

Lawrence Berkeley National Laboratory

LBL Publications

Title

Complexation of thorium(IV) with malonate at variable temperatures

Permalink

<https://escholarship.org/uc/item/2d97s14q>

Author

Rao, Linfeng

Publication Date

2004-08-20

COMPLEXATION OF THORIUM(IV) WITH MALONATE AT VARIABLE TEMPERATURES

Linfeng Rao^a, Thandankorai G. Srinivasan^a, PierLuigi Zanonato^b

^a Lawrence Berkeley National Laboratory, Berkeley, CA, U.S.A. L.Rao@lbl.gov

^b Università di Padova, Padova, Italy

The temperature of the high-level nuclear wastes in the storage tanks or in the geological repository could be significantly higher than the ambient temperature due to the decay energy of radioactive materials. Thus, reliable models for predicting the chemical behavior of actinides in the waste processing and disposal must properly take into consideration the temperature effect on the interactions of actinides with various ligands that may be present. Unfortunately, very few data are currently available on the complexation of actinides at elevated temperatures. To extend the thermodynamic database for the complexation of actinides to higher temperatures, we have initiated investigations on the complexation of actinides with a series of organic and inorganic ligands at variable temperatures. This paper presents the results on the complexation of Th(IV) with malonate from 10 to 85°C.

The stability constants and the enthalpy of complexation for three Th(IV)/malonate complexes, $ML_j^{(4-2j)+}$ where L stands for malonate and $j = 1 - 3$, have been determined by variable-temperature potentiometry and calorimetry. From these data, the entropy and heat capacity of complexation are calculated. Results show that the complexation of Th(IV) with malonate is endothermic and entropy-driven. As the temperature is elevated, the complexation becomes more endothermic, but stronger due to the increasingly more positive entropy at higher temperatures. These results are discussed in terms of the temperature effect on the structure of water and its solvation of actinide ions [1,2].

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, under U.S. Department of Energy Contract No. DE-AC03-76SF0098 at the Lawrence Berkeley National Laboratory.

[1] P. Zanonato, P. Di Bernardo, A. Bismondo, L. Rao, G. R. Choppin, *J. Solution Chem.* **2001**, 30, 1.

[2] L. Rao, A. Yu. Garnov, J. Jiang, P. Di Bernardo, P. Zanonato, A. Bismondo, *Inorg. Chem.* **2003**, 42, 3685.