



Impact of molecular structure of two natural phenolic isomers on the protective characteristics of electropolymerized nanolayers formed on copper



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ABSTRACT

A comparative study of the electropolymerization of two natural phenolic isomers, carvacrol (Carv) and thymol (TOH) on copper was made. They are components of *Origanum vulgare* and *Thymus vulgaris* essential oils. Polymerized layers (polyCarv and polyTOH) were attained by cyclic voltammetry (CV). Electrochemical techniques complemented by ATR-FTIR, XPS, SEM and AFM surface analyses were used to evaluate the composition and protective characteristics of the films. Results revealed that the electrochemical response in chloride solutions was dissimilar. Copper ions release by polyCarv in chloride solutions was lower than 30% of that obtained with TOH treatments. PolyCarv is a highly protective, transparent film, remarkably different from the brownish, rough and non-protective film obtained with TOH. ATR-FTIR results showed that the oxidation of adsorbed Carv and TOH led to cetonic structures while after electropolymerization ether bonds were also found. However, polyCarv and polyTOH showed important differences in ν -OH band. Deconvolution of C1s signal of XPS spectra led to four contributions with different proportions for polyCarv and polyTOH. Accordingly, $C_{(ph)}-O$ is 50% of total C1s for polyCarv and 30% for polyTOH. C1s/O1s relationships were also different. AFM and SEM observations showed the presence of round flakes, smaller for polyCarv (5 nm height) than for TOH (35 nm height). A compact layer was found in case of polyCarv but cauliflower and sticks structures with cracks were found for polyTOH. In summary, results showed the important impact of the molecular structure on the composition, structure and protective characteristics of the polymeric layers. A mechanism is proposed to interpret these results.

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1. Introduction

Copper and copper-based alloys are materials suitable for versatile purposes. They are used in construction for outdoor applications due to their attractive appearance and advantageous mechanical, thermal and conductivity properties together with their simple fabrication and joining. For industrial purposes they are extensively applied in piping, tubing, condensers and heat

exchangers because of their adequate resistance to corrosion and biofouling. They have also been proposed for containers for nuclear wastes buried and exposed to ground-waters [1]. Other advantages are their reduced maintenance costs, prolonged service life, increased reliability and high recyclability [1–3].

In spite of its valuable properties copper is vulnerable against corrosion in chloride environments [4]. Apart from the economical costs involved in substitution or repair of the copper-containing system, corrosion process leads to the release of copper ions that contaminate aqueous environments and represents a potential risk for biological systems [5]. Chloride ions adsorb on copper and CuCl is formed which may lead to soluble $CuCl_2^-$ complex or hydrolyze to form atacamite ($Cu_2(OH)_3Cl$) [4].

Several kinds of coatings have been proposed to reduce corrosion when metals are susceptible to environmental

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interactions [6]. Coating may act as ionic filter able to mitigate current transfer between anodic and cathodic areas, or obstruct the diffusion of oxygen to inhibit cathodic reaction. Several organic inhibitors form thin films of adsorbed molecules that cover copper active sites hindering the adsorption of chlorides and the formation of corrosion products. Many of them are hetero-cycles that are added to the corrosive solutions [7–11]. Several Inhibitory treatments were also developed with the aim of improving the shielding action achieved with adsorptive films. However, due to the more strict environmental regulations that have been implemented in recent years, corrosion inhibitors are required to have an environmentally friendly profile. They are expected to be non bioaccumulative, biodegradable and have a low toxicity level. Thus, current research is focused to the exploration of environmentally compatible, nonpolluting corrosion inhibitors. This search leads to natural factories like plants, rich sources of phytocompounds that can readily satisfy these requirements. Natural compounds are frequently low-cost, eco-compatible, renewable and readily available. Importantly, they can be extracted inexpensively by simple procedures. Consequently, substantial effort has been made in recent years to investigate the corrosion inhibiting efficacy of these natural products with low or “zero” environmental impact [12–18]. It is well known that aromatic plants like *Origanum vulgare* and *Thymus vulgaris* are sources of phenolic compounds (PC). Interestingly, electrochemical studies with some synthetic PC have revealed that they can be electropolymerized on metallic surfaces and showed excellent corrosion protection [19,20]. Thus, new strategies based in electropolymerization process of natural PC with low effect in the environment may be developed. Among non synthetic compounds two of the main components of *Origanum vulgare* and *Thymus vulgaris* essential oils (carvacrol and thymol) are PC that seem to be suitable for the development of an ecofriendly treatment [21]. Considering previous reports about different substituted PC [22], we hypothesized that both carvacrol (Carv) and thymol (TOH), due to their phenolic structures, are able to form electropolymerized layers on copper surface but their shielding action against corrosion may be different. Thus, the aim of this work is to elucidate if the molecule structure of these structural isomers impacts on their electropolymerization mechanism and on the protective characteristics of the nanolayers formed on copper. Apart from the importance of the fundamental aspects of this investigation, related the electropolymerization mechanisms of two PC isomers, Carv and TOH, results should be very useful in relation to the selection of the species of the aromatic plants that will be the best sources of the essential oils to be used as corrosion inhibitors. For example, they will provide information to select the best species between, *Origanum vulgare*, reach in Carv and *Origanum X apalii* or *Thymus vulgaris* whose main component is TOH [23–25].

2. Experimental

2.1. Chemicals

Carv (Sigma, St. Louis, MO, USA), and TOH (Sigma, St. Louis, MO, USA) which chemical structures are shown in Fig. 1 were used in the experiments. All chemicals consumed in the assays were of analytical grade and ultrapure water was employed to prepare the solutions.

2.2. Cu samples and generation of electropolymerized layers.

Cylindrical copper bars (99.7% electrolytic metal copper, 0.9 cm diameter) (Merck, Darmstadt, Germany), whose lateral surfaces were covered with polyoxymethylene, leaving an exposed area of

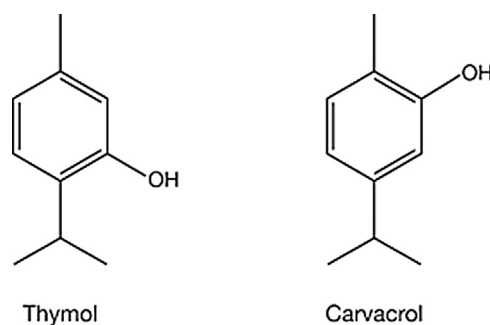


Fig. 1. Chemical structure of thymol and carvacrol.

0.626 cm² were used as working electrodes for electrochemical experiments. Each electrode was mechanically polished with emery paper of different grain sizes using water as lubricant and then washed with water and ethanol, and dried with nitrogen. The electrode surface was carefully observed under optical microscope (Olympus BX51, Olympus Corp., Tokyo, Japan), before and after the experiments, to evaluate possible changes in color and/or texture of copper.

Electrochemical assays were made in a conventional cell with double wall to allow the circulation of water at constant temperature. A platinum foil was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The potential values in the text are referred to the SCE.

Electropolymerized films of Carv and TOH (polyCarv and polyTOH) were attained using cyclic voltammetry (CV) by successive cycling the electrode potential at 50 mV s⁻¹ (39 cycles) within 0.3 V–1.0 V potential range. This electrochemical methodology was a modification of that reported by Guenbour [26,27]. In our case 0.1 M Carv or 0.1 M TOH, 70:30 water/ethanol (EtOH) alkaline solution (0.3 M NaOH) [26–28] was used as electrolyte for CV electropolymerization treatment. The presence of EtOH in Carv and TOH solutions is necessary to improve PC solubility. Each test was run in triplicate to verify the reproducibility of the data. In all cases a potentiostat-galvanostat TEQ03 was used. Control experiments using 0.3 M NaOH with and without EtOH were also recorded.

For surface analysis and copper ion release measurements, copper disks obtained from a pure copper sheet (99.7%, 0.1 mm thick, 6 mm diameter) (Merck, Darmstadt, Germany) were used. These disks were washed with (5% v/v) H₂SO₄, vigorously rinsed with ultrapure water and then dried with nitrogen. The polyCarv/polyTOH formation on the disks was carried out with the copper sheets as previously described for cylindrical copper samples.

2.3. Measurement of copper ions release

The copper ion release from the copper disks covered by polyCarv or polyTOH films (polyCarvCu, polyTOHCu) after their immersion in 3 ml of KCl solution (0.136 M) for 1 day, 3 days and 6 days at room temperature was measured by colorimetric analysis and by atomic absorption spectroscopy. Colorimetric method is based on the addition of 1-(2 pyridylazo)-2-naphthol (PAN) to the samples. This dye forms colored complexes with Cu(II) which are suitable for spectrophotometric analysis. Briefly, an appropriate volume of H₂SO₄ was added to each sample to reach a final concentration of 0.25 M. An aliquot of 100 µl of these acidic samples was mixed with 100 µl of 4 mM PAN ethanolic dissolution and 800 µl of water. The absorbance was measured in a Shimadzu UV 1800 spectrometer at λ=560 nm, maximum of the absorption spectra of the copper(II)–PAN complex. The copper content in an

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