A Theoretical Study of Polyoxometalates and Dendrizyme Model Compounds

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Abstract We firstly report on a density functional study of molecular structures and other properties of several molybdenum and tungsten polyoxometalates. These are, respectively, of the Lindqvist, α-Keggin, α-Wells–Dawson, and Preyssler type. A force field for classical molecular dynamics (MD) simulations is derived from quantum chemical data for two α-Keggin tungstates. The second part of this report is devoted to results from MD simulations performed for eight dendrimer-encapsulated polyoxometalates in trichloromethane solution. These neutrally charged ion clusters are model compounds for ‘dendrizymes’, a novel class of biomimetic supramolecular catalysts with enzyme-like activity profile. The influence of dendrimer type and number on the solvent molecule distribution within the dendrimer shell is studied. Our approach may prove helpful in searching potentially promising dendrizyme compounds without requiring to perform separate MD simulations for every dendrizyme/substrate combination.

1 Introduction

The polyoxometalates (POM) of molybdenum and tungsten form a large class of compounds, members of which have found applications in such diverse fields like, e.g., catalysis, biochemistry and pharmacology, see [1–4] and references therein. Of particular importance for the present study is the fact that several of these compounds are potent regioselective homogeneous oxidation catalysts, see reviews [5–9] and references therein. In order to attempt to introduce substrate selectivity, and to circumvent the difficulties of attaching substrate recognizing groups directly to the metal–oxygen cluster via chemical modification, Volkmer and coworkers [10] combined a catalytically active POM with amphiphilic cationic dendrimers. The resulting neutrally charged ion cluster, a prototype dendrizyme [11], indeed shows regioselectivity and substrate selectivity in olefin epoxidation, with hydrogen peroxide as oxidizing agent, but slow degradation occurs under reaction conditions [12]. Nevertheless, such dendrizymes may become valuable artificial homogeneous catalysts with enzyme-like substrate selectivity, regioselectivity, and stereoselectivity: the central polyoxometalate, the core of the dendrizyme, provides the catalytic activity, like the active center of a metalloenzyme, whereas the surrounding dendrimers,

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the shell of the dendrizyme, influence or restrict access of potential substrate molecules to the core, like parts of the peptide chain in an enzyme.

The aim of the present study is to improve our understanding of the effect of the dendrimer shell on small molecules (solvent, substrate) approaching the polyoxometalate core from the surrounding bulk phase. In general, the study of the interaction between substrate molecules and the dendrimer shell for every dendrizyme compound is prohibitive. Therefore, it would be highly welcome to have a criterion that is directly obtainable from a dendrizyme under study and suitable for comparison of different dendrizymes. The dendrimer shell exhibits a size exclusion effect, i.e., smaller molecules more likely succeed to approach the core than larger ones. We propose to study the spatial distribution of solvent molecules in the dendrimer shell, as obtained from molecular dynamics (MD) simulations, in order to study similarities and differences between different dendrimer shells in different dendrizymes. The distribution of single solvent molecules, of pairs, triples, etc. of solvent molecules within the dendrimer shell provides useful insight into the structure of this outer part of the dendrizyme. Such data, available for a series of solvent molecules differing in size, rigidity, polarity, etc., may help to select potentially promising dendrizyme compounds.

Our study is a first step into the direction just outlined. We firstly report on results from a quantum chemical study of several molybdenum and tungsten polyoxometalates, based on standard Kohn–Sham density functional theory (KS-DFT). The polyoxometalates are, respectively, of the Lindqvist, \( \alpha \)-Keggin, \( \alpha \)-Wells–Dawson, and Preyssler type, see Fig. 1. A force field (FF) was successfully derived from the quantum chemical data for the two \( \alpha \)-Keggin heterotungstates \([\text{XO}_4]\text{W}_{12}\text{O}_{36}]^{q-}\) (\(X = P, q = 3\); \(X = Zn, q = 6\)). Combination of these two POMs with four kinds of dendritic cations, shown in Fig. 2, leads to eight different dendrizyme model compounds, two of which are shown in Fig. 4. The next part of our report deals with the MD simulations for these eight compounds in trichloromethane solution (NVE...