

# Abstract

Azoles and their derivatives are known for their corrosion inhibition of copper. For this reason the bonding of imidazole, triazole, and tetrazole—used as archetypal models of azole corrosion inhibitors—on various  $\text{Cu}_2\text{O}(111)$ - and  $\text{Cu}_2\text{O}(110)$ -type surfaces was characterized using density functional theory (DFT) calculations. Both non-dissociative and dissociative adsorption modes were considered. We find that molecules bind much stronger to unsaturated Cu sites compared to saturated ones. Dissociated molecules bind considerably stronger to the surface compared to non-dissociative molecules, although even the latter can bind rather strongly to specific unsaturated (CUS) Cu sites. All three azole molecules display similar non-dissociative adsorption energies, but significant difference between them appears for dissociative adsorption mode. It was found that N–H dissociative adsorption is favorable only for triazole and tetrazole, but only at oxygen vacancy sites, where it proceeds barrierlessly (or almost so). This observation may suggest that, for imidazole, only the neutral form, but, for triazole and tetrazole, also their deprotonated forms are the active species for inhibiting corrosion under near neutral pH conditions, where copper surfaces are expected to be oxidized. In addition, we also addressed the bonding of Cl, which can be seen as a corrosion activator. The calculations indicate that only dissociated triazole and tetrazole bind strong enough to rival the Cl–surface bonds. An ab initio thermodynamics approach was used to construct two-dimensional phase diagrams for all three molecules. Although dissociated molecules bind to surfaces more strongly, none of the considered structures that involve dissociated molecules appear on the phase diagrams. According to the calculated phase diagrams for  $\text{Cu}_2\text{O}(111)$ -type surfaces, the three azole molecules adsorb to specific CUS sites and stabilize them, under all conditions at which molecular adsorption is stable. This tentatively suggests that their corrosion inhibition capability may stem, at least in part, from their ability to passivate reactive surface sites. We also addressed the adsorption of non-dissociated and dissociated water molecules on three (111)-type surface models. Non-dissociative water molecules form O–Cu bond only with unsaturated Cu surface sites. If the surface model lacks these sites, water forms hydrogen bonds with surface oxygen ions. Dissociation of water molecules was found to be exothermic only at oxygen vacancy sites.

**Keywords:** DFT calculations, azoles, adsorption, copper-oxide, corrosion.