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Theoretical study of the adsorption of substituted guaiacol and catechol radicals on a graphite surface

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ABSTRACT

Adsorption of radicals obtained from catechol and guaiacol derivatives, on a graphite surface, was theoretically analyzed in the context of electrografting process. It was determined that the phenoxy type radicals preferred to link to the surface by aligning the oxygen ($O^{\bullet}$) radical on top of a carbon atom of the surface; also, it was found that the main contribution to the radical-surface stabilization, in the studied systems, comes from van der Waals interactions. In addition, the calculated free energies and overpotentials, related to the first oxidation process of catechol and guaiacol type of structures on the surface, provide insights about the behavior of these molecules and more complex derivatives of them in cyclic voltammetry experiments in glassy carbon electrode.

1. Introduction

The electrografting of organic species is a powerful tool to modify the surface of solid conducting substrates [1]. The chemisorption of amines [2–4], carboxylates [5–7], alcohols [8,9], vinylics [10] and diazonium salts [11,12] are among the most studied electrografting processes, and some of them have found interesting applications [1]. In this sense, the understanding of the role of the experimental conditions and the mechanisms of the electrochemical reactions between different types of compounds and the substrates can contribute to achieve efficient functionalized surfaces.

Theoretical-experimental studies have been carried out in order to describe molecular adsorption on a graphite surface, for example: adenine [13], methane [14,15], water [16,17], Ar, H_2, and N_2 [18]. Radical systems have been also studied, such as alyl, benzyl, diphenilmethyl, perinaphtylene [19], hydrogen, oxygen [20], hydroperoxyl ($^{\bullet}OOH$) [21], hydroxyl ($^{\bullet}OH$) [22], and methyl [23,24], where the last two radicals are considered to interact through van der Waals forces. Adsorption of phenol was studied through the Monte Carlo method, where two adsorption sites were determined: one of them corresponds to the oxygen centered on the carbon cycle; and the other site between two carbon atoms [25]. Chakarova-Käck *et al.* [26] carried out the study of adsorbing phenol on the (0001) graphite surface using Density Functional Theory (DFT), including van der Waals correction terms; they found an adsorption distance of 3.47 Å and an adsorption energy of 0.56 eV, thus concluding that this type of study is key in the understanding of interactions between organic molecules and biologically relevant surfaces and interfaces.

On the other hand, several mechanistic studies on the electrochemical oxidation of ferulic and caffeic acids (**FA** and **CA**, in Fig. 1) have been documented in the literature [27–32], since their antioxidant activity could be related to electron transfer processes. From these studies, it is known that the electroactive units are the guaiacol and catechol moieties (**G** and **C**, in Fig. 1), and that the oxidation of this type of compounds on a Glassy Carbon Electrode (GCE) followed a mechanism known as ECE (*electron transfer – chemical reaction – electron transfer*). Our group has also investigated the electrochemical behavior of esters and amides derivatives of **FA** and **CA** including one [33] or more feruloyl [34,35] or caffeoyl [36] moieties in their structures (see compounds **1**–**4** in Fig. 1). In those studies, we documented that a chemisorption process also occurs during the electrochemical oxidation of these **FA** derivatives after a few scans [34,35]. In contrast, the dimeric caffeoyl derivatives reacts with the electrode surface during its oxidation, but a desorption phenomenon occurred at cathodic potentials which suggests that the reactive site [36], in the case of the **CA** derivative, could be different to that generated from their **FA**

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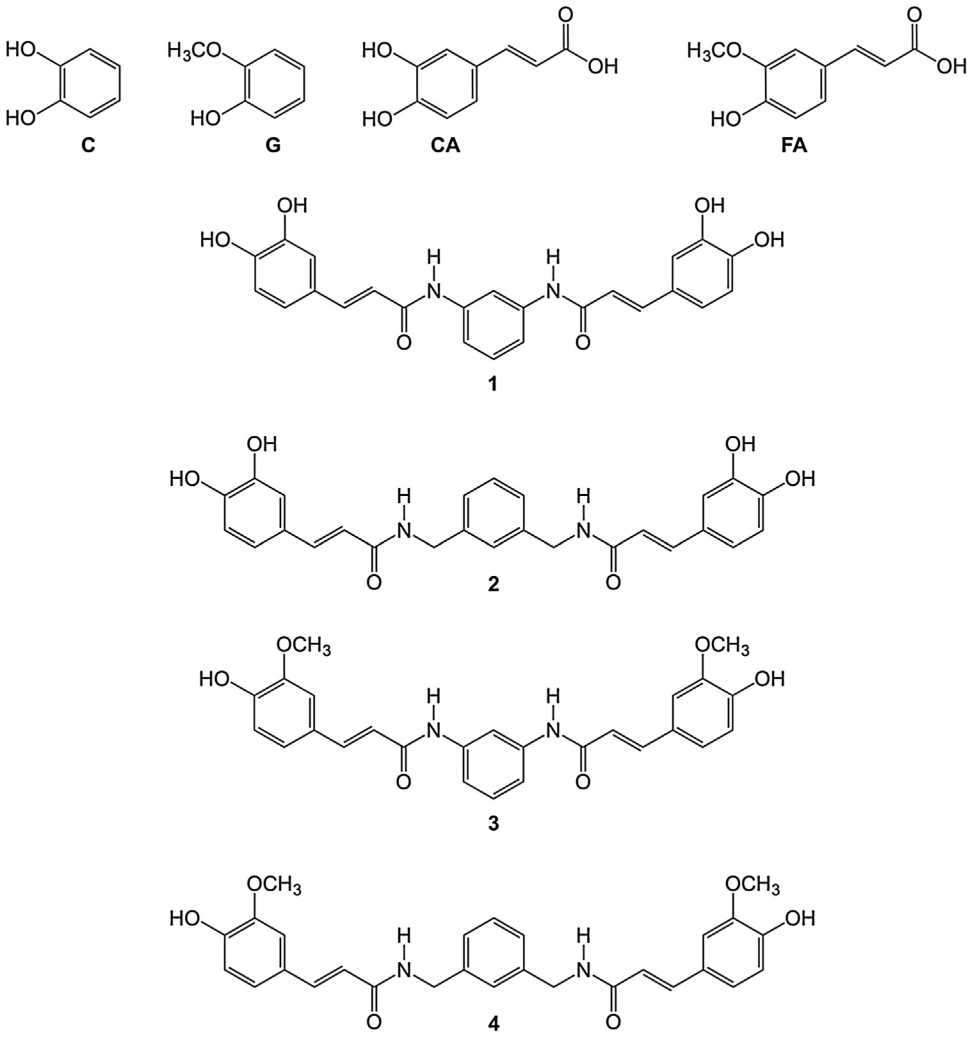

Fig. 1. Catechol (**C**), guaiacol (**G**), caffeic acid (**CA**), ferulic acid (**FA**) and *bis*-amide systems of **CA** (**1** and **2**) and **FA** (**3** and **4**).

analogs. The proposed mechanisms for the electrochemical oxidation of both type of compounds is summarized in Fig. S1a and Fig. S1b in the Supplementary Information (SI).

Nevertheless, the reactivity and structural differences between the oxidized species of **FA** and **CA** derivatives raised the need of obtaining more information with respect to their electrochemical oxidation, i.e., the reversibility of their interaction between them and the GCE, as well as their rate constants for the deprotonation process. Therefore, in this work, Density Functional Theory (DFT) under periodic conditions methodology is applied to better comprehend the first step of the oxidation mechanism (for systems **1**-**4** in Fig. 1) through the adsorption of radical systems

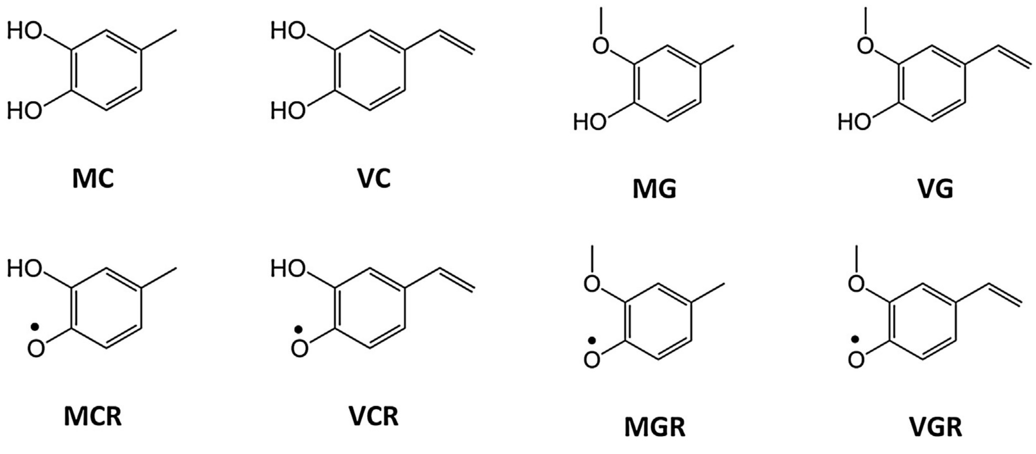

Fig. 2. Representative systems and its corresponding radical forms for compounds **1** to **4** of Fig. 1: **MC**, methyl catechol; **MCR**, methyl catechol radical; **VC**, vinyl catechol; **VCR**, vinyl catechol radical; **MG**, methyl guaiacol; **MGR**, methyl guaiacol radical; **VG**, vinyl guaiacol; and **VGR**, vinyl guaiacol radical.