

Continuum solvation models for computational electrochemistry: recent advances

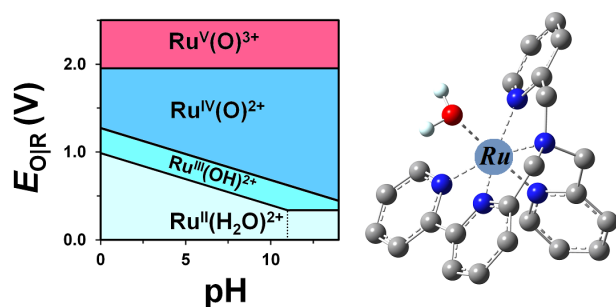
A. V. Marenich, C. J. Cramer, D. G. Truhlar

Department of Chemistry and Supercomputing Institute,
University of Minnesota
207 Pleasant Street S.E., Minneapolis, MN 55455, USA

The presentation will cover our most recent developments and applications in the area of computational electrochemistry. One application is predicting the standard reduction potentials of electron transfer reactions including proton-coupled electron transfer reactions in aqueous solution.

We consider computational protocols that combine quantum mechanical electronic structure methods (such as density functional theory) and both continuum solvation models and mixed discrete–continuum solvation models. Emphasis is placed on the use of these protocols for computing standard redox potentials in systems containing transition metals.

In one example, we will discuss our recent successful application [1] of the SMD continuum model [2] and the M11 density functional approximation [3] for predicting the redox potential E_{OR} -pH equilibrium diagrams (also known as Pourbaix diagrams) for some ruthenium-based water-oxidation catalysts in aqueous solution and their derivatives (see the figure). It will be shown how the resulting improved accuracy for transition-metal complexes opens new opportunities for the use of theory in understanding and designing catalysts containing transition metals, especially when experimental data are missing or uncertain due to the difficulty of experimental work on these complex systems.



References

- [1] Marenich, A. V.; Majumdar, A.; Lenz, M.; Cramer, C. J.; Truhlar, D. G. Construction of Pourbaix Diagrams for Ruthenium-Based Water-Oxidation Catalysts by Density Functional Theory. *Angew. Chem. Int. Ed.* **2012**, in production; DOI: 10.1002/anie.201206012.
- [2] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378.
- [3] Peverati, R.; Truhlar, D. G. Improving the Accuracy of Hybrid Meta-GGA Density Functionals by Range Separation. *J. Phys. Chem. Lett.* **2011**, *2*, 2810.