Probing Mineral/Fluid Interfaces by Molecular Dynamics Simulations with Effective Polarization: Rutile (TiO_2) and Quartz (SiO_2) Surfaces

D.BIRIUKOV[1*],O.KROUTIL[1,2],M.PŘEDOTA[1]

[1]Institute of Physics, Faculty of Science, University of South Bohemia, Branišovská 1760, 370 05 České Budějovice, Czech Republic (*correspondence: dbiriukov@prf.jcu.cz)
[2]Faculty of Chemistry, Materials Research Centre, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic

Introduction

For many years, molecular dynamics (MD) simulations serve to explore complex processes occuring at a narrow interfacial region between a solid substance and liquid phace. As a part of eternal challenge to model large-scale systems with a reasonable accuracy and within adequate simulation time, nonpolarizable MD force fields have been widely used to decode these interfacial phenomena. Recent studies have introduced a simple, but surprisingly effective approach (known as Electronic continuum correction, ECC) to incorporate electronic polarization, usually absent in classical MD simulations, via scaling atomic charges of charged ionic species. Our group has presented the first application of this approach to modeling mineral-fluid interfactions [1], and this contribution includes both a methodological part and numerous computational results shortly detailed below [2-4].

Results

Here, we present a vast collection of simulation data about the interfacial behavior of atomic and molecular ions adsorbed to two metal-oxides, TiO_2 and SiO_2, modeled as rutile (110) and quartz (101) surfaces. These results include pH and temperature dependent structural and dynamical properties, thermodynamics calculations, and zeta potential predictions. Special attention will be devoted to controversial inner- and outer-sphere modes of molecular adsorption on rutile [3-4]. Comparison of MD data with *ab initio* and experimental data proves a better performance of simulations with effective polarization, i.e. 'ECC' model, compared to widely used 'full charge' models.

[1] Biriukov et al. (2018) *Phys. Chem. Chem. Phys.* **20**, 23954-23966.
[2] Kroutil et al. (2017) *J. Mol. Model.* **23**, 327-334.
[3] Machesky et al. (2019) *Langmuir. Accepted manuscript.* 10.1021/acs.langmuir.8b03982
[4] Biriukov et al. (2019) *Langmuir. Submitted manuscript.*