1981

The coordination chemistry of several radius-sensitive complexones and applications to lanthanide-actinide separations

Michael Wayne Potter
Iowa State University

Recommended Citation

Potter, Michael Wayne, "The coordination chemistry of several radius-sensitive complexones and applications to lanthanide-actinide separations " (1981). *Retrospective Theses and Dissertations*. 6846.
https://lib.dr.iastate.edu/rtd/6846

INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.

2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame. If copyrighted materials were deleted you will find a target note listing the pages in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in "sectioning" the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.

University
Microfilms
International

300 N. ZEEB RD., ANN ARBOR, MI 48106

8122555

POTTER, MICHAEL WAYNE

THE COORDINATION CHEMISTRY OF SEVERAL RADIUS-SENSITIVE COMPLEXONES AND APPLICATIONS TO LANTHANIDE-ACTINIDE SEPARATIONS

Iowa State University PH.D. 1981

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

The coordination chemistry of several radius-sensitive complexones and applications to lanthanide-actinide separations

by

Michael Wayne Potter

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1981

TABLE OF CONTENTS

INTRODUCTION

The Necessity of Lanthanide-Actinide Separations in Nuclear Fuel Reprocessing

In recent years the problems surrounding the treatment of nuclear-fission wastes have been viewed with increasing interest by both the scientific community and the general public. This dissertation concerns the development and evaluation of several ligands of possible use in separation processes germane to that cause. In a larger sense, the stability constants and ion-exchange phenomena reported herein provide insights into the nature of bonding in tervalent lanthanide and actinide complexes, and into the origin of differences in the coordination chemistry of these two series.

One of the most formidable problems posed by spent fuel reprocessing concerns the partitioning of trivalent actinides, americium and curium, from the trivalent lanthanide fission products. It is felt by many that secondary processing in this fashion would significantly decrease the long-term hazards associated with the geological storage of fission wastes. The difficulties associated with this separation and the possible application of the present work to this problem are, however, more clearly developed after a short discussion of the present reprocessing scheme.

Figure 1 (1) illustrates the basis of the current approach to reprocessing. After removal from the reactor, the spent fuel elements are held in storage for a period of time to allow the short-lived fission products to decay. The fuel elements are then opened mechanically and the fuel cores are dissolved in a strong nitric acid solution, leaving behind

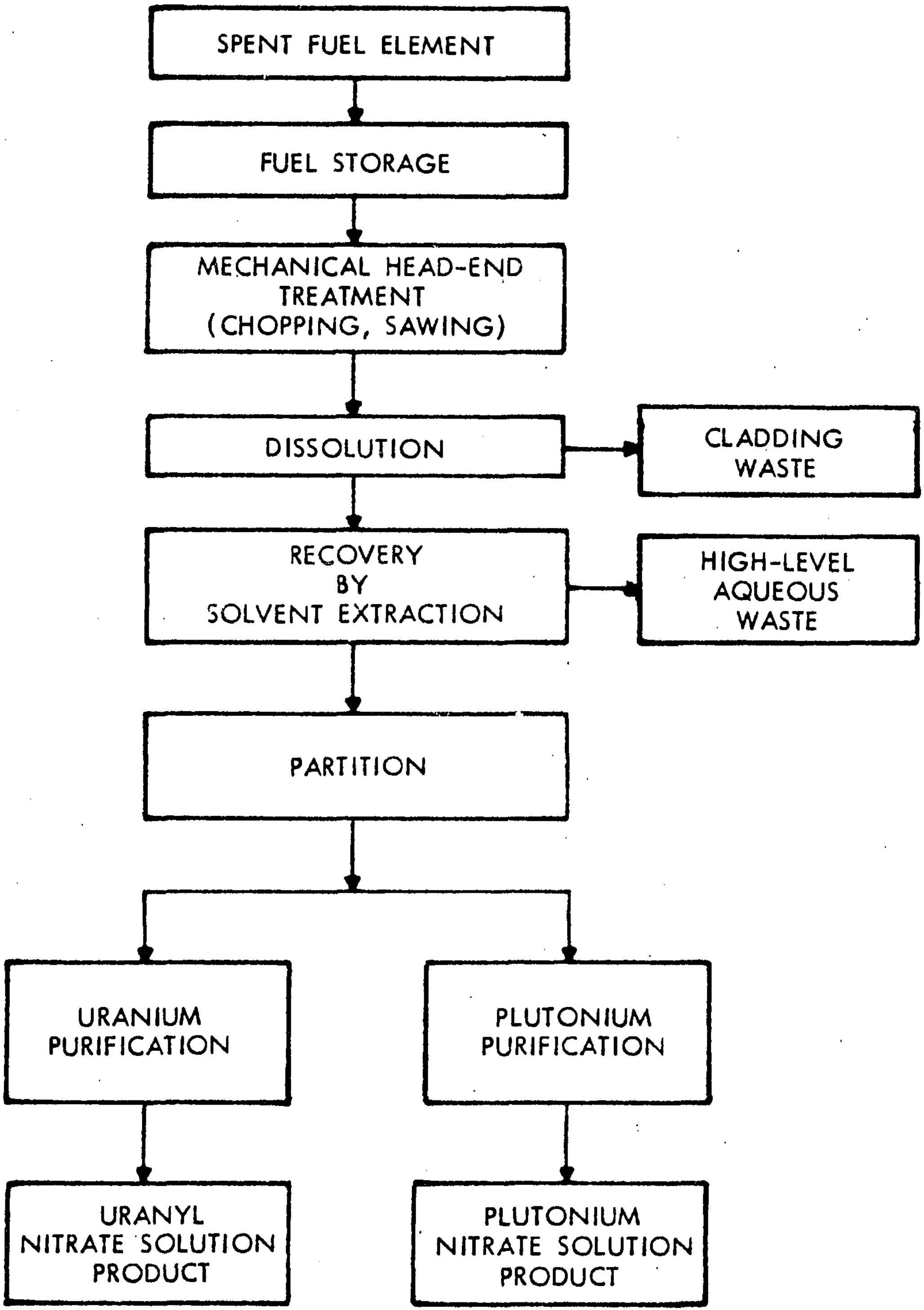


Figure 1. The current approach to reprocessing.

the undissolved metal cladding. At this point, the majority of uranium and plutonium is recovered from the acid stream by utilization of the PUREX process. In this process, uranium and tetravalent plutonium are selectively extracted from the fission-product mixture by tributyl phosphate (TBP). The separation of uranium and plutonium is subsequently accomplished by the addition of an appropriate reductant, capable of reducing Pu(IV) to Pu(III) which is much less soluble in TBP. This permits the convenient recovery of uranium from the organic phase and plutonium from an aqueous phase. Since both the uranium and plutonium recovered in this manner represent potential reactor fuels, the waste generated by the PUREX process is largely confined to the raffinate resulting from the initial TBP solvent extraction step. It is the disposal of the constituents of this high-level liquid waste stream (HLLW) which is of greatest concern in the treatment of nuclear power plant waste.

The exact composition of the HLLW depends on several factors (irradiation time, fuel configuration, amount of recycled material, etc.), but much can be inferred by considering the projected HLLW analysis for the Barnwell reprocessing facility. Table 1 (2) depicts the mass fraction, production rate, and concentration of elements expected to occur in the PUREX raffinate after a three-year cooling period. The waste stream is composed of several distinct classes of elements, differing in origin. Large amounts of iron, and lesser amounts of chromium and nickel, result from corrosion of irradiated reactor components. Secondly, a wide variety of elements is derived directly from the fission of uranium. The fission-produced lanthanides (as well as some natural Gd which is added during reprocessing as a neutron poison), a host of transition metals, and Sr,

Table 1. Barnwell HLLW composition after 3-year cooling period

Element	g/tonne	Kg/day	Concentration in waste, *M*
H	2,600	13.0	4.58
Na	5,000	25.0	0.383
Fe	20,000	100.0	0.631
Cr	200	1.0	0.0067
Ni	80	0.4	0.0025
Se	14.4	0.072	0.0003
Br	13.7	0.069	0.0003
Rb	347	1.74	0.0071
Sr	828	4.14	0.0163
Y	416	2.08	0.0082
Zr	3.710	18.55	0.0701
Mo	3,560	17.80	0.0643
Tc	822	4.11	0.0146
Ru	2,330	11.65	0.0402
Rh	505	2.53	0.0086
Pd	1,520	7.60	0.0254
Ag	82	0.41	0.0013
Cd	136	0.68	0.0021
In	1.6	0.008	
Sn	25.7	0.13	0.0004
Sb	10.8	0.054	0.0002
Te	535	2.68	0.0073

Table 1. Continued

Element	g/tonne	Kg/day	Concentration in waste, M
Cs	2,600	13.00	0.0340
Ba	1,750	8.75	0.0224
La	1,320	6.60	0.0167
Ce	2,540	12.70	0.0317
Pr	1,280	6.40	0.0160
Nd	4,180	20.90	0.0507
Pm	35.6	0.18	0.0004
Sm	1,010	5.05	0.0119
Eu	174	0.87	0.0020
Gd	9,122	45.61	0.1021
Tb	1.3	0.006	
Hg	10	0.050	0.0001
Np	482	2.41	0.0036
U	10,000	50.00	0.0740
Pu	100	0.50	0.0007
Am	525	2.63	0.0038
Cm	25	0.125	0.0002
NO^{-3}	288,945	1,444.75	8.21
PO_4^{-3}	2,000	10.0	0.0372
TOTAL	368,837	1,844.23	

Cs, and Ba, are all major contributors to the mass of the HLLW. A final group of great import consists of the actinides not removed in the PUREX process. A considerable amount of unextracted uranium, along with lesser amounts of the neutron-capture products, Np, Pu, Am, and Cm, is found in the HLLW stream.

The preceding groups are seen to represent a wide variety of chemical families and origins. It is not surprising, then, that much diversity is also present in their radiolytic toxicities. Most fission products require safe containment for about 10^3 years, a time scale well within the credibility of many geological storage sites (3). The necessary containment period is extended to 10^5 years, however, by the presence of the long-lived, alpha-emitting actinide group (4, 5, 6). This disparity in the required containment period of the fission wastes has prompted a call for the separation, and separate disposal of the residual actinide elements by more stringent means (i.e., transmutation or special geological containment). Inherent in any such actinide isolation plan is the need to separate americium and curium from the chemically similar lanthanide elements which compose a third of the mass of the HLLW. The next section of this work will explore the factors underlying the difficulty of this separation, and will review the solutions suggested to date.

The Chemical Basis for Lanthanide-Actinide Separations

Large-scale separation processes for metal ions rely almost exclusively on differences in complex-forming ability to provide the driving force for separation. In light of this criterion and the known chemistry of these elements, it is quite extraordinary that any scheme for separating the trivalent lanthanides, and americium and curium exists. The ions in question are all considered "hard acids" in the Pearson sense and thus their chemistry is dominated by electrostatic bonding. It follows that, since the charge on the cations to be separated is equal (+3), the radius of the ion is the paramount factor in determining the strength of the complex formed with a ligand. With this in mind, the prime cause for the difficulty of the lanthanide-actinide separation becomes apparent in the crystallographic radii shown in Figure 2 (7). Due to radius contractions in both the lanthanide (Ln) and actinide (An) series, americium and curium are interspersed within the lanthanide sequence, having radii approximate to neodymium and promethium. The gist of this discussion is then that, if these primary chemical factors are the only forces operating, one would expect ions of equal radius to form complexes of equal strength, and thus no separation of the lighter lanthanides from americium and curium would be possible.

Fortunately, secondary forces do exist which endow some trivalent actinide complexes with greater stability than those complexes formed by the lanthanide ions of the same radius (8). The origin of this additional stability is not well understood, and at least two different effects may be operating. Currently the consensus is that covalent interactions with the more available actinide 5f orbitals are responsible for the increase in stability. Indeed, there exists some evidence that this type of interaction is possible. Electron paramagnetic resonance experiments with UF_3 and NdF_3 in a CaF_2 lattice (9) have displayed complex hyperfine structure, due to fluorine nuclei, in the spectrum of the actinide cation. No such effect is observed for the lanthanide counterpart, implying that the

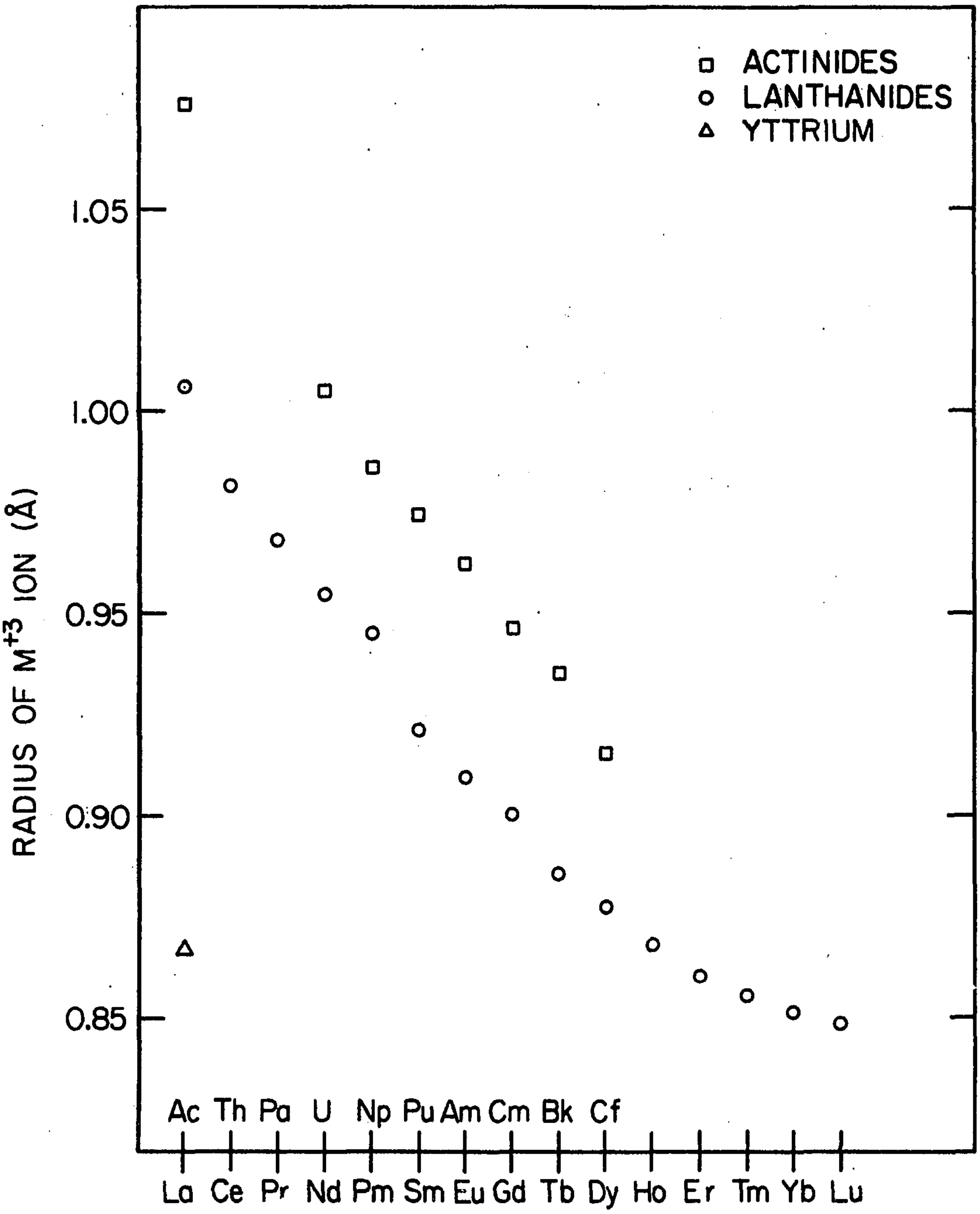


Figure 2. Radii of trivalent lanthanides, actinides and yttrium.

lanthanide 4f orbitals do not exhibit the same ability to interact with ligand atoms as the analogous actinide 5f orbitals. A second indication of trivalent actinide covalence has appeared in the ability of relatively soft ligands containing nitrogen donors to extract the actinides on a tracer scale (10). Discussion of these ligands will be deferred until the next section.

While increased covalency is a plausible explanation for the excess stability in actinide complexes, there are certain experimental results which temper enthusiasm for this view. Tris(cyclopentadienide)Am(III) is a well-characterized compound which might be expected to exhibit considerable covalent nature. In opposition to the expected result, Nugent et al. (11) has estimated that, on the basis of the absorption spectrum, the covalent interactions in $Am(C_5H_5)_3$ account for less than 3% of the bonding in this complex. This lack of covalent character in trivalent actinide organometallic compounds has been reiterated in a recent review by Baker et al. (12) in which it is stated: "Although there is evidence for some appreciable f-orbital contribution to the bonding in the early actinide(IV) complexes, there is essentially none in actinide(III) or lanthanide(III) complexes." One must conclude that the extent to which significant 5f participation occurs in other trivalent actinide complexes is a matter of some doubt.

A closer look at the relationship between the lanthanide complexes and those of another trivalent cation, yttrium, would seem to indicate an alternative explanation to the origin of discrepancies in complex strength. Y(III), with a radius equivalent to Ho(III), would be expected to form complexes of comparable strength. This is not the case.

In the vast majority of instances, the formation constants of the yttrium complexes are substantially smaller than those of the analogous holmium complex. Since there is no evidence for covalent interactions for either ion in question, this phenomena is almost certainly due to the greater effective nuclear charge (Z_{eff}) associated with the holmium cation. One might then also speculate that the observed differences in the Am(III) and Nd(III) complex stabilities might be a result of dissimilarities in the values of Z_{eff} for these cations. Durrant and Durrant have calculated the values of Z_{eff} for the lanthanide cations (13) using the method proposed by Slater (14). A comparison of these values to ones calculated for Y(III) and Am(III), by the same method, provides evidence for an effect based solely on electrostatic interactions. Yttrium and its radius cognate, holmium, produce quite different values of Z_{eff}, 10.90 and 12.40, respectively. The effect is much less pronounced, but still evident in the neodymium, americium pair, with the resulting values being 11.35 and 11.80. The agreement between the magnitude of the effective charge and the observed stabilities of the complexes is apparent, although it must be noted that the Slater treatment represents a very coarse approximation, especially for these heavy ions. Nevertheless, the possible importance of electrostatic interactions in the relative behavior of these complexes, is aptly illustrated by its use.

Evidence has been presented that supports either 5f covalency or increased electrostatic interaction as being the source of increased complex strength in the trivalent actinide complexes, relative to the complexes formed by lanthanide cations of the same radius. The observed effect may, in fact, be a combination of these effects and others. It should be emphasized that this question represents more than just an interesting theoretical exercise. The development of effective lanthanide-actinide separation schemes will depend on the design and synthesis of ligands which maximize these small bonding differences in the coordination chemistry of the two families.

A Review of Ln-An Separation Agents

The numerous proposals for Ln-An separation processes which occur in the literature (15, 16, 17) are based on relatively few chemical phenomena. The intent of this section is to review these chemical bases by citing appropriate examples of their application in ion-exchange and solvent-extraction techniques.

Before beginning the discussion of particular chemical separating agents, it is instructive to enumerate the qualities necessary for a ligand to serve in such a capacity.

1. It should provide adequate separation factors for partitioning Am and Cm from the lanthanides, especially lanthanum through gadolinium.

2. It should be applicable to the acidic media resulting from the extraction of the trivalent lanthanides and actinides from the other fission products. A low pH range is necessary to prevent substantial hydrolysis of these cations.

3. It should possess the necessary chemical and radiation stability to allow its use for an extended period.

4. It should not be highly corrosive, viscous or flammable, or possess other physical properties which make its use impractical.

5. It should exhibit good exchange kinetics and thus allow for realistic residence times.

No known ligand fulfills all of these requirements. The few which most nearly satisfy the first one will be the subjects of the following discussions.

Chloride

The ability of trivalent americium and curium to form more stable chloride complexes than the lanthanides was first observed by Seaborg and Street (18) in their initial experiments with the transplutonium elements. They noted that at high HCl concentrations (13 M) the actinides had a markedly lower affinity for a strong-acid cation exchanger (Dowex 50) than did the lanthanides. This separation technique was improved by the incorporation of 20% ethanol in the eluent, which provided greater separation factors and longer retention times (19). Further investigations into mixed solvent cation-exchange systems have been made (20), but no large-scale use of the chloride cation-exchange technique has developed.

Anion-exchange separations involving the chloride complexes, on the other hand, have seen widespread use in the nuclear industry. Hulet and coworkers (21) investigated the use of an aqueous 10 M LiCl solution as an eluent in the anion-exchange separation of trivalent lanthanides and actinides, and found it to be superior to HCl. Distribution coefficients (Dowex 1) for the lanthanides ranged from 0.25 (La) to 0.90 (Lu), while Am and Cm were found to be 5.0 and 4.0, respectively. Further studies by Marcus (22) concluded that the complex species in the resin was

$AmCl_4^-$. The addition of 0.1 M NH_2OH and 5% methanol by chemists at the Oak Ridge TRU facility (23) has proven effective in suppressing the persistent problems of tetravalent cerium and radiolytic gas. Use of these improvements has made possible the purification of multigram amounts of americium and curium by the chloride anion-exchange technique (24).

The disparity in the aqueous An-Ln chloride complex strength has also been utilized in several solvent extraction systems. Tributyl phosphate (TBP) (17, p. 200), mono-2-ethylhexylphosphoric acid (MEHPA) (25), di-2-ethylhexylphosphoric acid (DEHPA) (26), trioctylphosphine oxide (TOPO) (26), and diamylmethylphosphonate (DAMP) (26) have all been investigated as extraction agents for use in concentrated LiCl solutions containing these trivalent metals. Schemes incorporating these phosphorus based reagents have, however, failed to equal the exceptional separation factors obtained with amine extractants (26). Work with these reagents done by Moore (27), at an analytical level, and Baybarz (28), on a larger scale, led to the development of the widely used TRAMEX process (23) for separating the lanthanide and actinide families. Figure 3 (23) illustrates the striking differences in extractability of these cations from a slightly acidified 10 M LiCl solution, by the tertiary amine hydrochloride, Alamine 336-HCl, in a diethylbenzene diluent. The ratio of the distribution coefficients of the least extractable actinide, Cm, and the most extractable lanthanide, Eu, indicates that the Ln-An group separation factor exceeds one hundred. This represents one of the largest group separation factors observed to date.

One might expect the amine extraction mechanism to be analogous to the anion-exchange equilibrium discussed earlier in which the resin phase

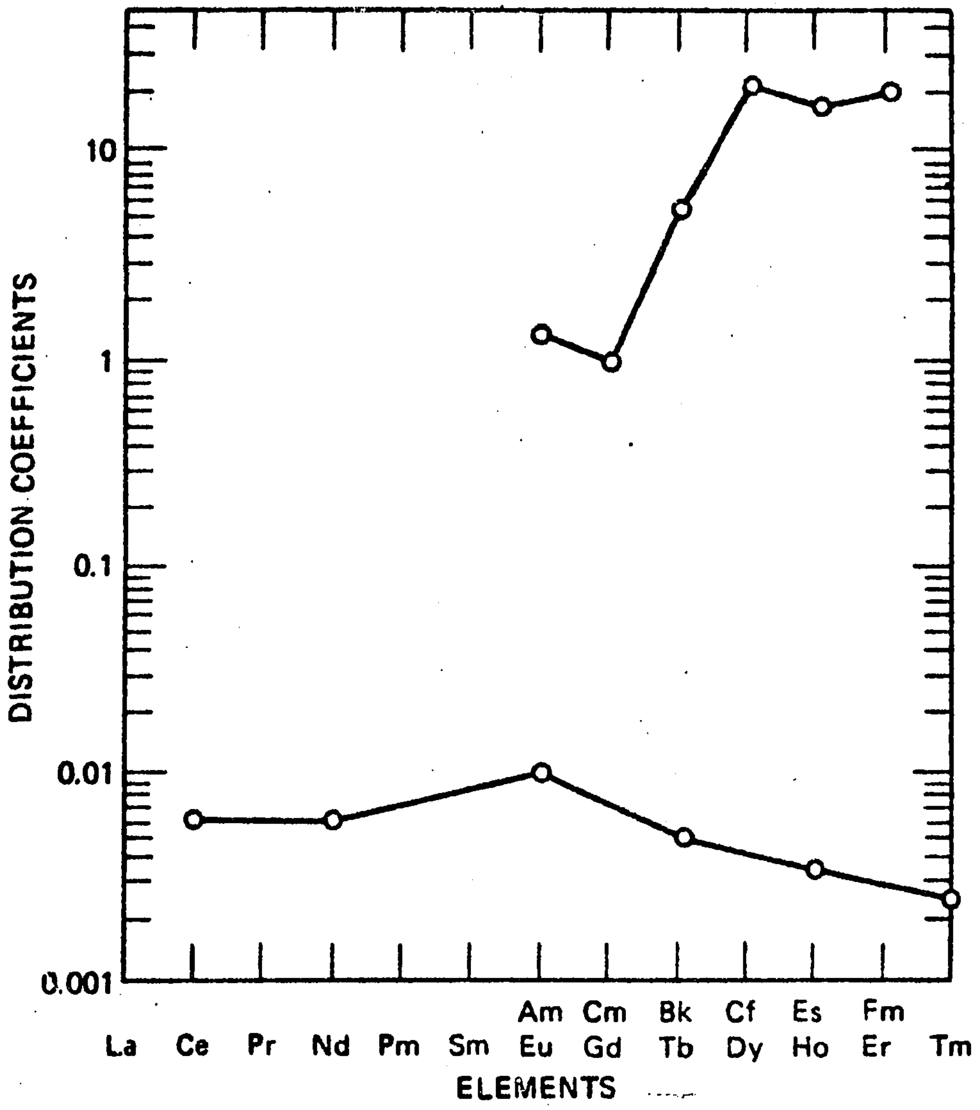


Figure 3. Relative extractability of the lanthanides and actinides from 10 M LiCL solution by 0.6 M Alamine 336·HCL in diethylbenzene.

species was postulated to be MCl_4^-. Surprisingly, experimental results (29) have revealed that the americium distribution coefficient varies as the square of the amine concentration, indicating that this is not the case. At present, the extraction equilibrium is thought to be (22):

$$AmCl_2{}^+{}_{(aq)} + 2Cl^-{}_{(aq)} + Li^+{}_{(aq)} + 2(R_3NHCl)_pR_3NHCl_{org}$$
$$\rightleftarrows [(R_3NHCl)_pR_3NH]_2LiAmCl_{6\ org}.$$

This interpretation has been further supported by the coextraction of substantial amounts of LiCl which has been observed in recent experiments involving macro amounts of americium (30).

Although the TRAMEX process enjoys excellent theoretical separation factors, it is fraught with practical problems (17, p. 229). Radiolysis effects which hamper the process include the rapid destruction of HCl, and the production of strong oxidants which promote the formation of extractable ceric chloride species (23). Tantalum or other such inert process equipment is necessary to prevent the formation of insoluble corrosion products and emulsions in the concentrated chloride solution. The presence of nitrate ion impurities rapidly compromises the Ln-An separation factors from 100, in the absence of nitrate, to 1 (no separation), when the nitrate concentration reaches 0.7 M (28). These problems proved sufficient to convince workers at the Savannah River Laboratory to abandon hope of continuous multicycle TRAMEX operation, in favor of high-pressure displacement-chromatographic cation-exchange systems for the purification of Am and Cm (17, p. 229). In addition to these factors, TRAMEX use on a scale applicable to reprocessing, would require recycle of the LiCl salt to prevent the mass of waste to be stored from becoming prohibitive (31).

Thiocyanate

The previous discussion noted that concentrated chloride solutions display a marked ability for Ln-An separation, and that their use is limited by their corrosive nature. The pseudohalide, thiocyanate, possesses a similar affinity for actinide complex formation, while minimizing the corrosive tendency of halide solutions. Evidence exists for the formation of the mono-, di-, tri-, and tetrathiocyanate species in aqueous solution, and as with all known actinide complexes, the thiocyanate ligand appears to be nitrogen bound (32).

Cation-exchange processes incorporating the thiocyanate ligand have not been closely studied. Surls and Choppin (33) note that in elutions of Ln-An mixtures with 2 $\underline{M}$ NH_4SCN, Am elutes between Pm and Lu, at a position coincident with Ho. Elution orders using more concentrated solutions are not available, although Keenan (34) reports the elution of Am with 8 $\underline{M}$ NH_4SCN as a preparative method for anion exchange feedstocks.

Anion-exchange techniques with the actinide thiocyanate complexes have enjoyed considerable popularity among researchers in transplutonium chemistry. Work performed by Thompson and coworkers (19), Coleman and coworkers (35), and Keenan (34) is representative of the development of the thiocyanate anion-exchange method from analytical to gram scale. The degree to which the anionic americium complexes are preferentially sorbed by an anion-exchange resin (Dowex 1) is illustrated in Figure 4 (36). At NH_4SCN concentrations between 0.5 and 5.0 $\underline{M}$, the Am-Eu separation factor.

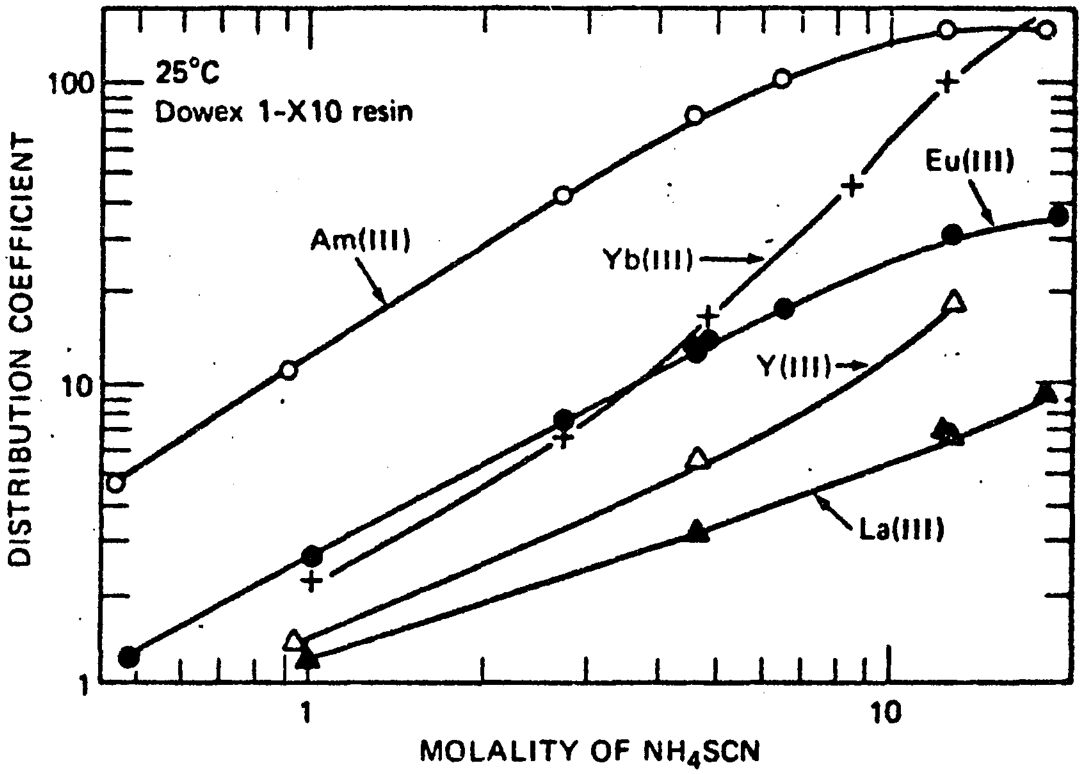


Figure 4. Anion-exchange absorption from aqueous NH_4SCN solutions.

rises gradually from approximately 4 to 6. Noted also was an unexplained rise of the Yb distribution coefficient with increasing thiocyanate concentration.

Russian scientists (37, 38, 39) have investigated the effects of alcohol addition on anion separations incorporating NH_4SCN and NH_4SCN-HNO_3 solutions as eluents. Guseva et al. observed a doubling of the Am-Eu separation factor by using 1 M NH_4SCN eluents in which the methanol content was varied from zero to 70% (37). This author has subsequently reported an ion-exchange process for separating americium from irradiated plutonium targets (40). In this scheme, trivalent lanthanides and actinides were loaded onto a strong-base anion exchanger from a 1 M HNO_3 - 90% methanol solution, and the group separation was attained by the elution of the lanthanide fraction from the resin with a 0.5 M NH_4SCN - 0.1 M HCl - 80% methanol solution. Americium and curium were then recovered by a final elution with 0.5 M HNO_3 in 80% methanol.

Solvent extraction methods exploiting thiocyanate complexes have been devised, although, they have not found widespread application. Sekine (41) studied the distribution of Am and Eu between 5% TBP in hexane, and NaSCN solutions. His results indicated that a mixture of extracting species, $Eu(SCN)_3(TBP)_3$ and $Eu(SCN)_3(TBP)$, were present. Am was observed to extract to a greater extent than Eu at very low NaSCN concentrations, however, this differentiation disappeared as the thiocyanate concentration increased. Later work by Khopkar and Narayanankutly (42) investigated the extraction of trivalent La, Eu, Am, and Lu from 1 M NH_4SCN by TBP, TOPO, and tributylphosphine oxide (TBPO). In all cases, the distribution coefficient for Am fell between those of Eu and Lu. The relationship between the distribution coefficients and extractant concentration revealed that La was extracted as a $R_4M(SCN)_3$ species by TOPO and TBPO, and as $R_5M(SCN)_3$ by TBP. Europium and americium were extracted as $R_4M(SCN)_3$ species by TBP, TBPO, and higher concentrations of TOPO, however at lower TOPO concentrations, a transition to a $R_3M(SCN)_3$ species was observed. Lutetium was extracted as $R_3M(SCN)_3$ by all three reagents. DAMP (26), DEHPA (26), and MEHPA (26, 43) have also been the subjects of minor investigations, however, none has proven competitive as a Ln-An separation method.

The use of amine extractants similar to those used in the TRAMEX process have been investigated by several workers. Moore (44) has shown that the order of decreasing extractability by 30% Aliquat 336-SCN in xylene from a 0.6 <u>M</u> NH_4SCN solution is:

$$\mathrm{Cf > Bk > Am,Cm \gg Yb > Tm > Eu > Pm > Y > Ce > La.}$$

The extracting species varied with increasing thiocyanate concentration, and moieties containing $Am(SCN)_4^-$, $Am(SCN)_5^{2-}$, and $Am(SCN)_6^{3-}$ were observed. Gerontopulos <u>et al</u>. (45) reported the strong dependence of distribution coefficients in the same system on temperature, diluent and contaminant anions. In spite of these effects, separation factors between americium and the lanthanides remained relatively constant. As is the case with all thiocyanate solvent extraction systems, no large-scale use of these amine extractants has been made.

The ion-exchange and solvent-extraction methods involving thiocyanate are all plagued by a common flaw. While thiocyanate provides workable separation factors between Am and Cm, and the lanthanides, the ligand is not sufficiently stable to alpha radiation. The presence of macro amounts of Am and Cm initiates the formation of polymeric sulfur, which renders these separation techniques unworkable at the scale required for reprocessing (34, 46). Other difficulties include radiolytic gas formation (34), and handling and disposing of viscous, concentrated thiocyanate solutions (17, p. 237).

DTPA

The aforementioned difficulties associated with thiocyanate and chloride based systems prompted further work in Ln-An separation chemistry. Much of this effort was directed toward the use of the aminocarboxylate ligands which had proven so successful in the large-scale separation of the pure lanthanide elements (47). The actinide selectivity of a variety of these ligands has been investigated, however the steep monotonic increase in complex strength generally exhibited by these chelates across the lanthanide sequence inhibits their usefulness by interspersing Am and Cm within the lanthanide series. Fortunately an important exception to this behavior was discovered in the case of diethylenetriaminepentaacetic acid (DTPA). Figure 5 illustrates the results of An and Ln stability constant determinations performed by Moeller and Thompson (48), and Baybarz (49), which formed the basis for several important ion-exchange and solvent-extraction systems. Stability constants for ethylenediaminetetraacetic acid (EDTA) (50) and 1,2-cyclohexanediaminetetraacetic acid (CDTA) (50, p. 236) are included for comparison. In the cases of EDTA and CDTA, the continuance of the increase in complex stability throughout the heavy lanthanon range causes

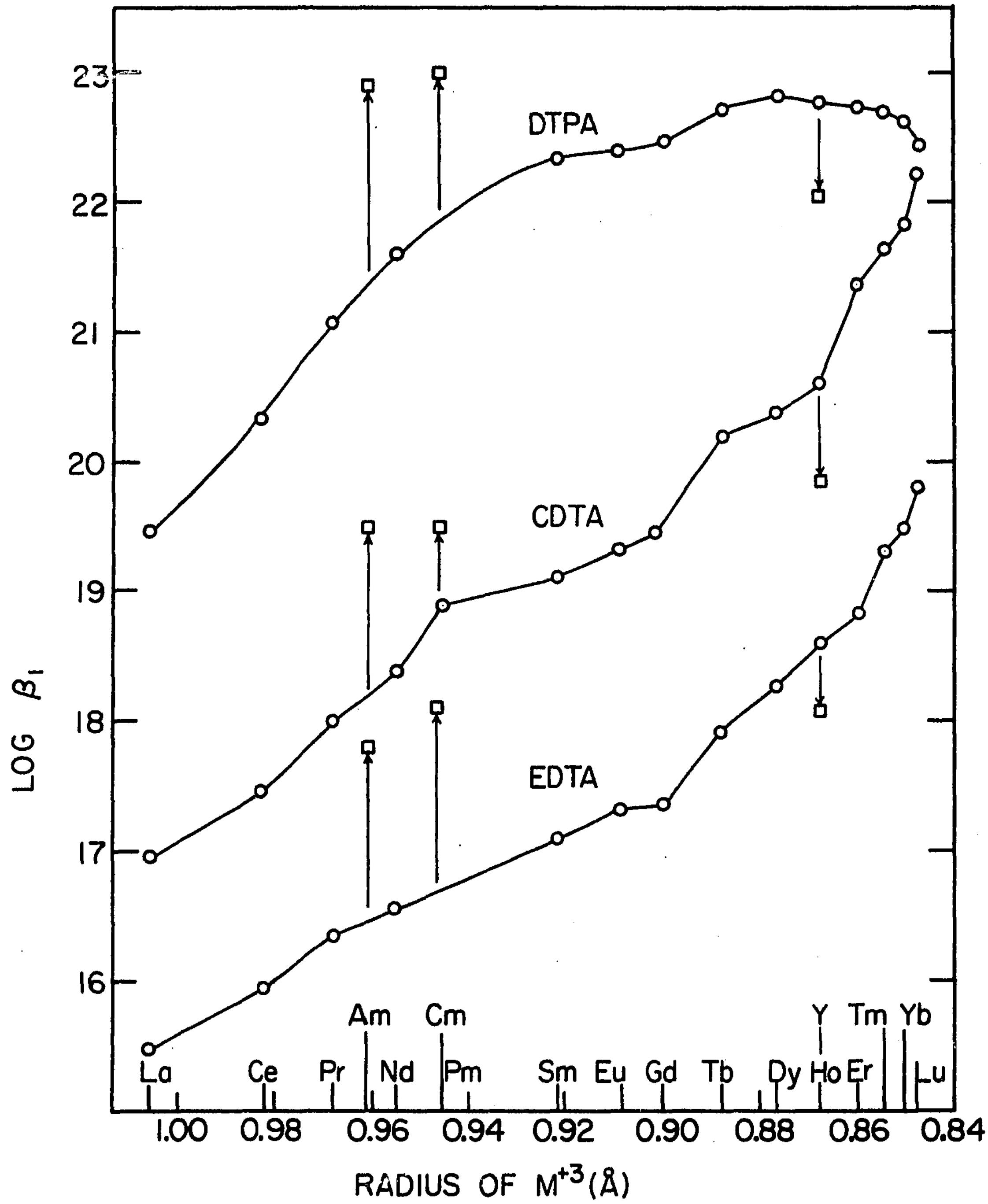


Figure 5. Stability constants of the rare-earth complexes formed by several aminocarboxylates.

the americium value to be intermediate between gadolinium and terbium. This phenomena makes a clean separation of americium from the entire lanthanide family impossible. In opposition to the monotonic trend observed in these aminocarboxylates, the maximum lanthanide stability constant for the DTPA sequence occurs at dysprosium (log K=22.82). This allows the slightly larger value of the Am-DTPA stability constant (log K=22.90) to be a sufficient basis for separation of this element from the entire lanthanide family.

DTPA has been proven by a number of workers to be a useful cation-exchange reagent for Ln-An separations. This utility is a consequence not only of the inherent Ln-Am,Cm separation factors, but also of its ability to be used in a displacement development mode. In this form of cation-exchange chromatography the mixture to be separated is eluted as a compact band by the use of a dilute complexone solution of relatively high pH, and a resin bed saturated with a retaining ion. As the elution progresses, discrete bands of pure material form, and are eluted from the resin in the order of decreasing stability of the ligand-metal complex. In the case of DTPA at 25°C one would expect the elution order to be: Cm, Am, Dy, Ho, Er, Tb, etc. Portions of this expected elution order have been observed by James, Powell, and Burkholder (51), however, no mention of Am displacement experiments employing eluents at this temperature was found. Wheelwright and Roberts (52) at Hanford, and Lowe <u>et al</u>. (53) at Savannah River, have used the DTPA displacement technique at 70°C, and pH = 6.0, for production of multigram amounts of Pm, Am, and Cm. Work at such elevated temperatures offered improved kinetics and thus lower resin requirements, although these benefits seem to have been obtained at the price of decreased selectivity. Hale and Hammer (54) reported a substantially different elution order at 70°C, pH = 6.0: Cm, (Yb, Tm, Ho, Er), Dy, Lu, Am, Tb, (Gd, Eu), Sm, Pm, Nd, Pr, Ce, La. High pressure operations with fine resin have been developed by several authors (55, 56) in an effort to improve exchange kinetics further and thus minimize radiolytic gassing and resin decomposition. Current flowsheets (57) for reprocessing consider the DTPA displacement cation-exchange technique the method of choice for Ln-Am,Cm separations.

In contrast to ligands discussed in previous sections, anion-exchange techniques utilizing DTPA have played no part in Ln-An separations. Early work done by Baybarz (57) reported that the DTPA-metal complexes did not readily sorb on anion-exchange resins. In spite of the contrast between this finding and Baybarz's later reports of strong sorption with EDTA complexes (58), little has been done to reconcile this anomaly.

The role of DTPA in solvent extraction systems has been principally one of sequestering Am and Cm in the aqueous phase, while allowing extraction of the lanthanides. Processes utilizing TBP (59, 60), DEHPA (61), or trilauryl amine (59) to extract the lanthanides preferentially from concentrated nitrate salt-DTPA solutions have been investigated. Unfortunately, these nitrate-containing systems are only marginally effective in separating the actinides from the heavy lanthanides, and are plagued with very slow kinetics (i.e. equilibrium times approaching 30 minutes for the Eu-DEHPA system).

In 1968, Weaver and Kappelman published a study (62) describing the preferential DEHPA extraction of the lanthanides from Ln-An mixtures in DTPA-carboxylic acid solutions. The substitution of carboxylic acids for the nitrate salts used in the previous systems, improved the kinetic problems associated with those techniques and retained the desired selectivity between Am and the heavy lanthanides. The significant Ln-An discrimination observed for the DEHPA-lactate-DTPA system is graphically depicted in Figure 6. The ratio of the distribution coefficients for the least extractable lanthanide, and Am and Cm, indicates a group separation factor on the order of 70. The use of lactic acid, in preference to other carboxylic acids, was suggested by the increased ability of hydroxycarboxylic acids to retard the extraction of americium (62), and due to the substantial solubility of the lactate-Ln complexes relative to those formed by other hydroxycarboxylic acids (17, p. 212). DEHPA may be replaced by 2-ethylhexylphenylphosphoric acid (62), or diisodecylphosphoric acid (63) to obtain similar separation factors with higher distribution coefficients.

The kinetics of the TALSPEAK process, as it is now commonly called, has been investigated briefly (64). The initial, and slowest step in the extraction mechanism, calls for the formation of a lactate-metal complex by displacement of the DTPA ligand:

$$\text{Ln-DTPA} + \text{lactate} \rightleftarrows \text{Ln-lactate} + \text{DTPA}.$$

The extraction is completed by the rapid reaction of two DEHPA molecules with the monolactate complex, to form the organic soluble species:

$$2\ \text{DEHPA} + \text{Ln-lactate}^{2+} \rightleftarrows \text{Ln-lactate(DEHPA)}_2 + 2H^+.$$

The reaction rate for lanthanide extraction decreases rapidly with increasing atomic number. From La to Eu, a tenfold drop in rate constant

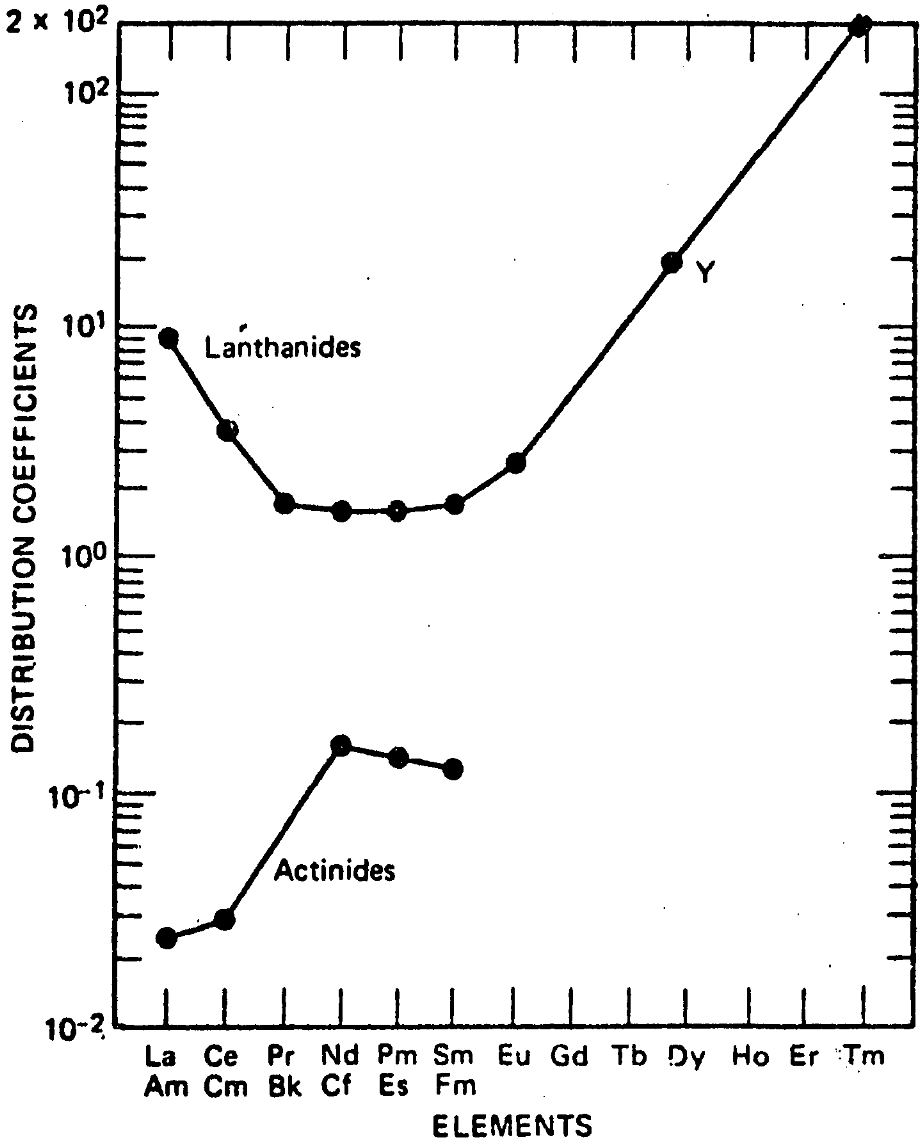


Figure 6. Extractability of lanthanides and actinides from 1 M lactic acid - 0.005 M DTPA solution at pH 2.0 by DEHPA in diisopropylbenzene.

is evident, although it is unknown whether this trend continues throughout the heavy lanthanons.

The radiation effects on TALSPEAK type extractions have recently been explored by Tachimori and Nakamura (65). Their studies of the effect of 5×10^5 rad/hr Co^{60} gamma radiation on Nd-Am separations concluded that the radiation-induced rise in the Nd and Am distribution coefficients and the decrease in the Nd-Am separation factor were both suppressed by the presence of lactic acid in the aqueous phase. The presence of nitrate ion, in contrast, enhanced both of these effects. The main chemical effect of ionizing radiation on the extraction appeared to be the production of MEHPA from DEHPA, and the destruction of DTPA, both of which are inhibited by lactic acid. The Japanese dispute the deleterious effect of MEHPA on the Ln-An separation factors reported by Fardy and Pearson (66), and claim that in doses below 200 watts/L these radiolytic effects may be ignored.

TALSPEAK and its modifications appear, at present, to be the only real challenge to the DTPA displacement development technique (67). The extraction method has not, however, been operated with actual waste feed, or at the scale necessary for reprocessing. Process problems such as those which plagued the solvent extractions systems in previous sections appear to be the rule, rather than the exception, and thus considerable investigation must be completed before TALSPEAK becomes a proven method.

Amine extractants have not been widely used in conjunction with DTPA, in fact, only two reports are to be found. In 1966, Moore (68) reported the extraction of tracer quantities of Am and Eu from 0.004 $\underline{M}$ DTPA solutions with 20% Aliquat 336 in xylene. The Am-Eu separation factors at all pH's were very poor, however, it is curious that a DTPA-metal complex could be extracted at all. No further mention of this type of DTPA extraction was found. Russian scientists have recently reported the use of DTPA and other aminocarboxylates as aqueous sequesterants for the transplutonium elements, in amine-based extraction systems from concentrated $LiNO_3$ solutions (69). The observed Am-Eu separation factor was high (8.0), but inferior to TALSPEAK, and no heavier lanthanides were investigated.

DTPA has proven itself to be an effective Ln-An separator in a variety of ion-exchange and solvent-extraction methods. Its major shortcomings appear to be kinetic in nature, arising from extreme stability of its lanthanide and actinide complexes. In addition, the general inability to extract DTPA-metal complexes, demands the rather inefficient operation of extracting the majority component of the mixture, the lanthanides, in order to separate it from a small amount of material (Am and Cm). A reverse configuration would be more desirable.

Miscellaneous

A number of reports have been published describing processes, unrelated to the previous discussions, which have shown some capability in separating Am and Cm from the lanthanides. In all cases, this work is still in a formative stage and the details are quite sketchy. These citings may, however, provide a glimpse at future possibilities for Ln-An separations.

In 1966 Sekine and Dyrssen (70) reported screening a variety of phenol-type chelating acids for possible use in separating Am and Eu by solvent extraction. In contrast to most of the chelates examined, 5,7-dichloroxine (5,7-dichloro-8-hydroxyquinoline, HDCO) was observed to extract tracer quantities of Am tenfold more effectively than Eu. Ten years later, two citings (31, 71) revived interest in HDCO and a similar compound, 5-nitroxine (5-nitro-8-hydroxyquinoline, H5NO), by reporting Ln-An separation factors of 53.7 (Am-Eu) and 4.9 (Am-Tb) for H5NO in chloroform. The extracting species was determined, by the pH dependence of the distribution coefficient, to be the neutral $M(H5NO)_3$ molecule. Americium separation factors for lanthanons heavier than Tb were not determined, although Am was assumed to extract coincidently with Dy. On this basis, a two-step solvent extraction method for separating Am from the lanthanides, was suggested. In the first step, DEHPA was proposed as an extractant to separate the light lanthanides and americium, from the heavy lanthanides. Subsequent extraction with H5NO would be used to separate americium from the lighter lanthanons. Unfortunately, the practical application of such a system is severely limited by the low acid strength of H5NO. Significant extraction with this reagent does not begin until the pH exceeds four, a value precariously close to the pH (5-6) at which hydrolysis dominates the aqueous chemistry of these trivalent cations.

Musikas et al. recently reported the ability of azide and orthophenanthroline ligands to form stronger complexes with Am than with any of the lanthanides (10). Orthophenanthroline was then incorporated in a solvent extraction system with nonanoic acid in nitrobenzene, and utilized in tracer scale Am-Eu separations. In the pH range where extraction occurred (4.5-5.0), Am was extracted approximately eighteen times more efficiently than Eu.

Some rather exotic separation techniques have been employed in the final two works to be discussed in this section. Foos and Mesplede (72) have described the preferential extraction of the lanthanides by tetraphenylbutylene disphospinate ($(C_6H_5)_2PO(CH_2)_4PO(C_6H_5)_2$) from a $LiNO_3$-KNO_3 molten salt phase at 160°C. The trivalent actinides Am, Cm, and Cf are not significantly extracted under these conditions. And, in work with inorganic sorbents, Schulz, Koenst, and Tallant (73) concluded that Am and Cm have a slightly greater affinity for $H(Ti_2O_5H)$, $H(Zr_2O_5H)$, and $H(Nb_2O_5H)$ phases than do the lanthanides they investigated (La, Pm, Gd, Eu). The separation factors are small (1.2), and problems relating to concentration and kinetic effects appear to be formidable.

Traits Apparent in Effective Ln-An Separation Agents

If one attempts to generalize the characteristics common to the ligands successful in Ln-An separations, two traits emerge. First, all successful ligands exhibit a lanthanide stability constant sequence which attains its maximum value in the mid-lanthanon range. This is apparent in the maximum extractibility of the europium complex for TRAMEX, in the maximum thiocyanate (3 M) anion-exchange distribution coefficient with $Eu(SCN)_4^-$, and in the minimum TALSPEAK extraction of Nd, Pm, and Sm from DTPA solutions. Since a maximum in the lanthanide stability constant sequence is seldom observed before Eu, the second characteristic necessary to a useful ligand is the maximization of the increased relative stability of actinide complexes discussed earlier. It follows that the desired separations are only possible when, by shifting the Ln stability maximum toward the lighter lanthanons and maximizing the actinide complex strength relative to its radius, the ligand affinity for Am and Cm is allowed to rise above that of all the lanthanides. The following sections of this dissertation describe the investigation of several ligands which exhibit some measure of these desired characteristics.

PART I. THE AQUEOUS COORDINATION CHEMISTRY OF 2,3-DIHYDROXY-2,3-DIMETHYLBUTANOATE WITH THE TRIVALENT LANTHANIDES, AMERICIUM AND YTTRIUM

INTRODUCTION

Hydroxycarboxylic acids are well known for their applicability as eluents in cation-exchange processes. Aliphatic monoprotic hydroxyacids (i.e., α-hydroxyisobutyric acid) have been especially valuable in the intragroup fractionation of the lanthanide and actinide elements (74). The utility of these reagents has, unfortunately, not extended into the An-Ln separation problem described earlier. Actinide and lanthanide hydroxyacid complexes exhibit a continuous rise in stability across these series, similar to that displayed by EDTA and CDTA. Analogous to the behavior of those aminocarboxylates, the hydroxyacids also intersperse the trivalent actinides within the lanthanide elution sequence, making the reagents worthless for An-Ln group separations (74).

In 1975 Powell, Farrell, and Kulprathipanja (75) reported the anomalous lanthanide stability sequences of the 2,3-dihydroxy-2-methylpropanoato (DHMP) and 2,3-dihyroxy-2-methylbutanoato (DHMB) chelate species. As can be seen in Figure 7, the K_1 values of the dihydroxy acid chelates did not exhibit the monotonic increase displayed by the 2-hydroxy-2-methylbutanoato (HMB) species (75). The first formation constants of the dihydroxycarboxylate complexes revealed an increase in stability from lanthanum to samarium and a subsequent decrease from europium to terbium or dysprosium, followed by an increase throughout the rest of the series. An explanation for this behavior was presented in terms of a gradual change from tridentate ligandcy, involving both hydroxyl groups and a carboxylate oxygen atom, to a bidentate chelation incorporating the 2-hydroxyl group and a carboxylate oxygen. This

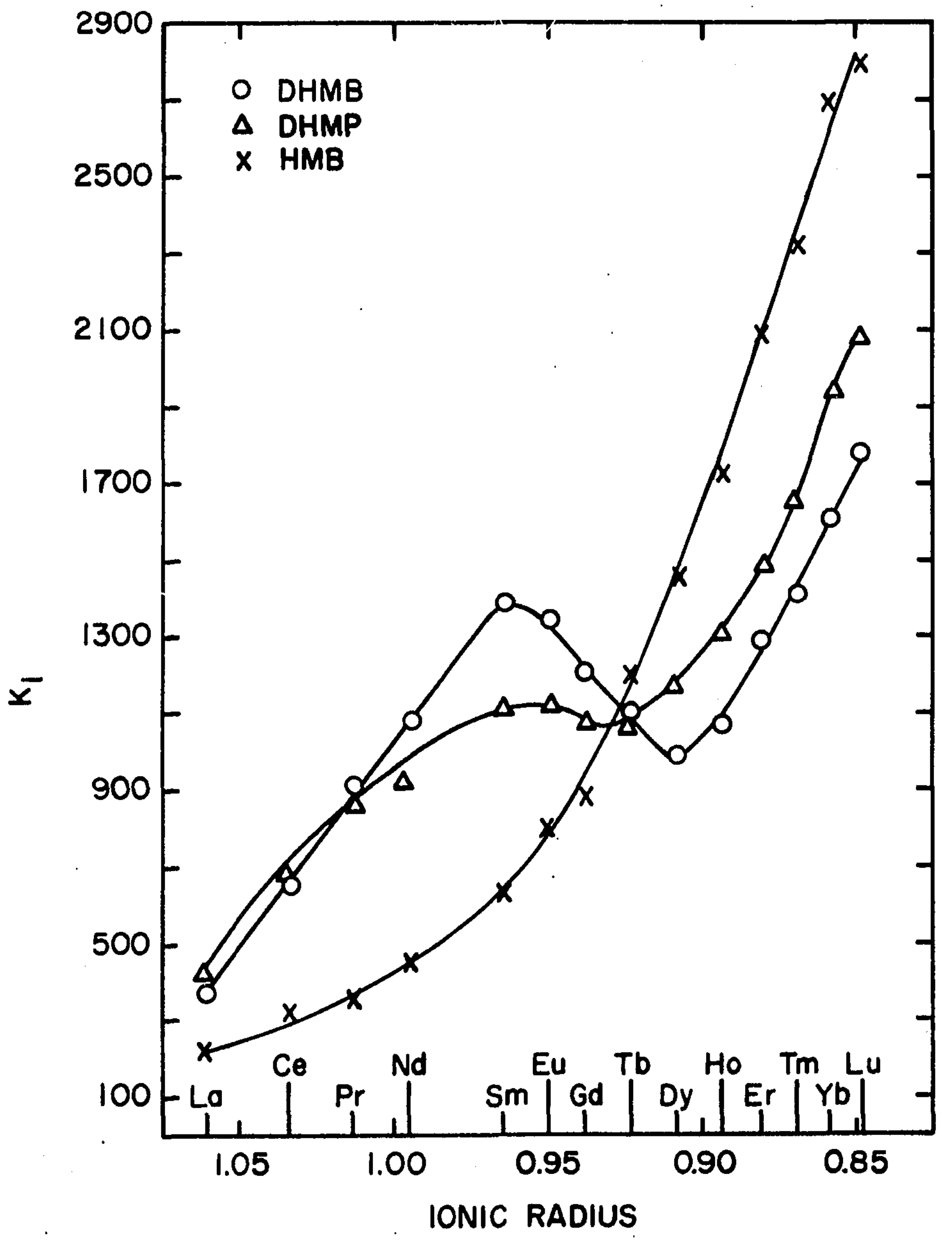


Figure 7. K_1 values of the 1:1 lanthanide chelate species formed by several hydroxycarboxylates.

transition in chelation mode was felt to be indicative of a change in lanthanide coordination number similar to that observed by other authors (76, 77).

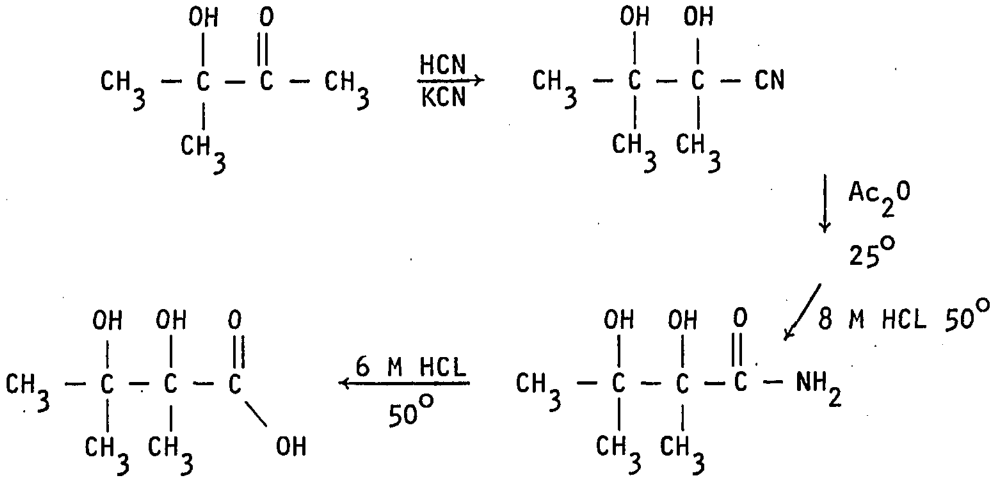
Taga et al. (78) has also recently reported experiments which display the importance of the 3-hydroxyl group in the chelation properties of a similar dihydroxycarboxylic acid, 2,3-dihyroxypropanoic acid (glyceric acid). He proposed tridentate behavior in the aqueous 1:1 europium(III) glycerate complex, based on calculations describing the lanthanoid induced ^{1}H NMR shifts. These calculations indicated that the 3-hydroxyl oxygen atom is more tightly held than the 2-hydroxyl oxygen atom (2.33 Å vs 2.42 Å).

The appearance of the relative maximum observed at samarium or europium in the dihydroxycarboxylate stability sequences was encouraging in its similarity to the curve shape exhibited by the known effective An-Ln separation agents. In addition, the effect was enhanced by increased methyl substitution of the three position carbon atom. Comparison of the DHMB curve with that of DHMP revealed a shift of the relative maximum from europium back to samarium, and an increase in the magnitude of this maximum with respect to the heavy lanthanides. These phenomena motivated the investigation of the complex stabilities and An-Ln separation chemistry of the 2,3-dihydroxy-2,3-dimethylbutanoate chelates.

EXPERIMENTAL

2,3-dihydroxy-2,3-dimethylbutanoic Acid

The 2,3-dihydroxy-2,3-dimethylbutanoic acid (DHDMB) was first synthesized by Powell *et al*. (79) using the following route:



The acid, kindly provided by the above, had been purified by ion exclusion on beds of hydrogen cycle, Dowex 50W-X8 cation-exchange resin, followed by sorption on an acetate form anion exchanger, displacement by 0.25 *M* HCL, and recrystallization from chloroform. The purified DHDMB exhibited an equivalent weight of 148.95 ($C_6H_{12}O_4$ = 148.16), and melted between 102-104°C. The carbon, hydrogen and oxygen weight percents: C, 48.4; H, 8.3; O, 43.3, closely matched those calculated for $C_6H_{12}O_4$: C, 48.64; H, 8.16; O, 43.20.

Reagents

Trivalent rare-earth nitrate solutions

Approximately 0.1 *M* rare-earth nitrate solutions were prepared by dilution of available stock solutions. These concentrated solutions had, in turn, been prepared from the corresponding oxides by Mr. James Farrell, using the method described by Adolphson (80). The dilute metal nitrate solutions were standardized either by a gravimetric technique in which the metal was precipitated as the oxalate, and ashed to the oxide, or by complexometric titration with EDTA, using xylenol orange as an indicator (81).

Potassium hydroxide solutions

Various standard potassium hydroxide solutions utilized throughout this work were prepared by dilution of ampoules of carbonate-free KOH (Anachemia) with boiled distilled water. The resulting solutions were standardized by repeated titrations of primary standard grade potassium acid phthalate and protected from CO_2 by an Ascarite/Drierite trap.

Potassium nitrate solution

The approximately 1.0 $\underline{M}$ solution of potassium nitrate, used for ionic strength adjustment, was prepared by dissolution of reagent grade KNO_3 in boiled distilled water. This salt solution was then standardized by passing aliquots through a well-washed, hydrogen-form, cation exchanger (Dowex 50) and titrating the resulting acid washings with standard base.

Nitric acid solutions

The nitric acid solutions were prepared from reagent grade HNO_3 and standardized by titration with standard base.

DHDMB buffer solutions

Buffer solutions utilized in the anion protonation constant and complex formation constant determinations were prepared by dissolving a weighed amount of purified DHDMB sufficient to produce an approximately 0.1 M solution. Standard potassium hydroxide was then added to produce the desired anion concentration. The remaining free acid concentration was confirmed by titration of aliquots of the buffer solution with standard base.

DHDMB eluents

Eluents used in the ion-exchange experiments were prepared by dissolution of the necessary amount of purified DHDMB to produce a 0.4 M solution. The pH of these eluents was adjusted to the desired value by the dropwise addition of concentrated NH_4OH.

^{241}Am nitrate solution

Approximately one millicurie of americium nitrate ($t_{\frac{1}{2}}$ = 458 yr) was purchased from New England Nuclear and received on 4/24/79. Convenient specific activities for the tracer-scale ion-exchange experiments were produced by dilution of the received sample to one milliliter, and subsequent dilution of a 100 μl aliquot of this primary stock solution in a 10 ml volumetric flask. These dilutions, which were kindly and expertly executed by Mr. Ken Malaby, produced an activity of approximately 10 μCi/ml. The remaining primary stock solution is presently stored in the Ames Laboratory hot canyon.

^{155}Eu nitrate solution

Approximately one millicurie of europium nitrate ($t_{\frac{1}{2}}$ = 1.81 yr) was purchased from New England Nuclear and received on 4/24/79. A 10 μCi/ml solution was produced in a fashion analogous to that described for the americium solution. The remaining stock solution of ^{155}europium is also presently stored in the Ames Laboratory hot canyon.

Liquid scintillation cocktail

The dioxane-based scintillation cocktail used in counting the ion-exchange effluent was a "Bray's Solution" purchased from New England Nuclear.

DHDMB Anion Protonation Constant

Knowledge of the DHDMB anion protonation constant (α = [HA]/[H][A]) is a prerequisite to the investigation of the DHDMB-metal complex formation equilibria. This constant, which described the equilibrium

$$H^+ + A^- \rightleftarrows HA$$

was obtained from pH_c measurements on a series of independently prepared DHDMB solutions, each containing a different amount of the DHDMB buffer stock solution. These solutions were adjusted to 0.1 $\underline{M}$ ionic strength by the addition of appropriate amounts of KNO_3 which were calculated from an estimated protonation constant value, using the iterative computer program ALFA (87). To insure attainment of equilibrium, the DHDMB solutions were conditioned in a water bath, thermostatted to 25.00 ± .05°C, for at least twelve hours prior to measurement.

The pH_c measurements were accomplished by the use of a Corning Model 101 Digital Electrometer equipped with a Beckman glass electrode, a Beckman sleeve-type reference electrode, and a platinum solution ground. This electrode arrangement was placed inside a closed thermostatted vessel with provisions for the introduction and removal of the sample, and a protective nitrogen atmosphere. The system was calibrated and sloped by utilizing a series of standard HNO_3 solutions adjusted to 0.1 M ionic strength. Standardization of the instrument in this fashion results in the determination of the hydrogen ion concentration rather than its activity. Each sample was measured repeatedly until stable values were obtained.

Rare Earth-DHDMB Complex Stability Constants

The first, second, and third formation constants for the DHDMB anion and the trivalent cations of the lanthanides and yttrium were determined from pH_c measurements of solutions containing fixed amounts of metal and variable amounts of the DHDMB buffer stock. The solutions were also adjusted to 0.1 M ionic strength by the addition of the required amounts of KNO_3. These amounts were, in turn, calculated from estimated stability constant values, by using the computer program BETA (82). Equilibration and measurement of the pH_c values for the metal-buffer solutions was done as described previously for the DHDMB anion protonation constant determination. The stability constants were calculated using a multiple linear regression scheme incorporated into the computer program OMEGA (82). The equations underlying this method are discussed in a subsequent section.

Tracer Cation-Exchange Experiments

Cation-exchange experiments incorporating tracer-level ^{241}Am and ^{155}Eu were performed to determine the feasibility of An-Ln separations with DHDMB. An Altex 2 mm X 500 mm chromatograph column, septum injection port, and Teflon tubing and fittings were all purchased from

Ranin Corporation. The injection port was attached directly to the top of the column and surrounded by a spill guard. Analytical grade Dowex 50W-8 200-400 mesh was employed as the cation-exchange resin. The effluent collection was achieved using a drop-counting type Packard sample collector which was modified to accept scintillation vials.

Prior to injection of the tracers, the cation exchanger was equilibrated by passing at least ten column volumes of eluent through the column. The scintillation vials used for sample collection were then filled with 10 ml aliquots of the scintillation cocktail, and loaded into the sample collector. The column, photometric drop counter, and turntable were aligned to insure the successful collection of all of the effluent.

The tracer mixture injected onto the cation exchanger was prepared by pipetting 10 $\mu\ell$ each of the tracer stock solutions onto an indented glass slide. The individual drops were mixed together with the point of the injection syringe, drawn into the syringe, and injected through the septum injector onto the top of the column. The eluent pump was then started (flow rate = 3 drops/min) and sample collection was begun. Seventy-five ten-drop samples were collected and counted by the liquid scintillation technique.

Although the liquid scintillation counting technique is not widely used for discriminative counting of heavy isotopes, a recent reference involving the detection of americium and plutonium in biological samples indicated that this technique might be feasible for counting the effluent (83). Figure 8 displays the scintillation spectrum observed for ^{155}Eu and ^{241}Am on the Beckman liquid scintillation counter kindly made

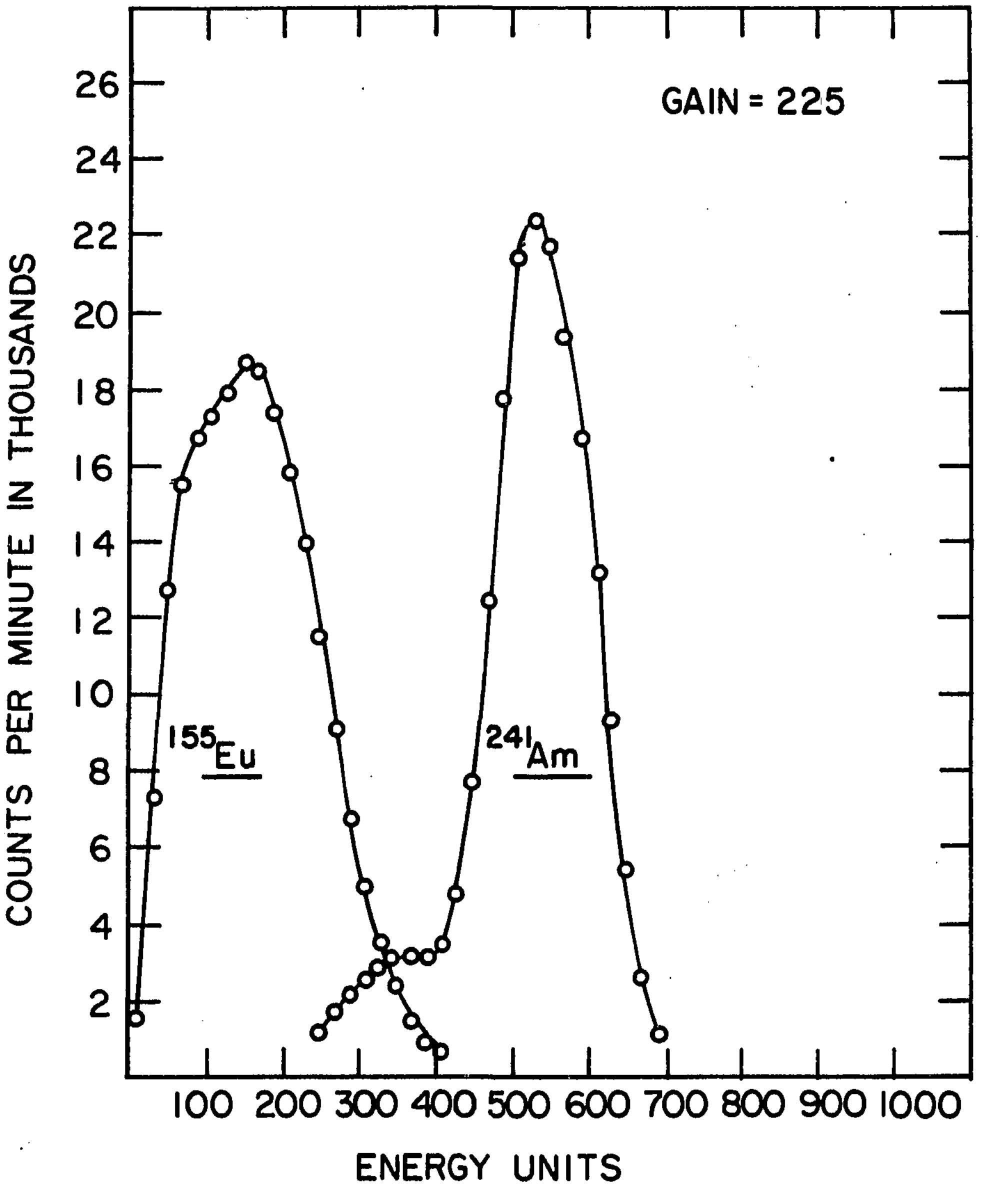


Figure 8. Liquid scintillation spectra of ^{155}Eu and ^{241}Am.

available by the Health Physics group. This spectrum clearly shows the feasibility of discriminating between ^{155}Eu (0-250 energy units) and ^{241}Am (400-700 energy units) at a gain setting of 225. The window settings used in counting the ion-exchange experiments utilized these values.

All radiochemical manipulations were conducted in a spill tray covered with absorbent paper. Gloves and a film badge were worn at all times. Numerous surveys for contamination were made both by the author and by the Health Physics group. Thanks to careful experimentation, and the advice and encouragement of Mr. Bob Staggs, no such problems arose.

Calculations

This section of the dissertation introduces the mathematical methods by which the DHDMB anion protonation constant and the DHDMB-rare earth complex stability constants were calculated. The computer programs which incorporate these principles were developed by previous members of this research group (82). The following mathematical methods are discussed both for the sake of completeness and for comparison to a method developed in a subsequent section.

DHDMB anion protonation constant

The equilibrium defining the affinity of the DHDMB anion (A) for protons is conveniently written:

$$H + A \rightleftarrows HA.$$

The equilibrium constant for this formulation is commonly called α, where $\alpha = [HA]/[H][A]$. The determination of α is performed by measuring the pH_c values of solutions of known stoichiometry which contain partially neutralized DHDMB acid. The mass balance equations for these solutions are:

total titratable hydrogen

$$H_t = [H] + [HA]$$
$$= [H] + \alpha[H][A]$$

total anion

$$A_t = [A] + [HA]$$
$$= [A] + \alpha[H][A].$$

The ratio of these two equations eliminates the [A] term and, after rearrangement, allows the direct computation of the protonation constant from the relation:

$$\alpha = ([H] - H_t)/(H_t - [H] - A_t)[H].$$

Rare earth-DHDMB stability constants

The equilibria which describe the formation of the DHDMB-rare earth complexes may be viewed as one of two different sets of simultaneous reactions. The first set:

$$M + A \rightleftarrows MA$$
$$MA + A \rightleftarrows MA_2$$
$$MA_2 + A \rightleftarrows MA_3$$

is described by the equilibrium constants:

$$K_1 = [MA]/[M][A]$$
$$K_2 = [MA_2]/[MA][A]$$

$$K_3 = [MA_3]/[MA_2][A].$$

The second set of equilibria which may be used to describe the system consists of the reactions:

$$M + A \rightleftarrows MA$$
$$M + 2A \rightleftarrows MA_2$$
$$M + 3A \rightleftarrows MA_3.$$

These reactions are, in turn, described by the equilibrium constants:

$$\beta_1 = [MA]/[M][A]$$
$$\beta_2 = [MA_2]/[M][A]^2$$
$$\beta_3 = [MA_3]/[M][A]^3.$$

It is not difficult to show that the equilibrium constants defining the two sets are related by:

$$\beta_N = \pi_1^N K_N.$$

The overall stability constants (β_1, β_2, and β_3) allow a more compact computational formation of the simultaneous equilibria. The stepwise stability constants (K_1, K_2, and K_3) are usually more helpful in conceptualizing the chemistry of the complex formation.

The mass balances necessary for the computation of β_1, β_2, and β_3 are:

$$A_t = [A] + [HA] + [MA] + 2[MA_2] + 3[MA_3]$$

and

$$M_t = [M] + [MA] + [MA_2] + [MA_3].$$

Equivalently,

$$A_t = [A] + \alpha[H][A] + \beta_1[M][A] + 2\beta_2[M][A]^2 + 3\beta_3[M][A]^3$$

and

$$M_t = [M] + \beta_1[M][A] + \beta_2[M][A]^2 + \beta_3[M][A]^3.$$

Since the individual terms of the ligand and metal mass balances are separable in terms of [H] and [M], rearrangement of the ligand balance and division by the metal balance results in a formulation independent of [M]:

$$\frac{A_t - [A] - \alpha[H][A]}{M_t} = \frac{\sum_{x=1}^{3} x\ \beta_x[A]^x}{1 + \sum_{x=1}^{3} \beta_x[A]^x} .$$

Cross multiplication and simplification yields:

$$[A] + \alpha[H][A] - A_t = \sum_{x=1}^{3} (A_t - [A] - \alpha[H][A] - XM_t)[A]^x\ \beta_x$$

which is of the form

$$Y = J_1\beta_1 + J_2\beta_2 + J_3\beta_3.$$

Since [H] is measured and [A] can be calculated from the relation $[A] = (H_t - [H])/\alpha[H]$, the values of Y, J_1, J_2, and J_3 are known for each solution. Knowledge of three such data sets would allow an algebraic solution of the system for β_1, β_2, and β_3.

In practice more than three solutions are measured, and the then overspecified system of equations is solved using a least-squares multiple linear regression. This regression, as described by Draper and Smith (84) and implemented in the OMEGA program by J. H. Miller (82), proceeds by minimizing the sum of the squares of the residuals ε_i. By definition the residual of the ith observation is:

$$\varepsilon_i = Y_i - (J_{1i}\beta_1 + J_{2i}\beta_2 + J_{3i}\beta_3).$$

The sum of the squares of these residuals is minimized by setting the partial derivatives with respect to each β_x equal to zero. Thus:

$$s = \Sigma\, \varepsilon_i^{\,2} = \Sigma\, (Y_i - \beta_1 J_{1i} - \beta_2 J_{2i} - \beta_3 J_{3i})^2$$

$$\frac{\delta s}{\delta \beta_1} = -2\, \Sigma\, J_{1i}(Y_i - \beta_1 J_{1i} - \beta_2 J_{2i} - \beta_3 J_{3i}) = 0$$

$$\frac{\delta s}{\delta \beta_2} = -2\, \Sigma\, J_{2i}(Y_i - \beta_1 J_{1i} - \beta_2 J_{2i} - \beta_3 J_{3i}) = 0$$

$$\frac{\delta s}{\delta \beta_3} = -2\, \Sigma\, J_{3i}(Y_i - \beta_1 J_{1i} - \beta_2 J_{2i} - \beta_3 J_{3i}) = 0.$$

Collecting terms yields:

$$\Sigma\, \beta_1 J_{1i}^{\,2} + \Sigma\, \beta_2 J_{1i} J_{2i} + \Sigma\, \beta_3 J_{1i} J_{3i} = \Sigma\, J_{1i} Y_i$$

$$\Sigma\, \beta_1 J_{2i} J_{1i} + \Sigma\, \beta_2 J_{2i}^{\,2} + \Sigma\, \beta_3 J_{2i} J_{3i} = \Sigma\, J_{2i} Y_i$$

$$\Sigma\, \beta_1 J_{3i} J_{1i} + \Sigma\, \beta_2 J_{3i} J_{2i} + \Sigma\, \beta_3 J_{3i}^{\,2} = \Sigma\, J_{3i} Y_i.$$

In matrix form:

$$\begin{vmatrix} \Sigma\, J_{1i}^{\,2} & \Sigma\, J_{1i} J_{2i} & \Sigma\, J_{1i} J_{3i} \\ \Sigma\, J_{1i} J_{2i} & \Sigma\, J_{2i}^{\,2} & \Sigma\, J_{2i} J_{3i} \\ \Sigma\, J_{1i} J_{3i} & \Sigma\, J_{2i} J_{3i} & \Sigma\, J_{3i}^{\,2} \end{vmatrix} \begin{vmatrix} \beta_1 \\ \beta_2 \\ \beta_2 \end{vmatrix} = \begin{vmatrix} \Sigma\, J_{1i} Y_i \\ \Sigma\, J_{2i} Y_i \\ \Sigma\, J_{3i} Y_i \end{vmatrix} .$$

Matrix equations of this form are easily solvable for β_1, β_2, and β_3 by using the Gaussian elimination subroutine DGELG, available at the Iowa State University Computation Center.

In an effort to allow for differences in the inherent error of the individual solution stoichiometries, the regression is weighted relative to A_t, [A], and M_t. The weighting factors are calculated from:

$$w_i = 1/\delta_i^{\,2}$$

where δ_i, the standard error, is given by:

$$q_i = \frac{\delta\varepsilon_i}{\delta A_t} q'_{A_t} + \frac{\delta\varepsilon_i}{\delta[A]} q'_{[A]} + \frac{\delta\varepsilon_i}{\delta M_t} q'_{M_t}$$

$$q'_c = \frac{\sigma_c}{C} C \quad (C = A_t,\ [A],\ M_t).$$

The variable σ_c is the standard deviation of c, and the quotient σ_c/C is the calculated average relative error in c. Since the values of β_1, β_2, and β_3 appear in the partial derivitives, an iterative scheme is used in which assumed values of β_1, β_2, and β_3 are used to calculate the w_i values which are, in turn, used to calculate new values for β_1, β_2, and β_3.

RESULTS AND DISCUSSION

The Protonation and Rare-Earth Complex Formation Constants

The protonation and rare-earth complex formation constants of the DHDMB anion were calculated from the data in Appendix A. The value obtained for the DHDMB anion protonation constant, α, was 2.44×10^3. This result can also be expressed in a more familiar manner by taking the inverse of α, and thus obtaining the acid dissociation constant, K_a, of the DHDMB acid. The resulting value is 4.10×10^{-4}.

The individual step formation constants computed for the 1:1, 2:1, and 3:1 DHDMB-rare earth chelates are given in Table 2. These values are the results of the three parameter multiple linear regression procedure described previously.

The plot of log K_1 vs crystal ionic radius is given in Figure 9 for the lanthanide DHMP, DHMB, and DHDMB complexes. The change in dentate character observed for DHMP and DHMB is again evident in the DHDMB 1:1 chelate series. It is also apparent that the inductive effect of an additional methyl group in the 3 position has resulted in a significant increase in the first formation constant of the DHDMB complexes compared to those formed by DHMB. The magnitude of this increase underscores the importance of the coordination of the lanthanide ion by the, now more electron-rich, 3-hydroxyl group. Further evidence of the strength of this bond is found by comparison of the log K_1 values in the region from terbium to lutetium. It was previously proposed that the decreased value of K_1 for DHMB with respect to DHMP in this region was due to steric effects which arose from a transition from tridentate to bidentate (75)

Table 2. Formation constants of rare-earth DHDMBA chelate species (25°; I = 0.1).

Cation	K_1	K_2	K_3	K_1/K_2	log K_1
Y^{3+}	1510[a]	196[a]	51[a]	7.7	3.18
La^{3+}	652	71	4	9.2	2.81
Ce^{3+}	1190	88	16	13.5	3.08
Pr^{3+}	1720	126	13	13.6	3.24
Nd^{3+}	2350	160	21	14.7	3.37
Pm^{3+}					
Sm^{3+}	3280	271	22	12.1	3.52
Eu^{3+}	3110	286	55	10.9	3.49
Gd^{3+}	2660	345	53	7.7	3.42
Tb^{3+}	2020	368	35	5.5	3.31
Dy^{3+}	2000	390	41	5.1	3.30
Ho^{3+}	2130	317	59	6.7	3.33
Er^{3+}	2400	275	55	8.7	3.38
Tm^{3+}	2780	204	65	13.6	3.44
Yb^{3+}	3160	257	16	12.3	3.50
Lu^{3+}	3790	293	20	12.9	3.58

[a] The listed K_1 values are estimated to be reliable to ± 2% of the value reported; K_2 to ± 5%; K_3 to ± 20%.

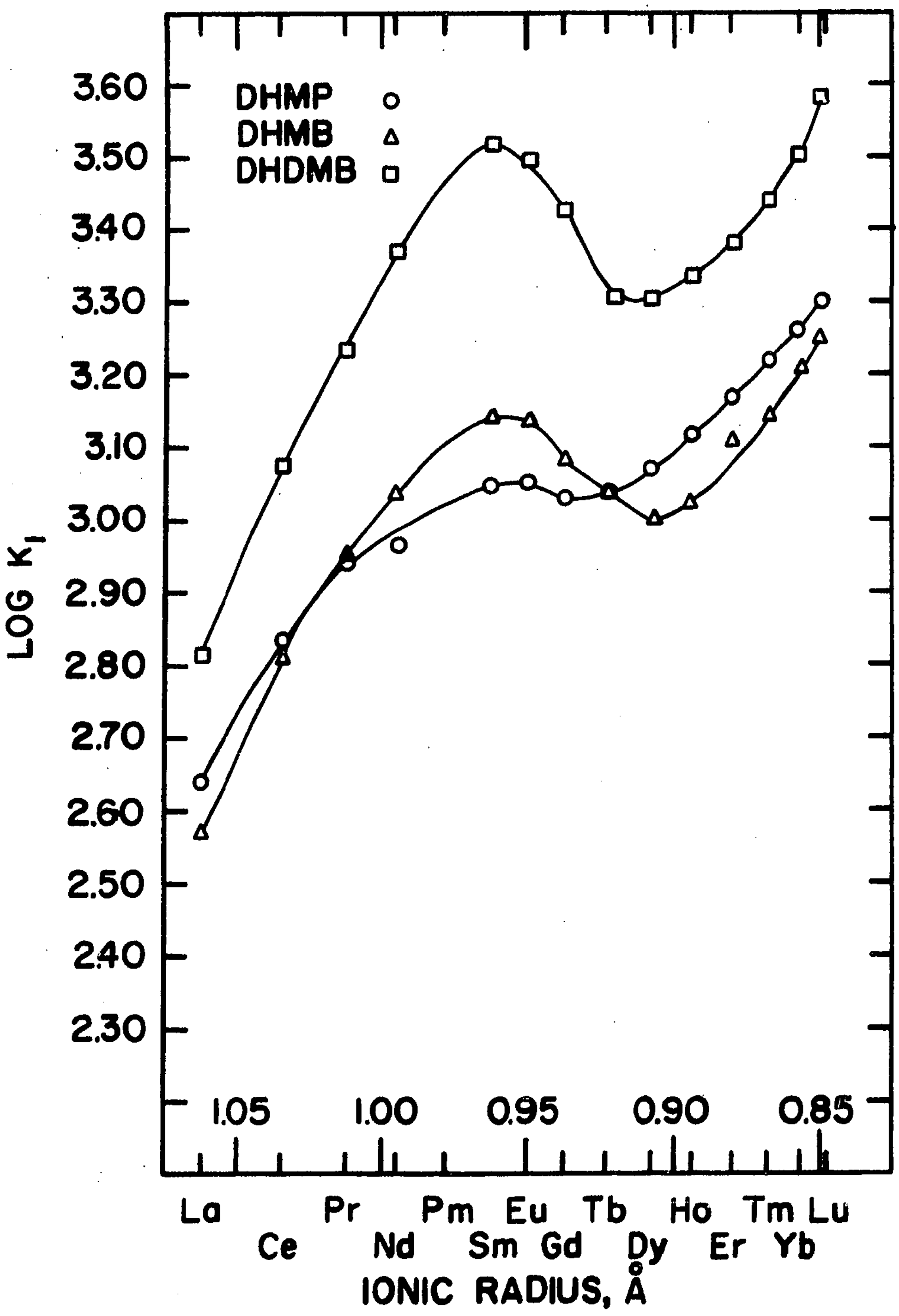


Figure 9. Log K_1 values for the 1:1 lanthanide chelate species formed with several dihydroxycarboxylates.

coordination. This transition freed the 3-hydroxyl group producing an adverse steric effect which increased with the size of the uncoordinated part of the ligand and attenuated the coordinative power of DHMB as compared to DHMP. Continuing along this line of reasoning, one would expect the K_1 values for DHDMB in this region to be even smaller than those for DHMB as a result of the increased substitution at the 3 position. This behavior was not observed, in fact, the K_1 values obtained were considerably higher than with either of the previous dihydroxyacids investigated. The explanation for these unexpected results lies in the strong coordination of the dimethyl substituted 3-hydroxyl group. In the previous cases involving bidentate behavior of DHMP and DHMB, the coordination of the 2-hydroxyl group was favored over that of the 3-hydroxyl group due to its proximity (formation of a five-membered ring) and the equal or greater substitution of the 2-position by electron donating methyl groups. This is no longer the case for DHDMB in which the 3 position has two methyl substituents. Molecular models also reveal that a transition from tridentate coordination to a "3-hydroxyl bidentate" situation could easily be accomplished, without disruption of the 3-hydroxyl-lanthanide bond or increased steric hindrance, by a simple rotation of the 2-hydroxyl group around the carbon chain. The resulting coordination of the 3-hydroxyl group and one carboxylate oxygen would prevent an adverse steric effect and thus explain the present observations.

Similar transitions in coordinative behavior are evident in the graph of K_2 values for DHMP, DHMB, and DHDMB shown in Figure 10. In the region from lanthanum to neodymium all three dihydroxyacids follow a trend

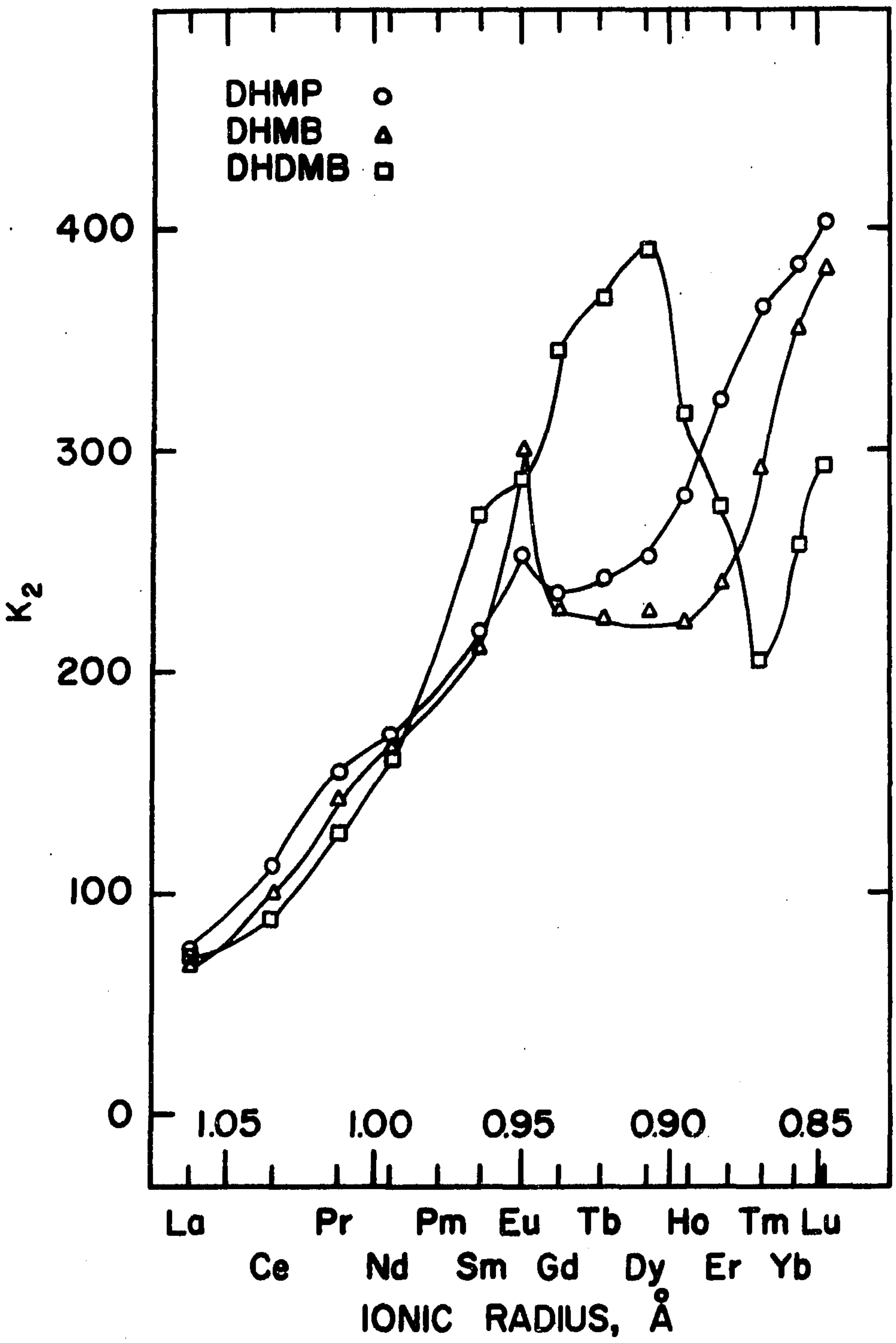


Figure 10. K_2 values for the 2:1 lanthanide chelate species formed with several dihydroxycarboxylates.

of slightly decreased K_2 value with increased methyl substitution, indicating some adverse steric effect. The coordination with these lanthanons is probably best characterized as tridentate, however the 3-hydroxyl group must not be exceptionally strongly bound compared to the steric effect experienced. Between samarium and dysprosium a marked increase in K_2 is seen for DHDMB contrasting with the behavior of the other two acids. This signals a significant increase in the bonding of the 3-hydroxyl group, and stands in opposition to the trend established in which the DHMP K_2 values were greater than those observed for DHMB. It is noted that the K_1/K_2 ratio for DHDMB steadily decreases in this region while K_2 steadily increases, indicating a growing similarity in bonding between the first complexed ligand and the second. This relationship is reiterated by the coincident positions of the K_1 curve minimum and the K_2 curve maximum at dysprosium. These factors are fully accounted for by a gradual change from tridentate to a "3-hydroxylbidentate" behavior which finds its most favorable radius at dysprosium.

If the second coordinated DHDMB ligand were to remain complexed in a "3-hydroxyl bidentate" fashion throughout the rest of the lanthanide series, one would expect a monotonic increase in K_2 values corresponding to the increased polarizing power of the lanthanide ion resulting from the successive contraction in cationic radius. The observed results show a decrease in K_2 from a maximum at dysprosium to a minimum at thulium, and a subsequent increase through lutetium. This might be viewed as a second transition in coordination, resulting from the increased steric hindrance caused by the shrinking lanthanide ion radius. If this transition was from a "3-hydroxyl bidentate" coordination mode to a "2-hydroxyl bidentate" mode, one would expect a decrease in K_2 value with increasing β-methyl substitution due to an adverse steric effect of this now uncoordinated part of the ligand. Scrutiny of Figure 10 reveals that this is indeed the case in the region from thulium to lutetium where the trend in K_2 values is clearly DHMP > DHMB > DHDMB.

Finally, it is interesting to note the continuing "abnormal" trend in the acid dissociation constants of the dihydroxyacids in Table 3.

Table 3. Acid dissociation constants at 25°C. I = 0.1 (unless otherwise indicated).

Acid	K_a	Ref.
2.3-dihydroxypropanoic (0.2 M)	3.02×10^{-4}	85
2,3-dihydroxy-2-methylpropanoic	2.65×10^{-4}	75
2,3-dihydroxy-2-methylbutanoic	3.06×10^{-4}	75
2,3-dihydroxy-2,3-dimethylbutanoic	4.10×10^{-4}	this work

The inductive effect of methyl substitution at the alpha position produces the expected decrease in acid strength of 2,3-dihydroxypropanoic acid (glyceric acid) compared with that of DHMP. The subsequent acids, however, show a striking and unexpected increase in K_a with increased β-methyl substitution. (DHMP < DHMB < DHDMB) This trend may reflect a combination of two phenomena. First, the increased substitution of the ligand may increase the propensity for disruption of the carboxylate H-O bond by a steric interaction (collision). Secondly, the increased electron donating ability of the hydroxyl groups may effectively draw the proton away from the carboxylate function whereupon it can more easily solvated by water molecules.

^{241}Am - ^{155}Eu DHDMB Cation-Exchange Elutions

The chromatograms obtained using eluents of 0.4 M DHDMB at pH's of 3.49 and 3.97 are shown in Figures 11 and 12. While the chromatographic and counting techniques are quite successful, the elution order observed for the Am-Eu pair was disappointing. It had been hoped that DHDMB would elute americium before europium and thus show some capacity for separating americium from both the light and middle lanthanides. This is not the case. If it is assumed that the elution is controlled by the formation of a 3:1 DHDMB-metal species, the observed separation factors of 1.4 and 1.7 would indicate a β_3 value for americium which is intermediate between that of samarium and europium. From this position one may conclude that while the radius sensitive aspects of DHDMB provide a lanthanide stability maximum in the desired region, the ligand does not enhance the americium complex stability enough to surpass the stability observed with cations in the mid-lanthanon range.

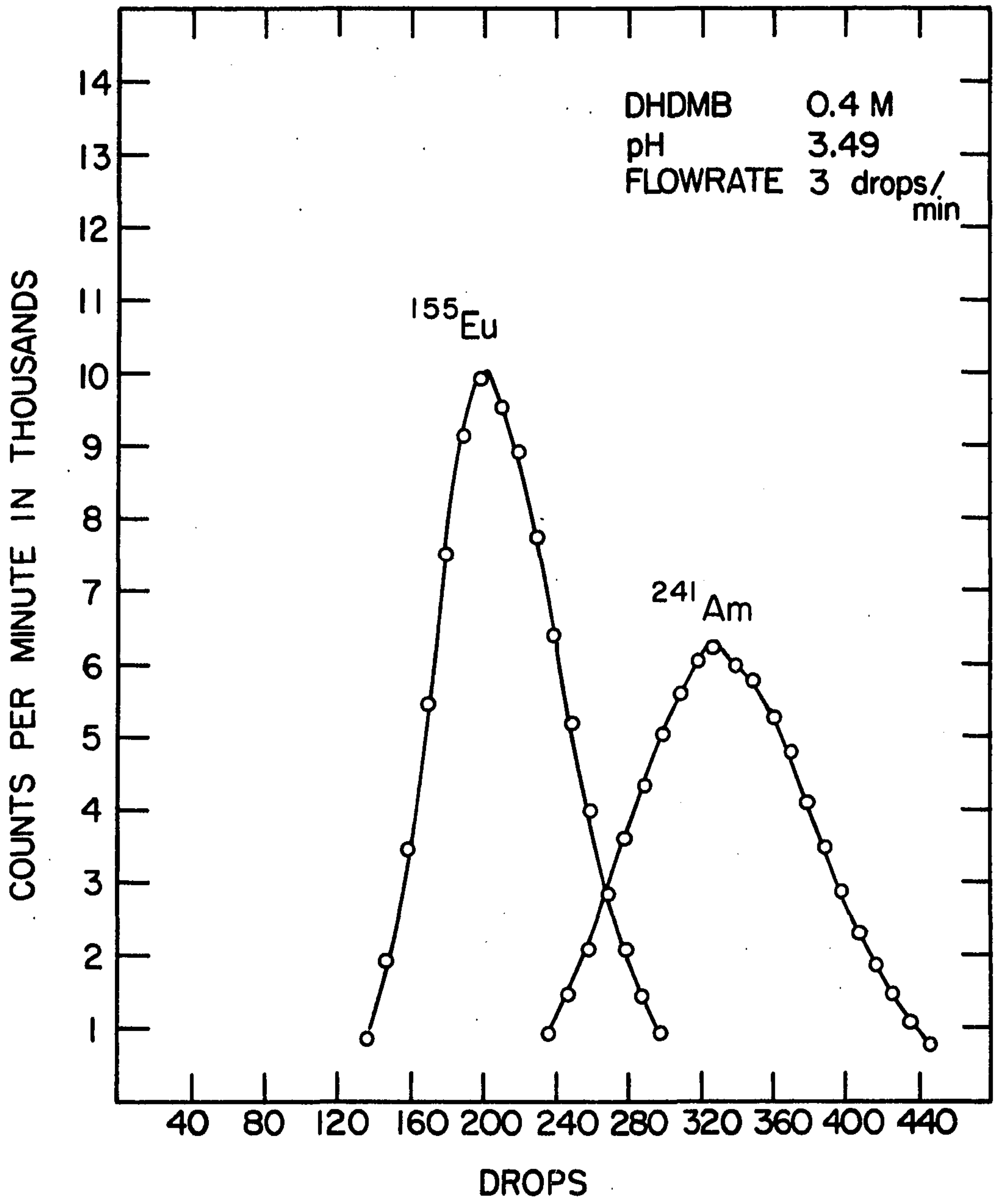


Figure 11. Cation-exchange elution of a ^{155}Eu - ^{241}Am mixture by DHDMB solution, pH = 3.49.

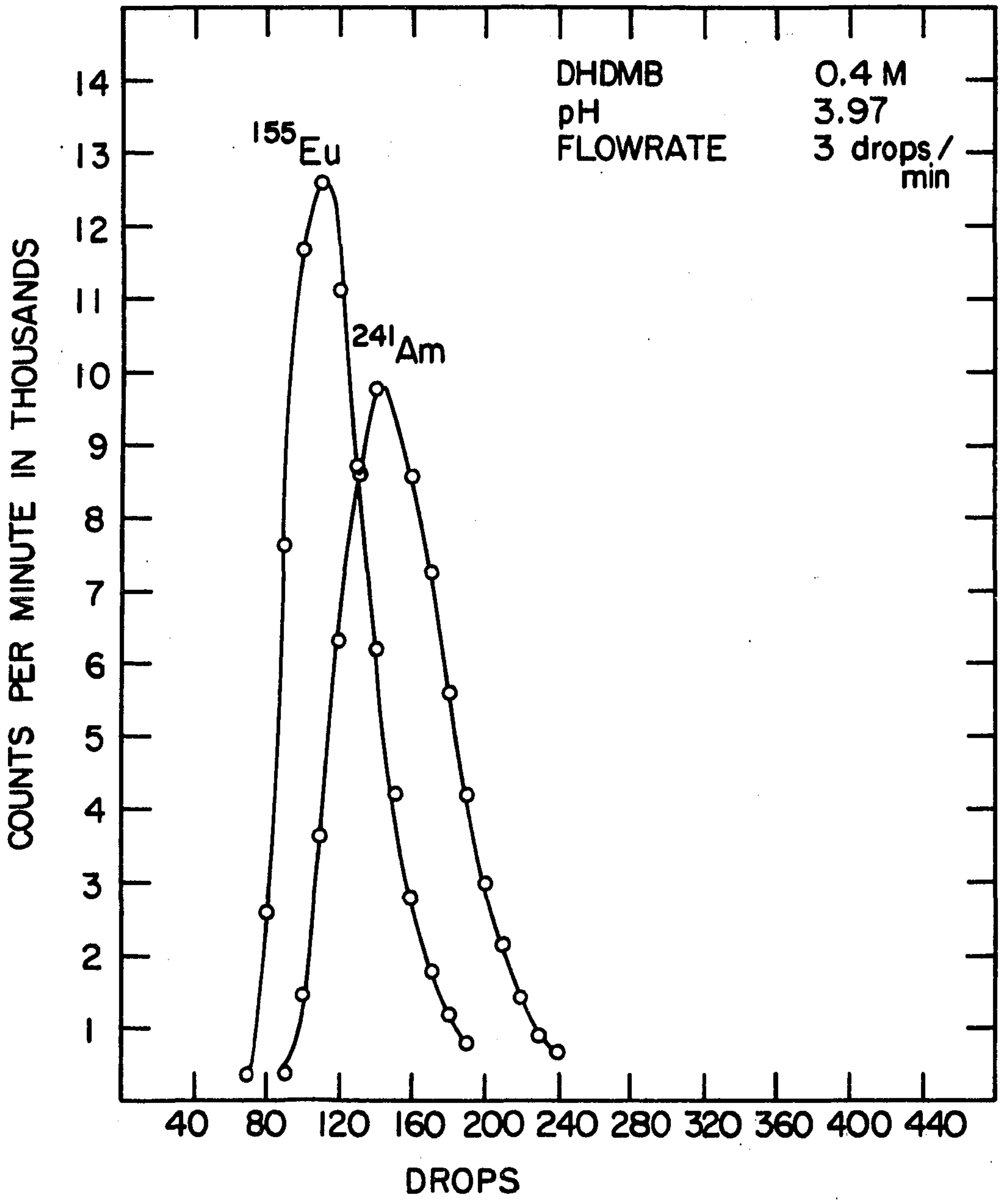


Figure 12. Cation-exchange elution of a ^{155}Eu - ^{241}Am mixture by DHDMB solution, pH = 3.97.

PART II. THE CATION-EXCHANGE SEPARATION OF AMERICIUM FROM THE TRIVALENT LANTHANIDES BY THE USE OF 2,2'-DIAMINODIETHYLETHER-N,N,N',N'-TETRAACETIC ACID

INTRODUCTION

The introductory part of this dissertation included a discussion of the anomalous lanthanide stability sequence observed for DTPA, and its utility in An-Ln separation schemes. A careful survey of the literature revealed that another aminopolycarboxylate existed which also exhibited its maximum lanthanide stability constant in the mid-lanthanon range.

During their investigations into new chelating agents for use in separating the individual rare-earths, Spedding and Powell (86) reported the lanthanide elution sequence of 2, 2'-diaminodiethylether-N,N,N',N'-tetraacetic acid (EEDTA) to be: Tb, Dy, (Sm, Er, Gd, Ho), Tm, Yb, Lu, Y, Nd, Pr, Ce, La, and noted the similarity of this elution sequence to that of DTPA. Later Mackey, Hiller, and Powell (87) observed that this complexone attained its maximum stability constant value at Eu and Tb. Surprisingly, no record of any An-Ln separation technique which incorporated this ligand could be found. This part of the dissertation reports the results of several tracer-level cation-exchange experiments, which were performed to determine the feasibility of An-Ln separations employing EEDTA.

EXPERIMENTAL

2,2'-Diaminodiethylether-N,N,N'N'-Tetraacetic Acid

Although previously test marketed under the trade name CHEL ME, EEDTA is no longer commercially available and as a result, a method for its synthesis was developed, based on that used by Yashunskii _et al_. (88).

The first step of the EEDTA synthesis, concerns the production of the diphthalmide derivative of the commercially available 2,2'-dichlorodiethyl ether (Aldrich):

$$\mathrm{Cl\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}Cl + 2C_8H_4O_2NK}$$
$$\rightarrow \mathrm{C_8H_4O_2N\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}NO_2H_4C_8.}$$

This reaction was accomplished by heating a mixture of 143 g of 2,2'-dichlorodethylether and 349 g of potassium phthalimide for 10 hours. The temperature was maintained at 140-150°C by means of a mineral oil bath, and the thick slurry was vigorously stirred. Five 2-ml aliquots of diethylamine were added at two-hour intervals to catalyze the reaction. After this period, the mixture was allowed to cool and the resulting solid was refluxed for one hour with 1.5 l of distilled water. The remaining precipitate was filtered, washed with water, and air dried. This procedure yielded 333 g of the yellow diphthalimide derivative which melted at 152-156°C.

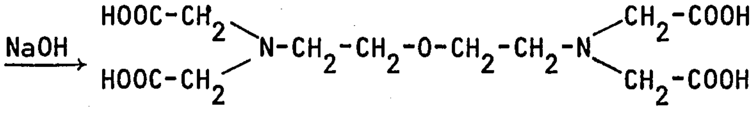
In the second phase of the EEDTA synthesis the diphthalimide derivative was decomposed with hydrazine and treated with HCL, to produce the 2, 2'-diaminodiethylether dihydrochloride:

$$\mathrm{[C_8H_4O_2N\text{-}CH_2\text{-}CH_2]_2\text{-}O} \xrightarrow{\mathrm{NH_2\text{-}NH_2}} \xrightarrow{\mathrm{HCl}} \mathrm{[HCl \cdot NH_2\text{-}CH_2\text{-}CH_2]_2\text{-}O}$$

Three hundred grams of the diphthalimide was slurried in 1.5 l of 95% ethanol, and treated with 53 g of anhydrous hydrazine. This mixture was then refluxed for three hours, cooled to room temperature, treated with 275 ml of concentrated HCl, and cooled to 0°C. The precipitate which formed was filtered, washed with cold ethanol and discarded. The ethanol fractions were then combined and evaporated. A small amount of extraneous precipitate formed rapidly and was filtered out. The remaining alcoholic solution was evaporated to a thick syrup and diluted with 250 ml of methanol. The addition of diethyl ether to this solution precipitated the desired 2, 2'-diaminodiethylether dihydrochloride without entraining any of the yellow color present in the methanol solution. One hundred and eighteen grams of the white, crystalline dihydrochloride which melted at 225-230°C were obtained in this fashion.

In the final step of the synthesis, the dihydrochloride adduct was neutralized to the free diamine and condensed with four moles of chloroacetic acid to produce the EEDTA:

$$[HCl\cdot NH_2\text{-}CH_2\text{-}CH_2]_2\text{-}O + 4Cl\text{-}CH_2\text{-}COOH$$



$$\xrightarrow{NaOH} \begin{matrix} HOOC\text{-}CH_2 \\ HOOC\text{-}CH_2 \end{matrix} \rangle N\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}N \langle \begin{matrix} CH_2\text{-}COOH \\ CH_2\text{-}COOH \end{matrix}$$

Ninety grams of the dihydrochloride were dissolved in 35 ml of water, cooled in an ice bath, and neutralized with 30% NaOH to a pH of 9. Likewise 270 g of chloroacetic acid (Aldrich) were dissolved in 250 ml of water, cooled, and neutralized to a pH of 5. These solutions were combined in a three-liter flask and maintained at 40°C. The pH of the reaction mixture was monitored and 30% NaOH was added as needed to obtain a pH between 10 and 11. After 48 hours no further change in the pH was noted (310 ml of base added), the solution was diluted to 4 l, and loaded on three (2" x 4') hydrogen-form cation-exchange columns (Dowex 50). As the mixture was loaded and washed with water, an easily distinguishable light colored band of EEDTA formed immediately ahead of the sodium band. The desired EEDTA product was obtained by displacing the complexone from the system with 0.2 M NH_4OH. The resulting samples were titrated with base, and those containing acid fractions were evaporated, yielding 168 g of EEDTA·$2H_2O$. Heating at 108°C overnight produced the anhydrous EEDTA. Elemental analysis and equivalent weight determination shown in Table 4 confirmed the high purity of the product.

Table 4. EEDTA analyses.

		C%	H%	N%
EEDTA·$2H_2O$				
	calculated	38.72	6.45	7.53
	found	38.73	6.62	7.60
	equivalent weight			
	calculated		372.33	
	found		377.18	
EEDTA				
	calculated	42.86	6.00	8.33
	found	43.04	6.11	8.31
	equivalent weight			
	calculated		336.30	
	found		334.09	

Cation-Exchange Elution Experiments

^{241}Am, ^{155}Eu, and ^{160}Tb solutions

The ^{241}Am and ^{155}Eu tracer solutions described in Part I were used again for the EEDTA experiments. The ^{160}Tb ($t_{\frac{1}{2}}$ = 72 d) stock solution was made by dilution of a 250 µl aliquot of the 0.47 µCi/ml $^{160}TbCl_3$ solution purchased from New England Nuclear and received on 10/22/79. The resulting 10-ml stock solution had a specific activity of 11.7 µCi/ml. Periodically, additional tracer was added to the stock solution to maintain a convenient activity. All of the original $^{160}TbCl_3$ has now been used in this fashion.

EEDTA eluent solutions

The EEDTA eluent solutions were prepared by dissolution of weighed portions of EEDTA and sufficient NH_4ClO_4 to produce solutions 0.1 $\underline{M}$ in the perchlorate salt. The addition of the salt insured an approximately constant ionic strength. The pH of the eluents was adjusted to the desired value with concentrated NH_4OH. The best results were obtained with a 0.02 $\underline{M}$ EEDTA solution at a pH of 3.06.

Chromatographic techniques

The column preparation and injection techniques used were analogous to those outlined for the DHDMB ion-exchange experiments in Part I. Only two minor changes were required. The volume of tracer injected was increased from 10 to 40 µl, to provide sufficient count rates for each isotope in the tertiary mixture. The eluent flow rate was also slowed from 3 to 2 drops/min to allow for the slower exchange kinetics of EEDTA.

Counting procedures

Initial EEDTA ion-exchange experiments employed only Am and Eu, and were counted by the liquid scintillation technique described previously. An attempt was made to expand the technique to permit the simultaneous counting of Am, Eu, and Tb. Unfortunately, the substantial overlap of the ^{160}Tb scintillation spectrum with that of the other isotopes, depicted in Figure 13, rendered the liquid scintillation counting method unworkable. For this reason, the ion-exchange experiments involving tertiary mixtures were counted by gamma spectroscopy. The Ge-Li detector and Canberra multichannel analyzer, kindly provided by Mr. Ken Malaby, were used to simultaneously count Eu, Am, and Tb by selecting the following discrete gamma energies:

^{241}Am -- 59.5 Kev
^{155}Eu -- 105.3 Kev
^{160}Tb -- 298.6 Kev.

Ten-minute sample counting times proved sufficient to provide reliable results. In order to minimize the number of samples to be counted in this fashion, all samples collected were first counted by the liquid scintillation technique. This practice eliminated the necessity of gamma counting samples with little or no activity. The combination of these counting techniques provided a quick and accurate method for the simultaneous determination of all three isotopes.

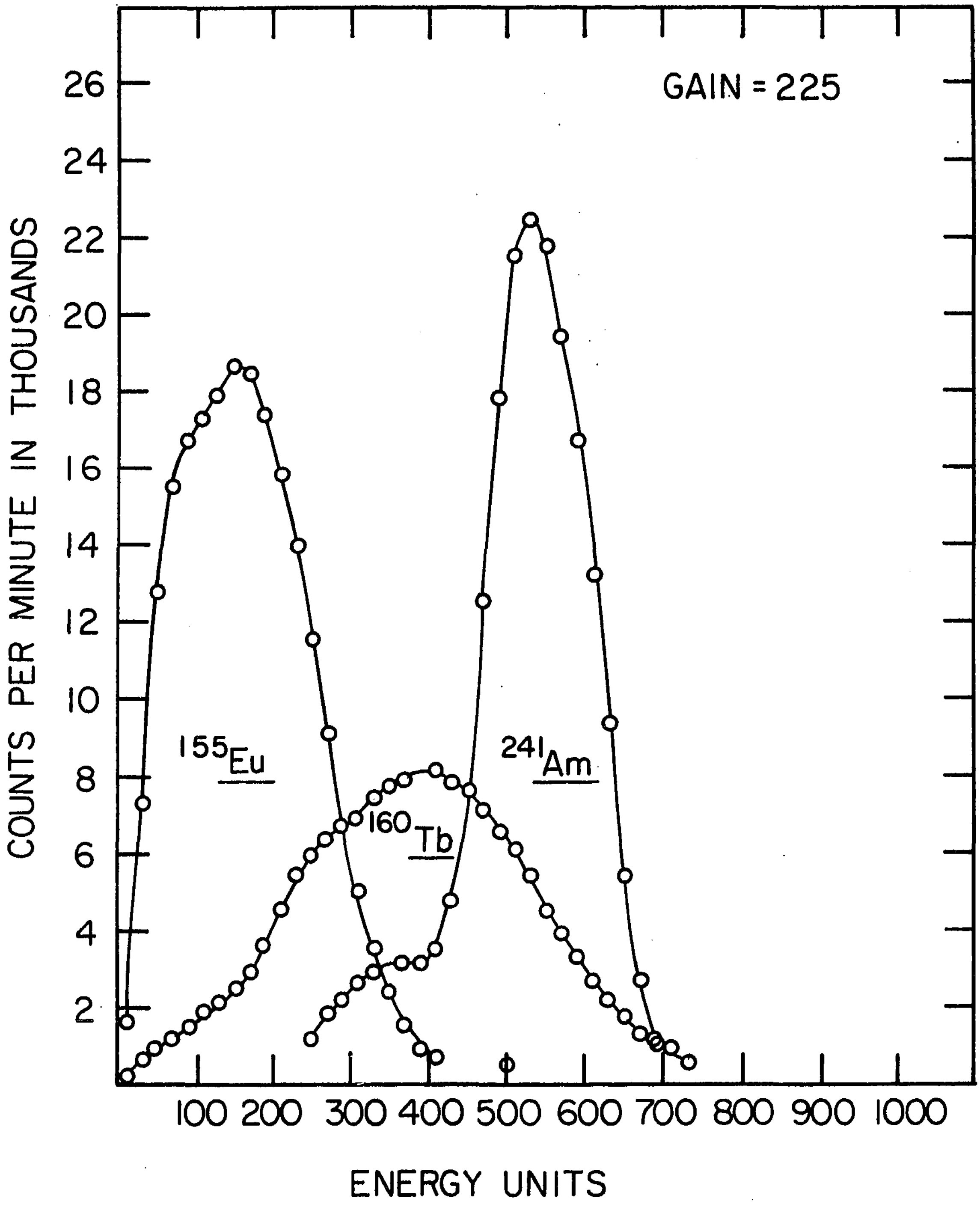


Figure 13. Liquid scintillation spectra of ^{155}Eu, ^{160}Tb, and ^{241}Am.

RESULTS AND DISCUSSION

Preliminary elution experiments employing Am and Eu were performed in which the EEDTA concentration and eluent pH were varied to produce acceptable elution volumes. These initial experiments also indicated that indeed, Am eluted before Eu as had been hoped. The equivalence of the Tb and Eu formation constants (87), and the observation of Tb as the leading lanthanide element in EEDTA elutions (86), caused some concern that Am would not be well-separated from Tb. In an effort to define the relative elution positions and separation factors of these three elements, an experiment was performed with a tertiary isotope mixture. The results of this elution are seen in Figure 14.

The chromatogram revealed the desired elution order of Am, Tb, and Eu; with Tb and Am well-separated. The equivalence of the Tb and Eu EEDTA formation constants was confirmed by the coincidence of their elution peaks. By employing the Am-Tb separation factor calculated from the chromatogram (1.71) and the EEDTA stability constants reported in (87), the separation factor between americium and each of the lanthanides was calculated. These appear in Table 5 along with the separation factors observed for cation-exchange systems at 70-80°C (53, 56), and values calculated from the DTPA stability constants discussed previously (48, 49). The average value measured for α_{Eu}^{Am} with DTPA at 25°C is 2.35 (49). The α_{Ln}^{Am} values in parentheses are normalized to this value, and are thus probably more reliable than those calculated from the absolute magnitude of the Am stability constant given in (49).

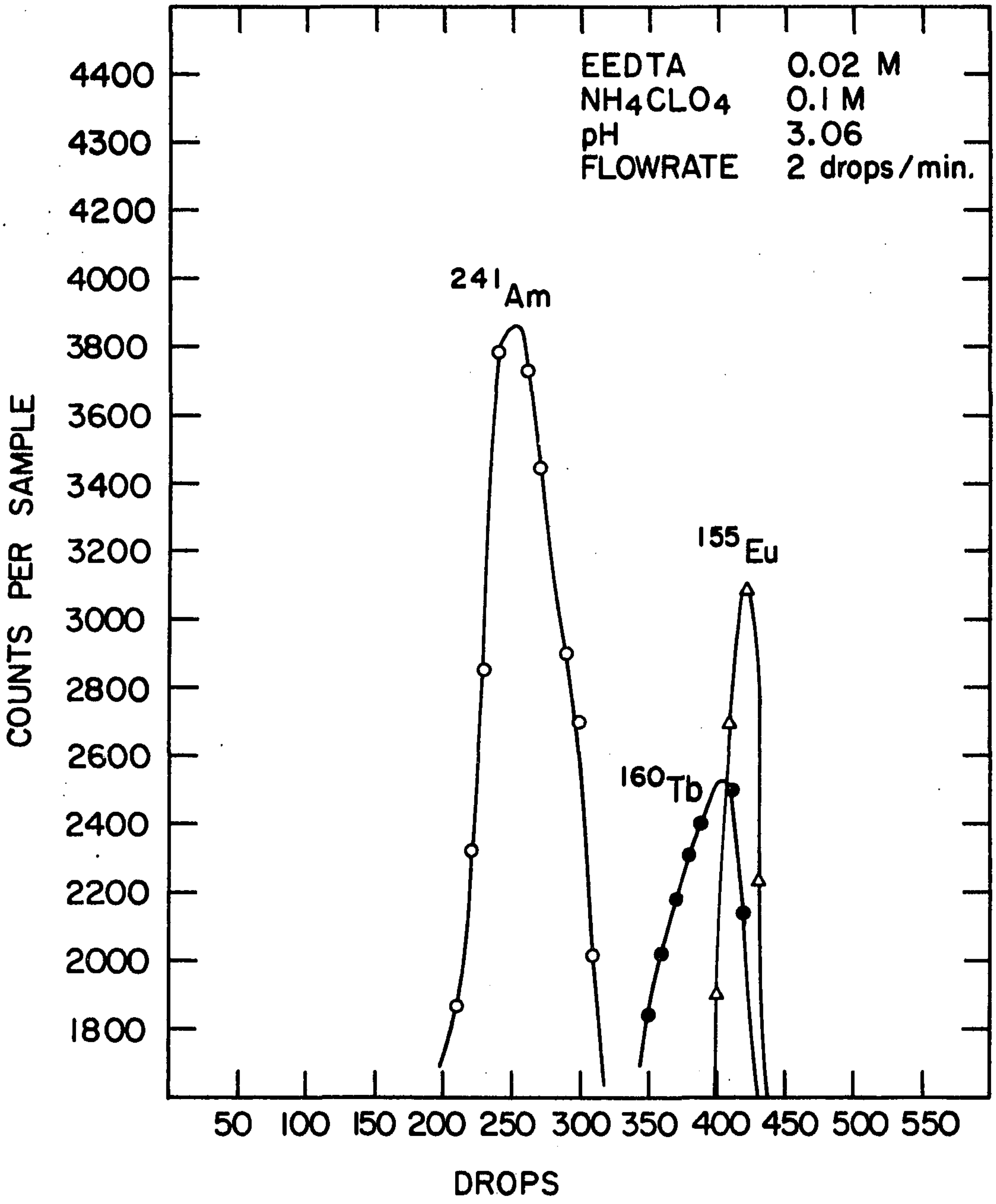


Figure 14. Cation-exchange elution of a ^{155}Eu - ^{160}Tb - ^{241}Am mixture using an EEDTA solution.

Table 5. α_{Ln}^{Am} for EEDTA and DTPA.

M	EEDTA 25°	DTPA 25°		DTPA 70°-80°
La	349.14	(1907.75)	2630.26	1202.0
Cr	71.28	(269.48)	371.54	162.0
Pr	15.24	(49.04)	67.61	40.74
Nd	7.46	(14.47)	19.95	13.80
Pm				6.46
Sm	2.25	(2.63)	3.63	3.02
Eu	1.71 (measured 1.78)	(2.35)	3.24	2.04
Gd	2.59	(1.99)	2.75	2.00
Tb	1.71 (measured)	(1.12)	1.55	
Dy	2.15	(0.870)	1.20	
Ho	2.59	(0.957)	1.32	
Er	3.57	(1.052)	1.45	less than 1.00 at 70°C
Tm	5.16	(1.095)	1.51	
Yb	4.93	(1.385)	1.91	
Lu	6.21	(2.089)	2.88	

As seen in the table EEDTA, like DTPA, exhibits excellent separation factors between Am and the light lanthanides. In the heavy lanthanide range EEDTA attains separation factors greater than 2.00 for the entire group from Dy - Lu. This behavior is clearly superior to DTPA which achieves a separation factor of this magnitude only at Lu. It is clear that by exhibiting a minimum An-Ln separation factor of 1.71, EEDTA promises to be a ligand of great utility in waste processing.

In addition to the impressive separation factors, EEDTA has other attributes which may encourage its use. The acid form of EEDTA is quite soluble in water, allowing the use of hydrogen ion as a retaining ion in a displacement development cation-exchange system. As evidenced in its synthesis, EEDTA is protonated and sorbed in the presence of a hydrogen-form cation exchanger. This phenomenon will cause the formation of a EEDTA band immediately ahead of the Am band in a displacement system, and will permit a convenient recovery and recycle of the ligand. Finally, the ten thousand-fold decrease in the magnitude of the stability constants of the EEDTA complexes, relative to those of DTPA, should translate into improved exchange kinetics for both ion-exchange and Talspeak-type extraction methods which could be developed with EEDTA.

PART III. THE COORDINATION CHEMISTRY AND CATION ELUTION BEHAVIOR OF THE LANTHANIDES, AMERICIUM AND YTTRIUM WITH 1,5-DIAMINOPENTANE-N,N,N',N'-TETRAACETIC ACID

INTRODUCTION

The successful separation of Am from the lanthanides in the EEDTA cation-exchange experiments prompted an attempt to discover which structural properties common to EEDTA and DTPA were responsible for their actinide selectivity. It was conjectured that the fall of the EEDTA and DTPA stability constant values for the heavy lanthanons (Tb or Dy - Lu) was essential to their selectivity, and that this phenomena was related to a gradual detachment of some ligand chelating group as the lanthanide radius decreased. Two possibilities for the failing chelating group are evident in a structural comparison of EEDTA and DTPA. Both ligands consist of two terminal iminodiacetate groups connected by a five membered chain. It is possible that this particular chain length between the terminal nitrogen atoms is such that the coordination of one of the terminal carboxylate groups fails due to steric constraints resulting from the decreasing lanthanide radius. A second possible explanation of the decreasing heavy lanthanide stability constants would predict a gradual failure of the coordination of the EEDTA ether-oxygen atom and the corresponding failure of the DTPA mid-chain nitrogen atom or carboxylate group. The paucity of data on other ligands with similar structural features makes it impossible to decide between these two possibilities at this time. In an attempt to examine the importance of the mid-chain chelating moeity the 1,5-diaminopentane-N,N,N',N'-tetraacetic acid (PMDTA) ligand was synthesized, its cation elution behavior was investigated, and its lanthanide complex formation constants were determined.

EXPERIMENTAL

1,5-diaminopentane-N,N,N',N'-tetraacetic acid

The 1,5-diaminopentane-N,N,N',N'-tetraacetic acid was synthesized by the condensation of chloroacetic acid and 1,5-diaminopentane (Aldrich) in a manner similar to that used in the final step of the EEDTA synthesis. The diaminopentane starting material (25 g) was first dissolved in 100 ml of water. To this solution 115 g of chloroacetic acid, which had been dissolved in 100 ml of water, cooled, and neutralized with NaOH, were added. The resulting mixture was warmed to 40°C on a hot plate, and maintained at a pH of 10 by timely additions of 10 M NaOH. Over a twenty-four hour period, 122 ml of base were added in this fashion.

Previous attempts at the synthesis of PMDTA by Schwarzenbach and Ackermann (89) and most recently by Peerce and coworkers (90) have proceeded in the manner just described, however, in both cases, the authors were unable to iosolate the free acid form of PMDTA in purities of greater than 80%. Fortunately, cation-exchange techniques analogous to those described for EEDTA have now allowed the production of high purity PMDTA in good yield. The reaction mixture described above was diluted to 2 l and loaded on five (1" x 4') Dowex 50, hydrogen-form, cation-exchange columns. The resulting HCl and unreacted chloroacetic acid were flushed from the system with distilled water. As in the case of EEDTA, a light-colored, easily discernible band of PMDTA formed, and was displaced from the resin by elution with 0.2 M NH_4OH. The acidic fractions of the eluate were collected, evaporated to a hard glass, and recrystallized from water. The resulting white powder (59 g) was characterized by equivalent weight and C, H, and N analyses, and determined to be PMDTA·H_2O. The anhydrous PMDTA was obtained by heating the monohydrate overnight at 108°C. The pertinent analyses are shown in Table 6.

Table 6. PMDTA analyses.

		C%	H%	N%
PMDTA·H_2O				
	calculated	44.31	6.88	7.95
	found	44.17	6.99	7.95
	equivalent weight, calculated		--	352.39
	found		--	352.58
PMDTA				
	calculated	46.69	6.65	8.38
	found	45.61	6.78	8.17
	equivalent weight, calculated		--	334.37
	found			335.73

Cation-Exchange Elution Experiments

The PMDTA elution order and separation factors for ^{241}Am, ^{160}Tb, and ^{155}Eu were determined by employing the chromatographic methods and gamma counting techniques developed for EEDTA. The optimum eluent was determined to be a 0.04 M - 0.1 M NH_4ClO_4 PMDTA solution adjusted to a pH of 5.06 with concentrated NH_4OH.

PMDTA Anion Protonation Constants

The PMDTA ligand exhibited two buffer regions, one at high pH (9-10), and another at low pH (2-3). The large difference between these regions allowed α_1 and α_2 pair to be determined from a set of solutions at high pH, and the α_3 and α_4 pair to be determined from a set of solutions at low pH. Each series of solutions was prepared by the combination of aliquots of PMDTA stock solution, standard KOH or HNO_3 solution, and sufficient KNO_3 solution to produce a 0.1 M ionic strength. The volume of KNO_3 solution needed was calculated by using program ALPHA, described in Part I. The pH_c values of the equilibrated solutions (25.00 ± 0.05°C) were measured in the manner previously described, and used in conjunction with program OMEGA to calculate the desired values for α_1, α_2, α_3, and α_4. The basis of the calculation method will be described in a subsequent section. Appendix B contains the pH_c data and results of program OMEGA.

Rare Earth-PMDTA Complex Stability Constants

The equilibrium constants for the formation of the ML^- and MHL species were calculated from pH_c measurements like those used in the study of the DHDMB - rare earth stability sequence. Appropriate volumes of metal nitrate, PMDTA, KOH, and KNO_3 calculated by program BETA were combined and equilibrated at 25.00 ± 0.05°C for at least twelve hours. The pH_c measurements were made as described previously with the exception of the standardization procedure which was accomplished by using the technique employed by Johnson (91). The formation of the MHL species complicated the calculation of the stability constants, and required the development of a new calculation method which was incorporated into the computer program HCMPLX. The solution data and a listing of HCMPLX are found in Appendix B and C. The mathematical method employed in this program will be discussed in the next section.

CALCULATIONS

PMDTA Anion Protonation Constants

The protonation of the PMDTA anion (L) can be described by the following four equilibria:

$$L + H \rightleftarrows HL$$

$$L + 2H \rightleftarrows H_2L$$

$$L + 3H \rightleftarrows H_3L$$

$$L + 4H \rightleftarrows H_4L$$

The resulting equilibrium constants are:

$$\alpha_1 = \frac{[HL]}{[H][L]}$$

$$\alpha_2 = \frac{[H_2L]}{[H]^2[L]}$$

$$\alpha_3 = \frac{[H_3L]}{[H]^3[L]}$$

$$\alpha_4 = \frac{[H_4L]}{[H]^4[L]}$$

The pertinent mass balances then become:

$$H_t = [H] + [HL] + 2[H_2L] + 3[H_3L] + 4[H_4L]$$

$$= [H] + \alpha_1[H][L] + 2\alpha_2[H]^2[L] + 3\alpha_3[H]^3[L] + 4\alpha_4[H]^4[L]$$

$$H_t - [H] = [L] \sum_{1}^{4} N\alpha_N[H]^N$$

and

$$L_t = [L] + [HL] + [H_2L] + [H_3L] + [H_4L]$$

$$= [L] + \alpha_1[H][L] + \alpha_2[H]^2[L] + \alpha_3[H]^3[L] + \alpha_4[H]^4[L]$$

$$= [L](1 + \sum_1^4 \alpha_N[H]^N).$$

Division of the mass balances yields:

$$\frac{H_t - [H]}{L_t} = \frac{\sum_1^4 N\alpha_N[H]^N}{1 + \sum_1^4 \alpha_N[H]^N}.$$

Rearrangement gives:

$$\sum_1^4 (H_t - [H] - NL_t)[H]^N\alpha_N = [H] - H_t$$

This equation is of the form:

$$Y = J_1\alpha_1 + J_2\alpha_2 + J_3\alpha_3 + J_4\alpha_4$$

and as such, may be treated by a multiple linear regression analogous to that described in Part I. This formulation is implemented in program OMEGA, and has been discussed in detail previously (91).

The linear regression model is needed only when two or more buffer regions of the ligand acid overlap. In the case of PMDTA, the buffer regions corresponding to the first and second protonations of the anion overlap in a high pH region, and the buffer regions resulting from the third and fourth protonation of the anion overlap in a low pH region. The difference in pH of the two apparent buffer regions requires the simultaneous computation of only two protonation constants within each of the regions, instead of four. In this fashion the α_1 and α_2 pair, and the α_3 and α_4 pair were calculated by utilizing a two parameter approach for data within the respective buffer regions.

Rare Earth-PMDTA Stability Constants

The computation of the rare earth-PMDTA stability constants was complicated by the formation of a protonated complex species, MHL, in addition to the 1:1 chelate ML^-. The equilibria used to describe this system are:

$$L + M \rightleftarrows ML$$

$$HL + M \rightleftarrows MHL$$

The resulting equilibrium constants are:

$$\beta_1 = \frac{[ML]}{[M][L]}$$

$$\beta_H = \frac{[MHL]}{[M][HL]}$$

The metal mass balance now becomes:

$$\begin{aligned} M_t &= [M] + [MHL] + [ML] \\ &= [M] + \beta_H[M][H][L]\alpha_1 + \beta_1[M][L] \end{aligned}$$

if

$$X = M_t/[M]$$

then

$$[L] = (X - 1)/(\beta_H[H]\alpha_1 + \beta_1)$$

The ligand mass balance is:

$$L_t = [L] + [HL] + [H_2L] + [H_3L] + [H_4L] + [MHL] + [ML]$$

$$= [L] + [L]\ \Sigma\ \alpha_N [H]^N + [L]\ \beta_H [M][H]\ \alpha_1 + [L]\beta_1 [M]$$

$$= [L](1 + \Sigma\ \alpha_N [H]^N + \alpha_1 \beta_H [H]\ \frac{M_t}{X} + \beta_1\ \frac{M_t}{X})$$

Finally, the hydrogen balance is:

$$H_t = [H] + [HL] + 2[H_2L] + 3[H_3L] + 4[H_4L] + [MHL]$$

$$H_t - [H] = [L](\Sigma\ N\alpha_N [H]^N + \beta_H [H][M]\alpha_1)$$

$$= [L](\Sigma\ N\alpha_N [H]^N + \beta_H [H]\ \frac{M_t}{X}\ \alpha_1)$$

Previous complexones investigated in this laboratory did not form appreciable amounts of a protonated chelate species. This allowed the elimination of the free metal concentration by combination of the metal and ligand mass balances. Since no metal containing species occurred in the hydrogen mass balance, the free ligand concentration [L] could be calculated from the measured hydrogen-ion concentration [H], and the predetermined protonation constants α_N. With the knowledge of [L], the combined metal and ligand mass balances could be solved for the stability constants (i.e. the DHDMB-rare earth system in Part I). Unfortunately, the mass balances just derived for the PMDTA system must be treated in a different manner.

The first step in the solution of the PMDTA system requires the substitution of the M_t mass balance into the L_t mass balance:

$$L_t = \frac{(X - 1)}{(\beta[H]\alpha_1 + \beta_1)}\ [1 + \Sigma\ \alpha_N [H]^N + \alpha_1 \beta_H [H]\ \frac{M_t}{X} + \beta_1\ \frac{M_t}{X}\ ]$$

Simplification yields a quadratic equation in terms of X:

$$0 = (1 + \Sigma\, \alpha_N [H]^N) X^2$$
$$+ (\alpha_1 \beta_H [H] M_t + \beta_1 M_t - 1 - \Sigma\, \alpha_N [H]^N - L_t \beta_H [H] \alpha_1 - L_t \beta_1) X$$
$$+ (-\alpha_1 \beta_H [H] M_t - \beta_1 M_t)$$

This is of the form

$$0 = AX^2 + BX + C$$

where

$$A = [1 + \Sigma\, \alpha_N [H]^N]$$
$$B = B_1 \beta_H + B_2 \beta_1 + B_3$$
$$B_1 = [\alpha_1 [H] M_t - L_t [H] \alpha_1]$$
$$B_2 = [M_t - L_t]$$
$$B_3 = [-\Sigma\, \alpha_N [H]^N - 1]$$
$$C = C_1 \beta_H + C_2 \beta_1$$
$$C_1 = [-\alpha_1 [H] M_t]$$
$$C_2 = [-M_t]$$

Similar substitution of the M_t mass balance into the H_t mass balance yields:

$$H_t - H = \frac{(X - 1)}{(\beta_H [H] \alpha_1 + \beta_1)} [\Sigma\, N\alpha_N [H]^N + \beta_H [H] \frac{M_t}{X} \alpha_1]$$

This can be rewritten as:

$$0 = (\Sigma\, N\alpha_N [H]^N) X^2$$
$$+ (\beta_H [H] M_t \alpha_1 - \Sigma\, N\alpha_N [H]^N - H_t \beta_H [H] \alpha_1$$
$$- H_t \beta_1 + \beta_H [H]^2 \alpha_1 + \beta_1 [H]) X$$
$$+ (-\beta_H [H] M_t \alpha_1)$$

This is of the form:

$$0 = DX^2 + EX + F$$

where

$$D = [\Sigma N\alpha_N[H]^N]$$

$$E = E_1\beta_H + E_2\beta_1 + E_3$$

$$E_1 = [[H]M_t\alpha_1 - H_t[H]\alpha_1 + [H]^2\alpha_1]$$

$$E_2 = [[H] - H_t]$$

$$E_3 = [-\Sigma N\alpha_N[H]^N]$$

$$F = F_1\beta_H$$

$$F_1 = [-[H]M_t\alpha_1]$$

The unknown free metal concentration term contained in X may now be eliminated by equating the solutions of the two quadratic equations just derived. Since X is positive, the solutions to the equations

$$\frac{-B \pm (B^2 - 4AC)^{\frac{1}{2}}}{2A} = X$$

and

$$\frac{-E \pm (E^2 - 4DF)^{\frac{1}{2}}}{2D} = X$$

are positive. From their definitions, the terms A and D are positive, and the terms C and F are negative. It follows that the terms $(B^2 - 4AC)$ and $(E^2 - 4DF)$ are positive, and that $(B^2 - 4AC)^{\frac{1}{2}} > |B|$ and $(E^2 - 4DF)^{\frac{1}{2}} > |E|$. The correct solutions to be equated must then be:

$$\frac{-B + (B^2 - 4AC)^{\frac{1}{2}}}{2A} = \frac{-E + (E^2 - 4DF)^{\frac{1}{2}}}{2D}$$

This can be simplified to:

$$0 = A^2F^2 - 2CDAF + C^2D^2 + FB^2D - AEFB$$
$$- CEBD + AE^2C$$

The substitution of the concentration variables into this equation, and the collection of the resulting terms is a lengthy and tedious task and will not be duplicated here. The final results of the campaign is an equation of the form:

$$0 = R\beta_1{}^3 + S\beta_1{}^2\beta_H + T\beta_1{}^2 + U\beta_1\beta_H$$
$$+ V\beta_1 + W\beta_H + X\beta_H{}^2 + Y\beta_1\beta_H{}^2 + Z\beta_H{}^3$$

where:

$$R = [AC_2E_2{}^2 - DC_2E_2B_2]$$

$$S = [B_2{}^2DF_1 - AF_1E_2B_2 - DC_1E_2B_2 - DC_2E_1B_2 - DC_2E_2B_1$$
$$+ AC_1E_2{}^2 + 2AC_2E_1E_2]$$

$$T = [C_2{}^2D^2 - DC_2E_2B_3 - DC_2B_2E_3 + 2AC_2E_2E_3]$$

$$U = [2C_1C_2D^2 - 2ADC_2F_1 + 2B_2B_3DF_1 - AF_1B_2E_3$$
$$- AF_1E_2B_3 - DC_1E_2B_3 - DC_1B_2E_3 - DC_2E_1B_3$$
$$- DC_2E_3B_1 + 2AC_1E_2E_3 + 2AC_2E_1E_3]$$

$$V = [AC_2E_3{}^2 - DC_2B_3E_3] = 0$$

$$W = [B_3{}^2DF_1 - AFB_3E_3 - DC_1B_3E_3 + AC_1E_3{}^2] = 0$$

$$X = [A^2F_1{}^2 - 2ADC_1F_1 + C_1{}^2D^2 + 2B_1B_3DF_1$$
$$- AF_1E_1B_3 - AF_1E_3B_1 - DC_1E_1B_3 - DC_1E_3B_1$$
$$+ 2AC_1E_1E_3]$$

$$Y = [2B_1B_2DF_1 - AF_1E_1B_2 - AF_1E_2B_1 - DC_1E_1B_2$$

$$- DC_1E_2B_1 - DC_2E_1B_1 + AC_2E_1^2 + 2AC_1E_1E_2]$$

$$Z = [B_1^2DF_1 - AB_1E_1F_1 - E_1B_1C_1D + AC_1E_1^2]$$

The following relationships were also noted and used in HCMPLX:

$$B_3 = -A$$

$$B_1 = \alpha_1[H]B_2$$

$$C_1 = \alpha_1[H]C_2$$

$$E_3 = -D$$

$$F = C_1$$

Each experimental solution of known stoichiometry and pH produces a similar third-order bivariant equation in β_1 and β_H. Fortunately, an efficient numerical technique has been developed for solving systems of equations of this kind (92). This technique is currently available via the IMSL software subroutine, ZSYSTM, which is maintained at the Iowa State University Computational Center. A computer program, HCMPLX, was written which takes all combinations of two data points from the submitted data, calculates the necessary coefficients, and solves the resulting system of two equations for β_1 and β_H, by using ZSYSTM. The combined results for all pairs of data points are then used to compute an average value.

Only one problem has been encountered with this mathematical method. The subroutine ZSYSTM requires an initial guess of the values of β_1 and β_H to begin its computation. If the initial guesses are too small, ZSYSTM tends to converge to the trivial solution: $\beta_l = 0$, $\beta_H = 0$. It is therefore advantageous to choose the initial values given to ZSYSTM slightly larger than the expected values for β_l and β_H to prevent convergence to this undesired solution.

RESULTS AND DISCUSSION

PMDTA Cation-Exchange Elutions

From the onset it was apparent that the behavior of the PMDTA ligand was remarkably different than that of EEDTA. Preliminary ion-exchange experiments revealed that elutions with thirty column volumes of 0.02 $\underline{M}$ PMDTA solutions at pH's of 3.0 (optimum for EEDTA), 4.0, or 4.8 were insufficient to remove the Am, Eu, and Tb tracers from the resin bed. An acceptable chromatogram was obtained only after the PMDTA concentration was increased to 0.04 $\underline{M}$ and the pH was increased to 5.07. These more severe conditions foreshadowed significant differences in the magnitude of the PMDTA and EEDTA protonation and lanthanide chelate formation constants.

The PMDTA chromatogram depicted in Figure 15 also reveals substantial differences in the PMDTA and EEDTA elution orders for the lanthanide and actinide tracers. Unlike EEDTA which eluted Am well ahead of a poorly separated Eu-Tb mixture, PMDTA eluted Tb first followed by an unresolved Am-Eu band. The separation factor calculated from the position of the Tb and Am peaks indicated a Tb-Am separation factor of 1.5. The relative position of these peaks showed that the PMDTA-Ln chelate system did not possess a sufficient decline in stability across the heavy lanthanons to allow the elution of Am ahead of Tb. It was, however, unknown as to whether this was indicative of a monotonic increase of the PMDTA complex stabilities across the lanthanons, or simply a displacement of the chelate failure to a less favorable position in the lanthanide

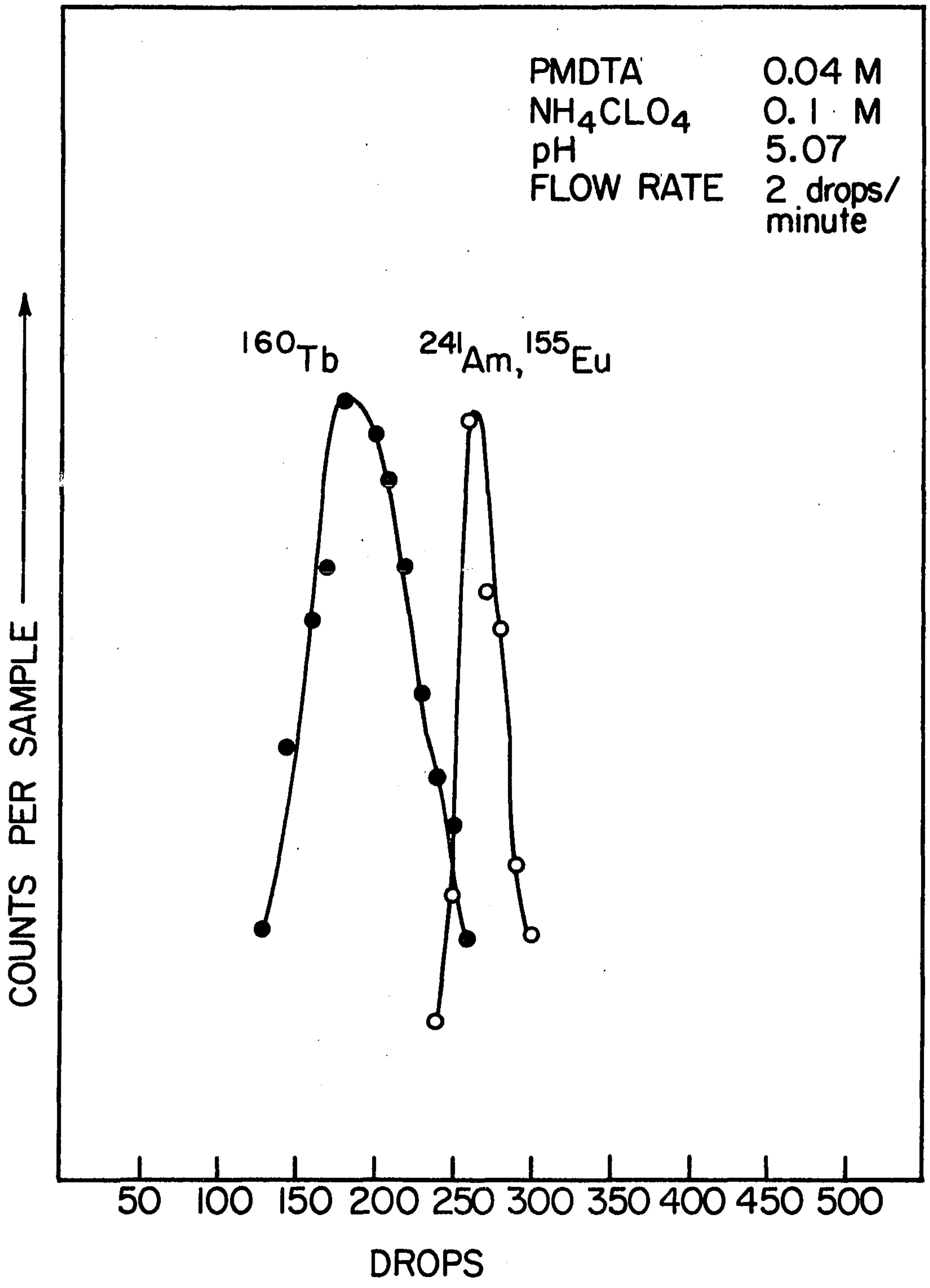


Figure 15. Cation-exchange elution of a ^{155}Eu - ^{160}Tb - ^{241}Am mixture using a PMDTA solution.

sequence. An investigation of the lanthanide-PMDTA solution equilibria was undertaken to decide between these possibilities.

Protonation and Rare-Earth Stability Constants

The protonation constants necessary for the study of the metal-ligand interactions were computed from the data in Appendix B. The results are displayed in Table 7.

Table 7. Protonation constants for the PMDTA anion.

	σ		Ref. 98
$\alpha_1 = 0.157 \times 10^{11}$	2.02%	$\log \frac{[HL]}{[H][L]} = 10.20$	10.58
$\alpha_2 = 0.350 \times 10^{20}$	1.32%	$\log \frac{[H_2L]}{[H][HL]} = 9.35$	9.50
$\alpha_3 = 0.180 \times 10^{23}$	2.32%	$\log \frac{[H_3L]}{[H][H_2L]} = 2.71$	2.7
$\alpha_4 = 0.311 \times 10^{25}$	2.65%	$\log \frac{[H_4L]}{[H][H_3L]} = 2.24$	2.2

The values for the log of the first and second stepwise protonation constant are somewhat different than those observed by Schwarzenbach and Ackermann (98). It is unclear whether this difference is due to the presence of impurities inherent in the previous PMDTA synthesis, or merely different standardization techniques. Differences similar in both magnitude and direction are found in the values of the first and second stepwise protonation constants of hexamethylenediamine-N,N,N',N'-tetraacetic acid (HMDTA) as determined recently by Brücher et al. (93), and previously by Schwarzenbach et al. (94) and Anderegg (95). The third and fourth stepwise protonation constants measured for PMDTA are in complete agreement with the values determined previously.

The values of β_H and β_1 for each of the tripositive lanthanides and yttrium are shown in Table 8. These values were computed from data in Appendix B by use of the computer program HCMPLX. It is apparent that the stability constant sequence for both the protonated and unprotonated PMDTA-Ln complexes increases continuously across the entire family. The complete reversal of the decreasing trend exhibited by the DTPA-Ln and EEDTA-Ln chelates in the heavy lanthanon region underscores the importance of the mid-chain chelating moiety which PMDTA lacks. Further comparisons are evident in Figure 16, which displays plots of log β_1 versus lanthanide cationic radius for DTPA (48), EEDTA (87), HMDTA (93), diethylenetriamine-N'-propanoic-N,N',N'',N''-tetraacetic acid (DTPTA) (96), and PMDTA; and the log β_2 values for N-methyliminodiacetic acid (MIDA) (97). The most striking feature of this graph is the 10^7-fold decrease in β_1 value directly attributable to the replacement of the ether oxygen atom in EEDTA with a methylene group. The stability constants of the PMDTA ligand bear little resemblance to those of DTPA and EEDTA, and instead parallel the values exhibited by HMDTA and MIDA. It is evident from this phenomenon that the two additional five-membered chelate rings formed by the mid-chain chelating group are essential to the high stability and actinide selectivity shown by EEDTA and DTPA. Unfortunately, it is still impossible to determine the exact role played by this group in the decrease in complex stability displayed in the heavy lanthanides. Molecular models show that chelation

Table 8. Stability constants of rare earth PMDTA chelate species (25°; I = 0.1).

M	β_H	log β_H	β_1	log β_1
Y	$.663 \times 10^{7}$	6.82[a]	$.227 \times 10^{11}$	10.36[a]
La	$.123 \times 10^{7}$	6.09	$.910 \times 10^{9}$	8.96
Ce	$.218 \times 10^{7}$	6.34	$.321 \times 10^{10}$	9.51
Pr	$.282 \times 10^{7}$	6.45	$.510 \times 10^{10}$	9.71
Nd	$.334 \times 10^{7}$	6.52	$.588 \times 10^{10}$	9.77
Pm				
Sm	$.462 \times 10^{7}$	6.66	$.149 \times 10^{11}$	10.17
Eu	$.496 \times 10$	6.70	$.166 \times 10^{11}$	10.22
Gd	$.611 \times 10^{7}$	6.79	$.232 \times 10^{11}$	10.37
Tb	$.771 \times 10^{7}$	6.89	$.344 \times 10^{11}$	10.53
Dy	$.960 \times 10^{7}$	6.98	$.560 \times 10^{11}$	10.75
Ho	$.115 \times 10^{8}$	7.06	$.678 \times 10^{11}$	10.83
Er	$.137 \times 10^{8}$	7.14	$.106 \times 10^{12}$	11.03
Tm	$.172 \times 10^{8}$	7.24	$.154 \times 10^{12}$	11.19
Yb	$.207 \times 10^{8}$	7.32	$.213 \times 10^{12}$	11.33
Lu	$.214 \times 10^{8}$	7.33	$.231 \times 10^{12}$	11.36

[a] Values are estimated to be reliable to ±.05.

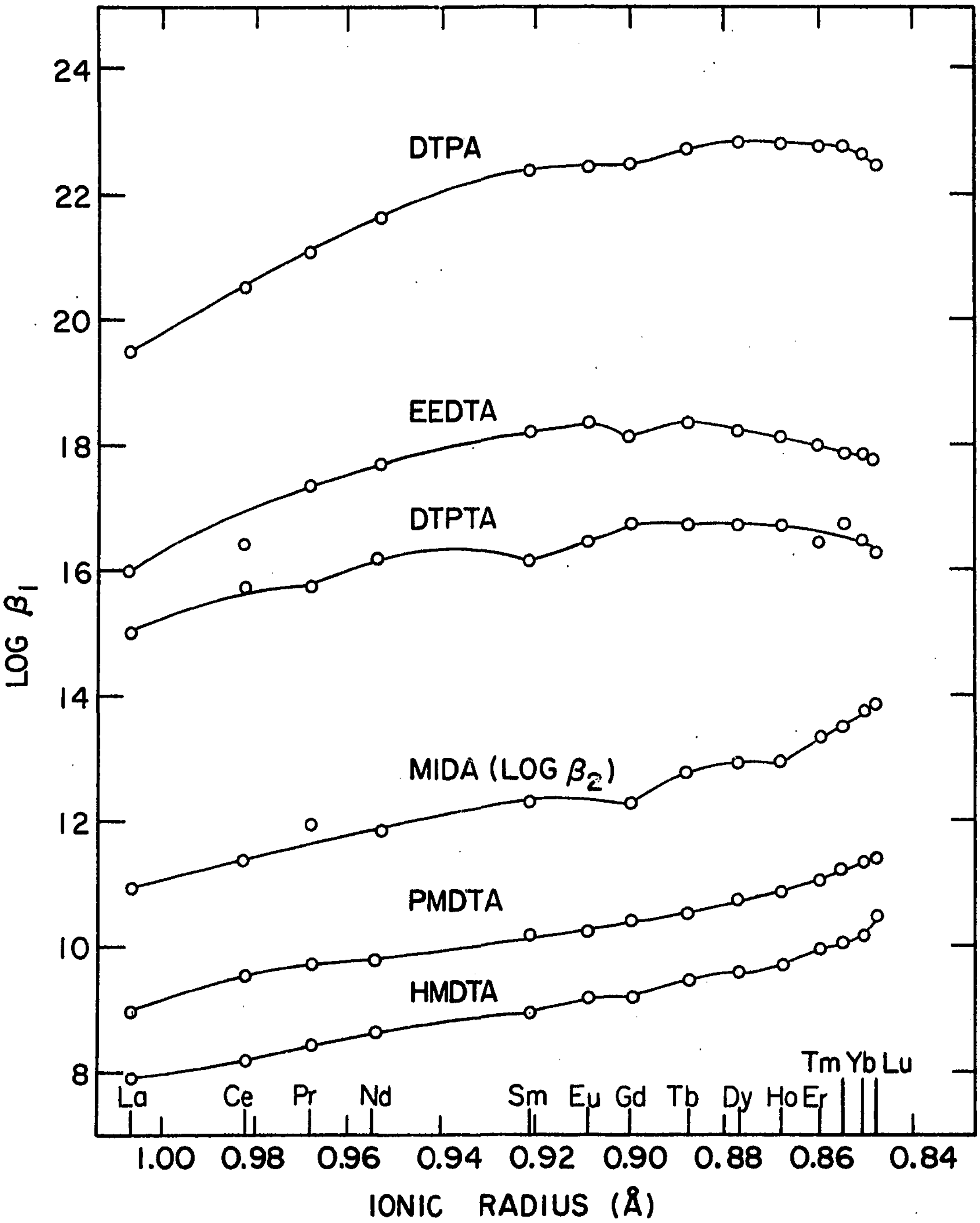


Figure 16. Stability constants of the lanthanide chelates formed by several aminocarboxylates.

of the mid-chain group introduces considerable strain in the coordination of the iminodiacetate groups, but present data does not offer conclusive evidence as to which group fails as the cationic radius decreases.

The literature contains only two other citings which offer further evidence as to the mode of chelation in these ligands. In 1979, Choppin, Baisden, and Khan (98) published ^{1}H and ^{13}C NMR spectra for the DTPA complexes of La and Lu. They concluded that the middle carboxylate group was unbound, implying heptadentate coordination of the metal cation by three nitrogen atoms and an average of four carboxylate groups. Unfortunately, if one accepts this view, it becomes very difficult to rationalize the 10^4-fold increase of β_1 values of DTPA over those of EEDTA without invoking the coordination of the fifth carboxylate group. The only other indication of the chelation mode of these aminocarboxylates appears in the stability constants reported for DTPTA (96). This ligand has a structure equivalent to DTPA with one terminal acetate group replaced by propanoate. Surprisingly, this minor change reduced the stability of the lanthanide complexes to a position below that of EEDTA, approximately 10^5 less than DTPA. In addition, the decrease observed within the heavy lanthanon region for EEDTA and DTPA seems to be retained in DTPTA, although the data in this region are obviously poor. If one assumes that the decrease in the overall magnitude of the DTPTA constants is due to the failure of the propanoate group to bond, the retention and equivalence of the decreasing trend in the heavy lanthanons, might be indicative of a gradual failure of the mid-chain group to coordinate. At present, all that is certain is that the mid-chain chelating group plays an important role in the behavior of these ligands, and that the continued collection of reliable data for the complexes of DTPTA, and other DTPA and EEDTA analogues is imperative to resolving the chelation modes of these ligands.

CONCLUSIONS

Summary

The relationships between the lanthanide complex formation equilibria and lanthanide-actinide separation applications of three radius sensitive ligands have been studied. The consecutive stepwise formation constants of the 1:1, 2:1, and 3:1 chelate species formed by the interaction of the DHDMB anion and the tripositive lanthanides and yttrium were determined potentiometrically. The results indicate that three different coordination modes, one tridentate and two bidentate, are in evidence.

Tracer level ^{241}Am-^{155}Eu cation-exchange experiments utilizing DHDMB eluents have indicated that this dihydroxycarboxylate does not form a sufficiently strong americium complex to elute that actinide ahead of europium. The overall stability of the americium 3:1 complex appears to be intermediate between samarium and europium.

Cation exchange elutions of ^{241}Am, ^{155}Eu, and ^{160}Tb mixtures with EEDTA solutions prove that the EEDTA ligand is capable of eluting americium ahead of all other tripositive lanthanide cations. The minimum separation occurs with terbium, where the americium-terbium separation factor is 1.71.

The successful synthesis of PMDTA was accomplished by the use of cation-exchange purification techniques. A new mathematical method was developed to calculate the formation constants of the protonated and unprotonated PMDTA-Ln complexes from potentiometric data. The results for both cases display a monotonic increase across the entire lanthanide series.

Cation-exchange elutions of tracer quantities of Am, Eu and Tb with PMDTA solutions revealed that terbium is eluted ahead of both americium and europium. This elution order illustrates that the mid-chain chelating groups of DTPA and EEDTA are necessary to their actinide selectivity.

Future Work

The results reported in this dissertation suggest a variety of interesting experiments which could be accomplished in the future. The dihydroxy acid investigations should be completed by studying the lanthanide complex formation equilibria of glyceric acid and 2,3-dihydroxy-3-methylbutanoic acid. In addition, NMR studies of the 1:1 lanthanide-dihydroxycarboxylates similar to those of Taga et al. (78) might provide definitive proof of the various coordination modes.

The study of analogs of EEDTA seems to hold the most exciting future, both in terms of nuclear waste separations and fundamental aspects of lanthanide and actinide chemistry. Measurement of the lanthanide formation constants and Am-Ln separation factors exhibited by the EEDTA analogs in which the ether-oxygen atom has been replaced by methylamine or sulfur will offer a unique opportunity to test the extent of covalent interactions in americium complexes. If indeed actinide covalency is a significant factor, one would expect the Am-Ln separation factors to increase with these "softer" donors. Comparative NMR studies of the EEDTA analogs are also called for.

Finally, solvent extraction experiments should be performed to determine the possible benefits of replacing DTPA with EEDTA in the systems described in the Introduction. In addition, if the methylamine EEDTA analog proves to be a successful Ln-An separator, one can imagine amine-based solvent extraction systems involving long chain amine EEDTA analogs which form organic soluble metal complexes, while retaining their actinide selectivity.

BIBLIOGRAPHY

1. Bond, W. D.; Claiborne, H. C.; Leuze, R. E. Nucl. Tech. 1974, 24, 362.
2. Wheelwright, E. J.; Bray, L. A.; Van Tuyl, H. H.; Fullam, H. T. Richland, Wash., May 1974, AEC Report BNWL-1831.
3. Claiborne, H. C. Oak Ridge, Tenn., Jan 1975, AEC Report ORNL-TM-4724.
4. Blomek, J. O.; Nichols, J. P.; McClain, W. C. Phys. Today 1973, 26, 36.
5. Rochlin, G. I. Science 1977, 195, 23.
6. Tedder, D. D.; Finney, B. C.; Blomek, J. D. In "Actinide Separations", Navratil, J. D., Ed.; American Chemical Society Symposium Series, 117, American Chemical Society: Washington, D.C., 1980; Chapter 27.
7. Brown, D. In MTP International Review of Science, Inorganic Chemistry Series One, "Vol. 7, Lanthanides and Actinides", Emeleus H. J.; Bagwell, K. W., Eds.; University Park Press: Baltimore, 1972, Chapter 3.
8. Moskvin, A. I. Soviet Radiochem. 1967, 9, 677.
9. Bleaney, B.; Llewellyn, P. M.; Jones, D. A. Proc. Phys. Soc. London 1956, 69B, 858.
10. Musikas, C.; Le Marois, G.; Fitoussi, R.; Cullerdier, C. In "Actinide Separations", Navratil, J. D., Ed.; American Chemical Society Symposium Series, 117, American Chemical Society: Washington, D.C., 1980, Chapter 10.
11. Nugent, L. J.; Laubereau, P. G.; Werner, G. K.; Vander Slius, K. L. J. Organometal. Chem. 1971, 27, 365.
12. Baker, E. C.; Halstead, G. W.; Raymond, K. N. Strut. Bonding 1976, 25, 63.
13. Durrant, P. J.; Durrant, B. "Introduction to Advanced Inorganic Chemistry", 2nd ed.; Longman Group LTD: London, 1970.
14. Slater, J. C. "Quantum Theory of Matter", McGraw-Hill: New York, 1953.
15. Petrizolova, H.; Ustav Jaderneho Vyzkumum Rez, (Czechosolvakia), Nov 1966, DOE Report UJV-3683-CH.

16. Barlett, J. W.; Bray, L. A.; Burger, L. L.; Burns, R. E.; Ryan, J. L. Richland Wash., Nov 1973, AEC Report BNWL-1776.

17. Schulz, W. W. "The Chemistry of Americium", ERDA Technical Information Center: Oak Ridge, Tenn., 1976.

18. Seaborg, G. T.; Street, K. J. Amer. Chem. Soc. 1950, 72, 2790.

19. Thompson, S. G.; Harvey, B. G.; Choppin, G. R.; Seaborg, G. T. J. Amer. Chem. Soc. 1954, 76, 6229.

20. Guseva, L. L.; Tikhomirova, G. S. Soviet Radiochem. 1972, 14, 197.

21. Hulet, E. K.; Gutmacher, R. G.; Coops, M. S. J. Inorg. Nucl. Chem. 1961, 17, 350.

22. Marcus, Y. J. Inorg. Nucl. Chem. 1966, 28, 209.

23. Lueze, R. E.; Lloyd, M. H. In "Progress in Nuclear Energy", Series III Process Chemistry, Vol. 4, Stevenson, C. E.; Mason, E. A.; Gresky, A. T., Eds.; Pergamon Press: New York, 1970; p. 549.

24. Burch, W. D.; Bigelow, J. E.; King, L. J. Oak Ridge, Tenn., April 1969, AEC Report ORNL-4376.

25. Baybarz, R. D.; Leuze, R. E. Nucl. Sci. Eng. 1961, 11, 90.

26. Bureev, E. S.; Dedov, V. B.; Karpachevas, S. M.; Shvetsov, I. K.; Ryzhov, M. V.; Trukchlayev, R. S.; Yakovlev, G. N.; Lebedev, I. A. In "Progress in Nuclear Energy", Series III Process Chemistry, Vol. 4, Stevenson, C. E.; Mason, E. A.; Gresky, A. T., Eds.; Pergamon Press: New York, 1970; p. 631.

27. Moore, F. L. Anal. Chem. 1961, 33, 748.

28. Baybarz, R. D.; Weaver, B. S.; Kinser, H. B. Nucl. Sci. Eng. 1963, 17, 457.

29. Mueller, W.; Duyckaerts, G.; Fuger, J. In "Solvent Extraction Chemistry of Metals", McKay, H. A. C.; Healy, T. V.; Jenkins, I. L.; Naylor, A., Eds.; Macmillan and Company Limited: London, 1965; p. 233.

30. Harmon, H. D.; Peterson, J. R.; McDowell, W. J.; Coleman, C. F. J. Inorg. Nucl. Chem. 1976, 38, 155.

31. Hulet, E. K. Livermore, Calif., 1976, ERDA Report UCRL-78332.

32. Bagnall, K. W. In MTP International Review of Science, Inorganic Chemistry Series One, "Vol. 7, Lanthanides and Actinides", Emeleus, H. J.; Bagnell, K. W., Eds.; University Park Press: Baltimore, 1972; Chapter 4.

33. Surls, J. P.; Choppin, G. R. J. Inorg. Nucl. Chem. 1957, 4, 62.

34. Keenan, T. K. J. Inorg. Nucl. Chem. 1961, 20, 185.

35. Coleman, J. S.; Penneman, R. A.; Keenan, T. K.; La Mar, L. E.; Armstrong, D. E.; Asprey, L. B. J. Inorg. Nucl. Chem. 1957, 3, 327.

36. Coleman, J. S.; Asprey, L. B.; Chisholm, R. C. J. Inorg. Nucl. Chem. 1969, 31, 1167.

37. Guseva, L. I.; Tikhomirova, G. S. Soviet Radiochem. 1968, 10, 233.

38. Moskvin, L. N.; Novikov, V. T. Soviet Radiochem. 1972, 14, 102.

39. Guseva, L. I.; Tikhomirova, G. S. Soviet Radiochem. 1974, 16, 152.

40. Lebedev, I. A.; Myasoedov, B. F.; Guseva, L. I. J. Radioanal. Chem. 1974, 21, 259.

41. Sekine, T. Bull. Chem. Soc. Japan 1965, 38, 1972.

42. Khopkar, D. K.; Narayanankutly, P. J. Inorg. Nucl. Chem. 1972, 34, 2617.

43. Mason, G. W.; Peppard, D. F. Nucl. Sci. Eng. 1963, 17, 247.

44. Moore, F. L. Anal. Chem. 1964, 36, 2158.

45. Gerontopulos, P. T.; Rigali, L.; Barbano, P. G. Radiochemica Acta 1965, 4, 75.

46. Hulet, E. K.; Bode, D. D. In MTP International Review of Science, Inorganic Chemistry Series One, "Vol. 7, Lanthanides and Actinides", Emeleus, H. J.; Bagnell, K. W., Eds.; University Park Press: Baltimore, 1972; Chapter 1.

47. Powell, J. E.; Spedding, F. H. Trans. Met. Soc. AIME 1959, 215, 457.

48. Moeller, T.; Thompson, L. C. J. Inorg. Nucl. Chem. 1962, 24, 499.

49. Baybarz, R. D. J. Inorg. Nucl. Chem. 1965, 27, 1831.

50. Martell, A. E.; Smith, R. E. "Critical Stability Constants", Plenum Press: New York, 1974; Vol. 1, p. 204.

51. James, D. B.; Powell, J. E.; Burkholder, H. R. *J. Chromatogr.* 1968, 35, 423.

52. Wheelwright, E. J.; Roberts, F. P. Richland, Wash., July 1969, AEC Report BNWL-1072.

53. Lowe, J. T.; Hale, W. H.; Hallman, D. F. *Ind. Eng. Chem. Process Des. Develop.* 1971, 10, 131.

54. Hale, W. H. Jr.; Hammer, C. A. *Ion Exch. Membranes* 1972, 1, 81.

55. Harbour, R. M.; Hale, W. H. Jr.; Burney, G. A.; Lowe, J. T. *At. Energy Rev.* 1972, 10, 379.

56. Kelley, J. A. Savannah River, Ga., March 1973, AEC Report DP-1308.

57. Baybarz, R. D. Oak Ridge, Tenn., 1965, AEC Report ORNL-3739.

58. Baybarz, R. D. *J. Inorg. Nucl. Chem.* 1966, 28, 1723.

59. Koehly, G.; Hoffert, F. Dec 1967, AEC Report ANL-TRANS-628.

60. McKibben, J. M.; Holcomb, H. P.; Orth, D. A.; Prout, W. E.; Scotten, W. C. Savannah River, Ga., Aug 1974, AEC Report DP-1361.

61. Moore, F. L.; Bray, L. A.; Robert, F. P. In "Solvent Extraction Chemistry of Metals", McKay, H. A. C.; Healy, T. V.; Jenkins, I. L.; Naylor, A., Eds., Macmillan and Company Limited: London, 1965; p. 401.

62. Weaver, B.; Kappelman, F. A. *J. Inorg. Nucl. Chem.* 1968, 30, 263.

63. Ishimori, T. In "Actinide Separations", Navratil, J. D., Ed.; American Chemical Society Symposium Series, 117, American Chemical Society: Washington, D.C., 1980; Chapter 24.

64. Kolarik, Z.; Koch, G.; Kuhn, W. *J. Inorg. Nucl. Chem.* 1974, 36, 905.

65. Tachimori, S.; Nakamura, H. *J. Radioanal. Chem.* 1979, 52, 343.

66. Fardy, J. J.; Pearson, J. M. *J. Inorg. Nucl. Chem.* 1973, 35, 2513.

67. Bond, W. D.; Leuze, R. E. In "Actinide Separations", Navratil, J. D., Ed.; American Chemical Society Symposium Series, 117, American Chemical Society; Washington, D.C., 1980; Chapter 31.

68. Moore, F. L. *Anal. Chem.* 1966, 38, 905.

69. Kopyrin, A. A.; Murashov, V. D.; Demidov, V. D.; Shvedov, V. P. *J. Radioanal. Chem.* 1979, 51, 27.

70. Sekine, T.; Dyrssen, D. Talanta 1964, 11, 867.

71. Kasting, G. B.; Hulet, E. K.; Heppert, J. A.; Wild, J. F. J. Inorg. Nucl. Chem. 1979, 41, 745.

72. Foos, J.; Mesplede, J. J. Inorg. Nucl. Chem. 1972, 34, 2051.

73. Schulz, W. W.; Koenst, J. W.; Tallant, D. R. In "Actinide Separations", Navratil, J. D., Ed.; American Chemical Society Symposium Series, 117, American Chemical Society: Washington, D.C., 1980; Chapter 3.

74. Korkisch, J. "Modern Methods for the Separation of Metal Ions", Pergamon Press: New York, 1969.

75. Powell, J. E.; Farrell, J. L.; Kulprathipanja, S. Inorg. Chem. 1975, 14, 786.

76. Spedding, F. H.; Pikal, M. J.; Ayers, B. D. J. Phys. Chem. 1966, 70, 2440.

77. Mioduski, T.; Siekierski, S. J. Inorg. Nucl. Chem. 1975, 37, 1647.

78. Taga, T.; Kuroda, Y.; Ohashi, M. Bull. Chem. Soc. Japan 1978, 51, 2278.

79. Powell, J. E.; Osuch, C.; Burkholder, H. R.; Kulprathipanja, S.; Miller, J. H.; Stadherr, L. G.; Baughman, R. G. J. Org. Chem. 1978, 43, 3166.

80. Adolphson, M. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1969.

81. Fritz, J. S.; Schenk, G. H. "Quantitative Analytical Chemistry", Allyn and Bacon: Boston, 1969.

82. Miller, J. H. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1977.

83. Lindenbaum, A.; Smyth, M. A. In "Organic Scintillators and Liquid Scintillation Counting", Horrocks, D. C.; Peng, C. T., Eds.; Academic Press: New York, 1971; p. 951.

84. Draper, N. R.; Smith, H. "Applied Regression Analysis", Wiley: New York, 1966.

85. Cannan, R. K.; Kibrick, A. J. Amer. Chem. Soc. 1938, 60, 2314.

86. Spedding, F. H.; Powell, J. E. Ames, Iowa, April 1969, AEC Report ISC-1116.

87. Mackey, J. L.; Hiller, M. A.; Powell, J. E. J. Phys. Chem. 1962, 66, 311.

88. Yashunskii, V. A.; Smolin, D. D.; Ermolaeva, V. G.; Shchukina, M. N. J. Gen. Chem. USSR 1960, 30, 3872.

89. Schwarzenbach, G.; Ackermann, H. Helv. Chim. Acta 1948, 31, 1029.

90. Peerce, P. J.; Gray, H. B.; Anson, F. C. Inorg. Chem. 1979, 18, 2593.

91. Johnson, D. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1973.

92. Brown, K. M. SIAM J. Num. Anal. 1969, 6, 560.

93. Brücker, E.; Király, R.; Varga, Z. Magy. Kem. Folyoirat 1975, 81, 339.

94. Schwarzenbach, G.; Senn, H.; Anderegg, G. Helv. Chim. Acta 1957, 40, 1886.

95. Anderegg, G. Helv. Chim. Acta 1967, 50, 2333.

96. Vasil'eva, V. F.; Lavrova, O. Yu.; Dyatlova, N. M.; Yashunskii, V. G. J. Gen. Chem. USSR 1966, 36, 688.

97. Thompson, L. C.; Shafer, B. L.; Edgar, J. A.; Mannila, K. D. In "Lanthanide/Actinide Chemistry", Fields, P. R.; Moeller, T., Eds.; American Chemical Society Symposium Series, 71, American Chemical Society; Washington, D.C., 1967; Chapter 13.

98. Choppin, G. R.; Baisden, P. A.; Khan, S. A. Inorg. Chem. 1979, 18, 1330.

ACKNOWLEDGMENTS

I would like to express my thanks to Dr. J. E. Powell for his encouragement and counsel. Most of my understanding of the art of chemical research is directly attributable to his patient teaching.

My thanks are also extended to Harvey Burkholder, Jim Miller, Pui Kwan Tse, Scott Stoner, Don Thompson, Bob Staggs, Ken Malaby, and Bill Carroll for their respective parts in making my graduate career a pleasurable and rewarding one.

Finally, my ever growing admiration to my wife, Evelyn, with whom I have shared the agonies and ecstasies of graduate school; and to my parents, who remain the finest teachers I have ever known.

APPENDIX A. SOLUTION DATA FOR THE PROTONATION CONSTANT AND RARE-EARTH COMPLEX STABILITY CONSTANTS OF DHDMB

```
        ALPHA 1 - DHDMB
BUFFER ACID CONCENTRATION =                 0.04864  BUFFER ANION CONC =  0.05110
ORIGINAL STRONG ACID CONCENTRATION =        0.00000  KNO3 CONCENTRATION = 1.05200
FINAL VOLUME =                             100.000   IONIC STRENGTH =      0.100
METAL CONCENTRATION=                        0.00000  METAL VOLUME =       0.000
 (I)    VBFR       VBASE      VHCL        P(H)     NBAR        ERROR   VOL KNO3
  1      1.000      0.000      0.000     3.7430     0.306        0.20     9.450      3.388
  2      2.000      0.000      0.000     3.6220     0.368       -0.01     9.408      3.387
  3      3.000      0.000      0.000     3.5610     0.396       -1.34     9.369      3.377
  4      4.000      0.000      0.000     3.5370     0.415        0.08     9.330      3.388
  5      5.000      0.000      0.000     3.5140     0.426       -0.28     9.292      3.385
  6     10.000      0.000      0.000     3.4680     0.454       -0.01     9.105      3.387
  7     15.000      0.000      0.000     3.4570     0.464        0.97     8.917      3.395
  8     20.000      0.000      0.000     3.4470     0.470        0.90     8.732      3.394
  9     25.000      0.000      0.000     3.4460     0.473        1.54     8.544      3.400
 10     35.000      0.000      0.000     3.4390     0.477        1.51     8.173      3.399
        (I)     BETA(I)        K(I)        PK(I)
         1     0.2438E 04    0.4101E-03    3.387
```

```
        Y - DHDMB
BUFFER ACID CONCENTRATION =                 0.04730  BUFFER ANION CONC =   0.05069
ORIGINAL STRONG ACID CONCENTRATION =        0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                            100.000    IONIC STRENGTH =       0.100
METAL CONCENTRATION=                        0.10560  METAL VOLUME =        2.000
 (I)   VBFR       VBASE      VHCL       P(H)     NBAR       ERROR   VOL KNO3
  1     2.000     0.000      0.000     3.3530    0.470      -0.22     8.344
  2     3.000     0.000      0.000     3.2860    0.627       0.39     8.380
  3     5.000     0.000      0.000     3.2410    0.866      -0.30     8.412
  4     6.000     0.000      0.000     3.2340    0.966      -0.18     8.414
  5     8.000     0.000      0.000     3.2310    1.142       0.56     8.401
  6    10.000     0.000      0.000     3.2380    1.279      -0.03     8.372
  7    12.000     0.000      0.000     3.2460    1.401      -0.07     8.330
  8    14.000     0.000      0.000     3.2540    1.510       0.15     8.279
  9    15.000     0.000      0.000     3.2590    1.554      -0.25     8.251
 10    16.000     0.000      0.000     3.2630    1.600      -0.20     8.221
 11    20.000     0.000      0.000     3.2780    1.759      -0.10     8.090
 12    25.000     0.000      0.000     3.2940    1.916      -0.12     7.906
 13    30.000     0.000      0.000     3.3070    2.040      -0.07     7.707
 14    35.000     0.000      0.000     3.3170    2.152       0.53     7.500
 15    40.000     0.000      0.000     3.3270    2.216      -0.34     7.284
 16    45.000     0.000      0.000     3.3340    2.294       0.16     7.065
 17    50.000     0.000      0.000     3.3400    2.363       0.62     6.842
     (I)     BETA(I)        K(I)       PK(I)          VBETA(I)
      1    0.1505E 04   0.1952E-01   1.710         0.80326E 01
      2    0.2960E 06   0.5083E-02   2.294         0.20397E 04
      3    0.1517E 08   0.6646E-03   3.177         0.21691E 06

     WEIGHTING OPTION USED =    -1
```

```
        LA - DHDMB
BUFFER ACID CONCENTRATION =                0.04730  BUFFER ANION CONC =  0.05069
ORIGINAL STRONG ACID CONCENTRATION =       0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                           100.000   IONIC STRENGTH =      0.100
METAL CONCENTRATION=                       0.10403  METAL VOLUME =       2.000
 (I)    VBFR       VBASE      VHCL        P(H)     NBAR       ERROR   VOL KNO3
  1      1.000      0.000      0.000     3.5950    0.196        0.11     8.253
  2      2.000      0.000      0.000     3.4490    0.331       -0.40     8.282
  3      4.000      0.000      0.000     3.3560    0.537        0.42     8.300
  4      5.000      0.000      0.000     3.3390    0.618        0.33     8.297
  5      6.000      0.000      0.000     3.3300    0.688       -0.06     8.289
  6      8.000      0.000      0.000     3.3230    0.805       -0.61     8.258
  7     10.000      0.000      0.000     3.3210    0.910        0.18     8.214
  8     12.000      0.000      0.000     3.3240    0.989       -0.44     8.161
  9     14.000      0.000      0.000     3.3270    1.063       -0.28     8.101
 10     15.000      0.000      0.000     3.3280    1.101        0.32     8.070
 11     16.000      0.000      0.000     3.3300    1.130        0.21     8.037
 12     18.000      0.000      0.000     3.3340    1.184       -0.04     7.967
 13     20.000      0.000      0.000     3.3370    1.239        0.46     7.895
 14     30.000      0.000      0.000     3.3520    1.428        0.38     7.502
 15     35.000      0.000      0.000     3.3580    1.493       -0.02     7.293
 16     40.000      0.000      0.000     3.3630    1.547       -0.38     7.079
 17     45.000      0.000      0.000     3.3670    1.598       -0.37     6.861
     (I)      BETA(I)         K(I)        PK(I)           VBETA(I)
      1     0.6520E 03    0.2296E 00     0.639          0.21684E 01
      2     0.4605E 05    0.1416E-01     1.849          0.44429E 03
      3     0.2005E 06    0.1534E-02     2.814          0.25900E 05

     WEIGHTING OPTION USED =    -1
```

```
        CE - DHDMB
BUFFER ACID CONCENTRATION =                    0.04730  BUFFER ANION CONC =  0.05069
ORIGINAL STRONG ACID CONCENTRATION =           0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                               100.000    IONIC STRENGTH =      0.100
METAL CONCENTRATION=                           0.10539  METAL VOLUME =        2.000
 (I)    VBFR       VBASE      VHCL        P(H)     NBAR       ERROR   VOL KNO3
  1      1.000     0.000      0.000      3.5420    0.251        0.26    8.271
  2      3.000     0.000      0.000      3.3290    0.549       -0.32    8.343
  3      4.000     0.000      0.000      3.3010    0.657        0.15    8.354
  4      5.000     0.000      0.000      3.2890    0.746       -0.05    8.354
  5      6.000     0.000      0.000      3.2840    0.822       -0.04    8.347
  6      8.000     0.000      0.000      3.2840    0.949        0.03    8.317
  7     10.000     0.000      0.000      3.2900    1.048       -0.38    8.274
  8     12.000     0.000      0.000      3.2960    1.137       -0.11    8.220
  9     14.000     0.000      0.000      3.3020    1.215        0.20    8.161
 10     15.000     0.000      0.000      3.3050    1.250        0.27    8.129
 11     16.000     0.000      0.000      3.3080    1.283        0.27    8.096
 12     25.000     0.000      0.000      3.3290    1.521        0.59    7.768
 13     30.000     0.000      0.000      3.3380    1.614        0.15    7.569
 14     35.000     0.000      0.000      3.3460    1.680       -1.04    7.362
 15     40.000     0.000      0.000      3.3510    1.764       -0.33    7.152
     (I)      BETA(I)        K(I)       PK(I)          VBETA(I)
      1     0.1189E 04   0.6139E-01    1.212          0.40503E 01
      2     0.1051E 06   0.1132E-01    1.946          0.90632E 03
      3     0.1711E 07   0.8409E-03    3.075          0.69393E 05

     WEIGHTING OPTION USED =    -1
```

```
        PR - DHDMB
BUFFER ACID CONCENTRATION =                0.04745  BUFFER ANION CONC =  0.05110
ORIGINAL STRONG ACID CONCENTRATION =       0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                           100.000    IONIC STRENGTH =       0.100
METAL CONCENTRATION=                       0.10090  METAL VOLUME =       2.000
 (I)     VBFR       VBASE       VHCL        P(H)     NBAR        ERROR   VOL KNO3
  1      3.000      0.000       0.000      3.2980    0.638        0.21     8.422
  2      4.000      0.000       0.000      3.2740    0.755        0.21     8.433
  3      5.000      0.000       0.000      3.2660    0.848       -0.27     8.434
  4      6.000      0.000       0.000      3.2640    0.930       -0.23     8.426
  5      8.000      0.000       0.000      3.2690    1.062       -0.18     8.393
  6     10.000      0.000       0.000      3.2780    1.167       -0.23     8.346
  7     12.000      0.000       0.000      3.2870    1.257       -0.09     8.289
  8     14.000      0.000       0.000      3.2950    1.336        0.28     8.226
  9     15.000      0.000       0.000      3.3000    1.363       -0.30     8.192
 10     16.000      0.000       0.000      3.3030    1.401        0.19     8.158
 11     18.000      0.000       0.000      3.3090    1.468        0.85     8.086
 12     20.000      0.000       0.000      3.3150    1.524        1.06     8.011
 13     30.000      0.000       0.000      3.3390    1.711        0.19     7.606
 14     35.000      0.000       0.000      3.3480    1.766       -1.00     7.390
 15     40.000      0.000       0.000      3.3550    1.814       -1.83     7.171
      (I)      BETA(I)         K(I)        PK(I)           VBETA(I)
       1     0.1715E 04    0.7456E-01    1.128          0.16767E 02
       2     0.2171E 06    0.7901E-02    2.102          0.25994E 04
       3     0.2911E 07    0.5831E-03    3.234          0.23725E 06

      WEIGHTING OPTION USED =    -1
```

```
              ND - DHDMBA
BUFFER ACID CONCENTRATION =                   0.04745  BUFFER ANION CONC =  0.05110
ORIGINAL STRONG ACID CONCENTRATION =          0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                               100.000   IONIC STRENGTH =       0.100
METAL CONCENTRATION=                          0.10020  METAL VOLUME =         2.000
 (I)    VBFR       VBASE      VHCL      P(H)     NBAR      ERROR   VOL KNO3
  1      2.000     0.000      0.000    3.3250    0.540     -0.06     8.425
  2      3.000     0.000      0.000    3.2670    0.701      0.27     8.457
  3      4.000     0.000      0.000    3.2460    0.823      0.02     8.470
  4      6.000     0.000      0.000    3.2410    1.006     -0.34     8.464
  5      8.000     0.000      0.000    3.2500    1.144     -0.37     8.432
  6     10.000     0.000      0.000    3.2610    1.257     -0.10     8.385
  7     12.000     0.000      0.000    3.2720    1.351      0.03     8.329
  8     14.000     0.000      0.000    3.2810    1.439      0.67     8.267
  9     15.000     0.000      0.000    3.2860    1.473      0.50     8.233
 10     16.000     0.000      0.000    3.2910    1.503      0.16     8.198
 11     18.000     0.000      0.000    3.2990    1.565      0.15     8.127
 12     20.000     0.000      0.000    3.3060    1.622      0.18     8.052
 13     25.000     0.000      0.000    3.3210    1.733     -0.24     7.854
 14     30.000     0.000      0.000    3.3320    1.829     -0.23     7.647
 15     35.000     0.000      0.000    3.3420    1.885     -1.49     7.431
      (I)     BETA(I)        K(I)        PK(I)          VBETA(I)
       1     0.2354E 04   0.4757E-01    1.323        0.14904E 02
       2     0.3748E 06   0.6281E-02    2.202        0.37094E 04
       3     0.7879E 07   0.4248E-03    3.372        0.35420E 06

      WEIGHTING OPTION USED =    -1
```

```
        SM - DHDMB
BUFFER ACID CONCENTRATION =                  0.04864  BUFFER ANION CONC =  0.05110
ORIGINAL STRONG ACID CONCENTRATION =         0.00000  KNO3 CONCENTRATION = 1.05200
FINAL VOLUME =                               100.000  IONIC STRENGTH =       0.100
METAL CONCENTRATION=                         0.10060  METAL VOLUME =       2.000
 (I)    VBFR       VBASE      VHCL        P(H)     NBAR        ERROR    VOL KNO3
  1      1.000      0.000      0.000     3.4490    0.356        0.61      8.501
  2      2.000      0.000      0.000     3.2770    0.599       -0.35      8.579
  3      5.000      0.000      0.000     3.1890    1.029       -0.36      8.643
  4      7.000      0.000      0.000     3.1960    1.208       -0.08      8.627
  5      8.000      0.000      0.000     3.2030    1.281        0.04      8.610
  6     11.000      0.000      0.000     3.2260    1.458        0.36      8.538
  7     13.000      0.000      0.000     3.2420    1.540       -0.24      8.477
  8     14.000      0.000      0.000     3.2460    1.596        0.97      8.445
  9     16.000      0.000      0.000     3.2600    1.654        0.09      8.374
 10     19.000      0.000      0.000     3.2770    1.727       -0.86      8.259
 11     20.000      0.000      0.000     3.2790    1.775        0.54      8.221
 12     25.000      0.000      0.000     3.2980    1.880        0.28      8.015
 13     35.000      0.000      0.000     3.3240    2.011       -1.05      7.576
 14     40.000      0.000      0.000     3.3320    2.075       -0.74      7.351
 15     45.000      0.000      0.000     3.3390    2.121       -0.97      7.122
     (I)      BETA(I)        K(I)        PK(I)          VBETA(I)
      1     0.3284E 04    0.4473E-01     1.349         0.23623E 02
      2     0.8881E 06    0.3698E-02     2.432         0.99262E 04
      3     0.1986E 08    0.3045E-03     3.516         0.91115E 06

     WEIGHTING OPTION USED =    -1
```

```
       EU - DHDMB
BUFFER ACID CONCENTRATION =                 0.04730  BUFFER ANION CONC =  0.05069
ORIGINAL STRONG ACID CONCENTRATION =        0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                            100.000    IONIC STRENGTH =      0.100
METAL CONCENTRATION=                        0.10104  METAL VOLUME =       2.000
 (I)    VBFR       VBASE      VHCL       P(H)     NBAR      ERROR   VOL KNO3
  1      2.000     0.000      0.000     3.2870   0.588       0.05     8.442
  2      3.000     0.000      0.000     3.2240   0.769      -0.30     8.484
  3      4.000     0.000      0.000     3.1980   0.914       0.05     8.505
  4      5.000     0.000      0.000     3.1890   1.036       0.28     8.513
  5      6.000     0.000      0.000     3.1890   1.138       0.16     8.513
  6      8.000     0.000      0.000     3.1990   1.308      -0.07     8.494
  7     10.000     0.000      0.000     3.2120   1.451       0.13     8.457
  8     12.000     0.000      0.000     3.2270   1.563      -0.35     8.409
  9     14.000     0.000      0.000     3.2390   1.670       0.02     8.351
 10     15.000     0.000      0.000     3.2460   1.709      -0.43     8.320
 11     16.000     0.000      0.000     3.2510   1.756      -0.12     8.288
 12     18.000     0.000      0.000     3.2610   1.838       0.13     8.219
 13     20.000     0.000      0.000     3.2710   1.901      -0.17     8.146
 14     25.000     0.000      0.000     3.2900   2.048       0.13     7.952
 15     30.000     0.000      0.000     3.3050   2.160       0.25     7.746
 16     35.000     0.000      0.000     3.3170   2.249       0.29     7.532
 17     40.000     0.000      0.000     3.3260   2.335       0.97     7.313
     (I)     BETA(I)        K(I)       PK(I)         VBETA(I)
      1    0.3112E 04    0.1808E-01   1.743        0.17272E 02
      2    0.8887E 06    0.3501E-02   2.456        0.47708E 04
      3    0.4916E 08    0.3214E-03   3.493        0.68387E 06

     WEIGHTING OPTION USED =    -1
```

```
         GD - DHDMB
BUFFER ACID CONCENTRATION =                0.04724  BUFFER ANION CONC =   0.05069
ORIGINAL STRONG ACID CONCENTRATION =       0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                            100.000   IONIC STRENGTH =      0.100
METAL CONCENTRATION=                       0.08388  METAL VOLUME =        2.000
 (I)    VBFR      VBASE     VHCL      P(H)    NBAR      ERROR   VOL KNO3
  1      1.000     0.000     0.000    3.4940   0.378     -0.08     8.540
  2      3.000     0.000     0.000    3.2700   0.826     -0.16     8.629
  3      4.000     0.000     0.000    3.2440   0.983      0.32     8.641
  4      5.000     0.000     0.000    3.2350   1.110      0.16     8.642
  5      6.000     0.000     0.000    3.2340   1.217     -0.14     8.635
  6      8.000     0.000     0.000    3.2400   1.399      0.05     8.602
  7     10.000     0.000     0.000    3.2520   1.536     -0.40     8.554
  8     12.000     0.000     0.000    3.2620   1.663      0.31     8.496
  9     14.000     0.000     0.000    3.2740   1.753     -0.22     8.430
 10     15.000     0.000     0.000    3.2790   1.797     -0.19     8.395
 11     16.000     0.000     0.000    3.2840   1.835     -0.30     8.358
 12     18.000     0.000     0.000    3.2920   1.915      0.17     8.283
 13     20.000     0.000     0.000    3.3000   1.977      0.10     8.204
 14     30.000     0.000     0.000    3.3280   2.215      0.59     7.784
 15     35.000     0.000     0.000    3.3380   2.290      0.40     7.563
     (I)     BETA(I)        K(I)       PK(I)         VBETA(I)
      1    0.2655E 04   0.1872E-01   1.728        0.13280E 02
      2    0.9174E 06   0.2895E-02   2.538        0.51542E 04
      3    0.4902E 08   0.3766E-03   3.424        0.71740E 06

     WEIGHTING OPTION USED =   -1
```

```
      TB - DHDMB
BUFFER ACID CONCENTRATION =                  0.04724  BUFFER ANION CONC =  0.05069
ORIGINAL STRONG ACID CONCENTRATION =         0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                             100.000    IONIC STRENGTH =       0.100
METAL CONCENTRATION=                         0.10582  METAL VOLUME =       2.000
 (I)     VBFR       VBASE      VHCL       P(H)     NBAR       ERROR   VOL KNO3
  1      3.000      0.000      0.000     3.2390    0.709       0.10    8.419
  2      4.000      0.000      0.000     3.2050    0.859       0.15    8.448
  3      5.000      0.000      0.000     3.1900    0.987      -0.04    8.465
  4      6.000      0.000      0.000     3.1850    1.098      -0.21    8.472
  5      8.000      0.000      0.000     3.1890    1.284      -0.20    8.462
  6     10.000      0.000      0.000     3.2000    1.436       0.30    8.431
  7     12.000      0.000      0.000     3.2160    1.549      -0.23    8.385
  8     14.000      0.000      0.000     3.2310    1.643      -0.49    8.329
  9     15.000      0.000      0.000     3.2360    1.696       0.28    8.298
 10     16.000      0.000      0.000     3.2430    1.733       0.08    8.265
 11     18.000      0.000      0.000     3.2540    1.811       0.56    8.196
 12     20.000      0.000      0.000     3.2650    1.870       0.46    8.123
 13     30.000      0.000      0.000     3.3040    2.083       0.19    7.718
 14     35.000      0.000      0.000     3.3180    2.140      -0.74    7.501
 15     40.000      0.000      0.000     3.3290    2.184      -1.57    7.280
     (I)      BETA(I)       K(I)        PK(I)           VBETA(I)
      1     0.2018E 04   0.2888E-01    1.539         0.27456E 02
      2     0.7430E 06   0.2717E-02    2.566         0.56635E 04
      3     0.2573E 08   0.4954E-03    3.305         0.81901E 06

     WEIGHTING OPTION USED =   -1
```

```
        DY - DHDMB
BUFFER ACID CONCENTRATION =                  0.04724  BUFFER ANION CONC =  0.05069
ORIGINAL STRONG ACID CONCENTRATION =         0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                             100.000    IONIC STRENGTH =      0.100
METAL CONCENTRATION=                         0.10220  METAL VOLUME =       2.000
 (I)    VBFR       VBASE      VHCL       P(H)     NBAR      ERROR   VOL KNO3
  1      2.000     0.000      0.000     3.3160    0.541      0.00    8.409
  2      3.000     0.000      0.000     3.2440    0.725      0.18    8.454
  3      4.000     0.000      0.000     3.2110    0.877     -0.19    8.482
  4      5.000     0.000      0.000     3.1950    1.010     -0.01    8.497
  5      8.000     0.000      0.000     3.1930    1.316     -0.02    8.491
  6     10.000     0.000      0.000     3.2050    1.466     -0.06    8.459
  7     12.000     0.000      0.000     3.2190    1.589      0.00    8.411
  8     14.000     0.000      0.000     3.2330    1.689      0.02    8.354
  9     15.000     0.000      0.000     3.2400    1.731     -0.13    8.323
 10     16.000     0.000      0.000     3.2450    1.781      0.47    8.290
 11     18.000     0.000      0.000     3.2580    1.844     -0.10    8.219
 12     20.000     0.000      0.000     3.2680    1.910      0.14    8.145
 13     25.000     0.000      0.000     3.2900    2.030     -0.19    7.947
 14     30.000     0.000      0.000     3.3060    2.129     -0.06    7.737
 15     35.000     0.000      0.000     3.3190    2.199     -0.40    7.520
     (I)      BETA(I)         K(I)        PK(I)          VBETA(I)
      1     0.2003E 04     0.2421E-01    1.616         0.95942E 01
      2     0.7792E 06     0.2571E-02    2.590         0.31434E 04
      3     0.3219E 08     0.4992E-03    3.302         0.38676E 06

     WEIGHTING OPTION USED =    -1
```

```
        HO - DHDMB
BUFFER ACID CONCENTRATION =                  0.04745  BUFFER ANION CONC =  0.05110
ORIGINAL STRONG ACID CONCENTRATION =         0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                             100.000    IONIC STRENGTH =       0.100
METAL CONCENTRATION=                         0.09840  METAL VOLUME =       2.000
 (I)    VBFR       VBASE       VHCL        P(H)     NBAR       ERROR   VOL KNO3
  1      2.000      0.000       0.000      3.3220    0.555       0.01     8.447
  2      3.000      0.000       0.000      3.2560    0.734      -0.34     8.487
  3      4.000      0.000       0.000      3.2240    0.888       0.46     8.509
  4      5.000      0.000       0.000      3.2120    1.013      -0.09     8.520
  5      6.000      0.000       0.000      3.2070    1.126       0.12     8.521
  6      8.000      0.000       0.000      3.2110    1.312      -0.06     8.505
  7     10.000      0.000       0.000      3.2210    1.465       0.01     8.470
  8     14.000      0.000       0.000      3.2460    1.692      -0.54     8.365
  9     15.000      0.000       0.000      3.2510    1.744      -0.25     8.333
 10     16.000      0.000       0.000      3.2560    1.792      -0.05     8.300
 11     18.000      0.000       0.000      3.2650    1.881       0.54     8.231
 12     20.000      0.000       0.000      3.2750    1.946       0.15     8.157
 13     25.000      0.000       0.000      3.2940    2.093       0.35     7.959
 14     30.000      0.000       0.000      3.3090    2.204       0.44     7.749
 15     35.000      0.000       0.000      3.3220    2.273      -0.36     7.530
 16     40.000      0.000       0.000      3.3320    2.335      -0.70     7.306
       (I)     BETA(I)        K(I)        PK(I)          VBETA(I)
        1     0.2133E 04   0.1690E-01    1.772         0.16465E 02
        2     0.6750E 06   0.3160E-02    2.500         0.45922E 04
        3     0.3995E 08   0.4688E-03    3.329         0.64121E 06

       WEIGHTING OPTION USED =    -1
```

```
        ER - DHDMB
BUFFER ACID CONCENTRATION =               0.04745  BUFFER ANION CONC =  0.05110
ORIGINAL STRONG ACID CONCENTRATION =      0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                           100.000   IONIC STRENGTH =      0.100
METAL CONCENTRATION=                      0.10546  METAL VOLUME =       2.000
 (I)    VBFR       VBASE      VHCL        P(H)     NBAR       ERROR   VOL KNO3
  1      1.000      0.000      0.000     3.4770    0.318       0.02     8.309
  2      2.000      0.000      0.000     3.3030    0.544       0.01     8.383
  3      3.000      0.000      0.000     3.2370    0.718      -0.27     8.427
  4      4.000      0.000      0.000     3.2080    0.861      -0.18     8.452
  5      5.000      0.000      0.000     3.1940    0.988       0.72     8.463
  6      6.000      0.000      0.000     3.1930    1.089      -0.04     8.467
  7      8.000      0.000      0.000     3.1990    1.265      -0.13     8.453
  8     10.000      0.000      0.000     3.2100    1.413       0.10     8.421
  9     12.000      0.000      0.000     3.2240    1.530      -0.39     8.376
 10     14.000      0.000      0.000     3.2360    1.637      -0.23     8.322
 11     15.000      0.000      0.000     3.2420    1.684      -0.28     8.292
 12     20.000      0.000      0.000     3.2660    1.892       0.52     8.123
 13     25.000      0.000      0.000     3.2860    2.040       0.56     7.931
 14     30.000      0.000      0.000     3.3030    2.137      -0.30     7.724
 15     35.000      0.000      0.000     3.3150    2.233       0.01     7.510
     (I)      BETA(I)        K(I)        PK(I)           VBETA(I)
      1     0.2400E 04    0.1807E-01    1.743          0.13258E 02
      2     0.6591E 06    0.3642E-02    2.439          0.54199E 04
      3     0.3648E 08    0.4166E-03    3.380          0.73790E 06

     WEIGHTING OPTION USED =    -1
```

```
       TM - DHOMB
BUFFER ACID CONCENTRATION =                0.04730  BUFFER ANION CONC =  0.05069
ORIGINAL STRONG ACID CONCENTRATION =       0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                           100.000    IONIC STRENGTH =       0.100
METAL CONCENTRATION=                       0.10109  METAL VOLUME =       2.000
 (I)    VBFR      VBASE      VHCL       P(H)     NBAR      ERROR   VOL KNO3
  1      2.000     0.000      0.000     3.3030    0.565       0.24    8.429
  2      3.000     0.000      0.000     3.2440    0.732      -0.44    8.467
  3      4.000     0.000      0.000     3.2200    0.867      -0.19    8.485
  4      5.000     0.000      0.000     3.2110    0.981       0.27    8.490
  5      6.000     0.000      0.000     3.2100    1.078       0.43    8.488
  6      8.000     0.000      0.000     3.2180    1.240       0.20    8.466
  7     10.000     0.000      0.000     3.2290    1.376       0.11    8.430
  8     12.000     0.000      0.000     3.2420    1.484      -0.78    8.383
  9     14.000     0.000      0.000     3.2520    1.590      -0.68    8.328
 10     15.000     0.000      0.000     3.2560    1.643      -0.29    8.298
 11     16.000     0.000      0.000     3.2590    1.699       0.52    8.267
 12     35.000     0.000      0.000     3.3170    2.248       0.85    7.529
 13     40.000     0.000      0.000     3.3270    2.315       0.21    7.311
 14     45.000     0.000      0.000     3.3340    2.397       0.92    7.090
 15     50.000     0.000      0.000     3.3420    2.418      -0.54    6.862
       (I)    BETA(I)        K(I)       PK(I)          VBETA(I)
        1    0.2778E 04   0.1530E-01    1.815        0.25125E 02
        2    0.5668E 06   0.4901E-02    2.310        0.67795E 04
        3    0.3705E 08   0.3600E-03    3.444        0.10587E 07

       WEIGHTING OPTION USED =    -1
```

```
      YB - DHOMB
BUFFER ACID CONCENTRATION =                  0.04724  BUFFER ANION CONC =  0.05069
ORIGINAL STRONG ACID CONCENTRATION =         0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                             100.000    IONIC STRENGTH =      0.100
METAL CONCENTRATION=                         0.10025  METAL VOLUME =       2.000
 (I)    VBFR       VBASE      VHCL       P(H)     NBAR       ERROR   VOL KNO3
  1      1.000      0.000      0.000     3.4640    0.347      -0.33     8.375
  2      2.000      0.000      0.000     3.2900    0.589       0.19     8.448
  3      3.000      0.000      0.000     3.2290    0.766       0.20     8.487
  4      4.000      0.000      0.000     3.2070    0.903       0.08     8.505
  5      5.000      0.000      0.000     3.2020    1.013      -0.17     8.510
  6      6.000      0.000      0.000     3.2030    1.109       0.20     8.506
  7      8.000      0.000      0.000     3.2180    1.252      -0.55     8.478
  8     10.000      0.000      0.000     3.2330    1.372      -0.23     8.433
  9     12.000      0.000      0.000     3.2470    1.473       0.28     8.377
 10     14.000      0.000      0.000     3.2610    1.550       0.14     8.313
 11     15.000      0.000      0.000     3.2670    1.586       0.23     8.279
 12     16.000      0.000      0.000     3.2730    1.616       0.13     8.244
 13     20.000      0.000      0.000     3.2920    1.729       0.47     8.094
 14     30.000      0.000      0.000     3.3250    1.898      -0.36     7.679
 15     35.000      0.000      0.000     3.3360    1.951      -0.96     7.461
     (I)     BETA(I)        K(I)        PK(I)         VBETA(I)
      1    0.3161E 04    0.5978E-01    1.223        0.15048E 02
      2    0.8119E 06    0.3894E-02    2.410        0.55674E 04
      3    0.1358E 08    0.3163E-03    3.500        0.64954E 06

     WEIGHTING OPTION USED =   -1
```

```
       LU - DHDMB
BUFFER ACID CONCENTRATION =                    0.04724  BUFFER ANION CONC =  0.05069
ORIGINAL STRONG ACID CONCENTRATION =           0.00000  KNO3 CONCENTRATION = 1.06800
FINAL VOLUME =                                100.000   IONIC STRENGTH =      0.100
METAL CONCENTRATION=                           0.10210  METAL VOLUME =        2.000
 (I)    VBFR        VBASE       VHCL        P(H)      NBAR        ERROR    VOL KNO3
  1      2.000       0.000       0.000     3.2690     0.608        -0.07     8.443
  2      3.000       0.000       0.000     3.2060     0.793         0.27     8.485
  3      4.000       0.000       0.000     3.1850     0.933        -0.04     8.506
  4      5.000       0.000       0.000     3.1810     1.045        -0.23     8.513
  5      8.000       0.000       0.000     3.2000     1.293        -0.28     8.484
  6     10.000       0.000       0.000     3.2160     1.421         0.51     8.440
  7     12.000       0.000       0.000     3.2350     1.509        -0.22     8.385
  8     14.000       0.000       0.000     3.2490     1.595         0.28     8.322
  9     15.000       0.000       0.000     3.2570     1.623        -0.24     8.288
 10     16.000       0.000       0.000     3.2630     1.658        -0.07     8.253
 11     18.000       0.000       0.000     3.2740     1.720         0.17     8.179
 12     20.000       0.000       0.000     3.2840     1.771         0.17     8.103
 13     25.000       0.000       0.000     3.3030     1.884         0.75     7.902
 14     35.000       0.000       0.000     3.3310     2.001        -0.90     7.471
 15     40.000       0.000       0.000     3.3400     2.050        -1.17     7.249
     (I)      BETA(I)          K(I)        PK(I)          VBETA(I)
      1     0.3788E 04    0.5049E-01    1.297          0.28287E 02
      2     0.1110E 07    0.3413E-02    2.467          0.83094E 04
      3     0.2198E 08    0.2640E-03    3.578          0.92710E 06

     WEIGHTING OPTION USED =    -1
```

APPENDIX B. SOLUTION DATA FOR THE PROTONATION CONSTANTS AND RARE-EARTH COMPLEX STABILITY CONSTANTS OF PMDTA

```
        PMDTA - ALPHA 1, 2
ORIGINAL ACID CONCENTRATION =                 0.04881  ORIGINAL BASE CONC = 0.05532
ORIGINAL STRONG ACID CONCENTRATION =          0.03890  KNO3 CONCENTRATION = 1.06800
METAL CONCENTRATION=                          0.0      METAL VOLUME =       0.0
FINAL VOLUME =                               200.000   IONIC STRENGTH =      0.100
 (I)    VACID      VBASE      VHCL        P(H)     NBAR       ERROR    VOL KNO3
  1      5.000     10.500      0.0       9.0020    1.63 -0.1423E 01   17.826
  2      5.000     11.000      0.0       9.1930    1.52  0.3931E-01   17.740
  3      5.000     11.500      0.0       9.3300    1.42  0.3211E 00   17.663
  4      5.000     12.000      0.0       9.4520    1.31  0.5793E 00   17.584
  5      5.000     12.500      0.0       9.5550    1.21  0.1322E-01   17.510
  6      5.000     13.000      0.0       9.6690    1.11  0.1001E 01   17.423
  7      5.000     13.500      0.0       9.7630    1.01  0.4727E 00   17.346
  8      5.000     14.000      0.0       9.8470    0.91 -0.1059E 01   17.274
  9      5.000     14.500      0.0       9.9460    0.82 -0.4152E 00   17.190
 10      5.000     15.000      0.0      10.0400    0.74 -0.5839E-02   17.108
 11      5.000     15.500      0.0      10.1300    0.65  0.2000E 00   17.029
        (I)      BETA(I)        K(I)        PK(I)            VBETA(I)
         1     0.1573E 11    0.4489E-09    9.348           0.31706E 09
         2     0.3504E 20    0.6357E-10   10.197           0.46114E 18

     WEIGHTING OPTION USED =   -1   HTIT = 4     FIRST DATA POINT =  1
```

```
        PMDTA - ALPHA 3, 4
ORIGINAL ACID CONCENTRATION =              0.04881  ORIGINAL BASE CONC = 0.05532
ORIGINAL STRONG ACID CONCENTRATION =       0.03890  KNO3 CONCENTRATION = 1.06800
METAL CONCENTRATION=                       0.00000  METAL VOLUME =         0.000
FINAL VOLUME =                           200.000    IONIC STRENGTH =       0.100
 (I)    VACID     VBASE     VHCL        P(H)     NBAR      ERROR    VOL KNO3
  1     5.000     0.000    10.000      2.4990    0.996 0.2774E 01    18.126
  2     5.000     0.000     9.000      2.5220    0.971 0.3176E 01    18.153
  3     5.000     0.000     8.000      2.5440    0.933 0.2107E 01    18.179
  4     5.000     0.000     7.000      2.5650    0.884-0.4362E 00    18.203
  5     5.000     0.000     6.000      2.5910    0.855-0.2320E 00    18.228
  6     5.000     0.000     5.000      2.6170    0.817-0.9619E 00    18.252
  7     5.000     0.000     4.000      2.6460    0.786-0.6296E 00    18.275
  8     5.000     0.000     3.000      2.6770    0.754-0.7201E-01    18.298
  9     5.000     0.000     2.000      2.7070    0.710-0.1450E 01    18.319
 10     5.000     0.000     1.000      2.7400    0.668-0.2211E 01    18.340
 11     5.000     0.000     0.000      2.7760    0.627-0.2584E 01    18.360
 12     5.000     1.000     0.000      2.8350    0.575-0.1281E 01    18.334
 13     5.000     2.000     0.000      2.9000    0.515-0.8116E 00    18.306
 14     5.000     3.000     0.000      2.9750    0.452-0.4477E-01    18.276
 15     5.000     4.000     0.000      3.0620    0.383 0.4562E-01    18.243
 16     5.000     5.000     0.000      3.1700    0.313 0.1301E 01    18.207
 17     5.000     6.000     0.000      3.3080    0.237 0.2061E 01    18.168
     (I)      BETA(I)        K(I)        PK(I)          VBETA(I)
      1     0.5131E 03    0.5773E-02     2.239         0.97592E 01
      2     0.8888E 05    0.1949E-02     2.710         0.20478E 04

     WEIGHTING OPTION USED =    -1    HTIT = 2     FIRST DATA POINT =  1
```

PMDTA Stability Constant Data

Ligand volume = 5.00

Ligand concentration = 0.04699

Base concentration = 0.06059

Salt concentration = 1.066

Rare-earth volume = 2.00

Final volume = 100.00

V base	pH	V salt	V base	pH	V salt
Yttrium concentration = 0.10500					
8.00	4.120	7.75	9.50	5.374	8.12
8.50	4.663	7.87	10.00	5.626	8.23
9.00	5.082	8.00	10.50	5.865	8.32
Lanthanum concentration = 0.10403					
8.00	4.505	7.76	9.50	6.094	8.13
8.50	5.373	7.88	10.00	6.339	8.27
9.00	5.792	8.01	10.50	ppt	8.33
Cerium concentration = 0.10539					
8.00	4.358	7.74	9.50	5.806	8.12
8.50	5.148	7.87	10.00	6.087	8.22
9.00	5.548	8.00	10.50	ppt	8.32
Praseodymium concentration = 0.10786					
8.00	4.299	7.71	9.50	5.690	8.09
8.50	5.030	7.84	10.00	5.948	8.20
9.00	5.421	7.97	10.50	6.187	8.30

V base	pH	V salt	V base	pH	V salt
Neodymium concentration = 0.1002					
8.00	4.222	7.80	9.50	5.689	8.17
8.50	4.992	7.92	10.00	5.944	8.27
9.00	5.410	8.05	10.50	6.219	8.36
Samarium concentration = 0.10726					
8.00	4.201	7.72	9.50	5.489	8.09
8.50	4.818	7.85	10.00	5.723	8.21
9.00	5.206	7.98	10.50	5.967	8.30
Europium concentration = 0.13174					
8.00	4.136	7.46	9.50	5.324	7.85
8.50	4.694	7.58	10.00	5.562	7.97
9.00	5.050	7.72	10.50	5.773	8.08
Gadolinium concentration = 0.10218					
8.00	4.167	7.78	9.50	5.418	8.15
8.50	4.719	7.90	10.00	5.656	8.25
9.00	5.117	8.03	10.50	5.891	8.35
Terbium concentration = 0.10582					
8.00	4.114	7.74	9.50	5.290	8.11
8.50	4.636	7.86	10.00	5.539	8.22
9.00	4.996	7.99	10.50	5.776	8.32
Dysprosium concentration = 0.1022					
8.00	4.106	7.78	9.50	5.212	8.15
8.50	4.579	7.90	10.00	5.458	8.25
9.00	4.944	8.03	10.50	5.722	8.35

V base	pH	V salt	V base	pH	V salt
		Holmium concentration = 0.10497			
9.00	4.838	8.00	9.75	5.261	8.18
9.25	4.999	8.06	10.00	5.383	8.23
9.50	5.108	8.12	10.25	5.518	8.28
		Erbium concentration = 0.10546			
9.00	4.745	7.99	9.75	5.172	8.17
9.25	4.906	8.05	10.00	5.296	8.22
9.50	5.041	8.11	10.25	5.420	8.27
		Thulium concentration = 0.10459			
9.00	4.676	8.00	9.75	5.099	8.18
9.25	4.820	8.06	10.00	5.220	8.23
9.50	4.945	8.12	10.25	5.356	8.28
		Ytterbium concentration = 0.10025			
9.00	4.631	8.05	9.75	5.031	8.22
9.25	4.782	8.11	10.00	5.178	8.27
9.50	4.920	8.17	10.25	5.311	8.32
		Lutetium concentration =			
9.00	4.609	8.03	9.75	5.010	8.20
9.25	4.765	8.09	10.00	5.157	8.25
9.50	4.879	8.15	10.25	5.279	8.30

APPENDIX C. COMPUTER PROGRAM HCMPLX

```
C PROGRAM HCMPLX
C THIS PROGRAM CALCULATES BMHLAND BML FOR METAL ION AND ACIDS OF THE FORM H4L
C THE DATA DECK CONSISTS OF
C CARD 1                     TITLE
C CARD2
C      COL  1   F10.5        LIGCON
C      COL 11   F10.5        BASCON
C      COL 21   F10.5        METCON
C      COL 31   F10.5        SLTCON
C      COL 41   F10.5        FINVOL
C      COL 51   F10.5        IONSTR
C CARD 3
C      COL  1   I2           N           NUMBER OF DATA POINTS
C      COL 11   E10.5        ALPHA(1)
C      COL 21   E10.5        ALPHA(2)
C      COL 31   E10.5        ALPHA(3)
C      COL 41   E10.5        ALPHA(4)
C      COL 51   E10.5        TBETA(1)   BETA(MHL)
C      COL 61   E10.5        TBETA(2)   BETA(ML)
C CARD 4  THROUGH N+3
C      COL  1   F10.5        LIGVOL(N)
C      COL 11   F10.5        BASVOL(N)
C      COL 21   F10.5        METVOL(N)
C      COL 31   F10.5            PH(N)
       IMPLICIT REAL*8 (A-H,O-Z),INTEGER(I-N)
       REAL*8 IONSTR,LIGCON,LIGVOL,METCON,METVOL,MTOT
       DIMENSION R(10),S(10),T(10),U(10),V(10),W(10),X(10),Y(10),Z(10),AL
      1PHA(4),TBETA(2),PAR(18),WA(20),TITLE(20),LIGVOL(10),BASVOL(10),MET
      2VOL(10),PH(10)
       EXTERNAL AUX
C   TRAPS ALLOWS  THE PROGRAM TO CONTINUE AFTER AN EXPOTENTIAL UNDERFLOW
       CALL TRAPS(0,0,32767,0,0)
```

```
  400 READ(5,10,END=2000)(TITLE(I),I=1,20)
      READ(5,20)LIGCON,BASCON,METCON,SLTCON,FINVOL,IONSTR
      READ(5,30)N,ALPHA(1),ALPHA(2),ALPHA(3),ALPHA(4),TBETA(1),TBETA(2)
      READ(5,40)(LIGVOL(I),BASVOL(I),METVOL(I),PH(I),I=1,N)
      WRITE(6,50)
      WRITE(6,10)(TITLE(I),I=1,20)
      WRITE(6,60)LIGCON,BASCON,METCON
      WRITE(6,70)SLTCON,FINVOL,IONSTR
      WRITE(6,80)(I,ALPHA(I),I=1,4)
      WRITE(6,90)TBETA(1)
      WRITE(6,100)TBETA(2)
      WRITE(6,110)
      WRITE(6,120)(I,LIGVOL(I),BASVOL(I),METVOL(I),PH(I),I=1,N)
C  THIS DO LOOP CALCULATES COEFFICIENTS A-F
      DO 500 I=1,N
      H=10.0**(-PH(I))
      MTOT=METCON*METVOL(I)/FINVOL
      ATOT=LIGCON*LIGVOL(I)/FINVOL
      HTOT=(LIGCON*4.0*LIGVOL(I)/FINVOL)-(BASCON*BASVOL(I)/FINVOL)
      A=1.0+ALPHA(1)*H+ALPHA(2)*H**2.0+ALPHA(3)*H**3.0+ALPHA(4)*H**4.0
      B2=(MTOT-ATOT)
      C2=(-MTOT)
      D=ALPHA(1)*H+2.0*ALPHA(2)*H**2.0+3.0*ALPHA(3)*H**3.0+4.0*ALPHA(4)*
     1H**4.0
      E1=ALPHA(1)*H*(MTOT-HTOT+H)
      E2=H-HTOT
      B3=-A
```

```
      B1=ALPHA(1)*H*B2
      C1= ALPHA(1)*H*C2
      E3=-D
      F=C1
      R(I)=A*C2*E2*E2-D*C2*E2*B2
      S(I)=B2*B2*D*F-A*F*E2*B2-D*C1*E2*B2-D*C2*E1*B2-D*C2*E2*B1+A*C1*E2*
     1E2+2.0*A*C2*E1*E2
      T(I)=C2*C2*D*D-D*C2*E2*B3-D*C2*B2*E3+2.0*A*C2*E2*E3
      U(I)=2.0*C1*C2*D*D-2.0*A*D*C2*F+2.0*B2*B3*D*F-A*F*B2*E3-A*F*E2*B3-
     1D*C1*E2*B3-D*C1*B2*E3-D*C2*E1*B3-D*C2*E3*B1+2.0*A*C1*E2*E3+2.0*A*C
     22*E1*E3
      V(I)=0.0
      W(I)=0.0
      X(I)=A*A*F*F-2.0*A*D*C1*F+C1*C1*D*D+2.0*B1*B3*D*F-A*F*E1*B3-A*F*E3
     1*B1-D*C1*E1*B3-D*C1*E3*B1+2.0*A*C1*E1*E3
      Y(I)=2.0*B1*B2*D*F-A*F*E1*B2-A*F*E2*B1-D*C1*E1*B2-D*C1*E2*B1-D*C2*
     1E1*B1+A*C2*E1*E1+2.0*A*C1*E1*E2
      Z(I)=B1*B1*D*F-A*B1*E1*F-E1*B1*C1*D+A*C1*E1*E1
  500 CONTINUE
C THIS SECTION NOW PICKS TWO POINTS AT A TIME AND CALCULATES BMHL AND BML
      FBETA1=TBETA(1)
      FBETA2=TBETA(2)
      M=N-1
      DO 1000 I=1,M
      L=I+1
      DO 900 J=L,N
      WRITE(6.130)I.J
```

```
      PAR(1)=R(I)
      PAR(2)=S(I)
      PAR(3)=T(I)
      PAR(4)=U(I)
      PAR(5)=V(I)
      PAR(6)=W(I)
      PAR(7)=X(I)
      PAR(8)=Y(I)
      PAR(9)=Z(I)
      PAR(10)=R(J)
      PAR(11)=S(J)
      PAR(12)=T(J)
      PAR(13)=U(J)
      PAR(14)=V(J)
      PAR(15)=W(J)
      PAR(16)=X(J)
      PAR(17)=Y(J)
      PAR(18)=Z(J)
      EPS=1.0D-70
      NSIG=4
      K=2
      ITMAX=20
      IER=0
      CALL ZSYSTM(AUX,EPS,NSIG,K,TBETA,ITMAX,WA,PAR,IER)
      WRITE(6,140)ITMAX
      WRITE(6,150)IER
      WRITE(6,160)TBETA(1)
      WRITE(6,170)TBETA(2)
      TBETA(1)=FBETA1
      TBETA(2)=FBETA2
  900 CONTINUE
 1000 CONTINUE
      GO TO 400
```

```
 2000 STOP
   10 FORMAT(20A4)
   20 FORMAT(6F10.5)
   30 FORMAT(I2,8X,6D10.4)
   40 FORMAT(4F10.5)
   50 FORMAT('1******************************  PROGRAM  HCMPLX   *******
     1************************')
   60 FORMAT(' LIGCCN = ',F10.5,' BASCCN = ',F10.5,' METCON = ',F10.5)
   70 FORMAT(' SLTCON = ',F10.5,' FINVOL = ',F10.5,' IONSTR = ',F10.5)
   80 FORMAT(' ALPHA ',I2,' = ',D10.4)
   90 FORMAT(' TRIAL BETA MHL = ',D28.16)
  100 FORMAT(' TRIAL BETA ML = ',D28.16)
  110 FORMAT('  (I)',T15,'LIGVOL',T25,'BASVOL',T35,'METVOL',T45,'PH')
  120 FORMAT   (I2,T10,F10.4,T20,F 10.4,T30,F10.4,T40,F10.4)
  130 FORMAT(' POINTS USED ARE ',I2,' AND ',I2)
  140 FORMAT(' NUMBER CF ITERATIONS = ',I3)
  150 FORMAT(' IER = ',13)
  170 FORMAT(' BML = ',D28.16)
  160 FORMAT(' BMHL = ',D28.16)
      END
```

```
      DOUBLE PRECISION FUNCTION AUX (TBETA,K,PAR)
      INTEGER K
      REAL*8 TBETA(2),PAR(18)
C   TRAPS ALLOWS  THE PROGRAM TO CONTINUE AFTER AN EXPOTENTIAL UNDERFLOW
      CALL TRAPS(0,0,32767,0,0)
      GO TO (10,20),K
   10 AUX=PAR(1)*TBETA(2)**3+PAR(2)*(TBETA(2)**2)*TBETA(1)+PAR(3)*TBETA(
     12)**2+PAR(4)*TBETA(2)*TBETA(1)+PAR(5)*TBETA(2)+PAR(6)*TBETA(1)+PAR
     3(7)*TBETA(1)**2+PAR(8)*(TBETA(1)**2)*TBETA(2)+PAR(9)*TBETA(1)**3
      RETURN
   20 AUX=PAR(10)*TBETA(2)**3+PAR(11)*(TBETA(2)**2)*TBETA(1)+PAR(12)*TBE
     1TA(2)**2+PAR(13)*TBETA(2)*TBETA(1)+PAR(14)*TBETA(2)+PAR(15)*TBETA(
     21)+PAR(16)*TBETA(1)**2+PAR(17)*(TBETA(1)**2)*TBETA(2)+PAR(18)*TBET
     3A(1)**3
      RETURN
      END
```