

Study of the electrochemical passivation by phenolics compounds using QSPR

Reinaldo F. Teófilo*, Rudolf Kiralj, Lauro T. Kubota, Márcia M.C. Ferreira
teofilo@iqm.unicamp.br

Instituto de Química, Universidade Estadual de Campinas

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It is well known that the oxidation of phenolic compounds (PCs) at solid electrodes produces phenoxy radicals, which couple to form a passivating polymeric film on the electrode surfaces.¹ During the oxidation the radical is formed causing a polymerization and consequently the surface fouling, which is a problem in electroanalysis and electrooxidation of phenols. Gattrell and Kirk² assume that the OH species react with adsorbed phenol slowly oxidizing it and releasing further sites for OH electrosorption and thus accelerate the chemical reaction. This assumption is based on the concept of a chemical reaction of organic compounds with reversibly deposited OH at open Pt metal sites.

Although the majority of the studies prioritizes the analysis of the obtained polymeric films, this work presents a proposal studying the PCs molecular structures relating to the electrochemical passivation. Quantitative Structure Property Relationship (QSPR) model was built to relate the phenolic molecular descriptors and electrochemical passivation properties.

The electrochemical passivation was monitored using the amperometric method with platinum electrode. The potential was fixed 50 mV more positive than the PC oxidation peak. The oxidation was carried out in a concentration of 5.0×10^{-4} mol L⁻¹ PC in 0.05 mol L⁻¹ phosphate buffer solution at pH 6.5, for 90 s measuring in each 0.2 s. The investigated PCs were: catechol, chloroguaiacol, dopamine, guaiacol, hydroquinone, L-dopa, *o*-aminophenol, *o*-nitrophenol, *p*-aminophenol, paracetamol, phenol, resorcinol, serotonin, 5-hydroxyindole, *o*-cresol, *p*-chloro-*m*-cresol, *m*-cresol, *p*-cresol, *o*-chlorophenol and L-tyrosine. The difference between the current density after 15 s and 90 s of oxidation was considered as a parameter of passivation measurement (Δj). The measures were carried out in triplicate and the mean value was used. The average of the mean triplicate results was of 33.6 μ A, presenting as minimum and maximum values, 10.3 and 53.8 μ A, respectively and standard deviation of 14.3 μ A. The negative logarithm of the means was used as dependent variable ($p\Delta j$).

Molecular structures of 20 compounds in neutral state were modeled according to their or similar structures from the Cambridge Structural Database. Geometry optimization was performed at *ab initio* level (DFT with B3LYP functional and 6-31G** basis set) and various molecular descriptors were calculated. The partial least square (PLS) regression model was built with autoscaled data and cross-validated by leave-one-out method. Systematic variable selection resulted in four descriptors, *i.e.*, NPA atomic charge of the carbon atom chemically bound to the OH group (Qcnpa); Julg's aromaticity index (Ar); sum of squares of the O atomic orbital (s, px, py, pz) coefficients in the LUMO+1 (Clumo+1) and bending frequency for the angle H–O–C (fCOH). The mean relative error was of 2.53%, and the Q and rmseCV was of 0.76 and 0.14, respectively. The selected molecular descriptors are moderately (corr. coeff. 0.42–0.76) correlated with the dependent variable. The final PLS model has satisfactory statistics and predicted values (no compounds with relative error greater than 7.0% by cross-validation). The first oxidation is crucial for the whole process. Molecules that are more difficult to oxidize (higher oxidation potential E_{ox}) have smaller values of dependent variable ($< p\Delta j$).

The descriptors selected suggest that a compound could be easier oxidized at the OH group if: i) the electron delocalization between the benzene ring and OH is weakened by substituents, so the ring is by itself highly aromatic (high Ar values); ii) the C–O bond polarization is pronounced, so O is negatively and first C positively (high Qcnpa values) charged, *i.e.* O is relatively electron-rich; iii) O atom is electron-rich and can be easily excited as it has significant contribution to frontier orbitals like LUMO+1 (high LUMO+1); iv) the existing interactions among O, H, and C are weakened, what results in more flexibility of this group and higher bending frequency (higher fCOH). In fact, all descriptors show that if the O from OH can be easily oxidized because its connection with the ring is weakened, the first phenolic radical will be formed and, in this way, a lower oxidation potential will be necessary, and a lower passivation process will be observed.

QSPR is a promising tool in passivation studies in electrochemistry, contributing to the elucidation of phenolic oxidation mechanism and supplying information to minimize the passivation.

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References

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