

Chemical Kinetics in Reactor Cooling Loops: Electron Transfer in the Reactions of Hexaaquo Transition Metal Ions with the Hydrated Electron

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Chemical kinetics data of all possible reactions taking place in the cooling loops of nuclear reactors are required to complete the radiolysis simulation for nuclear reactors. This simulation aids in the prediction of reactor corrosion potentials. As part of possible reactions present in reactor cooling loops, reactions of the hydrated electron with divalent aqueous transition metal ions: Zn²⁺, Ni²⁺, Cu²⁺, Co²⁺ and Mn²⁺ were studied using a pulse radiolysis technique. The kinetics study was carried out at a constant pressure of 120 bar with temperatures up to 300°C. The rate constants at room temperature agree with those reported in the literature. None of the reactions are diffusion-controlled at any temperature studied. The activation energies obtained from the Arrhenius plots are in the range of 14.5 ± 0.5 to 37.0 ± 1.0 kJ/mol. Pre-exponential factors are quite large, between 1x10¹³ and 7x10¹⁶ M⁻¹s⁻¹. There appears to be a large degree of entropy-enthalpy compensation in the activation as the larger pre-exponential factors correlate with higher activation energy.

Keywords Hydrated electron; Reaction rates; Water radiolysis; High temperature; Transition metal ions

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Elucidation of the Structural and Molecular Properties of Levan Oligosaccharides of Various Lengths

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Levan oligosaccharides (LO) have various potentials in pharmaceutical and biological applications. Previous studies found that LOs have beneficial properties such as prebiotic effects, boosting mineral absorption and colorectal cancer inhibition. These properties are determined by the lengths and structures of LOs. In this study, molecular dynamics simulation technique (AMBER) was used to build possible models and to elucidate the structural and molecular properties of LOs with the chain length from 3 to 15 residues. MMTSB tool set, employing k-meanclustering algorithm, was used to cluster the structures from 30 ns simulations based on their structural similarities that were measured by their structural root mean square deviations. The clustering results revealed that the representative structures (centroids) of LOs were observed to be “coils”, “helices” or combinations of both. The size of each LO was measured by its radius of gyration (ROG). The ROG values of these LOs tended to increase until the length around 10 residues before they converged, indicating the compactness of LOs with the chain lengths ≥ 10 residues. Among the three dihedral angles between two fructosyl units [φ (C4'-C2'-O6-C6), ψ (C2'-O6-C6-C5) and ω (O6-C6-C5-C4)], the dihedral angles distributions showed that ω was the most flexible dihedral angle and probably responsible for the conformational differences of LOs of various lengths. The tendency of LO to form a helix-like structure was evaluated by the closeness between the measured dihedral angles (φ , ψ , ω) of LO and those of the observed helix-like centroids. This tendency was prone to slightly decrease as the chain length increased. Our results may be beneficial in the selection of LO with appropriate length for specific pharmaceutical and biological applications. Moreover, the constructed LO structures could also be used in future simulation studies.

Keywords Levan oligosaccharides; Molecular dynamics; Structural properties

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Hydrogen Adsorption and Dissociation Pathway on Ni/Co-Promoted MoS₂ Catalyst: a Periodic DFT Study

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Hydrogen dissociation on MoS-based catalysts is among the most important steps for hydrodeoxygenation (HDO) reaction of oxygenated biomass compounds. In this study, the hydrogen gas adsorption pathways on NiMoS and CoMoS catalysts under HDO conditions were investigated through a density functional theory (DFT). The periodic DFT calculations were performed with the Vienna Ab-initio Simulation Package (VASP) using the projector augmented wave (PAW) method. First, hydrogen adsorptions on metal edge of Ni/Co-MoS nanoclusters were systematically investigated. Then, the energy barrier of hydrogen dissociation and migration on catalyst surface were studied using nudged-elastic bands (NEB) method. We found that Ni and Co promoters play a key role in enhancing the catalytic activities of hydrogen adsorption and dissociation. The partially occupied S atoms under HDO condition also enhance hydrogen dissociation reactivity by exposing reactive Mo and Ni/Co atoms to hydrogen gas. This study is expected to provide an insight to the microkinetic profile of hydrogen gas adsorption and dissociation on Ni/Co-MoS catalysts, which will be beneficial for HDO and hydrodesulfurization (HDS) experiments and studies.

Keywords Hydrogen adsorption; Hydrodeoxygenation (HDO); NiMoS; CoMoS; DFT

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Electronic Spectra of a Series of Substituent-Altered *Meso*-tetraphenylporphyrin: a DFT Prediction

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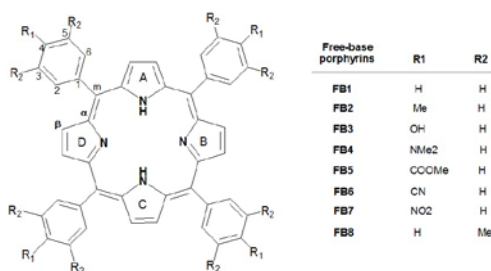
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A design of new dye sensitizers in solar cells based on *meso*-tetraphenylporphyrin (H₂TPP) were carried out. The geometrical structures and electronic spectra of H₂TPP derivatives namely **FB1-8** are predicted by the density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. No notable changes in the geometrical structures can be observed in the substituent - altered derivatives compared to the original H₂TPP. The introduction of strong electron-donating and -withdrawing substituents, i.e. dimethylamino and nitro groups in this study, to the four phenyl rings leads to the splits in the first major absorption band (namely B band in porphyrin spectroscopy) of the derivatives and a major rearrangement of the molecular orbitals. The dimethylamino groups in **FB4** (see table and figure below) dramatically increase the intensity of the second major peak (Q band), which are the outcome of strong charge transfer from the substituents to the porphyrin center upon the electronic excitations. According to the DFT prediction of electronic spectra, **FB4** has potential to make the best template for the metalloporphyrin-based dye among other derivatives.



Keywords Porphyrin; Dye-sensitized solar cells (DSSCs); DFT; TD-DFT

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Effect of Magnetic Field on the Cyclic Voltammogram and Chronoamperogram of the $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ Electrochemical System

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From the basic knowledge, paramagnetic species is attracted by applied magnetic field and the diamagnetic species is slightly repelled instead. It is interesting to study the effect of magnetic field on a redox couple such as $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (ferri/ferro cyanide) which composes of the paramagnetic species $K_3[Fe(CN)_6]$ and diamagnetic species $K_4[Fe(CN)_6]$. Therefore, the effect of magnetic field on electrical current in the cyclic voltammogram and chronoamperogram of the ferri/ferro cyanide electrochemical system was investigated. The effect of magnetic field was observed by using cyclic voltammetry and chronoamperometry. The cyclic voltammograms and chronoamperograms show significant current shift with applied the magnetic field up to 0.185 T. The current in the low potential region of voltammogram is enhanced to be more negative and the fluctuation of current in chronoamperogram is decreased. Furthermore, the quantitative effect of the magnetic field will be discussed based on the consideration of the convective-diffusion equation.

Keywords Magnetic field effect; Cyclic voltammetry; Chronoamperometry

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