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RESEARCH IN ACTINIDE CHEMISTRY

PROGRESS REPORT

of

Contract EY-76-S-05-1797

for the period

March 1, 1980 - February 28, 1981

MASTER

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Submitted by

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INTRODUCTION

The primary purpose of the research under this contract is the study of the behavior of actinide cations in aqueous solution. The interaction of trivalent actinides with a wide variety of both inorganic and organic ligands has been investigated with emphasis on the thermodynamics and kinetics of complexation at tracer concentrations using radiochemical techniques. In order to expand the scope of the experimental techniques, thereby obtaining additional understanding of the fundamental processes involved, we have conducted non-radioactive experiments with the trivalent lanthanides. Visible spectroscopy, nmr (^1_1H , $^{13}_6\text{C}$, $^{139}_{57}\text{La}$) spectroscopy, potentiometry, and calorimetry are examples of techniques for these lanthanide studies which have allowed much more thorough interpretation of the actinide tracer data due to the close chemical similarity of the lanthanide and actinide families of trivalent cations.

In the last several years, we have expanded our studies to include actinides in the IV, V and VI oxidation states. A significant part of the research during this time has been directed to investigation of actinide interaction with naturally occurring polyelectrolytes such as humic and fulvic acids. Since redox reactions seemingly occur in some of these interactions, a study of plutonium and neptunium redox behavior in the presence of organic complexing agents has been started.

I. THERMODYNAMICS

A. Inorganic Complexes

1. Inner vs outer sphere:

In previous Progress Reports and publications we have reported a correlation for trivalent lanthanide and actinide ions between ligand basicity and the inner (direct metal-ligand contact) vs outer (metal-H₂O-ligand structure) sphere character of the complex. This correlation was first noted in the interpretation of thermodynamic data for a number of inorganic complexes of these trivalent cations. To define the correlation more precisely, we have studied the halate and chloroacetate complexes since in both families of ligands we can span a range of ligand basicities with no change in ligand structure. These complexes were studied by our standard thermodynamic methods of potentiometry, calorimetry, and solvent extraction. The interpretation from these data of the relative degree of inner vs outer sphere complexations was confirmed by subsequent studies of the nmr shifts of ¹³⁹La. For both the halate (ClO₃¹⁻, BrO₃¹⁻, IO₃¹⁻) and chloroacetate (OAc⁻, ClOAc⁻, Cl²OAc⁻, Cl₃OAc⁻) complexes, it was found that inner sphere formation is dominant when the pK_a value exceed 2.5. However, for ligands with pK_a < 1, the complex has significant outer sphere character and when pK_a ≤ 0, the outer sphere character is dominant. These observations all pertain to the trivalent lanthanide and actinides. To extend these correlations, we have initiated investigations of Ca⁺², UO₂⁺², and Th⁺⁴ with

the same anions. For UO_2^{+2} and Th^{+4} , we find the order for the strength of complexation by the halates to be $\text{IO}_3 > \text{BrO}_3 > \text{ClO}_3$. However, until temperature coefficient studies have been completed, thereby allowing us to calculate entropy values, this order of complexation cannot be correlated directly with the relative degrees of inner vs outer sphere formation.

During the past year, studies with the chloroacetate system with thorium were initiated also. This has proven to involve a number of problems as a result of the extent of hydrolysis of thorium even at the relatively low pH values (2 to 3) with which these studies are conducted. Experiments with various "inert" electrolytes which might reduce the extent of hydrolysis and with various extracting agents have failed to yield a more useful system. The complexation constants are instead being determined with correction for the hydrolysis.

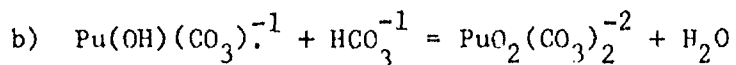
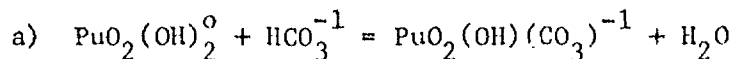
Calorimetric experiments of the heat of complexation of UO_2^{+2} with the halate ions have been completed and are being calculated. Similar measurements with the chloroacetate ligands and uranyl are in progress and should be completed by January. The calorimetric determination of Ca^{+2} complexation by these ligands will be studied.

2. Plutonium carbonate/bicarbonate:

In collaboration with Dr. J.D. Sullivan of Argonne National Laboratory we have investigated the interaction of Pu(VI) with carbonates and bicarbonates. From spectrophotometric data Sullivan and co-workers calculated that at pH 8.3 and an ionic strength of 0.1 M, PuO_2^{2+} forms a 1:1 complex with bicarbonate anion with a stability constant of 6463 ± 60 . At F.S.U. a 0.0052 M solution of $^{242}\text{PuO}_2^{+2}$ adjusted to pH 8.3 was titrated in a Peltier

cooled minicalorimeter (described in previous Progress Reports). NaHCO_3 solution, also at pH 8.3 and ionic strength 0.1 M was used as titrant. In separate runs, the heats of dilution of the metal and of the ligand solutions were determined. From the data, it is possible to calculate the heats of complexation. In May 1979 we conducted initial experiments on this system. In October 1980 more detailed and better titrations were conducted. Analysis of the calorimetric data is proceeding at present.

The calorimetric data does not agree with formation of a single complexed species, nor does preliminary analysis support a model of formation of simply $\text{PuO}_2(\text{HCO}_3)^+$ and $\text{PuO}_2(\text{HCO}_3)_2^0$. At this pH we estimate that initially the plutonyl is present predominantly as $\text{PuO}_2(\text{OH})_2$. An explanation which seems consistent with the calorimetric data is the reactions.



This and other models for the possible reactions are being tested for fit with the calorimetric and spectrophotometric data to ascertain the likely species of PuO_2^{+2} in basic aqueous solutions of the conditions found in natural systems.

B. Organic Complexes

1. Benzoates: The actinide cations are hard acids and interact in aqueous solution most strongly with oxygenated ligands. Since many organic complexing agents are used in actinide separation schemes, we have been concerned with studying a variety of organic carboxylate systems to better understand the fundamental principles in actinide - carboxylate interactions. There were

little data in the literature on the complexation of actinides and lanthanides by the simplest of aromatic carboxylate ligands, benzoic acid; so we have studied the thermodynamics of complexation of the trivalent lanthanides by this acid. Benzoic acid is a somewhat stronger acid than acetic acid and, accordingly, the stability constants for the formation of the lanthanide benzoates are slightly smaller than those for the corresponding acetates. The values for $\log \beta_1$ range from 1.92(La) to a maximum of 2.21(Sm) and down to 1.9(Lu). The enthalpies of formation for the monobenzoate complexes range from 8.0(La) to 12.6(Yb) kJ M^{-1} . The entropy for formation values are 63(La), to 79(Yb) $\text{J M}^{-1} \text{K}^{-1}$. These ΔH and ΔS values are rather similar to the analogous acetate data and reflect the effect of dehydration of the cation upon complexation.

The corresponding entropy data which we measured 3 years ago for the dicarboxylate phthalate complexation is approximately double that for the benzoate. This relationship agrees with our earlier observation for the aminopolycarboxylate complexation that the entropy of formation in the 1:1 polycarboxylate systems is a multiple of the monocarboxylate entropy. We interpreted such an effect as indicating the primary influence of dehydration in the entropy term wherein each carboxylate causes approximately the same amount of dehydration.

2. Aliphatic dicarboxylates: In order to expand our understanding of the effect of structure of chelating ligands on the complexation of actinide and lanthanide ions we are measuring the thermodynamic parameters of complexation of a series of aliphatic dicarboxylate acids in which the length of the carbon chain separating the two carboxylate groups is increased regularly. Potentiometry and calorimetry were used to study the thermodynamic formation constants for trivalent lanthanide ions with succinic, glutaric, and adipic acids. For these three systems the carboxylate groups are separated by chains

of 2,3, and 4 carbons. Malonate (with only 1 carbon between the carboxylates) had been studied earlier in this laboratory, giving us, then, a measure of the effect of increase in chelate ring size from 6 (malonate) to 9 (adipate). The stability constants of the 1:1 complexes are comparable except for the malonate system which is more stable. The log of the stability constants for the 1:2 diacetate (no chelation) and the 1:1 phthalate, succinate, gluturate, and adipate complexes had fairly similar values while that for the 1:1 malonate complex was approximately 10 times more stable. The chelate ring of the malonate complex confers extra stability which is, more or less, completely absent in the other chelates.

In the enthalpy and entropy data for these systems, the malonate values were significantly higher than the others. Succinate and gluturate had approximately the same value as the diacetate whereas the adipate data were somewhat smaller. These data support the interpretation of greatest stability for the five membered chelate ring of the malonate complex whereas succinate and gluturate apparently have chelate rings which are already large enough to allow the carboxylates to operate more or less independently (as they do in the 1:2 diacetate). The somewhat lower values for adipate complexation may reflect a decreased probability of bonding of the second carboxylate when they are separated by such a relatively large carbon chain length. These measurements have been completed and are in the process of preparation for publication.

3. Benzene polycarboxylates:

During the past year while the PI was on sabbatical leave at the Institute for Transuranium Elements in Karlsruhe, West Germany, his primary research interest was a study of the explanation for the incomplete extraction of

plutonium in the purex reprocessing of carbide fuels. It was possible to show that of the various organic acids formed in dissolution of a carbide fuel by nitric acid, oxalic acid interacts sufficiently with plutonium to account for the observed problems. Another oxidation product of the carbide that is present in significant amounts in the purex solutions is mellitic acid. This benzene hexacarboxylic acid is very likely to be a good complexing agent of the uranyl and plutonium(IV) cations present in the carbide solution. However, under the strong acid conditions (4 M) in the purex system, it was found to have no retarding effect on the TBP solvent extraction.

Although mellitic acid does not seem to be significant in purex reprocessing, it is interesting as a model monomeric compound of the type of polyelectrolytes studied in this laboratory in the past few years. Accordingly, we have initiated studies of the complexation of mellitic acid related benzene polycarboxylates with lanthanides as a prelude to their study with actinides.

The protonation constants of hemimellitic (1,2,3 benzene tricarboxylic acid) and pyromellitic (1,2,4,5 benzene tetracarboxylic acid) were determined by computer analysis of acid-base titration curves. In the case of the hemimellitic acid, potentiometry and calorimetry have been used to obtain values for the thermodynamic parameters of complexation. Although this is a tricarboxylic acid ligand, it should form bidentate chelates with the actinide and lanthanide ions due to steric constraints. However, due to the pi electron system of the benzene ring, it is possible for the third, noncomplexing carboxylate to transmit negative charge, thereby increasing the stabilization of the complex. In fact, we observe that the hemimellitate and the pyromellitate complexes are comparable in stability and both are approximately ten times more stable than the corresponding phthalate. This increased stability compared to

phthalate complexes supports the model of transfer of charge from the non-complexing carboxylates. The agreement in stability for the hemi (1,2,3 tricarboxylate) and pyro (1,2,4,5 tetracarboxylate) would indicate that the same extent of charge is transferred. From the possible canonical forms of the hemi and pyro acids, it would seem that only a single carboxylate group, which is para to one of the chelating groups, can be involved in charge transfer. This would seem to explain our observed stabilities. From models we confirmed that complexation via three carboxylate groups is not possible. However, the entropy data for the 1:1 hemimellitic complex is roughly three times that of the monobenzoate complexing and 150% larger than that for monophthalate complexation. The net charge on the carboxylate apparently affects directly the dehydration of cations.

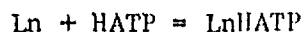
4. AMP and ATP:

The interaction of actinide and lanthanide ions with phosphate and phosphonate ligands has been studied lately due to the use of such ligands in solvent extraction systems. At the same time, interest in the behavior of actinides in biological system has developed rapidly. We are studying the complexation of lanthanide ions by AMP (adenosine monophosphate), ADP (adenosine diphosphate) and ATP (adenosine triphosphate) since these involve phosphate interaction and, also, are of biological interest. ATP is one of the most important chemical entities in biological systems, since it is involved in divergent functions of mechanical motion, light production, and synthesis of organic compounds. ATP and its analogs exist in solutions of biological fluids as a mixture of anions and metal complex species. Their interactions with Mg^{2+} and Ca^{2+} are particularly important. The chemical similarity between alkaline earth ions and the trivalent actinides and lanthanides

has indicated that a study of adenosine phosphate interaction might be of value in understanding the bio-inorganic chemistry of the lanthanide and actinide ions.

In the case of lanthanide-ATP systems, there is precipitation at relatively low concentrations, indicating an approximate K_{sp} value on the order of 10^{-7} . This will be of no problem in the study of the complexation of the actinides using tracer techniques but does put limitations on the concentrations in macroscopic studies by calorimetry and potentiometry. The precipitate was shown by thermal, base titration and metal analysis to be $\text{Ln}(\text{HATP})$.

In the pH range of 4-5 it was found that the complexes formed correspond to either $\text{LnATP} + \text{LnHATP}$ or $\text{LnHATP} + \text{Ln}(\text{HATP})_2$. These same complexes apparently were formed in the AMP and ADP systems. If we assume $\text{LnATP} + \text{LnHATP}$ complexes, the $\log \beta$ for formation of LnATP ranges from 5.8 to 6.4 across the lanthanide series. The value for $\log \beta$ for LnHATP varied from 9.9 to 10.2. Thus at a pH of approximately 4 there would be equal concentrations of the two species. For the AMP complexes, the corresponding ranges and $\log \beta$ values were for LnAMP 3.5 - 4.2 and 8.9 - 9.0. If we assume LnHATP and $\text{Ln}(\text{HATP})_2$ we find for the reaction



$\log \beta \sim 10^4$. For ADP the value of $\log \beta \sim 10^{2.5-3}$ and for AMP it is $\sim 10^{1.5}$. At present time the data is not extensive enough to allow us to speculate on the structural characteristics in bonding modes of these complexes but the adenosine base does not seem to be involved, only the phosphate groups are.

5. Humate:

Studies of the interaction of the actinides ions with humic acid has

continued. Since the initial studies with Am(III) were done with an cation exchange resin counter phase, we have begun to repeat these studies using the more accurate solvent extraction method developed for the thorium and uranium systems. However, before initiating that study, we have spent much of the past year trying to develop a reproducible method to obtain the binding capacity of the humic acids. The literature methods, which involved neutralizations with calcium acetate and filtration of the precipitated calcium humate followed by titration of the liberated acetic acid, were found to give questionable results. The first method did not show high reproducibility between various samples while the answers of the second were found to be dependent on the amount of excess calcium acetate added. Presently, we are investigating a system of immediate titrant additions with no time delay for the slow equilibrium process that we have observed. This technique may not provide the full carboxylate capacity; however, the relative values for different samples may be an accurate measure of the relative binding capacities. Moreover, we are hopeful of finding a constant ratio between the measured capacity by the fast titration technique and the total capacity obtained by a slow equilibration process which would allow us to use the rapid titration technique as an absolute method.

C. Solvent Extraction

1. Benzoic Acid:

Studies of extraction of organic acids from aqueous solutions into organic solvents have a long history. For example, Hendrixson in 1897 reported constants for the distribution of benzoic acid and for its dimerization in benzene. However, few of these studies have involved more than a single

solvent and fewer have attempted to characterize in detail the species present. Our attention to this problem arose from a distribution study of Eu(III) and Am(III) in which it was apparent that benzoic acid adducts in the organic phase produced synergistic extraction effect. (2)

In collaboration with Dr. Yuko Hasegawa of Science University of Tokyo, we have used potentiometric and spectral methods to measure the H_2O and benzoic acid (HB) concentrations in several organic solvents. Our data support the presence of HB, $HB(H_2O)$, $HB(H_2O)_2$, $(HB)_2$, $(HB)_2(H_2O)$ and $(HB)_2(H_2O)_2$ in the wet solvents. We find that the formation constants (from monomeric HB) for $HB(H_2O)$, $HB(H_2O)_2$, $(HB)_2$ and $(HB)_2(H_2O)$ vary inversely with the solubility of water in the organic solvent. However, the constant for the monomer HB equilibrium between water and the wet organic solvent increases. These relationships are understandable if $[H_2O]_o$ measures the solvating power of the solvent. As the latter increases, dimerization and hydration should decrease while simple monomer solubility would increase. If we assume that adduct formation leading to synergism in solvent extraction is related to reaction with the unhydrated monomer, synergism should increase with water solubility in the organic phase or, equivalently, with the solubility parameter of the solvent. However, the opposite trend is observed e.g. synergism is decreased with increased $[H_2O]_{o,T}$, (HB = adduct). This is in agreement with the interpretation that the increased hydrophobic character of the extracted species in synergism is more important than the concentration of adduct in the organic phase.

This work is completed and a manuscript is in final stages of preparation.

D. Redox

The redox behavior of neptunium and plutonium under conditions encountered in the ecosphere and at tracer level concentrations is a subject of much interest but of few definitive experiments.

It has been shown that oxalic, ascorbic, and humic acids reduce Np(VI) and Pu(VI) to lower oxidation states. In all these cases, work was done with macro concentrations of the elements. At tracer level concentrations the chemistry can be different due to the greater difficulty with which disproportionation reactions can occur.

Preliminary investigations into the interaction of Np(VI) tracer with certain carboxylate ligands have been carried out using coprecipitation techniques as a means of identifying the extent of metal reduction. LaF_3 carries the (VI) and (IV) oxidation states of Np, leaving the (VI) state in the supernatant, whereas $\text{Zr}_3(\text{PO}_4)_4$ carries the (IV) state only. Therefore, a combination of the two coprecipitation procedures should allow determination of reduction of Np(VI), and to which oxidation state.

Table I is a summary of the preliminary data for reduction of Np(VI) with the organic ligands. Other researchers have found no evidence of reduction of Np(VI) with benzoic acid, whereas the tracer level coprecipitation experiments showed significant reduction with benzoate. Either this is a case in which tracer level experiments for some reason yield different results, or the reduction was due to impurities in the benzoic acid. These experiments will be repeated using recrystallized reagents and water distilled over KMnO_4 .

TABLE I

adic	pH	elapsed time(hrs)	copptn* technique	%cpm in ppt control/acid	conclusion
acetic	4.0	2.0	LF	42/44	no redn.
oxalic	0	5.0	LF	50/92	reduction
		4.5	ZP	6/13	reduction
	4.0	2.0	LF	27/92	reduction
malonic	4.0	2.0	LF	27/99	reduction
succinic	4.0	2.0	LF	25/70	reduction
maleic	4.0	2.0	LF	27/88	reduction
benzoic	4.1	5.0	LF	56/98	reduction
		13.1	ZP	8/9	no redn.
	3.0	2.0	LF	30/57	reduction
salicylic	4.0	2.0	LF	30/97	reduction
phthalic	4.0	2.0	LF	30/49	reduction
trimesic	4.7	3.0	LF	55/80	reduction
mellitic	2.0	3.0	LF	41/80	reduction
		18.0	ZP	9/5	no redn.

* LF = lanthanum fluoride copptn.; ZP = zirconium phosphate copptn.

While the data above are preliminary, a few conclusions may be drawn. First, reduction in the control, as indicated by a substantial amount of Np carried by LaF_3 which increases with time, points to the presence of reducing impurities in the laboratory distilled water supply. This can be remedied by a second distillation of the water from KMnO_4 . (At the recent Savannah River meeting on plutonium in the environment, it was pointed out that all glassware used tracer level experiments with hexavalent neptunium and plutonium should be treated with a KMnO_4 wash prior to use.) Secondly, reduction of Np(VI) occurs quite easily with the aromatic and chelating

aliphatic ligands listed above.

The only ligand which demonstrates a complete lack of reduction is acetic acid, possibly indicating that with non-aromatic ligands, a chelate effect is necessary to effect reduction. Support for this conclusion is evident in the fact that significantly less reduction occurs for salicylic acid than occurs for other dicarboxylates which are known to form stronger chelates.

INCIDENT REPORT

There have been no incidents (as specified in attachment A) in this period of the report.

COMMENTS

The Principle Investigator spent the period August 1, 1979 to July 1, 1980 at the Institute for Transuranium Elements (Euratom) as a Von Humboldt Awardee. In March, 1980, he spent a week at Florida State University and reviewed the progress of the research under this contract.

Between March 1, 1980 and July 15, 1980 he lectured on the research of this contract at the Universities of Mainz, Munich, Marburg and Saarbruchen in Germany as well as at the German nuclear laboratory (Karlsruhe) and the Hahn-Meitner Institute in West Berlin. Talks were also given at the Swiss Nuclear center, at the Saclay, Fontenay-aux-Roses, and Curie Institutes in Paris, at the Universities of Liege and Leuven in Belgium, at the Chalmers University of Technology in Sweden, and as a plenary lecturer at a symposium on Pollution in the Mediterranean in Rovinj, Yugoslavia. A talk is being given at the University of Vienna on November 26, 1980.

In November, the P.I. is attending a small consultants meeting of the I.A.E.A. in Vienna to plan a critical review of thermodynamic data of actinide-organic ligand interaction. This Fall he was a member of the Panel to advise on the waste form for final disposal of the HAW at Idaho Falls. He is also a member of the steering committee to plan a national conference on the transportation of hazardous wastes to be held February, 1981.

During this contract period, four graduate students were engaged in research. Dr. Ahmad Dadgar left in September and Dr. Emil Rizkallah (Egypt) joined the group. Dr. Janina Legendyiewicz (Poland) came to the laboratory in October for a year (on F.S.U. funds). Dr. H. Aly (Egypt) and Dr. Y Hawegawa (Japan) were summer research visitors. In addition, two new students joined the group in September (both are on Fellowships from other sources).

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4. G.R. Choppin and D. Ensor, The Thermodynamics of Complexing of Ln(III) and Am(III) by Chloroacetates, *J. Inorg. and Nucl. Chem.* 42, 1477(1980)
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6. "Binding of Ln and Ac Polyelectrolytes:, The Rare Earths in Science and Technology, Vol. 2. Ed., G.J. McCarthy, et al., Plenum Press, New York, 1979 pp. 69-77
7. G.R. Choppin, "Interaction of Actinides and Humic Acid:", *Trans. Am. Nucl. Soc.*, 32, 166(1979).
8. G.R. Choppin, S.A. Kahn and G.C. Levy, "Studies of Protonation of Some Aminopolycarboxylates by C-13 Spectroscopy", *Spectros. Letters*, 13, 205(1980).
9. G.R. Choppin and K.L. Nash, "Dissociation Kinetics of Thorium and Humic Acid:", *J. Inorg. Nucl. Chem.*, In Press
10. G.R. Choppin and P.M. Shanbhag, "Binding of Ca(II) by Humic Acid", *J. Inorg. Nucl. Chem.*, In Press.