1983

Design and synthesis of some polyaminopolycarboxylic acids and the structural influence of their anions on the separation of actinides and lanthanides

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Iowa State University PH.D. 1983

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Design and synthesis of some polyaminopolycarboxylic acids and the structural influence of their anions on the separation of actinides and lanthanides

by

Pui-Kwan Tse

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ABSTRACT

Investigation of some methods for the preparation of four polyaminopolycarboxylic acids: thiobis(ethylenenitrilo)-N,N,N',N'-tetraacetic acid, N,N-bis(2-aminoethyl)aniline-N',N',N",N"-tetraacetic acid, bis (3-aminopropyl)ether-N,N,N',N'-tetraacetic acid and N,N-bis [N',N'-dicarboxymethyl-3-aminopropyl]-N-methylammonioacetate are reported. The coordinating properties of their anions with regard to lanthanide ions have been examined.

Polyaminopolycarboxylates form 1:1 chelate species with trivalent lanthanide ions in aqueous media. The stability constants of their metal chelate species depend upon the size the the chelating rings formed, the basicity of the middle atom in the chain, and the number of coordination points between anion and metal cation.

Tracer level ^{241}Am-^{155}Eu cation-exchange experiments explore how the relative magnitude of the chelate stability constants affects the separation of members of the lanthanide and actinide series.

INTRODUCTION

Nuclear energy can play a major role in solving our energy needs during the next several decades; but its impact on the environment has been questioned by many individuals. Whether or not nuclear fission wastes can be safely managed is of primary interest to both the scientific community and the general public. The problem of disposing of high-level wastes from fuel reprocessing is particularly complex. While many of the nuclides produced are relatively short-lived, others remain biologically hazardous for thousands of years. Rapid decay of short-lived fission products and their daughter products can compromise the integrity of a geological repository via thermal effects and thus initiate a release of longer-lived species to the biosphere. The long-term hazard of a repository is associated principally with the presence of transuranic actinide elements and removal of trivalent actinide species from high-lived waste is an important step toward reducing the likelihood of accidentally contaminating the biosphere in years to come. The trivalent actinides which are removed from nuclear wastes conceivably can either be recycled repeatedly to nuclear reactors for ultimate burn-up [that is conversion to shorter-lived fission products (1)] or disposed in a special manner (2).

This dissertation examines the development and evaluation of several organic ligands which may offer a practical means of separating trivalent actinides away from other nuclear wastes. The stability constants and ion exchange phenomena reported herein provide an insight into the nature of the bonding of trivalent lanthanide and actinide cations to ligands and reveal certain differences in the coordination chemistry of these two related series.

Current Approach in Nuclear Waste Separation

In order to remove trivalent actinides from high-level nuclear wastes, studies show that secondary processing is required in addition to that currently employed as shown in Figure 1 (3). After removal of the spent fuel elements from the reactor, they are stored for a period of time with efficient cooling to allow many of the short-lived fission products to decay. The fuel elements are then opened by mechanical shearing or sawing, whereupon some volatile fission products such as krypton and xenon may be released unless adequate precautions are taken. The fuel and perhaps some of its cladding are then dissolved in a strong nitric acid solution. The objectives of fuel dissolution are: to bring the uranium and plutonium in the fuel element completely into aqueous solution; to separate the fuel components from the inert cladding; to allow the determination of the amounts of uranium and plutonium being charged to reprocessing; and to convert uranium, plutonium and the various fission products into chemical states most favorable for their subsequent separation. After complete dissolution, nearly all of the uranium and plutonium are recovered by the PUREX process. In the process, hexavalent uranium and tetravalent plutonium are selectively extracted from the fission-product solution by tributylphosphate (TBP) in a diluent. The next step in the PUREX process is the separation of plutonium from uranium. This is done by the addition of an appropriate reductant (such as Fe^{2+}, U^{4+} or hydroxylamine) or by cathodic reduction to reduce plutonium to the trivalent state, which is inextractable by TBP, while leaving the uranium in its extractable hexavalent condition. This allows the convenient recovery

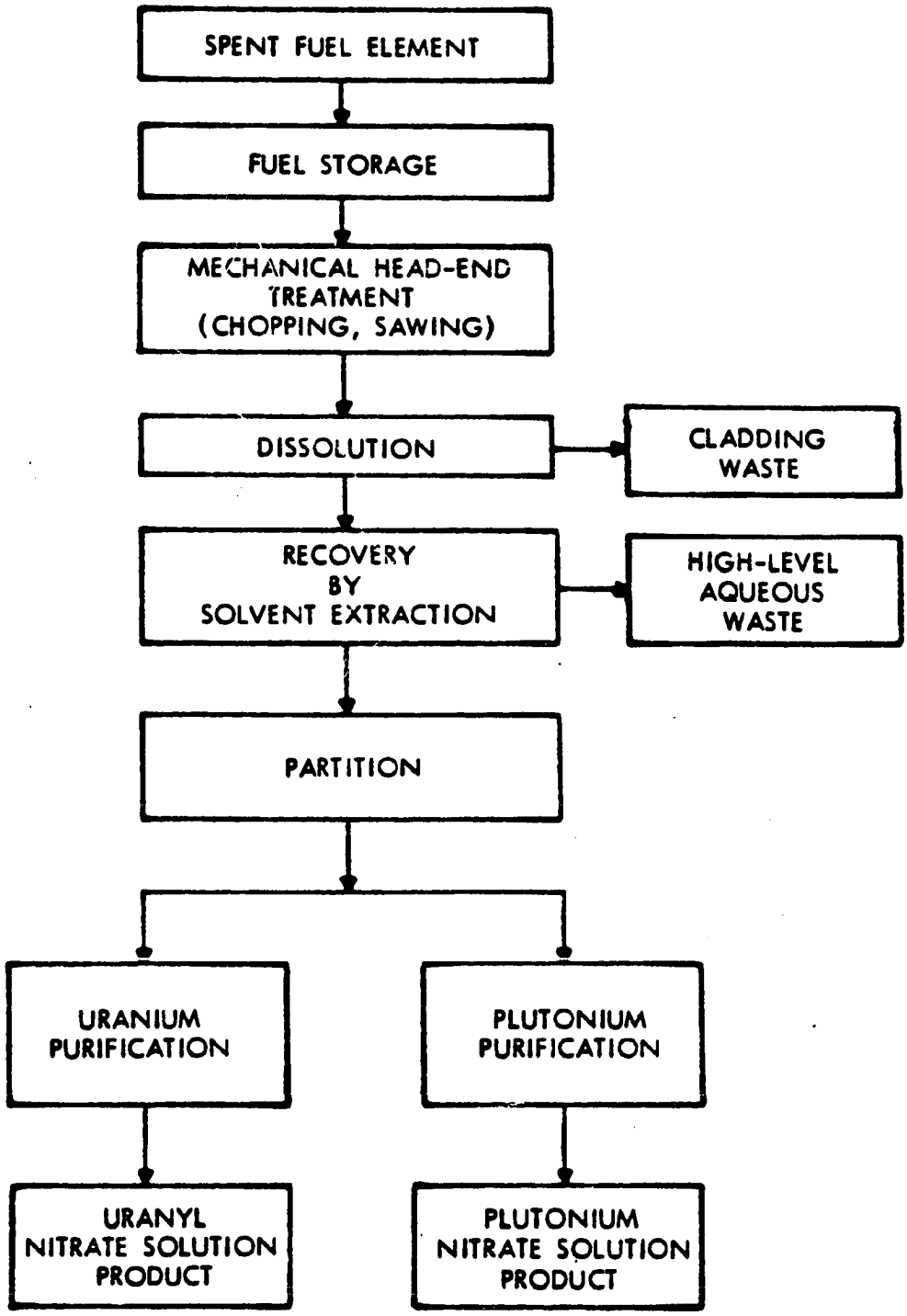


Figure 1. The current approach to reprocessing

of uranium from the organic phase and plutonium from an acidic aqueous layer. Both the recovered uranium and plutonium have the potential of being used further as reactor fuels, but the disposal of the highly radioactive and complex waste generated by the PUREX process (mostly as the initial TBP solvent extraction raffinate) is a difficult problem connected with the long-range operation of nuclear power plants.

The exact composition of high-level liquid waste (HLLW) depends upon several factors (irradiation time, fuel input composition, the recycling process, etc.), but it can be inferred from the Barnwell reprocessing experience. Table 1 (4) shows the mass fraction, product rate, and concentration of elements expected to be found in the PUREX raffinate after a three-year cooling period. The waste is comprised of several classes of elements: representative metals, transition metals, lanthanides and unremoved actinides. It contains a considerable amount of unextracted uranium and its neutron capture (followd by β-decay) products, Np, Pu, Am and Cm which are of utmost concern in the HLLW solution. The radioactivity of the waste is no direct measure of its relative radiotoxicity or its ultimate hazard. This is characterized by the ingestion hazard index, defined as the radioactivity divided by the allowed radioactivity concentration limit for drinking water. Figure 2 (5) shows the ingestion hazard index of HLLW as a function of time up to 10^6 years. After 500 years, the actinide radiotoxicity clearly dominates.

Prediction of tectonic stability of many geological storage sites is that they will remain unbreached for up to 10^3 years (6). However, the presence of the long-lived, alpha-emitting, actinide group elements

Table 1. Barnwell HLLW composition after three-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	

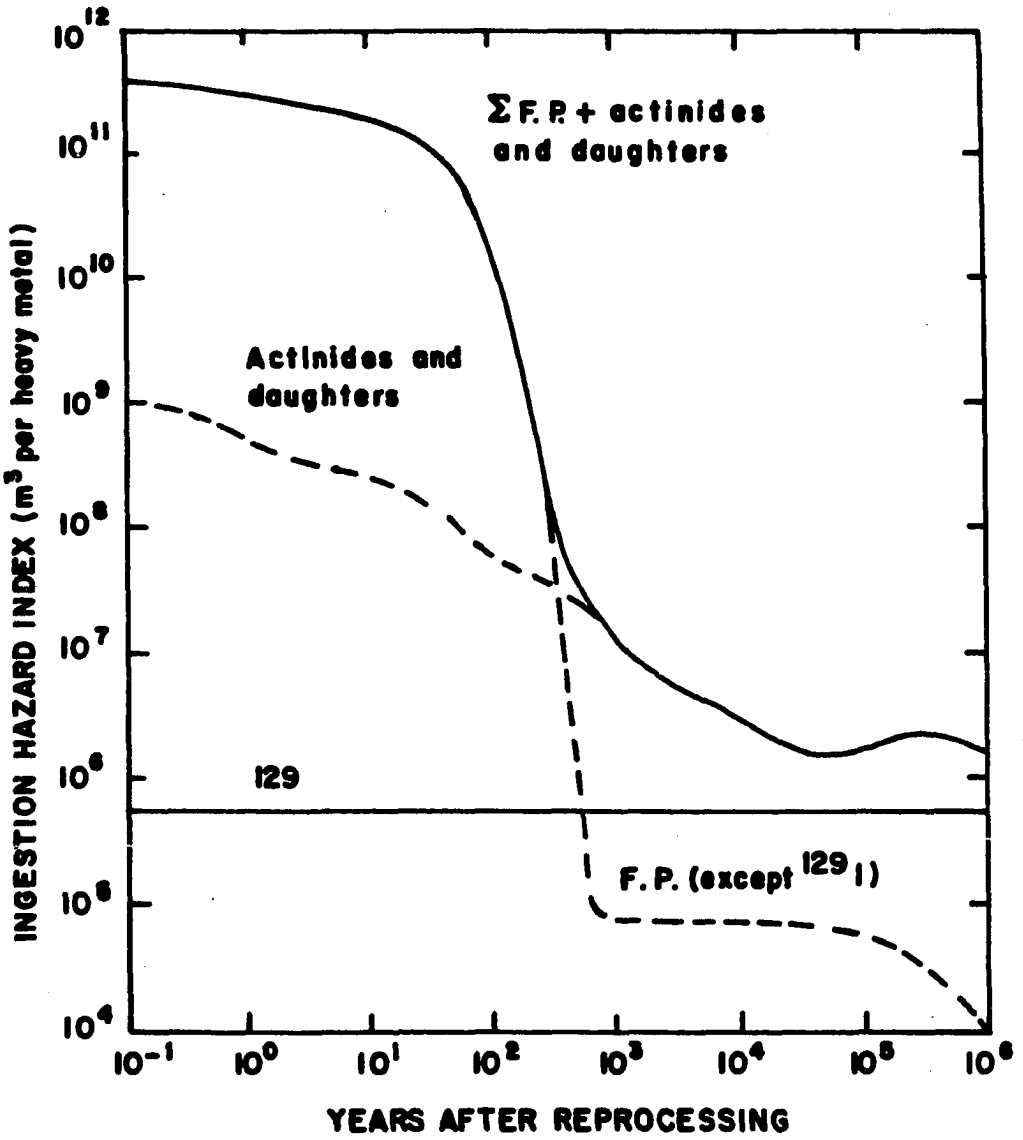


Figure 2. Effect of age of high-level wastes from light water reactor

dictates that the containment period must extend for at least 10^5 years (7-9). Obviously, removal of the long-lived alpha-emitters from the much more abundant, but shorter-lived, beta-emitters would remove the need to retain most of the waste beyond a thousand years. Table 1 shows that about one-third of the fission product waste consists of lanthanide elements whose chemistry closely parallels that of the tervalent actinons. Consequently, actinides can rather easily be recovered from solution by a group separation of lanthanides plus actinides from all other elements. Precipitation with oxalic acid could be used for this purpose (10). What remains to be worked out is an adequate, economical process for isolating the tervalent actinides from the 100-fold more abundant lanthanides obtained from a group recovery. Americium and curium are the most abundant of the transuranic actinides that must be dealt with at this point.

The Difficulty of Lanthanide-Actinide Separations

The chemical properties of lanthanides and trivalent actinides are, unfortunately quite similar, and individual actinides resemble individual lanthanides chemically as closely as adjacent lanthanides resemble each other. In modern separation processes for lanthanides, the driving force depends on small differences in their individual abilities to form complexes with ligands such as ethylenediaminetetraacetate and related polyaminopolycarboxylate anions. Trivalent americium and curium cations, like the tervalent lanthanons from which they must be separated, are "hard acids" according to the Pearson definition (11) and their chemistry is dominated by electrostatic bonding. Therefore, with the same charge (+3),

the separation factor for individual species are derived from the complexation strengths of the complexes formed with the ligand. The difficulty of lanthanide and trivalent actinide separations can be foreseen by comparison of their ionic radii which are shown in Figure 3 (12). Due to radius contractions in both the lanthanide and actinide series, the radii of both americium and curium fall within the lanthanide radii sequence. Am^{3+} and Cm^{3+} have radii approximate to Nd^{3+} and Pm^{3+}, respectively. If there was no other form of electrostatic force operating, little separation of americium from neodymium and curium from promethium would be possible.

Fortunately, other factors do exist so that the trivalent actinides form somewhat more stable complexes with most ligands than do lanthanide cations with the same radii. The origin of these extra forces is not well-understood but at least two different effects may operate. First, x-ray spectra of the atoms suggest that 5f orbitals are less penetrating than 4f orbitals (13). The 4f sub-shell of the lanthanides is inside the 6s valence sub-shell (as well as the 5s sub-shell towards the end of the series) while the 5f orbitals have a greater spatial extension relative to the 7s and 7p orbitals. The greater spatial extension of 5f orbitals has been revealed experimentally. The electron paramagnetic resonance spectrum of UF_3 in a CaF_2 lattice shows that there is interaction of fluorine nuclei with the electron spin of the U^{3+} ion. However, in the case of NdF_3 this kind of interaction is not observed (14). Because 4f electrons in the lanthanides occupy inner orbitals, they are not as accessible as 5f orbitals for covalent bonding. Secondly, trivalent

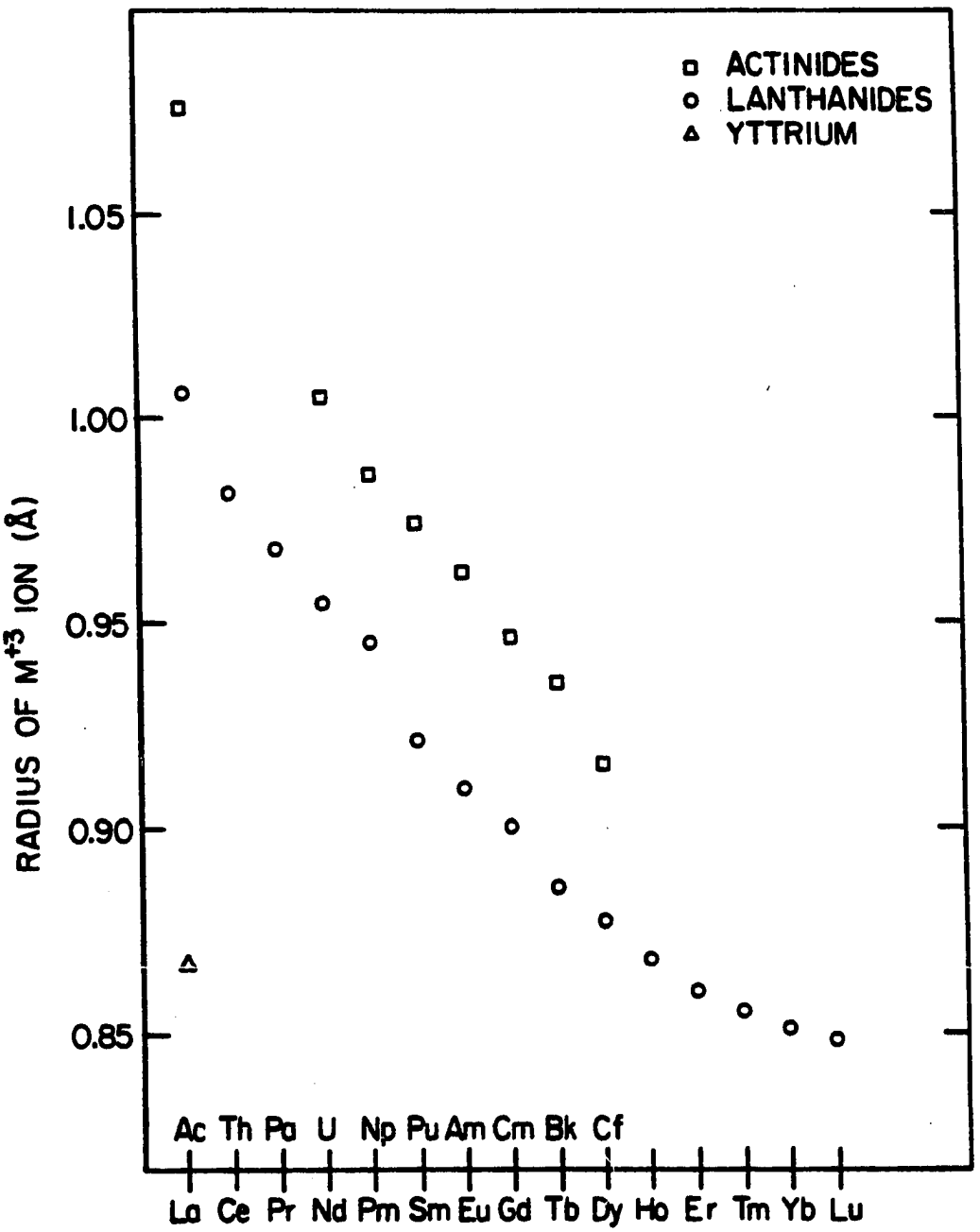


Figure 3. Radii of trivalent lanthanides, actinides and yttrium

actinide ions appear to be able to form stronger complexes with relatively soft ligands containing nitrogen and sulfur donor atoms in tracer-scale extraction processes (15).

By virtue of increased covalency, it is possible to explain the excess stability of actinide versus lanthanide complexes. There are some experimental results to support this view. Tris(cyclopentadienide)Am(III) is a well-characterized compound which might be considered to have a somewhat covalent nature. Based upon the absorption spectrum, however, Nugent et al. (16) suggest that the covalent interactions in $Am(C_5H_5)_3$ is only about 3% of the overall bonding in this complex. This lack of covalent character in trivalent actinide organometallic compound has been reiterated in a paper by Baker et al. (17) 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." However, the absorption spectra from f-f transitions show that the actinides divide into two groups: (1) Am^{3+} and heavier actinides which have spectra that resemble those of lanthanides (sharp, line-like); (2) Pu^{3+} and lighter actinides which have spectra somewhat more broadened, like those observed with the transition metal ions (18). Apparently, the greater exposure of the 5f orbitals in the lighter actinide elements results in greater ligand-metal orbital interaction and some broadening from vibrational effects. As the nuclear charge increases, the 5f orbitals of actinides behave more like the 4f orbitals of the lanthanide ions (13). From the above evidence, one may conclude that the lighter actinides exhibit

significant 5f orbital participation while the heavier trivalent actinides probably do not.

As mentioned before, metals with the same ionic radius should form complexes of identical strength. Yttrium should not separate from holmium in ion-exchange elutions with complexants because their radii are equivalent. The formation constant of yttrium complexes, in general, are substantially lower than those of the corresponding holmium complexes. Since there is no evidence for covalent interactions for either yttrium or holmium, the difference of effective nuclear charge (Z_{eff}), 11.90 and 12.40 for yttrium and holmium, respectively (19-20), may be the explanation. This argument may also be applied to the neodymium and americium separation (Z_{eff} = 11.35 and 11.80, respectively), even though the Slater treatment (20) is only a very coarse approximation for heavier elements.

Evidence has been presented that either 5f covalency or increased effective electrostatic forces could be the source of the increased stability in the trivalent actinide versus lanthanide complexes. The development of effective lanthanide-actinide separations can then be approached on the theoretical basis that chelating agents can be designed which maximize the small differences in bonding capability exhibited between these two families.

The Ideal Chelating Agent

Numerous schemes for lanthanide-actinide separation have been proposed in the literature (21-30). To be useful in the separation, a chelating agent must possess the following characteristics:

1. The reagent and its metal chelates must be reasonably soluble in some inexpensive but compatible solvent.

2. Complexation by the ligand should provide adequate separation factors for partitioning Am and Cm from the lanthanides (especially lanthanum through gadolinium, the more abundant lanthanide elements found in fission products).

3. The reagent should be applicable in acidic media, since a low pH range is necessary to prevent substantial hydrolysis of the trivalent lanthanide and actinide cations.

4. The reagent should be stable enough in the presence of radiation to permit it to accomplish its task.

5. The reagent must not be highly corrosive, flammable or viscous.

6. The cation exchange rate with the ligand should be reasonably rapid so that the residence time is not prohibitive.

A chelating agent which fulfills all the above requirements is not yet known, but a few which satisfy the first two conditions have been reviewed by Potter (31). Some that have been used will be discussed in the coming section.

Review of Some Chelating Agents

Diethylenetriaminepentaacetic acid (DTPA)

Diethylenetriaminepentaacetic acid is one of the most widely used aminocarboxylate chelating agents in Ln-An separations. Figure 4 illustrates the results of Ln and An stability constant determinations done by Moeller and Thompson (32) and Baybarz (33), which provided the fundamental

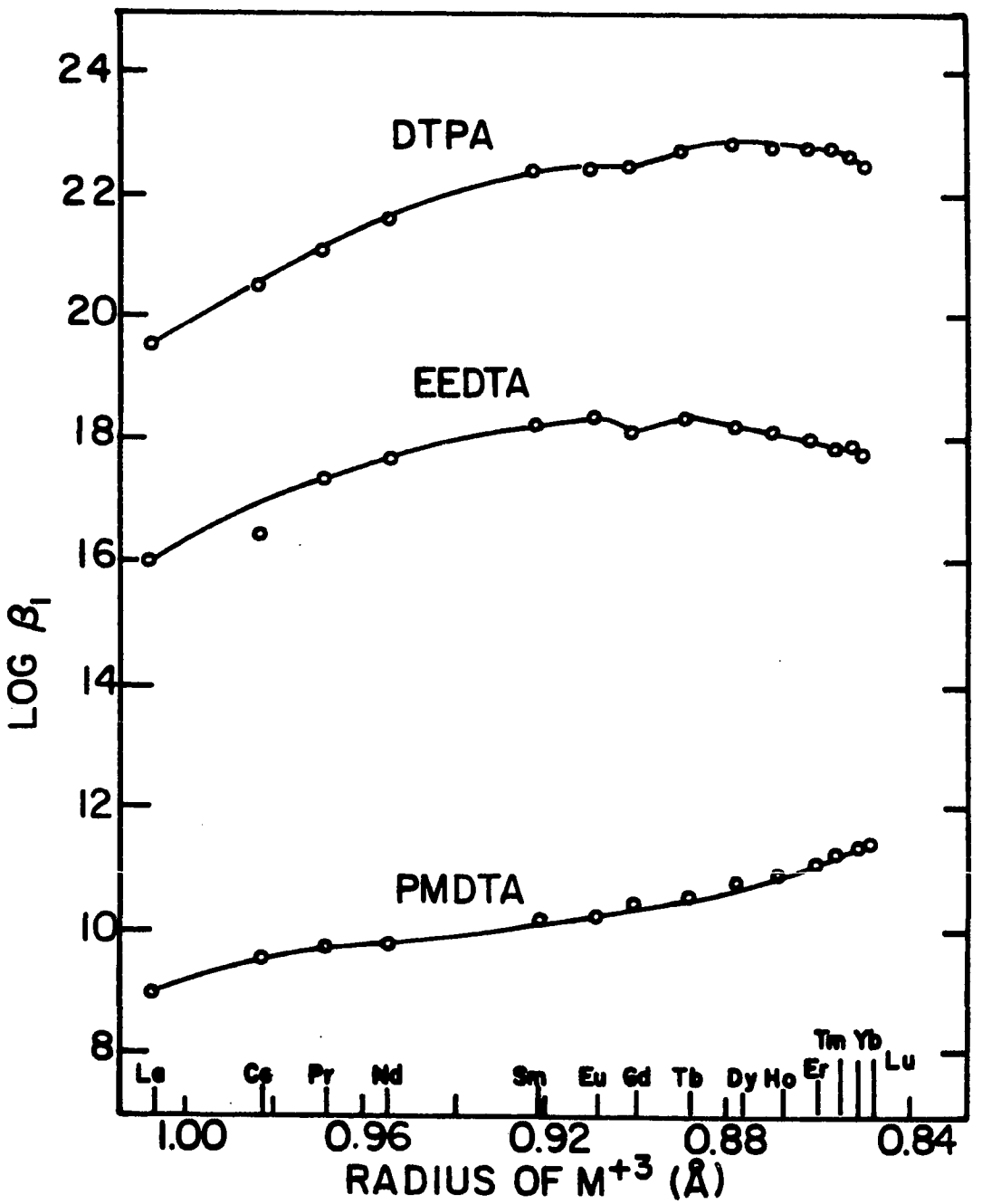


Figure 4. Stability constants of the lanthanide chelates formed by several aminocarboxylates

basis for several important ion-exchange and solvent-extraction separation systems. Observe that the lanthanide-DTPA complex stabilities exhibit a steady increase from lanthanum through dysprosium [up to log K (Dy^{3+}) = 22.82] but there pass through a maximum and decrease. Both americium and curium form more stable complexes [log K (Am^{3+}) = 22.92, log K (Cm^{3+}) = 22.99] than any of the lanthanides.

By way of cation-exchange chromatography, a mixture to be separated is eluted as a compact band using a dilute complexone solution at a certain pH, and a resin bed saturated with a retaining ion. As the elution progresses, discrete bands of pure sorbed species form on the exchanger bed, and are eluted eventually from the resin bed in the order of decreasing stability of the metal-ligand complexes. In the DTPA case, from their stability constants, the elution order would be predicted to be: Cm, Am, Dy, Ho, Er, etc. James, Powell and Burkholder (34) have performed the elution experiment of lanthanide ions with DTPA at pH = 8.74 at 25°C and the expected order was observed. Wheelwright and Roberts (35) at Hanford, and Lowe et al. (36) at Savannah River, however, individually reported that the Ln-An sequence with 0.05 M DTPA at pH = 6.5 and 70°C is Dy, Cm, Ho, Er, Am, Gd, Eu, Sm, Y, Pm, Nd, Pr, Ce, La. Note that Cm and Am did not actually elute ahead of Dy and the other lanthanide elements as predicted. The extreme stability of all lanthanide and actinide DTPA complexes introduces a kinetic factor which necessitates operating at an elevated temperature and at a lower pH than used by James et al. (34) Under these conditions, the selectivity of the chelating agent DTPA for metal ions decreases. High pressure operations with fine resin have been

developed to improve exchange kinetics (and also to minimize radiolytic gassing and resin damage) (37-38). Recently, Chmutov et al. (39) reported on the influence of citric acid on the Cm, Am, Eu and Ho-DTPA separation process. The addition of citric acid to the DTPA eluant permits an increase in the pH value within the system and increases the concentrations of the lanthanide and actinide elements in the eluant. This accelerates the movement of the band down the column. From computer simulations, DTPA elution on cation-exchange resin columns appears to be the technique of choice of Ln-An separations at this time (40).

Besides being used in cation-exchange chromatography for Ln-An separation, DTPA has also been employed as a chelating agent in solvent extraction processes (41-44), which have been reviewed recently (31).

DTPA has proven to be an effective Ln-An separation agent in both ion-exchange and solvent-extraction methods. Its major defects lie in its slow cation-exchange kinetics which arise from the very high stability of its complexes with lanthanides and actinides and its limited solubility in water. Therefore, ligands capable of exchanging partners more rapidly than DTPA does, and whose combinations are more soluble in aqueous media, are being sought.

2,2'-Diaminodiethylether-N,N,N',N'-tetraacetic acid (EEDTA)

This compound was synthesized by Yashunskii et al. (45) and the formation constants of its complexes with lanthanide ions were measured by Mackey, Hiller and Powell (46) more than two decades ago. The results of the latter work are shown in Figure 4. DTPA and EEDTA exhibit stability curves of a similar type, but the stability maximum for EEDTA

species occurs with Eu and Tb instead of Dy (as was the case with DTPA). Later, Spedding and Powell (47) reported the lanthanide elution sequence for lanthanides with EEDTA to be: Tb, Dy, (Sm, Er, Gd, Ho), Tm, Yb, Lu, Y, Nd, Pr, Ce, La and noted the similarity of the elution sequence to that of DTPA. Surprisingly, no report on Ln-An separations with this compound were reported for more than a decade. Recently, Potter (31), using tracer isotope cation-exchange techniques, determined the separation factor for ^{241}Am-^{155}Eu, ^{160}Tb. ^{241}Am is eluted ahead of both ^{155}Eu and ^{160}Tb from a cation-exchange column and the ^{155}Eu and ^{160}Tb appear in the eluant at the same time. The separation factors for Am-Eu and Am-Tb are both 1·71. The stability constants of EEDTA-Ln species are about ten thousand fold lower than those of corresponding DTPA-Ln complexes, which suggests strongly that exchange kinetics should be much improved. In addition, the acid form of EEDTA is quite soluble in water, allowing the use of hydrogen ion as a retaining ion in displacement cation-exchange systems. EEDTA thus shows much promise as a ligand in secondary nuclear waste processing.

1,5-Diaminopentane-N,N,N'N'-tetraacetic acid (PMDTA)

The successful separation of Am from the lanthanides in the EEDTA cation-experiments, led Potter (31) to study ligand structural properties related to the separation chemistry of Ln-An mixtures. The stability constants of various lanthanide complexes with PMDTA are shown in Figure 4. The stability of such complexes increases regularly with decreasing cationic radius. The highest chelate stability occurs with Lu. The stability sequence with PMDTA is different than the sequences

with EEDTA and DTPA. Chromatography experiments involving this ligand with Am, Eu and Tb have also been reported (31). Tb is eluted before unresolved Am and Eu. This ligand does not show any promise for Ln-An separations.

From the above discussion, one realizes that ligand characteristics are predominant in the separation of Ln-An mixtures by cation-exchange elution technique. In general, there are two effects that lead to successful separations. First, the ligands DTPA and EEDTA exhibit lanthanide stability sequences wherein maximum stability occurs in the mid-lanthanon range. Secondly, increasing relative stability of the complex species formed enhances the selection of the complexant for actinide species over lanthanide species of the same charge and radius (e.g., Am^{3+} vs. Nd^{3+} and Cm^{3+} vs. Pm^{3+}). A combination of the two effects cited above allows Am^{3+} and Cm^{3+} to elute from a cation-exchange column (under the influence of an appropriate ligand) ahead of all of the tervalent lanthanons. The design and synthesis of some ligands and the structural features which influence the Ln-An separation will be discussed in the following sections.

PART I. SYNTHESIS OF SOME POLYAMINOPOLYCARBOXYLIC ACIDS

INTRODUCTION

As mentioned in the first part of this dissertation, polyaminopolycarboxylic acids are promising chelating agents in the separation of actinides and lanthanides. The main defect of DTPA and EEDTA lies in the very high stabilities of their complexes with polyvalent metal ions, so that the rate of separation is kinetically slow. It has been noticed, however, that the stability constants of species formed from these complexing agents change markedly with the donor atom located at the central position of such compounds (i.e., N→O→C) (Figure 4). The reason for this change is still not clear; therefore, further study of such compounds is essential. Unfortunately, only a limited number of this class of chelating agents has been synthesized and almost none are commercially available. Therefore, methods to prepare compounds in which the central donor-O-atom has been replaced by -S-, RN< or ArN< are required. In this section, the design and synthesis of four polyaminopolycarboxylic acids will be discussed. Of these, only thiobis(ethylenenitrilo)tetraacetic acid (TEDTA) was prepared according to literature directions with no more than slight modifications (48-50). The other three were synthesized by methods described in the next section.

MATERIALS

Both N,N-bis(2-chloroethyl)aniline and N,N-bis(3-amino-propyl)-methylamine were purchased from Alfa Products. β,β'-Dicyanoethylether was obtained from Pfaltz and Bauer, Inc. and chloroacetic acid was obtained from Aldrich Chemical Co. These chemicals were used without further purification. Tetrahydrofuran (THF) was dried over calcium hydride, distilled under dry nitrogen at 64°∿65°C, and used immediately. Other reagent grade solvents were used without any additional purification.

Physical Measurements

Mass spectra were recorded on a Finnigan 400 GC MS DS. Nuclear magnetic resonance spectra were obtained by using either the Joel FX 90Q Fourier Transform NMR Spectrometer or the Bruker WM300. All the elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Molecular weights of product acids were determined by the potentiometric titration method, using standardized carbonate-free potassium hydroxide as the titrant.

Experimental

Ethyleneimine

Three moles of diluted H_2SO_4 (H_2SO_4/H_2O = 1:1) were added slowly to three moles of ethanolamine/H_2O (1:1) over an hour period. The reaction was quite exothermic. The resulting mixture was then heated rapidly over a Bunsen burner until the solution turned brown (∿240°C). On cooling, the clear brown liquid solidified to a hard white cake. A volume of 400 ml of

60% ethanol was added to the solidified cake which was then macerated, filtered by suction, and finally washed with ethanol until the leachate was colorless. The residue (β-aminoethylsulfuric acid) was dried in air; yield 300 g (70%).

$$HOCH_2CH_2NH_2 + H_2SO_4 \rightarrow HO_3SOCH_2CH_2NH_2 + H_2O$$

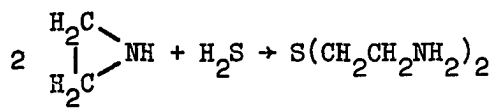
$$HO_3SOCH_2CH_2NH_2 + NaOH \rightarrow \begin{matrix} H_2C \\ | \\ H_2C \end{matrix}\!\!>\!NH + NaHSO_4 + H_2O$$

Three hundred grams of β-aminoethylsulfuric acid were heated with 822 g of 40% NaOH in a 3-L flask. As the mixture started to boil, the reaction began, and heating was discontinued. When the initial reaction ceased, heating was resumed slowly. The reaction was very vigorous and about 150 ml of solution distilled out between 75°∿105°C. Solid potassium hydroxide was then added to the distillate. Two layers formed and 50 ml of a colorless liquid were collected by a redistillation at 55°∿75°C. The process was repeated after the addition of more KOH to the colorless liquid, and finally a 20-g portion of ethyleneimine was obtained at 55°∿57°C.

Bis(2-aminoethyl)sulfide

A solution of 41.9 g ethyleneimine in 50 ml of water was saturated with hydrogen sulfide in a three-neck flask. The H_2S was introduced by passing it through a wash bottle filled with water to eliminate any trace of mineral acid. The saturated solution was stirred vigorously and the rate of addition was adjusted so that the temperature of the reaction mixture could be maintained at 17°∿20°C in a water bath. After the theoretical weight of H_2S (16.57 g) had been added, the rate of the

reaction was controlled by discontinuing the addition of H_2S and introducing N_2. The reaction required 14 hours. The water was distilled out under reduced pressure and the sulfide was finally collected by distilling at a temperature of 87°∿90°C at 2 torr; yield 35.1 g (60%).



$$2\ \mathrm{H_2C(CH_2)NH} + H_2S \rightarrow S(CH_2CH_2NH_2)_2$$

Thiobis(ethylenenitrilo)tetraacetic acid (TEDTA)

The required 146.25 ml (1.46 moles) of 10 M NaOH was added slowly to 138.2 g (1.46 moles) of chloroacetic acid in 150 ml of water at pH∿5 and at a temperature below 10°C. After neutralization of the acid, 35.1 g (0.293 mole) of bis(2-aminoethyl)-sulfide was added to the solution, whereupon the color of the solution changed to greenish. In a period of six hours, 150 ml of 10 M NaOH was added to the solution to maintain the pH above 10, while the temperature was kept under 40°C. After the addition was completed, the solution was diluted to 2 L and loaded on four (1" x 4') Dowex 50-W hydrogen-form cation-exchange columns. As the solution was loaded and washed with water, a distinguishable light band of TEDTA formed in front of (below) the sodium ion band. Highly pure TEDTA was next obtained by eluting the complexone from the column with 0.1 M NH_4OH. After the eluate was evaporated, white crystalline TEDTA was obtained. The product was dried in an oven at 100°C overnight; yield 53.3 g (51.8%). The molecular weight was found by titration to be 352.8 g/mole which compared very well to the expected 352.36 g/mole. The solubility of TEDTA in water is only 1.0×10^{-2} M at 25°C.

$$ClCH_2COOH + NaOH \rightarrow ClCH_2COONa + H_2O$$

$$4ClCH_2COONa + S(CH_2CH_2NH_2)_2 \rightarrow S[CH_2CH_2N(CH_2COONa)_2]_2 + 4HCl$$

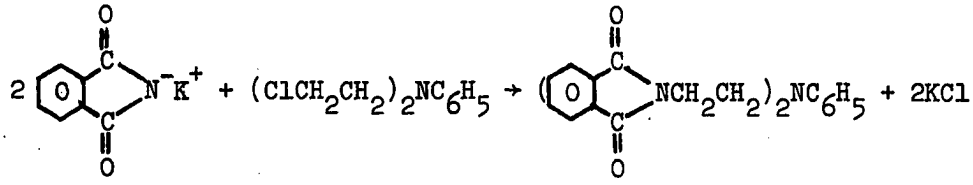
$$S[CH_2CH_2N(CH_2COONa)_2]_2 + 4H^+ \rightarrow S[CH_2CH_2N(CH_2COOH)_2]_2 + 4Na^+$$

The elemental analysis of $C_{12}H_{20}N_2O_8S$ was:

	C%	H%	N%
found	40.64	5.87	7.95
calculated	40.95	5.73	7.96

N,N-Bis(2-phthalimidoethyl)aniline

A mixture of 25.0 g (0.115 mole) N,N-bis(2-chloroethyl)aniline and 50.1 g (0.271 mole) potassium phthalimide in 75 ml N,N-diethylformamide, in a 1-L round-bottom flask, was heated with stirring for four hours at 130°∿140°C. The color of the mixture changed from white to yellow and then to tan. After cooling, 400 ml of boiled water was added, whereupon a yellow precipitate formed. The resulting solid was heated under reflux for half an hour. The precipitate, when filtered, washed with distilled water and dried in air, yielded 49.0 g (0.112 mole, 97.3%) of yellow solid melting at 210°∿212°C.

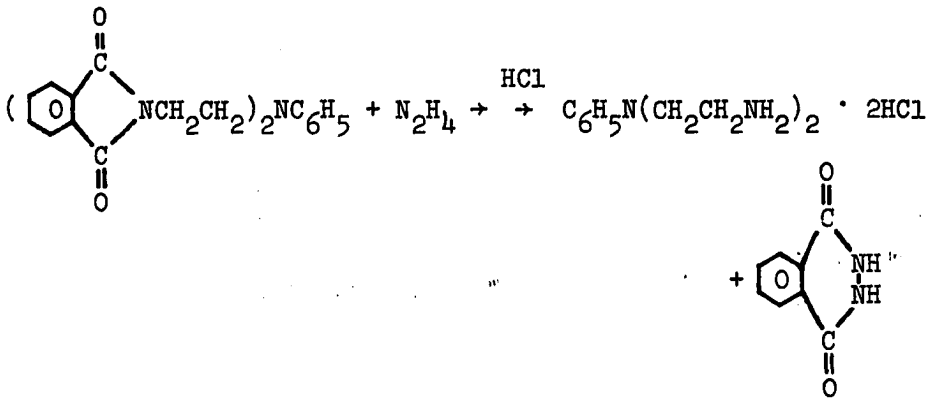


The elemental analysis of $C_{26}H_{21}N_3O_4$ was:

	C%	H%	N%
found	71.19	4.89	9.52
calculated	71.07	4.78	9.57

N,N-Bis(2-aminoethyl)aniline dihydrochloride

In a 500-ml round-bottom flask, a mixture of 54.1 g (0.123 mole) of N,N-bis(2-phthalimidoethyl)aniline, 14.5 g of 85% hydrazine hydrate and 300 ml of 95% ethanol was heated under reflux, with stirring, for three hours. During the heating, a voluminous white precipitate formed and the solvent color changed from colorless to yellowish. After cooling to room temperature, ethanol was removed by rotatory evaporation. The spongy residue was heated for 15 minutes on a steam bath with excess diluted hydrochloric acid. Phthalylhydrazide was removed by filtration and the greenish filtrate was evaporated to dryness under reduced pressure. The resulting grey solid was recrystallized from concentrated HCl/abs. ethanol and dried in air, producing a yield of 23.3 g (0.0925 mole, 88.9%). The finely crushed powder was observed to decompose at about ∿270°C.



The elemental analysis of $C_{10}H_{17}N_3 \cdot 2HCl$ was:

	C%	H%	N%	Cl%
found	47.41	7.44	16.50	28.17
calculated	47.62	7.54	16.67	28.30

N,N-Bis(2-aminoethyl)aniline-N',N',N",N"-tetraacetic acid·0.25 hydrate (BEATA)

The synthetic method followed was similar to that used in the case of TEDTA except that the cation-exchange eluant was 0.05 M NH_4OH. The product was a violet, finely crystalline solid at a yield of 75.6%. The product was dried in an oven at 100°C overnight, and found to decompose at 235°C. The molecular weight determination indicated 418.7 g/mole, which compared well with the calculated 415.9 g/mole.

$$C_6H_5N(CH_2CH_2NH_2)_2 + 4ClCH_2COOH \rightarrow C_6H_5N[CH_2CH_2N(CH_2COOH)_2]_2 + 4HCl$$

The elemental analysis of $C_{18}H_{25}N_3O_8 \cdot \frac{1}{4}H_2O$ was:

	C%	H%	N%	O%
found	52.00	6.44	9.96	31.77
calculated	51.98	6.17	10.10	31.73

Bis(3-aminopropyl)ether

A three-liter, three-necked flask was equipped with a reflux condenser, a mechanical stirrer and a dropping funnel. The reaction was carried on under dry N_2. The flask in which 26.6 g (0.70 mole) of lithium aluminium hydride were dissolved in 1 L of dry THF was placed in an ice bath. Then, 34.3 g (0.35 mole) of 100% H_2SO_4 was slowly added to the dry THF solution with vigorous stirring over a period of 30 min. Hydrogen gas was evolved during this time. To this aluminum hydride solution, 31.0 g (0.25 mole) of β,β'-dicyanoethylether in 70 mL of dry THF was slowly introduced through a dropping funnel over 45 minutes. During the addition of the ether solution, hydrogen gas was not evolved. After completion, the solution was stirred vigorously for three hours. The

solution color changed to light yellow during this time. Excess NaOH solution was added carefully to destroy the excess hydride and to coagulate the precipitated aluminum hydroxide. The precipitate was then separated by filtration, and the light yellowish filtrate was concentrated and treated with 140 mL HCl/H_2O (1:1). The aqueous layer was then concentrated to a viscous mass. Ethyl ether was added, followed by saturated potassium hydroxide solution. The light yellowish ether extract obtained was dried over anhydrous potassium carbonate, potassium hydroxide pellets, and then sodium metal. The product was finally distilled at a temperature of 83°~85°C/5 torr and yielded 20.0 g (0.151 mole, 60.5%) of product.

$$2LiAlH_4 + H_2SO_4 \rightarrow Li_2SO_4 + 2AlH_3 + 2H_2$$

$$2AlH_3 + O(CH_2CH_2CN)_2 \xrightarrow{OH^-/H_2O} 2Al(OH)_3 + O(CH_2CH_2CH_2NH_2)_2$$

Bis(3-aminopropyl)ether-N,N,N',N'-tetraacetic acid monohydrate (BPETA)

This compound had been prepared by Schwarzenbach *et al.* (51); however, no detailed experimental preparation method was reported.

BPETA was prepared in a manner similar to that used to prepare TEDTA and BEATA by the treating of 19 g (0.144 mole) bis(3-aminopropyl)ether with excess chloroacetic acid. The white product was recrystallized from H_2O/abs. ethanol and dried in an oven at 80°C overnight. The pure compound decomposed at about 99°C and weighed 47.6 g (0.125 mole, 86.6%). The determined molecular weight was 385.4 g/mole which was quite close to the calculated 382.4 g/mole.

$$O(CH_2CH_2CH_2NH_2)_2 + 4ClCH_2COOH \rightarrow O[CH_2CH_2CH_2N(CH_2COOH)_2]_2 + 4HCl$$

The result of the elemental analysis of $C_{14}H_{24}N_2O_9 \cdot H_2O$ was:

	C%	H%	N%	O%
found	43.82	6.91	7.20	41.94
calculated	43.98	6.85	7.33	41.84

N,N-Bis(N',N'-dicarboxymethyl-3-aminopropyl)-N-methylammonioacetate monohydrate (BCPA)

The procedure for preparation of BCPA was the same as for TEDTA with 25.0 g (0.172 mole) of N,N-bis(3-aminopropyl)methylamine and 97.6 g (1.03 mole) of chloroacetic acid to yield 66.5 g (0.147 mole, 85.5%) of pure product after drying in an oven at 100°C for five hours. In a melting point tube, the white powder decomposed at 120°C. Its experimental molecular weight was 451.8 g/mole which agreed well with the calculated 453.4 g/mole for the monohydrate.

$$H_3CN(CH_2CH_2CH_2NH_2)_2 + 5ClCH_2COOH \rightarrow {}^{-}OOCH_2C(CH_3)\overset{+}{N}[CH_2CH_2CH_2N(CH_2COOH)_2]_2 + 5HCl$$

The analysis of $C_{17}H_{29}N_3O_{10} \cdot H_2O$ was:

	C%	H%	N%
found	44.98	7.01	9.42
calculated	45.05	6.98	9.27

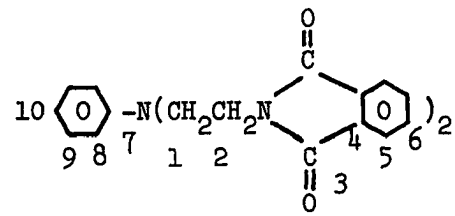
RESULTS AND DISCUSSION

BEATA

Both N,N-bis(2-phthalimidoethyl)aniline and N,N-bis(2-aminoethyl)aniline dihydrochloride were obtained in high yields. The preparation of these two compounds followed the method of Gabriel (52), who originally explored this simple method for preparing pure primary amines. The mass spectrum of N,N-bis(2-phthalimidoethyl)aniline exhibits the following major fragments: m/e 439 (parent peak), 279(100), 174, 119 and 77. The base peak, m/e 279, corresponds to the β cleavage on either side of the aniline nitrogen atom. Besides the favorable β cleavage, α cleavage on the aniline nitrogen atom or γ cleavage on the amide nitrogen atom is also observed, m/e 174.

The chemical shifts of carbon-13 nuclear magnetic resonance of these two compounds are noted in Table 2 and Table 3.

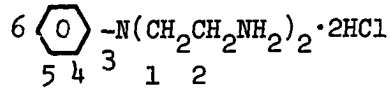
Table 2. Chemical shifts of N,N-bis(2-phthalimidoethyl)aniline[a]



C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
35.10	48.27	168.21	133.92	132.07	129.42	147.19	112.63	123.25	117.18

[a]At 90 MHz in $CDCl_3$ with TMS as an internal reference; chemical shifts are in δ units (ppm).

Table 3. Chemical shifts of N,N-bis(2 aminoethyl)aniline dihydrochloride[a]



C1	C2	C3	C4	C5	C6
37.32	49.46	147.30	119.94	130.72	121.02

[a]At 90 MHz in D_2O with CD_3CN as an internal reference.

Due to the low solubility of N,N,-bis(2-aminoethyl)aniline-N',N',N",N"-tetraacetic acid in both water and common organic solvents, nuclear magnetic resonances cannot be recorded in a solvent. The experimental results of molecular weight determination and elemental analysis, however, were close to the calculated values.

BPETA

Normally, lithium aluminum hydride would appear to be the reagent of choice for the reduction of nitrile compounds. However, in some cases, where the molecule contains groups which are relatively stable to aluminum hydride, the slow reaction time may be a handicap in the reduction. In the case of preparation of bis(3-aminoethyl)ether by direct addition of β,β'-dicyanoethylether to lithium aluminum hydride-tetrahydrofuran solution at room temperature, a large amount of hydrogen gas was evolved. After complete addition, the mixture was stirred vigorously for three hours at 30°C and allowed to stand overnight. A negligible yield of desired amine was collected. A large amount of hydrogen gas evolved, indicating that the nucleophilic agent, aluminum hydride anion, attacks the

active hydrogen of the α position of the nitrile (53-56). This is believed to be responsible for the decreased yield related to the reduction of nitrile by lithium aluminum hydride.

The difficulty can be overcome by the use of mixed hydride $ClAlH_2$ (57) or aluminum hydride (58-59). However, it appears that aluminum hydride may offer a more economical method in large-scale syntheses. With the use of AlH_3, the mechanism of the reaction is also different from that with $LiAlH_4$. Because the AlH_3 is an electrophilic agent which attacks on the nitrogen atom of the nitrile group to form $\sim CH{=}N{-}AlH_2$, no hydrogen gas is evolved.

The assignments of both the ^1H NMR and ^{13}C NMR resonances of bis(3-aminopropyl)ether are given in Table 4.

Table 4. NMR assignments of bis(3-aminopropyl)ether[a]

$O(CH_2CH_2CH_2NH_2)_2$
1 2 3 4

	1	2	3	4
^1H	3.49 (t^b, $^3J_{HH}$ = 6.2)	1.70 (q^b, $^3J_{HH}$ = 6.5)	2.78 (t^b, $^3J_{HH}$ = 6.7)	1.38 (s^b)
^{13}C	68.72	33.23	39.30	

[a]At 90 MHz in $CDCl_3$ with TMS as an internal reference; chemical shifts are in δ units (ppm), and coupling constants are in hertz.

[b]q = quintet, t = triplet, s = singlet

The mass spectrum reveals the following fragments: m/e 133, 103, 76(100), 74, 59 and 57. Normally, the aliphalic amine parent peak is very weak, therefore, it is not surprising that it does not appear with this aminoether. Instead, aliphatic amines have a strong tendency to undergo protonation at a moderately high pressure to the characteristic $(M + H)^+$ peak i.e., m/e 133 (60).

When bis(3-aminopropyl)ether condensed with a one-mole excess of chloroacetic acid, a very good yield of bis(3-aminopropyl)ether-N,N,N',N'-tetraacetic acid was obtained. This compound is very soluble in water and its NMR data are given in Table 5.

Table 5. NMR assignments of bis(3-aminopropyl)ether-N,N,N',N'-tetraacetic acid

$O[CH_2CH_2CH_2N(CH_2COOH)_2]_2$
1 2 3 4 5

	1	2	3	4	5
^1H[a]	3.72 ($t, ^3J_{HH} = 5.3$)	2.06 ($q, ^3J_{HH} = 5.7$)	3.44 ($t, ^3J_{HH} = 6.7$)	4.01	
^{13}C[b]	70.04	24.58	56.38	56.71	169.80

[a]At 300 MHz in D_2O with TMS as an internal reference; chemical shifts are in δ units (ppm), and coupling constants are in hertz.

[b]At 90 MHz in D_2O with CD_3CN as an internal reference.

BCPA

When one mole of N,N-bis(3-aminopropyl)methylamine reacted with four or five moles of chloroacetic acid, an unidentified white glassy product was obtained that was apparently not a single substance. This product reacted with an extra mole of chloroacetic acid to give the very unusual quarternary ammonium substance N-N-bis(N',N'-dicarboxymethyl-3-aminopropyl)-N-methyl-ammonioacetate $[(HOOCCH_2)_2NCH_2CH_2CH_2]_2\overset{+}{N}(CH_3)CH_2COO^-$. This acid can also be prepared by using six moles of chloroacetic acid with one mole of the original amine. The unidentified substance first obtained may be the result of incomplete reaction between the amine and chloroacetic acid. Under basic conditions, chloroacetic acid does not only react with sodium hydroxide to form sodium chloroacetate. Nucleophilic substitution also occurs with chloroacetic acid, forming glycolic acid. Therefore, only part of the chloroacetic acid provided reacts with amine to produce the unidentified (probably mixed) product. With an excess of chloroacetic acid, the reaction goes to completion forming the above identified ammonioacetate derivative.

The carbon-13 nuclear magnetic resonance shows that there are two peaks with the ratio (1:4) at the carboxyl carbon region (δ = 169.86 and 168.24 ppm, respectively, in D_2O with CD_3CN as internal reference). This distinctly shows that there are two types of carboxyl carbons. One of them (the more intense) corresponds to the four terminal carboxyl carbons of the same symmetry. The other (less intense) relates to the carboxyl carbon of the acetate group which is attached to the central nitrogen atom. In addition to these two peaks, there are six more peaks at the high field

region (δ = 61.78, 60.15, 57.10, 53.52, 49.94 and 18.79 ppm respectively). Four of them correspond to the propylene and the methyl carbons. The other two peaks must be due to the methylene carbons of the two kinds of acetate groups.

The proton nuclear magnetic resonance chemical shifts with TMS as internal reference are: δ = 4.04 (s), 4.00 (s), 3.71 (t), 3.43 (t), 3.24 (s) and 2.27 (q) ppm, respectively. When the protons at δ = 2.27 were irradiated, the peak δ = 3.71 and 3.43 became singlets. When either of the protons at δ = 3.71 and 3.41 were irradiated, the peak at δ = 2.27 changed from quintet to triplet. These decoupling results indicate that the odd acetate group does not bond to any of the propylene carbons. If the acetate group is attached to the central nitrogen atom, the nitrogen atom becomes quarternary. The protons of the methyl carbon bonded to the quarternary nitrogen should shift downfield because these protons would be more deshielded by a quarternary nitrogen than by the nitrogen atom of a tertiary amine. Normally, methyl protons of tertiary amines are observed in the vicinity of δ = 2.0 ppm (61). The experimental result shows that the methyl proton peak is at δ = 3.34 ppm. This suggests that the methyl protons are more deshielded and that the nitrogen atom to which the methyl group is bonded is indeed a quarternary amine nitrogen.

In the potentiometric titration method used to determine the molecular weight of this compound, there are only two types of acidic protons apparent, one at high pH and the other at low pH. There are an equal number of different titratable protons, two of each kind. These four protons may be assumed to come from the four terminal carboxylic acid

groups. The first two protons titrated are merely carboxylate associated; the second two are zwitterionic. The acetate group bonded to the central nitrogen (i.e., to a plus quarternary ammonium moiety) is an anionic radical ($-CH_2COO^-$) with no attached proton. Because of this, there is a strong dipole at the center of the ligand ($^+NCH_2COO^-$) which renders the molecule especially soluble in water. It is probably this dipole which accounts for the isolation of the product as a fairly stable monocrystalline monohydrate.

PART II. MATHEMATICAL METHODS TO CALCULATE THE PROTONATION CONSTANTS OF POLYAMINOPOLYCARBOXYLIC ACIDS AND THE FORMATION CONSTANTS OF THE SPECIES THEIR ANIONS FORM WITH LANTHANIDE IONS

INTRODUCTION

Before proceeding to the experimental determination of the protonation constants of the synthesized polyaminopolycarboxylic acids and the formation constants of complexes of their anions with individual lanthanide ions, this section introduces the mathematical methods by which these constants were calculated. The computer programs associated with this task were developed by previous members of this research group (31, 62-63) by incorporating gradual improvements.

ANION PROTONATION CONSTANTS CALCULATION

The protonation of the polyaminopolycarboxylate anion (L) can be described by four equilibria.

$$L + H \rightleftarrows HL$$

$$L + 2H \rightleftarrows H_2L$$

$$L + 3H \rightleftarrows H_3L$$

$$L + 4H \rightleftarrows H_4L$$

The equilibrium constants which are commonly designated as alpha (α_n) 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 mass balances of total proton, H_t, and total anion, L_t, are:

$$H_t = [H] + [HL] + 2[HL] + 3[HL] + 4[HL]$$

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

$$H_t - [H] = [L]\sum_1^4 N\alpha_N[H]^N$$

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

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

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

Taking the ratio of the mass balances to eliminate [L] gives:

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

With cross multiplication and rearrangement the above gives:

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

This equation can be written:

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

The value of [H] is obtained from experimental measurement so that the values of Y, J_1, J_2, J_3 and J_4 are known for each solution. The only unknowns are α_1, α_2, α_3 and α_4 which can in theory be solved by measuring four solution sets. However, in practice, more than four solutions are measured and the equations are solved by using a least-squares multiple linear regression. The multiple linear regression which has been described by Draper and Smith (64), was incorporated into the computer program OMEGA by Johnson (62) and Miller (63). The least-square analysis proceeds by minimizing the sum of the squares of the individual residuals ε_i. The residual is defined as the difference between the observed Y_i and the predicted Y_i which is used to calculate α's.

$$\varepsilon_i = Y_i - (J_1\alpha_1 + J_2\alpha_2 + J_3\alpha_3 + J_4\alpha_4)$$

The sum of the squares is minimized by taking the individual partial derivatives and setting them equal to zero.

$$S = \Sigma\varepsilon_i^2 = \Sigma(Y_i - J_{1i}\alpha_1 - J_{2i}\alpha_2 - J_{3i}\alpha_3 - J_{4i}\alpha_4)^2$$

$$\frac{\partial S}{\partial \alpha_1} = -2\Sigma J_{1i}(Y_i - J_{1i}\alpha_1 - J_{2i}\alpha_2 - J_{3i}\alpha_3 - J_{4i}\alpha_4) = 0$$

$$\frac{\partial S}{\partial \alpha_2} = -2\Sigma J_{2i}(Y_i - J_{1i}\alpha_1 - J_{2i}\alpha_2 - J_{3i}\alpha_3 - J_{4i}\alpha_4) = 0$$

$$\frac{\partial S}{\partial \alpha_3} = -2\Sigma J_{3i}(Y_i - J_{1i}\alpha_1 - J_{2i}\alpha_2 - J_{3i}\alpha_3 - J_{4i}\alpha_4) = 0$$

$$\frac{\partial S}{\partial \alpha_4} = -2\Sigma J_{4i}(Y_i - J_{1i}\alpha_1 - J_{2i}\alpha_2 - J_{3i}\alpha_3 - J_{4i}\alpha_4) = 0$$

Rearranging gives:

$$\Sigma J_{1i}^2\alpha_1 + \Sigma J_{1i}J_{2i}\alpha_2 + \Sigma J_{1i}J_{3i}\alpha_3 + \Sigma J_{1i}J_{4i}\alpha_4 = \Sigma J_{1i}Y_i$$

$$\Sigma J_{1i}J_{2i}\alpha_1 + \Sigma J_{2i}^2\alpha_2 + \Sigma J_{2i}J_{3i}\alpha_3 + \Sigma J_{2i}J_{4i}\alpha_4 = \Sigma J_{2i}Y_i$$

$$\Sigma J_{1i}J_{3i}\alpha_1 + \Sigma J_{2i}J_{3i}\alpha_2 + \Sigma J_{3i}^2\alpha_3 + \Sigma J_{3i}J_{4i}\alpha_4 = \Sigma J_{3i}Y_i$$

$$\Sigma J_{1i}J_{4i}\alpha_1 + \Sigma J_{2i}J_{4i}\alpha_2 + \Sigma J_{3i}J_{4i}\alpha_3 + \Sigma J_{4i}^2\alpha_4 = \Sigma J_{4i}Y_i$$

Now, the system has four equations and four unknowns which can be represented in matrix form.

$$\begin{vmatrix} \Sigma J_{1i}^2 & \Sigma J_{1i}J_{2i} & \Sigma J_{1i}J_{3i} & \Sigma J_{1i}J_{4i} \\ \Sigma J_{1i}J_{2i} & \Sigma J_{2i}^2 & \Sigma J_{2i}J_{3i} & \Sigma J_{2i}J_{4i} \\ \Sigma J_{1i}J_{3i} & \Sigma J_{2i}J_{3i} & \Sigma J_{3i}^2 & \Sigma J_{3i}J_{4i} \\ \Sigma J_{1i}J_{4i} & \Sigma J_{2i}J_{4i} & \Sigma J_{3i}J_{4i} & \Sigma J_{4i}^2 \end{vmatrix} \begin{vmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \\ \alpha_4 \end{vmatrix} = \begin{vmatrix} \Sigma J_{1i}Y_i \\ \Sigma J_{2i}Y_i \\ \Sigma J_{3i}Y_i \\ \Sigma J_{4i}Y_i \end{vmatrix}$$

The α_1, α_2, α_3 and α_4 in these matrix equations can easily be solved for by using the Gaussian elimination subroutine DGELG which is available at Iowa State University Computation Center.

However, in order to allow for differences in the inherent error of

the individual relative errors, the regression is weighted relative to H_t, [H], and L_t. The weighing factors W_i are obtained from the standard errors q_i:

$$W_i = \frac{1}{q_i^2}$$

The standard errors are derived from the individual residuals ε_i:

$$q_i = (\frac{\partial \varepsilon_i}{\partial H_t})q'_{H_t} + (\frac{\partial \varepsilon_i}{\partial [H]})q'_{[A]} + (\frac{\partial \varepsilon_i}{\partial L_t})q'_{L_t}$$

where q' is:

$$q'_c = (\frac{\sigma_c}{C})C \qquad (C = H_t, [H], L_t)$$

σ_c is the standard deviation of C and the quotient $(\frac{\sigma_c}{C})$ is the calculated average relative error in C. Since the values of α_1, α_2, α_3 and α_4 need to be known to calculate W_i, an iterative method is used in which the values of α_1, α_2, α_3 and α_4 are first estimated, in order to calculate W_i, and then in turn the latter value is used to calculate new values of α_1, α_2, α_3 and α_4.

The linear regression method is only applied when two or more buffer regions in the ligand acid overlap. However, for all the ligand acids discussed in this dissertation there are two distinct pH regions which must be dealt with this way. The first and second protonations of the anion overlap in a high pH region, and the third and fourth protonations of the anion overlap in a low pH region. The great difference in pH of the two buffer regions allows simultaneous solution for only two a_n's at a time instead of four, that is α_1 and α_2 as a pair, and α_3 and α_4 as a separate group.

METAL-ANION STABILITY CALCULATION

The equilibrium between the lanthanide ions (M) and polyaminopolycarboxylate anions (L) is:

$$M + L \rightleftarrows ML$$

The equilibrium constant for this formulation is defined as:

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

The value of β is determined by measuring the pH values of solutions of known stoichiometry in which the acid ligand is progressively partially neutralized. The mass balances which are necessary to calculate β are:

$$M_t = [M] + [ML]$$

$$= [M] + \beta[M][L]$$

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

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

$$= [L](1 + \sum_i^4 \alpha_N[H]^N) + \beta[M][L]$$

$$H_t = [H] + [L]\sum_i^4 N\alpha_N[H]^N$$

$$[L] = \frac{H_t - [H]}{\sum_i^4 N\alpha_N[H]^N}$$

Elimination of [M] gives:

$$\frac{M_t}{L_t - [L](1 + \sum_i^4 \alpha_N[H]^N)} = \frac{(1 + \beta[L])}{\beta[L]}$$

Then cross multiplication and substitution for [L] yields:

$$\beta = \frac{\dfrac{L_t(\sum_i^4 N\alpha_N[H]^N)}{H_t - [H]} - (1 + \Sigma\alpha_N[H]^N)}{\left\{\dfrac{H_t - [H]}{\sum_i^4 N\alpha_N[H]^N}(1 + \sum_i^4 \alpha_N[H]^N) + M_t - L_t\right\}}$$

The value of [H] is obtained from pH measurement in each case so that the only unknown, β, can be calculated.

However, if more than one species of metal complex is formed, the computation of the equilibrium constants is more complicated. In some cases, in addition to the 1:1 chelate, ML^-, a protonated species MHL is also formed. The equilibria of these two species are:

$$M + L \rightleftarrows ML$$

$$M + HL \rightleftarrows MHL$$

The equilibrium constants of these two individual species are:

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

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

The mass balances of metal, ligand and hydrogen are:

$$M_t = [M] + [MHL] + [ML]$$

$$= [M] + \beta_H[M][H][L]\alpha_1 + \beta_1[M][L]$$

let

$$X = \frac{M_t}{[M]}$$

then

$$[L] = \frac{X - 1}{\beta_H[H]\alpha_1 + \beta_1}$$

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

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

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

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

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

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

In the previous computations, metal concentration does not occur in the hydrogen mass balance, so that the free [L] can be calculated from the measured hydrogen-ion concentration [H] and the predetermined protonation constants α_N. On the other hand, when the metal concentration occurs in the hydrogen mass balance, the treatment is different.

The approach of this case is to substitute the M_t mass balance into the L_t mass balance and also into the H_t mass balance. The L_t mass balance becomes:

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

This can be rearranged to a quadratic equation in terms of X:

$$0 = (1 + \Sigma\alpha_N[H]^N)X^2$$

$$+ (\alpha_1\beta_H[H]M_t + \beta_1M_t - 1 - \Sigma\alpha_N[H]^N - L_t\beta_H[H]\alpha_1 - L_t\beta_1)X$$

$$+ (-\alpha_1\beta_H[H]M_t - \beta_1M_t)$$

This is of the form:

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

where

$$A = [1 + \Sigma\alpha_N[H]^N]$$

$$B = B_1\beta_H + B_2\beta_1 + B_3$$

$$B_1 = [\alpha_1[H]M_t - L_t[H]\alpha_1]$$

$$B_2 = [M_t - L_t]$$

$$B_3 = [-\Sigma\alpha_N[H]^N - 1]$$

$$C = C_1\beta_H + C_2\beta_1$$

$$C_1 = [-\alpha_1[H]M_t]$$

$$C_2 = [-M_t]$$

The H_t mass balance gives:

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

or

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

This is of the form:

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

where

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

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

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

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

$$E_3 = (-\Sigma N\alpha_H[H]^N)$$

$$F = F_1\beta_H$$

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

By equating two quadratic equations, the X term can be eliminated from the unknown free-metal concentration. The value of X must be positive so that the solutions to the equations

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

and

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

are positive. As shown above, the terms A and D are positive, and C and F are negative, and, therefore, the values of $(B^2 - 4AC)$ and $(E^2 - 4DF)$ must be positive, and that $(B^2 - 4AC)^{\frac{1}{2}} > |B|$ and $(E^2 - 4DF)^{\frac{1}{2}} > |E|$. The solutions to be equated are:

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

This can be simplified to:

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

All the concentration variables are substituted into the above equation and the terms are grouped to give:

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

where:

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

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

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

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

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

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

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

$$Y = [2B_1B_2DF_1 - AF_1E_1B_2 - AF_1E_2B_1 - DC_1E_1B_2 - DC_1E_2B_1 - DC_2E_1B_1 + AC_2E_1^2 + 2AC_1E_1E_2]$$

$$Z = [B_1^2DF_1 - AB_1E_1F_1 - E_1B_1C_1D_1 + AC_1E_1^2]$$

The following relationships were also noted and used in the HCMPLX program:

$$B_3 = -A$$

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

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

$$E_3 = -D$$

$$F = C_1$$

The calculation of this system is very complicated, but an efficient numerical technique has been developed and is available via IMSL software subroutine, ZSYSTM, which is stored at Iowa State University Computational Center. The subroutine ZSYSTM requires an initial guess as to the values of β_1 and β_H in order for the computation to be initiated. If the values provided initially are too small, ZSYSTM tends to converge to the trivial solution: $\beta_1 = 0$, $\beta_H = 0$. It has also been noticed that if the expected value β_H in the system is very small (so that it could probably be ignored) ZSYSTM will tend to give large errors.

PART III. STUDY OF THE BEHAVIOR OF THIOBIS(ETHYLENENITRILO)-N,N,N',N'-TETRAACETIC ACID AND N,N-BIS(2-AMINOETHYL)ANILINE-N',N',N",N"-TETRAACETIC ACID WITH THE LANTHANIDES, AND THEIR ANIONS' INFLUENCE ON LANTHANIDE-AMERICIUM SEPARATIONS

INTRODUCTION

Diethylenetriaminepentaacetic acid (DTPA) has been known for several decades to be a promising chelating agent for lanthanide and actinide separations. Since the first DTPA studies, a limited number of additional polyaminopolycarboxylic acids have been prepared, but only a few of them have been studied with regard to their potential use in lanthanide-actinide separations. As noted in the first section of this dissertation, Figure 4, there are two types of stability trends for lanthanide chelate species: (1) "ideal," such as with lanthanide-PMDTA complexes, where the behavior appears to be based on a simple electrostatic or acid-base concept of cationic size and charge (a uniform increase in chelate stability accompanying decreased cationic radius); (2) "nonideal," such as with lanthanide-DTPA and EEDTA chelates, where the curve shapes first parallel the type 1 behavior for lighter lanthanides (usually with a break at gadolinium) but deviate in the case of the heavier lanthanides, with chelate stability decreasing with increasing atomic number. Experimental results show that type 2 chelating agents are the most promising agents for promoting lanthanide-actinide separation (65). The properties of type 2 chelating agents will be discussed in detail in the following sections.

Reagents

Trivalent lanthanide nitrate solutions

Approximately 0.1 M lanthanide nitrate solutions were prepared by dilution of concentrated stock solutions. These concentrated reagents

were originally prepared from the corresponding oxides which had been purified up to 99.999% purity in this laboratory by our technical staff, using the method described by Adolphson (66). The diluted metal nitrate solutions were standardized by both a gravimetric technique in which the metal ion was precipitated as the oxalate and ashed to the oxide and by complexometric titration with EDTA, using xylenol orange as an indicator (67).

Potassium hydroxide solution

Standard potassium hydroxide solution was prepared by dilution of ampules of carbonate-free KOH (Anachemia) with degassed distilled water. The resulting solution was standardized repeatedly by titration of solutions prepared from primary standard grade potassium acid phthalate (67) and protected from carbon dioxide by an Ascarite/Drierite trap.

Potassium nitrate solution

Approximately 1.0 M solution of potassium nitrate which was used for ionic strength adjustment, was prepared by dissolution of analytical grade KNO_3 into degassed distilled water. The solution was then standardized by passing aliquots through a well-washed, hydrogen-form, cation exchanger (Dowex 50-W) and titrating the resulting effluent and rinsings with standardized KOH.

Nitric acid solution

The nitric acid solution was prepared by dilution from concentrated reagent-grade HNO_3 and was standardized by titration with standard base.

Polyaminopolycarboxylic acid solutions

Various polyaminopolycarboxylic acid solutions for protonation constant and complex formation determinations were obtained by dissolving weighed amounts of the acids in degassed distilled water solution. The concentrations of the resulting solutions were determined by titration with standard base.

Polyaminopolycarboxylic acid eluants

Eluants used in cation-exchange experiments were prepared by dissolving the necessary amounts of pure polyaminopolycarboxylic acid to produce the desired concentration and adjusting the pH with concentrated NH_4OH. Sufficient NH_4NO_3 was added to produce a concentration 0.1 M in nitrate to insure an approximately constant ionic strength.

^{241}Am nitrate solution

One millicurie of americium-241 ($t_{1/2}$ = 458 yr.) as the nitrate was purchased from New England Nuclear. Appropriate specific activities for the tracer-scale ion-exchange experiments were produced by dilution of the received sample to one milliliter, and subsequent dilution of 100-µL aliquots of this primary stock solution in a 10-mL volumetric flask to provide an activity of approximately 10 µCi/mL. These dilutions were carried out by Mr. Ken Malaby.

^{155}Eu nitrate solution

One millicurie of europium-155 ($t_{1/2}$ = 1.81 yr.) as the nitrate was purchased from New England Nuclear and a 10 µCi/mL solution was prepared

by the procedure described in the case of ^{241}Am.

^{160}Tb chloride solution

A 250 µL aliquot of 0.47 mCi/mL terbium chloride ($t_{\frac{1}{2}}$ = 72 days) solution was obtained from New England Nuclear also. A specific activity of 11.7 µCi/mL was prepared from this material.

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.

Experimental

Protonation constants of polyaminopolycarboxylate anions

The polyaminopolycarboxylic acids which were synthesized in this dissertation exhibited two buffer regions, one at high pH (9-10), and another at low pH (2-3). This large difference in pH regions allowed the 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 from low pH solutions. Each series of solutions was prepared by combination of polyaminopolycarboxylic acid stock solution, standard KOH or HNO_3 solution, and sufficient KNO_3 to produce a 0.1 M ionic strength (I). The required volume of KNO_3 solution was calculated as described in the previous section in conjunction with program ALPHA, Appendix A. To insure the attainment of equilibrium, the prepared solutions were equilibrated in a water bath, thermostatted to 25.00 ± 0.05°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. Electrodes were 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. The desired values for α_1, α_2, α_3 and α_4 were calculated as described previously by mean of the computer program OMEGA.

Lanthanide-polyaminopolycarboxylate stability constants

Appropriate volumes of lanthanide nitrate, polyaminopolycarboxylic acid, KOH and enough KNO_3 to adjust the ionic strength to 0.1 M were combined in a series of volumetric flasks. The requisite KNO_3 were calculated from estimated stability constant values by means of the computer program BETA. The solutions were equilibrated at 25.00 ± 0.05°C for 12 hours and the pH_c of each was determined as in the case of the protonation constant experiment above. The formation constants of ML^- or of ML^- and MHL species were calculated by computer programs OMEGA and HCMPLX.

Tracer cation-exchange

An Altex 2 mm x 500 mm chromatographic column, a septum injection port and a Teflon tube and fittings were all obtained from Rainin

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

The cation-exchanger was equilibrated by passing a portion of the eluant through the column before injection of the well-mixed tracers. The scintillation vials used for sample collection were filled with 5-mL aliquots of the scintillation cocktail and loaded in the sample collector. The column photometric drop counter and turntable were aligned to assure successful collection.

Approximately 3~5 μL of well-mixed tracers were injected into the top of the column by a syringe. Eluant was then pumped through the column from the top by using a HPLC pump at a flow rate 3~4 drops/min. In each elution experiment, 50~75 samples were collected.

When the collection was completed, the individual samples were counted by gamma-ray spectrometry. The Ge-Li detector and Canberra multi-channel analyzer used were provided by the Health Physics group. The analyzer can count Eu, Am and Tb simultaneously by selecting the following discrete gamma energies:

^{241}Am -- 59.5 Kev

^{155}Eu -- 105.3 Kev

^{16a}Tb -- 298.6 Kev

Less than ten-minute sample counting times proved sufficient to provide reliable results.

RESULTS AND DISCUSSION

Protonation and Lanthanide Stability Constants

TEDTA

The protonation constants for TEDTA had been determined by other groups (51, 68, 69), however, in order to verify their results, the measurements were performed once again under the conditions mentioned in the experimental section. The results of this experiment and the literature values are displayed in Table 6.

Table 6. Protonation constants for the TEDTA anion at I = 0.1

25°C		25°C (69)	20°C (51, 68)
$\alpha_1 = \frac{[HL]}{[H][L]} = 0.195 \times 10^{10}$	$\log \frac{[HL]}{[H][L]} = 9.29$	9.33	9.42
$\alpha_2 = \frac{[H_2L]}{[H]^2[L]} = 0.430 \times 10^{18}$	$\log \frac{[H_2L]}{[H][HL]} = 8.34$	8.39	8.47
$\alpha_3 = \frac{[H_3L]}{[H]^3[L]} = 0.207 \times 10^{21}$	$\log \frac{[H_3L]}{[H][H_2L]} = 2.68$	--	2.52
$\alpha_4 = \frac{[H_4L]}{[H]^4[L]} = 0.191 \times 10^{23}$	$\log \frac{[H_4L]}{[H][H_3L]} = 1.97$	--	1.80

The values of the first and second stepwise protonation constants at 25°C are quite close to those reported in Martell and Smith (69). Unfortunately, Martell and Smith did not record the values of the third and fourth protonation constants at 25°C. For comparison purposes, the values of all four stepwise protonation constants at 20°C are displayed in Table 6. The values which were determined in this work are slightly different from those determined by Anderegg (68). The difference may be due to the different standardization techniques and conditions.

The values of each of the trivalent lanthanide stability constants (β_1) are shown in Table 7. It is apparent that the stability constants in the sequence of Ln-TEDTA complexes increase gradually up to Eu and drop at Gd (the "gadolinium break"). This could be attributed to the small ligand-field stability energy associated with splitting of partially filled f orbitals. However, the main reason for this change is not well-understood. After Gd, the complex stability constant of Ln-TEDTA increases slightly. Both the Tb and Dy complexes exhibit the same stability. After that, the complex stability constant decreases continuously for the remainder of the sequence. Plots of log β_1 versus lanthanide cationic radius for TEDTA chelates, DTPA (32) chelates, EEDTA (46) chelates and PMDTA (31) chelates are displayed in Figure 5 for comparison purposes. The shape of the TEDTA curve is similar to those of DTPA and EEDTA but differs from that of PMDTA. As it was mentioned in the introductory part of this section, the TEDTA plot is a type 2 curve, "nonideal." The most surprising features of this graph are the large stability constant differences between DTPA-EEDTA and EEDTA-TEDTA. The difference of each pair is a factor of *ca.* 10^4, due in

Table 7. Stability constants of trivalent lanthanide-TEDTA (at 25°C; I = 0.1)

M	β_1	log β_1	Lit. log β	Ref.	separation factor α_Z^{Z+1}
La	0.400×10^{13}	12.60[a]	12.8 at 20°C	(68)	La - Ce = 7.30
Ce	0.292×10^{14}	13.47			Ce - Pr = 3.18
Pr	0.930×10^{14}	13.97			Pr - Nd = 1.76
Nd	0.164×10^{15}	14.22	14.7 at 18°-20°C	(70)	Nd - Sm = 3.51
Pm					
Sm	0.576×10^{15}	14.76			Sm - Eu = 1.14
Eu	0.656×10^{15}	14.82			Eu - Gd = 0.88
Gd	0.579×10^{15}	14.76			Gd - Tb = 1.17
Tb	0.675×10^{15}	14.83			Tb - Dy = 1.00
Dy	0.677×10^{15}	14.83			Dy - Ho = 0.70
Ho	0.471×10^{15}	14.67			Ho - Er = 0.69
Er	0.327×10^{15}	14.51			Er - Tm = 0.78
Tm	0.255×10^{15}	14.41			Tm - Yb = 0.81
Yb	0.207×10^{15}	14.32			Yb - Lu = 0.61
Lu	0.126×10^{15}	14.10			

[a]Values are estimated to be reliable to ± 0.05.

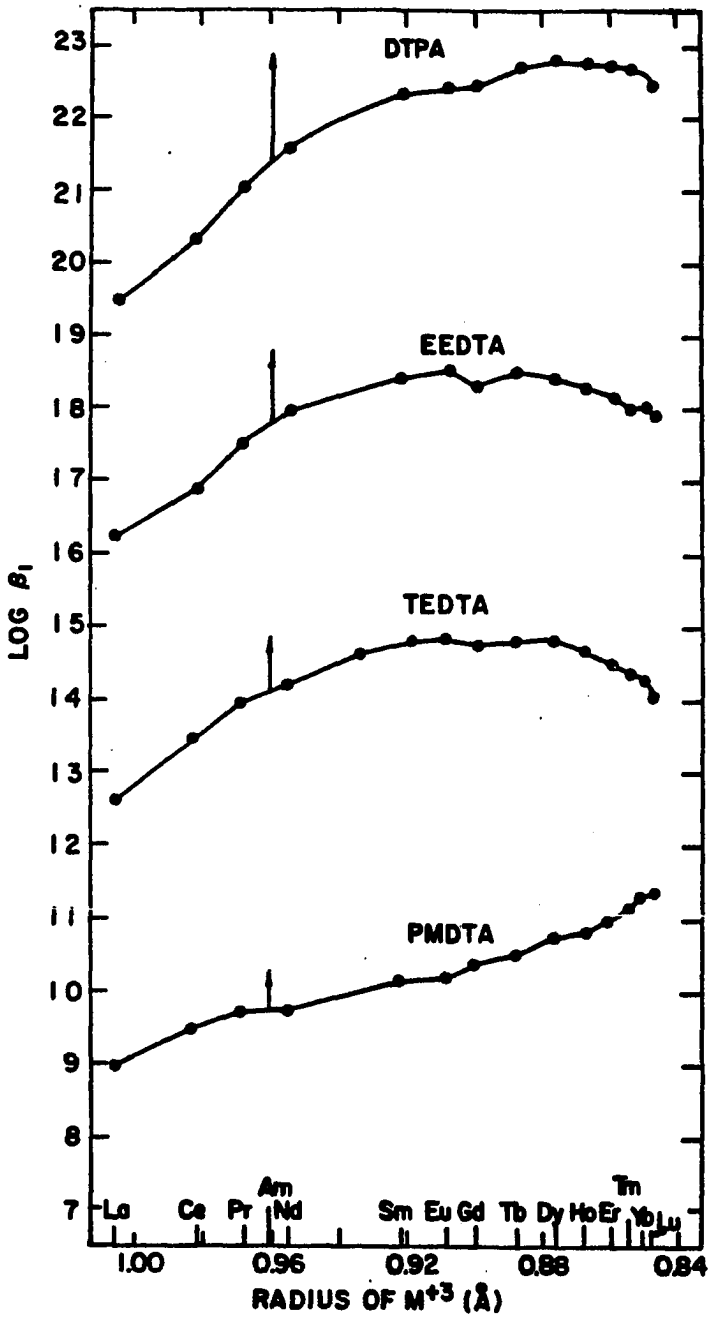


Figure 5. Stability constants of lanthanides with several polyamino-polycarboxylates

one instance to the direct replacement of the amine nitrogen atom and a CH_2COO^- in DTPA with the ether oxygen atom in EEDTA and in the other case by replacement of the ether oxygen atom by a sulfur atom. Comparison of these three strategically placed atoms shows that all have at least one set of lone pair of electrons. X-ray crystallographic determinations of the bond angles of substances having resemblances to these moieties, however, show that the bond angle of the central atom C-X-C (X = O, N or S) does not vary drastically; $O(CH_3)_2 = 111^\circ \pm 3^\circ$, $N(CH_3)_3 = 108^\circ \pm 4^\circ$ and $S(CH_3)_2 = 105^\circ \pm 3^\circ$ (71). The bond angle does not seem to be the essential cause for such large differences in stability constants of the complexes. It is easy to rationalize that the stability constants of Ln-EEDTA complexes should be higher than those of the Ln-TEDTA complexes since the greater polarization effect should cause the central oxygen atom to be more strongly attracted to a metal ion than the sulfur atom is. The difference between the Ln-EEDTA and Ln-DTPA stability constants is more subtle and will be discussed later.

Both Ln-EEDTA and Ln-TEDTA complexes exhibit a decreasing trend in the stability with the heavy lanthanides. As the cationic radius becomes smaller and smaller toward the end of the family, steric effects become more critical. In order to account for this decreasing affinity, it would seem that one of the bonds of the heptadentate ligand must be gradually compromised or broken. In the Ln-PMDTA sequence, where a methylene group

replaces either oxygen or sulfur, but provides no lone pair of electrons to form the two additional five-membered chelate rings, the chelate stability constants decrease tremendously (10^7 with respect to EEDTA, Figure 5) (65). Because of this, it appears that the gradual down turn (in the case of DTPA, EEDTA and TEDTA) midway through the stability sequences must mean that one of the four terminal carboxylate groups is partially or completely detached so that one five-membered chelate ring is removed. This explanation seems more reasonable than does a gradual failure of the coordination of the central atom (i.e., O, N or S).

BEATA

The values of the stepwise protonation constant of BEATA are shown in Table 8 and the stability constants of the Ln-BEATA complexes are displayed in Table 9.

Table 8. Protonation constants for the BEATA anion at 25°C, I = 0.1

$\alpha_1 = \frac{[HL]}{[H][L]} = 0.141 \times 10^{11}$	$\log \frac{[HL]}{[H][L]} = 10.15$
$\alpha_2 = \frac{[H_2L]}{[H]^2[L]} = 0.215 \times 10^{20}$	$\log \frac{[H_2L]}{[H][HL]} = 9.18$
$\alpha_3 = \frac{[H_3L]}{[H]^3[L]} = 0.613 \times 10^{23}$	$\log \frac{[H_3L]}{[H][H_2L]} = 3.46$
$\alpha_4 = \frac{[H_4L]}{[H]^4[L]} = 0.500 \times 10^{25}$	$\log \frac{[H_4L]}{[H][H_3L]} = 1.91$

Table 9. Stability constants of trivalent lanthanide-BEATA at 25°C, I = 0.1

M	β_1	log β_1	separation factor α_Z^{Z+1}
La	0.126×10^{14}	13.10	La - Ce = 6.51
Ce	0.820×10^{14}	13.91	Ce - Pr = 8.06
Pr	0.661×10^{15}	14.82	Pr - Nd = 1.90
Nd	0.126×10^{16}	15.10	Nd - Sm = 3.62
Pm			
Sm	0.456×10^{16}	15.66	Sm - Eu = 1.12
Eu	0.512×10^{16}	15.71	Eu - Gd = 0.51
Gd	0.263×10^{16}	15.42	Gd - Tb = 1.16
Tb	0.304×10^{16}	15.48	Tb - Dy = 0.74
Dy	0.225×10^{16}	15.35	Dy - Ho = 0.46
Ho	0.104×10^{16}	15.02	Ho - Er = 0.62
Er	0.642×10^{15}	14.81	Er - Tm = 0.97
Tm	0.620×10^{15}	14.79	Tm - Yb = 1.21
Yb	0.753×10^{15}	14.88	Yb - Lu = 0.73
Lu	0.550×10^{15}	14.74	

The plots of log β_1 versus lanthanide cationic radius for BEATA, [(octylimino)bis(ethylenenitrilo)]tetraacetic acid, $H_{17}C_8N[CH_2CH_2N(CH_2COOH)_2]_2$, (BEOTA) (72), [(benzylimino)bis(ethylenenitrilo)]tetraacetic acid, $C_6H_5CH_2N[CH_2CH_2N(CH_2COOH)_2]_2$, (BEBTA) (72), N'-(β-carboxyethyl)diethylenetriamine-N,N,N",N"-tetraacetic acid, $HOOCCH_2CH_2N[CH_2CH_2N(CH_2COOH)_2]_2$, (CDTA) (73) and N'-(β-hydroxyethyl)diethylenetriamine-N,N,N",N"-tetraacetic acid, $HOCH_2CH_2N[CH_2CH_2N(CH_2COOH)_2]_2$, (HEDTA) (74) are displayed in Figure 6. It is surprising that the stability constants (log β_1) of these five chelating agents ($\sim 1 \times 10^{16}$ to 1×10^{18}) are so much lower than that of DTPA ($\sim 1 \times 10^{22}$). Choppin *et al.* (75) published ^1H and ^{13}C NMR spectra for the DTPA complexes of La and Lu. They concluded that the middle carboxylate group was unbound and suggested heptadentate coordination of the metal ion by three nitrogen atoms and an average of four carboxylate groups. Comparison of these six compounds, BEATA, BEOTA, BEBTA, CDTA, HEDTA and DTPA reveals that, the only difference among them is the substitution group on the central nitrogen atom. The substituents can be classified into two classes: (1) electron donor, $C_{17}H_{18}$ and $C_6H_5CH_2$ groups; (2) electron withdrawing, $HOOCCH_2CH_2$, $HOCH_2CH_2$, C_6H_5 and $HOOCCH_2$ groups. Since an electron donor group enhances the basicity of the lone-pair of the middle nitrogen atom, one expects that this group of compounds will bind much more tightly to a metal ion, resulting in a higher stability constant. The experimental results agree with this view, since both BEBTA and BEOTA complexes have stability constants higher than those of the corresponding chelate species of HEDTA, CDTA and BEATA. DTPA chelates have the highest formation constants of all probably due to a -5 formal charge compared to

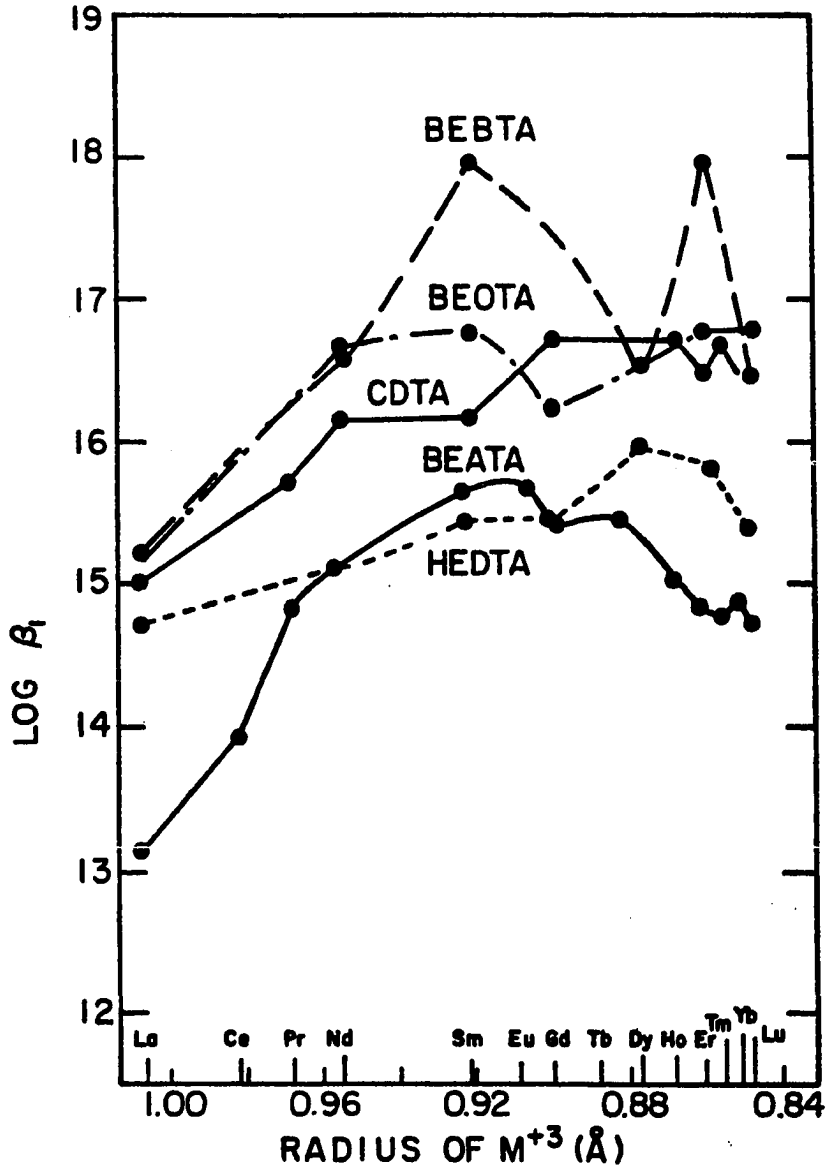


Figure 6. Stability constants of lanthanides with $C_6H_5N[CH_2CH_2N(CH_2COOH)_2]_2$ and different N-substituent chelates

-4. There is without doubt heptadentate coordination of BEBTA, BEOTA and BEATA to the lanthanons by three nitrogen atoms and all four carboxylate groups. If one accepts Choppin et al.'s view on the DTPA complexes, it is extremely difficult to explain a more than 10^4-fold decrease of β_1 values with the other amino compounds in Figure 6, even though some of the data reported by Vasil'eva et al. (72-74) are obviously poor and incomplete. DTPA probably bonds octadentately rather than heptadentately. The highest stability constant for Ln-BEATA complexes is at Eu while for the Ln-DTPA complexes is at Dy. The shift of the highest stability constant to the lighter lanthanon ion provides the insight of steric constraints of these two chelating agents (DTPA vs. DEATA). The flexibility of the phenyl group in DEATA is much less than the carboxylate group in DTPA. As the radius of the metal ion becomes smaller and smaller along the lanthanide family, the steric stress increases and one of the bonds is gradually compromised to relieve this stress. In the DTPA case, with the fifth carboxylate group binding to the metal ion, the hold on the lanthanon is so tenacious that compromise of a bonding moiety occurs later in the sequence. When detachment occurs, it is difficult to be absolutely sure which donor (a carboxylate oxygen or the central nitrogen) is removed from the coordination sphere. Nevertheless, it appears that the fifth carboxylate group does play a role in DTPA in bonding, otherwise the 10^4-fold increase in stability does not make sense.

TEDTA and BEATA Cation-Exchange Elutions

The behaviors of these two chelating agents towards lanthanide metal ions are quite similar. The stability constants of BEATA complexes of

lanthanide ions are but about 7-fold higher than those of the corresponding TEDTA species. Therefore, in the Am-Ln cation-exchange elution, one would expect that there would be only slight differences between these two chelating agents when used as eluting agents. The experimental results and the best conditions of these two individual chelating agents (TEDTA and BEATA) are depicted in Figure 7 and Figure 8, respectively. The conditions used in the TEDTA experiment were much more severe than with BEATA. If the concentration of BEATA is as much as 2.0×10^{-2} at pH 3.8, a solid complex deposits in the column. It was also noted that BEATA reacts with the column resin to form an unknown violet-colored material which cannot be removed from the system by common mineral acids or bases.

The chromatogram of Am, Eu and Tb with TEDTA shows that all three metal ions elute at the same rate (Figure 7). As predicted, from the same stability constants, the separation factor equals one. Therefore, Am cannot be separated from Eu and Tb with TEDTA as was done in the case of the EEDTA system (65). However, with BEATA, Am was eluted slightly ahead of Eu, but there was a considerable amount of overlapping (Figure 8). The separation factor calculated from the positions of the Am and Eu peaks with BEATA eluant indicated an Am-Eu separation factor of 1.16.

Of the two chelating agents (TEDTA and BEATA), BEATA is the better agent for Ln-Am separation, but the low solubility of this agent in water and its tendency to react with the resin are two major deterrents to the use of this compound in any separation scheme.

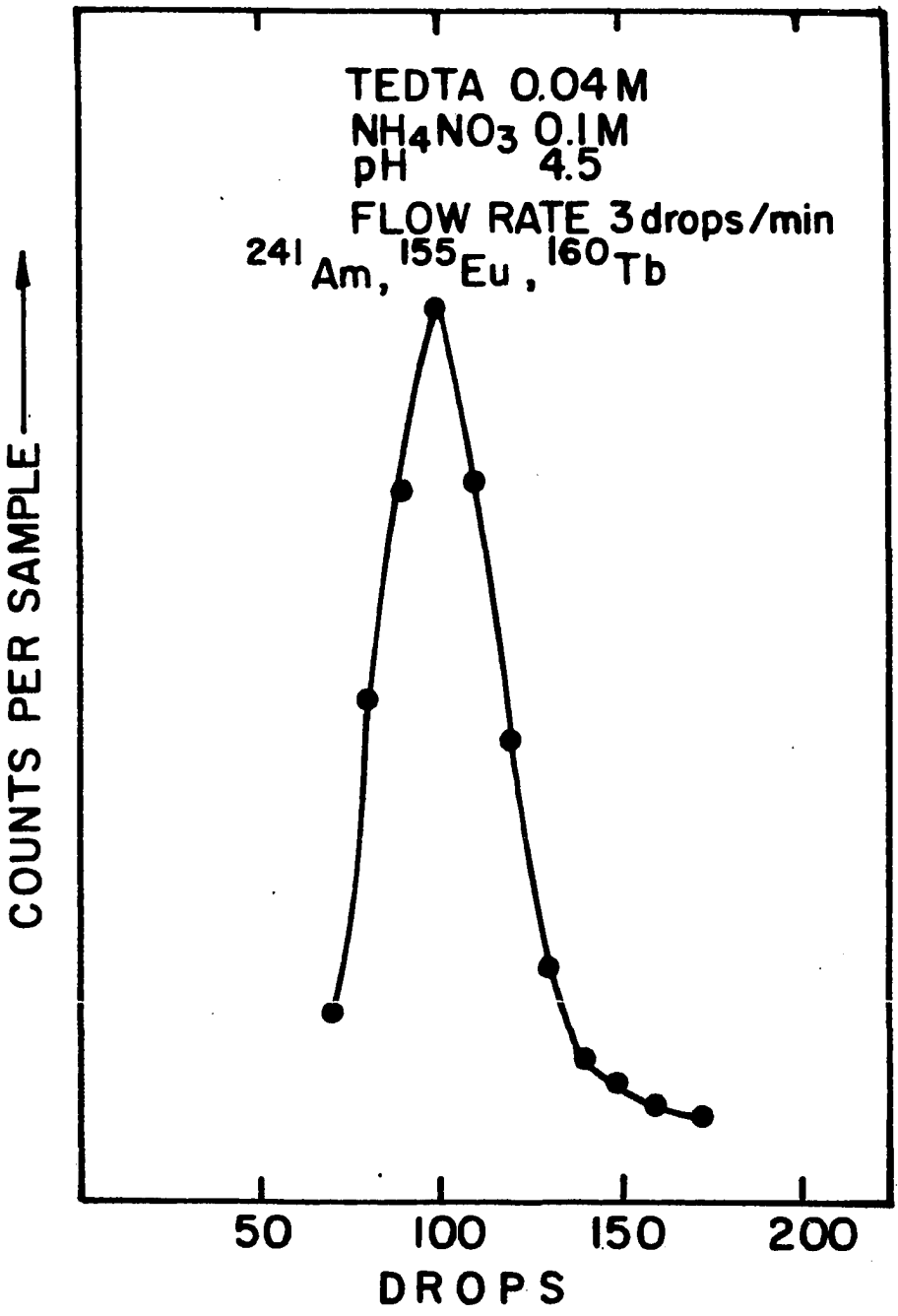


Figure 7. Cation-exchange elution of ^{155}Eu-^{160}Tb-^{241}Am with $S[CH_2CH_2N(CH_2COOH)_2]_2$

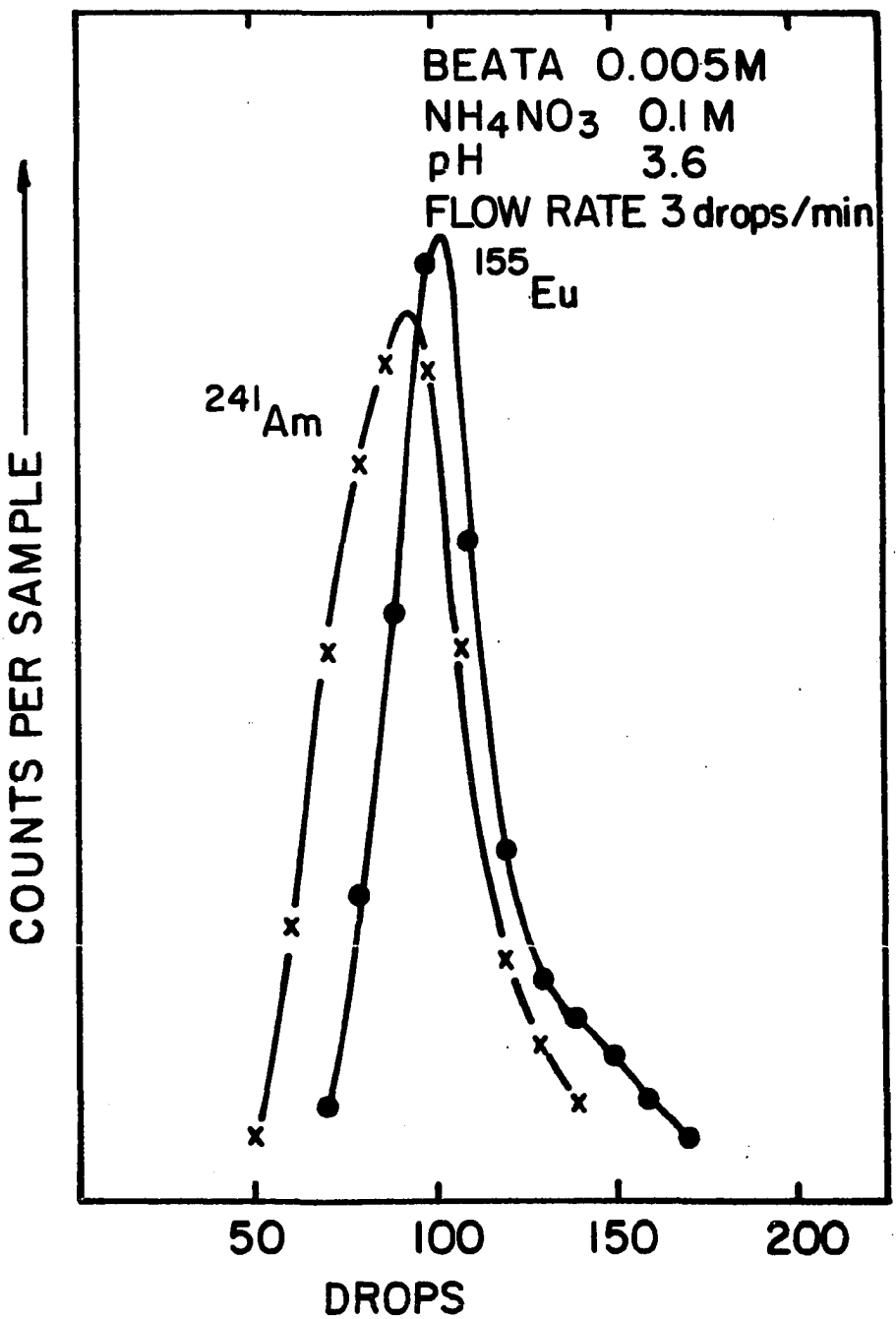


Figure 8. Cation-exchange elution of ^{155}Eu-^{241}Am mixture with $C_6H_5N[CH_2CH_2(CH_2COOH)_2]_2$

PART IV. STUDIES OF THE PROTONATION CONSTANTS AND STABILITY CONSTANTS OF SPECIES FORMED BETWEEN LANTHANIDES AND BIS(3-AMINOPROPYL)ETHER-N,N,N',N'-TETRAACETATE (BPETA) AND N,N-BIS(N',N'-DICARBOXYMETHYL-3-AMINOPROPYL)-N-METHYL-AMMONIOACETATE (BCPA)

INTRODUCTION

Polyaminopolycarboxylic acids have long been known to be potential chelating agents in lanthanide and actinide separations; and, in the area of cation-exchange separations, certain polyaminopolycarboxylic acids (EDTA, DTPA, EEDTA) surpass most other reagents (e.g., phosphoric acids, hydroxcarboxylic acids and amines) in effectiveness. The study of polyaminopolycarboxylic acids has been concentrated in the past mainly on reagents with an ethylene (EDTA) or diethylene (DTPA and EEDTA) backbone. The compounds form multiple five-membered rings with metal ions in the complexones. To establish the ring-size influence on the selectivity of a complex-forming reagent, an investigation of another ring size (besides five-membered) is necessary. In this section, a study of the stability constants of lanthanide chelates with bis(3-aminopropyl)ether-N,N,N',N'-tetraacetate (BPETA) and N,N-bis[N',N'-dicarboxymethyl-3-aminopropyl]-N-methylammonioacetate (BCPA) is discussed, as well as the performance of these ligands as selective eluants in lanthanide-actinide separations.

Experimental

All the reagent preparations and experimental procedures are the same as described in Part III of this dissertation.

RESULTS AND DISCUSSION

Protonation Constants and Stability Constants

BPETA

The protonation constants of BPETA have been determined before by two other groups (51, 76) at different conditions. The verified values of these constants are revealed in Table 10. Even though the conditions differ by 5°C, the values obtained in this work agree well with the earlier data. The pK values of EEDTA are 9.47, 8.84, 2.76 and 1.8. Comparison of pK values for BPETA and EEDTA indicates that bis(3-aminoethyl)ether-N,N,N',N'-tetraacetic acid is a more basic compound due to the reduced inductive effect of the ether oxygen atom when it is in a less proximate location (i.e., the 3 position rather than the 2 position of the chain which connects the iminodiacetate moieties).

Table 10. Protonation constants of $O[CH_2CH_2CH_2N(CH_2COOH)_2]_2$ at 25°C, I = 0.1

		20°C (51)	20°C (76)
$\alpha_1 = \frac{[HL]}{[H][L]} = 0.108 \times 10^{11}$	$\log \frac{[HL]}{[H][L]} = 10.03$	10.17	10.14
$\alpha_2 = \frac{[H_2L]}{[H]^2[L]} = 0.817 \times 10^{20}$	$\log \frac{[H_2L]}{[H][HL]} = 9.88$	9.67	9.64
$\alpha_3 = \frac{[H_3L]}{[H]^3[L]} = 0.366 \times 10^{23}$	$\log \frac{[H_3L]}{[H][H_2L]} = 2.65$	2.7	2.74
$\alpha_4 = \frac{[H_4L]}{[H]^4[L]} = 0.767 \cdot 10^{25}$	$\log \frac{[H_4L]}{[H][H_3L]} = 2.32$	2.1	2.0

The stability constants of BPETA chelates involving lanthanide ions are displayed in Table 11 and a plot of log β_1 values versus the metal ionic radius is shown in Figure 9. The ligand-cation affinity rises to a maximum at samarium, falls to a minimum at terbium, and then increases again. The stability constants of BPETA chelates with lanthanons are about 10^6-fold less than those of EEDTA. The great difference of stability constants between homologues may be caused by two factors: the inductive effect and the influence of ring size. Upon replacing the ethylene linkages of EEDTA by propylene in BPETA, the acidity of the chelating agent is lessened (Table 10) because the inductive effect of the ether oxygen atom is attenuated (77). Secondly, with EEDTA, a heptadentate ligand, six 5-membered chelating rings involve the metal ion. With BPETA, one more methylene group is present in each connection between ether-O and amino-N donor atoms. Therefore, two of six 5-membered chelating rings are converted to 6-membered chelating rings. Experimental results (78) have shown that, in metal chelating complexes, a five-membered ring provides a higher stability than any other size of chelating ring. Combination of the two effects above renders BPETA a much less effective chelate for lanthanide ions than EEDTA.

The stability constant curve of BPETA in Figure 9 resembles those of the lanthanide-hydroxycarboxylates which were studied by Powell *et al.* (79, 80). As the metal ion becomes smaller, the steric stress becomes more pronounced, and affects the stability constant of the complexes. The gradual decrease in stability constant starting at samarium and continuing until terbium suggests a progressive change of coordination within the

Table 11. Stability constants of lanthanides with $O[CH_2CH_2CH_2N(CH_2COOH)_2]_2$ at 25°C, I = 0.1

M	β_H	log β_H	β_1	log β_1	separation factor α_Z^{Z+1}
La	0.391×10^7	6.59	0.474×10^{11}	10.68[a]	La - Ce = 3.93
Ce	0.680×10^7	6.83	0.186×10^{12}	11.27	Ce - Pr = 1.85
Pr	0.967×10^7	6.99	0.345×10^{12}	11.54	Pr - Nd = 1.32
Nd	0.108×10^8	7.03	0.458×10^{12}	11.66	Nd - Sm = 1.63
Pm					
Sm	0.159×10^8	7.20	0.744×10^{12}	11.87	Sm - Eu = 0.88
Eu	0.198×10^8	7.30	0.655×10^{12}	11.82	Eu - Gd = 0.83
Gd	0.195×10^8	7.30	0.545×10^{12}	11.74	Gd - Tb = 0.91
Tb	0.364×10^8	7.56	0.498×10^{12}	11.70	Tb - Dy = 1.05
Dy	0.507×10^8	7.71	0.524×10^{12}	11.72	Dy - Ho = 1.07
Ho	0.625×10^8	7.80	0.561×10^{12}	11.75	Ho - Er = 1.31
Er	0.700×10^8	7.85	0.735×10^{12}	11.87	Er - Tm = 1.32
Tm	0.847×10^8	7.93	0.972×10^{12}	11.99	Tm - Yb = 1.23
Yb	0.123×10^9	8.09	0.119×10^{13}	12.08	Yb - Lu = 1.17
Lu	0.135×10^9	8.13	0.139×10^{13}	12.14	

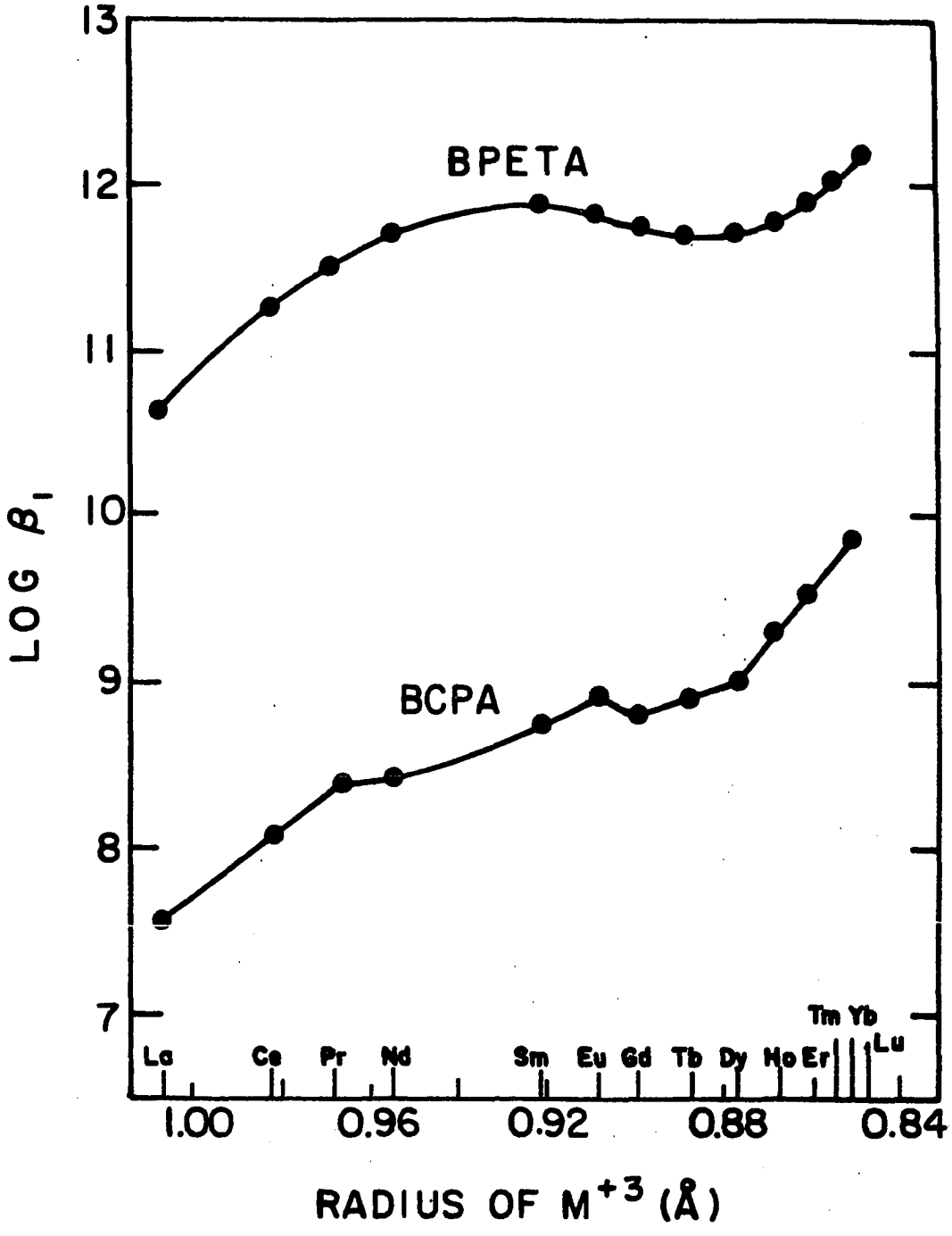


Figure 9. Plots of log β_1 vs. radius of M^{3+} of BPETA and BCPA

metal complex. One of the seven attachments of the chelating agent to the metal (via electron donor atoms) is gradually compromised and eventually broken. After terbium, the continued increasing charge density of the lanthanons (whose size is diminishing) results again in an increasing affinity for those donor atoms that can be accommodated with little stress. Note that while even the smallest lanthanon, Lu^{3+}, can accommodate about at least eight oxygen atoms from water molecules, not all the donor atoms of a polydentate ligand can be forced into an array that will replace such H_2O molecules on a one to one basis. Accommodation of the potential donor O's and N's of a polydentate ligand is less constrained in the case of larger cations, where the coordination sphere is larger and the close packing of a greater number of donor atoms of whatever origin provides more flexibility. In reducing dentate character from heptadentate to hexadentate, it is more likely that a terminal (carboxylate) O will detach rather than either the ether O or a tertiary amine N, because ruination of fewer rings occurs. The destruction of two chelate rings would decrease the stability of a complex tremendously (65). Therefore, it appears to be more reasonable to assume that one of the carboxylate group is released rather than an atom associated with a greater number of rings.

BCPA

The protonation constants of BCPA are shown in Table 12. The values for this compound are lower than those of bis(2-aminoethyl)methylamine-N,N,N',N'-tetraacetic acid (pK_1 = 10.89, pK_2 = 7.39, pK_3 = 3.65, pK_4 = 2.8 at 20°C, I = 0.1) (51) which indicates that this acid is more acidic

Table 12. Protonation constant of $^{-}OOCH_2C(CH_3)\overset{+}{N}[CH_2CH_2CH_2N(CH_2COOH)_2]_2$ at 25°C, I = 0.1

$\alpha_1 = \frac{[HL]}{[H][L]} = 0.690 \times 10^9$	$\log \frac{[HL]}{[H][L]} = 8.84$
$\alpha_2 = \frac{[H_2L]}{[H]^2[L]} = 0.617 \times 10^{17}$	$\log \frac{[H_2L]}{[H][HL]} = 7.95$
$\alpha_3 = \frac{[H_3L]}{[H]^3[L]} = 0.410 \times 10^{20}$	$\log \frac{[H_3L]}{[H][H_2L]} = 2.82$
$\alpha_4 = \frac{[H_4L]}{[H]^4[L]} = 0.569 \times 10^{23}$	$\log \frac{[H_4L]}{[H][H_3L]} = 2.14$

than $CH_3N[CH_2CH_2N(CH_2COOH)_2]_2$. Its acidic properties are also much different from those of EEDTA and BPETA. The difference is apparently due to the introduction of a carboxylate group on the central nitrogen atom. The electron withdrawing effect of the carboxylate group at the middle nitrogen atom causes protons on the terminal carboxylate groups and at the terminal amine to be more acidic.

The stability constants of complexes formed by BCPA with lanthanide ions are much lower than those formed by other polyaminopolycarboxylates which have been reported, and the values are listed in Table 13. Comparing the β_1 values of BCPA and PMDTA (65) in Figure 9 and Figure 5, it is seen that the stability constants of BCPA are about ten times lower than those of PMDTA which is a hexadentate ligand. That the dipolar ligand, BCPA, exhibits properties similar to PMDTA indicates that BCPA is also a hexadentate ligand. This is not surprising because the central nitrogen atom

Table 13. Stability constants of lanthanide-BCPA at 25°C, I = 0.1

M	β_H	log β_H	β_1	log β_1	separation factor α_Z^{Z+1}
La	0.129×10^6	5.11	0.379×10^8	7.58	La - Ce = 3.20
Ce	0.216×10^6	5.33	0.121×10^9	8.08	Ce - Pr = 1.93
Pr	0.274×10^6	5.44	0.234×10^9	8.37	Pr - Nd = 1.16
Nd	0.313×10^6	5.50	0.271×10^9	8.43	Nd - Sm = 1.90
Pm					
Sm	0.462×10^6	5.67	0.516×10^9	8.71	Sm - Eu = 1.55
Eu	0.456×10^6	5.64	0.802×10^9	8.90	Eu - Gd = 0.77
Gd	0.471×10^6	5.67	0.618×10^9	8.79	Gd - Tb = 1.21
Tb	0.606×10^6	5.78	0.744×10^9	8.87	Tb - Dy = 1.34
Dy	0.102×10^7	6.02	0.995×10^9	9.00	Dy - Ho = 2.24
Ho	0.130×10^7	6.12	0.223×10^{10}	9.35	Ho - Er = 1.56
Er	0.160×10^7	6.20	0.348×10^{10}	9.54	Er - Tm = 1.42
Tm	0.216×10^7	6.34	0.494×10^{10}	9.69	Tm - Yb = 1.42
Yb	0.257×10^7	6.41	0.701×10^{10}	9.85	Yb - Lu = 0.97
Lu	0.271×10^7	6.43	0.680×10^{10}	9.83	

is a quaternary ammonium atom and is without a lone-pair of electrons. One would expect that the carboxylate group of the acetate attached to the central N atom could play a major role in bonding to lanthanons as does a comparable group in DTPA. However, experimental results suggest that this is not the case. If that carboxylate bonded to the metal ion, BCPA would become a heptadentate instead of hexadentate ligand and chelation would result in additional (albeit nine-membered) rings. Although the effect of nine-membered rings on the stability of the metal complex might be small, it should be positive. BCPA would bond more tenaciously than PMDTA to lanthanons if its fifth carboxylate O were involved in chelation. This is apparently not the case since the lanthanide-BCPA stability constants are approximately 10-fold less stable than their PMDTA counterparts. The trend of stability with BCPA complexes mimics the trend observed with PMDTA rather than that characteristic of EEDTA (46) and BPETA chelates, in which additional rings are formed and make the structure less flexible.

Cation-Exchange Elution

BPETA

The experimental conditions and results of a BPETA elution of Am^{3+} and Eu^{3+} are displayed in Figure 10. ^{241}Am eluted slightly ahead of ^{155}Eu and the Eu-Am separation factor is 1.10. By employing this calculated Eu-Am separation factor, the stability constant ($\log \beta_1$) of Am is estimated to be 11.86, which interposes it between Sm and Eu, as well as between Ho and Er. Am, therefore, cannot be separated easily from the lanthanide family by elution with BPETA. The ligand, however, exhibits a

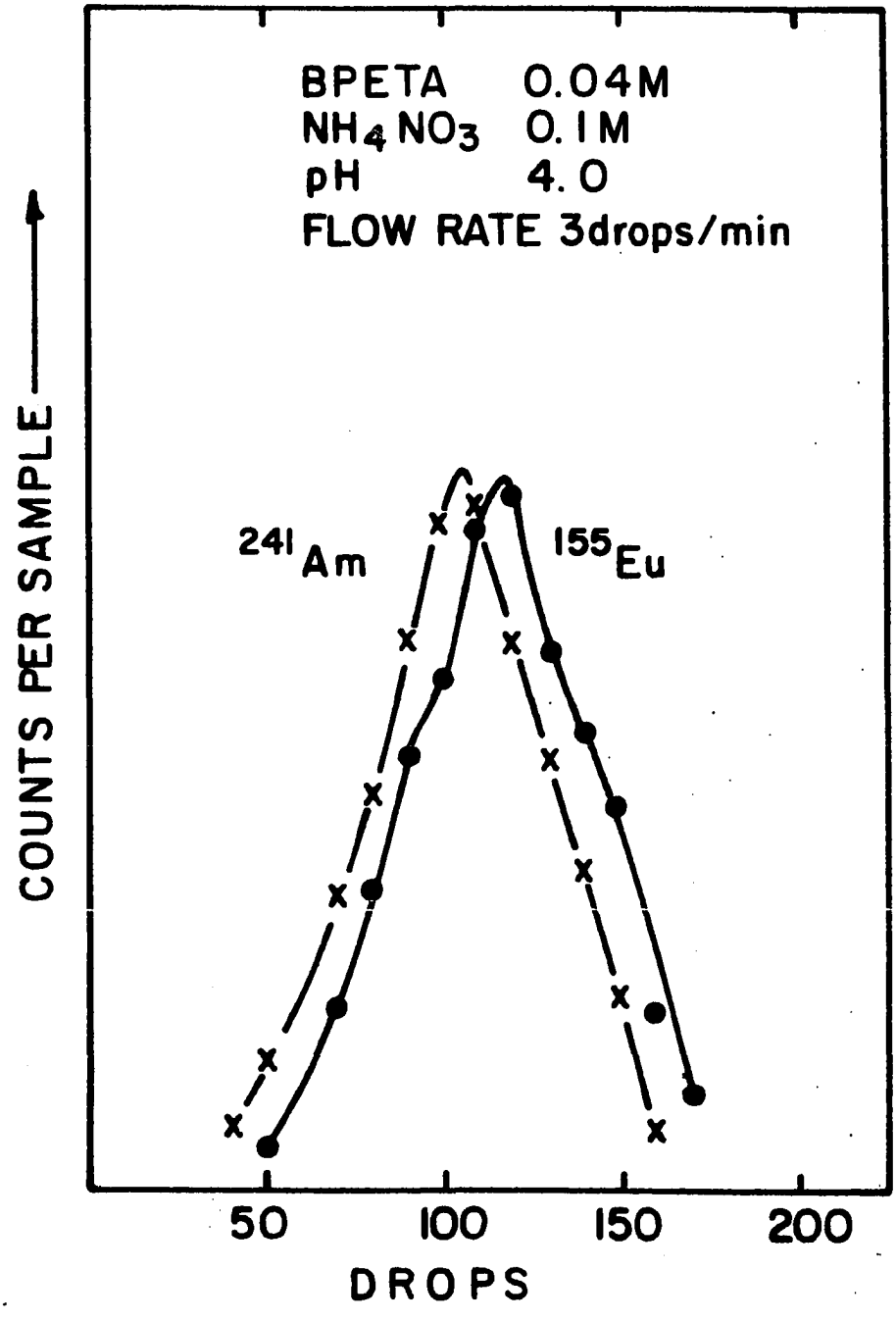


Figure 10. Cation-exchange elution of ^{241}Am and ^{155}Eu with BPETA

good separation factor for the light lanthanides. Besides that, BPETA is very soluble in water in room temperature, allowing the use of hydrogen ion as a retaining ion in displacement cation-exchange schemes.

BCPA

The experimental conditions for BCPA are different from those of BPETA. Both ^{241}Am and ^{155}Eu eluted coincidentally under necessarily more basic conditions. The results are shown in Figure 11. Preliminary elutions with 25 column volumes of 0.04 M BCPA solution at pH's of 3.0, 4.0, 5.0 or 6.0 were insufficient to remove the Am and Eu tracers from the resin bed. The higher pH requirements reflect the 1000-fold lower affinity of BCPA (compared to BPETA) for tervalent cations.

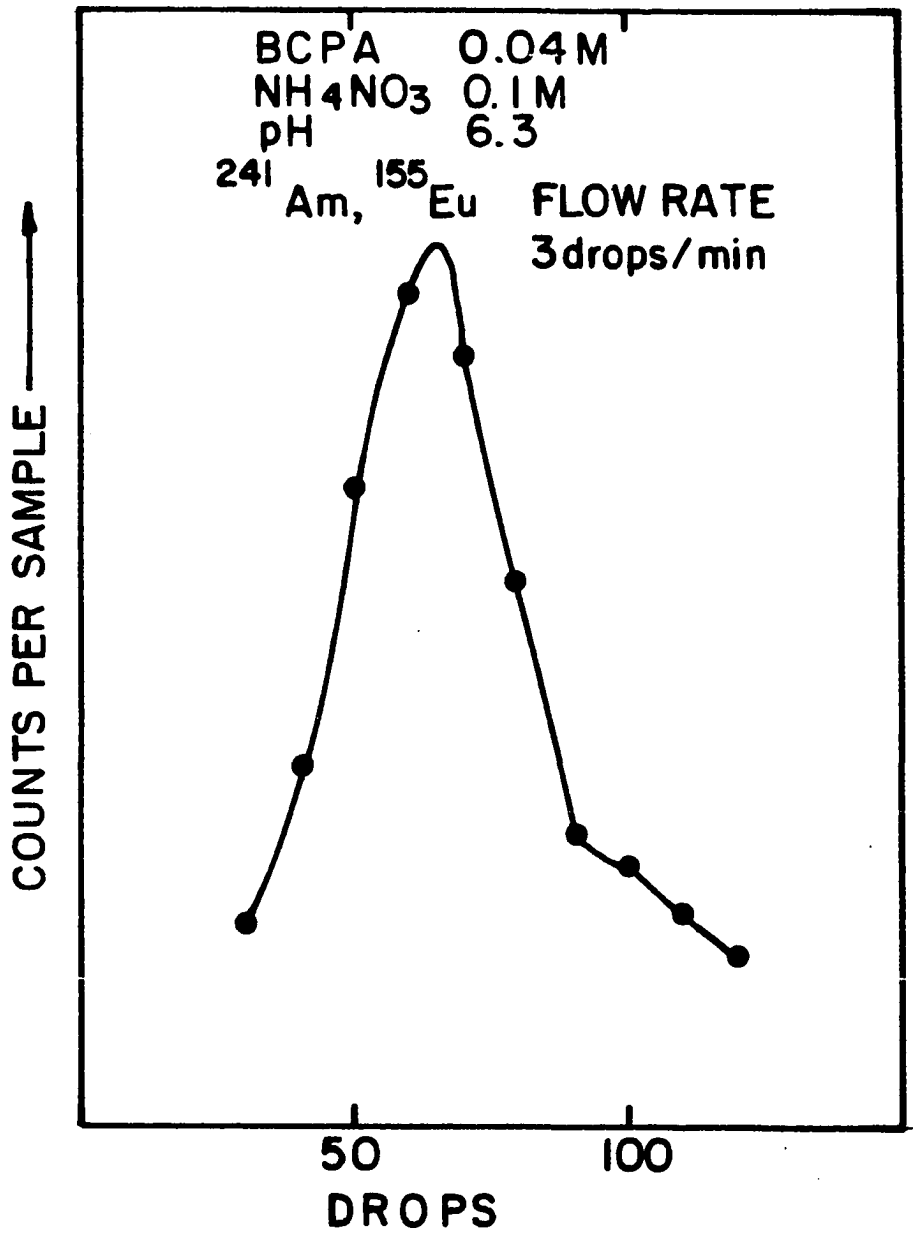


Figure 11. Cation-exchange elution of ^{241}Am and ^{155}Eu with BCPA

CONCLUSIONS

Summary

The coordination properties of some polyaminopolycarboxylates toward lanthanide ions have been examined and reported. Polyaminopolycarboxylates, TEDTA, BEATA, BPETA and BCPA, which form soluble 1:1 chelate species with trivalent lanthanide ion in aqueous media, were studied under identical conditions, 25°C and 0.1 M ionic strength. The stability constants of metal chelate species were found to depend upon the chelate ring size, electronegativity of the central atom (N, S, O) and the coordination number of the ligand to metal ion. Five-membered chelating rings provide the most stable complexes. Chelate ring sizes beyond five-membered exhibit lesser affinity for lanthanons (EEDTA vs. BPETA). Electronegativity of the central donor atom plays an important role in the overall stability of the complex, e.g. EEDTA has a higher affinity (by $\sim 10^4$) than does TEDTA. The difference is due primarily to the fact that the ether oxygen atom in EEDTA is more basic than the thio sulfur atom in TEDTA, because the other structural features are the same. The coordination number of ligands to metal also affects the stability constant. TEDTA, a heptadentate type, forms chelate complexes about 10^4 more stable than PMDTA, a hexadentate ligand, does.

Heptadentate or higher dentate ligands such as DTPA, EEDTA, TEDTA, BEATA and BPETA exhibit a turning point in the mid-lanthanon range. The turning point corresponds to onset of a gradual change of coordination number of the ligand anion to metal cation. One of the terminal

carboxylate groups is the most likely candidate for cleavage due to the steric effect which arises as the metal ion becomes smaller and smaller. Ligands which do not have an electron donor atom in the middle of the chain, such as PMDTA and BCPA, do not exhibit any turning point along the stability sequence.

Tracer level ^{241}Am-^{155}Eu cation-exchange experiments, utilizing four individual ligands (TEDTA, BEATA, BPETA and BCPA) as eluants, indicate that the "nonideal" ligands are eluting agents which have a potential in lanthanide-actinide separations. With the "ideal" type ligands, PMDTA and BCPA, the stability constants of americium chelating complexes do not possess a sufficient enhanced affinity for the ligand to permit separation from all the lanthanons.

In the "nonideal" type of chelating agents, the separation factor between Am and lanthanide ions of comparable radius increases as the stability constants of the chelate complexes increase. Experimental results show that the separation factors of ^{241}Am-^{155}Eu-^{160}Tb, with TEDTA as eluent, equal one. Ligands exhibiting affinities lower than those of TEDTA, such as BEATA, interpose Am^{3+} in the lanthanide elution series. In order for the separation of lanthanides and americium to occur, the stability constants of the lanthanide complexes must be higher than those formed with TEDTA.

Future Work

The study of the affinity of polyaminopolycarboxylate species toward members of the lanthanide series provides some fundamental insight regarding lanthanide and actinide chemistry. However, there are still a lot

of uncertainties regarding structural features of species formed by lanthanide ions with individual donor atoms. Polyaminopolycarboxylate ligands with a nitrogen atom in the middle of the "backbone" chains are the most interesting compounds to examine. Substitutions on this central nitrogen will no doubt affect its electronegativity and the accessibility of its lone-pair of electrons for attachment to Lewis acids such as metal cations. An overly bulky substitution may also cause considerable steric effects so that the turning point in the lanthanide chelate stability series will occur earlier in the sequence (i.e., shift toward the lighter lanthanons) and increase the likelihood that actinons will separate cleanly from lanthanons in cation-elution systems.

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APPENDIX A. COMPUTER PROGRAM ALFA

```
C                    PROGRAM ALPHA
C
C      THIS PROGRAM IS DESIGNED TO CALCULATE SAMPLE KNO3 VOLUMES FOR RUNS
C      DETERMINING LIGAND PROTONATION CONSTANTS USING TRIAL ALPHAS FOR ANY
C      POLYBASIC LIGAND
C      APPROXIMATION IS USED IN VARIABLE OTHER
C   ************************DATA SET MAKEUP ************************************
C      CARD    VARIABLE   COL   FORMAT              EXPLANATION
C     ------------------------------------------------------------------------
C        1        TITE    1-80      A80        ANY TITLE
C        2           N     1-5       I5        NUMBER OF DATA POINTS
C                   NN      10       I1        NUMBER OF ALPHAS INPUT
C                 HTIT      15       I1        NUMBER OF TITRATABLE H PER LIGAND
C                CACID   21-30    F10.4        MOLARITY OF LIGAND ACID SOLN
C                CBASE   31-40    F10.4        MOLARITY OF BASE SOLN
C                CHNO3   41-50    F10.4        MOLARITY OF STRONG ACID SOLN
C                 FINV   51-60    F10.4        FINAL VOLUME
C                CKNO3   61-70    F10.4        MOLARITY OF KNO3 SOLN
C                   US   71-80    F10.4        IONIC STRENGTH DESIRED
C        3   ALPHA(I)    1-10    E10.4        1 TO NN ASSUMED ALPHAS USED, ONE
C                                                PER CARD
C        4   VACID(I)    1-10    F10.5        VOLUME OF LIGAND ACID SOLN USED
C            VBASE(I)   11-20    F10.5        VOLUME OF BASE SOLN USED
C            VHNO3(I)   21-30    F10.5        VOLUME OF STRONG ACID SOLN USED
C    (REPEAT UNTIL I=N)
      DIMENSION ALPHA(6),VACID(100),VBASE(100),VHNO3(100),TITE(20),CNBAR
     1(100),APH(100),VKNO3(100)
      INTEGER HTIT
      DOUBLE PRECISION BOT,TOP,OTHER,UA
      READ(5,1)(TITE(I),I=1,20)
      READ(5,2)N,NN,HTIT,CACID,CBASE,CHNO3,FINV,CKNO3,US
      READ(5,3)(ALPHA(I),I=1,NN)
      READ(5,4)(VACID(I),VBASE(I),VHNO3(I),I=1,N)
      ERR=0.001
```

```
      DO 100 M=1,N
      AT=(CACID/FINV)*VACID(M)
      HT=(CACID/FINV)*VACID(M)*HTIT+(CHNO3/FINV)*VHNO3(M)-(CBASE/FINV)*
     1VBASE(M)
      H=0.0
      HFAC=10.0
      WRITE (6,500) M, HT
  500 FORMAT (1X, 'M=',I4,'HT=', F8.3)
   10 HINC=HT/HFAC
   20 H=H+HINC
      HPH=-ALOG10(H)
      ANBAR=(HT-H+10**(-13.8069+HPH))/AT
      BOT=1.0
      TOP=0.0
      DO 40 K=1,NN
      BOT=BOT+ALPHA(K)*H**K
      TOP=TOP+K*ALPHA(K)*H**K
   40 CONTINUE
      BNBAR=TOP/BOT
      TEST=ANBAR-BNBAR
      IF(ABS(TEST).LE.ERR) GO TO 70
      IF(TEST.GT.0.0) GO TO 20
      H=H-HINC
      HFAC=HFAC*10
      GO TO 10
   70 CONTINUE
      A=AT/BOT
      CNBAR(M)=BNBAR
      APH(M)=-ALOG10(H)
      OTHER=(HTIT)**2*A*.5
      DO 80 K=1,NN
      OTHER=OTHER+(K-HTIT)**2*ALPHA(K)*H**K*A*.5
   80 CONTINUE
```

```
      UA=.5*(CBASE/FINV)*VBASE(M)+.5*(CHNO3/FINV)*VHNO3(M)+OTHER
     1+.5/10.0**APH(M)+.5*10.0**(-13.8069+APH(M))
      VKNO3(M)=((US-UA)/CKNO3)*FINV
  100 CONTINUE
      WRITE(6,200)
      WRITE(6,201)(TITE(I),I=1,20)
      WRITE(6,202)CACID,CBASE
      WRITE(6,203)CHNO3,CKNO3
      WRITE(6,204)FINV,US
      WRITE(6,205)
      WRITE(6,206)(L,VACID(L),VBASE(L),VHNO3(L),APH(L),CNBAR(L),VKNO3(L)
     1,L=1,N)
      WRITE(6,207)NN
      WRITE(6,208)(IW,ALPHA(IW),IW=1,NN)
    I FORMAT(20A4)
    2 FORMAT(I5,4X,I1,4X,I1,5X,6F10.4)
    3 FORMAT(E10.4)
    4 FORMAT(3F10.5)
  200 FORMAT('1**********TRIAL CALCULATION OF VKNO3 FROM ASSUMED
     1 ALPHAS**********')
  201 FORMAT(' ',20A4/)
  202 FORMAT(T2,'ORIGINAL ACID CONCENTRATION =',T40,F8.5,T55,'ORIGINAL B
     1ASE CONCENTRATION =',T90,F8.5)
  203 FORMAT(T2,'ORIGINAL STRONG ACID CONCENTRATION =',T40,F8.5,T55,
     1'POTASSIUM NITRATE CONCENTRATION =',T90,F8.5)
  204 FORMAT(T2,'FINAL VOLUME =',T39,F7.3,T55,'IONIC STRENGTH =',T90,
     1F8.5/)
  205 FORMAT('  (I)',T9,'VACID',T19,'VBASE',T29,'VHNO3',T41,
     1'PH',T48,'NBAR',T56,'VOL KNO3')
  206 FORMAT(' ',I3,T8,F7.3,T18,F7.3,T28,F7.3,T38,F7.4,T48,F6.3,T58,
     1F7.3)
  207 FORMAT('0ASSUMED PROTONATION CONSTANTS  ALPHA(1)-ALPHA(',I2,')'/)
  208 FORMAT(6X,I2,6X,E12.5)
      RETURN
      END
```

APPENDIX B. COMPUTER PROGRAM BETA

```
C
C                    PROGRAM BETA
C
C     THIS PROGRAM IS DESIGNED TO CALCULATE SAMPLE KNO3 VOLUMES FOR RUNS
C     DETERMINING STABILITY CONSTANTS.USING KNOWN ALPHAS AND ASSUMED BETAS
C
C ********************** DATA SET MAKEUP *********************************
C     CARD    VARIABLE   COL    FORMAT              EXPLANATION
C    ------------------------------------------------------------------------
C       1        TITE    1-80      A80       ANY TITLE
C       2       VACID    1-10    F10.5       VOLUME OF LIGAND ACID SOLN USED
C              CACID   11-20    F10.5       MOLARITY OF LIGAND ACID SOLN USED
C               VMET   21-30    F10.5       VOLUME OF METAL SOLN USED
C               CMET   31-40    F10.5       MOLARITY OF METAL SOLN
C               CKND   41-50    F10.5       MOLARITY OF KNO3 SOLN
C              CBASE   51-60    F10.5       MOLARITY OF BASE SOLN
C               FINV   61-70    F10.5       FINAL VOLUME
C                 US   71-80    F10.5       IONIC STRENGTH DESIRED
C       3          N     1-5       I5       NUMBER OF DATA POINTS
C                 NN      10       I5       NUMBER OF BETAS INPUT
C                NNN      15       I5       NUMBER OF ALPHAS INPUT
C               HTIT      20       I5       NUMBER OF TITRATABLE H PER LIGAND
C                 ZC      25       I5       CHARGE ON METAL CATION
C                 ZA      30       I5       CHARGE ON LIGAND ANION
C       4   ALPHA(I)    1-10    E10.4       1 TO NNN ALPHAS USED.ONE PER CARD
C       5    BETA(I)    1-10    E10.4       1 TO NN ASSUMED BETAS USED. ONE
C                                             PER CARD
C       6   VBASE(I)    1-80    F10.4       1 TO N BASE VOLUMES USED. EIGHT
C                                             PER CARD
C
      DIMENSION TITE(20),ALPHA(6),BETA(5),VBASE(50),CNBAR(50),APH(50),
     1VKNO(50)
      REAL MT
      INTEGER HTIT,ZC,ZA
    9 READ(5,1,END=300)(TITE(IR),IR=1,20)
```

```
      READ(5,2)VACID,CACID,VMET,CMET,CKNO,CBASE,FINV,US
      READ(5,3)N,NN,NNN,HTIT,ZC,ZA
      READ(5,4)(ALPHA(I),I=1,NNN)
      READ(5,4)(BETA(I),I=1,NN)
      READ(5,5)(VBASE(I),I=1,N)
      ERR=0.001
      MT=(CMET/FINV)*VMET
      AT=(CACID/FINV)*VACID
      DO 100 M=1,N
      HT=(CACID/FINV)*VACID*HTIT-(CBASE/FINV)*VBASE(M)
      H=0.0
      HFAC=10.0
   10 HINC=HT/HFAC
   20 H=H+HINC
      ALPTO=0.0
      DO 30 I=1,NNN
   30 ALPTO=ALPTO+ALPHA(I)*I*H**I
      A=(HT-H)/ALPTO
      BOT=1.0
      TOP=0.0
      DO 40 K=1,NN
      BOT=BOT+BETA(K)*A**K
   40 TOP=TOP+K*BETA(K)*A**K
      BNBAR=TOP/BOT
      ALFTO=1.0
      DO 50 J=1,NNN
   50 ALFTO=ALFTO+ALPHA(J)*H**J
      ANBAR=(AT-A*ALFTO)/MT
      TEST=ANBAR-BNBAR
      IF(ABS(TEST).LE.ERR)GO TO 70
      IF(TEST.LT.0.0) GO TO 20
      H=H-HINC
      HFAC=HFAC*10.
      GO TO 10
   70 CONTINUE
```

```
      CNBAR(N)=BNBAR
      APH(N)=-ALOG10(H)
      OTHER=(HTIT)**2*A
      DO 80 K=1,NNN
      OTHER=OTHER+(K-HTIT)**2*ALPHA(K)*H**K*A
   80 CONTINUE
      UA=0.5*OTHER
      UB=0.5*CBASE*VBASE(N)/FINV
      UC=0.5*10.0**(-APH(N))
      UD=0.5*10.0**(-13.8069+APH(N))
      UE=0.5*ZC*MT
      UF=0.5*MT*(ZC-BNBAR*ZA)**2
      UA=UA+UB+UC+UD+UE+UF
      VKNO(N)=((US-UA)/CKNO)*FINV
  100 CONTINUE
      WRITE(6,199)
      WRITE(6,200)
      WRITE(6,201)(TITE(I),I=1,20)
      WRITE(6,202)CACID
      WRITE(6,203)CMET
      WRITE(6,204)CBASE
      WRITE(6,205)CKNO
      WRITE(6,212)VACID
      WRITE(6,213)VMET
      WRITE(6,214)LS
      WRITE(6,215)FINV
      WRITE(6,206)
      WRITE(6,207)(L,VBASE(L),APH(L),CNBAR(L),VKNO(L),L=1,N)
      WRITE(6,208)(IW,ALPHA(IW),IW=1,NNN)
      WRITE(6,209)(IX,BETA(IX),IX=1,NN)
      GO TO 9
  300 STOP
    1 FORMAT(20A4)
    2 FORMAT(8F10.5)
    3 FORMAT(6I5)
```

```
  4 FORMAT(E10.4)
  5 FORMAT(8F10.4)
199 FORMAT('1**  TRIAL CALCULATION OF VKNO3 FROM **')
200 FORMAT(T2,'**  KNOWN ALPHAS AND ASSUMED BETAS  **'/)
201 FORMAT(' ',20A4/)
202 FORMAT(T2,'ORIGINAL  ACID CONCENTRATION =',T35,F8.5)
203 FORMAT(T2,'ORIGINAL METAL CONCENTRATION =',T35,F8.5)
204 FORMAT(T2,'ORIGINAL MBASE CONCENTRATION =',T35,F8.5)
205 FORMAT(T2,'ORIGINAL MKNO3 CONCENTRATION =',T35,F8.5)
212 FORMAT(T2,'VOLUME OF ACID SOLN USED =',T35,F8.5)
213 FORMAT(T2,'VOLUME OF METAL SOLN USED =',T35,F8.5)
214 FORMAT(T2,'IONIC STRENGTH =',T35,F8.5)
215 FORMAT(T2,'FINAL VOLUME =',T35,F7.3/)
206 FORMAT(' (I)',T9,'VBASE',T21,'PH',T30,'NBAR',T36,'VOL KNO3')
207 FORMAT(' ',I3,T8,F7.3,T18,F7.4,T28,F6.3,T38,F6.3)
208 FORMAT('0',',ALPHA(',I1,') =',4X,E12.5)
209 FORMAT('0',',BETA(',I1,') =',5X,E12.5)
    RETURN
    END
```

APPENDIX C. COMPUTER PROGRAM OMEGA

```
C
C                    PROGRAM OMEGA
C
C
C  **********DATA SET MAKEUP**********
C     CARD  VARIABLE   COL   FORMAT              EXPLANATION
C    ------------------------------------------------------------------
C       1          N     1-3      I3        NUMBER OF DATA POINTS
C                 NN       5      I1        NUMBER OF COSTANTS TO BE DETERMINED
C               IFUN       6      I1        OPTION TO BE USED
C                                           =1 CALCULATE KNO3 VOL FOR STABILITY
C                                              CONSTANTS BASED ON TRIAL PH
C                                           =2 CALCULATION OF PROTONATION
C                                              CONSTANTS(ALPHAS)
C                                           =3 CALCULATION OF STABILITY CONSTANTS
C                                              (BETAS)
C             BETA1   8-17  E10.4        IF IFUN=2,BETAS ARE ALL SET TO ZERO
C             BETA2  18-27  E10.4
C             BETA3  28-37  E10.4
C             BETA4  38-47  E10.4
C             BETA5  48-57  E10.4
C              HTIT     60     I1        NUMBER OF TITRATABLE H PER LIGAND
C                ZC     65     I1        CHARGE ON METAL CATION,=0 IF IFUN=2
C                ZA     70     I1        CHARGE ON LIGAND ANION,=0 IF IFUN=2
C       2     TITLE   1-80    A80        ANY TITLE
C       3     CACID   1-10  F10.5        MOLARITY OF LIGAND ACID SOLN
C             CBASE  11-20  F10.5        MOLARITY OF BASE SOLN
C              CHCL  21-30  F10.5        MOLARITY OF STRONG ACID
C              FINV  31-40  F10.5        FINAL VOLUME
C              CKNO  41-50  F10.5        MOLARITY OF KNO3
C                US  51-60  F10.5        IONIC STRENGTH DESIRED
C              VMET  61-70  F10.5        VOLUME OF METAL SOLN USED
C              CMET  71-80  F10.5        MOLARITY OF METAL SOLN
C       4  VACID(I)   1-10  F10.5        VOLUME OF LIGAND ACID SOLN USED
C          VBASE(I)  11-20  F10.5        VOLUME OF BASE SOLN USED
C           VHCL(I)  21-30  F10.5        VOLUME OF STRONG ACID SOLN USED
C            HPH(I)  31-40  F10.5        MEASURED PH
```

```
C     (REPEAT  UNTIL I=N)
C      N+4      RELAT    1-10  F10.5       RELATIVE ERROR IN ATOT / MTOT
C               RELHT   11-20  F10.5       RELATIVE ERROR IN HTOT / ATOT
C               RELPH   21-30  F10.5       RELATIVE ERROR IN PH  / A
C               IWEIT   39-40     I2       WEIGHTING OPTION TO BE USED FOR DATA
C                                          SECOND SET USED FOR IFUN=3
C                                          =-1 WEIGHTING WITH ALL ERROR PARAMETERS
C                                          =0  WEIGHTING ON PH (A) ONLY
C                                          =1 NO WEIGHTING OF DATA
C      N+5      ALFA1    1-10  E10.4       USED ONLY IF IFUN=3
C               ALFA2   11-20  E10.4
C               ALFA3   21-30  E10.4
C               ALFA4   31-40  E10.4
C               ALFA5   41-50  E10.4
C               ALFA6   51-60  E10.4
C
C     THIS PROGRAM NOW LOOPS TO HANDLE DIFFERENT SETS OF THE
C     SAME DATA LIST.  THE FOLLOWING CARDS MUST BE ADDED.
C       CARD  N+6     NNCA  =  NUMBER OF SETS TO BE TREATED
C     CARD  N+7  NEWST = THE NUMBER OF THE FIRST SAMPLE TO BE CONSIDERED
C                NEWN    NUMBER OF DATA POINTS THIS SET
C                NEWNN = NUMBER OF CONSTANTS TO BE DETERMINED THIS SET
C                NEWTIT = NUMBER OF TITRATABLE HYDROGEN
C                NEWIW = WEIGHTING OPTION FOR THIS SET
C     ..................................................................
C        SUBROUTINE DGELG
C           PROGRAM SUPPLIED BY COMPUTER
C
C        PURPOSE
C           SOLVE GENERAL SYSTEM OF SIMULTAEOUS LINEAR EQUATIONS
C
C        USAGE
C           CALL DGELG(R,A,M,N,EPS,IER)
C
```

```
C        DESCRIPTION OF PARAMETERS
C           R - DOUBLE PRECISION M BY N RIGHT HAND. SIDE MATRIX(DESTROYED)
C               ON RETURN CONTAINS SOLUTIONS OF THE EQUATIONS
C           A - DOUBLE PRECISION M BY N COEFFICIENT MATRIX (DESTROYED)
C           M - NUMBER OF EQUATIONS IN SYSTEM
C           N - NUMBER OF RIGHT HAND SIDE VECTORS
C           EPS - SINGLE PRECISION INPUT CONSTANT USED AS RELATIVE
C                 TOLERANCE FOR TEST ON LOSS OF SIGNIFICANCE
C           IER=0 - NO ERROR
C           IER=-1 - NO RESULT DUE TO M LESS THAN 1, OR PIVOT ELEMENT AT
C                    ANY ELIMINATION STEP EQUAL TO 0
C           IER=5 - WARNING DUE TO POSSIBLE LOSS OF SIGNIFICANCE
C                   INDICATED AT ELIMINATION STEP K+1 WHERE PIVOT ELEMENT
C                   WAS LESS THAN OR EQUAL TO INTERNAL TOLERANCE EPS
C                   TIMES ABSOLUTELY GREATEST ELEMENT OF MATRIX A
C
C        REMARKS
C           SEE IBM BULLETIN
C
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C           NONE
C
C        METHOD
C           SOLUTION IS DONE BY GAUSS-ELIMINATION WITH COMPLETE PIVOTING
C
C     ..................................................................
C
      DIMENSION TITLE(20),VACID(100),VBASE(100),VHCL(100),
     &HPH(100),ETA(100),PERCE(100),AK(4),PK(4),VKNO3(100),BETAN(6),
     &XTX(36),SXTX(36),DUMM(50)
      DIMENSION NEWN(30),NEWIW(30),NEWNN(30),NEWST(30),NEWTIT(30),
     CTVACID(100),TVBASE(100),TVHCL(100),TPH(100)
      INTEGER HTIT,ZA,ZC
```

```
      COMMON /TRID/ X(100),Y(100),Z(100),BETA(6),N,NN,IER,
     1PHI(100),E(100),VBETA(6),RELAT,RELHT,RELPH,IWEIT,IFUN,ALFA(6),
     &CH(100)
      DOUBLE PRECISION Q(100,6),XTX
      ITEST=0                                                          0440
  250 READ(5,1,END=300) NZ,NN,IFUN,BETA(1),BETA(2),BETA(3),BETA(4),
     &BETA(5),HTIT,ZC,ZA
      READ(5,2)(TITLE(I),I=1,20)
      READ(5,3)CACID,CBASE,CHCL,FINV,CKND,US,VMET,CMET
      READ(5,4)(VACID(I),VBASE(I),VHCL(I),HPH(I),I=1,NZ)
      READ(5,6)RELAT,RELHT,RELPH,IWEIT
      IF (IFUN.EQ.3)  READ(5,5)(ALFA(I),I=1,6)
      READ(5,763)NNCA
      DO 762 I=1,NNCA
  762 READ(5,763)NEWST(I),NEWN(I),NEWNN(I),NEWTIT(I),NEWIW(I)
  763 FORMAT(20I4)
      DO 50 INCA=1,NNCA
      NEW1=NEWST(INCA)-1
      N=NEWN(INCA)
      IWEIT=NEWIW(INCA)
      NN=NEWNN(INCA)
      HTIT=NEWTIT(INCA)
      DO 30 I=1,NZ
      IF (IFUN.EQ.3) GO TO 18
      Z(I)=(VACID(I)/FINV)*CACID
      X(I)=1.0/10.0**HPH(I)
      Y(I)=HTIT*(VACID(I)/FINV)*CACID+(VHCL(I)/FINV)*CHCL
     1-(VBASE(I)/FINV)*CBASE+10.0**(-13.8069+HPH(I))
      GO TO 19
   18 CONTINUE
      CH(I)=1./10.**HPH(I)
      BH=CH(I)
      Z(I)=VMET/FINV*CMET
      Y(I)=VACID(I)*CACID/FINV
```

```
      X(I)=(HTIT*Y(I)-VBASE(I)/FINV*CBASE-BH)/(ALFA(1)*BH+2.*ALFA(2)*
     &BH**2+3.*ALFA(3)*BH**3+4.*ALFA(4)*BH**4+5.*ALFA(5)*BH**5+
     &6.*ALFA(6)*BH**6)
      Y(I)=VACID(I)/FINV*CACID-X(I)*(ALFA(1)*BH+ALFA(2)*BH**2+ALFA(3)*
     &BH**3+ALFA(4)*BH**4+ALFA(5)*BH**5+ALFA(6)*BH**6)
   19 CONTINUE
      ETA(I)=(Y(I)-X(I))/Z(I)
   30 CONTINUE
   20 CONTINUE
      DO 133 I=1,N
      ETA(I)=ETA(NEW1+I)
      TVHCL(I)=VHCL(NEW1+I)
      TVACID(I)=VACID(NEW1+I)
      TVBASE(I)=VBASE(NEW1+I)
      TPH(I)=HPH(NEW1+I)
      X(I)=X(NEW1+I)
      Z(I)=Z(NEW1+I)
  133 Y(I)=Y(NEW1+I)
      IF (IFUN.NE.1) CALL CFIT(Q,XTX,SXTX)
      DO 40 I=1,N
C  DON'T GET EXCITED, JUST USING PERCE HERE TO SAVE CORE
      PERCE(I)=1.0
      PHI(I)=0.0
      DO 45 K=1,NN
      PHI(I)=PHI(I)+K*BETA(K)*X(I)**K
      PERCE(I)=PERCE(I)+BETA(K)*X(I)**K
   45 CONTINUE
      PHI(I)=PHI(I)/PERCE(I)
      PERCE(I)=(ETA(I)-PHI(I))/PHI(I)*100.0
   40 CONTINUE
      IF (NN.EQ.1) GO TO 61
      NM=NN-1
      DO 60 I=1,NM
      AK(I)=BETA(NN-I)/BETA(NN-I+1)
      IF (AK(I).LE.0.0) PK(I)=0.0
      IF (AK(I).GT.0.0) PK(I)=-ALOG10(AK(I))
```

```
50 CONTINUE
61 CONTINUE
   AK(NN)=1.0/BETA(1)
   IF (AK(NN).GT.0.0) PK(NN)=-ALOG10(AK(NN))
   IF (AK(NN).LE.0.0) PK(NN)=0.0
   IF (IFUN.LE.2) GO TO 83
   DO 41 I=1,N
   UA=.5*(VBASE(I)*CBASE/FINV+VHCL(I)*CHCL/FINV+
  &ZC*VMET*CMET/FINV+CH(I)+X(I)*ZA**2+X(I)*(ALFA(1)*(ZA-1)**2*CH(I)+
  1ALFA(2)*CH(I)**2*(ZA-2)**2+ALFA(3)*CH(I)**3*(ZA-3)**2+ALFA(4)*
  2CH(I)**4*(ZA-4)**2+ALFA(5)*CH(I)**5*(ZA-5)**2+ALFA(6)*CH(I)**6*
  3(ZA-6)**2)+Z(I)*(ZC-PHI(I)*ZA)**2)
   VKNO3(I)=(US-UA)*FINV/CKNO
41 CONTINUE
83 CONTINUE
   IF (IFUN.GT.2)  GO TO 47
   DO 42 IS=1,N
   UA=.5*(VBASE(IS)/FINV)*CBASE+.5*(VHCL(IS)/FINV)*CHCL
  1+.5/10.0**HPH(IS)+.5*(VACID(IS)/FINV)*CACID*
  2(HTIT-PHI(IS))**2+0.5*10**(-13.8069+HPH(IS))
   VKNO3(IS)=((US-UA)/CKNO)*FINV
42 CONTINUE
47 CONTINUE
   IF (IFUN.EQ.1)WRITE(6,98)
   WRITE(6,101)(TITLE(I),I=1,20)
   WRITE(6,102)CACID,CBASE
   WRITE(6,103)CHCL,CKNO
   WRITE(6,108)CMET,VMET
   WRITE(6,110)FINV,US
   WRITE(6,104)
   WRITE(6,105)(I,TVACID(I),TVBASE(I),TVHCL(I),TPH(I),
  IETA(I),PERCE(I),VKNO3(I),E(I),I=1,N)
   IF(NN.EQ.1) GO TO 48
   GO TO 49
48 WRITE(6,111)
   WRITE(6,109)(I,BETA(I),AK(I),PK(I),I=1,NN)
```

```
      GO TO 50
 49   WRITE(6,106)
      WRITE(6,107)(I,BETA(I),AK(I),PK(I),VBETA(I),I=1,NN)
      WRITE(6,112)IWEIT,HTIT,NEWST(INCA),N
112   FORMAT('0',5X,'WEIGHTING OPTION USED =',3X,I2,3X,'HTIT =',I2,5X,
     C'FIRST DATA POINT =',I3,5X,'NUMBER OF POINTS =',I3)
 50   CONTINUE
      GO TO 250                                                          03090
300   STOP
 98   FORMAT('1********************************************** KNO3 CALCULA
     &TION **********************************')
101   FORMAT (20A4)
102   FORMAT (T2,'ORIGINAL ACID CONCENTRATION =',T40,F8.5,T50,
     1'ORIGINAL BASE CONCENTRATION = ',T90,F8.5)
103   FORMAT (T2,'ORIGINAL STRONG ACID CONCENTRATION = ',T40,
     1F8.5,T50,'POTASSIUM NITRATE CONCENTRATION =',T90,F8.5)
104   FORMAT ('  (I)',T9,'VACID',T19,'VBASE',T29,'VHCL',T40
     1,'P(H)',T48,'NBAR',T58,'ERROR',T66,'VOL KNO3')
105   FORMAT (' ',I3,T8,F7.3,T18,F7.3,T28,F7.3,T38,F7.4,T48,
     CF6.3,T53,E12.4,T68,F6.3,T78,F6.3)
106   FORMAT (T7,'(I)',T15,'BETA(I)',T30,'K(I)',T40,'PK(I)',T55,
     1'VBETA(I)')
107   FORMAT (T8,I2,T12,E12.4,T26,E12.4,T40,F6.3,T53,E12.5)
108   FORMAT(T2,'METAL CONCENTRATION= ',T40,F8.5,T50,'METAL VOLUME =',
     &T90,F6.3)
109   FORMAT(T8,I2,T12,E12.4,T26,E12.4,T40,F6.3)
110   FORMAT (T2,'FINAL VOLUME =',T40,F7.3,T50,'IONIC STRENGTH =',T90,
     1F7.3)
111   FORMAT (T7,'(I)',T15,'BETA(I)',T30,'K(I)',T40,'PK(I)')
  1   FORMAT(I3,1X,2I1,1X,5E10.4,2X,I1,4X,I1,4X,I1)
  2   FORMAT(20A4)
  3   FORMAT(8F10.5)
  4   FORMAT(4F10.5)
  5   FORMAT (6E10.4)
  6   FORMAT(3F10.5,8X,I2)
      END
```

```
      SUBROUTINE CFIT (Q,XTX,SXTX)
      COMMON /TRID/ X(100),Y(100),Z(100),BETA(6),N,NN,IER,
     1PHI(100),E(100),VBETA(6),RELAT,RELHT,RELPH,IWEIT,IFUN,ALFA(6),
     &CH(100)
      DIMENSION XT(600),EA(100),EH(100),EP(100),ET(100),YT(100),
     &XTX(NN,NN),BETAN(6),SXTX(NN,NN),LI(10),MI(10)
      DOUBLE PRECISION V(100),Q(N,NN),W(100),YT,XT,SST,
     1XTX,SSR,BETAN,XBETA(100)
      WRITE(6,1)NN
      WRITE(6,500)(I,BETA(I),I=1,NN)
      DO 45 II=1,10
      DO 29 I=1,N
      SIGAT=0.0
      SIGHT=-1.0
      SIGPH=1.0
      DO 70 M=1,NN
      SIGPH=SIGPH-M*(Y(I)-X(I)-M*Z(I))*X(I)**(M-1)*BETA(M)+
     1X(I)**M*BETA(M)
      SIGHT=SIGHT-X(I)**N*BETA(M)
      SIGAT=SIGAT+M*X(I)**M*BETA(M)
   70 CONTINUE
      IF(IFUN.NE.3)GO TO 370
      SIGA=0.0
      DO 470 MM=1,5
      SIGA=SIGA+CH(I)**MM*X(I)*ALFA(MM)
  470 CONTINUE
      SIGAP=1.+SIGA
      DO 570 JJ=1,NN
      SIGAP=SIGAP-JJ*(Y(I)-X(I)-JJ*Z(I))*X(I)**(JJ-1)*BETA(JJ)+
     &(1.+SIGA)*X(I)**JJ*BETA(JJ)
  570 CONTINUE
      SIGPH=SIGAP
  370 CONTINUE
      EA(I)=SIGAT*RELAT*Z(I)
      EH(I)=SIGHT*RELHT*Y(I)
```

```
      EP(I)=SIGPH*RELPH*X(I)
      IF(IWEIT)71,72,73
   71 ET(I)=EA(I)+EP(I)+EH(I)
      GO TO 75
   72 ET(I)=EP(I)
      GO TO 75
   73 ET(I)=1.0
   75 CONTINUE
      DO 27 J=1,NN
      W(I)=1./ET(I)**2
  302 V(I)=X(I)-Y(I)
  303 Q(I,J)=(Y(I)-X(I)-J*Z(I))*X(I)**J
   27 CONTINUE
   29 CONTINUE
      IF (NN.NE.1) GO TO 40
      SUMQ=0.0
      SUMV=0.0
      DO 39 I1=1,N
      SUMQ=SUMQ+Q(I1,1)*W(I1)
      SUMV=SUMV+V(I1)*W(I1)
   39 CONTINUE
      BETA(1)=SUMV/SUMQ
      GO TO 50
   40 CALL WLSQ (Q,V,BETA,W,N,NN,XT)
   50 CONTINUE
      WRITE(6,500)(I,BETA(I),I=1,NN)
   45 CONTINUE
      IF (NN.NE.1)  GO TO 60
      DO 59 I=1,N
      TEM=V(I)/Q(I,1)
      IF (TEM.LE.0.) TEM=1.
      E(I)=ALOG10(TEM)
   59 CONTINUE
      GO TO 80
   60 DO 90 J=1,NN
   90 BETAN(J)=BETA(J)
```

```
      CALL DGMTRA(V,YT,N,1)
      DO 99 I=1,N
   99 YT(I)=YT(I)*W(I)
      CALL DGMPRD(YT,V,SST,1,N,1)
      CALL DGMPRD(Q,BETAN,XBETA,N,NN,1)
      CALL DGMPRD(YT,XBETA,SSR,1,N,1)
      CALL DGMPRD(XT,Q,XTX,NN,N,NN)
      SS=SNGL((SST-SSR)/(N-NN))
      SSRD=SSR/NN
      WRITE(6,381)SS,SSRD,SST,SSR
      DO 91 J=1,NN
      DO 92 L=1,NN
      SXTX(J,L)=SNGL(XTX(J,L))
   92 CONTINUE
   91 CONTINUE
      CALL MINV(SXTX,NN,D,LI,MI)
      DO 61 M=1,NN
      VBETA(M)=SQRT(SXTX(M,M)*SS)
   61 CONTINUE
      DO 94 I=1,N
   94 E(I)=10**9
   80 RETURN
  500 FORMAT(T2,'ALHPA',I1,'=',E10.4)
  381 FORMAT(' ',5X,'MSE=',E10.4,5X,'MSR=',E10.4,5X,'SST=',E10.4,5X,'SSR
     &=',E10.4)
    1 FORMAT ('1**********************************************',I2,'PAR
     1AMETER PROGRAM USED**********************************')
      END

      SUBROUTINE WLSQ (X,Y,BETA,W,N,NN,XT)
      DIMENSION XT(600),XTX(36),DETA(6),X(1),Y(1),W(1),BETA(1),
     &XV(600)
      DOUBLE PRECISION XT,XTX,DETA,XV,X,Y,W
      CALL DGMTRA (X,XT,N,NN)
      IJ=0
      DO 31 I=1,N
```

```
      DO 32 J=1,NN
      IJ=IJ+1
      XT(IJ)=XT(IJ)*W(I)
   32 CONTINUE
   31 CONTINUE
      CALL DGMPRD(XT,Y,DETA,NN,N,1)
      CALL DGMPRD (XT,X,XTX,NN,N,NN)
      CALL DGELG(DETA,XTX,NN,1,.1E-15,IER)
      IF (IER.NE.0) WRITE(6,15) IER
      DO 4 IS=1,NN
      BETA(IS)=SNGL(DETA(IS))
    4 CONTINUE
      RETURN
   15 FORMAT(*  JOB BOMBED IER=*,I2)
      END
C                                                                       GMTR  10
C     ..................................................................GMTR  20
C                                                                       GMTR  30
C        SUBROUTINE DGMTRA                                              GMTR40
C                                                                       GMTR  50
C        PURPOSE                                                        GMTR  60
C           TRANSPOSE A GENERAL MATRIX                                  GMTR  70
C                                                                       GMTR  80
C        USAGE                                                          GMTR  90
C           CALL DGMTRA(A,R,N,M)                                        GMTR 100
C                                                                       GMTR 110
C        DESCRIPTION OF PARAMETERS                                      GMTR 120
C           A - NAME OF MATRIX TO BE TRANSPOSED                         GMTR 130
C           R - NAME OF RESULTANT MATRIX                                GMTR 140
C           N - NUMBER OF ROWS OF A AND COLUMNS OF R                    GMTR 150
C           M - NUMBER OF COLUMNS OF A AND ROWS OF R                    GMTR 160
C                                                                       GMTR 170
C        REMARKS                                                        GMTR 180
C           MATRIX R CANNOT BE IN THE SAME LOCATION AS MATRIX A         GMTR 190
C           MATRICES A AND R MUST BE STORED AS GENERAL MATRICES         GMTR 200
C                                                                       GMTR 210
```

```
C         SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                    GMTR 220
C            NONE                                                          GMTR 230
C                                                                          GMTR 240
C         METHOD                                                           GMTR 250
C            TRANSPOSE N BY M MATRIX A TO FORM M BY N MATRIX R              GMTR 260
C                                                                          GMTR 270
C     ..................................................................GMTR 280
C                                                                          GMTR 290

      SUBROUTINE DGMTRA(A,R,N,M)                                           GMTR 300
      REAL*8 A(1),R(1)                                                     GMTR 310
C                                                                          GMTR 320
      IR=0                                                                 GMTR 330
      DO 10 I=1,N                                                          GMTR 340
      IJ=I-N                                                               GMTR 350
      DO 10 J=1,M                                                          GMTR 360
      IJ=IJ+N                                                              GMTR 370
      IR=IR+1                                                              GMTR 380
   10 R(IR)=A(IJ)                                                          GMTR 390
      RETURN                                                               GMTR 400
      END                                                                  GMTR 410
C                                                                          GMPR  10
C     ..................................................................GMPR  20
C                                                                          GMPR  30
C        SUBROUTINE DGMPRD
C                                                                          GMPR  50
C         PURPOSE                                                          GMPR  60
C            MULTIPLY TWO GENERAL MATRICES TO FORM A RESULTANT GENERAL     GMPR  70
C            MATRIX                                                        GMPR  80
C                                                                          GMPR  90
C         USAGE                                                            GMPR 100
C                                                                          GMPR 120
C         DESCRIPTION OF PARAMETERS                                        GMPR 130
C            A - NAME OF FIRST INPUT MATRIX                                GMPR 140
C            B - NAME OF SECOND INPUT MATRIX                               GMPR 150
C            R - NAME OF OUTPUT MATRIX                                     GMPR 160
```

```
C           N - NUMBER OF ROWS IN A                                          GMPR 170
C           M - NUMBER OF COLUMNS IN A AND ROWS IN B                         GMPR 180
C           L - NUMBER OF COLUMNS IN B                                       GMPR 190
C                                                                            GMPR 200
C        REMARKS                                                             GMPR 210
C           ALL MATRICES MUST BE STORED AS GENERAL MATRICES                  GMPR 220
C           MATRIX R CANNOT BE IN THE SAME LOCATION AS MATRIX A              GMPR 230
C           MATRIX R CANNOT BE IN THE SAME LOCATION AS MATRIX B              GMPR 240
C           NUMBER OF COLUMNS OF MATRIX A MUST BE EQUAL TO NUMBER OF ROWGMPR 250
C           OF MATRIX B                                                      GMPR 260
C                                                                            GMPR 270
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                       GMPR 280
C           NONE                                                             GMPR 290
C                                                                            GMPR 300
C        METHOD                                                              GMPR 310
C           THE M BY L MATRIX B IS PREMULTIPLIED BY THE N BY M MATRIX A      GMPR 320
C           AND THE RESULT IS STORED IN THE N BY L MATRIX R.                 GMPR 330
C                                                                            GMPR 340
C     ..........................................................................GMPR 350
C                                                                            GMPR 360

      SUBROUTINE DGMPRD(A,B,R,N,M,L)                                         GMPR 370
      REAL*8 A(1),B(1),R(1)                                                  GMPR 380
C                                                                            GMPR 390
      IR=0                                                                   GMPR 400
      IK=-M                                                                  GMPR 410
      DO 10 K=1,L                                                            GMPR 420
      IK=IK+M                                                                GMPR 430
      DO 10 J=1,N                                                            GMPR 440
      IR=IR+1                                                                GMPR 450
      JI=J-N                                                                 GMPR 460
      IB=IK                                                                  GMPR 470
      R(IR)=0                                                                GMPR 480
      DO 10 I=1,M                                                            GMPR 490
```

```
      JI=JI+N                                                    GMPR 500
      IB=IB+1                                                    GMPR 510
   10 R(IR)=R(IR)+A(JI)*B(IB)                                    GMPR 520
      RETURN                                                     GMPR 530
      END                                                        GMPR 540
```

APPENDIX D. 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)
1       IMPLICIT REAL*8 (A-H,O-Z),INTEGER(I-N)
2       REAL*8 IONSTR,LIGCON,LIGVOL,METCON,METVOL,MTOT
3       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)
4       EXTERNAL AUX
C    TRAPS ALLOWS  THE PROGRAM TO CONTINUE AFTER AN EXPOTENTIAL UNDERFLOW
5       CALL TRAPS(0,0,32767,0,0)
```

```
 6      400 READ(5,10,END=2000)(TITLE(I),I=1,20)
 7          READ(5,20)LIGCON,BASCON,METCON,SLTCON,FINVOL,IONSTR
 8          READ(5,30)N,ALPHA(1),ALPHA(2),ALPHA(3),ALPHA(4),TBETA(1),TBETA(2)
 9          READ(5,40)(LIGVOL(I),BASVOL(I),METVOL(I),PH(I),I=1,N)
10          WRITE(6,50)
11          WRITE(6,10)(TITLE(I),I=1,20)
12          WRITE(6,60)LIGCON,BASCON,METCON
13          WRITE(6,70)SLTCON,FINVOL,IONSTR
14          WRITE(6,80)(I,ALPHA(I),I=1,4)
15          WRITE(6,90)TBETA(1)
16          WRITE(6,100)TBETA(2)
17          WRITE(6,110)
18          WRITE(6,120)(I,LIGVOL(I),BASVOL(I),METVOL(I),PH(I),I=1,N)
      C  THIS DO LOOP CALCULATES COEFFICIENTS A-F
19          DO 500 I=1,N
20          H=10.0**(-PH(I))
21          MTOT=METCON*METVOL(I)/FINVOL
22          ATOT=LIGCON*LIGVOL(I)/FINVOL
23          HTOT=(LIGCON*4.0*LIGVOL(I)/FINVOL)-(BASCON*BASVOL(I)/FINVOL)
24          A=1.0+ALPHA(1)*H+ALPHA(2)*H**2.0+ALPHA(3)*H**3.0+ALPHA(4)*H**4.0
25          B2=(MTOT-ATOT)
26          C2=(-MTOT)
27          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
28          E1=ALPHA(1)*H*(MTOT-HTOT+H)
29          E2=H-HTOT
30          B3=-A
```

```
31          B1=ALPHA(1)*H*B2
32          C1= ALPHA(1)*H*C2
33          E3=-D
34          F=C1
35          R(I)=A*C2*E2*E2-D*C2*E2*B2
36          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
37          T(I)=C2*C2*D*D-D*C2*E2*B3-D*C2*B2*E3+2.0*A*C2*E2*E3
38          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
39          V(I)=0.0
40          W(I)=0.0
41          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
42          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
43          Z(I)=B1*B1*D*F-A*B1*E1*F-E1*B1*C1*D+A*C1*E1*E1
44        500 CONTINUE
      C THIS SECTION NOW PICKS TWO POINTS AT A TIME AND CALCULATES BMHL AND BML
45          FBETA1=TBETA(1)
46          FBETA2=TBETA(2)
47          M=N-1
48          DO 1000 I=1,M
49          L=I+1
50          DO 900 J=L,N
51          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(I)
      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(' LIGCON = ',F10.5,' BASCON = ',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,F10.4,T30,F10.4,T40,F10.4)
  130 FORMAT(' POINTS USED ARE ',I2,' AND ',I2)
  140 FORMAT(' NUMBER OF ITERATIONS = ',I3)
  150 FORMAT(' IER = ',I3)
  170 FORMAT(' BML = ',D28.16)
  160 FORMAT(' BMHL = ',D28.16)
      END
```

```
104           DOUBLE PRECISION FUNCTION AUX (TBETA,K,PAR)
105           INTEGER K
106           REAL*8 TBETA(2),PAR(18)
      C    TRAPS ALLOWS  THE PROGRAM TO CONTINUE AFTER AN EXPOTENTIAL UNDERFLOW
107           CALL TRAPS(0,0,32767,0,0)
108           GO TO (10,20),K
109        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
110           RETURN
111        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
112           RETURN
113           END
```