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FINAL REPORT

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Research in Actinide Chemistry

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to

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I. INTRODUCTION

The present three-year grant period ('93-'96) has been a fruitful one for the laboratory as research entered some new areas while continuing in others in which the group has been successful. As in past grant periods, the principal focus has been on complexation of actinide elements with inorganic and organic ligands. The ligands to study have been chosen for their value (known or potential) in actinide separations or for their potential role in environmental behavior of the actinides. Since the radioactivity of some actinides limits the variety of techniques which can be used in their study, we have used "oxidation state analogs". These analogs have the same oxidation state and very similar chemical behavior but are stable or very long-lived. Also, the analogs are chosen for their redox stability to avoid uncertainties in interpretation of systems in which several oxidations may coexist (e.g., in the case of Pu). Examples of such analogs which we have used are: Nd(III), Eu(III) for Pu(III), Am(III), Cm(III); Th(IV) for U(IV), Pu(IV); NpO_2^+ for PuO_2^+; UO_2^{2+} for NpO_2^{2+}, PuO_2^{2+}. These analogs have allowed use of techniques which can increase significantly our understanding of actinide complexation.

Among the techniques we have employed in our studies are solvent extraction, potentiometric titration, calorimetric titration, nuclear magnetic resonance spectrometry, near-IR and vis absorption spectrometry, laser induced fluorescence spectroscopy-both spectral and time-resolved, stopped-flow kinetics, kinetics of redox and complexation reactions by optical spectroscopy.

During the past three-year period, the number of graduate students supported as Research Assistants required all the available salary funds. As a consequence no postdoctoral associates could be appointed. However, there were postdoctoral researchers associated with the BES program (from the actinide laboratory at JAERI in Japan, through an agreement whereby JAERI provides their support). In addition, Sandia National Laboratory supported postdoctoral associates as did Mallinckrodt Medical Corporation, but their research was separated from that of the OBES grant.

The research summaries follow.

II. f-ELEMENT COMPLEXATION

A. Silicate Binding

During this grant period, Mark Jensen completed his Ph.D. project on the "Competitive Complexation Studies of Eu(III) and U(IV) complexation by Aqueous Orthosilicic Acid." The abstract of his thesis follows.

> "The environmental chemistry of actinide elements is of considerable interest since the release of actinides into the environment is considered the primary long-term hazard of nuclear waste disposal in geological repositories. While numerous studies have examined a great variety of organic and inorganic actinide complexes, the possible significance of complexes with orthosilicic acid, found in all natural waters, has been largely ignored. The aqueous complexes formed between trivalent europium or hexavalent uranyl cations and orthosilicic acid were studied in 0.1 M ionic strength solutions to improve the models used to predict actinide migration in the environment.

Ligand competition experiments were employed to measure the stability constants of these f-element-orthosilicate complexes. Europium-orthosilicate complexation was studied by solvent extraction and laser-induced fluorescence spectroscopy. Measurable amounts of the 1:1 complex begin to form at pcH 4 in solutions containing millimolar orthosilicate concentrations. At pcH values greater than 8, europium bisorthosilicate complexes form. The stability constant of the 1:1 uranyl:orthosilicate complex also was measured between pcH 4 and 5 using absorption spectroscopy.

Speciation calculations show that europium orthosilicate complexes are important inorganic species for waters between pcH 6 and 7.5 that are in equilibrium with atmospheric carbon dioxide and contain at least 0.03 mM orthosilicate. Orthosilicate complexes are less important for uranyl cations than for europium cations owing to increased hydrolysis and carbonato complex formation of the former. The presence of 0.1 ppm humic acid completely inhibits formation of aqueous europium and uranyl orthosilicate complexes."

Table 1 lists the values obtained for the stability constants by the different methods. Figures 1 and 2 show the calculated speciation for the hydrolytic, carbonate and silicate competition as a function of pH. Such speciation calculations were done over the range of o-$Si(OH)_4$ concentrations found in natural waters (0.27 mM is an average value). For both UO_2^{2+} and Eu^{3+}, the presence of 0.1 ppm humic acid reduces the fractional contribution to the speciation by o-$Si(OH)_4$ to very small values. The behavior of Am^{3+} would resemble very closely that of Eu^{3+}.

A paper has been submitted to Radiochimica Acta on the results of the Eu^{3+} study and another is being prepared with the uranyl data. Mr. Jensen is presently a postdoctoral research associate in the Chemistry Division of Argonne National Lab.

Table 1. Summary of all stability constants determined in the present work.

Method[a]	Number of Trials	Competitive Ligand System	Species	Log β_n^{avg}
S.E.	3	Eu^{3+}-HDEHP	$Eu(OSi(OH)_3)^{2+}$	7.16±0.34
S.E.	3	Eu^{3+}-HDEHP	$Eu(OSi(OH)_3)(DEHP)_2$	-0.16±0.01[b]
S.E.	3	Eu^{3+}-HDBM	$Eu(OSi(OH)_3)^{2+}$	7.25±0.13
S.E.	3	Eu^{3+}-HDBM	$Eu(OSi(OH)_3)^{2+}$	11.7±0.4
Fluor.	3	Eu^{3+}-H_3TMA	$Eu(OSi(OH)_3)^{2+}$	7.36±0.15
Spect.	5	UO_2^{2+}-H_4PCV	$UO_2(OSi(OH)_3)^+$	6.70±0.05

[a] S.E. = solvent Extraction, Fluor. = Laser-Induced Fluorescence,
Spect. = Visible Absorption Spectroscopy

[b] Log $K_{ex,2}$

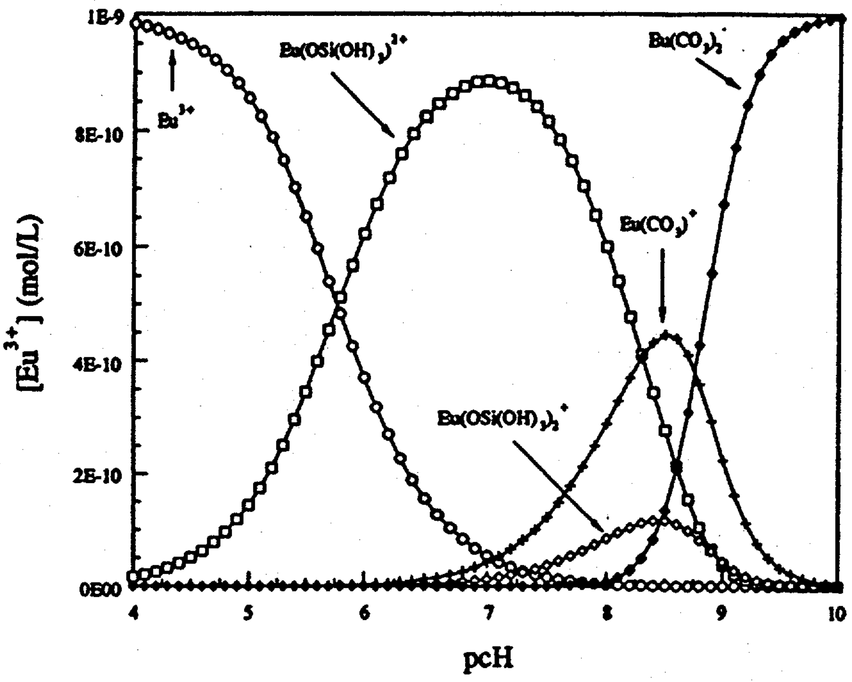


Figure 1. Eu^{3+} speciation diagram for water in equilibrium with atmospheric CO_2, $[Si(OH)_4]$ = 0.27 mM.

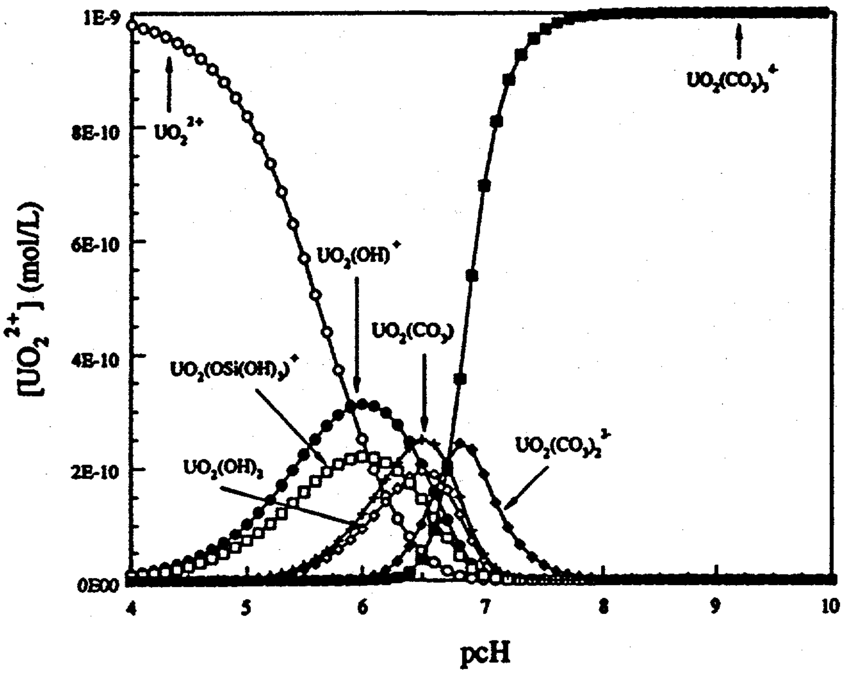


Figure 2. UO_2^{2+} speciation diagram for water in equilibrium with atmospheric CO_2. $[Si(OH)_4]$ = 0.27 mM.

B. Complexation in Brines

Miting Du received his Ph.D. this summer based on research on complexation of Eu^{3+} and UO_2^{2+} in high ionic strength solutions. The title of his dissertation was: "f-Element Complexation in Solutions to High Ionic Strengths". The abstract follows.

> "The complexation of f-elements with ligands in brine is of considerable interest since the release of actinides into the salt-bed environment is considered the primary hazard of radioactive wastes in a long-term geological disposal. To predict actinide migration in the environment, the aqueous complexes formed between trivalent europium or hexavalent uranyl cations with chloride, nitrate, fluoride and acetate were studied in a wide range of ionic strength, from 0.1 M to 9.0 M.
>
> Ligand competition experiments were employed to measure the stability constants of these f-element complexes: solvent extraction, titrations with pH electrode or ion selective electrode, as well as other techniques.
>
> Based on measured equilibrium constants and literature data, a Parabolic model was developed in this study to correlate equilibrium constants (pKa of acids, log β_1 of metal complexes, etc.) with ionic strength. This correlation was compared with that by the SIT and the Pitzer models. Possibilities of decomposing the coefficients $\Delta\varepsilon$ and $\Delta\delta$ into ε_1 and δ_1 were analyzed with a revision of the Pitzer's subequations.
>
> The speciation diagrams of Eu(III) and U(IV) in brines at $I = 0.7$ M and 5.0 M show that the f-element inorganic complexes studied in this work are

less important species for neutral brines at high ionic strengths owing to increased hydrolysis or carbonato complex formation. The influence of ionic strength on f-element speciation in brine solutions is reflected in the increased total concentration of chloride and the variation of log β_{ML} and pKa_{HL} values with ionic strength."

Mr. Du was supported partially by OBES and partially by Sandia National Lab. He analyzed his data using the Specific Interaction Model endorsed by the Nuclear Energy Agency (OECD) and the Pitzer Model employed by the WIPP project. He also showed that expansion of the SIT formalism to include a $\Delta\delta$ parameter for I^2 (I = ionic strength), his Parabolic Model, gave fits superior to the SIT and equivalent to the Pitzer modeling. His measured stability constants are listed in Table 2, while Table 3 shows the equations and parameters for each model. Figure 3 shows the fits to the experimental data of the three models for the fluoride, chloride, nitrate and acetate complexes (1:1) with Eu^{3+} and UO_2^{2+}. Tables 4 and 5 lists the values calculated for the parameters of the different models from the fits in the Figures.

The data are being prepared for publication. Mr. Du is on an ORINS postdoctoral research fellowship in the Chemistry Technology Division of Oak Ridge National Laboratory.

Table 2 Measured Equilibrium Constants of Eleven Complexes at Different I (M)

I (M) =	0.1	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
HAc	4.585±0.016	4.545±0.010	4.623±0.017	*4.78*	5.041±0.005	*5.27*	5.561±0.005		6.179±0.005	6.535±0.030	6.812±0.01
HF	*2.94*	*2.91*	3.03±0.03	*3.12*	*3.3*		*3.73*	*4.06*	4.21±0.04	4.6±0.1	*4.76*
H_2O	13.795±0.02	13.765±0.01	13.819±0.02	*13.96*	14.18±0.01		14.695±0.03		15.46±0.012	15.91±0.014	16.29±0.01
EuCl			*-0.1*		0.015±0.047 (-.011±.065)	*-0.06*	0.095±0.060 (.033±.076)		0.237±0.038 (.135±.067)		0.422±0.04(.243±.05)
UO_2Cl	*-0.17*	*-0.32*	*-0.31*	*-0.15*	0.09±0.03 (.054±.049)		0.332±0.09 (.286±.130)		0.707±0.104 (.570±.190)		0.930±0.19(.749±.140)
$EuNO_3$		*0.44*	*0.3*	*0.26*	0.22±0.03 (.193±.052)	*0.17*	0.297±0.070 (.241±.092)		0.453±0.057 (.358±.107)		0.676±0.04 (.538±.092)
UO_2NO_3		*-0.2*	*-0.3*		-0.180±.033 (-.208±.033)		-0.092±0.05 (-.152±.068)		-0.01±0.04 (-.082±.089)		
EuF	3.68±0.03	3.43±0.02	3.29±0.03	3.30±0.06	3.43±0.02	3.60±0.08	3.74±0.02	3.94±0.03	4.11±0.02	4.30±0.08	4.59±0.02
UO_2F		*3.3*	*3.19*		4.74±0.04	4.89±0.07	4.93±0.02	5.01±0.07	4.73±0.05	5.35±0.07	5.47±0.05
EuAc	2.16±0.04	2.10±0.01	2.38±0.05	*1.90*	2.39±0.05		3.05±0.07		3.08±0.14		3.08±0.05
UO_2Ac	2.50±0.09	2.43±0.07	2.62±0.10		2.71±0.07		3.05±0.10		3.11±0.07		

* The data in *italic* are the literature data. * The data in ( ) are those corrected to molality constants

Table 3. Equations of the Three Models

"SIT":

$$\log \beta_i = \log \beta_i^o + \Delta z^2 D(I_m) - \Delta\varepsilon\, I_m$$

$$\log \gamma_i = -z_i^2 D(I_m) + \varepsilon_i\, I_m$$

$$\Delta\varepsilon = \varepsilon_{MLi} - \varepsilon_M - i\varepsilon_L$$

$$\Delta z^2 = z^2_{MLi} - z^2_M - z^2_L$$

"Parabolic":

$$\log \beta_i = \log \beta_i^o + \Delta z^2 D(I_m) - \Delta\varepsilon\, I_m - \Delta\delta\, I_m^2$$

$$\log \gamma_i = -z_i^2 D(I_m) + \varepsilon_i\, I_m + \delta_i\, I_m^2$$

$$\Delta\delta = \delta_{MLi} - \delta_M - i\delta_L$$

"Pitzer":

$$\ln \beta_i = \ln \beta_i^o + \ln \gamma_M + i \ln \gamma_L - \ln \gamma_{MLi}$$

$$\ln \gamma_{ML} = \left|z_M z_L\right| * f + I_m[2(\nu_M \nu_L/\nu_{ML})(B_{ML} + /B^{\phi}_{ML})] + I_m 2[6(\nu_M \nu_L)^{3/2}\sqrt{}(z_M z_L)/\nu_{ML}]C_{ML}$$

$$\ln \gamma_M = z_M^2 f + I_m * (2B_{MClO4} + EC_{MClO4}) + I_m 2(z_M C_{NaClO4} + \Psi_{M,NaClO4}) + I_m * 2(\phi_{M,Na} + {}^E\phi_{M,Na}) + I_m z^2_M B'_{NaClO4}$$

$$\ln \gamma_L = z_L^2 f + I_m * (2B_{NaL} + EC_{NaL}) + I_m 2(z_L C_{NaClO4} + \Psi_{L,NaClO4}) + I_m * 2(\phi_{L,ClO4} + {}^E\phi_{L,ClO4}) + I_m z^2_L B'_{NaClO4}$$

$$f = -A_\Phi[\sqrt{I_m}(1+1.2\sqrt{I_m})] + 2/1.2 \ln(1+1.2\sqrt{I_m})$$

$$B_{ML} = \beta^{(0)}_{ML} + \beta^{(1)}_{ML} * g(\alpha, I_m)$$

$$g = 2[1-(1+\alpha\sqrt{I_m})e^{-\alpha\sqrt{Im}}]/(\alpha\sqrt{I_m})^2$$

$$B'_{ML} = (\beta^{(1)}_{ML}/2I_m^2)[-1+(1+2\sqrt{I_m}+2I_m)e^{-2\sqrt{Im}}]$$

$$B^{\Phi}_{ML} = \beta^{(0)}_{ML} + \beta^{(1)}_{ML} e^{-\alpha\sqrt{Im}}, \qquad C = 3C^{\Phi}/2$$

$$\ln \gamma_N = 2(\lambda_{N,Na} + \lambda_{N,ClO4})\, I_m, \qquad E = 1/2\sum m_i \left|z_i\right|$$

For pKa,	$\beta^{(0)}_{NaClO4}$	$\beta^{(0)}_{HClO4}$	$\beta^{(0)}_{NaL}$	$\phi_{H,Na}$	$\Psi_{H,NaClO4}$	$\lambda_{Na,HL}$
	$\beta^{(1)}_{NaClO4}$	$\beta^{(1)}_{HClO4}$	$\beta^{(1)}_{NaL}$	$\phi_{L,ClO4}$	$\Psi_{L,NaClO4}$	$\lambda_{ClO4,HL}$
	C^{Φ}_{NaClO4}	C^{Φ}_{HClO4}	C^{Φ}_{NaL}			
for log β,	$\beta^{(0)}_{NaClO4}$	$\beta^{(0)}_{MClO4}$	$\beta^{(0)}_{NaL}$	$\phi_{M,Na}$	$\Psi_{M,NaClO4}$	$\beta^{(0)}_{MClO4}$
	$\beta^{(1)}_{NaClO4}$	$\beta^{(1)}_{MClO4}$	$\beta^{(1)}_{NaL}$	$\phi_{L,ClO4}$	$\Psi_{L,NaClO4}$	$\beta^{(1)}_{MClO4}$
	C^{Φ}_{NaClO4}	C^{Φ}_{MClO4}	C^{Φ}_{NaL}			C^{Φ}_{MClO4}

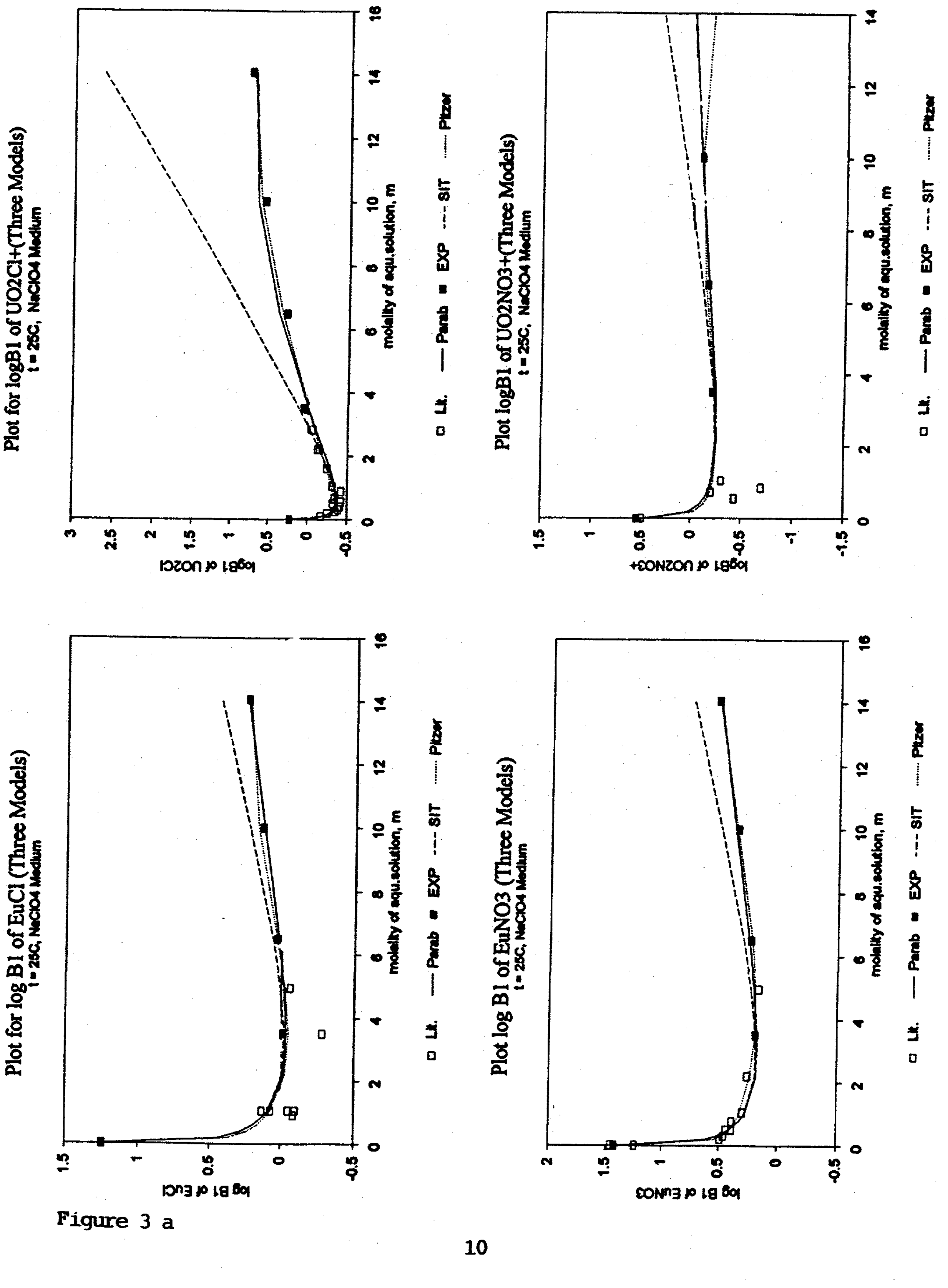
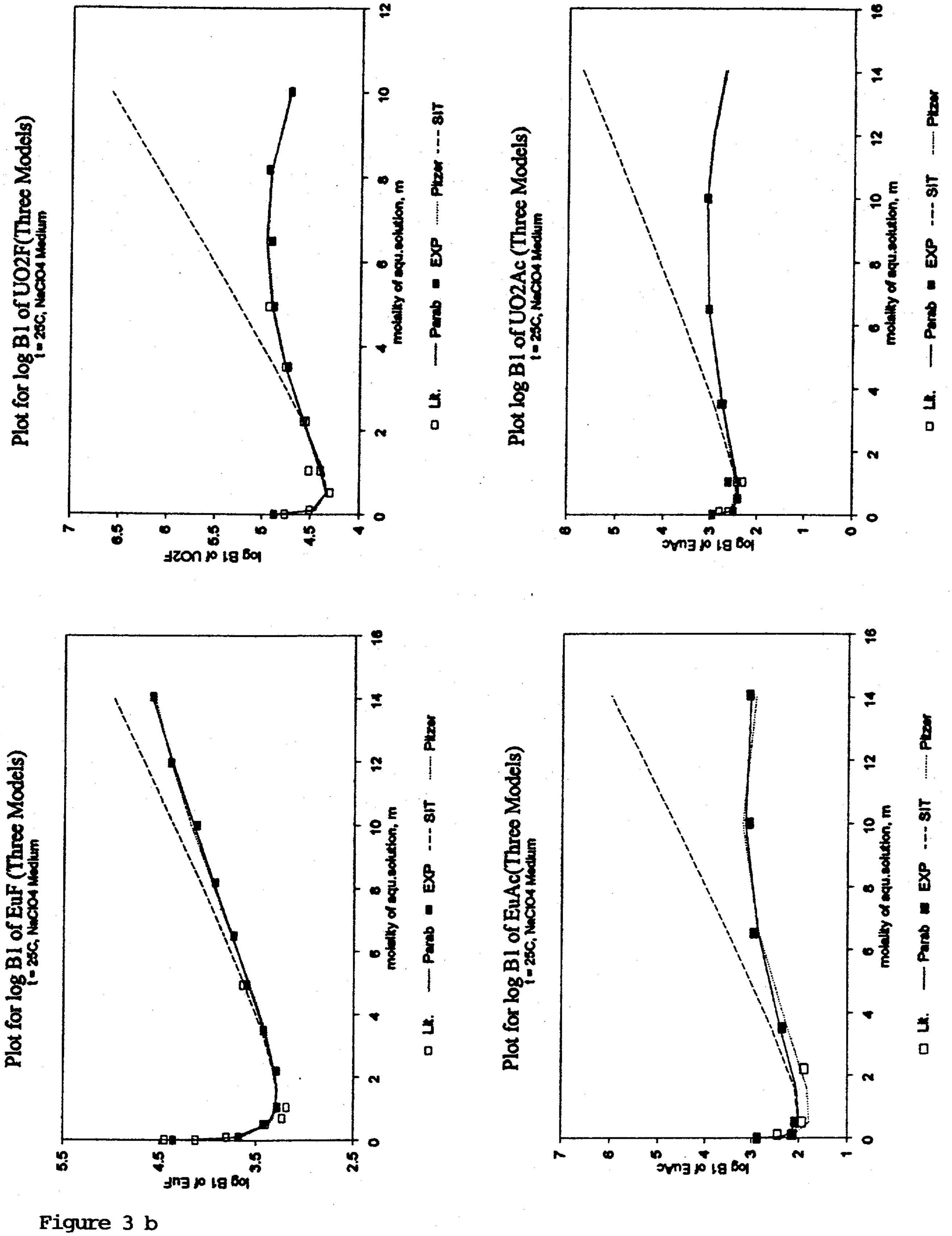
Plot log B1 of EuNO3 (Three Models)
t = 25C, NaClO4 Medium
log B1 of EuNO3
2
1.5
1
0.5
0
-0.5
0
2
4
6
8
10
12
14
16
molality of aqu.solution, m
□ Lit.
— Parab
■ EXP
--- SIT
...... Pitzer
Plot logB1 of UO2NO3+(Three Models)
t = 25C, NaClO4 Medium
logB1 of UO2NO3+
1.5
1
0.5
0
-0.5
-1
-1.5
0
2
4
6
8
10
12
14
molality of aqu.solution, m
□ Lit.
— Parab
■ EXP
--- SIT
...... Pitzer
Plot for log B1 of EuCl (Three Models)
t = 25C, NaClO4 Medium
log B1 of EuCl
1.5
1
0.5
0
-0.5
0
2
4
6
8
10
12
14
16
molality of aqu.solution, m
□ Lit.
— Parab
■ EXP
--- SIT
...... Pitzer
Plot for logB1 of UO2Cl+(Three Models)
t = 25C, NaClO4 Medium
logB1 of UO2Cl
3
2.5
2
1.5
1
0.5
0
-0.5
0
2
4
6
8
10
12
14
16
molality of aqu.solution, m
□ Lit.
— Parab
■ EXP
--- SIT
...... Pitzer

Figure 3 a



Plot for log B1 of EuF (Three Models)
t = 25C, NaClO4 Medium
log B1 of EuF
5.5
4.5
3.5
2.5
0
2
4
6
8
10
12
14
16
molality of aqu.solution, m
Lit.
Parab
EXP
SIT
Pitzer
Plot for log B1 of UO2F(Three Models)
t = 25C, NaClO4 Medium
log B1 of UO2F
7
6.5
6
5.5
5
4.5
4
0
2
4
6
8
10
12
molality of aqu.solution, m
Lit.
Parab
EXP
Pitzer
SIT
Plot for log B1 of EuAc(Three Models)
t = 25C, NaClO4 Medium
log B1 of EuAc
7
6
5
4
3
2
1
0
2
4
6
8
10
12
14
16
molality of aqu.solution, m
Lit.
Parab
EXP
SIT
Pitzer
Plot log B1 of UO2Ac (Three Models)
t = 25C, NaClO4 Medium
log B1 of EuAc
6
5
4
3
2
1
0
0
2
4
6
8
10
12
14
16
molality of aqu.solution, m
Lit.
Parab
EXP
SIT
Pitzer

Figure 3 b

Table 4 Regression Results of log β°, Δε, Δδ Values by Three Models

	SIT		SIT(lit.)		Parabolic			Pitzer
	log β°	Δε	log β°	Δε	log β°	Δε	Δδ	log β°
HAc	4.782	-0.2123	/	/	4.793	-0.20692	0.001403	4.713
H_2O	14.013	-0.1910	/	/	14.014	-0.1841	-0.00148	14*
HF	3.189	-0.1785	3.18	-0.16	3.184	-0.18905	0.00232	3.078
$EuCl^{2+}$	1.249	-0.06574	/	/	1.249	-0.06574	0.001	1.237
$EuNO_3^{2+}$	1.459	-0.067	/	/	1.427	-0.0755	0.0012	1.338
EuF^{2+}	4.359	-0.1685	/	/	4.359	-0.1685	0.00204	4.354
$EuAc^{2+}$	2.886	-0.3452	/	/	2.886	-0.3452	0.01494	2.86
UO_2Cl^+	0.223	-0.25433	0.17	-0.27	0.223	-0.25433	0.00983	0.112
$UO_2NO_3^+$	0.548	-0.0659	0.30(±.15)	-0.09(±.06)	0.548	-0.0659	0.0016	0.495
UO_2F^+	4.893.	-0.2815	5.02	-0.19	4.878	-0.3375	0.02406	4.825
UO_2Ac^+	3.024	-0.2221	/	/	2.954	-0.2789	0.01518	3.006

* using thermodynamic pK_w value.

Table 5 Pitzer parameters used and calculated in pK fittings of 11 complexes in $NaClO_4$

	HAc	H_2O	HF	$EuCl^{2+}$	$EuNO_3^{2+}$	EuF^{2+}	$EuAc^{2+}$	UO_2Cl^+	$UO_2NO_3^+$	UO_2F^+	UO_2Ac^+
$\beta^{(0)}_{NY}$ $\beta^{(1)}_{NY}$ C^{ϕ}_{NY}	$^{(6)}$0.0554 0.2755 -0.0012	$^{(6)}$0.0554 0.2755 -0.0012	$^{(6)}$0.0554 0.2755 -0.0012	$^{(6)}$0.0554 0.2755 -0.0012	$^{(6)}$0.0554 0.2755 -0.0012	$^{(6)}$0.0554 0.2755 -0.0012	$^{(6)}$0.0554 0.2755 -0.0012	$^{(6)}$0.0554 0.2755 -0.0012	$^{(6)}$0.0554 0.2755 -0.0012	$^{(6)}$0.0554 0.2755 -0.0012	$^{(6)}$0.0554 0.2755 -0.0012
$\beta^{(0)}_{MY}$ $\beta^{(1)}_{MY}$ C^{ϕ}_{MY}	$^{(5.5)}$0.1747 0.2931 0.00819	$^{5.5)}$0.1747 0.2931 0.00819	$^{5.5)}$0.1747 0.2931 0.00819	$^{(2)}$*0.77** *6.5333* *.005389*	$^{(2)}$*0.77** *6.5333* *.005389*	$^{(2)}$*0.77** *6.5333* *.005389*	$^{(2)}$*0.77** *6.5333* *.005389*	$^{(2.5)}$.61133 2.14425 .0108426	$^{(2.5)}$.61133 2.14425 .0108426	$^{(2.5)}$.61133 2.14425 .0108426	$^{(2.5)}$.61133 2.14425 .0108426
$\beta^{(0)}_{NL}$ $\beta^{(1)}_{NL}$ C^{ϕ}_{NL}	$^{(3.5)}$0.1426 0.3237 -0.00629	$^{(6)}$0.0864 0.253 0.0044	$^{(1)}$0.0215 0.2107 0.0	$^{(6)}$0.00765 0.2664 0.00127	$^{(6)}$0.0068 0.1783 -0.00072	$^{(1)}$0.0215 0.2107 0.0	$^{(3.5)}$0.1426 0.3237 -0.00629	$^{(6)}$0.00765 0.2664 0.00127	$^{(6)}$0.0068 0.1783 -0.00072	$^{(1)}$0.0215 0.2107 0.0	$^{(3.5)}$0.1426 0.3237 -0.00629
$\phi_{M,N}$ $\phi_{L,Y}$	$^{(5)}$0.036 ***-0.05065***	$^{(5)}$0.036 *-0.05***	$^{(5)}$0.036 ***0.0633***	*0* *0*	*0* *0*	*0* *0.0633*	*0* *-0.05065*	*0* *0*	*0* *0*	*0* *0.0633*	*0* *-0.05065*
$\psi_{M,NY}$ $\psi_{NY,L}$	***-0.01058*** ***0.00034***	***-0.011*** */*	***-0.0157*** ***-0.0046***	*0* *0*	*0* *0*	*0* *-0.0046*	*0* *0.00034*	*0* *0*	*0* *0*	*0* *-0.0046*	*0* *0.00034*
$\lambda_{N,ML}$ $\lambda_{Y,ML}$	*0* *0*	*0* *0*	*0* *0*	N/A N/A	N/A N/A	N/A N/A	N/A N/A	N/A N/A	N/A N/A	N/A N/A	N/A N/A
$\beta^{(0)}_{M'Y}$ $\beta^{(1)}_{M'Y}$ $C^{\phi}_{M'Y}$	N/A N/A N/A	N/A N/A N/A	N/A N/A N/A	***0.36397*** ***2.80981*** ***0.03133*** ($EuCl^{2+}$)	***0.43371*** ***1.91119*** ***0.0167*** ($EuNO_3^{2+}$)	***0.33222*** ***2.70624*** ***0.02512*** (EuF^{2+})	***0*** ***4.03*** ***0.085*** ($EuAc^{2+}$)	***0.27108*** ***-0.21238*** ***0.02933*** (UO_2Cl^+)	***0.37514*** ***0.498*** ***0.02348*** ($UO_2NO_3^+$)	***0.23707*** ***-0.0166*** ***0.05644*** (UO_2F^+)	***0.2942*** ***1.034*** ***2.0413*** (UO_2Ac^+)
pK(T)	***4.713***	14	***3.078***	***1.237***	***1.338***	***4.3537***	***2.86***	***0.1119***	***0.495***	***4.817***	***3.006***

-"NY":the background electrolyte $NaClO_4$; "M":H, Eu, UO_2, respectively; "L": Ac, OH, F, Cl, NO_3, respectively.
- Parameters (# in normal) are taken from Pitzer(1993); # in italic is the parameters estimated from literature;
\# in italic & bold is the fitted results; The supercript(#) is the highest molality for the pure electrolyte given by Pitzer
* Parameters for $Eu(ClO_4)_3$ are averaged from those for $Sm(ClO_4)_3$ and $Gd(ClO_4)_3$. ** using $\phi_{Cl,OH}$.

C. Plutonium - Vanadate Interaction

The interactions between alkaline solutions of V(V) and Cr(VI), Pu(VI), and U(VI) have been investigated during a research visit of Dr. J. Sullivan of the Argonne National Laboratory, with K.Schaab, a Ph.D. student.

A spectrophotometric method permitting simultaneous analysis of Cr(VI) and V(V) was developed. The timed absorbance spectra of solutions containing these two species showed a marked decrease in the absorbance band of the dichromate after a period of 24 hrs, indicating the formation of chromovanadates. Further evidence for the existence of chromovanadates was gained through high resolution ^{51}V NMR. ^{51}V spectra of solutions containing millimolar concentrations of Cr(VI) and V(V) at various ratios and pH's permitted assessment of the vanadate species. While unequivocal evidence for the formation of chromovanadates could not be obtained using ^{51}V NMR, the technique proved valuable in studying the interactions of vanadate with U(VI) (as an analog for Pu(VI)).

Solutions of millimolar concentrations of V(V) and U(VI) in a 2:1 ratio were investigated at pH=11 by ^{51}V NMR. The addition of U(VI) to alkaline solutions of V(V) resulted in the formation of a precipitate. Dissolution of this precipitate in DMSO and subsequent measurement by ^{51}V NMR gave rise to a single vanadate peak corresponding to the $V_2O_7^{4-}$ anion. Based on literature reports, the uranyl vanadate complex was assigned as carnotite, $Na_2(UO_2)_2V_2O_8$. The formation of plutonyl vanadates from solutions containing millimolar concentrations of V(V) and Pu(VI) in a 2:1 ratio was investigated at pH=11 using spectrophotometry. This study confirmed the presence of a 1.5:1 complex of vanadium:plutonium which precipitated upon addition of Pu(VI) to an alkaline V(V) solution.

It remains to be proven whether the reaction of U(VI) in the presence of sodium vanadate at pH=11 to form carnotite is analogous to the reaction of Pu(VI). The uranyl vanadate experiments have illustrated, however, the usefulness of ^{51}V NMR in analysis of metal-vanadate complexes as a fast tool for qualitative identification of vanadate in metal-vanadate complexes, and as a potentially powerful means for determining the types of vanadate species present in metal-vanadate complexes without decomposition of these complexes.

D. Th(IV)-DFT Complexation

Desferrithiamine, DFT, was synthesized by the group of Professor R. Bergeron at the University of Florida and sent to us for evaluation as an actinide chelator. We used potentiometry to determine the two pKa values for the DFT compound (3.02 and 9.81). DFT has absorption bands at 309 nm and at 386 nm which follow Beer's Law in the concentration range of 0 to 2e-4 M. For constant [DFT] at varying [Th]/[DFT] ratios, the intensity of the two bands of DFT decreased and a new band appeared at 336 nm which was assigned to the $Th(DFT)_2$ complex. Th-DFT complexation is quite strong so a competing ligand, oxalate, had to be used.

The calculations of the spectral data used the SQUAD program and gave a best fit for formation of 1:1 and 1:2 complexes with the values:

$$\log \beta_1 = 17.0 \pm 0.4$$

$$\log \beta_2 = 23.19 \pm 0.03$$

These values are reasonable; log β_1 has a larger error because the concentration of 1:1 complex was only 0.1 of the concentration of 1:2 complex under the present experimental conditions. DFT may be of interest as an actinide (IV) sequestering agent in biological systems based on its strong binding with An(IV) metal ions.

This work was performed by Dr. L.-F. Rao whose Ph.D. work was reported in the 1990-1993 FINAL PROGRESS REPORT. Dr. Rao is a Research Scientist at Pacific Northwest Lab in Hanford.

E. Cyanuric Tricarboxylate Complexation

Mr. Li Yao completed a course work M.S. degree in 1994 which included some research. He studied the complexation of Am^{3+}, Pm^{+3} and Eu^{3+} at several temperatures by cyanuric tricarboxylate ligand (this is a system in which N replaces the 1, 3 and 5 C-H groups in the benzene ring and carboxylates are bound to the three remaining (at the 2, 4 and 6 positions of the ring) carbons. Solvent extraction was used with f-element tracers. The results in Figure 4 show strong complexation, but no significant difference in the thermodynamic parameters of 4f and 5f trivalent cations.

Table 6. Thermodynamic Parameters of Cyanuric Tricarboxylic Acid Complexation with Pm, Eu, Am. I = 0.10 M($NaClO_4$), T = 298 K

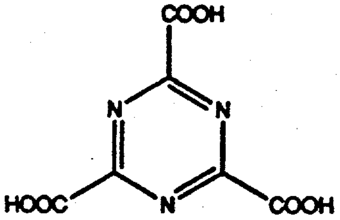
Ion	$\log \beta_{101}$	ΔG_{101}(kJ/m)	ΔH_{101}(kJ/m)	ΔS(J/K/m)
Pm(III)	4.96	—28.3±0.2	26.4±0.3	184
Eu(III)	5.13	—29.2±0.2	25.8±0.1	185
Am(III)	5.20	—29.7±0.2	25.2±0.3	184

pKa_1=6.54; pKa_2=4.37; pKa_3=3.01

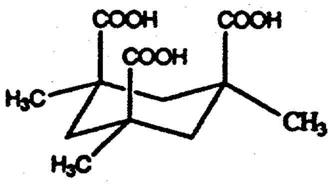
This ligand resembles trimesic acid whose complexation with trivalent f-element cations we had studied earlier. Trimesic acid is benzene-1,3,5 tricarboxylic acid. However, the cyanuric ligand forms stronger complexes which suggests it may be chelating via a nitrogen and a carboxylate group. The complex is very soluble and may be of some value in assessing the characteristics required in ligands useful in An/Ln separations and seems worthy of further study. The data are listed in Table 6.

F. Kemp Triacid

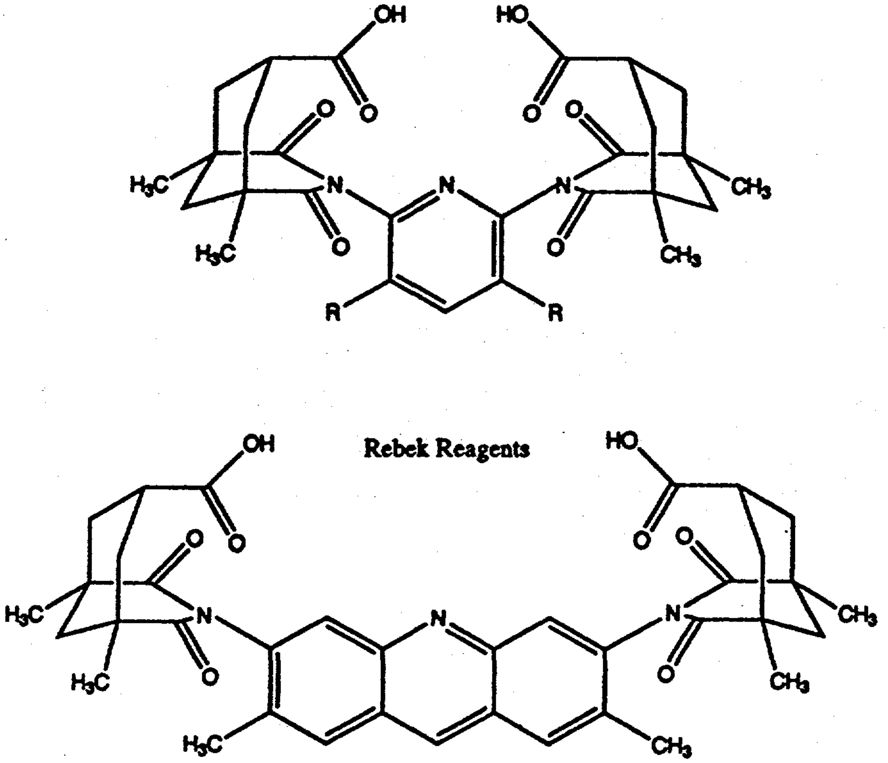
A few years ago Dr. P. Tanner, a sabbatical visitor from the University of West Florida for three months, investigated complexation with 1,3,5-cyclohexanetricarboxylic acid (Kemp triacid, KTA). The Ln complexes were not very soluble, but quite strong (log β_{101} = 7.75 (Eu)). To prepare to study the actinide complexes with this ligand using tracer methods where solubility is no problem, the protonation constants of KTA have been studied. Preliminary experiments using solvent extraction have begun to study metal complexation. The protonation constants agree with the earlier values within error. We have also begun studies to establish the conditions to study complexation of f-elements by this ligand by laser-induced fluorescence and NMR.



Cyuranic Tricarboxylic Acid



Kemp Triacid
(1,3,5-trimethyl-1,3,5-cyclohexanetricarboxylic acid)



Rebek Reagents

Figure 4. Structure of Ligands

G. Rebek's Reagents

J. Rebek (MIT) has reported a new class of ligands which bind very strongly to alkaline earths. Essentially, the simplest Rebek reagent binds two KTA molecules to m-xylidinediamine to form a basket for the cation (Figure 4). Tanner's preliminary investigation of this ligand with Ln(III) resulted in very insoluble complexes. The synthesis of the Rebek reagent was repeated and addition of sulfonic groups attempted to increase the solubility. Thus far, there has been little success in this area.

H. Acetate and Glycolate Complexation

In preparation for use of the high temperature calorimeter (see below), an M.S. thesis was completed by Mr. Jean-Marc Monsallier on Ln(III) complexation by acetate and glycolate at elevated (45° and 70°C) temperatures. Potentiometric titration was used with solutions of 2.0 M ($NaClO_4$) ionic strength. Both ML and ML_2 complexation was observed. The values for β_{101} and β_{102} at 45° and 70°C reflected an endothermic complexation with acetate and an exothermic reaction with glycolate, in agreement with earlier calorimetric data at 28°C. These values of β can be used with the data from calorimetric titrations at 45°C and 70°C (see Section III) to obtain the enthalpies as a function of temperature. This will allow us to obtain the value of ΔCp (Cp = heat capacity) which, in turn, will allow calculation of stability constants at temperatures in the 100 - 130 °C range for near field speciation. Acetate and glycolate would not be present in the near field, but are serving to test the calorimeter, etc.

I. Tetrahydroxamate Complexation

Smith et al (LANL)[1] has developed a series of tetrahydroxamate ligands with the purpose of sequestering actinides and lanthanides from process waste streams and the environment. In collaboration with the LANL group, room temperature calorimetry is currently being employed to determine the enthalpy and entropy of complexation between Nd and the ligand (THM) shown below.

Potentiometric titrations by Smith et al. determined that the MLH, MLH_2 and MLH_3 species exist in the basic region.

Initially, the calorimetric titrations were performed without a competing ligand at pH 4.6-6.4. From the protonation titration, the enthalpies of protonation were calculated. Data analysis was performed by fitting enthalpies to the experimental heats according to the speciation. The results were:

ΔH_6	-53.19 kJ/mol
ΔH_5	-28.69
ΔH_4	+2.03
ΔH_3	+36.53

A Nd-THM titration at pH 4.995 produced hydrolysis and a white precipitate was observed. Subsequent titrations at pH 4.00 produced no precipitate, but neither was there enough heat to determine the enthalpy of complexation with any reproducibility.

Currently, the enthalpy of complexation is being determined by using a PIPES buffer as well as a competitive ligand, EDTA. PIPES, an organosulfonic acid, does not appreciably chelate lanthanides and the EDTA-Nd stability constants are known to be lower than Nd-THM. Titrations with Th are presently being conducted.

References: [1] Smith, P. H., *J. Chem. Soc. Comm.*, 1266, (1992).

J. Humic Acid

The interaction of actinide ions with humic and fulvic acids in natural waters can be a significant factor in the speciation of the cations. Previously in this lab we studied the effect of complexation and redox by humics on An(III), An(IV) and AnO_2^{2+} cations. In this work Mr. L.-F. Rao studied complexation of NpO_2^+ by humic acid using spectrophotometry. The paper has been accepted for publication by *Radiochim. Acta.* The abstract of the paper entitled "Thermodynamic Study of the Complexation of Neptunium(V) with Humic Acids" follows.

> "Humic acid samples from two different sources were size-fractionated by ultrafiltration and characterized with the techniques of solid-state C-13 NMR and potentiometry. Protonation constants of both fractionated and unfractionated humic acids were determined by potentiometric titrations and were found to be pH-dependent. Binding constants for Np(V)-humate complexes in a pH range of 4.5 to 7.5 were determined by near-IR absorption spectrophotometry. After correction for the degree of ionization of humic acids at different pH values, the binding constants were found to be pH-independent, with log β values in the range of 2.15 to 2.44 for humic acids of different sources and different ranges of molecular weights. Calorimetric

titrations were performed to determine the enthalpy changes of protonation of these humic acids and their complexation with Np(V). Results from both the spectrophotometric and the calorimetric experiments suggested that Np(V) forms a single type of complex with humate, probably a 1:1 Np(V)-carboxylate complex, in the pH range of 4.5 to 7.5."

K. A Quinone Ligand for AnO_2^{2+} Complexation

A ligand which could bind actinyl ions (such as PuO_2^{2+}, UO_2^{2+}, NpO_2^{+}) with high strength and specificity could be most valuable in decontamination work. We have been attempting to synthesize a compound which is essentially a trimer of 2,7-diaminophenatrenequinone-3,6-disulfonic acid (Figure 5). This ligand would be planar with O-O distances for potential donors (labeled with a line above or below the 0 in the figure) of ca. 5.17 Å so the AnO_2^{n+} would fit in the cavity perpendicular to the ligand plane. The six oxygen donors would satisfy the coordination of the central An and the bulky structure would protect the complex from hydration attack which is the mechanism of dissociation of actinide complexes. Moreover, the aromatic substructures should serve as "antenna groups" to absorb light which energy would be transferred to the U of UO_2^{2+} and result in strong fluorescence. The result could be a highly sensitive reagent for UO_2^{n+} analysis at concentrations $\leq 10^{-12}$ M.

Figure 5 shows the synthetic scheme being used at present. The intermediate monomer (2,7-diaminophenatrenequinone-3,6-disulfonic acid) is underlined. Thus far, the monomer has been made in a 3 gram quantity and identified by ICP-MS and NMR analyses. At present, several trimerization schemes are being tried, including template synthesis using UO_2^{2+}.

L. Diphosphate Complexation

In a collaboration with Dr. Kenneth Nash of Argonne National Lab, we conducted calorimetric and fluorescence studies on Eu(III) complexes of several diphosphonate complexants which were being evaluated for use as TUCS (Thermally Unstable Complexant Systems) reagents for stripping trivalent actinides from TRUEX organic extraction phases. The paper, published in *Inorganic Chemistry* was entitled: "Calorimetric and Laser-Induced Fluorescence Investigation of Complexation Geometry of Selected Eu-gem-Diphosphonate Complexes in Acidic Solutions". The abstract follows.

> "Details of the coordination chemistry of europium comoplexes with methanediphosphonic acid (MDPA), vinylidene-1,1-diphosphonic acid (VDPA), and 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) in acidic aqueous solutions have been investigated by titration calorimetry and laser-induced fluorescnece. For the 1:1 complexes, thermodynamic parameters and complex hydration are consistent with those previously reported for europium complexes with the carboxylate structural analog malonate. In the 1:2 complexes, markedly different thermodynamic parameters and cation dehydration are observed. The second diphosphonate ligand adds to the 1:1 complex displacing four additional water molecules from the primary coordination sphere (as compared with two for the addition of a second

malonate). This reaction is also characterized by a nearly zero entropy change. The results are rationalized using molecular mechanics to suggest an unuaual geometry in which the diphosphonate ligands and bound water molecules are appreciably segregated in the europium coordination sphere. Intramolecular hydrogen bonding and second hydration sphere ordering are suggested to explain the low complexation entropies."

M. Theoretical Study of Concentrated Solutions

In connectin with our studies on the speciation behaviour of actinides in concentrated salt solutions, we developed a new model to evaluate activity coefficients of electrolytes in such systems. The article was titled "Activity Coefficients of Single Electrolytes in Concentrated Solutions Derived froma Quasi-Lattice Model" and was published in the *Journal of Solution Chemistry*. The abstract follows.

> "This paper describes a new model to calculate the mean activity coefficients of dissociated electrolytes in concentrated solutions. It is based on three assumptions: (i) quasi-lattice arrangments of ions in solution; (ii) a contribution from ion-water interactions to the mean activity coefficients; (iii) a concentration dependence of the dielectric constants. The mean activity coefficients of thirteen strong electrolytes from moderately dilute solutions to saturated solutions are found to correlate well by this model. For dilute solutions, a limiting equation in which only ion-specific parameters are required is proposed. It is suggested that specific ion-water interactions

might be the major source of the nonideality of strong electrolyte solutions at high concentrations."

III. HIGH TEMPERATURE CALORIMETRY

The high temperature calorimeter ($\geq$70°C) was developed to provide complexation data which could be used to model behavior at repository temperatures (> 100°C). During this contract period a standard operating procedure (SOP) has been developed to ensure reproducibility in operation. Also, a troubleshooting procedure has been put in place to keep the system on line more regularly. Several systems have been run to validate the results of the calorimeter. The data are listed in Table 7.

A. Ligand pKa Determinations

Determination of protonation constants using potentiometric methods at 45°C has been a challenge, but the experimental approach has been developed. The titration vessel is a thermostated jacketed cell with a thermostated lid. The pH electrode is calibrated using a three point calibration, (buffer 4, 7, 10), with NIST traceable buffers. We must determine the value of K_W at 45.0°C and I = 2.0 M $NaClO_4$ as the value for K_w directly affects the value of the pKa determined by potentiometric titrations. Originally the pKa's were determined for diglycolic acid at I = 1.0 M $NaClO_4$, but subsequently we decided to run all experiments at ionic strengths of 2.0 M $NaClO_4$ because there is more room temperature data at I = 2.0 M $NaClO_4$ for the ligands of interest.

Table 7. Date from the High Temperature Calorimeter

	a. 45° C	
THAM protonation:	(p.w.)	-46.7 ± 0.3 kJ/mol
	(lit.)	-46.0 ± 0.3 kJ/mol
Nd-EDTA complex:	(p.w.)	15.9 kJ/mol
	(lit.)	15.8 ± 0.1 kJ/mol
	b. 70°C	
THAM protonation:	(lit.)	-46.2 ± 0.3 kJ/mol
	(p.w.)	-46.3 ± 0.3 kJ/mol
BIS-TRIS protonation:	(lit.)	-29.3 ± 0.2 kJ/mol
	(p.w.)	-30.9 ± 0.3 kJ/mol

Lit.: J. R. Smith, P.L. Zanonato and G. R. Choppin, *J. Chem. Thermodynamics*, **24**, 99 (1992).

B. Lanthanide-diglycolate Complexes

These measurements involve basic titration calorimetry, where an aqueous lanthanide solution is in the calorimeter cup and the ligand is titrated in using an automated burette system. The entire calorimeter system is controlled by computer. The results are shown in Figure 6 where the values at 45°C are compared with 25°C data. This data closely follows trends observed at room temperature.

C. Hydroloysis

In collaboration with Dr. James Sullivan of Argonne National Laboratory, we have initiated studies of the thermodynamics of actinide hydrolysis at elevated temperatures using the FSU High Temperature Calorimeter.

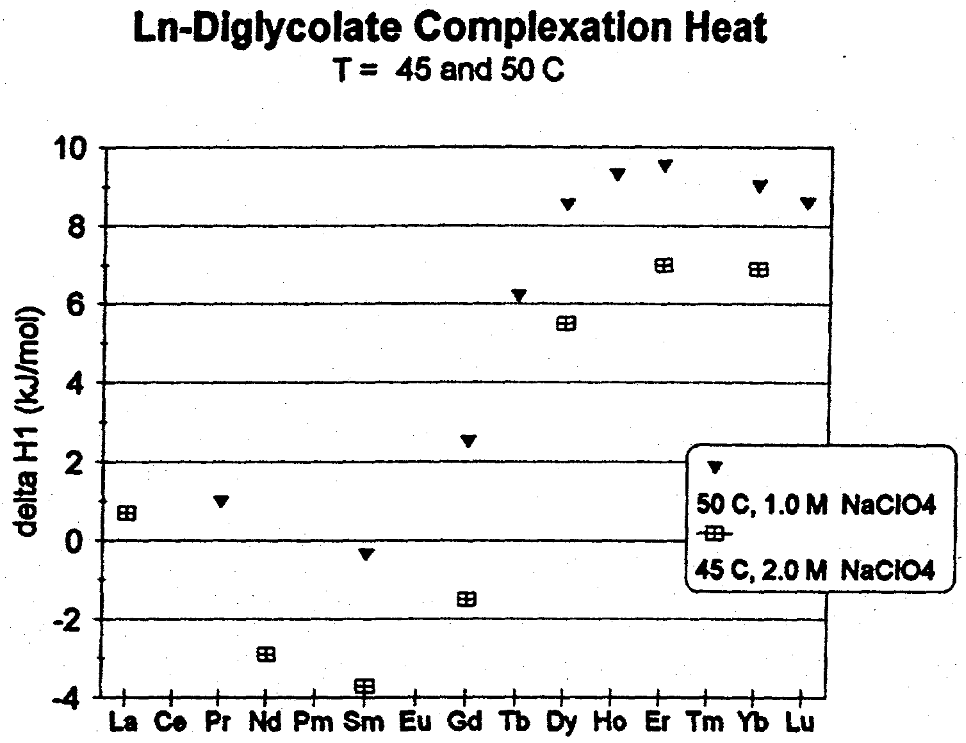


Figure 6. Ln-Diglycolate Complexation Heat

Previous work in this lab [2,3] had determined the enthalpies and entropies for UO_2^{2+} and $NpO_2$2+ hydrolysis at 25° C. Using the calorimeter developed in this laboratory, the hydroysis enthalpies were measured for the reactions below and are tabulated in Table 1. ΔH was calculated by plotting the aparent ΔH vs. $[OH^-]/[Np]_{total}$ where $\Delta H_{app} = \Sigma Q_{corr}/n_{Np\ total}$. A linear regression along the resulting line and subsequent extrapolation to 1 results in a ΔH value independent of the log β value.

$$2UO_2^{2+}\ 2H_2O \rightarrow [(UO_2)_2(OH)_2]^{2+} \tag{2}$$

$$NpO_2^{2+} + OH^- \rightarrow NpO_2OH \tag{3}$$

Table 8.

Actinide	Ionic Medium	ΔH(kJ/mol) 25° C	ΔH(kJ/mol) 45°C
NpO_2OH	1 M $(CH_3)_4NCl$	-22.1±0.4	-15.71±0.52
NpO_2OH	1 M $NaClO_4$	-16.77±0.31	-11.31±0.74
$(UO_2)_2(OH)_2$	1 M $(CH_3)_4NCl$	44.4±1.9	37.1±1

The entropies were not calculated at higher temperature because the log β for NpO_2OH and $[(UO_2)_2(OH)_2]^{2+}$ have not been determined at 45° C but will be determined via potentiometric titration in the next Progress Period. ΔCp was calculated for the NpO_2^+ and UO_2^{2+} species.

1. E. Rizkalla, et. al., *Radiochim. Acta*, **65**, 23 (1994).
2. J. Sullivan, et. al., *Radiochim. Acta*, **54**, 17 (1991).

IV. HETEROPOLYOXOMETALLATES

Research in the laboratory continues on heteropolyoxometallates and their interactions with f-elements. This year a paper was submitted and accepted for publication in *Radiochemica Acta.* It is co-authored with Dr. A. Saito of Tokyo Gakugai University and G. R.Choppin and has the title "Interaction of Metal Cations with Heteropolymolybdate Ions, $MnMo_9O_{32}^{6-}$ and $TeMo_6O_{24}^{6-}$". The abstract follows.

> "Stability constants for the binding of the metal cations Ca^{2+}, Eu^{3+} and Th^{4+} to two heteropolymolybdates, $MnMo_9O_{32}^{6-}$ and $TeMo_6O_{24}^{6-}$, have been determined by the solvent extraction technique. With both anions, Ca^{2+} and Eu^{3+} formed only 1:1 complex, whereas Th^{4+} formed 1:1 and 1:2 species. The stability constants increase with the positive charge of the cations, indicating that the interaction between metal cations and heteropoly anions is electrostatic. The magnitudes of the stability constants suggest the cations bind surface oxygen atoms in two types of geometrical arrangements in both anions."

As the research for his Ph.D., Mr. C. Van Pelt is studying the feasibility of using a large, soluble heteropolytungstate anion as a model for colloid sorption and mobility. He is attempting to synthesize and characterize $K_{28}Li_5H_7[P_8W_{48}O_{184}]\cdot 92H_2O$.

The synthesis of the P_8W_{48} heteropolytungstate goes through two intermediates, first $K_6P_2W_{18}O_{62}$ then $_{12}[H_2P_2W_{12}O_{48}]\cdot 12H_2O$. The P_2W_{18} compound has been made in large quantities (~150 grams) with yields around 67% and is easily isolated and purified by recrystallization from hot water. Characterization of this ligand uses thermogravimetric analysis (TGA) to determine the number of water molecules associated with each ligand. The determination of potassium involves precipitation as a tetraphenylborate salt. The tungsten determination is achieved by destroying the compound by boiling in 0.1 M NaOH and then precipitation of the tungsten with oxine as $[WO_2(C_9H_6ON)_2]$. This procedure has had limited success and is the primary hinderance in the work. The problem is associated with the fact that the taungstate-oxine complex precipitates only at certain pH (4.8) which is difficult to achieve in the procedure. ^{31}P NMR and high resolution mass spec are under study for characterization use. The synthesis of the P_2W_{12} also proceeds well with high recovery of product (90% yield and 63 grams recovered). The same problems are encountered in the characterization of this product.

The synthesis of the P_8W_{48} is completed by placing 950 mL water, 60 g (1 mole) glacial acetic acid, 21 g LiOH, 21 g LiCl and 28 g P_2W_{12} in a 2 liter beaker. The solution is covered with a watch glass and, after a week, crystals precipitate from solution. Approximately 3 grams of product have been isolated and analyzed.

Los Alamos National Lab has initiated a contract with the laboratory to support two projects. This has been accepted as one of the LANL projects.

IV. SEPARATION SCIENCE

A. Crown ethers bound to silica gel

Ms. P. Wong presented a report on this work as a poster at the Fall 1994 National American Chemical Society Meeting (Washington, D.C.). The abstract follows.

"While the study of liquid-liquid solvent extraction involving macrocyclic complexation to lanthanides is well established, there are drawbacks inherent to the system. The need for disposal of the organic phase after retrieval of the metal, loss of ligand to the aqueous phase, and the intrinsic difficulty of transporting a charged cationic species into an organic environment, present significant environmental, economical and chemical concerns. Silica gel bound crown ethers (SGBM) were prepared by bonding crown ethers 18C6 and 15C5 to silica gel according to the method of Bruening, et al. (Bruening, M.L., Mitchell, D. M., Bradshaw, J. S. and Izatt, R. M., *Anal. Chem.* **63**: 21-24 (1991). These SGBM provide an effective method for the separation of lanthanides and actinides in aqueous solution using column chromatography. The advantage of these gels over solvent extraction lies in their availability of multiple fractional plates, the absence of an organic phase, and regeneration of the SGBM. Studies demonstrate that the use of chelating eluants such as malonic acid, picolinic acid, and ethyl-diocy-diacetate complete with the SGBM for coordination to the metal, thereby achieving a more effective separation. Separation has been observed in both tracer as well as macroscopic quantities."

B. Soft Donor Extractants

A new compound diglycolic-diethyl-dimethylamide was synthesized, purified and evaluated as an extract for f-elements. The extraction studies were conducted with tracer

Eu(III) in perchlorate solution contacted with a benzene solution of TTA + amide. Studies of variation of extraction with pH, TTA concentration and amide (A) concentration indicate the extraction reaction to be:

$$Eu^{3+}{}_{(aq)} + xA_{(o)} + yHTTA_{(o)} + (3\text{-}4)ClO_4^-{}_{(aq)} =$$

$$Eu(TTA)y(ClO_4)_{3-y}\ \ (A)_{x(o)} + yH^+{}_{(aq)}$$

The extracted species are: $Eu(TTA)_3$ A, $Eu(TTA)_2(ClO_4)A_3$ and $Eu(TTA)(ClO_4)_2A_3$. Since the coordination number of Eu is 8 to 10, these species are consistent with a bidentate bonding of the amide to the Eu. These studies constituted the M.S. Thesis (1994) research for Ms. J. Yao. Her thesis title and abstract follow.

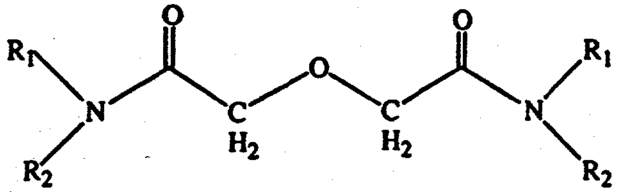
"Synergistic Extraction of Eu(III) and Am(III) by Thenoyltrifluoracetone and N,N-Dimethyl-N,N'-Dihexyl-3-Oxapentanediamide"

> "Extraction of Eu(III) and Am(III) from 0.1 N sodium perchlorate solution into toluene using thenoyltrifluoroacetone (HTTA) and N,N'-dimethyl-N,N'-dihexyl-3-oxapentanediamide (DMDHOPDA) has been studied. The extraction mechanism has been investigated. Species with a methyl:HTTA:DMDHOPDA ration of 1:3:1, 1:2:2, and 1:1:3 are extracted. Significant synergism has been reported."

This work was combined with that from an earlier study by R. Wharf on extraction of f-elements by ligands with sulfur donors, thiothenoyltrifluoroacetone and triisobutyl phosphine sulfide and presented at the Spring 1994 National Meeting of the American Chemical Society. The abstract of the publication which appears in a book of the symposium papers follows.

"Solvent Extraction of Eu(III) and Am(III) with Thio and Amide Extractants." (Published in: "Separations of f-Elements; K. Nash and G. R. Choppin, Eds. Plenum Publishing Co.: New York, 1995).

> "Extraction studies of trivalent f-elements are reported for two thio donor ligands for a diamide. The systems studied were tributylphosphate (TBP) + thiothenoyltrifluoracetone (HSTTA), triisobutyl phosphine sulfide (TiBPS) + thenoyltrifluoracetone (HTTA) and N,N'-dimethyl-N,N'-dihexyl-3-oxapentanediamide + HTTA. HSTTA and TiBPS were found to be much weaker extractants than the oxo analogs HTTA and TBP. Moreover, these soft donor ligands show little enhancement in Eu/An separation. A number of species were observed in diamide extraction the largest separation factor (α = 10) was obtained for the extraction of M(TTA)(DMDHOPDA)(ClO_4)$_2$ species."



R $_1$= R_2 = CH_2CH_3; N,N'-tetraethyl-3-oxapentanediamide (TEOPDA)
R_1 = C_6H_{11}, R_2 = CH_3; N,N'-dimethyl-N,N'-dihexyl-3-oxapentanediamide (DMDHOPDA)

R_1 = R_2 = O; Thenoyltrifluoroacetone (HTTA)
R_1 = O, R_2 = S; Thiothenoyltrifluoroacetone (HSTTA)

R_1 = Bu, R_2 = O; Tri-n-butylphosphate (TBP)
R_1 = *i*-Bu, R_2 = S; Tri-iso-butylphosphine sulfide (TBPS)

Figure 7. Structures of the Extraction Ligands

Table 9. Results of Extraction Studies of HSTTA and TiBPS Systems.
T = 25 °C; I = 0.1 M ($NaClO_4$).

	A. HSTTA(a)		
	HSTTA	pH	
Dependency:	2.8	2.1	
Species:	$M(STTA)_2(X)(HSTTA)$ ($X = ClO_4^-$ or OAc^-)		
	B. HSTTA + TBP(a)		
	HSTTA	pH	TBP
Dependency:	2.8	2.7	1.8
Species:	$M(STTA)_3(TBP)$ $M(STTA)_3(TBP)_2$		
	C. HTTA + TiBPS(a)		
	HTTA	pH	TiBPS
Dependency:	1.8	2.4	1.0
Species:	$M(TTA)_2(X)(TiBPS)$ ($X = ClO_4^-$ or OAc^-)		

(a)The values of Am and Eu agreed within the uncertainty of ±0.1 for these values.

Table 10. Extraction Constants for the HSTTA + TBP and TTA + TiBPS Systems.
T = 25.0 °C; I = 0.1 M ($NaClO_4$).

	Cation	Solvent	$\log K_{2,1}$	$\log K_{3,1}$	$\log K_{3,2}$
			A. HSTTA + TBP		
i.	Eu(III)	Cyclohexane	---	-4.85±0.02	-0.94±0.02
		Toluene	---	-7.55±0.13	-4.87±0.03
ii.	Am(III)	Cyclohexane	---	-4.71±0.10	-1.11±0.01
		Toluene	---	-7.37±0.11	-4.74±0.03
			B. HTTA + TiBPS		
i.	Eu(III)	Cyclohexane	-2.35±0.01	-7.80±0.08	---
ii.	Am(III)	Cyclohexane	-2.58±0.01	-8.34±0.13	---

Table 11. Extraction Constants of the HTTA + DMDHOPDA System.
T = 25 °C; I = 0.1 M ($NaClO_4$).

Species[(a)]	Constant	Eu(III)	Am(III)
$M(TTA)_3$	log $K_{3,0}$	-6.9±0.2	-6.6±0.2
$M(A)_4(X)_3$	log $K_{0,4}$	10.27±0.12	9.93±0.07
$M(TTA)_3(A)$	log $K_{3,1}$	-0.11±0.01	-0.11±0.01
$M(TTA)_2(A)_2(X)$	log $K_{2,2}$	5.40±0.01	5.18±0.01
$M(TTA)(A)_3(X)_2$	log $K_{1,3}$	10.7±0.05	9.71±0.04

[(a)] A = DMDHOPDA; X = ClO_4^-.

Dr. Yuji Sasaki (JAERI) spent 8 months in the laboratory on the soft donor extractant studies. His ligands were modifications of the DMDHOPDA extractant: DHSPDA (N,N'-dihexyl-3-sulfopentanediamide) and DHOPDA (N,N'-dihexyl-3-oxapentanediamide). Neither neutral ligand extracts alone so the system TTA + Extractant (in toluene) was used.

The DHSPDA was a much weaker extractant than DMDHOPDA when the same concentrations of TTA were present. The weakness of the extraction prevented assessment of the Am/Eu separation factor. The monoligand species with DHSPDA were extracted (i.e., $Am(TTA)_3 \cdot S$). The same species were found for the extraction with TTT+ DHOPDA. The K_{ex} values for UO_2^{2+} reflect the relative extraction strengths:

log K_{ex} = 49 (DHSPDA); 87 (DHOPDA); 300 (DMDHOPDA).

In summary, only DHDHOPDA would seem to have promise in separations which is surprising as the only difference between it and DHOPDA is the two methyl groups on the N atoms.

C. Extraction in Molten Paraffin

Professor J. Gao was sent by P.R. China to spend three months in our laboratory during which time he studied extraction of Ln(III) ions by dibenzoylmethane using molten paraffin as the organic solvent. Solidification of the paraffin after extraction provided excellent separation from the aqueous phase. A paper has been published in *Solvent Extraction and Ion Exchange* **13**, 495-501 (1994) with the title "Solvent Extraction behavior of Trivalent Nd, Eu, Ho and Yb with Dibenzoylmethane at 90°C." The abstract is presented below.

> "The extraction behavior of trivalent lanthanide ions (Nd, Eu, Ho and Yb) has been studied with dibenzoylmethane (DBM) at 80 °C using molten paraffin was as diluent. In the range of pH 7 to 8, the extraction of lanthanide cations is greater than 90%. The ratio for Ln:DBM in the extracted species was determined to be 1:3 by the slope analysis method. The $pH_{½}$ values of extraction and the extraction constants of Nd(III), Eu(III), Ho(III) and Yb(III) are reported."

Table 12. Extraction parameters for the formation of $Ln(DBM)_3$ in Paraffin Wax at 80±0.1°C: $C_{DBM} = 2 \times 10^{-3}$ M, I = 0.1 M $NaClO_4$.

Lanthanides	Z	$\log K_{ex}$	Slope	$pH_{½}$
Nd^{3+}	60	-11.64±0.15	2.88±0.24	6.58±0.15
Eu^{3+}	63	-11.58±0.17	2.97±0.17	6.56±0.17
Ho^{3+}	67	-11.55±0.08	3.07±0.17	6.55±0.08
Yb^{3+}	70	-11.40±0.22	2.91±0.44	6.50±0.22

We concluded that dibenzoylmethane can react with trivalent lanthanides to form a stable chelate which can be extracted quantitatively by molten paraffin wax. Equilibrium time is very short and the separation of the phases easily achieved. No emulsification or third phase formation was observed. However, no significant separation of individual lanthanides was obtained with this system.

D. Actinide Redox Speciation.

A major concern in modeling the environmental behavior of some actinide elements is the assignment of the correct oxidation states. We have published several separation systems for isolating the various states (e.g., Pu(III), Pu(IV), Pu(V) and Pu(VI) with minimal perturbation of the redox speciation present originally. However, these were for low ionic strength systems and, of relatively low (<4) pH. Natural waters have higher pH values and brines will be involved in some waste repositories (e.g., WIPP). Therefore, D. Wall has studied redox speciation for his M.S. research with emphasis on higher pH and ionic strengths. Initially redox stable analogs were used to develop the separation. There have been three main areas of concentration: separation of Eu(III), The(IV), Np(V) and U(VI) in 5 M NaCl by solvent extraction; separation of these ions by silica gel sorption; spectrophotometric determination of pH.

Extractions for Eu, Th, U, Np with 0.5 M DBM in toluene in the pH range 2- 3.6 showed that The and U are almost completely extracted while Eu and Np are not extracted at all. The extraction of Th and U occurs in brine solution at lower pH (by about 1.5 - 2 pH units) than in low ionic strength solution. However, in the pH range 2 - 3.6, uranium has a distribution ratio about twice that of Th.

Like the solvent extraction experiments, separation by sorption is pH dependent. As separations are done in near neutral systems, there is a problem of uncertainty in pH measurements which may be compounded by working with brine solutions. We used the buffers MES and HEPES, whose pKa values were determined at each ionic strength.

The kinetics of solvent extraction of The, U, Am from 4 molal NaCl into 0.5 molar DBM in toluene have been measured. In general these systems reach equilibrium after 10 - 15 minutes at pcH's of 2.8, 4.3 and 7 respectively.

Additionally the extraction dependence of Th, U, Np and Eu on pcH was determined in a 5 molal NaCl aqueous phase. These ions could be conveniently and quantitatively separated on this basis. Eu and Am are only extracted in the neutral region, so we used a spectrophotometric method to determine the pcH of the solutions in the Eu extraction experiments with very good results.

D. pcH measurements

To use the results of the pcH dependent solvent extraction experiments to examine the redox behavior of plutonium in high ionic strength solutions, it is necessary to have a reliable technique to measure the pcH in neutral solutions. Unfortunately, glass electrodes are relatively insensitive in the pH 6 - 8 range.

Previously researchers have considered the spectrophotometric method to measure hydrogen ion concentration by measuring the spectral absorbance changes of organic dyes which are also weak acids, however, little reliable data is available on the acid dissociation constants of these dyes, particularly in high ionic strength solutions.

We have measured the acid dissociation constants of two organic dyes, bromocresol green and bromocresol purple, in solutions of various ionic strengths. Basically, these dyes respond to changes in hydrogen ion concentration by linear changes in the concentration of the protonated and deprotonated form the dye molecule, which is directly proportional to the intensity of absorbance band for each form. Performing a simple titration of the dye and measuring concomitant changes in the spectra allow one to accurately determine the acid dissociation constant by plotting pcH vs. log[base]/[acid] which gives a y-intercept equal to pKa.

Finally, we used this method to measure pcH values in 5 molal NaCl for solvent extraction of europium with good results, i.e., good correlation of measured pcH and extraction of the metal ion.

VI. f-ELEMENT SPECTROSCOPY

Both absorption spectroscopy and laser-induced fluorescence spectroscopy are used in our research projects.

A. Studies of Organic Complexes

During this contract period, Mr. Zheming Wang obtained his Ph.D. The title and abstract of his dissertation follow.

"Spectroscopic Studies of Lanthanide Complexes with Organic Ligands."

"The effects of concentration of Eu(III) on its luminescence decay constant and complexation of trivalent lanthanides with aromatic (mellitic, pyromellitic, hemimellitic, trimellitic, trimesic, phtalic, isophthalic, terephthalic and benzoic) and aliphatic (malonic, succinic, glutaric and adipic) carboxylic acids and ethylenediamine were studied by luminescence, absorption and NMR spectroscopic methods and luminescence lifetime measurements.

At constant ionic strength (0.1 M $NaClO_4$), the Eu(III) luminescence decay constant increases as its concentration decreases from 0.2 M to 10^{-5} M but, the Eu(III) $^7F_0 \rightarrow {}^5D_0$ excitation spectra were unchanged. Such an increase of the decay constant at lower Eu(III) concentration was attributed to enhanced interactions between Eu(III) and inner sphere water molecules.

The luminescence spectra and decay constants indicate that mellitate, pyromellitate, hemimellitate, trimellitate, trimesate and terephthalate form ML complex while phthalate, isophthalate, benzoate and the aliphatic dicarboxylates form ML and ML_2 complexes at 25 °C and 0.1 M ionic strength (0.1 M $NaClO_4$). Using the SQUAD program, stability constants of Eu(III) with these carboxylate ligands were calculated from the $^7F_0 \rightarrow {}^5F_0$ excitation spectra of Eu(III). For the aromatic carboxylates, the stability constant linearly correlates with the basicity of the ligand. For the aliphatic dicarboxylates, the stability constant decreases as the carbon chain in the ligands lengthens. The luminescence decay constants indicate that aromatic carboxylates with adjacent carboxylates groups are bidentate and replace two water molecules upon complexation. Benzoate and terephthalate are unidentate. Isophthalate and trimesate replace *ca.* 1.5 water molecules, suggesting greater binding capability of these ligands due to the contribution from the non-binding carboxylate group(s). For the aliphatic dicarboxylates, as the carbon chain increases, the number of water molecules released from the inner sphere upon complexation decreases from 1.7 (malonate) to 1.8 (adipate).

The oscillator strengths of Nd(III) and Ho(III) complexes with carboxylates in the hypersensitive transition ranges were calculated. For the complexes of aromatic carboxylates, the oscillator strength is non-linearly proportional to the effective ligand basicity while for aliphatic carboxylates, the correlation is near linear. Ligand polarizability, along with other factors, were proposed to be responsible for the increase of oscillator strength.

Luminescence and NMR studies show that trivalent lanthanides form ML, ML_2, and ML_3 complexes with ethylenediamine in DMSO. The luminescence decay constants of Eu(III) and Tb(III) complexes of ethylenediamine show that N-H group strongly quenches Eu(III) and Tb(III) luminescence. The quenching effect is linearly proportional to the number of N-H groups in the inner sphere of the metal ion. The luminescence

> quenching efficiency of N-H is 150% and 52% of that of O-H, respectively, for Eu(III) and Tb(III).
>
> It was found that formation of Eu(III) complexes causes a shift of the maxima of Eu(III) ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra towards lower frequency. The magnitude of the shift linearly correlates with the total ligand coordination number."

Mr. Wang is a postdoctoral associate at Pacific Northwest Laboratory, Hanford. The research results have been reported in several papers of which the Abstracts are given below.

1. *J. Chem. Soc., Dalton Trans.* "Thermodynamics of Lanthanide (III) Complex Formation with Nitrogen-Donor Ligands in Dimethyl Sulfoxide."

> "Potentiometric and calorimetric data for the complexation of lanthanide(III) cations by the neutral nitrogen-donor ligands diethylenetriamine or triethylenetetramine in anhydrous dimethyl sulfoxide at 25 °C and in an ionic medium of 0.1 mol dm^{-3} NEt_4ClO_4 have been obtained. All the complexes are strongly enthalpy stabilized while the entropy changes are unfavorable. The results are discussed in terms of the charge density of the metal ions, the solvation changes along the lanthanide(III) series and the structural and conformation characteristics of the ligands."

2. *Thermochimica Acta.* "Luminescence Spectroscopic Study of Europium(III) and Terbium(III) with Ethylenediamine in Dimethyl Sulfoxide."

"The luminescence excitation and emission spectra of europium(III) and terbium(III) complexes of ethylenediamine (en) in dimethyl sulfoxide have been studied. the $^7F_0 \rightarrow {}^5D_0$ spectra of Eu(III) and the values of the luminescence decay constant confirmed that trivalent lanthanides form 1:1, 1:2 and 1:3 inner-sphere complexes with en. The quenching of the luminescence of Eu(III) and Tb(III) are linearly proportional to the number of N-H groups attached to the metal ions. The equations are $K_{obs}(Eu) = 0.759\ n_{N\text{-}H} + 0.416$ and $k_{obs}(Tb) = 0.073\ n_{N\text{-}H} + 0.299$. The quenching mechanism is assumed to be the same as that of the O-H groups, e.g., it involves coupling between the electronic transition energy of Eu(III) or Tb(III) and the vibrational overtones of N-H. Luminescence spectra and decay contents measured between 15 and 80 °C indicate decreased stability of the complexes with increased temperature, in agreement with the reported enthalpies of complexation."

3. *Inorganica Chimica Acta* "Spectroscopic Study of Ion Binding in Synthetic Polyelectrolytes Using Lanthanide Ions."

"Spectroscopic properties of Ln(III) bound to six polyacrylic acids of molecular weights ranging from 2000 to 7000000 daltons are described. These complexes were characterized using Nd(III) absorption of the hypersensitive band at ca. 575 nm and stopped-flow spectroscopy, as well as

Eu(III) luminescence life-time and selective excitation spectra. The luminescence lifetimes of Eu(III), the changes in the absorption of Nd(III) and the passage through columns of cation exchange resin gave a predominance of rapid, strong, binding of Eu(III) with about 3% more weakly bound. The variation of intensity of the Eu(III) $^5D_0 \rightarrow ^7F^0$ selective excitation spectra indicates a molar ratio of 1:3 for Eu(III):[Coo-} with three residual waters of hydration in the inner coordination sphere of the bound Ln(III). No significant changes in either the hydration number or the excitation spectra have been observed among the Eu/PAA complexes for varying PAA."

4. *Inorganic Chemistry*, "A Correlation between Ligand Coordination Number and the Shift of the $^7F_0 \rightarrow ^5D_0$ Transition Frequency in Eu(III) Complexes."

"The relative shift of the Eu(III) $^7F_0 \rightarrow ^5D_0$ transition towards lower energies due to the formation of inner sphere Eu(III) complexes is shown to be linearly proportional to the total ligand donor number of the ligand bound to Eu(III) for forty organic ligand complexed species in both water and DMSO solvents. Such a correlation allows estimation of the donor number, Cn_L, of organic ligands coordinated to Eu(III) from the relative frequency, $\Delta\upsilon$, of the Eu(III) $^7F_0 \rightarrow ^5D_0$ transition by the equation of $CN_L = 0.237\ \Delta\upsilon + 0.628$. The validity of the method has been confirmed by using shift data of other Eu(III) complex systems from the literature. The nature of the shift of $^7F_0 \rightarrow ^5D_0$ band upon complexation is discussed as possibly due to a small degree of covalency in the Eu-L bond of the complexes with organic ligands."

5. *Journal of Alloys & Compounds*, "Synthesis, characterization, spectroscopic and photophysical studies of ternary complexes of Eu(III) with 3-aminopyrazine-2-carboxylic acid (HL) and herobiaryl ligands (2,2'-bipyridine and 1,10-phenanthroline)."

> "The synthesis and spectroscopic properties of mixed ligand complexes of Eu(III) with 3-aminopyrazine-2-carboxylic acid (HL) and two heterobiaryl ligands (2,2'-bipyridine and 1,10-phenanthroline) are described. These complexes were characterized by means of chemical analysis, Ir, UV and luminescence spectra, $^5D_0 \rightarrow {}^7F_0$ selective excitation spectra and $^5D_0$ excited state lifetimes. The complexes show strong ligand-centered absorption in the UV range, efficient energy transfer from the ligands and intense metal-centered emission in the visible range. The structures of the complexes in the solid state and in solution were deduced from spectroscopic and lifetime data. It was found that the complexes exist as different linkage isomers depending on the medium. The high quantum efficiencies indicate that these complexes can be used as light conversion molecular devices either in the solid state or in solution."

C. Cm Luminescence Studies

Dr. T. Kimura spent a year in the laboratory under the agreement with JAERI. The emphasis in his research was to obtain a quantitative relation between the luminescent half-life of curium and the inner sphere hydration of the curium. We were able to use our experience with similar research on Eu(III) luminesce to do the Cm study properly. The results were reported at the Actinides '93 International Conference. The abstract of the article printed in *J. Alloys & Compounds* follows.

Luminescence Study on Determination of the Hydration Number of Cm(III).

> "A luminescence study of Cm(III) has shown a linear correlation between the decay constant k_{obs} (the reciprocal of the excited-state lifetime) and the number of water molecules $n_{(H}2_{0)}$ in the first coordination sphere of complexes. From measurements of k_{obs} of Cm^{3+} in D_2O-H_2O solutions and of Cm(III) doped lanthanum compounds, the following correlation for $k_{obs}(ms^{-1})$ vs. n_{H2O} was established: $n_{H20} = 0.65k_{obs} - 0.88$. This relationship was applied to study of the residual hydration of Cm(III) complexes of polyaminopolycarboxylate ligands. The hydration number of Cm(III) in these complexes is apparently larger than that of Eu(III)."

The report "Hydration Studies of Lanthanide(III) and Actinide(III) Ions by Laser-Induced Fluorescence Spectroscopy (LIF)" on further work was given at the WASH-94 Conference at JAERI, Tokai, Japan, and will appear in the Proceedings volume. The abstract follows:

"The quenching behavior of Sm^{3+}, Dy^{3+} and Cm^{3+} in D_2O/H_2O system is similar to those of Eu^{3+} and Tb^{3+} and is due mainly to energy transfer from the excited state to OH vibrators of H_2O molecules bound to the metal ion. From the measurements of the k_{obs} of lanthanide (III) and Cm(III) in D_2O/H_2O solutions and in lanthanide bromate, $Ln(BrO_3)_3\ 9H_2O$, the n_{H20} of Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+} and Cm^{3+} in H_2O were calculated to be 9.0±0.5, 9.1±0.5, 8,3±0.4, 8.4±0.4 and 9.1±0.5, respectively. From the assumption that for a given polyaminopolycarboxylate ligand the residual hydration of Sm(III) and formulae for the calibration of k_{obs} (ms^{-1}) vs. n_{H2O} were proposed as : $n_{H20} = 0.026K_{obs} - 1.6$ for Sm(III) and $n_{H2O} = 0.024K_{obs} - 1.3$ for Dy(III). From the measurements of the k_{obs}(ms^{-1}) of Cm(III) doped lanthanum compounds, the following correlation was established: $n_{H20} = 0.65k_{obs} - 0.88$. This relationship was applied to the study of hydration state of Cm(III) complexes of polyaminopolycarboxylate ligands. The total coordination number of Cm(III) is possible 0.7±0.2 larger than those of Eu(III) and Tb(III) in the complexes."

C. Other Studies.

Dr. S. Lis conducted a study during a stay in the lab the results of which were reported at the International f-Elements Conference, Helsinki 1994. The article "Luminescence Study of Europium(III) Complexes with Several Dicarboxylic Acids in Aqueous Solution" has appeared in *J. Alloys & Compounds.* The abstract follows.

> "Luminescence lifetimes of Eu(III) in complexes with dicarboxylate ligands and N, O of S donors have been measured in H_2O and D_2O solutions of varying pH and Eu-ligand ratio. The ligands were iminodiacetate (IDA), diglycolate (DGA), Thiodiglycolate (TDA), dipicolinate (DPA), benzene-1,2-bis(oxyacetate (BDODA), ethylenediaminediacetate (EDDA) and ethylene-1,2-dithiodiacetate (EDTDA). The lifetimes have been used to measure the number of water molecules coordinated to the Eu(III) ion in each complex. The results show that in the 1:1 and 1:2 complexes the ligands: IDA, DGA, and DPA are tridentate whereas the TDA complexes are bidentate. BDODA and EDDA form tetradentate 1:1 and bidentate 1:2 complexes, while EDTDA is bidentate in both the 1:1 and 1:2 complexes. These results indicate that the nitrogen and oxygen donors are bonded to lanthanide ions in the DGA, IDA, DPA and EDDA complexes, whereas the sulfur donors are not bonded in the TDA and EDTDA complexes."

Although performed with Eu(III) this study has been valuable for use in interpreting trivalent actinide behavior with these ligands. Such understanding is needed to evaluate the bonding and structural parameters which can guide us to design more specific complexing ligands for actinide separations, decontamination, etc.

C. Stopped-flow Instrument for Measurement of Chemical Kinetics

We have completed the design and construction of a stopped-flow system designed for investigating reaction rates which are too fast to monitor using non-automated acquisition techniques. A diagram of the overall system is presented in Figure 8. The system is equipped with an ultraviolet/visible light source and monochrometer, permitting the acquisition absorbance data at a single wavelength over the range 250-700 nm with 0.1 nm resolution, although it also possesses the capability for monitoring fluorescence data. A detailed schematic of the actual stopped-flow portion of the system is presented in Figure 9.

This home-built system has allowed us to incorporate several features tailored to the unique challenges of studying chemical reaction rates of the f-elements, including:

> The ability to obtain multiple repetitive sample measurements using fairly small sample volumes (~5 ml) of dilute solutions. This feature is useful in minimizing waste generated, especially in the case of radioactive f-elements.
>
> The stopped-flow portion of the overall system is small and compact, permitting operation in a glove-box (isolation box) environment.
>
> Two sampling ports: one parallel to the incident light (for spectrophotometric absorbance measurements), and another perpendicular to the incident light (for fluorescence emission measurements).

Systems Investigated:

The following are sample systems investigated using the stopped-flow instrument:

1. Measurement of instrument dead time

The experimental dead-time for a stopped-flow instrument is defined as: the time during which the physical and chemical processes initiated by rapidly mixing two reactants go undetected by the instrument.[4] and is a function of the physical separation of the mixer and the detector (sample chamber). It was necessary to know the dead-time of our stopped-flow instrument in order to gauge what portion of the first two half-lives of a chemical reaction were being observed, based on the measured experimental rate constant. This parameter was also a convenient means of comparison between our stopped-flow system and that of the commercially available system as reported in reference 4. Using the procedure in this reference, et. al., we determined the dead time of our instrument to be 4.9 s^{-1}, which compare to that measured for ra commercially available Durrum-Dionex Model D-110 of 4.1 s^{-1}.

2. Rate constant for Ni^{2+}/Chlorophosphonazo III

The first order rate constant for the formation of the nickel complex of chlorophosphonazo III in 0.1 M $HClO_4$ was determined to be 46 s^{-1} at 25 °C. The literature value is 45 s^{-1} at 25 °C.

3. Dissociation kinetics for polyelectrolyte systems.

Preliminary results for the dissociation of NpO_2^+ from humic acid demonstrate that nearly quantitative stripping of NpO_2^+ is achieved from purified Aldrich humic acid within 1s after rapid mixing of a solution containing $[NpO_2^+] = 5 \times 10^{-6}$ M bound to [Humate] = 2×10^{-5} M. Preliminary results indicate the dissociation behavior may be satisfactorily explained by a single first order rate constant of 5.7 s^{-1} at 25 °C and pH = 5.7 in 0.1 M MES buffer. This kinetic behavior is in sharp contrast to that observed in this laboratory for the stripping of the multivalent actinide cations [Th(IV)] [5] and $[UO_2^{2+}]$ [6] from humic acid by arsenazo III, in which the rate of dissociation required minutes for completion, and 5 - 7 independent first order kinetic processes for adequate fitting of the rate vs. time data.

We also have made initial investigations of the dissociation kinetics of Np(V) from solutions of polyacrylic acid as potential models for humic acid. Polyacrylic acids of two different molecular weight distributions (MW_{2000} and MW_{250000}) were chosen in order to investigate any differences in the rate of dissociation based on molecular weight. The first order rate constants for both molecular weight fractions were found to be identical ($k = 15\ s^{-1}$) within experimental errors for the dissociation of NpO_2^+ from PAA (50% ionization of carboxylic acid groups for both molecular weight fractions). These results were obtained using the same experimental methodology as employed for the humic acid work. It is interesting that the experimental first order rate constant for the PAA solutions is larger than that for aldrich humic acid under nearly identical conditions.

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RESEARCH PRESENTATIONS

The research under this grant has been described in a number of presentations during this three year period.

1993: *Spring National American Chemical Society Meeting, Denver (3)

Actinide Separations Conference, Hanford

*International Atomic Energy Agency Research Workshop, Poland

*Fall National American Chemical Society Meeting, Chicago (2)

*North American Rare Earth Conference, Kentucky (2)

*Actinides 93 International Conference, Santa Fe

*Palm Coast Environmental Conference, Florida

Migration of Radionuclides International Conference, Charleston, S.C. (3)

(indicates invited lecture, ( ) indicates number of presentations.)*

Seminars were given at University of Kentucky, Orsay (Paris), Florida Academy of Science, Los Alamos, San Jose State University, Washington University, and five lectures on an ACS Lecture Tour in the Southeast.

1994: *Spring National ACS Meeting, San Diego (2)

*Actinide Separations Conference, Durango, CO

*Workshop on Comparative Science of f-Elements, Germany

*International f-Element Conference, Finland (Plenary)

*International Trace Analysis Conference, Japan (Plenary)

Fall National ACS Meeting, Washington, D.C.

*Workshop on Humic Acid-Metal Interaction, OECD/NEA, Switzerland

*Congress on Environmental Science, Hungary (Plenary)

Seminars were given at Lawrence Berkeley National Laboratory, Japan Institute of Atomic Energy, Drexel University, and five lectures on ACS Lecture tour in the West.

1995: *Spring National ACS Meeting, Anaheim, CA (2)

*IAEA Research Workshop (Chair), Tallahassee, FL

*Symposium in Honor of K. Tominaga, University of Tokyo (3)

Fall National ACS Meeting, Chicago

*Oesper Award Symposia, University of Cincinnati

*Migration of Radionuclides International Conference, St. Malo, France (4)

Seminars were given at University of Cincinnati, Argonne National Lab, Pacific Northwest Laboratories, University of Kyushu, University of Dresden, and five lectures on the ACS Lecture Tour in the Southwest.

Publications

During this period, the following publications acknowledged OBES-DOE support.

1. J. N. Mathur and G. R. Choppin, "The Interaction of Crown Ethers with ß-Diketonate Complexes of f-Elements", Solv. Extr. Ion Exch., 11, 1-18 (1993).

2. B. E. Stout, G. R. Choppin, F. Nectoux, and M. Pages, "Cation-Cation Complexes of NpO", Radiochim. Acta, 61, 65-67 (1993).

3. E. N. Rizkalla and G. R. Choppin, "Thermodynamics, PMR, and Flourescences Studies for the Complexation of Trivalent Lanthanides, Ca^{2+}, Cu^{2+}, Zn^{2+} by Diethyltriaminepentaacetic Acid Bis(methylamide)", Inorg. Chem. 32, 582-586 (1993).

4. G. F. da Sa, L.H.A. Nunes, Z. M. Wang and G. R. Choppin, "Synthesis, characterization, spectroscopic and photophysical studies of Eu(III) with 3-aminopyrazine-2-carboxylic acid (HL) and heterobiaryl ligands (2,2'-bipyridine and 1, 10-phenanthroline)", J. Alloys and Compounds, 196, 17-23 (1993).

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6. A. Cassol, G. R. Choppin, P. Di Bernardo et al., "Thermodynamics of Lanthanide (III) Complex Formation with Nitrogen-Donor Ligands in Dimethyl Sulfoxide", J Chem. Soc. Dalton Trans., 1695, (1993).

7. G. R. Choppin, "Separation of f-Elements by Solvent Extraction", Proc. 1st Hanf. Sepn. Sci. Workshop, 1993, Pacific Northwest (Batelle) Laboratory, Hanford, Washington.

8. A. Cassol, G. R. Choppin, P. Di Bernardo, R. Portenova, M. Tolazzi, G. Tomat and P. Zononato, "Thermodynamics of Ln(III) Complex Formation with Nitrogen Donor Ligands in Dimethyl Sulfoxide", J. Chem. Soc. (Dalton Trans.), 1695-1698 (1993).

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