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Changes in electronic structures of flavonoids upon electrochemical oxidation and a theoretical model for the estimation of the first oxidation potential

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ABSTRACT

This paper studies the electronic structures of the 14 flavonoids and their cation and radical forms involved in the first electrochemical oxidation step, associated with the oxidation peak appearing at potential E_{p1}. The sum of differences in Net atomic charges on atoms in skeleton of cations and neutral flavonoids ($\sum_{s(C)} \Delta NAC_{Cat.-Neut.}$) and the sum of Atomic orbital electron and spin populations on atoms in skeleton of radicals ($\sum_{s(C)}$ AOEP and $\sum_{s(C)}$ AOSP) revealed that electron distribution between skeleton atoms and active OH oxygen is more evenly distributed in cations and radicals of flavonoids that are more prone to oxidation. Those less susceptible to oxidation are more polarized, i.e. the skeleton becomes more positively charged. Also, $\sum_{s(C)}$ AOSP proved to be an excellent descriptor for modelling the first oxidation potential, especially in combination with $\sum_{s(C)} p_z$AOEP (common model for pH = 3 and 7 yielded R^2 = 0.978 and S.E. = 0.43).

Keywords: oxidation potentials; polyphenols; QSPR; PM6; DFT

1. Introduction

Redox reactions play a crucial role in maintaining normal cellular functions and thus the proper functioning of biological systems. Flavonoids, a large group of polyphenolic secondary plant metabolites, can interfere with these redox reactions and consequently affect the cellular redox balance. In this regard, the ability of flavonoids to scavenge free radicals