

Quantitative Structure-Property Relationship (QSPR) study of phenolic passivation at the platinum electrode*Reinaldo F. Teófilo, Rudolf Kiralj, Márcia M. C. Ferreira, Lauro T. Kubota*

Laboratório de Quimiometria Teórica e Aplicada, Instituto de Química, Universidade Estadual de Campinas, Campinas SP, 13084-971, Brazil.

E-mail: marcia@iqm.unicamp.br

Keywords: electrochemical passivation, QSPR, chronoamperometry

Oxidation of phenolic compounds (PCs) at solid electrodes produces phenoxy radicals, which couple to form a passivation polymeric film on the electrode surfaces *via* mechanism of OH-mediated oxydation [1,2]. The current literature is concerned with the structure of the passivation products (polymeric films) and not with the structure of the reactants, which might contain useful information for prediction of passivation mechanisms and polymer yields from particular PCs.

This work consists of chronoamperometry coupled with Quantitative Structure-Property Relationship (QSPR) with the aim to build a regression model for prediction of phenolic electrochemical passivation rates. The passivation on the platinum electrode was monitored for 20 PCs at 50 mV above the PCs oxidation peaks (5.0×10^{-4} mol/L PC, 0.05 mol/L phosphate buffer, pH 6.5, 90 s measuring in each 0.2 s): 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 densities after 15 and 90 s of oxidation, normalized by the electric current mean and transformed into negative logarithm, was defined as the passivation rate $p\Delta_j$. Molecules of PCs were modeled and geometry-optimized at the B3LYP 6-31G** level. Various molecular descriptors were calculated, autoscaled and correlated with $p\Delta_j$ in systematic variable selection (leave-one-out crossvalidation). Obtained PLS (Partial Least Squares) regression model was used to predict $p\Delta_j$.

The parsimonious PLS model had one latent variable with 58% total variance, SEV=0.114, SEP=0.098, Q=0.845 and R=0.898. Only three compounds had $p\Delta_j$ predicted with errors above 10% but below 16%. Five descriptors were used: NPA atomic charge of the carbon chemically bound to the OH group (Qcnpa), Julg's aromaticity index (Ar), HOMO orbital energy (H), the number of acidic hydrogen atoms divided by the number of non-hydrogen atoms (HBD/N) and an unweighted 3D MoRSe signal 06 descriptor (Mor06u). The regression vector shows that pronounced electropassivation by PCs is related to: i) formation of more compact polymers (smaller PCs with less acidic hydrogen atoms), ii) formation of more stable phenoxide ions (from more stable ground states), iii) easier scission of the O-H bond due to higher C-O bond polarization and its weakened electron delocalization with the benzene ring.

Acknowledgement: CNPq, FAPESP.

References

- [1] Gatrell M., Kirk D. W., Habibi M. *J. Electrochem. Soc.* 1993, 140, 903-911.
- [2] Gatrell M., Kirk D. W., Habibi M. *J. Electrochem. Soc.* 1993, 140, 1534-1540.