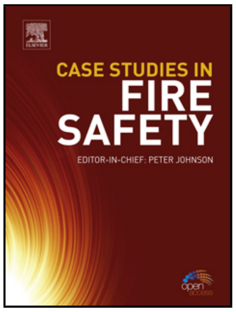

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PII: S0010-938X(16)30771-5
DOI: http://dx.doi.org/doi:10.1016/j.corsci.2017.04.021
Reference: CS 7068

To appear in:

Received date: 16-9-2016
Revised date: 6-4-2017
Accepted date: 7-4-2017

Please cite this article as: Nataša Kovačević, Ingrid Milošev, Anton Kokalj, How relevant is the adsorption bonding of imidazoles and triazoles for their corrosion inhibition of copper?, *<![CDATA[Corrosion Science]]>* (2017), http://dx.doi.org/10.1016/j.corsci.2017.04.021

# How relevant is the adsorption bonding of imidazoles and triazoles for their corrosion inhibition of copper?

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## Abstract

Imidazole, 1,2,4-triazole and their 1-methyl derivatives were evaluated as copper corrosion inhibitors in NaCl solution by corrosion experiments and their bonding to Cu(111) was characterised by DFT calculations. Deprotonated triazole adsorbs considerably stronger than 1-methyl-triazole, whereas deprotonated imidazole displays only slightly more exothermic aqueous-phase adsorption free energy than 1-methyl and neutral imidazole. This suggests that triazole should be a more efficient inhibitor than 1-methyl-triazole, whereas the efficiency of imidazole and 1-methyl-imidazole should be similar. The experimental measurements only partly support this inference, because 1-methyl-imidazole accelerates corrosion at higher concentrations.

*Keywords:* A. Copper, B. Modelling studies, B. Polarisation, C. Interfaces, C. Neutral inhibition

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## 1. Introduction

Azoles and particularly their derivatives are known as efficient corrosion inhibitors for copper [1–4]. In our previous publications the adsorption of plain azole molecules—imidazole, 1,2,3-triazole, tetrazole, and pentazole—in protonated, neutral, and deprotonated forms on Cu(111) has been characterised using density functional theory (DFT) calculations [5, 6]. Both vacuum/metal and water/metal interfaces were considered. We found that chemisorption bonding is by and large the strongest for deprotonated molecules. An exception is imidazole for which the aqueous-phase adsorption free energy of the neutral form is comparable to that of the deprotonated form. This suggests that for imidazole—due to its more basic nature—the neutral form and for triazole and tetrazole their deprotonated forms should be the active species for inhibiting copper corrosion [6].

The purpose of this work is to further scrutinise the proposition that imidazole is active in neutral and triazole in deprotonated form against corrosion of copper. Deprotonation of imidazole and triazole can be prevented by substituting the H1 atom by a methyl group and for this reason we compare the corrosion inhibition efficiency of plain imidazole and triazole with their 1-methyl derivatives for copper in 3 wt.% aqueous NaCl solution (respective molecular skeletal structures are shown in Fig. 1). We further try to associate the corrosion inhibition efficiency of these molecules with their adsorption bonding. For the sake of comparison with our previous publications, where we characterised by means of DFT calculations the bonding of plain azoles with bare Cu(111) [5–7], we have chosen to elucidate the bonding of the current molecules with the same surface, although the oxidised surface of copper would be more relevant in the context of corrosion under near-neutral pH conditions. In should be noted that in our previous publications [5, 6], we considered 1,2,3-triazole, while currently we consider 1,2,4-triazole and its 1-methyl derivative, because the former was not commercially available. 1,2,4-Triazole has a somewhat larger pKa constant than 1,2,3-triazole, 10.3 and 9.4, respectively [8].

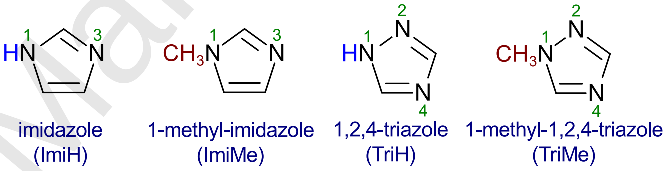

Figure 1: Skeletal structures of imidazole (ImiH), 1-methyl-imidazole (ImiMe), 1,2,4-triazole (TriH), and 1-methyl-1,2,4-triazole (TriMe). The numbering of N atoms is also indicated.

## 2. Technical details and definitions

### 2.1. Experimental details

Corrosion tests were performed on copper metal (99.9%) supplied by Goodfellow (Cambridge Ltd., UK). Copper was purchased in the form of 2 mm thick foil. All copper specimens were cut from the foil in the shape of discs of 15 mm diameter. Using a circulating device the specimens were mechanically ground under a stream of water with SiC papers of gradations 500, 800, 1000, 1200, 2400, and 4000. Further, the copper samples were cleaned with acetone in an ultrasonic bath for three minutes, double-rinsed with distilled water, and dried with nitrogen gas.

Samples were immersed in 3 wt.% aqueous NaCl solutions with or without the addition of inhibitors in various concen-

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