ELECTROCHEMICAL PROPERTIES OF ANILINE AND ORTHO-SUBSTITUTED ANILINES: COMPARATIVE EXPERIMENTAL AND THEORETICAL STUDIES

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In this work, we present an exhaustive study of the electropolymerization as well as the electronic properties of aniline and ortho-substituted (-CH₃, -OCH₃, -F, -OH) monomers, dimers obtained using several DFT based methods. With this aim, a series of ortho-substituted aniline monomers and dimers, have been optimized with the DFT B3LYP/6-311G(2d,2p) and 6-311++G(d,p) methods which produced considerable information on the three-dimensional structures, charge distributions, spin density distributions and molecular orbital energies (E_HOMO and E_LUMO). Band gaps (ΔE) and ionization potentials are also calculated. Besides, experimental electrochemical data were produced on a set of monomers by enforcing them to electropolymerize exactly at the same conditions [1]. The calculated band gap of o-aminophenol which is almost equal to the experimental band gap of polyaniline, can be considered to be a good approximation. The polymerization reactions were performed potentiodynamically via cyclic voltammetry (CV) on ITO coated glass electrode in 3 M H₃PO₄ at room temperature. Then, the correlations have been established between the experimental electrochemical data produced in this study and the calculated molecular orbital energies. The linear correlation between the Hammett parameters and the HOMO energies with high regression coefficient had shown the electronic effects of substituents to be important on redox behavior. Thus, Hammett parameters of substituents of the phenyl ring belonging to monomers have been correlated with the calculated HOMO, LUMO, HOMO–LUMO values. The correlations demonstrated that the calculated molecular orbital energies would be correlated successfully to experimental data such as I_a/I_c, E_a, E_c. This result was supported by DFT B3LYP/6-311G(2d,2p).

Figure 1. HOMO and LUMO of o-aminophenol at calculated of B3LYP/6-311G(2d,2p) method.

Reference