

Formation of Calcium Uranyl Carbonate Species at Variable Temperatures

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1. Introduction

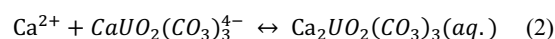
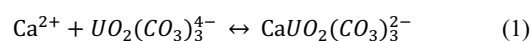
Due to geothermal gradient (typically + 3°C/100 m) and decay heat from radioactive waste, the temperature of repository system for high-level radioactive waste is likely to be elevated. However, thermodynamic data for elevated temperature effect are still scarce. Even though calcium uranyl carbonate species, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq.})$, have been regarded as the most dominant species in groundwater and seawater, the influence of temperature on the formation of $\text{Ca-UO}_2\text{-CO}_3$ has not been reported yet. In this work, thermodynamic data (formation constants at variable temperatures and reaction enthalpy) of $\text{Ca-UO}_2\text{-CO}_3$ species were determined by time-resolved laser fluorescence spectroscopy (TRLFS), UV/Vis absorption spectrophotometry, potentiometry using a Ca^{2+} -ion selective electrode, and calorimetry. In addition, the estimation to predict the temperature-dependent formation constants was modeled.

2. Experimental Methods

2.1 Sample preparation

Determination of formation constants at variable temperatures (10 – 85°C) was carried out by three different analytical methods, and the chemical condition of samples was set to be adjusted to the sensitivity of each method. Using TRLFS, the

experiment was conducted at a micromolar level of uranium concentration due to its high sensitivity. On the other hand, UV/Vis absorption spectrophotometry and potentiometry analysis were performed at millimolar U(VI) concentration. Initially, all uranium samples were set to form $\text{UO}_2(\text{CO}_3)_3^{4-}$ abundantly by adding sufficient carbonate ions, and then the quantitative spectrophotometric or potentiometric change with increasing calcium concentration was observed. As the Ca^{2+} ion concentration increases, a sequential complexation of calcium ions and $\text{UO}_2(\text{CO}_3)_3^{4-}$ may occur (equation 1 and 2).



2.2 Determination of formation constants of $\text{Ca-UO}_2\text{-CO}_3$ at variable temperatures

A laser wavelength of 266 nm from Nd:YAG pulse laser was utilized for TRLFS analysis. Time-resolved emissions from U(VI) samples were recorded with Czerny-Turner spectrometry with ICCD camera. An enhanced fluorescence in terms of intensity and lifetime with increasing $[\text{Ca}^{2+}]$ gives quantitative information on the formation of $\text{Ca-UO}_2\text{-CO}_3$.

Due to a large difference in molar absorptivity, absorption spectra were collected in the wavelength 220 – 400 nm and 360 – 500 nm with 1 cm cuvette

and 100 cm liquid waveguide capillary cell, respectively. The observed spectrophotometric data were processed with the software, HypSpec2014 [1,2].

Moreover, Ca^{2+} selective electrode was used to the potentiometric titration. The measured potential corresponds to the concentration of free Ca^{2+} , as shown in equation (3).

$$E = E_0 + S \cdot \log[\text{Ca}^{2+}] \quad (3)$$

(where E_0 is the standard potential of electrode in mV and S is the slope of the electrode response.)

Prior to potentiometric titration with uranium samples, a calibration titration was performed to obtain E_0 and S in equation 3. In order to avoid an interference of carbonate ion, argon-purged 0.1 m NaCl solution was utilized for the calibration. The potentiometric data were analyzed by Hyperquad2013 [1,2].

All experiments were conducted at various temperatures of 10, 25, 40, 55, 70, and 85°C using a water-jacketed cell by circulating the temperature-controlled water.

2.3 Calorimetry

Reaction enthalpies corresponding to equation 1 and 2 were measured with isothermal titration calorimeter and nano-calorimeter at 25°C. The measured heat flow was corrected by the subtraction of heat flow of titrant dilution and side reactions during titration. The reaction enthalpies were determined by U(VI) speciation using the formation constants obtained in this work and by least-squares regression.

3. Results and Discussion

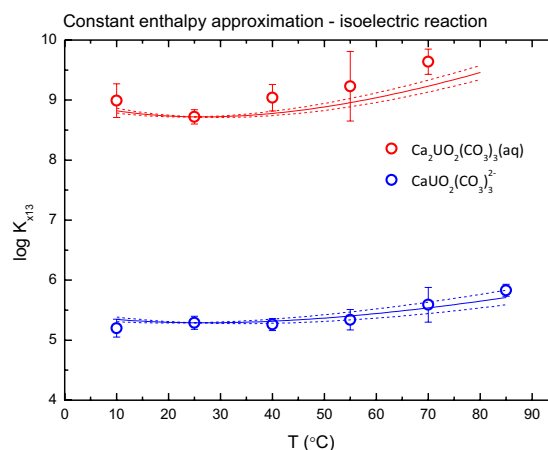


Fig. 1. Formation constants of calcium uranyl carbonate species (derived from TRLFS, UV/Vis absorption spectrophotometry, potentiometry) and estimation model for variable temperatures.

Figure 1 illustrates the formation constants of $\text{Ca-UO}_2\text{-CO}_3$ at various temperatures. Constant reaction enthalpy model in isoelectric reaction provided a successful prediction of the formation constants at variable temperatures.

ACKNOWLEDGEMENT

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REFERENCES

- [1] P. Gans, A. Sabatini, A. Vacca, *Talanta*, 43, 1739 (1996).
- [2] L. Alderighi, P. Gans, A. Ienco, D. Peters, A. Sabatini, A. Vacca, *Coord. Chem. Rev.*, 184, 311 (1999).