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Research in Actinide Chemistry

Progress Report, 1990-1993

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to

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from

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MASTER

Introduction

The general area of research under this Grant has been the behavior of the actinide elements in aqueous solution. The relatively high radioactivity of the transuranium actinides limits the concentrations which can be studied and, consequently, limits the variety of experimental techniques. However, oxidation state analogs - e.g., trivalent lanthanides, tetravalent thorium, and hexavalent uranium - do not suffer from these limitations and can be used with a wide range of experimental methods.

The questions of the behavior of actinides in the environment are a major USDOE concern, whether in connection with long-term releases from a repository, releases from stored defense wastes or accidental releases in reprocessing, etc. Accordingly, a principal goal of our research has been to expand the thermodynamic data base on complexation of actinides by natural ligands (e.g., OH^- , CO_3^{2-} , PO_4^{3-} , humates). To better model the environmental behavior requires an understanding of the factors which underly such complexation. This has led us to studies of the structure of the complexes, the kinetics of complexation, etc. It has also led to studies of ligands not likely to be found in nature but which can provide deeper understanding of actinide complexation. Perhaps a valid description of our approach is that we undertake fundamental studies of actinide complexes which directly or indirectly can serve to increase understanding of the environmental behavior of these elements.

During the 1990-1993 Grant period, the search group was in a period of change. After a period of 4 years in which no new graduate students had entered the group, four joined in the summer of 1990, four more in 1991, and two this summer. As a result, there are now five Ph.D. students on this Grant. This has meant eliminating post-doctoral associates requiring support although in 1992-1993, there were two "free" ones, Dr. T. Kimura of JAERI, Tokai, Japan, and Dr. T. Al-Ansi of the University of Saana, Yemen. In addition, there are 3 post-doctoral associates on a Contract with Sandia National Lab for the WIPP Project and one supported by Mallinckrodt Medical, Inc. (MRI research). The other students are also supported by these Contracts although their research is closely tied to that of the DOE Grant.

The activities of this research group in actinide separations and in the basic environmental science of the actinides has resulted in several professional activities of the P.I. At present, I am a member of the Waste Management External Advisory Committee of Westinghouse Hanford. This 6 person Committee meets every 3 months to review the progress and plans of WHC in regard to the remediation of the Hanford tanks. In June, I was a member of a similar committee that reviewed the Savannah River Lab treatment and vitrification plans for WSRC. I am also a member of the External Review Committee for the MST Division of LANL. We met at TA-55 in July to review their involvement in the Complex-21 reconfiguration plans. A major assignment has been service as a member of the NAS/NAE Panel on Separations Technology and Transmu-

tation Systems (STATS). This Panel is chaired by Prof. N. Rasmussen (MIT) and is completing an intensive year of meetings to assess the status of separations technologies applicable to the environmental restoration program of DOE and to the potential of transmutation of nuclear wastes by reactor or accelerator irradiation. I am responsible for the evaluation of potential separations technologies which might be of value but would require further R & D. I have also been asked by the Division of Geochemistry, ACS, to organize a symposium on the Geochemistry of the f-Elements for the Spring, 1993, Am. Chem. Soc. meeting in Denver and am a candidate for 1994 Chair of the Division of Geochemistry of the ACS. An additional duty in the area of actinide environmental research is service as the Scientific Chair of the 4th Intern. Conf. on Radionuclide Migration in the Geosphere (Charleston, S.C., Dec., 1994).

The following presentations on our DOE research were made in the 1990-93 time.

1990-91:

Plenary or Keynote Lectures were presented at: "The Chemistry in the Mediterranean Conference", Yugoslavia, May; "International Solvent Extraction Conference", Japan, July; "International Trace Element Conference", Japan, July; "f-Element International Conference", Belgium, September, 1990; "35th National Radiochemical Conference", Japan, October, 1990. Other invited lectures were presented in Japan, Poland, and The Netherlands as well as at both national American Chemical Society meetings.

1991-92:

Invited Lectures at "50th Anniversary of the Discovery of Plutonium", LBL, Feb.; "Actinides Sepn. Conference", Charleston, S.C., May; "Welch Conf. for High School Teachers" (on Pu), Houston, June; 1st Separations Workshop, Hanford, July; "3rd Intern. Radionuclide Migration in the Geosphere", Spain, Oct.; Departmental seminars at Florida State University, U. of Cincinnati, U. of Cal. (Berkeley), U. of Houston. In April I appeared before the NRC Committee on WIPP to discuss the validity of the actinide oxidation state analog approach in connection with Pu speciation studies. Invited talks were also presented at the two ACS national meetings.

1992-93:

A Keynote Lecture was presented at the "Choppin Symposium on Coordination Chemistry" of the Intern. f-Element meeting, Japan, June. Lectures were also given at Sci. U. of Japan, U. of Tokyo, JAERI (Tokai), and the U. of Ibaraki as well as at the Spr. ACS meeting, Sav. River Lab, and the RAS Institute of Inorg. Chem., Russia.

During each year of this Grant period, an ACS lecture tour (Southeast, Central, New England) was made. The title of the lecture was "Plutonium - The Element of Surprise". This lecture also appears as an invited article in Chemistry in Britain.

In addition to the USDOE-OBES Grant, the following support is available to our research.

Sandia National Laboratories - Studies in WIPP Brine Solutions; \$220,000, 1/1/92-12/31/92.

Mallinckrodt Medical, Inc. - Studies of Ln-MRI Agents; \$86,000,
5/1/92-4/30/93.

Research in Actinide Chemistry

Progress Report

Grant Period 1990-93

Since this report covers 1990-93, portions of the 1990-91 and 1991-92 Progress Reports are included (with some editing) plus the summary of the 1992-93 period. The progress in each year is indicated in each research area.

The focus of our research is the solution chemistry of the f-elements.

I. Inorganic Complexes

A. 1990-1991

A paper on the hydrolysis constants of UO_2^{2+} was the first to report a value for formation of $\text{UO}_2(\text{OH})_2$ as oligomer formation interferes with this complex when $[\text{UO}_2^{2+}]_T > 10^{-8}$ M. However, at trace levels likely to be present in the environment or far-field of a repository, this species must be included in geochemical modeling.

The calorimetric titration of UO_2^{2+} with base was conducted during 2 visits to the lab by Dr. James Sullivan (ANL). The data was analyzed based on different oligomeric speciation. The best correlation was obtained for formation of the dimeric $(\text{UO}_2)_2(\text{OH})_2^{2+}$. The reaction of $2\text{UO}_2^{2+} + 2\text{OH}^- = (\text{UO}_2)_2(\text{OH})_2^{2+}$ was calculated to have $\Delta H = -70 \pm 11$ kJ/m and $\Delta S = 181 \pm 18$ J/K/m. Similar titration data for NpO_2^{2+} and PuO_2^{2+} were taken during the second visit of J. S. The data indicate oligomer formation by UO_2^{2+} whereas PuO_2^{2+} remains in

mononuclear species. This is important for proper modeling of the hydrolytic behavior of these elements.

The titration calorimetry of NpO_2^+ by $(\text{CH}_3)_4\text{NOH}$ gave values of $\Delta H = -22.4 \pm 0.4 \text{ kJ/m}$ and $\Delta S = 16 \pm 5 \text{ J/K/m}$ for formation of NpO_2OH . With the van't Hoff equation, we calculate $\log \beta(\text{NpO}_2\text{OH}) = 4.00 \pm 0.07$ at 90°C and 3.67 ± 0.07 at 130°C which is the range of temperatures expected in the near field of the Yucca Mountain waste repository. These values are smaller than at 25°C and indicate that diffusion of NpO_2^+ (and of PuO_2^+) could be greater at the higher temperatures of the repository as it is less hampered by hydrolysis. Subsequently, a manuscript was prepared and accepted for publication.

B. 1991-1992

A major new endeavor in the area of inorganic studies was the measurement of the binding of actinides to monosilicic acid, H_4SiO_4 . This work was started with Dr. I. Satoh (Japan) who studied the binding of uranyl ion. His results were described in a paper published in *Inorganic Chemistry*. Since these studies may provide data of significant value in environmental research on actinide migration, they have been extended to other actinide cations by Mr. Mark Jensen for his Ph.D. research.

The solubility of orthosilicic acid (H_4SiO_4 or $\text{Si}(\text{OH})_4$) varies widely in contact with amorphous silica. This reflects the tendency of the monomeric $\text{Si}(\text{OH})_4$ to polymerize under the conditions desirable for use in binding studies. As a result, much of the past year has been devoted to determining the effect of pH,

ionic strength, etc. on silicic acid polymerization in order to define the optimum set of conditions for the stability of the monomer system. The conditions which are being used as a result of these studies include a maximum orthosilicic acid concentration of 8.3 mM, buffered with acetate at a pH of 4.6. GC/MS analysis of solutions of the above conditions showed that the dimer peak was less than 3% of the area of the monomer peak after 1.5 hours. Solvent extraction studies indicated similar results. Therefore, using $[\text{Si}(\text{OH})_4]_{\text{T}} \leq 10 \text{ mM}$ at pH 4.5-4.8 for the experimental conditions, over the time required for the extractions to study actinide binding, we anticipate that the solution should contain at least 95% orthosilicic acid.

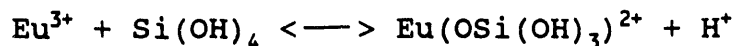
Initial experiments on the binding of Eu^{+3} to $\text{Si}(\text{OH})_4$, with release of a proton, gave an equilibrium constant of 3.8×10^{-3} . This may be compared with the value of 3.6×10^{-3} for uranyl binding. The similarity in these values is surprising and further experiments are necessary to verify that these are valid equilibrium constants.

A Ph.D. research program was initiated by Mr. Don Wall on the oxidation state speciation of plutonium as a function of ionic strength and pH. Over the past several years, reliable separation methods involving precipitation, solvent extraction, and sorption have been developed in this laboratory. Experience in these techniques is being gained using oxidation state analogs of the plutonium. After further experience with the separation techniques, studies on plutonium speciation will begin. This knowledge

is essential if the environmental behavior of Pu in systems ranging from zero ionic strength (e.g., YMP) to brines (e.g., WIPP) is to be understood.

C. 1992-1993

A primary goal has been to find a suitable solvent extraction system for measuring the equilibrium constant for the reaction



The systems studied were HDEHP in toluene, TTA in toluene, TTA-TBP in heptane, and TTA-TOPO in heptane. None of these systems are totally satisfactory and the different systems give different K_{eq} as summarized below:

K_{eq}	System	Comments
(3.8±0.9) E-3	HDEHP/Toluene	<200 ppm SiO ₂ , pH slope very low pH dependence exp. @ 0 & 500 ppm Bad points, Too low extr. @ 0 ppm, Kinetics exp. @ 0 and 500 ppm.
3.0 E-3	TTA/TBP/C ₇ H ₁₆	
8.5 E-4	TTA/Toluene	
7.2 E-4	TTA/Toluene	

In addition, the UO₂²⁺/Si(OH)₄/TTA system was studied and the pH dependence was too low (1.5-1.7). This cannot be accounted for by hydrolysis, though the slopes match those obtained earlier for this system.

Spectrophotometric and proton NMR experiments have demonstrated that 8.32 mM Si(OH)₄ is not extracted by 0.25 M TTA in toluene at pH 4.2 and 0.10 M NaCl after 90 minutes. However, under these same conditions, some of the silicate does polymerize. To address this problem a new extraction system at pH 6 using DBM and

TOPO is under investigation. The high pH allows a decrease of the $[\text{Si}(\text{OH})_4]$ to below the solubility of amorphous silica (100-130 ppm SiO_2).

Several techniques were evaluated for use in the study of the oxidation state speciation of plutonium as a function of pH (4 to 9) and ionic strength (0.1 to 7 M). Emphasis was given to the solvent extraction methods using TTA and DBM. Am^{3+} , Th^{4+} , NpO_2^+ , and UO_2^{2+} have been used as oxidation state analogs of the plutonium species in 0.1 M (NaClO_4) solutions at pH's of 4 through 9.

To evaluate stability constant data in WIPP brines, data is necessary over a range of ionic strengths. Potentiometric titrations with a fluoride electrode have been used to study the protonation constants of HF as a function of ionic strength (1.0-9.0 m NaClO_4). In addition, the stability constants of 1:1 complexation of Eu^{3+} , UO_2^{2+} , and Th^{4+} with F^- were measured over the same range of ionic strength. The values were analyzed by specific interaction theory which is used for treatment of such values by the Nuclear Energy Agency (OECD) for the nuclear waste thermodynamic data base. The SIT equation is:

where

$$\log \beta_1 = \log \beta_1^0 - \Delta Z^2 \cdot D - \Delta \epsilon \cdot I$$

$$\Delta Z^2 = (Z_{\text{ML}})^2 - Z_{\text{M}}^2 - Z_{\text{L}}^2$$

$$D = 0.509 I^{1/2} / (1 + 1.5 I^{1/2})$$

$$\Delta \epsilon = \epsilon_{\text{ML}} - \epsilon_{\text{M}} - \epsilon_{\text{L}}$$

and $\log \beta_1$ is the experimental stability constant at ionic strength I. From our analyses we obtain the values:

	<u>log β_1^0</u>	<u>$\Delta\epsilon$</u>
HF	3.169	0.169
UO ₂ F ⁺	4.944	0.240
ThF ₃ ³⁺	8.868	0.224

Good linear correlations are obtained for plots of $\log \beta_1 + \Delta Z^2 D$ vs I . The $\log \beta_1^0$ values, the intercepts, represent the equilibrium constant values at infinite dilution, the conventional Lewis standard state. A purpose of this study was to evaluate the validity of the SIT analysis for higher ionic strengths. The NEA recommends it only to ca. 2 M but it would be very helpful to be able to use it directly or with modifications to the ionic strength ranges of the WIPP brines.

A similar study using a solvent extraction technique has given values for UO₂F⁺ and EuF²⁺

	<u>log β_1^0</u>	<u>$\Delta\epsilon$</u>
HF	3.169	0.169
UO ₂ F ⁺	4.944	0.240
ThF ₃ ³⁺	8.868	0.224

The sources of the disagreements in the sets of values are being investigated.

A manuscript was prepared and accepted (J. Coord. Chem.) on the thermodynamics of complexation of Ca²⁺, Eu³⁺, and Th⁴⁺ by the halate anions. Several major reviews of actinide and/or lanthanide hydration and hydrolysis were also completed and published or are in press at present.

III. Organic Complexes

A. 1990-1991

In collaboration with Dr. Y. Hasegawa (Science University of Tokyo), the thermodynamics of formation of LnL^{2+} (L = phenylacetate, 3-phenylpropionate and salicylate) were measured. These ligands are models for the carboxylate binding sites in humic acids. A paper has been published in Bulletin of the Chemical Society of Japan.

Some years ago we measured the thermodynamics parameters for Ln^{3+} complexation with benzene dioxydiacetate. In the 1:1 complex, the Ln(III) bonds to the ether oxygens as well as the carboxylates whereas in the 1:2 complex, there is no bonding to the ether groups. This was explained by steric and electrostatic effects. Now, we have studied the complexation of UO_2^{2+} by this ligand. The thermodynamics and NMR data are consistent with formation only of the 1:1 complex with little or no interaction with the ether oxygens. The linear structure of UO_2^{2+} can account for these observations. A paper has been published in Inorganic Chemistry.

During a 2-week visit by J. Sullivan, the thermodynamics of complexation of NpO_2^+ with a series of dicarboxylates ($\text{X}(\text{CH}_2\text{CO}_2)_2$ where X = O, N, S, and also α -picolinate and dipicolinate) and with NTA were measured. The data is consistent with binding to the carboxylates and the O and N donors but not with the S. In fact, for the thiodiacetate, it seems only one of the carboxylates is bound.

The thermodynamics of complexation of lanthanide ions by ethylenetriaminepentapropionate (DTPP) was studied. In contrast to its acetate analog DTPA, DTPP forms only weak complexes with the trivalent ions ($\log \beta$ ca. 4 for MH_2L). To avoid hydrolytic competition, the measurements were obtained in the buffer region pH 3-6 which allowed calculation of equilibrium constants for LnH_2L and LnH_3L formation as well as the thermodynamic parameters. Fluorescence measurements showed a release of four water molecules upon complexation whereas EuDTPA formation causes loss of 8 H_2O 's. C. Musikas, of the French CEA, provided the sample of DTPP.

A high temperature titration calorimeter was designed and built on a contract from LLNL for the Yucca Mountain Project. The calorimeter is now being used for basic studies under this BES grant. To test the system, the complexation between Sm^{3+} and diglycolate (DGA) was studied at 45° and 70°C. The stepwise enthalpies for protonation of DGA were measured to be:

$$\Delta H_1 \text{ 5.61 kJ mole}^{-1}, \Delta H_2 \text{ 0.37 kJ mole}^{-1} \text{ at } 45^\circ\text{C};$$

$$\Delta H_1 \text{ 8.14 kJ mole}^{-1}, \Delta H_2 \text{ 2.82 kJ mole}^{-1} \text{ at } 70^\circ\text{C};$$

Stepwise enthalpies for Sm^{3+} -DGA complexation were:

$$\Delta H_1 \text{ -2.00 kJ mole}^{-1}, \Delta H_2 \text{ -7.53 kJ mole}^{-1}, \Delta H_3 \text{ -4.91 kJ mole}^{-1} \text{ at } 45^\circ\text{C};$$

$$\Delta H_1 \text{ -2.47 kJ mole}^{-1}, \Delta H_2 \text{ -5.62 kJ mole}^{-1}, \Delta H_3 \text{ -6.46 kJ mole}^{-1} \text{ at } 70^\circ\text{C};$$

These data are in good agreement with literature values obtained by Grenthe et al. at temperatures of 25° and 55°C. When the van't Hoff relation was applied to these data, we calculated that the

stability constant was almost invariant with temperature. This remains to be confirmed experimentally, but it indicates that there must be a much smaller (if any) temperature variation of the stability constant than expected. This can have major implication in geochemical modeling in which room temperature data is used with the van't Hoff relation to calculate stability constants at the elevated temperatures expected for near-field conditions in nuclear repositories. These results would indicate that at temperatures of 125°C, the EDTA speciation differ from that expected by the van't Hoff relation by 400%.

Investigation of the kinetics of dissociation of aminopolycarboxylate ligands has continued. These ligands are models for complexation at specific sites of natural polyelectrolytes such as humic acid and, also, are being used in nuclear medicine in magnetic resonance imaging. Previously, we reported the result on the kinetics of lengthening the chain length of the carboxylate arms and of the alkyl chain separating the nitrogen donors. A more thorough study of the latter has been conducted with trimethylenedinitrilotetraacetate and tetramethylenedinitrilotetraacetate. The rate of dissociation increases rapidly as the chain length separating the N donors increases but the mechanism remains the same. A paper on this study has been published in the Journal of Coordination Chemistry.

The dissociation kinetics of lanthanide complexes with triethylenetetraaminehexaacetate has been investigated. Both an acid dependent and an acid independent pathway was observed with

rather surprising high rates - comparable to EDTA. We interpret these rates to indicate that only 2 of the 4 nitrogen sites are binding with the lanthanide.

The kinetics of complexation with the phosphonic acid analog of EDTA (i.e., ethylenediaminetetra (methylenephosphonate, ENTMP) were studied. As with EDTA, both an acid dependent and an acid independent pathway were observed for dissociation of LnENTMP. However, while dissociation of LnEDTA is promoted by increasing $[H^+]$, that of LnENTMP is retarded. This surprising opposite behavior is probably due to the fact that in HLnEDTA, the proton binds to a nitrogen, disrupting the Ln-N bond. However, in HLnENTMP, the proton binds to a phosphonate group and the resulting decrease in net negative charge further stabilizes the complex. Other phosphonate ligands are being investigated in collaboration with K. Nash and P. Horwitz of ANL as they are of potential use in stripping actinides from CMPO extractants in the TRUEX process.

B. 1991-1992

In the 1990-1991 report, initial experiments on the thermodynamics of complexation of Np(V) by a series of dicarboxylic acid ligands were described. These studies have been completed and the data analyzed. In contrast to the UO_2^{2+} which interacts with the oxydiacetates through the ether oxygen, the thermodynamic, data indicated that the NpO_2^+ interacts only with the carboxylates. These results on such model system further confirms that the carboxylate functional groups in humic acid in natural waters are

the major binding groups for actinide ions of all oxidation states, including the pentavalent.

Several years ago we began studies of monophosphonic acid complexation to actinides and lanthanides. Previously, we reported the stability constants and enthalpy values for methylphosphonate, aminomethylphosphonate, and hydroxymethylphosphonate complexation. In all cases, the complexes were weaker than those for the analogous carboxylate ligands but surprisingly large for ligands as strongly acidic as these phosphonates. Nuclear magnetic resonance and Raman studies have been conducted to obtain better values of the first acid constant, which is quite low and difficult to obtain by direct potentiometric titration. At present, these measurements have provided values of $pK_1 = 2.1$ for methylphosphonic and $pK_1 = -0.6$ for aminomethylphosphonic acids.

We collaborated with Dr. Ken Nash of the Argonne National Laboratory on the thermodynamic (potentiometric + colorimetric) measurements of diphosphonate systems. These are the TUCS reagents developed at ANL for scrubbing the remaining actinides after the TRUEX solvent extraction process in reprocessing. We have also measured the fluorescent lifetimes of Eu^{+3} to determine the hydration of the various complexes. For the methyldiphosphonate (MDPA), we obtained a hydration number of 7.2 for the EuH_3L indicating that two waters have been lost upon complexation. The most likely structure is a bridging chelate structure involving an oxygen from each phosphonate group. A similar hydration number is obtained for the EuH_3L complex with the vinylidene diphosphonate

but the value for the hydroxy diphosphonate complex is smaller. For the 1:2 complex of these systems, the hydration number drops to 2.6 indicating that 6-7 waters have been lost. This would suggest that approximately 3 waters per ligand are replaced in the formation of the 1:2 complex. It is quite probable that the bulkiness of the 1:2 complex results in dehydration compared to which is more than twice as large as that of the 1:1 complex. These luminescent decay results are being used with the thermodynamic data to obtain a more complete picture of the nature of the species formed in these systems.

In January, 1991, four visiting scientists came to the lab from the Northwestern Teacher's University in Lanzhou, China on an international grant to study lanthanide complexation. They were given the assignment of synthesizing aza-phosphonates, ligands in which nitrogen donor groups are separated by ethylene groups in a cyclic structure. Each of the nitrogen atoms has a pendant methylenephosphonate group attached. A ligand with a triaminocyclic ring plus three pendant phosphonate groups was synthesized and its acid constants measured. The sum of the first five acid constants was 28.7. The potentiometry of the lanthanide complexes indicated formation of the LnHL species. The value of the log K of this complex varied from 11.1 (La) to 13.1 (Lu). To better evaluate this system, the non-cyclic nitrilotrimethylenephosphonic acid (the analog of nitrilotriacetic acid) was prepared. In this ligand, the three methylphosphonate groups are attached to a single ternary nitrogen. The sum of the first five pKa values was found

to be 30.5 indicating a somewhat more basic system than the cyclic aza system. However, the stability constants were found to be much lower, varying from 7.45 for LaHL to 8.21 for LuHL. The greater stability of the aza complex with the triamine ring reflects the role of these cryptate-type systems in increasing the complex strength. Other syntheses were attempted in which four nitrogen atoms were included in the aza ring, but thus far they have not been successful. The carboxylate analogs of these systems are being studied intensively in a number of radiopharmaceutical laboratories, as they hold promise for use as intensifying agents in magnetic resonance imaging of tumors, etc. The high stability constants of the phosphonate complexes, combined with their slow kinetics, suggest possible value in separations chemistry of actinides.

During the Spring semester of 1991, Dr. Peter Tanner, of the Chemistry Department at the University of West Florida, spent a sabbatical leave in the laboratory. He investigated two very interesting ligands for potential use with actinides. The simpler ligand is known as Kemp triacid (1,3,5-trimethyl,-1,3,5-cyclohexanetricarboxylic acid, KTA). The structure of this ligand is shown below.

We have previously studied the complexation of f-elements with 1,4-cyclohexyldicarboxylic acid and showed that the boat structure of the cyclohexane increases the stability of the complex. Since the three carboxylates in KTA are relatively isolated from each other, there is little interaction, and, as a result, the sum of the three protonation constants is rather large, 16.7. The complex constant with calcium was found to be 4.2 ($\log \beta$) which is quite high for calcium. Unfortunately, when lanthanide cations were added to solutions of KTA, precipitates immediately formed and it was very difficult to make any stability measurements. The value of the stability constant of the Eu complex was estimated to be about 7.75 ($\log \beta_{101}$) if we assume the formation of the EuL species. In fact, the EuHL complex may be forming in which case the $\log \beta_{111}$ value is estimated to be 12.04. Since it seems likely that the three methyl groups on the KTA were the source of the insolubility, we conducted similar studies with the 1,3,5-cyclohexanetricarboxylic acid (CTA). This is a somewhat less basic ligand for which the sum of the acid constants equals 13.2. The calcium stability constant is only 1.35 ($\log \beta_{101}$) and the lanthanide complexes were very insoluble - even more so than the KTA complexes - so no estimates could be obtained of the stability constants of the complexes. We retain an interest in the KTA type system since it may be possible to overcome the insolubility by attaching sulfonate groups to the cyclohexane.

Professor J. Rebek of MIT has used the KTA with the amines to form a basket type of ligand as shown below.

With Prof. Rebek's advice, we synthesized these two compounds and found that compound D contained a number of impurities and slowly decomposed in solution. The solution in CH_2Cl_2 showed extraction experiment. For ligand A we obtained a pure product as confirmed by the spectrum. However, ligand A was only slightly soluble and we could not obtain acid constants by potentiometry. The solubility was approximately 1×10^{-4} M in water, very high in CH_2Cl_2 but it was insoluble in CCl_4 , and in toluene. The CH_2Cl_2 solution did not extract La^{+3} at pH 5.5-7.5. The ligand was more soluble in the presence of lanthanide cations which suggests complex formation and it may be possible to obtain stability constants by methods other than potentiometry. Unfortunately, the extreme insolubility of these systems indicates that they hold little promise for practical separation technology. Several variations of these two ligands were prepared but in every case aqueous solubility presented a major obstacle to further studies.

C. 1992-1993

The 1,4,8,11-tetraazacyclotetradecane-N,N',N'',N'''-tetra(methylphosphonic acid) and the 1,4,7-triacid were recrystallized and titrated with base. The tetraaza acid solubility in

acidic and neutral solutions is quite limited but successful titrations were accomplished with it and the 1,4,7-triacid. The data is being analyzed to obtain the acid constants for both ligands. In addition, the proton NMR spectra have been taken at 0°, 25°, 40°, and 60°C for the H⁺, Y³⁺, La³⁺, and Lu³⁺ systems of these two ligands. Unfortunately, solubility problems at pH < 8 prevent measurement of the stability constants.

Measurement of the thermodynamics of lanthanide complexation with dimethylphosphinic acid was initiated using potentiometric and calorimetric titration.

IV. Humic Acid

A. 1990-1991

Studies of the interactions of actinides and lanthanides with humic acid were continued. Since near-field temperatures of 90-130°C are expected in waste repositories, the effect of temperature on humic acid was studied. Acid-base titration of the humic acid (after being heated in solution in a sealed tube at various temperatures up to 150°C for two days) indicated that structural changes in HA occurred when the temperature was above 120°C. The visible absorption spectra of the HA at 120° and 150°C showed different E4/E6 ratios from the HA treated at lower temperatures.

Complexation of An(III), An(IV), and AnO₂²⁺ by humic acid was found to be very fast (< 1 m). However, passage through ion exchange resin removed a fraction of the bound actinide; the amount eluted decreased with increase in the time of binding prior to passage through the column.

When the eluted fraction was stored for some time and then passed through the column again, an additional amount of the Eu^{3+} was retained on the column. The amount of Eu^{3+} further retained by the column increased with the storage time. A constant value of the fraction retained was reached after a storage period of minutes to hours, depending on the pH.

In the similar experiments with Eu^{3+} and polyacrylic acid (PAA) and with polymaleic acid (PMA), changes in the fraction of Eu^{3+} retained with time were not observed, probably because the equilibrium among different binding modes in those systems is much faster than those in Eu-HA system.

An isobestic point at 984 nm was observed in the optical absorption spectra of Np(V)-HA solutions at different pH's (4.5, 6.0, and 7.5, respectively). The peak at 989-990 nm is likely due to the "first complex" between Np(V) and HA. Preliminary processing of the data gave the following apparent stability constants: $\log \beta_{\text{app}}$: 2.43 + 0.20 (pH 4.5), 2.37 + 0.10 (pH 6.0), 2.53 + 0.10 (pH 7.5). It is interesting that no dependence on pH for $\log \beta$ is observed as it is expected from polyelectrolyte theory and occurs for binding of Am^{3+} , UO_2^{2+} , and Th^{4+} .

B. 1991-1992

The studies of the possible effects of thermal decomposition of humic acid were continued. Solutions of the humic acids at pH values of 6 or greater were sealed in glass vessels and placed in an oven at a constant temperature of 2 days. Temperatures of 25°, 50°, 75°, 100°, and 120°C were used in separate experiments. After

heating, the humic acid samples were characterized by acid base titration, visible absorption spectrometry, and C-13 solid-state NMR. The observations can be summarized as follows:

1. There was no significant change in the property of the humic acid treated at temperatures below 100°C. Significant changes were observed at higher temperatures.
2. By the acid base titration, it was observed that the apparent pKa of humic acid decreased and the apparent number of carboxylate equivalents per gram increased after the treatment at 120°C.
3. From the visible absorption spectrometry, it was seen that the E_4/E_6 ratio (ratio of the absorbance at wavelengths of 465 nm and 665 nm) decreased. This ratio is related to the aromatic vs aliphatic character such that a decrease indicates increased aliphatic nature.
4. The solid state C-13 NMR showed that the peaks corresponding to the carboxylate groups decreased in intensity.

All of these observations indicate that the humic acid undergoes some type of decomposition at temperatures above 100°C into fractions of small molecular weights. Treatment of an EDTA sample in a similar way showed that while the same number of equivalents of carboxylate were present after heating at 120°C, the successive protonations were not equally spaced in the titration curve indicating that the EDTA decomposed into smaller fractions of varying acid constant values. In terms of the repository effects, such decomposition on heating would result in smaller (fulvic acid

type) macromolecules which would have less sorption and higher migration rates.

We have described the studies using ultrafiltration and passage through cation exchange resin columns of the kinetics of metal ion complexation to humic acids. The combination of these two techniques indicated that although the metal binds extremely rapidly, the interaction can be described in terms of weak binding and strong binding since a significant fraction (weak) could be removed by the cation resin. If the mixture of metal in humic acid was passed through the cation resin immediately after mixing, as much as 60% of the Eu^{+3} was retained by the resin. However, as longer times were allowed between mixing and passage through the resin, this amount decreased until a two-day period was reached, after which there was no further change. At that time, about 40% of the Eu^{+3} was retained by the resin.

We have ascertained that when an aged (several days) solution of Eu(III)-humate complex was passed through the column and aliquots of the effluent passed through a second column, the Eu retained by the resin on the second column increased with the time delay between the two column elutions. In both types of experiments, the time required to see no further change was the same and the % of retained Eu also had the same value at the same pH. The equilibrium value of the % Eu(III) retention on the column decreased from 65% to 35% when the pH increased from 4.2 to 5.6. The time required to see no further change also decreased (from 50 hours to a few hours) when the pH increased from 4.2 to 5.6. These

results are evidence for an equilibrium between the two types of binding modes: territorial ("weak") and site-binding ("strong"), which is affected by pH. We have also repeated these experiments with uranyl and obtained similar results. At pH 4.2 about 50% of the uranyl passed through the column with the humic acid. Study of the kinetics with Ca^{+2} , and Zn^{+2} using the same humic acid showed that between pH 4.2 and 7.0, essentially 100% of both of these cations were retained on the cation exchange column, although ultrafiltration had shown that they had rapidly and completely bound to the humic acid.

These results correspond to that expected for condensation vs site binding. The condensation model of Manning indicates that for monovalent cations the binding can be described as essentially 100% condensed (i.e., labile, outer sphere complexation). However, as the charge density of the cation increases, the degree of site binding in which the cation is fixed to a specific carboxylate group or groups increases. Therefore, as one increases the cation charge, site binding should become increasingly a higher percentage of the total. These kinetic experiments have been very informative of the nature of metal interactions with humic acids. They are also providing important understanding about the role of humics in the retention or migration of radionuclides in natural waters and nuclear repository areas.

During these experiments, we attempted to ascertain how many metal ions were bound to a particular humic acid molecule. These studies led us to realize that we could use a combination of

ultrafiltration and tracer techniques to determine the apparent stability constants of the metal humic acid complex. For example, the stability constant of the uranyl-humic acid complex at pH 4.2 was measured to be $\log \beta = 5.2 \pm 0.1$ which agrees rather well with the literature values on similar humic acids. We are continuing to investigate the validity of this method for determination of stability constants with humic acids.

C. 1992-1993

Both Aldrich Humic and Lake Bradford Humic Acids were fractionated with ultrafiltration and characterized by C-13 NMR and pH-titration. The apparent stability constants of the complex between these fractions and Np(V) were measured with spectrophotometry on the Cary-14.

An invited lecture by the P.I. at the III Intern. Conf. on Radionuclide Migration (Spain) was published in Radiochim. Acta. The abstract follows.

The Role of Natural Organics in

Radionuclide Migration in Natural Aquifer Systems

The wide variety of organic compounds present in natural waters is assessed for the role they may play in radionuclide and, especially, actinide migration. Some natural analog and environmental data are briefly reviewed for evaluation of the effect of organics in these systems. The binding constants and the kinetics of complexation of actinides by humics are discussed in terms of probable effects on actinide migration. The role of organics in redox, and in sorption, is also considered.

V. Spectroscopic Studies

A. 1990-1991

During the 1990-1991 period, the investigation of systems using the luminescence lifetime of Eu(III) was a very active area. A paper was submitted reporting a joint study with H. Brittain (Squibb Lab.) of the residual hydration in solution of a series of Eu and Th aminopolycarboxylate complexes. It was shown that the number of waters lost correlated linearly with the ΔS of complexation.

A method was developed to analyze for small amounts of H₂O in DMF and DMSO solutions using Eu(III) as a luminescence probe. The luminescence lifetimes and relative intensities in D₂O and H₂O solutions were measured carefully for Sm(III), Eu(III), Gd(III), Tb(III), and Dy(III). We have also measured the lifetimes for Eu(III) in solutions of Eu:EDTA ratio from 0.5 to 6.0 and are using these data to develop better software to resolve the component decay curves.

A major emphasis was given to study of Eu(III) hydration in systems of interest in actinide separations. In solvent extraction systems, we found that Eu extracted into dinonylnaphthalene solution in heptane remained fully hydrated whereas upon extraction by diethylhexylphosphoric acid solutions in toluene, lost all of its hydration. Extraction into thenoyltrifluoroacetone + toluene left 3 water molecules attached to the Eu (which was confirmed by Karl Fischer titration). The synergistic extraction to form Eu(TTA)₃·TBP removed these last 3 waters. We also measured a

series of $\text{Eu}(\text{TTA})_3$ + crown ether extracts and found that $\text{Eu}(\text{TTA})_3 \cdot \text{CE}$ where CE = 12C4, 15C5, 18C6 left 1 H_2O on the Eu but DB18C6 and DB24C8 removed all H_2O 's. The paper appeared in Solvent Extraction and Ion Exchange.

Similar studies were conducted on $\text{Eu}(\text{III})$ in resin systems. For Dowex-50 (a sulfonic acid ion exchange resin), the hydration number of $\text{Eu}(\text{III})$ remained unchanged between pH 0 and 5 with a value of 9 for 4% DVB resin and 8 for 12% DVB. The hydration number decreased above pH 6 to a value of 6 for pH 9 (12% DVB). These values confirm the outer sphere interaction in these strongly acid resin. In Chelex-100 resin, a cation exchange resin with $-\text{N}(\text{CH}_2\text{CO}_2^-)$ chelating sides, the hydration number of Eu dropped rapidly from 8 to 3 as the pH increased from 0 to 1.8, then slowly decreased to a value of 2 as the pH increased to 5. These values indicate that two of the chelating sites must bind the Eu. In Amberlite XAD-7, a non-ionic resin, the hydration was 8.5 until pH 3.5, falling to 6.7 by pH 4 and 4.7 by pH 8. In this system, the Eu is sorbing as a neutral complex or is invading the aqueous phase of the resin matrix. The decrease between pH 3.5 and 6 probably represents a lower water activity in the resin (same explanation for the lower hydration in Dowex 50 4% DVB vs 12% DVB). Above pH 6, the decrease in hydration can be associated with hydrolysis of the Eu.

B. 1991-1992

The hypersensitive transitions of Nd and Ho complexes of benzenepolycarboxylic acids such as hexa (mellitic acid), the

1,2,4,5 tetra (pyromellitic), and two tri (1,2,3 and 1,2,4) carboxylates in which the carboxylates are in different positions about the benzene ring. This work was completed in 1992. All the oscillator strengths of the 1:1 complexes have been measured and a linear relationship was established between the oscillator strengths and the total ligand basicity. The modified Born equation was used to calculate the effective charges of the ligands and it was shown that the oscillator strength was directly proportional to this effective charge. Examination of the different isomers indicated that the inductive effect was more important than the resonance effect in the oscillator strength.

The hypersensitive transition oscillator strengths have been measured for a series of dicarboxylic acid complexes of the same two metal cations. Again, linear correlations were observed between the oscillator strength and the basicity of the ligands. These studies can provide the background for spectroscopic studies of f-element binding to fulvic and humic acids.

In connection with the study of a number of aminocarboxylate complexes of Eu, the luminescent lifetimes of the iminodiacetate complex were studied. For this system, which has an N-H group, it was observed that there was a stronger quenching than expected based on the probable residual hydration. This observation suggests that the N-H group is also a luminescent quencher of the excited Eu ion. Based on this interpretation, it was estimated that the quenching by the single N-H group represents approximately

0.7 ms⁻¹. This can be compared with the quenching by the O-H oscillator which is approximately 0.5 ms⁻¹.

In connection with a joint NATO Grant project with groups at the University of Padua and Udine in northern Italy, we have conducted luminescent decay experiments on lanthanide polyamine complexes in nonaqueous solvents. The Italian groups (Portanova and DiBernardo) determined the stability constants by potentiometry and the enthalpy and entropy changes by calorimetry. We are complementing these studies with luminescence as well as optical spectroscopic studies. The systems that have been studied include the complexes with the ethylenediamine, the diethylenetriamine, the triethylenetetraamine, and the tris(2-methylamino)amine ligands. The decay constants have been determined for the 1:1 and the 1:2 complexes of these systems with Eu using the stability constants measured in Italy. Our data confirms that each N-H oscillator has a quenching factor of approximately 0.7 ms⁻¹. These results indicate that the ethylenediamine and the diethylenetriamine are completely complexed with all nitrogen donor groups involved while the triethylenetetraamine has all donor groups involved while the triethylenetetraamine has all donor groups complexed in the case of the 1:1 complex but in the case of the 1:2 complex one of the ligands is only partially coordinated. Again, in all cases where the number of N-H oscillators varies from 4 to 12 in the complexes, a quenching constant of 0.7 ms⁻¹ was observed. This agrees with the previous study for the iminodiacetate complex.

Many papers in the literature have used this luminescence method to determine the residual hydration of Eu^{+3} and Tb^{+3} in complexes, assuming that the quenching is due solely to the O-H oscillators. As described in the previous paragraph, we have now ascertained that the N-H oscillator is an even more effective quencher.

In a paper published in the European Journal of Solid State Inorganic Chemistry, we report the results of the measurements in a variety of electrolyte solutions from low concentration to saturated. In the HClO_4 , NaClO_4 , and HCl solutions, the apparent hydration number increased with concentration of the electrolyte. For the HClO_4 , the increase corresponded to a calculated hydration number change from 9.2 in dilute solutions to 11.5 in concentrated solutions. It is unlikely that the hydration number increases to such a value. A more likely interpretation is that the high ionic concentrations of electrolytes results in a considerable weakening of the second and subsequent hydration spheres about the Eu cation. As a result, the bonding between the cation and the first hydration sphere increases, shortening the Eu-O distance. This increased interaction increases the quenching effect and changes the quenching factor. The opposite effect has recently been reported by G. Blasse who studied some solid tungstate systems in which there were two hydrate waters in the first coordination sphere of the Eu. In this case, x-ray structure data showed that the Eu-O distance was greater than normal and the quenching effect was correspondingly decreased. These observations indicate that one

must proceed with caution in using this method which is widely employed in both lanthanide and actinide chemistry to measure residual hydration of complexes.

The project which occupied a considerable amount of time and attention on our part during 1991-1992 was the development of adequate software combined with some new hardware to allow us to measure the luminescent lifetimes better, and also to obtain luminescent spectra and intensities. This took approximately 6 months of the year for development but has resulted in a duty cycle only 1/20 of the previous one which allows data to be obtained much faster with better statistics.

A new study was initiated in the laboratory in collaboration with Professor gilberto de Sá from Recife, Brazil. Professor de Sá spent two months as a visitor on a Brazilian grant, conducting research on "antenna" complexes. In this type of system, the europium is complexed with three aminopyrazine-2-carboxylic acid and hetero-biaryl ligands. The latter were 2,2'-bipyridine and 1,10-phenanthroline. These latter ligands serve as light collectors and transfer the collected photon energy efficiently to the europium. The combination of the carboxylic acid complex plus these ligands occupies all of the coordination sphere of the europium, eliminating the possibility of quenching of the fluorescence by the water. The antenna ligands are more efficient photon collectors than the europium itself, and, therefore, enhance the quantum yield as well as the lifetime. The luminescence lifetimes of these two systems are about 1.5 ms which may be compared to the

lifetime in water which is less than 1/10 of this value and in D₂O which is approximately double this value. Professor J. M. Lehn in Strassborg has also been studying these antenna systems and has reported a system with a lifetime of 0.8 ms. The quantum yield observed in our systems is about 15 times greater than in the aqueous system (both H₂O and D₂O). The compound that Lehn has had the most success with has a quantum yield about 25% of our new systems. It appears that this antenna system has the combination of a long lifetime with the highest quantum yield of any such system thus far studied. There is a considerable interest in such systems as light conversion molecular devices (LCMD). These two systems also have the advantage over the types of systems studied by Lehn in that they are much simpler than his macrobicyclic cryptates.

C. 1992-1993

Study of the complex formation of Ln(III) with strongly basic N-coordinating ligands and their thermodynamic and spectroscopic properties continued. A main focus in this period was luminescence quenching effect of N-H group on Eu(III) and Tb(III) luminescence, which is very important for luminescence study of biological systems when Eu(III) and Tb(III) are used as probes. Ln(III) and the amines form stable complexes in DMSO as evidenced from the excitation and emission spectra and lifetime data. A linear relationship between the decay constants and the number of N-H groups was observed and the luminescence quenching effect of N-H of ca. 65% and 130-140% of O-H for Tb(III) and Eu(III), respectively.

For the higher amines (with 4 or more N's) not all of the N's bonds to Ln(III) simultaneously. Formation of these amine complexes cause blue shifts of the f-f spectra. NMR experiments have been done on these complexes in solution and is continuing.

Luminescence studies using Cm-248 were initiated by Dr. T. Kimura (JAERI). To check the detection limit of curium by the multichannel detector, the emission spectra of various concentration of curium (^{248}Cm) in 1 M HClO_4 and 0.1 M Na_2CO_3 were measured. The curium concentration was determined quantitatively by liquid scintillation counting, discriminating the beta-activity region spectrometrically. Light of 396.5 and 399.4 nm was used for the excitation of curium in HClO_4 and Na_2CO_3 . The emission peak of curium was observed at 596 nm in HClO_4 and at 607 nm in Na_2CO_3 . Although the tailing of the 463 nm Raman band from H_2O disturbed the measurement of curium emission at the lower concentration, the emission peak of curium was resolved by a graphical method. The detection limit of curium was found to be 10^{-8} and 10^{-9} M in 1 M HClO_4 and 0.1 M Na_2CO_3 , respectively. Further, the fluorescence lifetime of curium in the presence of DTPA, TMDTA, EDTA, and NTA was measured to obtain the relationship between fluorescence decay constant $k_{\text{H}_2\text{O}}$ and number of water molecules in first coordination sphere $n_{\text{H}_2\text{O}}$. The correlation of $k(\text{Cm})$ with $k(\text{Eu})$ was non-linear which is surprising and indicates more study is needed to clarify the source of such a difference.

VI. Solvent Extraction

During the 1992-1993 period analysis of data on extractions by crown ethers + TTA was completed and the paper submitted. The abstract follows.

The interaction of UO_2^{2+} , Eu^{3+} , La^{3+} , and Th^{4+} complexes of TTA with several crown ethers have been investigated in benzene and chloroform. The thermodynamic (ΔG , ΔH , ΔS) parameters were measured by extraction and by titration calorimetry. The hydration of the complexes were determined by Karl Fischer and fluorescence techniques. NMR (H-1 and C-13) spectra were used to further clarify the nature of the complexes. These spectra indicated that the metal ion more often does not interact equally with all the ether oxygens and the "fit" of the cation to the CE cavity is not significant. The binding to the simple crowns by $\text{Ln}(\text{TTA})_3$ and $\text{UO}_2(\text{TTA})_2$ follows the CE basicity sequence but with DCh18C6 and DB18C6, steric effects become more important. Such effects are important for $\text{Th}(\text{TTA})_4$ interactions even in the interactions with the simple crown ether.

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