

## Rates of uranium electron transfer: A theoretical perspective

K.M. ROSSO, Z. WANG, C.C. AINSWORTH  
AND J.K. FREDRICKSON

Pacific Northwest National Laboratory, P.O. Box 999, MSIN  
K8-96, Richland, WA 99352, USA (kevin.rosso@pnl.gov,  
zheming.wang@pnl.gov, calvin.ainsworth@pnl.gov,  
jim.fredrickson@pnl.gov)

Redox transformation of U(VI) to U(IV) by metal reducing bacteria is a potentially important technological strategy for controlling uranium mobility in aqueous subsurface environments. Despite the well-known thermodynamic relationship between uranium oxidation state and its solubility, molecular-scale controls on the kinetics of uranium electron transfer (ET) have not been examined in detail. For example, equatorial ligands have the capacity to serve as ET bridges, steric hinderances, or to stabilize various oxidation states.

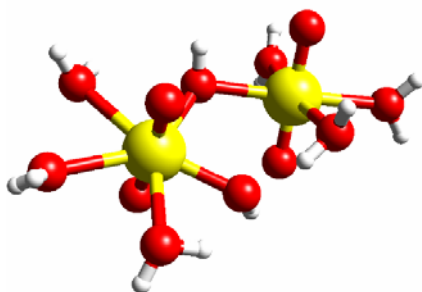


Figure 1. Ball and stick model of a calculated U(VI)-U(V) electron transfer encounter complex including solvation.

One of the hallmarks of Marcus' ET theory is the cross-relation, which describes the ET rate ( $k_{12}$ ) for  $A + B \rightarrow A^+ + B^-$  in terms of  $k_{11}$  and  $k_{22}$ , the separate self-exchange rates of the reactants (i.e.,  $A + A^+ \rightarrow A^+ + A$  and  $B + B^- \rightarrow B^- + B$ ). Hence, analysis of self-exchange ET is akin to accessing the intrinsic ET behavior of a species. In this study, we present the results of ab initio calculations on the kinetics of  $UO_2^{2+} - UO_2^+$  self-exchange ET, including a discussion of the roles of equatorial water, hydroxide,  $CO_3^{2-}$ ,  $SO_4^{2-}$ , and  $PO_4^{3-}$  ligands. The quantities that enter into Marcus' theory have been computed. Increasing the numbers of equatorial water ligands increases the reorganization energy. The electronic coupling matrix element is highly dependent on the structure of the encounter complex. Calculated second-order ET rates are slow ( $\sim 1 M^{-1} s^{-1}$ ), in accord with the limited available experimental data.

## Effects of metal cation binding on the colloidal stability of kaolinite-fulvic acid particles

RUBEN KRETZSCHMAR, ILONA HEIDMANN  
AND ISO CHRISTL

Institute of Terrestrial Ecology, ETH-Zurich, Switzerland.  
(kretzschmar@env.ethz.ch)

Adsorbed natural organic matter has a strong influence on trace metal sorption to mineral surfaces and the colloidal stability of clay particles. Mobile clay-organic colloids play an important role in trace element cycling in rivers, lakes, soils, and groundwater aquifers [1]. We investigated the effects of Cu(II) and Pb(II) on the colloidal stability of kaolinite colloids in the presence of adsorbed fulvic acid, an important component of natural organic matter. The effects of Cu and Pb on the aggregation rate and electrophoretic mobility of kaolinite-fulvic acid colloids were compared with that of Ca, a major divalent metal cation which is less strongly adsorbed. Kaolinite-fulvic acid suspensions (at pH 4 and 6) were spiked with solutions containing Cu, Pb, or Ca to give total divalent cation concentrations between  $10^{-5}$  and  $8 \times 10^{-3}$  M. The mass ratio of kaolinite to fulvic acid was 500:3 in all experiments. Starting with a well-dispersed suspension, the increase in average hydrodynamic radius was monitored by dynamic laser light scattering (DLS). Relative aggregation rates were determined from the slopes of the initial linear increase in average hydrodynamic radius with time. Addition of fulvic acid to the suspensions completely inhibited kaolinite aggregation at pH 4 and 6. Additions of Cu, Pb, and Ca resulted in strongly increased aggregation rates of kaolinite-fulvic acid colloids. Based on total concentrations, the potential of the three cations to enhance aggregation was much higher for Cu and Pb than for Ca. However, the relationship between electrophoretic mobility and aggregation rate was the same for all three divalent metal cations at pH 4. In the presence of Ca, an increase in pH from 4 to 6 resulted in decreased aggregation rates, while the opposite trend was observed for Cu and Pb. The effects of Cu, Pb, and Ca on the aggregation rates of kaolinite-fulvic acid colloids are explained by the sorption behavior of the three divalent metal cations to kaolinite-fulvic acid colloids [2].

### References

- [1] Kretzschmar, R., Borkovec, M., Grolimund, D., and Elimelech, M. (1999). *Adv. Agron.* 66: 121-194.
- [2] Heidmann, I., Christl, I., and Kretzschmar, R. (2005) *Environ. Sci. Technol.* (in press).