

Tetramer model of leukoemeraldine–emeraldine electrochemistry in the presence of trihalogenoacetic acids : DFT approach.

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Streszczenie

First results of the application of the DFT computational approach to the reversible electrochemistry of polyaniline are presented. A tetrameric chain was used as the simplest model of the polyaniline polymer species. The system under theoretical investigation involved six tetramer species, two electrons, and two protons, taking part in 14 elementary reactions. Moreover, the tetramer species were interacting with two trihalogenoacetic acid molecules. Trifluoroacetic, trichloroacetic, and tribromoacetic acids were found to impact the redox transformation of polyaniline as shown by cyclic voltammetry. The theoretical approach was considered as a powerful tool for investigating the main factors of importance for the experimental behavior. The DFT method provided molecular structures, interaction energies, and equilibrium energies of all of the tetramer–acid complexes. Differences between the energies of the isolated tetramer species and their complexes with acids are discussed in terms of the elementary reactions, that is, ionization potentials and electron affinities, equilibrium constants, electrode potentials, and reorganization energies. The DFT results indicate a high impact of the acid on the reorganization energy of a particular elementary electron-transfer reaction. The ECEC oxidation path was predicted by the calculations. The model of the reacting system must be extended to octamer species and/or dimeric oligomer species to better approximate the real polymer situation

Adres publiczny

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