Proceedings of the Korean Nuclear Society Autumn Meeting
Seoul, Korea, October 1998

The Effect of 4-Sulfonic Calix[6]arene on UO_2^{2+} Adsorption onto Goethite

Jinho Jung, Young Hwan Cho, and Pilsoo Hahn
Korea Atomic Energy Research Institute, P.O.Box 105 Yusung,
Taejeon 305-600, Korea

Abstract

The adsorption of UO_2^{2+} and 4-sulfonic calix[6]arene onto goethite, respectively, was well simulated by the triple layer model. With a inner-sphere surface complex of $SOUO_2^{+}$ ($\log\beta$ = 2.736), where SOH is the surface functional group, the model successfully explained the pH dependence of the UO_2^{2+} adsoption onto goethite. In the case of 4-sulfonic calix[6]arene, three outer-sphere surface complexes (SOH_2^{+}-$CalH_6$, SOH_2^{+}-$CalH_5^{-}$ and SOH_2^{+}-$CalH_4^{2-}$) were assumed to be formed. This model well predicted the dominant adsoption of 4-sulfonic calix[6]arene onto goethite in the acidic condition. In the presence of 4-sulfonic calix[6]arene the adsorption of UO_2^{2+} onto goethite decreased in the neutral and alkaline conditions.

I. Introduction

Uranium is an important radionuclide in the nuclear fuel cycle, where it starts as a source and results as a final waste component. It usually exists as two oxidation states, namely 4+ and 5+ in natural groundwater systems. The U(IV) ion is essentially insoluble in mildly acidic to alkaline groundwaters. On the other hand, the U(VI) is potentially much more mobile, due in part to the greater solubilities of most U(VI) minerals.[1] Thus, the mobility of uranium is enhanced in oxidizing environment by the formation of U(VI) species. In natural groundwater conditions, the adsorption of uranyl ions(UO_2^{2+}) onto mineral surface inhibits the mobility of U(VI). In this work, the effect of 4-sulfonic calix[6]arene (Cal^{6-}) on the adsorption of uranyl ions onto goethite was studied by using surface complexation modeling.

Calix[n]arenes (n = 5. 6) are found to have high selectivity for uranyl ions.[2,3,4] It was shown that these macrocycles formed extremely stable uranyl complex, and the stability is attributed to the quasi-planar arrangement of the 5 or 6 binding groups on the lower calixarene rim.[4] This arrangement coincides with the preferred hexa-coordinate planar geometry occuring perpendicular to the U-O bonds of the linear uranyl ion.

Traditionally, experimental adsorption data have been described by empirical means, including partition coefficients, isotherm equations, etc.[5] In order to fully describe the environmental behavior of uranium, a quantitative model for the adsorption of uranyl ions on mineral surfaces is necessary. The fundamental concepts upon which SCM is based is that the adsorption of metal ions on mineral surface takes place at specific coordination sites and adsorption reactions on solid surfaces can be described quantitatively by mass law equations.

II. Experimental

A number of mixtures were prepared with goethite (12 g / L), uranyl nitrate 6-hydrate (1.0×10^{-4} or 5.0×10^{-5} M), 4-sulfonic calix[6]arene (1.0×10^{-4} M) and potassium nitrate (0.1 M) in 30 ml polypropylene bottles (Nalgene). Goethite was purchased from High Purity Fine Chemical Inc. (Japan), and 4-sulfonic calix[6]arene was obtained from Acros organics (Belgium). All solutions were prepared from AR grade reagents and water with the resistivity of 18.3 MΩ cm (Milli-Q, Millipore).

After overnight pre-equilibration during which the system was stabilized under the appropriate conditions (pH, ionic strength, complexing ligands, etc.), uranyl nitrate was added. The mixtures were gently shaken for two days, and the final pH was determined. An aliquot of the samples was withdrawn with a 10 ml plastic syringe then expressed through a 0.45 μm syringe filter (Whatman). The uranium concentration in the filtrate was determined using ICP-AES (JY 50 P, Jobin yvon). Adsorption spectra of 4-sulfonic calix[6]arene and uranyl-4-sulfonic calix[6]arene complex were recorded on a 8452A Diode Array Spectrophotometer (Hewrett Packard).

III. Results and Discussion

Chemical speciation of U(VI) : Chemical speciation studies were carried out using the FITEQL program.[6] The thermodynamic data used in this study were taken from the work of Hall et al.[7] The uranyl-4-sulfonic calix[6]arene complex formation constants were determined by the fitting of experimental data of Shinkai et al. using the FITEQL program (Figure 1).[2,6]

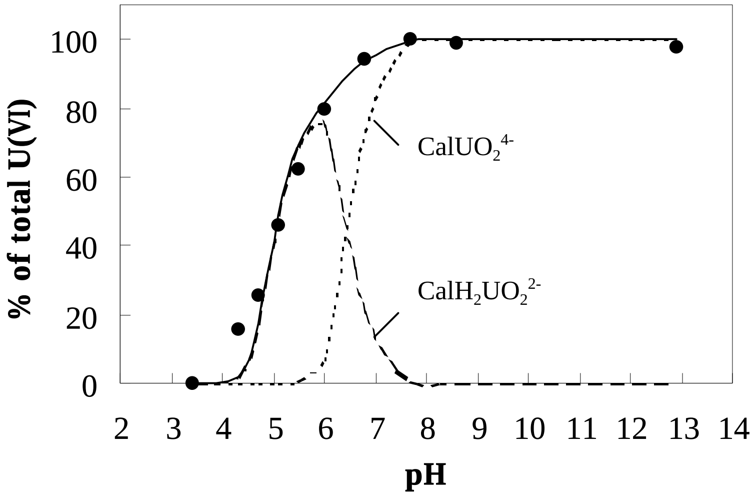

Figure 1. The simulation of uranyl-4-sulfonic calix[6]arene complex formation

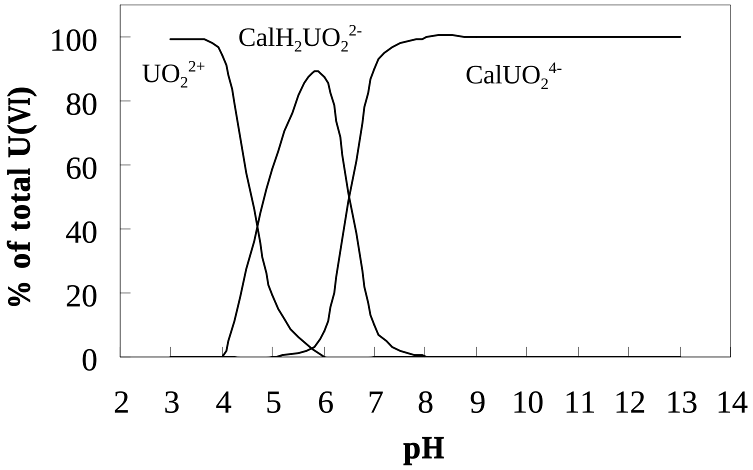

Figure 2. The chemical speciation modeling of 5.0×10^{-5} M $UO_2(NO_3)_2$ and 1.0×10^{-4} M 4-sufonic calix[6]arene in 0.1 M KNO3.

Using a thermodynamic database containing the 4-sulfonic calix[6]arene protonation and uranyl complexation constants, the chemical speciation of U(VI) in the presence of 4-sulfonic calix[6]arene at different pH values was obtained (Figure 2). It is clear from Figure 2 that uranyl-4-sulfonic calix[6]arene complexes are predominant above pH5 in the experimental conditions studied

U(VI) adsorption onto goethite : The sorption of UO_2^{2+} as a function of pH is shown in Figure 3. The sorption increased from near zero at pH 3.0 to greater than 99% of the total U(VI) at pH 5.5. The experimental data were fitted by the FITEQL program using the triple layer model (TLM).

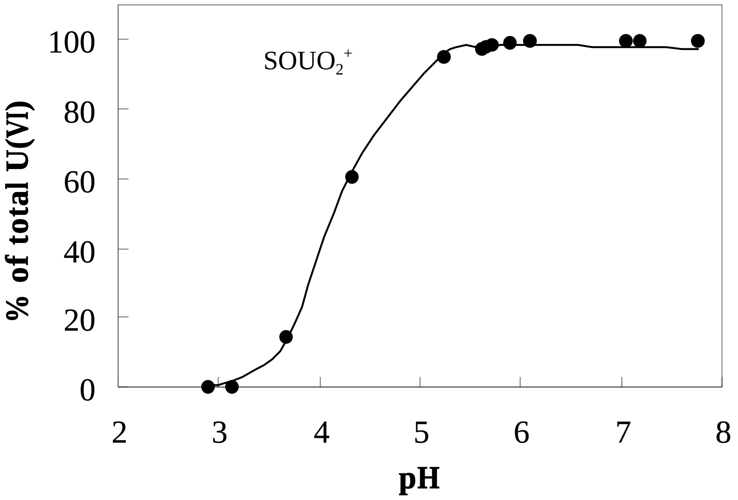

Figure 3. The adsorption of U(VI) onto goethite. Point is experimental data, and line is simulation result.

Three uranyl species, UO_2^{2+}, UO_2OH^+ and $(UO_2)_3OH_5^+$, were assumed to be adsorbed as inner-sphere complex onto goethite. Among them, the surface uranyl complex of $SOUO_2^+$ gave the best fit to the experimental data, and the formation constant calculated was 2.736 (Figure 3).

4-sulfonic calix[6]arene adsorption onto goethite : The effect of pH on 4-sulfonic calix[6]arene sorption onto goethite is shown in Figure 4. Increasing the pH value substantially reduced the sorption of 4-sulfonic calix[6]arene. Since 4-sulfonic calix[6]arene has negative charge, the adsorption is occurred in the acidic conditons where the surface of goethite is positively charged. The best fit to the experimental data was obtained with the combination of three outer-sphere complexes, SOH_2^+-$CalH_6$, SOH_2^+-$CalH_5^-$ and SOH_2^+-$CalH_4^{2-}$ (Figure 4).

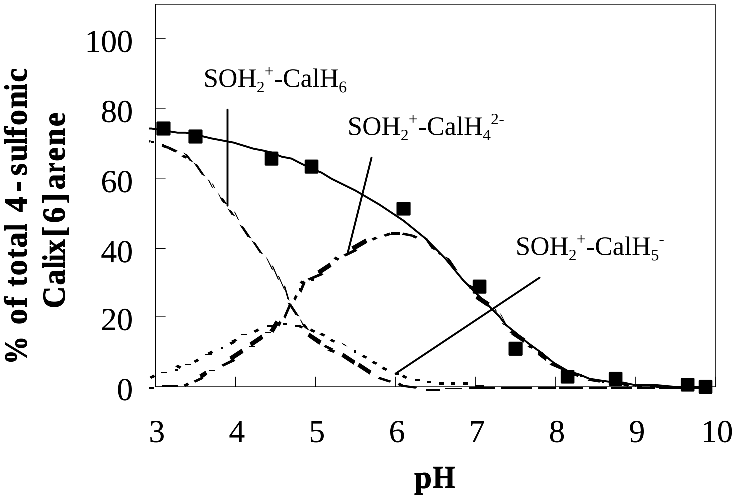

Figure 4. The adsorption of 4-sulfonic calix[6]arene onto goethite. Point is experimental data, and line is simulation result.

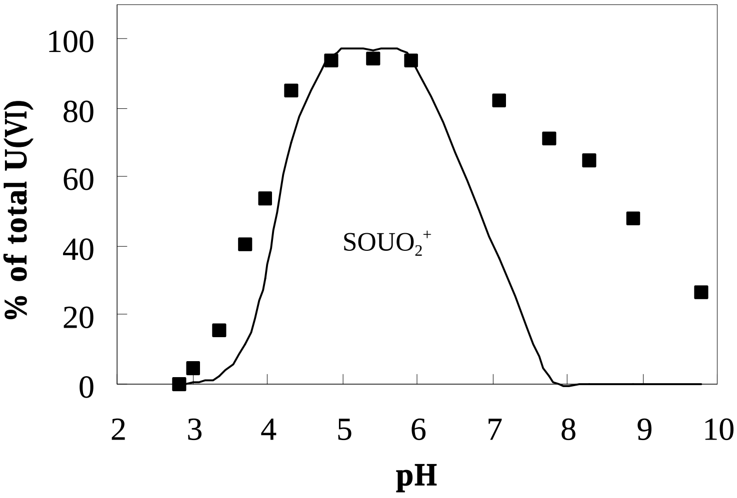

Figure 5. The adsorption of U(VI) onto goethite in the presence of 4-sulfonic calix[6]arene. No adsorption of uranyl-4-sulfonic calix[6]arene complexes is assumed. Point is experimental data, and line is simulation result.

Effect of 4-sulfonic calix[6]arene on UO_2^{2+} adsorption onto goethite : The adsorption of UO_2^{2+} onto goethite decreased by 4-sulfonic calix[6]arene in the neutral and alkaline conditions (Figure 5). The modeling began by assuming that no uranyl-4-sulfonic calix[6]arene complexes are adsorbed. As indicated in Figure 5, the simulation underpredicted the sorption above pH6. It was therefore assumed that uranyl-4-sulfonic calix[6]arene complexes are adsorbed as inner-sphere or outer-sphere surface complexes. However, the modeling studies gave unsatisfactory results. The higher sorption of UO_2^{2+} above pH6 might be caused by the slow complexation rate between UO_2^{2+} and 4-sulfonic calix[6]arene in comparison with the UO_2^{2+} adsorption onto goethite.[8,9]

Acknowledgement

The Nuclear R & D program of the MOST funded this study.

References

1. Osmond, J.K.; Ivanovich, M. In *Uranium-series Disequilibrium: Application to Earth, Marine, and Environmental Sciences*; Oxford University Press: Oxford, U.K., **1992**.
2. Shinkai, S.; Koreishi, H.; Ueda, K.; Arimura, T.; Manabe, O. *J. Am. Chem. Soc.* **1987**, *109*, 6391.
3. Nagasaki, T.; Arimura, T.; Shinkai, S *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2575.
4. Shinkai, S.; Koreishi, H.; Ueda, K.; Manabe, O. *J. Chem. Soc., Chem. Commun.* **1986**, 233.
5. Cho, Y.H.; Hahn, P.S.; Park, S.W. *J. Korean Nuclear Society* **1995**, *27*, 25.
6. Westall, J.C. FITEQL, *A Computer Program for Determination of Chemical Equilibrium Constants from Experimental Data*, Version 3.2; Oregon State University: Corvallis, U.S.A., **1996**; Report 96-01.
7. Hall, I.; Nicholson, G. P.; Piper, T.J.; Taylor, D.M.; Williams, G.; Williams, D.R. *Radiochim. Acta* **1995**, *69*, 225.
8. Nagasaki, T.; Kawano, K.; Araki, K.; Shinkai, S. *J. Chem. Soc. Perkin Trans.* **1991**, *2*, 1325.
9. Hall, I.; Nicholson, G. P.; Piper, T.J.; Williams, D.R.; Williams, G *Appl. Radiat. Isot.* **1994**, *45*, 1065.