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Complexation of uranium(VI) with the siderophore desferrioxamine B

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Siderophores are microbial produced low molecular weight iron chelators and strongly bind to hard Lewis acids. The siderophore desferrioxamine B (DFO) has hydroxamate functional groups, similar to acetohydroxamic acid (AHA), a ligand that is proposed for actinide complexation in advanced separations. In the proposed separation involving AHA, the exact role of the complex in the extraction behavior of actinides is unclear. DFO can be used to clarify the role of AHA if the fundamental interactions of DFO with actinides are determined. Experiments with uranyl are performed from pH 3.5 to pH 10 showing three complexes: UO_2DFOH_2, UO_2DFOH, and UOOHDFOH with stability constants of $\log \beta(UO_2DFOH_2) = 22.93\pm0.04$, $\log \beta(UO_2DFOH) = 17.12\pm0.35$, and $\log \beta(UO_2OHDFOH) = 22.76\pm0.34$.

Introduction

The ligand acetohydroxamic acid (AHA) is proposed as a complexing ligand to prevent Pu extraction into a TBP organic phase from low concentration nitric acid in nuclear fuel reprocessing.[1–3] The exact role of AHA in the extract is unclear. The Pu-AHA complex appears to have an unexpectedly quantifiable extraction into the organic phase. Furthermore, the role of AHA degradation to form hydroxylamine, which can reduce tetravalent Pu to the non-extracted trivalent state, needs to be evaluated. To investigate this behavior a ligand with hydroxamate functional groups that does not reduce actinides and extract the complex into organic phases can be exploited. The siderophore desferrioxamine B (DFO) (Fig. 1) is a ligand with these properties.[4] As a necessary initial step the complexation of DFO with actinides needs to be evaluated. In this work the complexation and speciation of uranium(VI) with DFO is examined as an initial step in further studies with actinides to compare with AHA complexation.

Siderophores usually contain anionic hydroxamate or catecholate functional groups that form hard oxodonors, which strongly bind to hard Lewis acids, resulting in complexes with remarkably high stability constants (β).[5] Since actinides form strong complexes with hard oxygen anions, it has been suggested that siderophores will bind actinides.[6] This has lead to investigations of biomimetic analogs based on siderophores as actinide sequestering agents.[7,8] The siderophores DFO and enterobactin have been shown to solubilize hydrous plutonium oxide and uranite.[9] Studies of UO_2^{2+} with DFO show the presence of the uranium DFO species through a large pH range.[10] For the trivalent actinides complexation experiments with Am have been performed and the complexation constant estimated to be $\log \beta \approx 16$ for the Am-DFO complex.[11]

Experimental

Reagents

The UO_2^{2+} is obtained in the nitrate form from Merck and purified by anion exchange. The desferrioxamine B is obtained as the mesylate salt from Monsanto. All other chemicals are purchased from Merck and used as received.

Spectrophotometric titration apparatus

The titrations are conducted in a 100 ml jacketed titration vessel, with the solution mixed by a magnetic stir bar. The pH is measured with an Orion electrode with an error of ±0.1. The titration is performed with a Metrohm Dosimat. The solution is monitored with a Cary UV-visible spectrophotometer as it is passed through a 10 mm×10 mm flow cell with a Gilson Minipuls 2 peristaltic pump. The temperature of the titration vessel is controlled with a MGW Lauda K4R thermostatic temperature regulator to ±0.1 °C.

Spectrophotometric titration procedure

The experiments are conducted in 50 ml of 0.1M $NaClO_4$, under argon atmosphere, at 20.0 °C. DFO and uranium are added to the solution, with final concentrations at 1.0 mmol/l and a volume of 50.0 ml. The pH is adjusted to 2.5 with the addition of 0.1M $HClO_4$. Titrant solution of 0.1M NaOH is added in 0.010 ml increments every ten minutes, during which time spectrophotometric measurements are taken of the solution as it passes through a flow cell beginning 6 minutes after the addition of titrant. The pH is measured prior to each addition of base.

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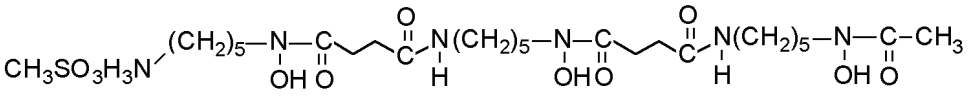

Fig. 1. The mesylate salt of DFO

The titration end point is pH 10. Four spectrophotometric titration measurements are made. Stability constants are determined from the titration data by a least squares fit to the pH with the program BETA.[12,13]

Redox examination

The possible reduction of UO_2^{2+} to U^{4+} by DFO is examined with DFO and uranium concentrations of 1 mmol/l. The samples are prepared under inert atmosphere conditions and examined at 2 hours, 1, 5, 10, and 120 days after mixing. Uranium reduction is determined with UV-visible spectroscopy employing a method based on the formation of complexes with the indicator dye Arsenazo-III.[14] From the uranium DFO solution, 200 µl samples are added to 20 µl of $1.25 \cdot 10^{-2}$ mol/l Arsenazo-III in 2 ml of pH 2 buffer or 4M HCl. Tetravalent uranium will complex with Arsenazo-III in 4M HCl with a molar absorptivity of $1.0 \cdot 10^5$ l/mol·cm at 670 nm. Hexavalent uranium forms complexes with Arsenazo-III at pH 2 with a molar absorptivity of $5.3 \cdot 10^4$ l/mol·cm at 665 nm.[14] Therefore, any reduction of the uranium will be observed in the 4M HCl solution, where the hexavalent uranium complexation to Arsenazo-III is eminently weak.

Results and discussion

Reduction

No reduction of UO_2^{2+} by DFO is observed which shows the stability of the complex. The detection limit of the tetravalent uranium with the Arsenazo-III indicator method is $(8.0 \pm 0.4) \cdot 10^{-8}$ mol/l.

Spectrophotometry

An example of the spectroscopic results is presented in Fig. 2. From this figure, the change in the absorption spectra with an increase in pH is observed. In the lower pH region, there is a peak near 490 nm. As the pH increases, this peak is transformed into a shoulder. Additionally, a change in the larger peak around 370 nm is observed with increased pH. At pH 3.5, this peak maximum is at 383 nm. As the solution becomes more alkaline, the peak shifts to shorter wavelengths, with a maximum of 361 nm at pH 10.0. Solely from the examination of the absorbance spectra, a change in the uranium DFO complex as a function of pH can be inferred. The wavelengths for the absorbance maxima of the two peaks through the experimental pH range are presented in Table 1.

Examining the absorbance maximum of the peaks as a function of pH (Fig. 3), an enhanced recognition of the pH effect on the uranium DFO species is discernible. It appears through the pH range studied, three different uranium DFO species are formed. From pH 3.0 to 4.5, the increase in the absorbance is reflective of the increase in the first uranium DFO species. This indicates the formation of one species in this pH range, dominating up to pH 4.5. Starting near pH 5.5, the absorbance rapidly increases, achieving a maximum near pH 7, implying the formation of a second species.

Table 1. Wavelength of uranium DFO absorbance maxima measured at different pH s-shoulder

pH	Peak 1, nm	Peak 2, nm
3.5	489	383
4.0	489	382
4.5	489	380
5.0	489	379
5.5	487	365
6.0-8.5	487 (s)	365
9.0	487 (s)	363
9.5	487 (s)	362
10.0	487 (s)	361

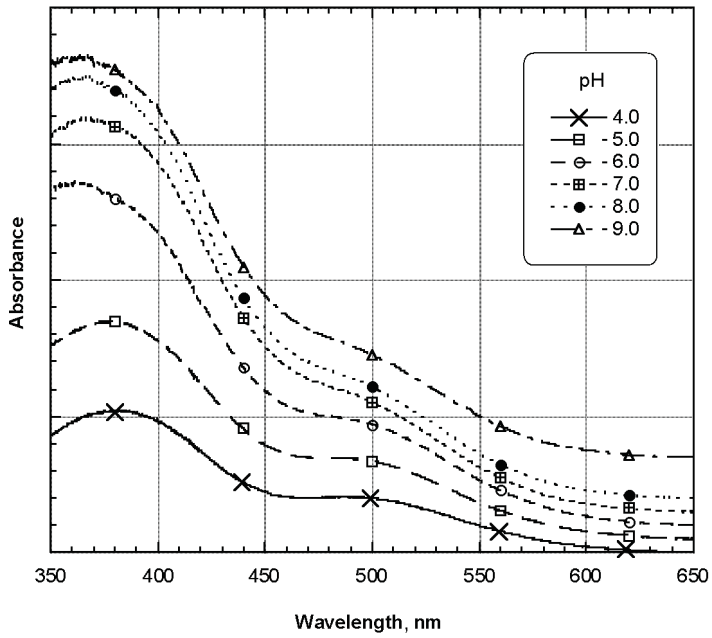

Fig. 2. Absorbance spectra of uranium DFO from pH 4.0 to 9.0. The total solution volume varies from 50.9 ml at pH 4.0 to 51.9 ml at pH 9.0 with 50 μmol of uranium and DFO. The lines are displaced along the y-axis to ease viewing

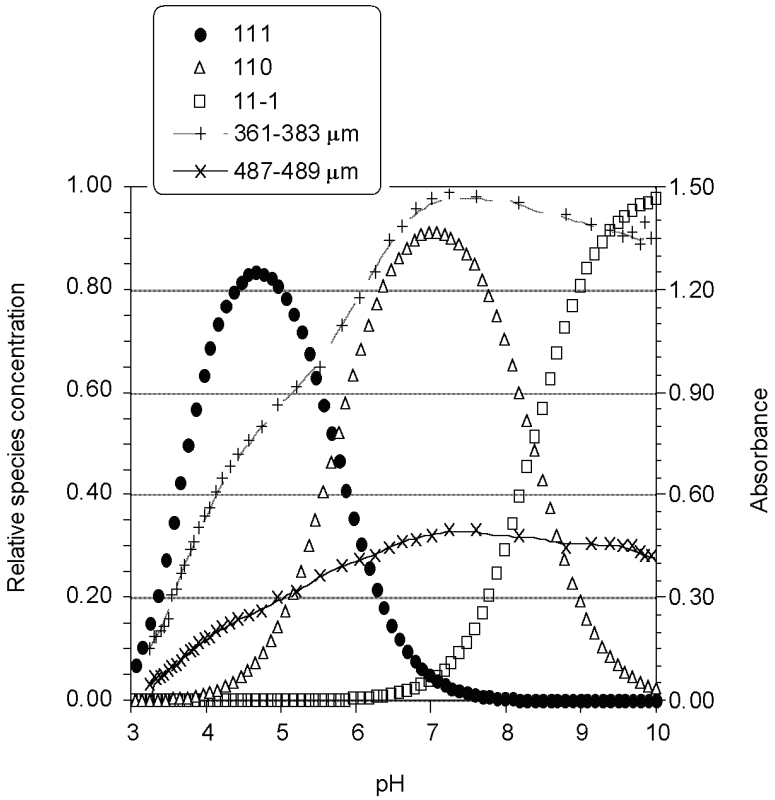

Fig. 3. Absorbance maximum and species distribution for uranium DFO complexes. Lines are absorbance, points are species distribution. Examination of the absorbance maxima for the two spectral peaks in relation to the species calculated with the stability constants shows a change in species concentration resulting in a corresponding change in absorbance. The species are listed as UO_2DFOH_2 = 111, UO_2DFOH = 110, $UO_2OHDFOH$ = 11-1

The absorbance remains high, up to pH 8. Above this pH, there is a slight but perceivable decrease in the absorbance maximum. This suggests the formation of a third uranium DFO species at high pH. These results are consistent with previous uranium DFO studies, which showed spectral changes in the uranium DFO absorbance as a function of pH.[15]

The variation in the absorbance spectra, particularly for the peak at the shorter wavelength, can be traced to a change in the charge of the ligand in the complex. An increase in the ligand charge due to deprotonation leads to an accompanying increase in the absorbance. For the uranium DFO complex, this is detected near the neutral pH region. The later slight decrease in the absorbance at high pH can be attributed to the formation of the first hydrolysis product. From the spectrophotometric results, this change is less dramatic than the increase in ligand charge.

Titration and stability constant determination

The titration data are used to determine the β of the uranium DFO species. The stability constant is defined as:

$$\beta = \frac{[M_xL_y]}{[M]^x[L]^y} \quad (1)$$

where the complexation reaction for metal M and ligand L, ignoring charge, is:

$$xM + yL \leftrightarrow M_xL_y \quad (2)$$

From the spectrophotometric measurements previously discussed, three different uranium DFO species are proposed. Since the initial metal ion to ligand ratio is unity, polynuclear metal ligand species can be excluded. The DFO is in the form of a mesylate salt, and hence, has 4 deprotonation constants. The full deprotonation of the ligand is not expected in the pH range examined. Furthermore, dihydroxouranyl species are not expected to form strong complexes with DFO. Therefore, uranium DFO species with a ratio of unity are proposed:

$$UO_2DFOH_2;$$
$$UO_2DFOH;$$
$$UO_2OHDFOH$$

where $DFOH_4$ represents protonated DFO and the mesylate group. These species are represented throughout the paper as 111, 110, and 11-1, respectively. This nomenclature ignores the last proton that remains on the ligand. The data for the hydrolysis constants of uranium[16] and the protonation constants[17] for the DFO ligand are shown in Tables 2 and 3.

The collected spectra are used along with the titration results to ascertain the β for the uranium DFO complexes by a least squares fit with the program BETA. Since the program BETA solves for the stability constant based on the pH, results for species with hydroxyl ligands must be corrected to find the stability constant. For a hydroxyl containing species, the program BETA uses the reaction:

$$xM + yHOH_{(l)} \leftrightarrow M_x(OH)_y + y\,H^+ \quad (3)$$

which results in the constant:

$$K_{\mathrm{BETA}_{Mx(OH)y}} = \frac{[M_x(OH)_y][H^+]^y}{[M]^x[HOH]_l^y} \quad (4)$$

The stability constant for the hydroxyl containing species is found by inserting K_w into Eq. (4).

$$\frac{[M_x(OH)_y]}{[M]^x - [OH]^y} = \beta_{M_x(OH)_y} = \frac{K_{\mathrm{BETA}_{Mx(OH)y}}}{K_w^v} \quad (5)$$

Equation (5) is used to normalize the hydrolysis constants for uranium for input into the program and evaluate the stability constant of the output for the mixed uranylhydroxo-DFO species (11-1). The calculated β for the three uranium DFO species are given in Table 4.

In comparison of the measured and calculated titration curves, the greatest variance is shown above pH 7, where the 110 and 11-1 species dominate. The difference manifests itself as relatively large errors for the β of the 110 and 11-1 complexes. In comparison, the excellent agreement where the 111 species is predominant results in the lower variance in the value of the stability constant for this complex.

Table 2. UO_2^{2+} complexation constants used for calculations[16]

Species	logβ
UO_2OH^+	8.5
$UO_2(OH)_2$	17.3
$UO_2(OH)_3^-$	22.6
$UO_2(OH)_4^{2-}$	23.1
$(UO_2)_2OH^{3+}$	11.0
$(UO_2)_2(OH)^{2+}$	22.0

Table 3. DFO protonation constants at 0.1M ionic strength

Species	pKa
pK_{a1}	8.50
pK_{a2}	9.24
pK_{a3}	9.69
pK_{a4}	11.48

Table 4. Stability constants of uranium DFO at 0.1M ionic strength

Species	Log β
111	22.9 ± 0.1
110	17.1 ± 0.4
11-1	22.8 ± 0.3

The value of the stability constant for Am-DFO is estimated to be $\log\beta \approx 16$ where the Am is complexed as the trivalent cation.[9] This value is less than the β for the non-hydrolyzed, cationic uranium DFO species. For hydrolysis and complexation strengths of the different oxidation states of uranium, the trend is $U^{4+}>UO_2^{2+}>U^{3+}$, with a net effective charge on the UO_2^{2+} metal center calculated to be +3.2±0.1.[18,19] This implies an increase in the equatorial bonding strength of uranyl greater than indicated by the net 2+ charge. Therefore, one should expect the stability of uranyl DFO to be greater than Am-DFO with respect to charge differences, as is observed. Additionally, the increase in positive charge on the central uranium atom must be compensated by increased negative charge on the uranyl oxo groups. This partial negative charge on the uranyl oxo groups has been used as hydrogen bonding receptors.[20] The negatively charged oxo groups may increase the stability of uranium DFO complex by hydrogen bonding to the protonated amine site of DFO. This interaction between the large net positive charge on the central uranium atom and increased negatively charged oxo groups can enhance the stability of the uranium DFO complex. The formation of the mixed monohydroxide species rather than the dihydroxide species at the highest pH is based on the strength of the resulting complex. The uranyldihydroxo species would have an overall neutral charge, with an associated decrease in metal center charge. Even though the charge density on uranium is 3.2, the accompanying increase of the anion charge of the uranyl moiety and the increased steric crowding of the uranyl equatorial plane due to an additional hydroxyl group would result in a weak complex.

Molar absorptivity determination and calculations

The molar absorptivity for the three uranium DFO species can be determined using the spectroscopic data and the β. From the β, the calculated species distribution is shown in Fig. 3. At peak maxima for each species or where the species has a relative concentration >95%, the molar coefficients can readily be determined by Eq. (6):

$$\mathrm{Abs}_{\mathrm{total}} = [111]\varepsilon_{111}+[110]\varepsilon_{110}+[11\text{-}1]\varepsilon_{11\text{-}1} \qquad (6)$$

The results are listed in Table 5. Comparison of measured and calculated absorbance values from Fig. 4 allows an evaluation of the calculated molar absorptivity. Good agreement is found, especially for the absorbance maximum of the peak centered near 490 nm. There are some deviations between the calculated and measured values for the peak centered near 380 nm between pH 5.5 and 6.5. However, the overall general agreement is further evidence for the three different uranium DFO species.

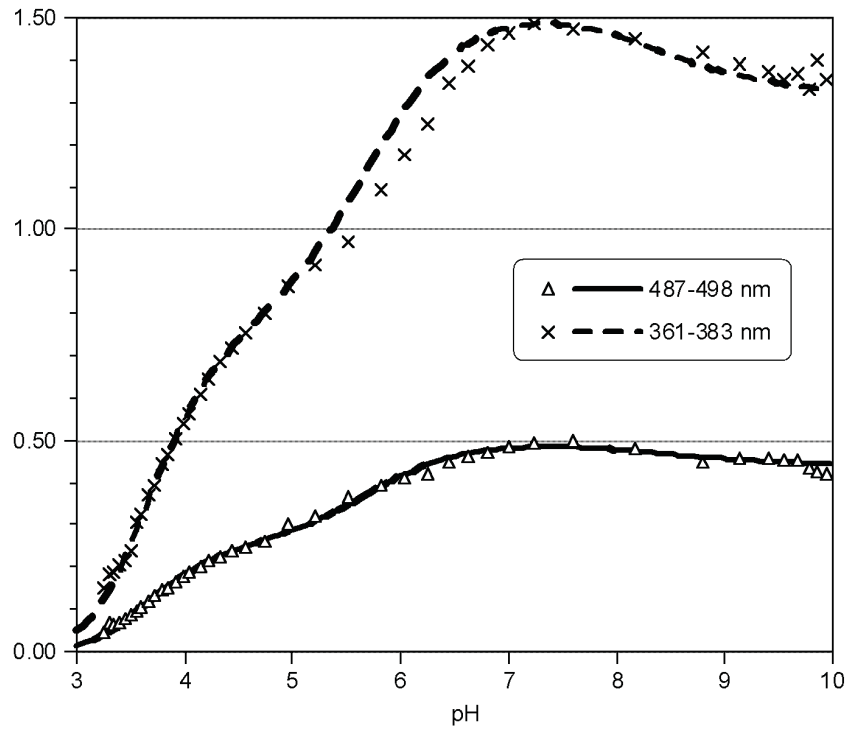

Fig. 4. Measured and calculated absorbance maximum values for uranium DFO. Lines are calculated values, points are determined from the spectrophotometric data

Table 5. Peak wavelengths and molar absorptivity for the uranium DFO species

Species	Peak 1		Peak 2	
	Peak, nm	ε, l·mol^{-1}·cm^{-1}	Peak, nm	ε, l·mol^{-1}·cm^{-1}
111	489	270 ± 4	381	823 ± 4
110	487	512 ± 8	365	1574 ± 7
11-1	487	471 ± 11	362	1411 ± 14

Conclusions

The β of the three uranium DFO species have been measured via spectrophotometric titrations. No reduction of UO_2^{2+} by DFO is observed. The three species found are UO_2DFOH_2, UO_2DFOH, and $UO_2OHDFOH$ where $DFOH_4$ is protonated DFO and the mesylate salt. The resulting data and techniques can be used to study the complexation of uranium and other actinides with hydroxamate ligands. Additionally, due to their large β, siderophores can have an important role in the development of actinide complexation agents. Furthermore, by understanding the fundamental chemistry of actinide interaction with DFO, the behavior in extraction systems that employ hydroxamate functional groups can be better understood.

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References

1. R. J. TAYLOR, I. MAY, Separ. Sci. Technol., 36 (2001) 1225.
2. D. G. KARRAKER, T. S. RUDISILL, M. C. THOMPSON, Technical Report WSRC-TR-2001-00509 (http://www.osti.gov/bridge/SRS).
3. M. C. THOMPSON, M. A. NORATO, G. F. KESSINGER, R. A. PIERCE, T. S. RUDISILL, J. D. JOHNSON, Technical Report WSRC-TR-2002-00444 (http://www.osti.gov/bridge).
4. A. TAKAHASHI, I. SHUKURO, Solv. Extr. Res. Dev., Japan, 6 (1999) 61.
5. W. R. HARRIS, C. J. CARRANO, K. R. RAYMOND, J. Am. Chem. Soc., 101 (1979) 2722.
6. K. R. RAYMOND, G. E. FREEMAN, M. J. KAPPEL, Inorg. Chim. Acta, 94 (1984) 193.
7. K. N. RAYMOND, Coord. Chem. Rev., 105 (1990) 135.
8. P. W. DURBIN, D. L. WHITE, N. JEUNG, F. L. WEITL, L. C. UHLIR, E. S. JONES, S. BRUENGER, K. N RAYMOND, Health Phys., 56 (1989) 839.
9. J. R. BRAINARD, B. A. STRIETELMEIER, P. H. SMITH, P. J. LANGSTON-UNKEFER, M. E. BARR, R. R. RYAN, Radiochim. Acta, 58/59 (1992) 357.
10. M. HAFEZ, F. PATTI, Bull. Soc. Chim. France, 4 (1969) 1419.
11. N. V. JARVIS, R. D. HANCOCK, Inorg. Chim. Acta, 182 (1991) 229.
12. W. R. HARRIS, K. N. RAYMOND, F. L. WEITL, J. Am. Chem. Soc., 103 (1981) 2667.
13. W. R. HARRIS, K. N. RAYMOND, J. Am. Chem. Soc., 101 (1979) 6534.
14. H. DE BEER, P. P. COETZEE, Radiochim. Acta, 57 (1992) 113.
15. G. A. SNOW, Biochem. J., 115 (1969) 199.
16. I. GRENTHE, J. FUGER, R. J. M. KONINGS, R. J. LEMIRE, A. B. MULLER, C. NGUYEN-TRUNG, H. WANNER, Chemical Thermodynamics of Uranium, Vol. 1, North-Holland, Amsterdam, (1992) 107.
17. D. E. KALINOWSKI, L. J. LIERMANN, S. L. BRANTLEY, A. BARNES, C. G. PANTANO, Geochim. Cosmochim. Acta, 64 (2000) 1331.
18. G. R. CHOPPIN, L. F. RAO, Radiochim. Acta, 37 (1984) 143.
19. G. R. CHOPPIN, Radiochim. Acta, 32 (1983) 43.
20. T. S. FRANCZYK, K. R. CZERWINSKI, K. N. RAYMOND, J. Am. Chem. Soc., 114 (1992) 8138.