Full Paper

Computational Electrochemical Oxidation of Some N-Hydroxy Compounds in Aqueous Solution

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Abstract- Density functional theory method at the level of B3LYP/6-31G(d,p) in combination with the polarizeable continuum model have been used to compute one-electron oxidation potentials for eighteen N-hydroxy compounds in aqueous solution. Analysis of correlation between the experimental oxidation potentials and the theoretically calculated values revealed that notable relations existed between the experimental potentials and the eigenvalues of SOMO's of the N-Hydroxy {-N (OH)-} derivatives.

Key words- N-hydroxy Compounds, Redox Potential, Polarizeable Continuum Model, Computational Studies

1. INTRODUCTION

The electron transfer process constitutes the basic feature of chemical, biochemical and, especially, electrochemical reactions. These electron transfers can be either oxidative or reductive. Thus, the assessment of electron transfer in the reactions of N-Hydroxy [-N (OH)-] compounds with electrophiles and oxidants requires values of the standard oxidation potentials. Cyclic voltammetry provides an experimental means for the measurement of redox potentials when the electron-transfer process is reversible. For non-reversible reactions, the experimental situation is more complicated. Thus, the ability to accurately predict redox potentials via using the theoretical methods for a given molecule in a number of different

areas is highly desirable, particularly where the experimental measurements are difficult [1-10]. The analysis of correlations between observable and calculated molecular descriptors has proved to be effective in the study of the electrochemical reaction mechanisms in the case of a variety of organic compounds [11-13]. This is commonly based on the fundamental relations between different important quantities, including the half-wave potential, $E_{1/2}$ (or the voltammetric peak potentials, E^a_p and E^c_p), the standard oxidation potential, E, the electron affinity of the reduced species in the gas phase, EA, the ionization potential for the reverse reaction, IP, the energy of the highest occupied molecular orbital (HOMO) and the energy of the lowest unoccupied molecular orbital (LUMO).

This article focuses on predicting the electrode oxidation potentials of a series of eighteen N-hydroxy compounds $\{-N (OH)-\}_1$ -- $\{-N(OH)-\}_{18}$ (Fig. 1) in water by quantum chemical density functional level of gas-phase calculations and the polarizable continuum model (PCM) for solvation energies. Traditionally, the metal ion-chelating property of these compounds has made them useful for extractive metallurgy, corrosion prevention, and nuclear fuel processing. The redox property of some -N (OH) - compounds, which is of great interest for the development of laccase-catalyzed pulp delignification, water/soil decontamination, and other biocatalyses in aqueous solution, has already been reported by Feng Xu *et al.* using cyclic and differential pulse voltammetry [14].

2. COMPUTATIONAL STUDIES

Gas-phase molecular geometries for all species were optimized at DFT-B3LYP level using 6-31G(d,p) basis set [15-17]. The calculations give internal energies at 0 K. In order to obtain gas phase free energies at 298.15 K, it is necessary to calculate the zero-point energies and thermal corrections together with entropies to convert the internal energies to Gibbs energies at this temperature [18-20]. These corrections for neutral and radical species were carried out using frequency calculations [21]. The ΔG_{solv}^{o} value was computed using the version of polarizable continuum model (PCM) to describe the solvent and its interaction with solutes [22-24]. The salvation calculations were carried out using the B3LYP/6-31G(d,p) method. In the PCM model, the solvation energy is partitioned into four components including electrostatic interaction (ΔG_{elec}), cavity term (ΔG_{cav}), dispersion (ΔG_{dis}) and repulsion energies (ΔG_{rep}), the last three terms indicating the non-electrostatic interactions between solute and solvent ($\Delta G_{non-elec}$). All quantum theoretical calculations were carried out by means of DFT-B3LYP/6-31G(d,p) level of theory, using the Gaussian 98 package of programs [25].