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# Experimental and theoretical studies on the corrosion inhibition of copper by two indazole derivatives in 3.0% NaCl solution

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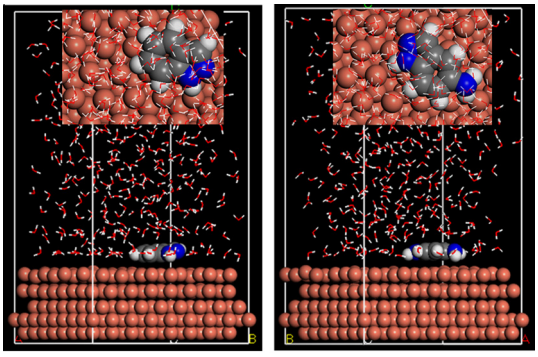
## GRAPHICAL ABSTRACT



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## ABSTRACT

Corrosion experiments and theoretical calculations were performed to investigate the inhibition mechanism of indazole (IA) and 5-aminoindazole (AIA) for copper in NaCl solution. The results obtained from weight loss and electrochemical experiments are in good agreement, and reveal that these compounds are high-efficiency inhibitors with inhibition efficiency order: AIA > IA, which was further confirmed by field emission scanning electronic microscope (FESEM) observation. Besides, the quantum chemical calculations and molecular dynamics (MD) simulation showed that both studied inhibitors are adsorbed strongly on the copper surface in parallel mode. The adsorption of these molecules on copper substrate was found to obey Langmuir isotherm.



## 1. Introduction

Corrosion, causing approximate 3% loss of the global gross domestic product (GDP) every year, is a serious global problem for any metallic material [1]. As a very classical example, copper is the most important metal used in marine engineering, including power stations, shipbuilding and seawater desalination, owing to their perfect electrical, thermal and mechanical properties [2,3]. However, copper can be corrode seriously in marine environment despite possessing excellent corrosive resistance, owing to the existence of huge amounts of aggressive chloride ions.

Among the numerous available methods to prevent copper from corrosion, the use of inhibitors is one of the most practical

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and cost-effective strategies. Organic compounds containing conjugated double bonds, several heteroatoms (i.e. sulfur, nitrogen, oxygen) and/or polar functional groups generally exhibit favorable inhibitive properties, so they can always be employed as inhibitor for corrosion of copper [4–6]. The most effective corrosion inhibitor relies extensively on benzotriazole (BTA), owing to its high inhibitive ability and low cost [7]. However, with increasing concern about environment pollution, the use of BTA and its derivatives has been restricted worldwide due to their high toxicity. This has resulted in high scientific interest and research activity in finding environment-friendly BTA replacements [8–18].

5-Nitroindazole has been proved as a green corrosion inhibitor for copper in 3% NaCl solution by our group [19]. Based on this structure, indazole (IA) and 5-aminoindazole (AIA), chemical intermediates whose derivatives are used as affinity reagents or inhibitors in medicinal chemistry [20–22], are also promising to improve corrosion resistance of copper.

Therefore, the purpose of the present work is to measure the inhibition performance and investigate the inhibition mechanism of both IA and AIA on copper in 3% NaCl solution, which has not been reported previously. Weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and FESEM techniques were used to evaluate the inhibitive performance of these inhibitors for copper corrosion in 3.0% NaCl solution at first. Then both quantum chemical calculations and molecular dynamics simulation were further adopted to investigate the active sites and adsorption properties of these inhibitors on copper surface. Based on the results of experiments and theoretical calculations, an inhibitive mechanism is further developed to interpret the protection effects of studied inhibitors for copper corrosion.

## 2. Experimental

### 2.1. Materials and sample preparation

Sodium chloride (NaCl, 99.9%), absolute ethanol ($C_2H_5OH$, 99.9%), indazole (IA, Aladdin, 99%) and 5-anminoindazole (AIA, Aladdin, 98%) incorporated in Fig. 1 were used as received. The copper coupons (99.8%) with dimensions of 1.00 $cm^3$ were embedded in epoxy resin leaving 1 $cm^2$ cross-sectional area exposed to the corrosive medium for electrochemical experiments. Besides, the copper specimens used for weight loss measurements were mechanically cut into 3.00 cm × 1.50 cm × 1.50 cm dimensions.

The testing solution was prepared by 3.0% NaCl solution with different concentrations (0.2–0.8 mM) of the inhibitors, and the solution without inhibitors was treated as blank for comparison. Prior to each experiment, the copper specimens were abraded consecutively with a series of emery papers (400, 800, 1600, 2000 grit). And then, they were washed ultrasonically with ultrapure water, degreased with acetone and dried at room temperature. All experiments were carried out at 298 ± 0.5 K by thermostat water bath.

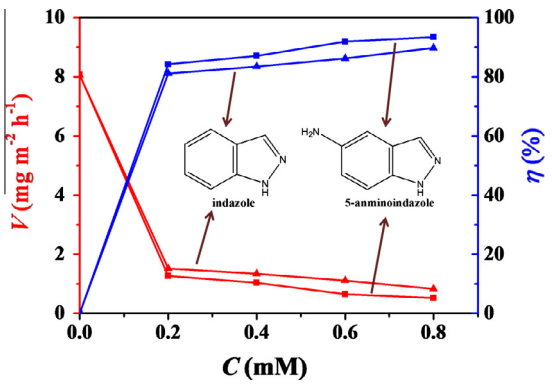


**Fig. 1.** Corrosion rates and inhibition efficiencies for copper electrode in 3% NaCl solution with different concentrations of IA and AIA at 298 K, together with molecular structure of these inhibitors.

### 2.2. Weight loss measurements

Weight loss experiments were carried out in 500 mL glass beakers placed in a water thermostat. Cleaned and weighed copper samples in triplicate were immersed in 3% NaCl solution for each inhibitor concentration at 298 K, respectively. Then the specimens were rinsed thoroughly in 0.1 mol/L HCl, water and acetone, subsequently dried and weighed by analytical balance. The mean corrosion rates were finally calculated by immersion time and the weight loss of each specimen.

### 2.3. Electrochemical measurements

A conventional three-electrode system assembly with copper working electrode, saturated calomel electrode (SCE) and platinum electrode was used for electrochemical measurements by CHI660B electrochemical workstation. Prior to each measurement, the working electrode (WE) was immersed in aggressive solution for 30 min at open circuit potential (OCP) to reach an almost steady state. Subsequently, EIS measurements were performed at the OCP in the frequency range from 100 kHz to 0.01 Hz using sinusoidal AC perturbation with amplitude of 5 mV. The EIS data were analyzed and fitted by Zsimpwin 3.10 software. At last, polarization experiments were performed in the potential range of ±250 mV versus the OCP with a scan rate of 2 mV $s^{-1}$. All potential values reported in present study were referred to SCE. The same experiment was carried out for 5 times to guarantee a favorable reproducibility.

### 2.4. Surface analysis

The surface morphology of the copper specimens before and after immersed in 3% NaCl solution without and with 0.2 mM IA and AIA at 298 K were observed by field emission scanning electron microscope (FESEM, JEOL-JSM-7800F-Japan).

### 2.5. Calculation methods

Quantum chemical calculations were carried out by Gaussian 03W software. The molecular structures of IA and AIA were geometrically optimized by density functional theory (DFT) using B3LYP [23] functional with 6-311++G(d,p) basis set in aqueous phase. The corresponding quantum chemical parameters including the energy of the frontier molecule orbital ($E_{HOMO}$, $E_{LUMO}$), energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$), and dipole moment ($\mu$) are considered.

Besides, the forcite module in Material Studio 7.0 software from Accelrys Inc. [24] was employed to study the interaction between the Cu (1 1 1) surface and the inhibitors. A (8 × 8) surface unit cell with a slab of five layers containing 300 water molecules was chosen to model the Cu (1 1 1) surface. The molecular dynamics (MD) simulation was performed in aqueous phase at 298 K, canonical ensemble (NVT), with a time step of 1.0 fs and simulation time of 500 ps.

The binding energy $E_{Cu\text{-}inhibitor}$ between the inhibitor molecule and the Cu (1 1 1) surface was calculated as following equation [25]:

$$E_{Cu\text{-}inhibitor} = E_{Total} - E_{Cu} - E_{Inhibitor} \quad (1)$$

where $E_{Total}$ was the energy of the copper crystal together with the adsorbed inhibitor molecule, $E_{Cu}$ was the energy of the copper