ELSEVIER

Journal of Alloys and Compounds 271–273 (1998) 765–768

Journal of ALLOYS AND COMPOUNDS

Interaction of uranium(VI) with silicic acid in aqueous solutions studied by time-resolved laser-induced fluorescence spectroscopy (TRLFS)

H. Moll*, G. Geipel, V. Brendler, G. Bernhard, H. Nitsche

Forschungszentrum Rossendorf e.V., Institute of Radiochemistry, P.O. Box 510 119, D-01314 Dresden, Germany

Abstract

We investigated for the first time the complex formation in the uranyl–silicate system by fluorescence spectroscopy. The interaction between soluble species of uranium(VI) with silicic acid was studied in 0.3 M $NaClO_4$ solution using time-resolved laser-induced fluorescence spectroscopy (TRLFS). Tetramethylorthosilicate (TMOS) was used as source of silicic acid in order to minimize the formation of polymeric silicon species. Fluorescence lifetimes were obtained for (a) the free uranyl cation of 1.7±0.3 μs, and (b) the 1:1 silicato–uranyl complex of 19.0±4 μs. The main fluorescence bands of the complex $UO_2OSi(OH)_3^+$ are centered at 500, 521, 544 and 570 nm. The stability constant of the complex $UO_2OSi(OH)_3^+$ was determined at pH 3.9, as $\log \beta° = -(1.67 \pm 0.20)$ using an uranyl concentration of 2.3×10^{-5} M, and a monosilicic acid concentration up to 5.4×10^{-3} M. © 1998 Elsevier Science S.A.

Keywords: Uranyl ion; Silicate; Silicic acid; Fluorescence spectroscopy; Complex formation

1. Introduction

Ground and surface waters contain silicon of approximately 10^{-3} M as a result of the weathering of different solid silicate phases [1]. The dissolved silicon is present under this conditions primarily as $Si(OH)_4$.

Presently, only very few data exist about the solution complexation of uranium(VI) with silicate [2–4]. The polymerization of silicates complicates the investigation of metal–silicate complexation.

The equilibrium constants determined by Porter and Weber [2] and Satoh and Choppin [4] are based on the reaction:

$$UO_2^{2+} + Si(OH)_4 \Leftrightarrow UO_2OSi(OH)_3^+ + H^+. \quad (1)$$

Porter and Weber applied a spectrophotometric technique to study the silicato–uranyl complex and determined $\log \beta° = -(2.25 \pm 0.13)$ at 25°C. Satoh and Choppin determined $\log \beta° = -(2.70 \pm 0.34)$ by using solvent extraction.

In Si-rich waters with uranium concentrations of about 2.5×10^{-5} M, found in seepage waters of mine tailing piles and waters of flooding uranium mines in Saxony and Thuringia, the uranyl/silicate complexation could possibly play a role in the migration of uranium in natural systems.

The goal of this work was to investigate the solution complexation of uranium(VI) with silicic acid at low silicic acid concentrations (<0.01 M) using TRLFS.

2. Experimental

2.1. Solutions and reagents

Orthosilicic acid was prepared by acid hydrolysis of tetramethylorthosilicate (TMOS), $Si(OCH_3)_4$ (98% purity from Aldrich) according to the procedure described by Jensen and Choppin [5]. Appropriate volumes of TMOS were added to solutions of $HClO_4$ between pH 2 and 3. No stock solution of $Si(OH)_4$ was used. The millimolar methanol concentrations did not affect the uranium(VI) complexation with silicic acid.

The uranium(VI) concentration was adjusted using a 0.04 M $UO_2(ClO_4)_2$ stock solution with a pH of 2.5. The stock solution was prepared by weighing the necessary amount of solid $Na_2U_2O_7$ and dissolving it in $HClO_4$. The ionic strength and the pH of the experimental solutions were kept constant at 0.3 M, using $NaClO_4$ (p.A., Merck),

---

*Corresponding author. Present address: Royal Institute of Technology (KTH), Dept. of Chemistry/Inorg. Chemistry, Teknikringen 30, S-10044 Stockholm, Sweden. Fax: +46 8 212626; e-mail: henrym@inorchem.kth.se

0925-8388/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII: S0925-8388(98)00203-5

and 3.9, respectively. The measurements were performed at pH 3.9 because, under these conditions, the formation of hydrolytic species of U(VI) is minimized. The pH of the test solutions was measured using a pH micro-electrode (U 402-M6-S7, Ingold Inc., Germany) and pH-meter (pH 3000, Wiss. Technische Werkstätten GmbH, Germany). The electrode was calibrated using standard buffers. The pH measurements were done at 20°C with a precision of 0.05 pH units. The pH of the test solutions were adjusted with NaOH (p.A., CO_2-free, Merck) and $HClO_4$ (Suprapur, Merck). At a constant uranium(VI) concentration of 2.3×10^{-5} M, a series of TRLFS spectra were measured at several different silicon concentrations ranging from 0 to 5.4×10^{-3} M. The TRLFS measurements were carried out immediately after the preparation of the samples. The test solutions were analyzed for uranium(VI) and silicon by ICP-MS and for silicon by the β-silicomolybdate method [6,7].

2.2. Time-resolved laser-induced fluorescence (TRLFS) measurements

The light source used was a Nd:YAG-MOPO system (Spectra Physics, Mountain View, CA, USA). The excitation wavelength of the uranyl fluorescence was 266 nm with an actual laser energy of 2.5–2.7 mJ. The fluorescence signal was measured in time-resolved mode with discrimination of the signal against the laser pulse using a delay generator and a gated array spectrometer. The focusing of the fluorescence signal into the spectrograph was realized with a fiber optic. A more detailed description of our laser equipment can be found in [8,9].

The TRLFS spectra were recorded in the range from 407.0 to 634.5 nm, with delay times ranging from 0.1 to about 15 μs after application of the laser pulse. The time steps between two recorded spectra was 0.5 μs. The gate time was set to 2 μs. One hundred laser shots were collected for each single spectrum and the result was divided by the number of laser shots.

The spectra were integrated from 450 to 620 nm. The fluorescence time dependencies of the spectra were calculated with ORIGIN 3.78 (Microcal Software Inc., USA). The spectra were deconvoluted using Excel 5.0 (Microsoft Inc., USA).

3. Results and discussion

Fig. 1 depicts a set of time-resolved fluorescence spectra with 2.3×10^{-5} M UO_2^{2+} and 5.4×10^{-3} M $Si(OH)_4$ ($I=0.3$ M). The interaction of U(VI) with silicic acid was clearly detectable by the red shift of the spectra with increasing time. This ligand influence of the U(VI) fluorescence was observed in all test solutions where silicic acid was added.

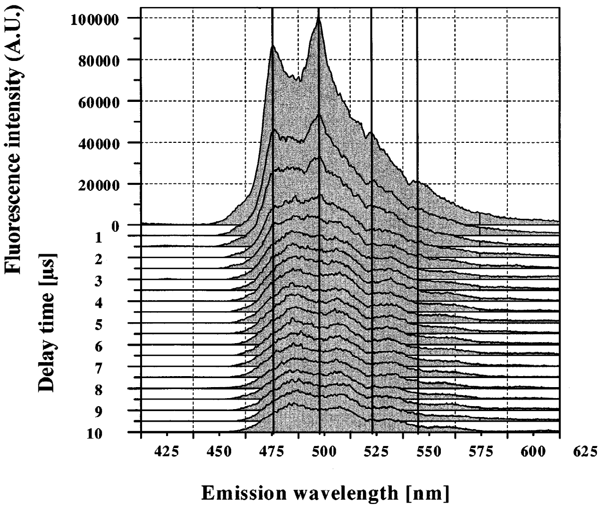

Fig. 1. Set of time-resolved fluorescence spectra with delay times between 0.1 and 10 μs for 2.3×10^{-5} M UO_2^{2+} and 5.4×10^{-3} M $Si(OH)_4$ at pH 3.9 ($I=0.3$ M).

The time-resolved measurements allow the discrimination of the fluorescence spectra from species which occur together. The integrated fluorescence signal from 450 to 620 nm, measured at different silicic acid concentrations, was fitted to a sum of exponential decay functions to calculate the lifetimes of the different species. The fluorescence decay of solutions containing silicic acid is much slower than in pure uranyl solutions. The time dependency of the measured fluorescence signal represent the sum of the fluorescence intensities of all species in solution:

$$A_0 = \sum_{i=1}^{n} A_i \cdot e^{-\frac{t}{\tau_i}} \qquad (2)$$

where A_0 is total fluorescence intensity at $t=0$, A_i is fluorescence intensity of the species i at $t=0$, and τ_i is lifetime of species i.

The spectra of solutions containing silicic acid in the range from 0 to 1×10^{-4} M showed a mono-exponential fluorescence decay. One main species dominated the time dependence of the measured fluorescence signals. We observed for the test solutions containing silicic acid ranging from 1.7×10^{-4} to 5.4×10^{-3} M a different fluorescence decay behavior (Fig. 2). The time-resolved fluorescence spectra showed a di-exponential fluorescence decay. Therefore, the spectra represent a mixture of two species. For the uranyl/silicate system no lifetimes are available in the literature for comparison. One species was determined with a lifetime of 1.7±0.3 μs. This lifetime is typical for the free uranyl ion [10]. For the postulated silicato–uranyl complex, $UO_2OSi(OH)_3^+$ [2–4], we determined a lifetime of 19±4 μs. The intensities of the integral fluorescence signals between 450 and 620 nm for the free uranyl ion and the silicato–uranyl complex have the following ratios:

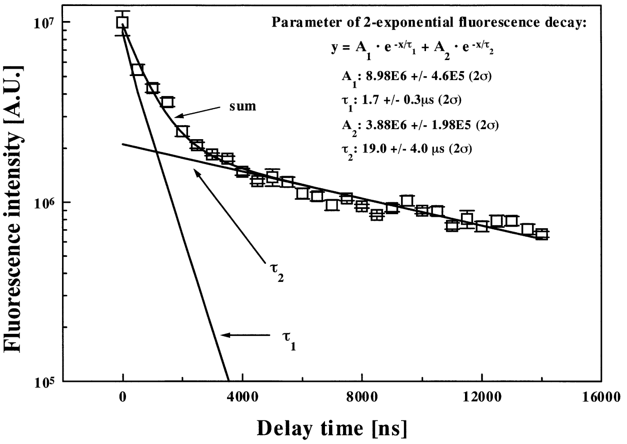

Fig. 2. Fluorescence decay (integrated signal from 450 to 620 nm) for a solution containing 2.3×10^{-5} M UO_2^{2+} and 1.1×10^{-3} M $Si(OH)_4$ at pH 3.9 ($I=0.3$ M).

$$UO_2^{2+} : UO_2OSi(OH)_3^+ = 1 : 0.95.$$

If sodium metasilicate was used as source of silicic acid the lifetime evaluation showed a third species with a fluorescence lifetime in the range of 90 to 200 μs [11]. Only about 80% of the total silicon concentration was detectable with the β-silicomolybdate method [6,7]. Therefore, the investigated system contained also about 20% adducts of polymeric silicic acid. This suggests that the third species is formed by an interaction of U(VI) with polymeric silicic acid. If TMOS was used as source of silicic acid, about 95±5% of the total silicon concentration was detectable with the β-silicomolybdate method. No interaction of U(VI) and polymeric silicic acid was observed under these conditions, because no adducts of polymeric silicic acid were present.

At high silicic acid concentrations (5.4×10^{-3} M) and delay times over 6 μs no significant fluorescence for the free uranyl-ion was observed. These spectra were used for the calculation of the unknown spectrum of the $UO_2OSi(OH)_3^+$ complex (Fig. 3). The main fluorescence bands of the complex $UO_2OSi(OH)_3^+$ are centered at 500, 521, 544 and 570 nm. The spectra of the free uranyl ion was known from earlier measurements. All measured spectra could be resolved into the individual spectral contributions of the two species involved, using conventional peak deconvolution (method of least squares). We observed, with increasing silicic acid concentration, an increasing fluorescence intensity of the deconvoluted spectra of the silicato–uranyl complex. The results of the peak deconvolution were used to calculate the concentrations of the species involved, $UO_{2\,\mathrm{free}}^{2+}$ and $UO_2OSi(OH)_3^+$. This approach is useable because the fluorescence yields of both species are about the same. The interaction of uranyl ions with monosilicic acid can be described by reaction (1) [2]. The stability constant log β can be calculated according to the relation:

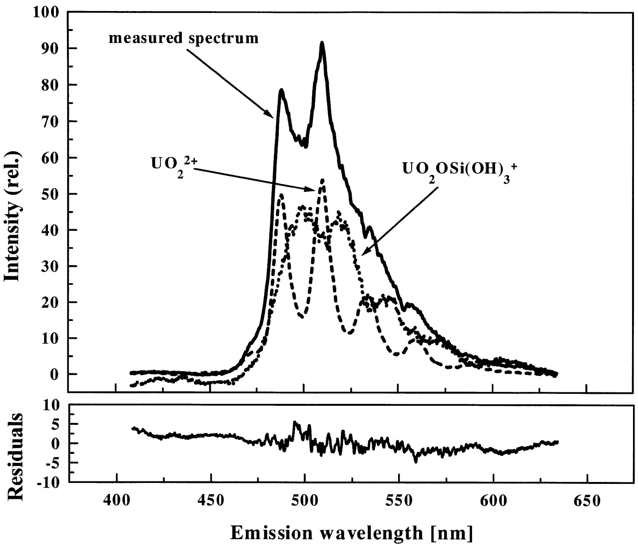

Fig. 3. Result of the peak deconvolution of the measured TRLFS spectra for a solution containing 2.3×10^{-5} M UO_2^{2+} and 5.4×10^{-3} M $Si(OH)_4$ at pH 3.9 ($I=0.3$ M).

$$\beta(I) = \frac{[UO_2OSi(OH)_3^+]\cdot[H^+]}{[UO_2^{2+}]_{\mathrm{free}}\cdot[Si(OH)_4]_{\mathrm{free}}} \tag{3}$$

The following linear equation can be derived by rearranging equation (3):

$$\log\left(\frac{[UO_2OSi(OH)_3^+]}{[UO_2^{2+}]_{\mathrm{free}}}\right) - \mathrm{pH} = \log[Si(OH)_4]_{\mathrm{free}} + \log\beta(I) \tag{4}$$

The stability constant of reaction (1) was calculated based on equation (4) using linear regression (Fig. 4). The linear function has a slope of 0.80±0.13. The difference to the ideal slope of one may results from additional U(VI) complexes which could not be detected by TRLFS. However, the results showed a predominant 1:1 complex

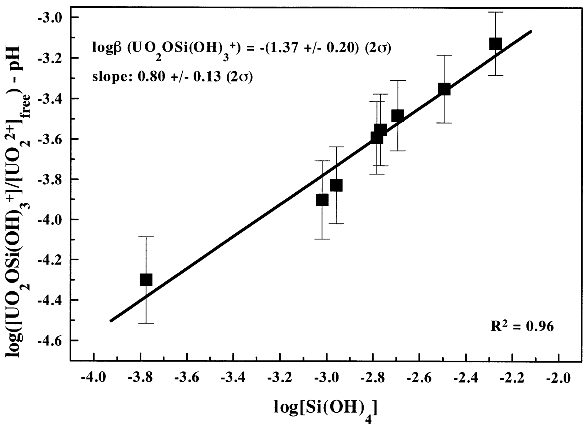

Fig. 4. Validation of the postulated complex formation reaction.

formation between uranyl ions and monosilicic acid. Our experiments support a stability constant of log β ($I = 0.3$ M) $= -(1.37 \pm 0.20)$ for reaction (1). The stability constant log $\beta° = -(1.67 \pm 0.20)$ at infinite dilution was calculated using the Davies equation.

The results of this study show that the TRLFS technique can be used to investigate the complexation of U(VI) with silicic acid at low concentrations ($c_{\mathrm{Si,total}} < 0.01$ M). Speciation calculations using the stability constants of the $UO_2OSi(OH)_3^+$ complex determined by Porter and Weber [2] as well as Satoh and Choppin [4] showed that the influence could be underestimated of the silicato–uranyl complex on the total U(VI) speciation (Fig. 5). This is one important result of our study. The relative amounts of the $UO_2OSi(OH)_3^+$ complex were 37 and 15% at pH 5.3 using the stability constants determined by Porter and Weber, log $\beta° = -(2.25 \pm 0.13)$ [2], as well as Satoh and Choppin, log $\beta° = -(2.70 \pm 0.34)$ [4], respectively. If we use our stability constant, we calculated that about 70% of the dissolved uranium(VI) is present as the silicato–uranyl complex. Therefore, our determined stability constant log $\beta° = -(1.67 \pm 0.20)$ suggests stronger complexation of U(VI) with silicic acid in natural systems from pH 3 to 7.

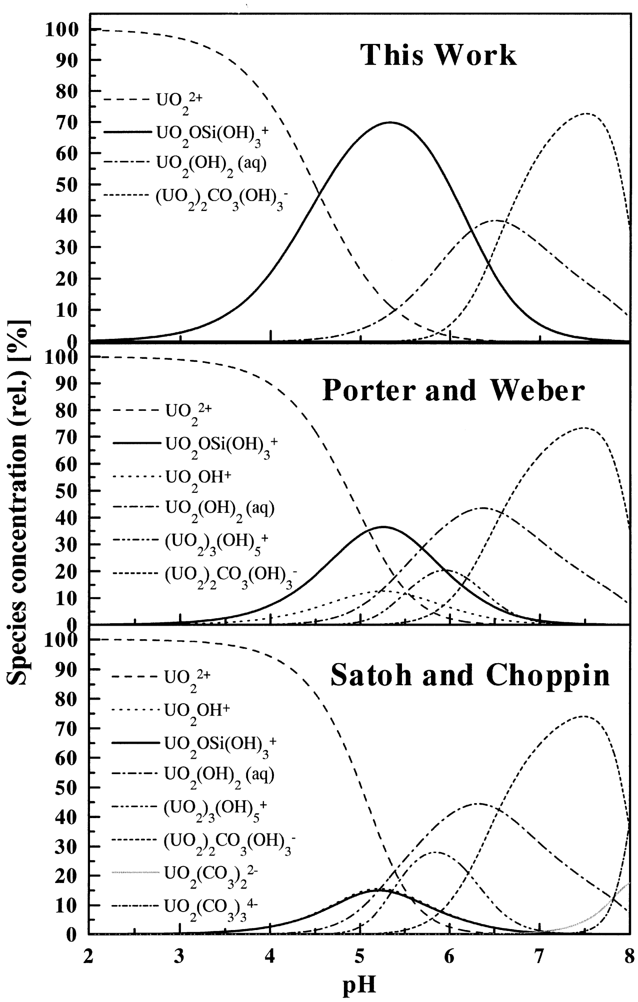

Fig. 5. Species distribution of uranium(VI) as a function of pH in a system containing $2 \cdot 10^{-3}$ M UO_2^{2+} and $3 \cdot 10^{-3}$ M $Si(OH)_4$ (I: 0.1 M $NaClO_4$, p_{CO_2}: $10^{-3.5}$ atm, EQ3/6, Database: NEA). Top, using log $\beta° = -(1.67 \pm 0.20)$ for $UO_2OSi(OH)_3^+$; middle, using log $\beta° = -(2.25 \pm 0.13)$ for $UO_2OSi(OH)_3^+$ determined by Porter and Weber [2]; bottom, using log $\beta° = -(2.70 \pm 0.34)$ for $UO_2OSi(OH)_3^+$ determined by Satoh and Choppin [4].

Acknowledgements

The authors would like to thank Dr W. Wiesener and Ms U. Schäfer, Department of Analytics, Forschungszentrum Rossendorf e.V., for the ICP-MS measurements.

References

[1] R.J. Finch, R.C. Ewing, Mater. Res. Soc. Symp. Proc. 257 (1992) 465.
[2] R.A. Porter, W.J. Weber, J. Inorg. Nucl. Chem. 33 (1971) 2443.
[3] I. Grenthe, J. Fuger, R.J.M. Konings, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, H. Wanner, Chemical Thermodynamics of Uranium, NEA OECD, 1992, p. 334.
[4] I. Satoh, G.R. Choppin, Radiochim. Acta 56 (1992) 85.
[5] M.P. Jensen, G.R. Choppin, Radiochim. Acta 72 (1996) 143.
[6] O.G. Koch, G.A. Koch-Dedic, Handbuch der Spurenanalyse Teil 2, Springer-Verlag, Berlin, 1974, p. 1099 ff.
[7] O. Weres, A. Yee, L. Tsao, Kinetics of silica polymerization, report LBL-7033, 1980.
[8] G. Bernhard, G. Geipel, V. Brendler, H. Nitsche, Radiochim. Acta 74 (1996) 87.
[9] G. Geipel, A. Brachmann, V. Brendler, G. Bernhard, H. Nitsche, Radiochim. Acta 75 (1996) 199–204.
[10] V. Eliet, G. Bidoglio, N. Omenetto, L. Parma, I. Grenthe, J. Chem. Soc. Faraday Trans. 91 (1995) 2275.
[11] H. Moll, Ph.D. Dissertation, Technical University of Dresden, 1997.