



# The corrosion inhibition of certain azoles on steel in chloride media: Electrochemistry and surface analysis



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## ABSTRACT

This study analyses the corrosion inhibition efficiency of certain azoles for C15 grade mild steel in 3 wt.% NaCl solution by employing immersion tests and different electrochemical techniques. The possible synergistic effect of azole inhibitors and metal salts was also investigated. It was found that tolyltriazole is the most effective corrosion inhibitor. Additional surface analyses were performed for specimens inhibited with tolyltriazole. ATR-FTIR analysis confirmed the adsorption of tolyltriazole on the steel surface and 3D-profilometry and AFM showed that tolyltriazole reduces surface roughness compared with non-inhibited solution. Contact angle analysis showed that tolyltriazole-inhibited steel specimens evidenced a hydrophilic character.

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## 1. Introduction

One of the most widely used methods of controlling corrosion is the addition of very small amounts of corrosion inhibitors in the corrosive medium [1–7]. Organic compounds have been extensively tested as corrosion inhibitors for decades [8–11]. Due to their structure, azoles have high potential for use as corrosion inhibitors. Azoles are heterocyclic compounds with a five-membered ring containing nitrogen and at least one other non-carbon atom (nitrogen, sulphur, or oxygen). Some azoles, such as 3-amino-1,2,4-triazole, 2-trifluoromethyl-4,5-dichlorobenzimidazole, and 1,3,4-thiadiazole, are used as herbicides. Moreover, 1,3,4-thiadiazole is used to clear roads, aerodromes, construction sites, and areas surrounding high voltage transmission lines. Some azoles are used as insecticides, especially against the plant louse and ticks. Derivatives of imidazole and 1,2,4-triazole are used in fungicides against fungal skin, nail, and hair infections as well as against infections with *Candida* and *Aspergillus* species [12].

Azole compounds have been used as corrosion inhibitors for various types of metals. Only a few studies related to the use of azole-type compounds as corrosion inhibitors for

lower-grade steels have been performed previously, mainly in acidic [13–18] and chloride-containing solutions [19–21]. Mahdavian et al. [19] studied the corrosion inhibition efficiency of 2-mercaptobenzimidazole (MBI) and 2-mercaptobenzoxazole (MBO) for the same mild steel as in [13] immersed in 1 M NaCl solution. It was shown that MBI is a more effective corrosion inhibitor than MBO. Abd El Haleem et al. [20] studied the corrosion inhibition efficiency of benzotriazole (BTA) and its derivatives, i.e. 5-chlorobenzotriazole (5-Cl-BTA) and 5-nitrobenzotriazole (5-NO<sub>2</sub>-BTA) for steel in saturated naturally aerated Ca(OH)<sub>2</sub> solution containing 0.0001 M or 0.05 M concentration of Cl<sup>-</sup>. It was observed that the corrosion inhibition efficiency depends on the type and concentration of the azole and on the concentration of Cl<sup>-</sup> in solution. The corrosion inhibition efficiency increases in the order 5-NO<sub>2</sub>-BTA < BTA < 5-Cl-BTA. Sahin et al. [21] studied the corrosion inhibition efficiency of 3-amino-1,2,4-triazole (3-AT), 2-amino-1,3,4-thiadiazole (2-ATDA), 5-(*p*-tolyl)-1,3,4-triazole (5-TTA), 3-amino-5-methylmercapto-1,2,4-triazole (3-AMTA), and 2-aminobenzimidazole (ABI) for steel in 2.5 wt.% and 3.5 wt.% NaCl solutions. The results showed that the corrosion inhibition efficiency increased with increasing inhibitor concentration and that ABI was the most effective inhibitor among the compounds tested in both 2.5 wt.% and 3.5 wt.% NaCl solutions.

Lower-grade steel materials are frequently subjected to corrosion conditions, such as the 3 wt.% NaCl solution employed herein

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**Table 1**

The composition of C15 grade mild steel specimen as specified by the supplier.

Element	C	Si	Mn	P	S	Fe
wt.%	0.140	0.200	0.470	0.006	0.003	balance

[22]. Based on this, C15 grade mild steel was employed in this study. There is always a need to find new corrosion inhibitors in a certain medium, and azoles due to the involvement of N-atoms in their structure, which act as binding centres are potential corrosion inhibitors. In this study, the corrosion inhibition efficiency of various azoles for C15 grade mild steel in 3 wt.% NaCl solution is explored. Moreover, the synergistic effect of azole-type corrosion inhibitors with metal salts (especially KI) was studied. This investigation started with immersion tests of specimens at 25 and 70 °C. Next, the behaviour of the most effective inhibitors was further studied using different electrochemical techniques. Finally, surface analysis of the most effective inhibitor was performed. Hitherto, to the best of our knowledge, no such systematic analysis with regard to C15 grade mild steel has been performed before.

## 2. Experimental

### 2.1. Immersion tests

C15 grade mild steel specimens with the composition given in Table 1 were supplied by Rocholl, Aglasterhausen, Germany. The specimen's dimensions were 50 × 20 × 1 mm.

Ethanol, NaCl, and KI (for analysis-ACS quality) were supplied by Carlo Erba Reagents (Milano, Italy). 2-mercaptobenzothiazole (MBT) with a purity 97 wt.%, 2-mercaptobenzoxazole (MBO) with a purity 95 wt.%, 2-mercaptobenzimidazole (MBI) with a purity 98 wt.%, tolyltriazole (TTA) with a purity 98 wt.%, benzotriazole (BTA) with a purity 99 wt.%, 2-methylimidazole (2-MI) with a purity 99 wt.%, 4(5)-methylimidazole (4-MI) with a purity 98 wt.%, 2-mercapto-1-methylimidazole (MMI) with a purity ≥99 wt.%, imidazole (IMD) with a purity ≥99.5 wt.%, 4-methyl-2-phenylimidazole (MePhI) with a purity 95 wt.%, 2-phenylimidazole (2-PhI) with a purity 98 wt.% were supplied by Sigma-Aldrich (St. Louis, Missouri, USA), 3-amino-1H-1,2,4-triazole (3-AT) with a purity 95 wt.%, 1,2,3-1H-triazole (TRI) with a purity 97 wt.%, 1,2,4-1H-triazole (TAH) with a purity 99.5 wt.%, 2-aminobenzimidazole (ABI) with a purity >99%, bismuth(III) oxide with a purity 99.9 wt.%, antimony(III) chloride ACS reagent, and tin(II) chloride with a purity 98 wt.% were supplied by ACROS Organics (New Jersey, USA), and ammonium iodide with a purity ≥99.0 wt.% by Fluka Analytical (St. Gallen, Switzerland).

Corrosion inhibitor structures are presented in Fig. 1. Specimens were exposed for 3 days to a stationary non-stirring medium at 25 °C or 70 °C in 100 mL closed-to-air polypropylene vials. Ultra-pure water with a resistivity of 18.2 MΩ cm was used to prepare all of the tested solutions (Milli-Q, Millipore Corporation, Massachusetts, USA). The tested solutions were: (a) 3 wt.% NaCl, (b) 3 wt.% NaCl containing 10 mM corrosion inhibitor (or saturated corrosion inhibitor in the case of MBT, MBO, MBI, MePhI, and 2-PhI), (c) 3 wt.% NaCl containing 10 mM (or saturated MBT, MBO, MBI, MePhI, 2-PhI) corrosion inhibitor with the addition of 0.5 wt.% KI, and (d) 3 wt.% NaCl containing 10 mM (or saturated MBT, MBO, MBI, MePhI, 2-PhI) corrosion inhibitor with the addition of 2 wt.% KI. The solubility of MBT was determined to be 0.598 mM, 1 mM for MBO, MBI, and 2-PhI, while for MePhI it was 2.375 mM. Before immersion, the specimens were cleaned ultrasonically in a bath of 50% ethanol and 50% Milli-Q water by volume, dried under a stream of air, and weighed. The specimens were aligned in such a way that they were in contact with the vial only at the four edges. After three days of immersion, the specimens were rinsed with water, lightly

brushed with a fibre-bristle brush to remove corrosion products, rinsed, dried under a stream of air, and weighed. At least three replicate measurements were performed (if any outlier was present, more replicate measurements were performed; outliers were discarded using the Grubbs' test [23]). As a result, the average mass loss and corrosion rate ( $v_{\text{corr}}$ ) were calculated.

### 2.2. Electrochemical analysis

Only the most effective corrosion inhibitors based on immersion tests were electrochemically tested. All electrochemical measurements were performed in 1 L solutions. Steel specimens were cut out in the shape of discs 15 mm in diameter. Using a manual grinder, the specimens were ground under a stream of water starting with 320-grit SiC paper and continued with 500, 800, 1200, 2400, and 4000-grit papers (Struers, Ballerup, Denmark). After grinding, the specimens were cleaned ultrasonically in a bath of 50% ethanol/50% Milli-Q water by volume and afterwards rinsed with Milli-Q water. The prepared specimens (working electrode) were embedded in a Teflon holder (PAR, Cambridge, UK) so that the area exposed to the solution was 1 cm<sup>2</sup>. Experiments were performed in a three-electrode cell under stagnant conditions at room temperature. A saturated calomel electrode was employed as a reference electrode. A graphite rod served as a counter electrode. Measurements were carried out with a Gamry 600™ potentiostat/galvanostat controlled by a Gamry Framework electrochemical program and analysed by EChem Analyst software.

Polarisation resistance ( $R_p$ ) and EIS measurements were performed in sequence after 1 h, 3 h, 5 h, 7 h, and 8 h of immersion.  $R_p$  measurements were carried out in the potential range of ±10 mV vs.  $E_{\text{oc}}$  at a 0.1 mV/s sweep rate. In between the  $R_p$  and EIS measurements, chronopotentiometry measurements were carried out, which also served for the stabilisation process. EIS spectra were obtained at the above-mentioned immersion times at  $E_{\text{oc}}$  in the frequency range of 1 MHz to 10 mHz with 10 points/decade and a 10 mV (peak to peak) amplitude of the excitation signal. The impedance measurements were interpreted by fitting the measured data using EChem Analyst software. Cyclic polarisation (CP) curves were recorded after 9 h of immersion. These measurements started at −250 mV vs.  $E_{\text{oc}}$  and continued in the anodic direction until a current density of 1 mA/cm<sup>2</sup> was reached. Then the potential scan was reversed in the cathodic direction until it reached −500 mV vs. SCE. A sweep rate of 0.1 mV/s was employed.

### 2.3. Surface analysis

For the surface analysis, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), 3D-profilometry, atomic force microscopy (AFM), and contact angle analysis using a tensiometer, were performed. To ensure the relevance of the results with regard to the performed electrochemical measurements, the same specimen preparation procedure was used. ATR-FTIR analysis was carried out with a Shimadzu IRAffinity-1 (Riverwood Dr. Colombia, USA) spectrometer. A profilometer, model Form Talysurf Series 2 (Taylor Hobson), was employed for the 3D-profilometry. The instrument has a vertical resolution of about 5 nm. The data were processed with TalyMap Gold 4.1 software. The average surface roughness was calculated and a surface profile created. To level the profile, corrections were made to exclude the general geometrical shape and possible measurement-induced misfits [24,25]. A profilometer measures the surface profile in one direction. The topography of the surface was obtained by combining several measurements in parallel directions 10 μm apart.

The surface morphology and roughness on a small scale of selected specimens were characterised by AFM in tapping mode with an Agilent 5500 AFM multimode scanning probe microscope

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