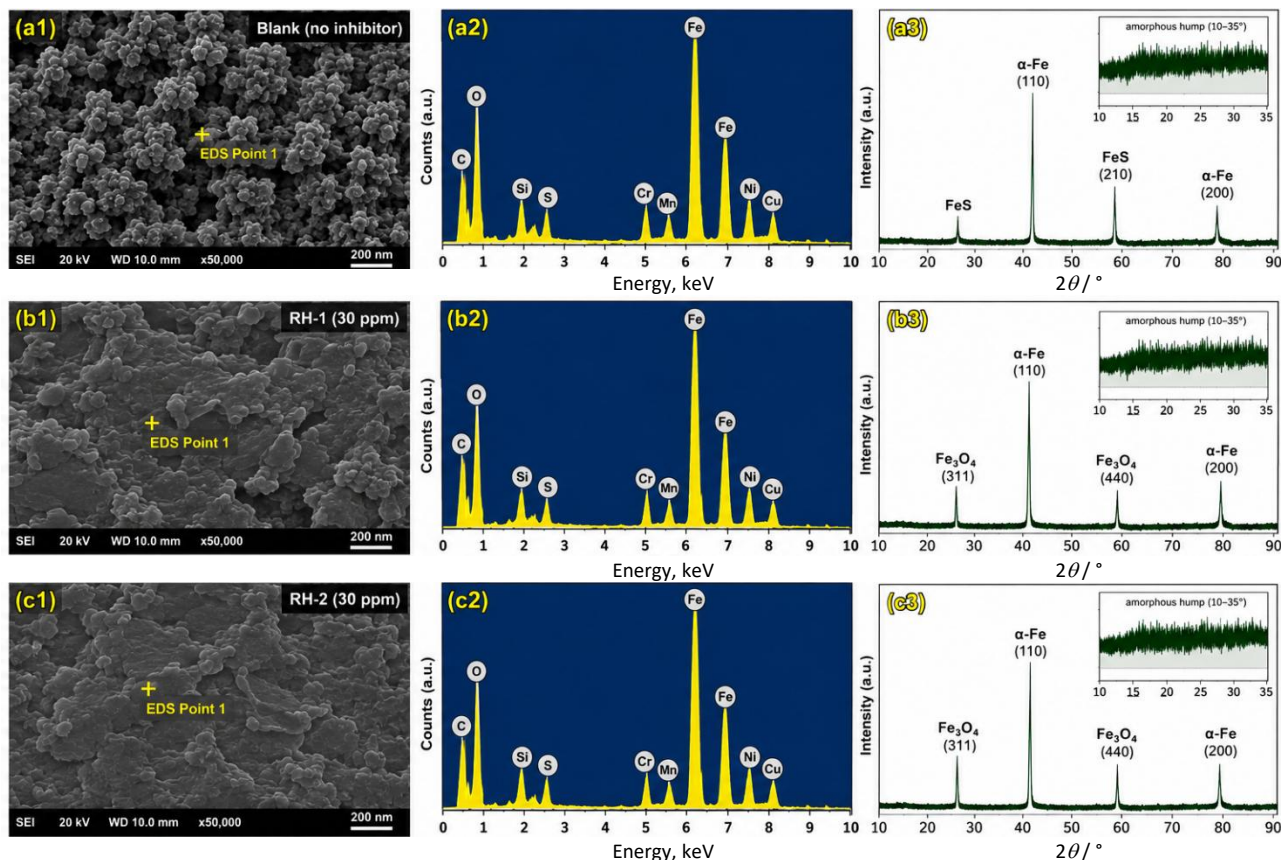


Figure 10. Comparative surface characterization of St-3 carbon steel after exposure to the H_2S -containing medium: (a1-a3) blank specimen without inhibitor, (b1-b3) specimen inhibited with 30 ppm RH-1 and (c1-c3) specimen inhibited with 30 ppm RH-2. Panels (a1), (b1) and (c1) show SEM micrographs with the marked EDS measurement positions; (a2), (b2) and (c2) show the corresponding EDS spectra and (a3), (b3) and (c3) show the corresponding XRD patterns

As shown in Figure 10a1, the uninhibited steel surface exhibits a highly heterogeneous and rough morphology with extensive accumulation of corrosion products, indicating severe surface degradation in the H_2S -containing medium. In contrast, the surfaces exposed in the presence of RH-1 and RH-2 (Figures 10b1 and 10c1) appear markedly more compact and less severely damaged, demonstrating the protective effect of the adsorbed inhibitor layers. The RH-1-treated surface exhibits a comparatively more continuous and compact morphology, consistent with its higher experimentally determined inhibition efficiency.

The EDS spectra recorded at the positions explicitly marked on the corresponding SEM micrographs (Figures 10a2 to 10c2) confirm that the analysed regions contain Fe together with O, C, S and minor alloying elements originating from the steel substrate. Comparison of the blank and inhibited specimens indicates changes in the surface composition associated with suppression of

corrosion-product accumulation and formation of inhibitor-containing protective layers. Importantly, the marked EDS acquisition positions establish a direct correspondence between the observed SEM morphology and the local elemental analysis.

The XRD patterns (Figures 10a3 to 10c3) provide further evidence of changes in the corrosion-product layer. The uninhibited specimen shows reflections attributable to α -Fe and FeS, consistent with sulphide-containing corrosion products formed in the H_2S environment. In the inhibited specimens, the patterns are dominated by α -Fe together with the indicated Fe_3O_4 reflections, while the broad low-angle contribution suggests a poorly crystalline or amorphous surface layer. Taken together, the SEM, EDS, and XRD observations demonstrate that both RH-1 and RH-2 substantially modify the steel surface after corrosion exposure and promote the formation of a more protective surface layer, with RH-1 showing the more compact surface morphology.

FTIR analysis was used to examine the chemical composition of the surface films formed on St-3 steel after exposure to the H_2S -containing medium. Spectra were recorded for the uninhibited steel and for specimens treated with 30 ppm RH-1 and RH-2, paying particular attention to changes in characteristic bands of surface species and the presence of functional groups associated with the inhibitors. The resulting FTIR spectra are shown in Figure 11.

The FTIR spectrum of the uninhibited specimen (Figure 11a) is dominated by bands at approximately 3430 , 1630 , 1080 and 620 cm^{-1} , which are associated with hydroxyl-containing surface species, adsorbed water and oxygen-containing/iron-containing corrosion products. In contrast, the spectra obtained after treatment with RH-1 and RH-2 contain additional absorption features attributable to the organic inhibitor layers. For RH-1 (Figure 11b), bands at approximately 2920 and 2850 cm^{-1} are assigned to aliphatic C-H stretching vibrations, while the band at approximately 2105 cm^{-1} is consistent with the $C\equiv C$ functionality characteristic of the propargyl-containing inhibitor.

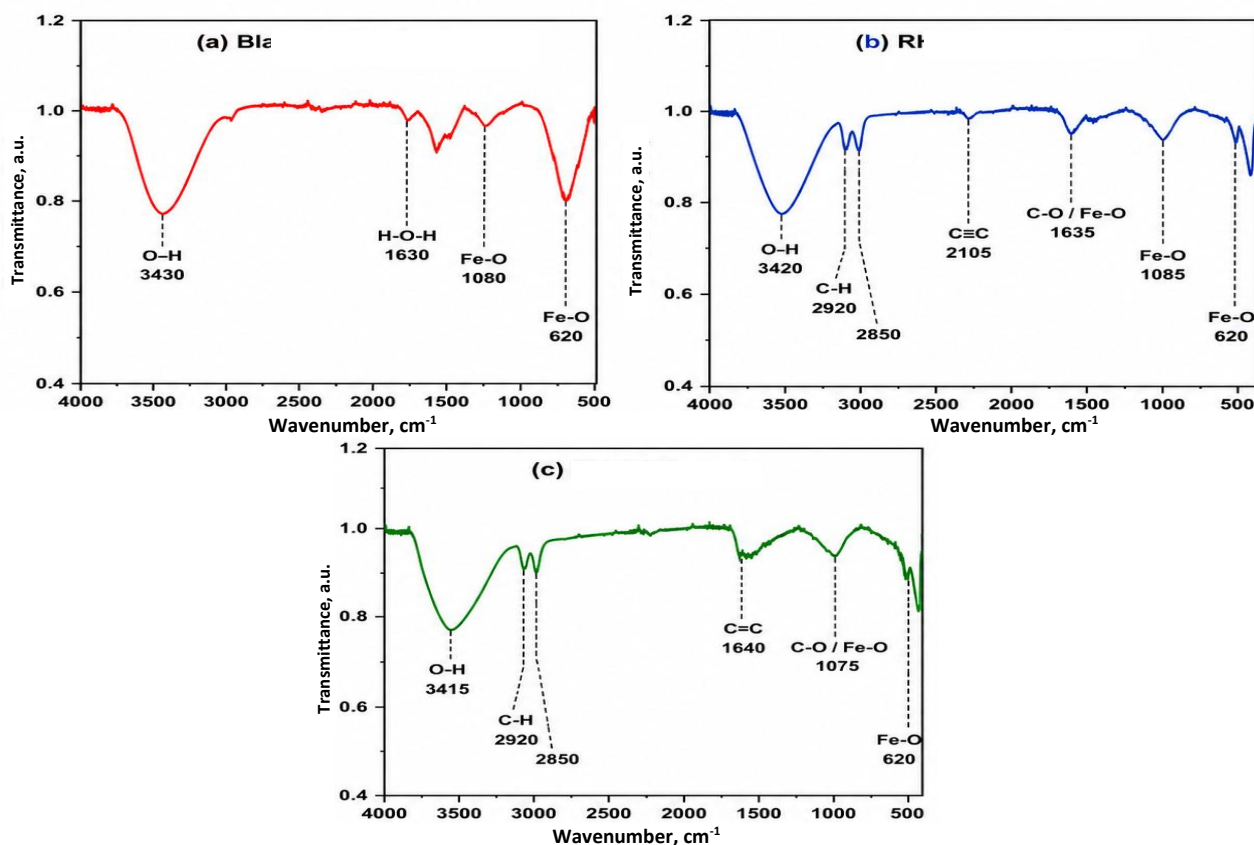


Figure 11. FTIR spectra of St-3 carbon steel surfaces after corrosion exposure to the H_2S -containing medium: (a) blank without inhibitor, (b) 30 ppm RH-1 and (c) 30 ppm RH-2

The band near 1635 cm^{-1} and the features in the lower-wavenumber region indicate contributions from C-O/Fe-O-containing surface species. For RH-2 (Figure 11c), the C-H bands at approximately 2920 and 2850 cm^{-1} are accompanied by a feature near 1640 cm^{-1} attributable to the C=C functionality of the allyl-containing inhibitor. The persistence of inhibitor-related bands on the steel surfaces after corrosion exposure supports the adsorption of both RH-1 and RH-2 and the formation of organic-containing protective surface layers.

XPS analysis was subsequently employed to obtain further information on the elemental composition and chemical states of the species present on the steel surface after corrosion exposure.

Survey spectra and high-resolution Fe 2p, O 1s, C 1s and S 2p spectra were recorded for the blank specimen and the specimens treated with 30 ppm RH-1 and RH-2. The corresponding spectra and surface atomic compositions are presented in Figure 12.

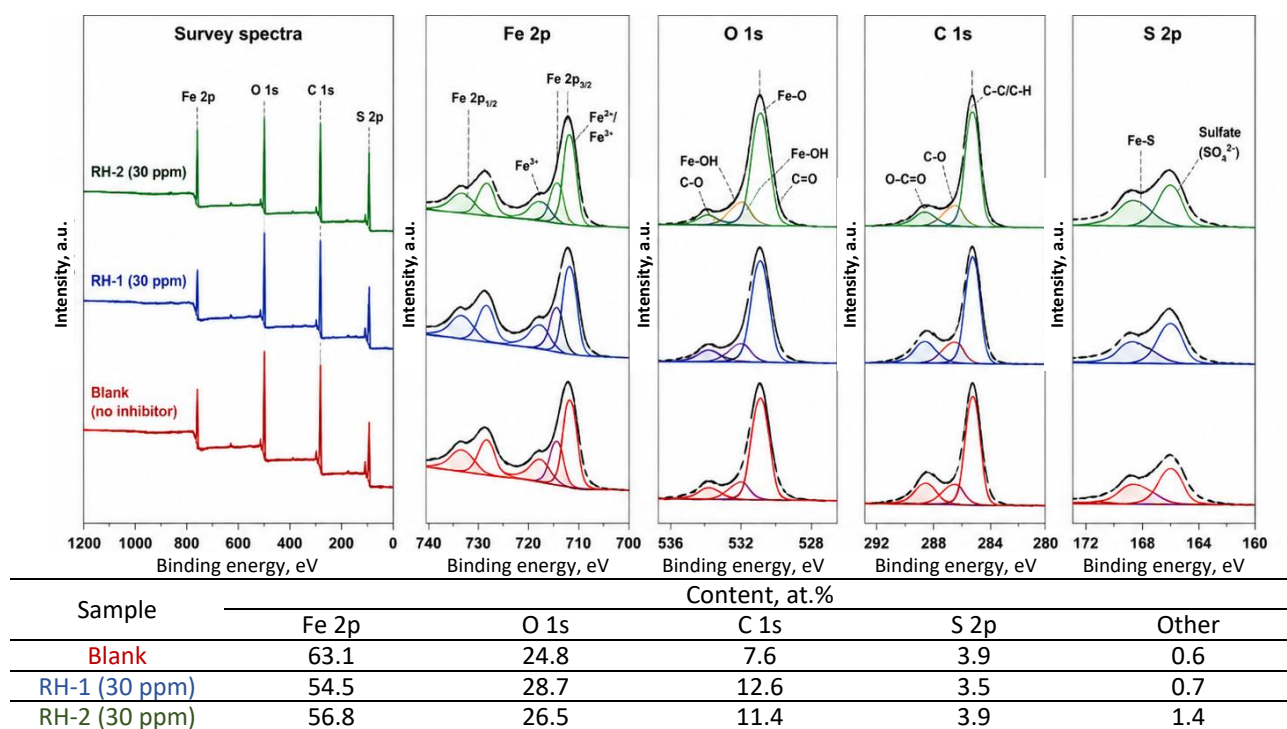


Figure 12. XPS characterization of St-3 carbon steel surfaces after corrosion exposure to the H_2S -containing medium in the absence and presence of 30 ppm RH-1 and RH-2: survey spectra and high-resolution Fe 2p, O 1s, C 1s and S 2p spectra, together with the corresponding surface atomic compositions

The XPS survey spectra confirm the presence of Fe, O, C and S on all investigated post-corrosion surfaces. The blank specimen contains 63.1 at.% Fe, 24.8 at.% O, 7.6 at.% C and 3.9 at.% S. Following treatment with RH-1, the surface carbon content increases markedly to 12.6 at.%, accompanied by a decrease in the Fe contribution to 54.5 at.%. A similar, although slightly less pronounced, change is observed for RH-2, for which the surface contains 11.4 at.% C and 56.8 at.% Fe. The increased carbon contribution and attenuation of the substrate Fe signal in the inhibited specimens are consistent with coverage of the steel surface by an organic-containing protective layer.

The high-resolution spectra provide additional information on the chemical nature of this layer. The Fe 2p region contains contributions associated with metallic iron and oxidized iron species, whereas the O 1s spectra reveal Fe-O/Fe-OH and oxygen-containing organic surface species. The C 1s spectra contain a dominant C-C/C-H contribution together with oxygen-containing carbon components, consistent with the molecular structure of the adsorbed inhibitors.

The S 2p region contains contributions associated with Fe-S and oxidized sulphur species, reflecting the interaction of the steel surface with the H₂S-containing corrosive medium. The combined changes in Fe, O, C, and S surface chemistry after inhibitor addition provide spectroscopic evidence that RH-1 and RH-2 modify the post-corrosion steel surface and form protective interfacial layers. The larger carbon enrichment and stronger attenuation of the Fe signal observed for RH-1 are also consistent with its higher inhibition efficiency relative to RH-2.

Density functional theory studies

To better understand the inhibition mechanism at the molecular level, DFT calculations were performed for RH-1 and RH-2. The calculated quantum chemical parameters provide information on the electronic properties of the inhibitor molecules, including their electron-donating and electron-accepting abilities, molecular reactivity, and adsorption tendency toward the steel surface. These theoretical descriptors are widely used to explain differences in corrosion inhibition performance and to support experimental observations obtained from gravimetric, electrochemical, and surface characterization analyses. The calculated DFT parameters are summarized in Table 5.

Table 5. Calculated DFT quantum chemical parameters of RH-1 and RH-2

Parameter	RH-1	RH-2
E_{HOMO} / eV	-5.41	-5.62
E_{LUMO} / eV	-2.84	-2.73
ΔE / eV	2.57	2.89
Ionization potential, eV	5.41	5.62
Electron affinity, eV	2.84	2.73
Electronegativity, eV	4.13	4.18
Global hardness, eV	1.29	1.45
Global softness, eV ⁻¹	0.78	0.69
Electrophilicity index, eV	6.61	6.02
Fraction of electrons transferred	1.11	0.94
$\Delta E_{\text{back-donation}}$ / eV	-0.32	-0.36

RH-1 has a slightly higher HOMO energy (-5.41 eV) than RH-2 (-5.62 eV), indicating a greater tendency to donate electrons to the iron surface. This is also reflected by its lower ionization potential and higher fraction of electrons transferred ($\Delta N = 1.11$), suggesting stronger interaction with the steel surface.

RH-1 also exhibits a smaller HOMO-LUMO energy gap (2.57 eV) than RH-2 (2.89 eV), indicating higher molecular reactivity. In addition, RH-1 has higher global softness ($\sigma = 0.78$ eV⁻¹) and lower chemical hardness ($\eta = 1.29$ eV) than RH-2. According to the HSAB concept, softer molecules generally interact more readily with the iron surface, resulting in stronger adsorption.

The electronegativity values of the two inhibitors are similar, whereas RH-1 shows a slightly higher electrophilicity index and a larger ΔN value. These parameters suggest that RH-1 has a greater tendency to donate electrons and adsorb on the steel surface than RH-2.

The frontier molecular orbitals were further analysed to identify the preferred adsorption sites of the inhibitor molecules. The calculated HOMO and LUMO distributions of RH-1 and RH-2 are presented in Figure 13.

As shown in Figure 13, the HOMO of both inhibitors is mainly distributed over the aromatic ring, oxygen atoms, and the unsaturated substituent, indicating that these regions are the primary electron-donating sites during adsorption on the steel surface. The LUMO is mainly localized on the aromatic framework and oxygen-containing groups, suggesting these regions can also interact with the metal surface.

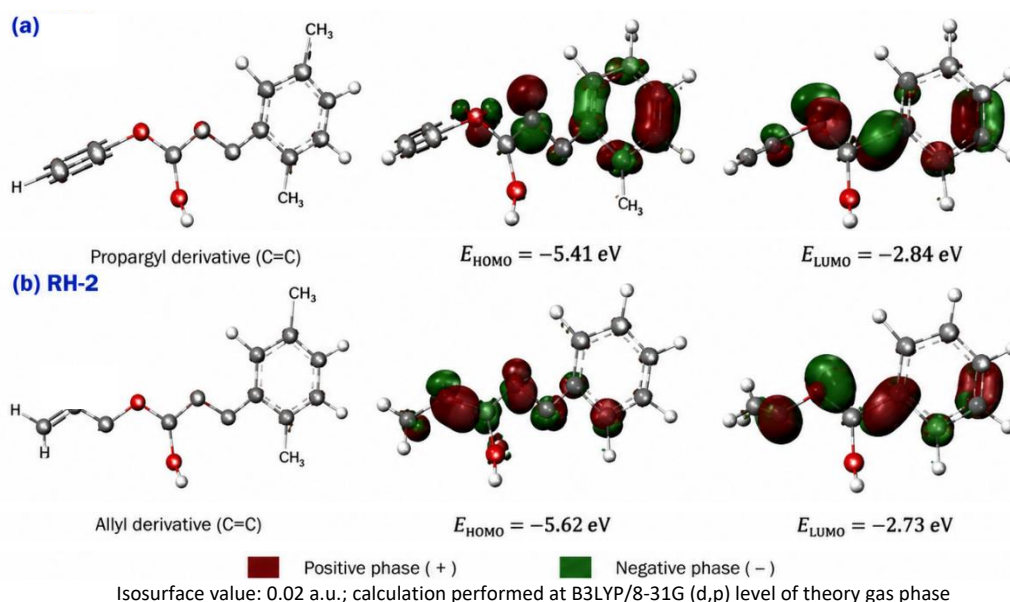


Figure 13. Optimized molecular structures together with the calculated frontier molecular orbitals (HOMO and LUMO) of (a) RH-1 and (b) RH-2 obtained by DFT calculations. The HOMO and LUMO distributions illustrate the electron-donating and electron-accepting regions responsible for adsorption on the carbon steel surface

A clear difference is observed between the two molecules. In RH-1, the HOMO extends over the propargyl (C≡C) group together with the aromatic ring and oxygen atoms, whereas in RH-2 the electron density is less delocalized because of the allyl (C=C) group. This agrees with the quantum chemical parameters in Table 5, where RH-1 shows a higher HOMO energy, a smaller HOMO-LUMO energy gap, and a larger ΔN value than RH-2. These features indicate stronger adsorption of RH-1 on the steel surface and explain its higher inhibition efficiency.

Conclusions

- Two aryloxy alcohol derivatives, RH-1 and RH-2, containing propargyl and allyl functional groups, respectively, were synthesized and characterized by FTIR, ^1H NMR and ^{13}C NMR spectroscopy. The spectroscopic results confirmed the proposed molecular structures.
- Both inhibitors reduced the corrosion of St-3 carbon steel in an H_2S -containing medium over the investigated temperature (25 to 50 °C) and concentration (10 to 30 ppm) ranges. Inhibition efficiency increased with inhibitor concentration and decreased gradually with increasing temperature. RH-1 showed higher inhibition efficiency than RH-2, reaching 97 % at 30 ppm and 25 °C.
- EIS and potentiodynamic polarization measurements showed that both compounds act as mixed-type corrosion inhibitors. Compared with RH-2, RH-1 exhibited higher charge-transfer resistance, lower double-layer capacitance, and lower corrosion current density, indicating stronger adsorption on the steel surface.
- SEM, EDS, XRD and DFT analyses supported the experimental results. The better performance of RH-1 is attributed to the propargyl (C≡C) group, which promotes stronger interaction with the steel surface than the allyl (C=C) group in RH-2. These results indicate that RH-1 is a suitable inhibitor for protecting carbon steel in H_2S -containing environments.

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