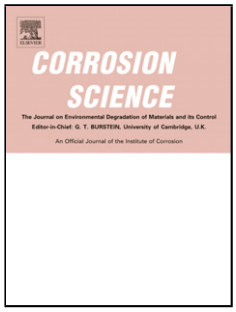

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PII: S0010-938X(15)00236-X
DOI: http://dx.doi.org/doi:10.1016/j.corsci.2015.05.041
Reference: CS 6328

To appear in:

Received date: 5-3-2015
Revised date: 20-5-2015
Accepted date: 22-5-2015

Please cite this article as: Nataša Kovačević, Ingrid Milošev, Anton Kokalj, The roles of mercapto, benzene, and methyl groups in the corrosion inhibition of imidazoles on copper: II. inhibitorndashcopper bonding, *Corrosion Science* (2015), http://dx.doi.org/10.1016/j.corsci.2015.05.041

The roles of mercapto, benzene, and methyl groups in the corrosion inhibition of imidazoles on copper: II. inhibitor–copper bonding

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Abstract

Bonding of five imidazole type molecules—imidazole, 1-methyl-imidazole, benzimidazole, 2-mercapto-1-methyl-imidazole, and 2-mercaptobenzimidazole—with copper surfaces and hydrated Cu^{2+} ions is characterized in detail by DFT calculations as to explain the corrosion inhibition efficiency trend of these inhibitors for copper, determined experimentally in the Part I. We find that mercapto-substituted imidazoles are prone to deprotonation upon adsorption. They bond stronger to the surface and display weaker tendency to form soluble complexes with hydrated Cu^{2+} ions than non-mercapto molecules. By encapsulating these two interactions into a simple model—the first interaction is deemed as beneficial and the second as detrimental—the inhibition efficiency trend is well captured.

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

1. Introduction

This is the second part of the two-part series of articles about the role of mercapto group, benzene, and methyl group on the inhibition efficiency of imidazole type corrosion inhibitors on copper; the term "benzene" is used pragmatically to distinguish between imidazoles and benzimidazoles. In the Part I [1], the issue has been investigated experimentally and corrosion inhibition characteristics of five different inhibitors (imidazole, benzimidazole, 1-methyl-imidazole, 2-mercapto-1-methyl-imidazole, and 2-mercaptobenzimidazole) were determined for copper in 3% (w/w) aqueous NaCl solution. It has been shown that mercapto group and benzene have a beneficial effect on corrosion inhibition, whereas the effect of methyl group is more intriguing: at lower inhibitor concentrations ($\lesssim$1 mM) the effect is weakly disadvantageous (compared to plain imidazole), but at larger concentrations the disadvantageous effect amplifies and 1-methyl-imidazole even accelerates the corrosion at 10 mM concentration. Composition of layers formed on copper surface was strongly affected by the type of the inhibitor added to solution, as revealed by X-ray photoelectron spectroscopy (XPS). Cupric compounds were formed in the presence of imidazole and 1-methyl-imidazole. In the presence of benzene and mercapto derivatives only cuprous compounds were formed.

In the current paper, we try to explain the reasons for experimentally observed trends. For the purpose of facilitating such interpretations, a molecular modeling of organic corrosion inhibitors has become very popular in last decade, e.g., see Review [2]. In large majority of cases the procedure consists of calculating several, presumably relevant, electronic parameters of inhibitor molecules without any consideration of the substrate and associating them to the experimentally determined trend of corrosion inhibition efficiency via some correlation analysis. This approach was criticized in Ref. 3, where it was pointed out that in general molecular electronic properties of inhibitors alone cannot be directly related to corrosion inhibition efficiency, because the actual relation is far more involved. Moreover, Lindsay et al. [4] recently stated that "*in terms of predictive power, such an approach has at best limited value, and is potentially simply misleading*". A step forward would be, for example, to rigorously model interactions between the components of corrosion system. Recently several attempts in this direction appeared [5–32].

Although the mechanism by which organic molecules inhibit the corrosion is usually not known, it is generally accepted that the strong interaction between an inhibitor molecule and a substrate is very important for achieving the inhibitory effect [33–35]. For this reason, we explicitly consider the interaction of the current inhibitors with copper surfaces (their molecular skeleton structures are shown in Fig. 1). As a starting point and for the sake of comparison with our previous publications, where we characterized the bonding of plain azoles with bare Cu(111) [10, 17], we choose to elucidate the bonding of the current inhibitor molecules with the same surface, although the oxidized surface of copper would be more relevant in the context of corrosion under near-neutral pH conditions.[2] In addition to Cu(111) we also consider the adatom de-

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[2]It should be noted that metallic surfaces are conceptually and structurally simpler than the oxidized surfaces. This is the basic premise behind our choice, which follows the reductionist *divide-and-conquer* approach, i.e., start with