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Synthesis, purification and characterization of a new polyaminopolycarboxylate and the determination of the stability constants of its anion-lanthanide complexes

Douglas James Sawyer
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Iowa State University, 1988

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Synthesis, purification and characterization of a new polyaminopolycarboxylate and the determination of the stability constants of its anion-lanthanide complexes

by

Douglas James Sawyer

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INTRODUCTION

The safe disposal of high-level wastes from nuclear power plants is a growing concern if nuclear power is to continue to be a major source of energy worldwide. Nearly all of the components of the high-level waste can be managed safely in geological repositories. Unfortunately, the transuranic actinide elements, which constitute a small fraction of the waste, cannot be buried safely. The duration of the radioactivity of these elements and their daughter products is very long compared to the other waste components. The presence of these actinides in geological repositories presents an unacceptable environmental hazard. A safe disposal process for the high-level waste must involve the removal of the transuranic actinide elements. Once these elements are removed, they can be transmuted in a high-flux nuclear reactor [1], or disposed in other ways [2].

The work described in this dissertation focuses on the development of a procedure which will remove the actinides from all of the other products of the high-level waste. Sufficient methods have been developed for removing the actinides from all of the waste components, except the lanthanides. Separation of actinides from the lanthanides is difficult, and is the main focus of this work.

Cation-exchange chromatography can be used to separate the actinide elements from the lanthanides. The key to a successful separation is the existence of a chelating agent that will bind the transuranic An(III) ions more tightly than any of the trivalent lanthanides. This dissertation describes the design, synthesis,

purification, and characterization of such a chelating agent. The stability constants of this ligand's complexes with the lanthanides are also reported. The data provide information about the nature of chelation across the lanthanide series. The ability of this chelating agent to participate in industrial-scale separations of nuclear waste is also discussed.

Nuclear Waste Processing

The treatment of the spent fuel elements from nuclear reactors is summarized in Figure 1 [3]. The spent fuel element is removed from the reactor and stored for a period of time that allows for most of the short-lived fission products to decay. After storage, the fuel element is opened with mechanical shearing or sawing. It is then dissolved in a nitric acid solution. Nearly all of the uranium and plutonium are recovered from the solution by solvent extraction. This extraction is carried out with tributylphosphate, and is known as the PUREX process. After the extraction, uranium and plutonium are separated and isolated. Both uranium and plutonium may be reused as reactor fuel, but the waste generated by the PUREX process, known as high-level liquid waste (HLLW), is a problem. Nearly all of this waste is the raffinate from the initial tributylphosphate extraction.

The exact composition of HLLW depends on several factors (irradiation time, original fuel composition, etc.). An example of the expected composition of HLLW from the PUREX process, after a three-year cooling period, can be seen in Table 1 [4]. All of the

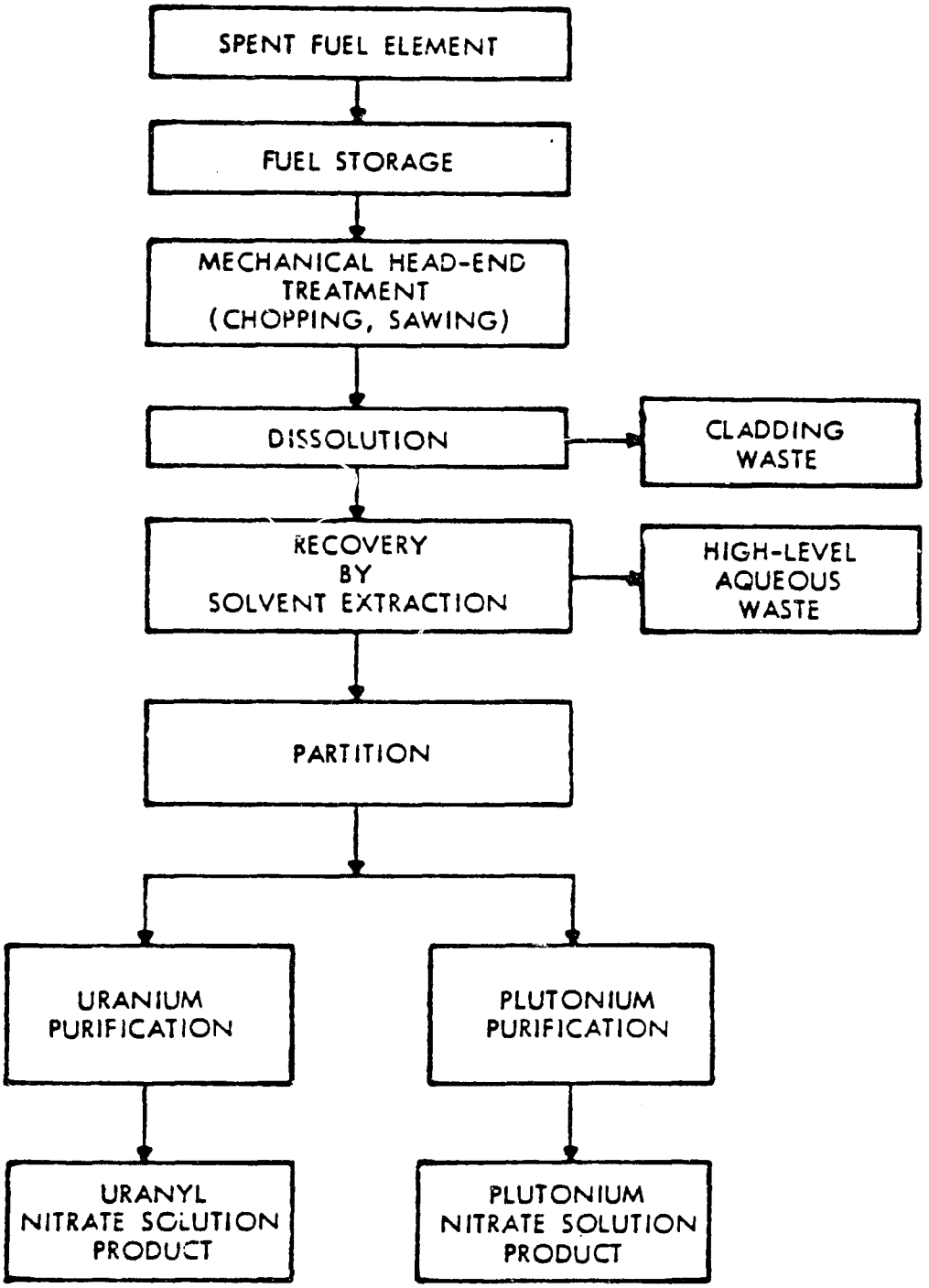


Figure 1. Current treatment of nuclear waste

Table 1. HLLW composition after three-year cooling period

Element	g/tonne	Concentration in waste, M
H	2,600	4.58
Na	5,000	0.383
Fe	20,000	0.631
Cr	200	0.0067
Ni	80	0.0025
Se	14.4	0.0003
Br	13.7	0.0003
Rb	347	0.0071
Sr	828	0.0163
Y	416	0.0082
Zr	3.710	0.0701
Mo	3,560	0.0643
Tc	822	0.0146
Ru	2,330	0.0402
Rh	505	0.0086
Pd	1,520	0.0254
Ag	82	0.0013
Cd	136	0.0021
In	1.6	--
Sn	25.7	0.0004
Sb	10.8	0.0002

Table 1. Continued

Element	g/tonne	Concentration in waste, M
Te	535	0.0073
Cs	2,600	0.0340
Ba	1.750	0.0224
La	1,320	0.0167
Ce	2,540	0.0317
Pr	1,280	0.0160
Nd	4,180	0.0507
Pm	35.6	0.0004
Sm	1,010	0.0119
Eu	174	0.0020
Gd	9,122	0.1021
Tb	1.3	--
Hg	10	0.0001
Np	482	0.0036
U	10,000	0.0740
Pu	100	0.0007
Am	525	0.0038
Cm	25	0.0002
NO^{-3}	288,945	8.21
PO_4^{-3}	2,000	0.0372
TOTAL	368,837	

components of the HLLW, except the actinides, can be stored in geological repositories effectively [2]. Most of these components decay to stable isotopes after 500 years, which is an acceptable duration of toxicity for geological storage. The long-lived alpha-emitting actinide elements, however, can constitute a toxic hazard for at least 10^5 years. Clearly, if the actinide elements could be separated from the other components of this waste, geological storage would be an acceptable disposal method for the remaining waste components.

The separation of the transuranic actinide elements from other components of HLLW has been investigated [5-18]. Many of these reports describe the removal of the actinides along with the lanthanide elements [5-11]. This is not surprising, as the chemistry of the trivalent lanthanides is very similar to that of the trivalent actinides.

Unfortunately, the presence of several of the lanthanide elements can limit the ultimate disposal of the actinides. Several of the lanthanides are known to have extremely large thermal neutron cross-sections [19]. The presence of these elements (Sm, Eu, Gd, and Dy) is highly undesirable if the actinides are to be disposed of by transmutation in a high-flux reactor. Transmutation is a very attractive disposal method because it is one of two proposed methods that provides complete disposal of the actinides [2]. The other method, rocketing the waste into space, is currently unattractive due to the unacceptable possibility of a launching accident.

The separation of the most abundant actinides, americium and curium, from the lanthanides has been investigated recently [12-18]. Most of the separations involve the use of HPLC or solvent extractions. Usuda [18] has described the successful separation of americium and curium from the lanthanides in concentrated HCl solutions, using anion-exchange chromatography. Hirayama et al. [13] have reported the development of an automatic chemical separation apparatus, which employs both cation- and anion-exchange chromatography. These reports, and others which utilize elution chromatography, describe good separation of Am and Cm from the lanthanides. However, elution chromatography cannot be implemented on an industrial scale without a significant loss of column efficiency and/or a tremendous increase in the cost of the separation [20].

Most of the solvent extraction experiments described in the literature have reported the separation of Am from a select few of the lanthanides, rather than from the entire series. Musikas [14], however, has studied the extraction of Am from all of the lanthanides. The extractant molecule described shows a lot of promise for lanthanide-actinide separations, but is soluble in water and not suitable for liquid-liquid extraction separations.

Although many interesting investigations have been performed, more work in this area is necessary. There is a clear need for a cost-efficient procedure that will provide for the large-scale separation of Am and Cm from mixtures of these elements with the lanthanides.

Chemical Aspects of Lanthanide-Actinide Separations

The reason for the similar chemical behavior of Am(III) and Cm(III) to that of the trivalent lanthanide is largely due to the similarities in ionic radii of Am(III) and Cm(III) to Pm(III) and Sm(III), respectively. Figure 2 shows the ionic radii for the trivalent lanthanide and actinide ions [21]. Little separation of Am(III) and Cm(III) from the trivalent lanthanides seems possible upon consideration of their ionic radii only. Separation of these ions depends on the ability to exploit the differences in nuclear charge between the two series.

Successful separation of actinides from lanthanides can be achieved by taking advantage of the small differences in the complex-forming ability that these ions have with polyaminopolycarboxylate ligands. The formation of lanthanide and actinide complexes with these ligands is governed by electrostatic and steric factors [22]. The larger nuclear charge of the actinide ions, therefore, explains why they form somewhat more stable complexes with polyaminopolycarboxyate ligands than do lanthanide ions with the same radii.

The successful chelating agent will bind Am(III) and Cm(III) more tightly than <u>any</u> of the trivalent lanthanide ions. Also, the chelating agent should (1) be soluble in aqueous acidic solutions; (2) be relatively stable in the presence of radiation; (3) not be highly corrosive, flammable or viscous; and (4) exchange rapidly with the lanthanides and actinides on a cation-exchange column.

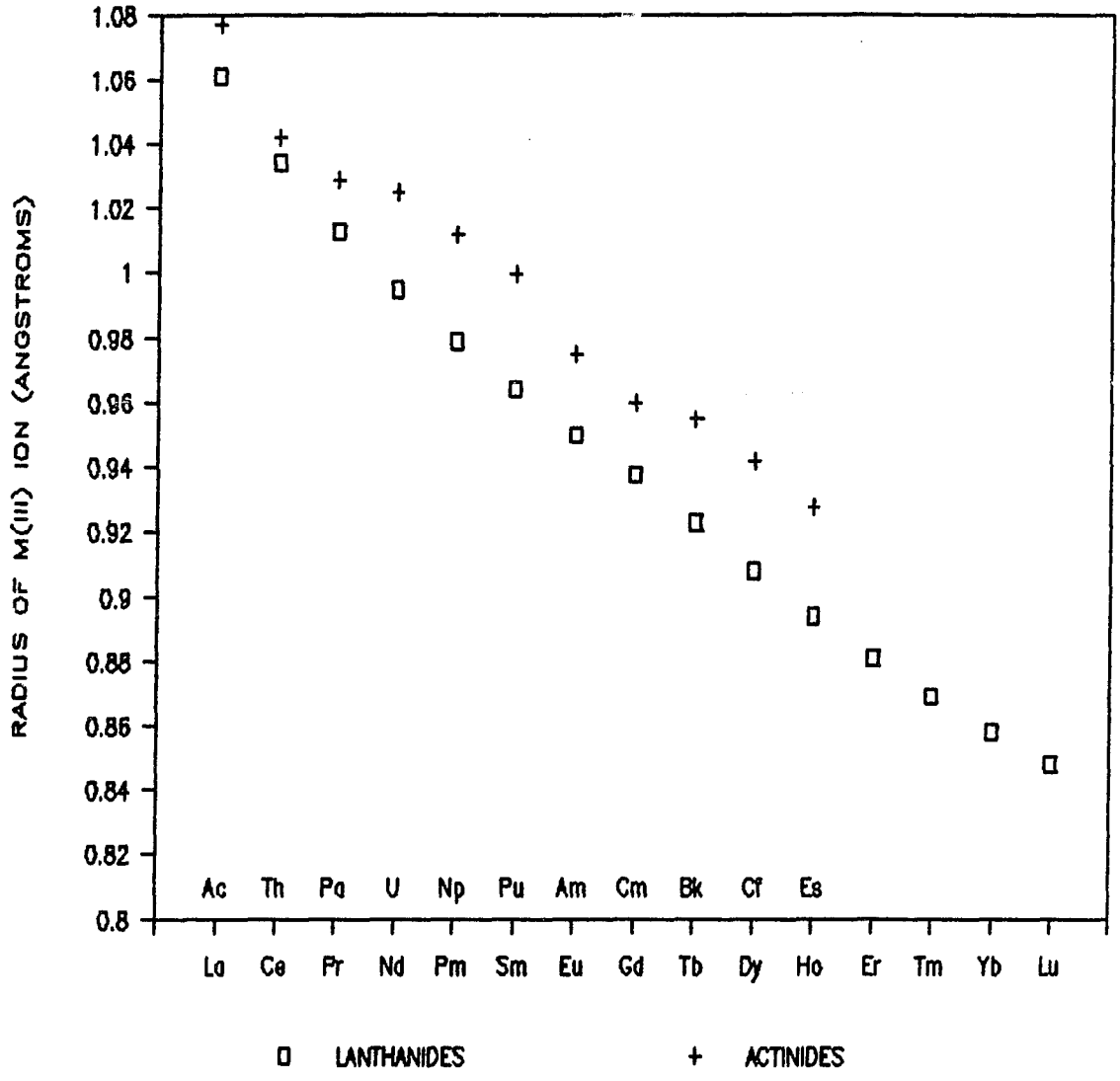


Figure 2. Radii of the trivalent lanthanide and actinide ions [21]

Several chelating agents which show promise for An/Ln separations are known. The focus of this work is to design and test a chelating agent that might improve the existing separation factors of Am and Cm from the lanthanides.

Some Chelating Agents

The stability constants for the lanthanide complexes of several polyaminopolycarboxylates have been studied [23-25]. The complexation behavior of four of these (DTPA, EEDTA, DETAP, and CEDTA) will be discussed.

Diethylenetriaminepentaacetic acid

Diethylenetriaminepentaacetic acid (DTPA) is a widely used potentially octadentate chelating agent. This ligand forms strong complexes with the trivalent lanthanides and actinides. Figure 3 shows a plot of the Ln-DTPA stability constants as a function of cationic radius [26]. The complex stabilities increase from La to Dy, and then decrease. Am and Cm both form more stable complexes than Dy:

Metal	log K (M-DTPA)
Dy	22.82
Am	22.90
Cm	23.00

From these data, one would predict that trivalent Am and Cm could be separated from a mixture of these elements with all of the lanthanides. Cation-exchange displacement chromatography would

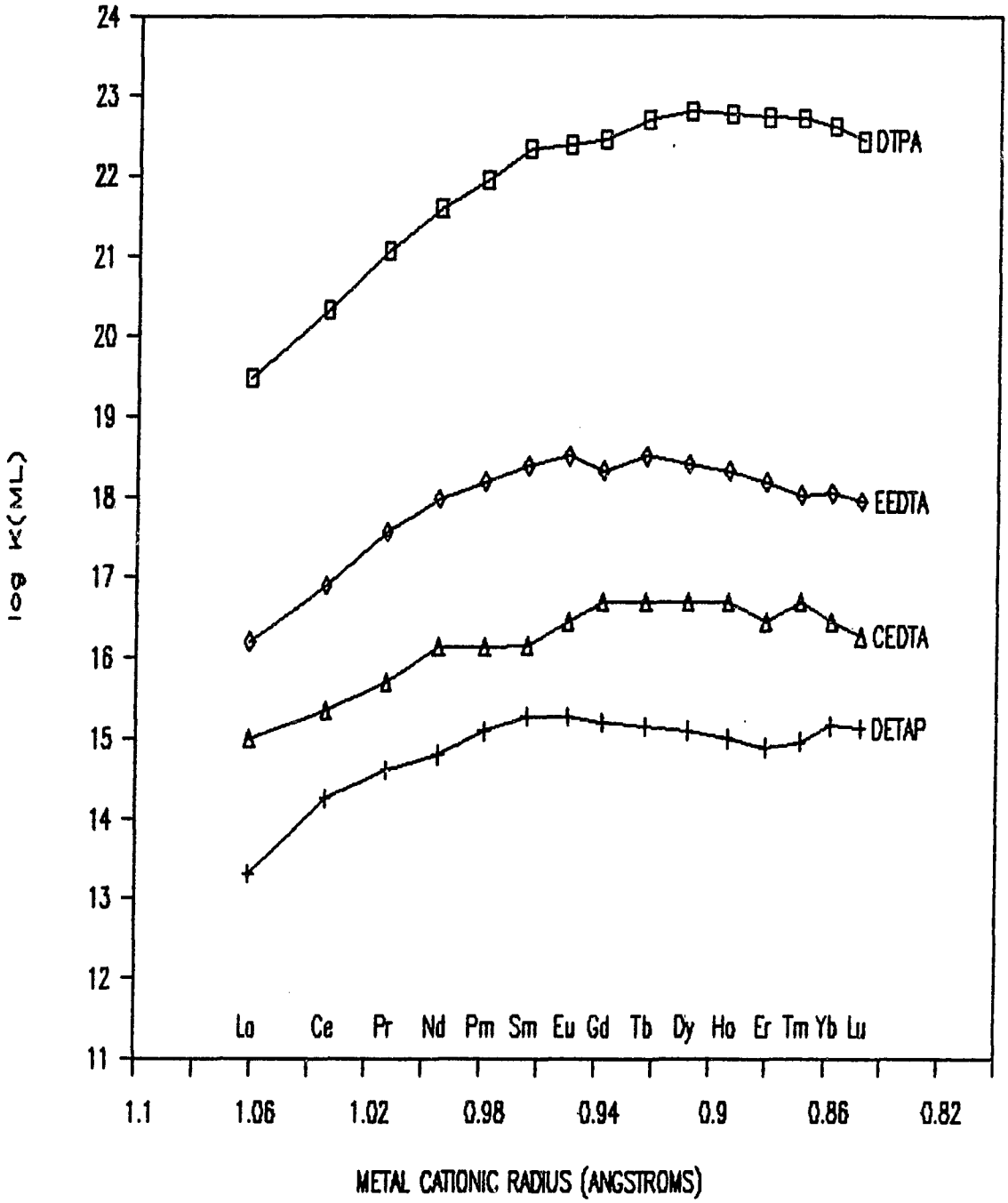


Figure 3. Lanthanide-anion stability constants for some polyaminopolycarboxylates as a function of metal cationic radius

accomplish the task by elution of a band containing a mixture of these ions with a dilute DTPA solution along a resin bed saturated with a retaining ion. The ions would elute in the order of decreasing metal-DTPA complex stability. The Am and Cm complexes are predicted to elute before any of the lanthanide complexes in a cation-exchange experiment of this type.

Such elution experiments with DTPA have been performed [27-29]. James et al. [27] report the order of elution expected from the stability constant data. The other two investigations report a different order of elution with Dy eluting before Am and Cm [28-29].

DTPA has also been used as a chelating agent in solvent-extraction separation experiments involving the actinides and lanthanides [17, 23, 30].

DTPA has proven to be a useful ligand in An/Ln separations. The downfall of this ligand results from its limited solubility in water and its extremely strong complex-forming ability with the f-block elements. The large formation constants of the metal-DTPA complexes results in slow exchange kinetics for the metal ion between the resin and the ligand phases, and in little selectivity of this ligand for the metal ions.

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

A plot of the Ln-EEDTA stability constants as a function of metal cationic radius is shown in Figure 3 [26]. This ligand shows a maximum stability earlier in the sequence than does DTPA. The maximum stability occurs at Eu and Tb. The Am-Eu and Am-Tb separation factors have been

determined by Powell et al. [31]. The separation factors are both 1.71 (separation factor (α) = $10^{(\log K_{(Am)} - \log K_{Ln})}$). This value represents an improvement over the calculated separation factors for the DTPA system. The overall stability of the Ln-EEDTA complexes is about 10^4 lower than the Ln-DTPA complexes. This would result in much improved exchange kinetics from the DTPA system. In addition, the acid form of EEDTA is very water-soluble. EEDTA represents an improvement over the DTPA system for An/Ln separations. This ligand shows the most promise for use in Ln/An separations to date.

Bis-(2-aminoethyl) ether-N, N, N'-triacetic acid-N'-(3-propionic acid) (DETAP)

DETAP represents a slight modification of the EEDTA ligand. In DETAP, one propionic acid group has replaced one of the acetic acid groups of EEDTA. This modification was employed in order to weaken one of the chelate rings of the EEDTA ligand and cause a shift of the stability constant maximum toward the lighter lanthanides. A plot of the Ln-DETAP stability constants vs. metal ion radius is plotted in Figure 3 for comparison with the other ligands [25]. The stability constant maximum has shifted for this ligand relative to EEDTA. The shift of the stability constant maximum is a desirable phenomenon. If the stability maximum could occur at Nd-Pm, then the maximum separation factor of Am from the Ln's would be realized, since Am(III) and Pm(III) possess essentially identical radii. Due to the unavailability of Pm, the Am-Nd separation factor gives a good point of reference. One assumes that the α_{Nd}^{Am} for this ligand is fixed, and all other Ln-DETAP

stabilities should be lower than that of Nd for the maximum separation to be realized. The Am-Sm separation factor for DETAP has been estimated to be 1.3 [25]. This is not as high as the separation factor observed for EEDTA for Am and the most stable lanthanide. The attenuation in overall stability for the DETAP complexes relative to the EEDTA complexes is about one thousand-fold. This lower stability would result in a lower selectivity of the actinide elements over the lanthanides. The overall stabilities observed for EEDTA are more useful for An/Ln separations. DETAP does not represent an improvement over EEDTA for use in Ln/An separations. This ligand does, however, provide some interesting information about lanthanide chelation, and about the effects of ring-size on the overall Ln-ligand stabilities.

N'-(β-carboxyethyl)-diethylenetriamine-N, N, N", N"-tetraacetic acid (CEDTA)

CEDTA is a derivative of DTPA where the acetic acid group on the middle nitrogen of DTPA has been replaced with a propionic acid group. A plot of the stability constants vs. metal ion radius for the metal-CEDTA complexes is shown in Figure 3 [32]. This ligand exhibits maximum stability with Gd-Ho. Replacement of the acetic acid group on the middle nitrogen, with a propionic acid group, once again has shifted the stability maximum towards the lighter lanthanides. The large million-fold attenuation in the overall stability of the CEDTA complexes relative to DTPA is observed. It appears that the lengthening of the chelate ring involving the middle nitrogen results in a larger attenuation than the lengthening of a chelate ring involving an

end nitrogen, as shown with the EEDTA-DETAP comparison.

The Design of a New Ligand

Two major factors affect the value of a chelating agent for use in Ln/An separations. If the ligand exhibits maximum Ln-ligand complex stability near Nd, then this would be favorable. Secondly, if the overall stability of the Ln-ligand complexes could be about one hundred-fold lower than that of the Ln-DTPA complexes, then the selection of the ligand for the actinide ions over the lanthanide ions would be enhanced over that of the ligands with lower overall stability. Furthermore, the exchange-kinetics should be acceptable in this range of stabilities ($K_{ML} = 10^{19} - 10^{20}$).

Modification of the DTPA ligand may accomplish the desired improvements needed for this separation problem. If one of the chelate rings of this ligand could be changed slightly, perhaps a shift of the stability constant maximum toward the lighter lanthanides could be accomplished.

Also, an attenuation in the overall stabilities would be expected from such a change. From the data of CEDTA, it seems that derivatizing the acetic acid group on the central nitrogen may cause a larger attenuation in overall stability than is desired. The focus, therefore, should be on one of the acetic acid groups on an end nitrogen. Replacement of one end-acetic acid of DTPA with a more bulky or longer substituent could cause the desired shift of the stability constant maximum and cause an attenuation in overall stability less than the 10^6

factor observed for CEDTA. Several replacements for an end-acetic acid group may accomplish the desired changes. A few examples are shown below:

2-methyl acetic acid	$-\underset{\displaystyle CH_3}{\underset{\vert}{CH}} - COOH$
2-phenyl acetic acid	$-\underset{\displaystyle \emptyset}{\underset{\vert}{CH}} - COOH$
propionic acid	$- CH_2CH_2 - COOH$.

Replacement of an end-acetic acid group with a propionic acid is expected to produce a chelating agent that will improve the existing Am-Ln separation factors. A shift of the stability constant maximum toward the lighter lanthanides would be expected from the comparison of DETAP and EEDTA, where one acetic acid group of EEDTA has been replaced with a propionic acid group. A less drastic attenuation of the overall stability is expected by replacing an acetic acid on an end nitrogen, rather than an acetic acid on the middle nitrogen.

The synthesis, purification and characterization of such a derivative of DTPA are described in the next sections of this dissertation.

PART I. SYNTHESIS, PURIFICATION, AND CHARACTERIZATION OF SEVERAL PRODUCTS OF THE REACTION BETWEEN DIETHYLENETRIAMINE AND 3-CHLOROPROPIONIC ACID

INTRODUCTION

The synthesis of the desired chelating agent could be carried out in two steps. In the first step, a monopropionic acid derivative of diethylenetriamine could be prepared. Once this intermediate is isolated, the remaining nitrogen sites could be carboxymethylated with chloroacetic acid.

Several reactions between diethylenetriamine and 3-chloropropionic acid were carried out in an attempt to prepare diethylenetriamine-N-propionic acid. A chloropropionate:diethylenetriamine ratio of 1.5 was used in the early attempts of this preparation. This section describes one such experiment. The characterization of three products of this reaction will be presented and discussed.

EXPERIMENTAL

Materials

3-chloropropionic acid

3-chloropropionic acid (98%) was purchased from Aldrich Chemical Company and used without further purification.

Sodium hydroxide

Reagent-grade sodium hydroxide pellets were purchased from Fisher Scientific and used without further purification.

Diethylenetriamine

Diethylenetriamine (95%) was purchased from Aldrich Chemical Company and used without further purification.

Hydrochloric acid

Reagent-grade concentrated hydrochloric acid was purchased from Fisher Scientific.

Absolute ethanol

Reagent-grade absolute ethanol was purchased from Midwest Grain Products, Inc.

Deionized water

All deionized water in this laboratory is prepared by passing condensed steam through a mixed bed of cation- and anion-exchange resins.

Experimental Procedure

A solution was prepared by dissolving 1.5 moles of 3-chloropropionic acid in a minimum of deionized water. The acid solution was then neutralized by slowly dripping a 50% NaOH solution (1.5 moles NaOH) into a 500-ml Erlenmeyer flask containing the swirling acid solution. During the neutralization, the temperature of the solution was kept below 20°C with the aid of an ice-water bath. The total volume of the neutral 3-chloropropionate solution was approximately 350 ml.

A second solution was prepared by adding deionized water to one mole of diethylenetriamine (103g) until a volume of approximately 150 ml was achieved.

A third solution was prepared by dissolving 1.5 moles of sodium hydroxide (60g) into enough deionized water to produce 150 ml of solution.

The diethylenetriamine solution was transferred to a clean, dry, two-liter, three-neck, round-bottom flask equipped with two addition funnels and one condenser. The solution was heated with a water bath to 50°C. The chloropropionate solution was added dropwise over a period of 1.5 hours to the swirling diethylenetriamine solution. During this addition, and throughout the reaction, the pH of the reaction mixture was kept between 8 and 10 with periodic additions of the NaOH solution. The mixture was stirred at 50°C under a cold-water condenser for 48 hours.

After the 48-hour reaction period, the solution was adjusted to pH $\approx$ 6 with concentrated H_2SO_4 in preparation for the separation of

products by cation-exchange displacement chromatography.

The solution was eluted through a series of cation-exchange chromatographic columns in order to separate the mixture of products. The mixture was first placed onto a 48" x 2" diameter column containing approximately 4.5 moles of Dowex 50-X8 cation-exchange resin capacity, 40-50 mesh, in the H^+ form. The mixture was then rinsed with deionized water to remove the highly acidic reaction product. The mixture was then displaced with .1 M NH_3 solution along the 2" diameter column and then, along two 48" x 1" diameter columns, each containing approximately 1.1 moles of Dowex 50W-X8 cation-exchange resin capacity in the H^+ form. The flow-rate of the displacing aqueous NH_3 solution was a slow 2.5 ml/min. NH_3 was a convenient displacing molecule, as it did not displace unreacted diethylenetriamine.

After several days, the lightly colored band reached the bottom of the third column. Fifty-one fractions of the effluent were collected over a period of four days.

RESULTS

Product Distribution

pH measurements

The volume and pH were measured for each fraction collected from the column chromatography separation described in the previous section. The results can be seen in Table 2. A plot of pH vs. effluent volume is seen in Figure 4. The pH vs. effluent volume function levels off at three distinct points.

^{13}C NMR

The ^{13}C NMR spectra of the samples 14-17 (pH $\approx$ 5) reveal an unresolved mixture of many products.

Samples 24-27 (pH $\approx$ 5.8) were all found to contain one substance of high purity. The proton-decoupled ^{13}C NMR spectrum of sample 25 may be seen in Figure 5. The chemical shifts of the five observed peaks are listed in Table 3.

Samples 38-48 (pH $\approx$ 9.7) were also found to contain one substance of high purity. The ^{13}C NMR spectrum of sample 39 may be seen in Figure 6. The chemical shifts of the seven observed peaks are listed in Table 4.

A ^{13}C NMR spectrum was also taken of sample 51. This sample was found to contain a product of >90% purity. The ^{13}C NMR spectrum of sample 51 may be seen in Figure 7. The chemical shifts of the five major observed peaks are listed in Table 5.

Table 2. Samples collected from the cation-exchange chromatographic separation of the products of reaction between 3-chloropropionate and diethylenetriamine

Sample	Volume (ml)	pH	
1	320	3.75	
2	320	3.84	
3	250	3.93	
4	240	4.03	
5	240	4.11	
6	275	4.20	
7	290	4.26	
8	300	4.31	
9	320	4.35	
10	285	4.50	
11	270	4.56	
12	240	4.66	
13	230	4.78	
14	240	4.91	
15	220	4.99	
16	240	5.00	
17	280	5.00	
18	325	5.11	
19	120	5.20	
20	340	5.30	
21	320	5.45	
22	310	5.63	
23	300	5.66	
24	300	5.71	
25	230	5.78	pure diethylenetriamine N, N"-dipropionic acid
26	270	5.80	
27	315	6.11	
28	290	6.41	

Table 2. Continued

Sample	Volume (ml)	pH	
29	280	7.10	
30	270	7.37	
31	250	7.40	
32	280	7.50	
33	280	7.65	
34	270	7.85	
35	270	8.30	
36	270	8.94	
37	270	9.43	
38	270	9.68	
39	270	9.72	
40	270	9.76	
41	270	9.73	
42	220	9.75	pure diethylenetriamine-N-monopropionic acid
43	200	9.73	
44	320	9.73	
45	350	9.73	
46	350	9.73	
47	340	9.73	
48	340	9.73	
49	320	9.90	
50	310	10.07	
51	290	10.20	95% diethylenetriamine-N'-monopropionic acid

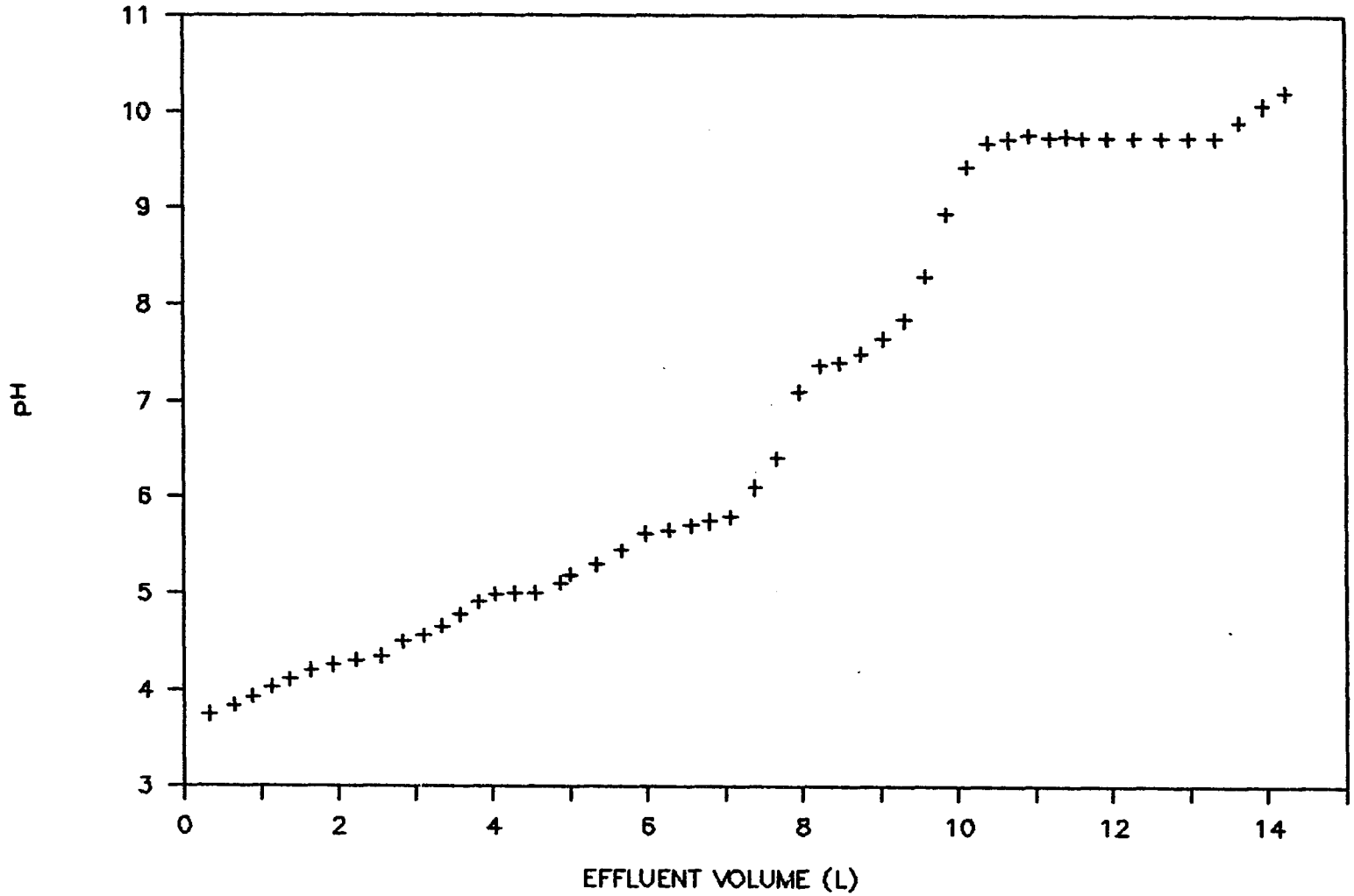


Figure 4. Plot of pH vs. effluent volume for the cation-exchange separation of the products of a reaction between 3-chloropropionic acid and diethylenetriamine

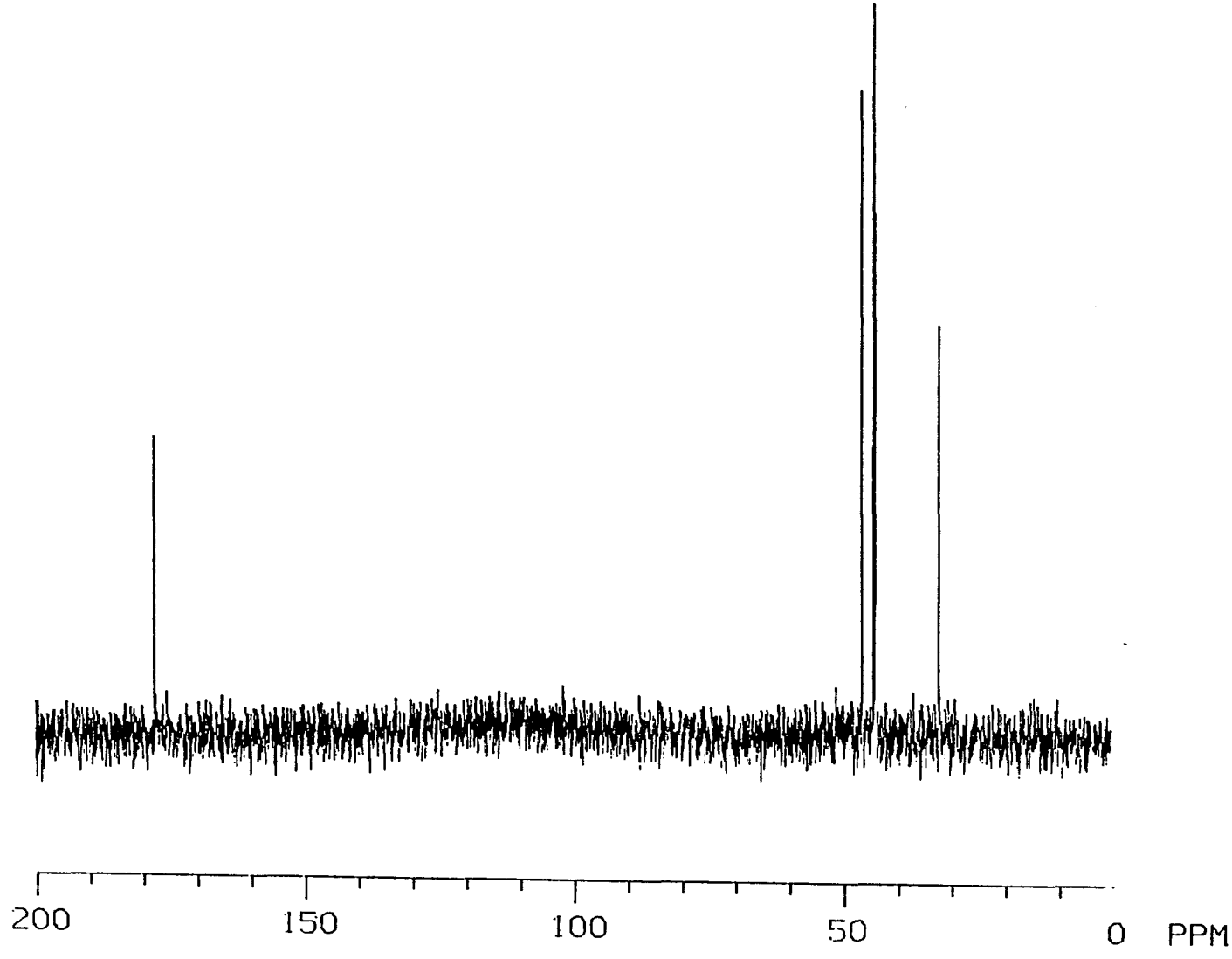


Figure 5. Proton-decoupled ^{13}C NMR spectrum of sample 25

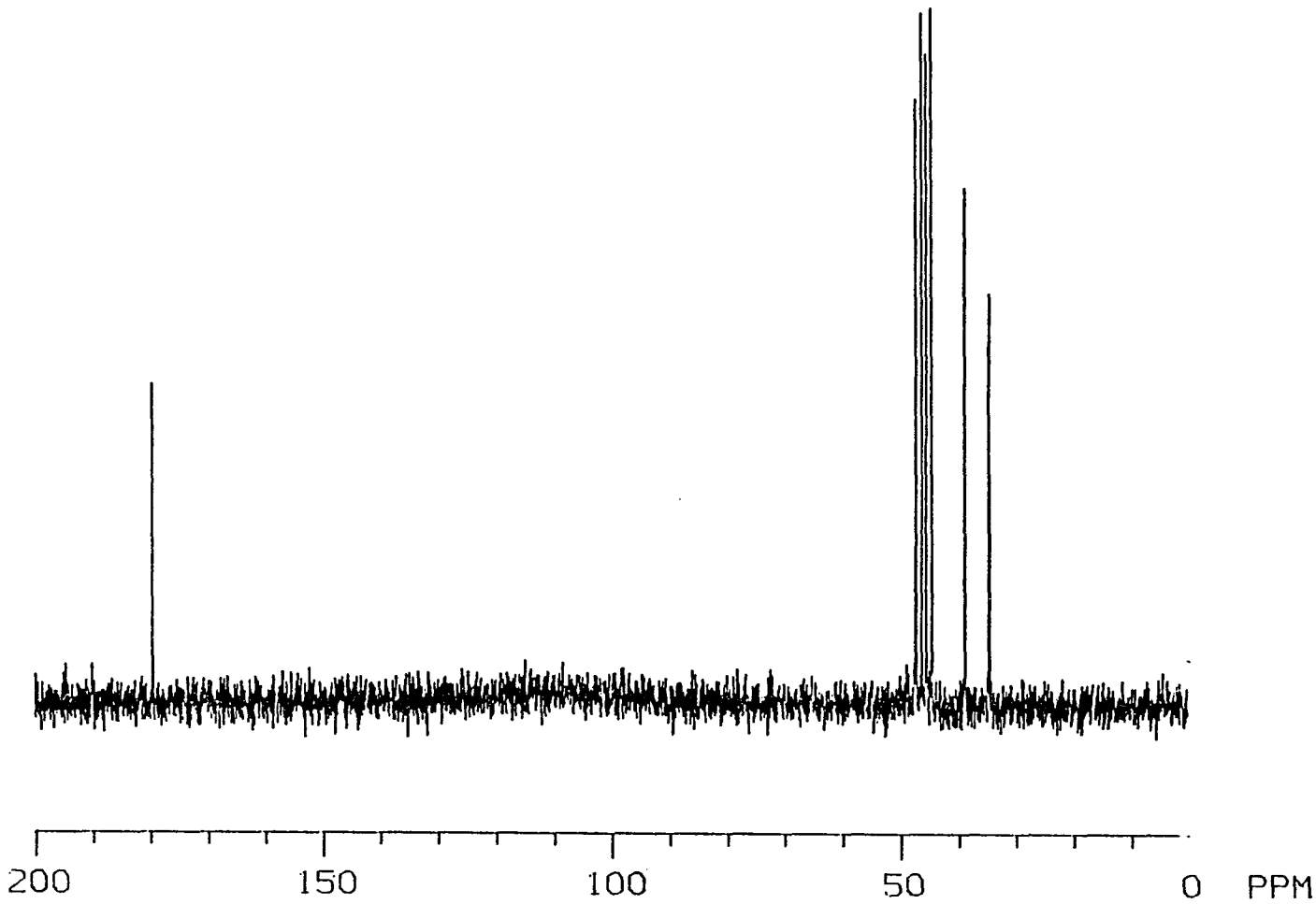


Figure 6. Proton-decoupled ^{13}C NMR spectrum of sample 39

Table 3. Chemical shifts observed in the ^{13}C NMR spectrum of sample 25

Peak	Chemical shift (ppm)
1	177.5
2	46.0
3	43.8
4	43.5
5	31.7

Table 4. Chemical shifts observed in the ^{13}C NMR spectrum of sample 39

Peak	Chemical shift (ppm)
1	179.4
2	47.2
3	46.2
4	45.5
5	44.5
6	38.7
7	34.5

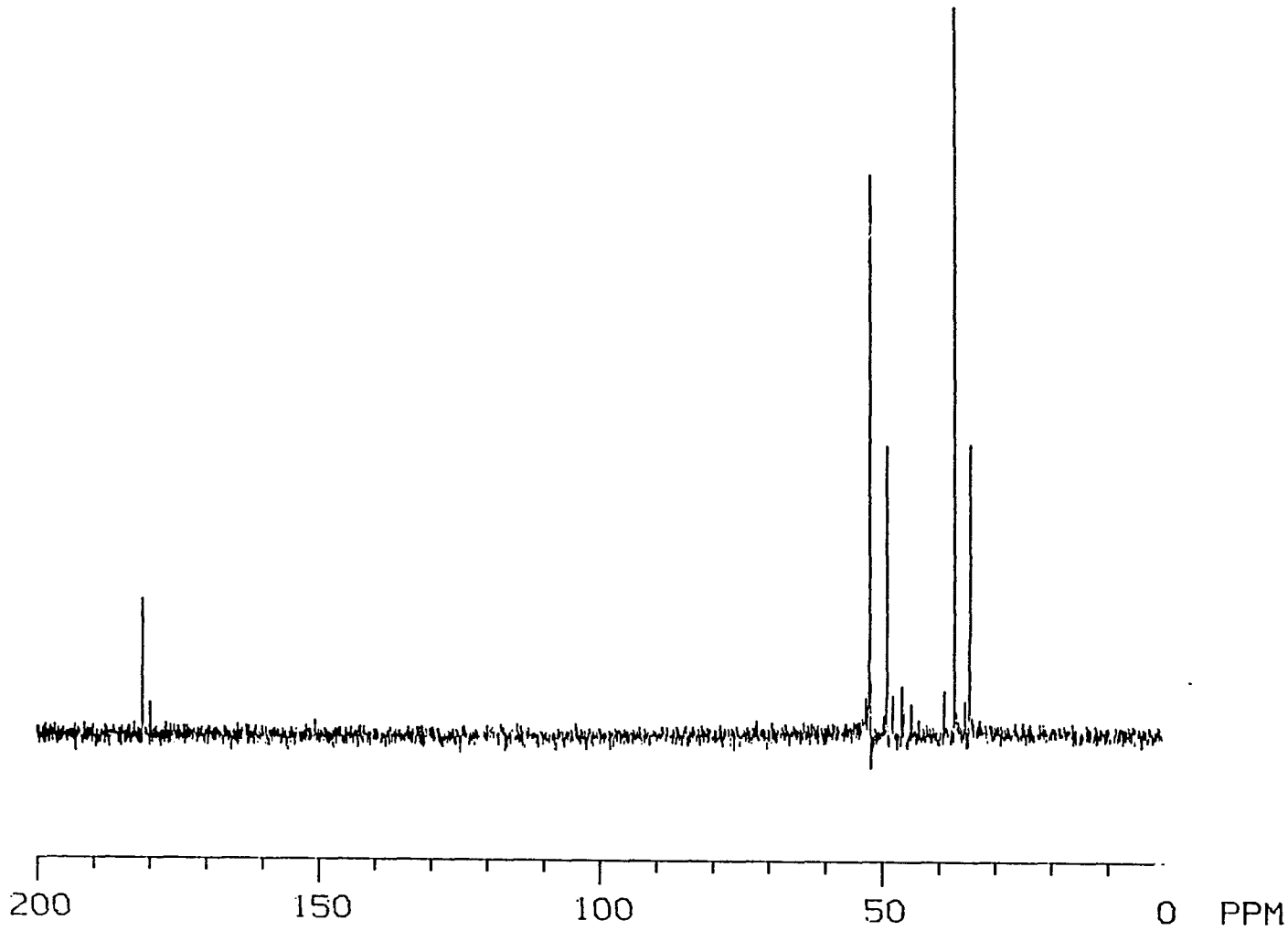


Figure 7. Proton-decoupled ^{13}C NMR spectrum of sample 51

Table 5. Chemical shifts observed in the ^{13}C NMR spectrum of sample 51

Peak	Chemical shift (ppm)
1	181.0
2	51.8
3	48.8
4	36.9
5	34.1

All ^{13}C spectra were recorded on a Nicolet 300 MHz Fourier-Transform NMR spectrometer. The chemical shifts are reported relative to a dioxane standard (66.5 ppm).

Elemental analysis

A solid was isolated from sample 25. The aqueous solution was evaporated to a syrup consistency. The syrup was then added slowly to a large excess of absolute ethanol. Upon addition of concentrated HCl solution, a precipitate formed.

solid mp = 246 - 248°C

The dried solid was submitted to Mic Anal for elemental analysis. The results are seen in Table 6.

A solid was isolated from sample 39 using the same procedure as for sample 25. The dried sample was submitted to Desert Analytics for elemental analysis. The results are seen in Table 7.

Table 6. Elemental analysis of the solid isolated from sample 25

	Found	Calculated for $C_{14}H_{32}N_3O_4Cl_3$
%C	39.90	40.73
%H	7.97	7.76
%N	10.20	10.18
%Cl	25.71	25.82

Table 7. Elemental analysis of the solid isolated from sample 39

	Found	Calculated for $C_7H_{20}N_3O_2Cl_3$
%C	29.79	29.53
%H	7.28	7.03
%N	14.77	14.76
%Cl	36.38	37.43

A solid isolated from sample 51 was found, using ^{13}C NMR, to contain the same impurity that was present in the aqueous sample.

DISCUSSION

The substances that exhibit the ^{13}C NMR spectra shown in Figures 5, 6 and 7 have been identified.

The ^{13}C NMR spectrum of sample 25 contains five peaks. The peak possessing a chemical shift of 177.5 ppm is in the region expected for the resonance of a carboxylic acid carbon [33]. The three resonances occurring between 46 and 43 ppm may correspond to carbon atoms adjacent to a nitrogen atom and to another carbon atom. The peak at 31.7 is near the region where one would expect α-carbon atoms of aliphatic carboxylic acids to resonate.

Diethylenetriamine-N, N"-dipropionic acid has been proposed as the molecule that exhibits the ^{13}C NMR structure seen in Figure 5:

$$NH(\overset{5}{CH_2}\overset{1}{CH_2}NHCH_2CH_2COOH)_2$$

diethylenetriamine-N, N"-dipropionic acid .

The proton-decoupled ^{13}C NMR spectrum containing five lines is expected for this compound. The carbons labeled 1 and 5 have been assigned to peaks 1 and 5, respectively. The remaining three nonequivalent carbons are expected to resonate in the region of the remaining peaks.

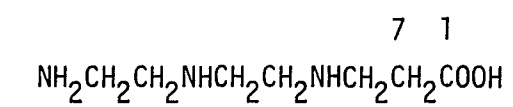
The elemental analysis for this compound indicates that it was isolated as the diethylester-trihydrochloride.

The synthesis of this compound has been reported previously by Gamp et al. [34]. In their procedure, two equivalents of acrylonitrile

were reacted with one equivalent of diethylenetriamine. The nitrile product was isolated as the trihydrochloride. The nitrile product was then hydrolyzed with 5M H_2SO_4 and isolated as the sulfate-hydrogen sulfate. The dipropionic acid was characterized by elemental analysis and 'H NMR.

The authors do not address the possibility of one of the propionate groups being attached to the central nitrogen. The results presented in this dissertation will show that a middle-end-substituted product is likely to be present, and is likely to co-precipitate with the desired product. Elemental analysis cannot distinguish these two isomers. The 'H NMR spectrum can distinguish the two isomers. Three chemical shifts are reported for the protons in this molecule, instead of the expected four. Unfortunately, the 'H NMR spectrum is not shown. These observations leave some question as to whether or not the desired end-end dipropionic acid was prepared in high enough purity for the stability constant and protonation constant determinations that were carried out.

The ^{13}C NMR spectrum of sample 39 contains seven peaks. This spectrum is believed to be that of the desired product: diethylenetriamine-N-propionic acid.



diethylenetriamine-N-propionic acid

The end-substituted monopropionic acid is the only product of this reaction that would give a proton-decoupled ^{13}C NMR spectrum containing seven lines. Peaks 1 and 7 have been assigned to the carbons labeled 1 and 7 above. The five remaining peaks occur in the region expected for the five remaining carbon atoms, each adjacent to an amine N and to a $-CH_2-$ group.

The elemental analysis of this compound indicates that it was isolated as the trihydrochloride: $C_7H_{20}N_3O_2Cl_3$.

The ^{13}C NMR spectrum of sample 51 contains five lines. This spectrum is believed to be that of diethylenetriamine-N'-propionic acid.

$$\overset{1}{HOOC}\overset{5}{CH_2}\overset{3}{CH_2}\overset{4}{N}(\overset{2}{CH_2}CH_2NH_2)_2$$

diethylenetriamine-N'-propionic acid

Five lines are expected in the ^{13}C NMR spectrum of this compound. All lines in the spectrum have been assigned based on their relative intensities and the expected chemical shifts of the carbon atoms in this compound [33]. The assignments are shown by the numbering of the carbon atoms above. The spectrum of sample 51 shows the presence of a small amount of the end-substituted monopropionic acid, indicating an incomplete separation of the two mono-substituted isomers.

This compound is distinguished from the end-end dipropionic acid by its higher affinity for the H^+-form cation-exchange resin. The middle-substituted monopropionic acid is the most highly basic of all expected products of the reaction, and is expected to elute after all

of the other substituted products.

A previous synthesis of the middle-substituted monopropionic acid has been reported by Vasil'eva et al. [32]. In their procedure, disalycylidene diethylenetriamine is reacted with acrylonitrile and trimethylbenzylammonium hydroxide. The reaction mixture is evaporated and then boiled with concentrated HCl. The compound was isolated as the monohydrate-trihydrochloride and characterized by elemental analysis. Due to the presence of the protector groups on the end-nitrogens, the production of isomers in this synthesis is not likely. However, more extensive characterization would leave even less doubt about the purity of the reported compound.

The reaction described between diethylenetriamine and 3-chloropropionate results in a mixture of many products. Among these is a new compound: diethylenetriamine-N-propionic acid. The yield of this product and other products can be optimized by adjusting the mole ratio of the starting materials. For example, when excess diethylenetriamine is used, the fraction of the two mono-substituted products is greatly enhanced.

The end-substituted monopropionate is expected to form in greater yield than the middle-substituted product. The 4:1 end to middle ratio of replacable protons in diethylenetriamine contributes to the observed dominance of the end-substituted product over the middle-substituted product.

^{13}C NMR spectra for three products of the reaction have been reported for the first time. These spectra, along with the other

evidence reported, allow for the unambiguous characterization of these three products.

This work illustrates the value of ^{13}C NMR spectroscopy as a characterization tool for compounds of this type. The ^{1}H NMR spectra of these polyamino-carboxylate compounds are often difficult to interpret. Unresolved multiplets are often observed, and the isolation of the pure compounds in the absence of water or HCl has not been achieved. Elemental analysis provides useful information, but is not an adequate characterization technique by itself. It is especially inadequate for characterizing products of a reaction where isomers are possible. The unambiguous characterization of these compounds in the absence of impurities (other than water) is accomplished when ^{13}C NMR spectroscopy is used as one of the characterization tools.

PART II. SYNTHESIS, PURIFICATION AND CHARACTERIZATION OF DIETHYLENETRIAMINE-N, N, N', N"-TETRAACETIC ACID-N"-MONOPROPIONIC ACID (DTTAP)

INTRODUCTION

This section describes the synthetic route taken for the first known preparation of diethylenetriamine-N, N', N', N"-tetraacetic acid-N"-monopropionic acid (DTTAP). The rather difficult purification of DTTAP is also described in this section. A detailed characterization of DTTAP is also described.

This part contains comments on the many difficulties encountered throughout the synthesis and purification of DTTAP, which contributed to a low yield of the >99.9% pure compound.

EXPERIMENTAL

This section describes the materials and experimental procedures used for the synthesis and purification of diethylenetriamine-N, N, N', N"-tetraacetic acid-N"-monopropionic acid (DTTAP).

Reagents

Diethylenetriamine

The diethylenetriamine used in this synthesis was of 95% purity, as purchased from Aldrich Chemical Company.

Sodium hydroxide

Reagent-grade sodium hydroxide pellets were purchased from Fisher Scientific.

Sulfuric acid

Reagent-grade concentrated sulfuric acid was purchased from Fisher Scientific and used without further purification.

3-chloropropionic acid

3-chloropropionic acid (98%) was purchased from Aldrich Chemical Company and used without further purification.

Amonium hydroxide

Solutions of .1M of NH_4OH were prepared by dilution of reagent-grade concentrated NH_4OH purchased from Fisher Scientific. Dilution was performed with deionized condensed steam. Deionization is achieved by

passing the water through a mixed bed of cation- and anion-exchange resins.

Hydrochloric acid

Reagent-grade concentrated hydrochloric acid was purchased from Fisher Scientific. A .10M HCl solution was prepared by dilution of the concentrated HCl with deionized condensed steam.

Absolute ethanol

Reagent-grade absolute ethanol was purchased from Midwest Grain Products, Inc. and used without further purification.

Chloroacetic acid

Reagent-grade chloroacetic acid was purchased from Fisher Scientific and used without further purification.

Experimental Procedure

Preparation of DTTAP

The preparation of DTTAP was carried out in two steps. An intermediate, diethylenetriamine-N-propionic acid, was prepared and purified in the first step. Next, the pure end-substituted monopropionate was reacted with four equivalents of chloroacetate to form the desired product.

Diethylenetriamine-N-propionic acid One mole of 3-chloropropionic acid (108.5g) was dissolved in a minimum of deionized water. The acid solution was then neutralized by slowly dripping a 50% NaOH solution (1.0 moles NaOH) into a 500-ml Erlenmeyer flask

containing the swirling acid solution. During the neutralization, the temperature of the solution was kept below 20°C with the aid of an ice-water bath. The total volume of the neutral 3-chloropropionate solution was approximately 250 ml.

A second solution was prepared by adding deionized water to three moles of diethylenetriamine (309.5g) until a volume of approximately 450 ml was achieved.

A third solution was prepared by dissolving one mole (40g) of NaOH in enough deionized water to produce 100 ml of solution.

The diethylenetriamine solution was transferred to a clean, dry, three-liter, three-neck, round-bottom flask equipped with two addition funnels and one condenser. The solution was heated with a water bath to 50°C. While the solution was stirring, the chloropropionate solution was added dropwise over a period of one hour. During this addition, and throughout the reaction, the pH of the reaction mixture was kept between 8 and 10 with periodic additions of the NaOH solution. The reaction mixture was stirred at 50°C under a cold-water condenser for 24 hours.

After the 24-hour reaction period, the solution was adjusted to pH = 2 by the addition of concentrated H_2SO_4. At this point, a precipitate formed which was identified by ^{13}C NMR spectroscopy as a protonated form of unreacted diethylenetriamine. The precipitate was separated by suction filtration and the filtrate was placed on a series of three columns containing cation-exchange resin in the H^+ form in order to separate the mixture of products.

Pure end-substituted monopropionic acid was isolated using the method described in Part II of this dissertation. The flow-rate of the .1M aqueous NH_3 eluent was a slow 2.5 ml/min. The light-colored band was displaced along one 48" x 2" diameter column followed by two 48" x 1" diameter columns.

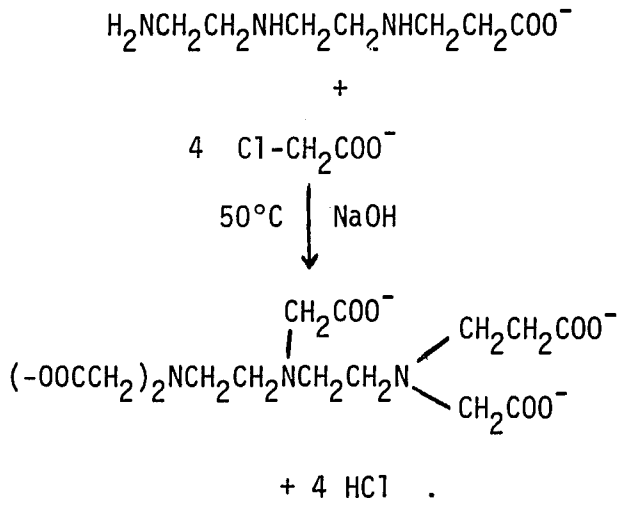
Thirty-four samples were collected over a period of three days. Each sample contained 200-250 ml of solution. The pH of each solution was measured. Samples 1-30 all were within 0.10 pH units (pH = 9.32 - 9.41). Samples 1-30 were combined after they were found to each contain the pure end-substituted monopropionate by ^{13}C NMR spectroscopy (see Figure 6). The yield of pure monopropionic acid was calculated by pH titration of the product with standard HCl solution. Yield = 50% (based on chloropropionic acid).

Final product preparation A concentrated solution was prepared by evaporating a solution containing 0.232 moles of the monopropionic acid intermediate to a syrup consistency. This solution was then adjusted to pH = 8 with 50% NaOH solution.

A second solution was prepared by dissolution of 1.02 moles chloroacetic acid in a minimum of deionized water. The acid was neutralized by slowly dripping 50% NaOH solution into the swirling solution. During the neutralization, the temperature was kept below 20°C with an ice-water bath.

A third solution was prepared by dissolving 1.02 moles of NaOH into enough deionized water to produce 150 ml of solution.

Dry nitrogen gas was then bubbled into each of the three prepared solutions. The monopropionate and chloroacetate solutions were then combined in a clean, dry 1000-ml three-neck, round-bottom flask equipped with an addition funnel and reflux condenser. The reaction mixture was heated to 50°C in a hot water bath. The reaction mixture was stirred at 50°C for two and one-half hours. During the reaction, dry nitrogen gas was bubbled through the solution. The pH of the reaction mixture was kept between pH = 8-10 by periodic additions of the NaOH solution, which drives the reaction:



After the two and one-half hour reaction time, the solution was adjusted to pH = 2 with concentrated HCl. The reaction mixture was then diluted to twice its original volume with deionized water in preparation for the separation of the mixture of products.

Purification of DTTAP The mixture was first placed on a series of two columns containing cation-exchange resin in an effort to separate

the polyaminopolycarboxylate products from the other substances.

The diluted reaction mixture was placed on a 48" x 2" diameter cation-exchange column containing approximately 4.5 moles of Dowex 50-X8 cation-exchange resin capacity in the acid form. The solution was washed with deionized water and then displaced with .15M NH_3 solution at a flow-rate of 3 ml/min. After passing through the two-inch diameter column, the light-colored band was displaced through a 48" x 1" diameter column containing approximately 1.1 moles of Dowex 50W-X8 cation-exchange resin capacity in the acid form.

All fractions collected from the above displacement within pH = 2-6 were combined and the mixture of polyaminopolycarboxylate products within were further separated by anion-exchange displacement chromatography.

The mixture was displaced through a series of six 48" x 1" diameter columns, each containing approximately 1.1 moles of Dowex-2 anion-exchange resin capacity in the hydroxide form. The mixture was displaced with .10M HCl solution at a flow-rate of 2 ml/min. Sixteen fractions of the effluent were collected within the range (pH = 1-3). The volume and measured pH of each sample are shown in Table 8. Samples 11-16 gave a positive test for Cl^- [35]. Samples 8-12 were found to contain a substance of >99.9% purity. This substance is characterized by its ^{13}C NMR spectroscopy pattern. The spectrum contains 13 peaks corresponding to a compound with 13 nonequivalent carbon atoms.

Table 8. Eluted samples from anion-exchange displacement chromatography experiment

Sample	Volume (ml)	pH
1	220	2.83
2	220	2.75
3	220	2.69
4	220	2.62
5	190	2.55
6	225	2.43
7	220	2.37
8	210	2.34
9	220	2.31
10	75	2.26
11	175	1.93
12	150	1.57
13	150	1.40
14	140	1.35
15	130	1.33
16	125	1.32

The samples 8-12 were combined and further purified by washing the mixture, with H_2O, onto a 12" x 1/2" diameter column containing Dowex 50W-X8 H^+-form cation-exchange resin, thereby removing Cl^- ion. The pure compound was then eluted through the cation-exchange system with .01M NaOH at a flow-rate of approximately 10 ml/min. Only samples of pH < 4 were recovered. The overall yield of pure DTTAP is 2% (based on original Cl-propionic acid).

RESULTS

Characterization

^{13}C NMR spectroscopy

The ^{13}C NMR spectrum of the Cl^--free product described in the previous section can be seen in Figure 8. The proton-decoupled spectrum consists of 13 peaks. Two of the peaks are of double intensity, thereby indicating the correct number of carbon atoms (15) in the desired product. Figure 9 shows the structure of DTTAP and a list of the ^{13}C NMR chemical shifts observed in the spectrum. The ^{13}C NMR spectrum was recorded on a Nicolet 300 MHz Fourier-Transform NMR spectrometer. The chemical shifts are reported relative to a dioxane standard (66.5 ppm). The sample was measured in solution with a 10% D_2O - 90% H_2O solvent.

Six of the 13 resonances have been assigned, as shown by the numbered carbons in Figure 5. The four peaks at 169-174 ppm are in the range expected for the carboxylic acid carbons. The eight peaks at 48-57 ppm are in the range expected for a carbon atom adjacent to a nitrogen atom. Finally, the peak at 28.17 ppm is located close to where one would expect the alpha carbon of a simple aliphatic carboxylic acid [33].

The peaks observed at 169.54 ppm and 56.21 ppm have been assigned to the carbons labeled 3 and 5, respectively. These two peaks are of double intensity compared to the others and are undoubtedly a result of the two equivalent acetate groups. The resonance at 169.22 ppm is

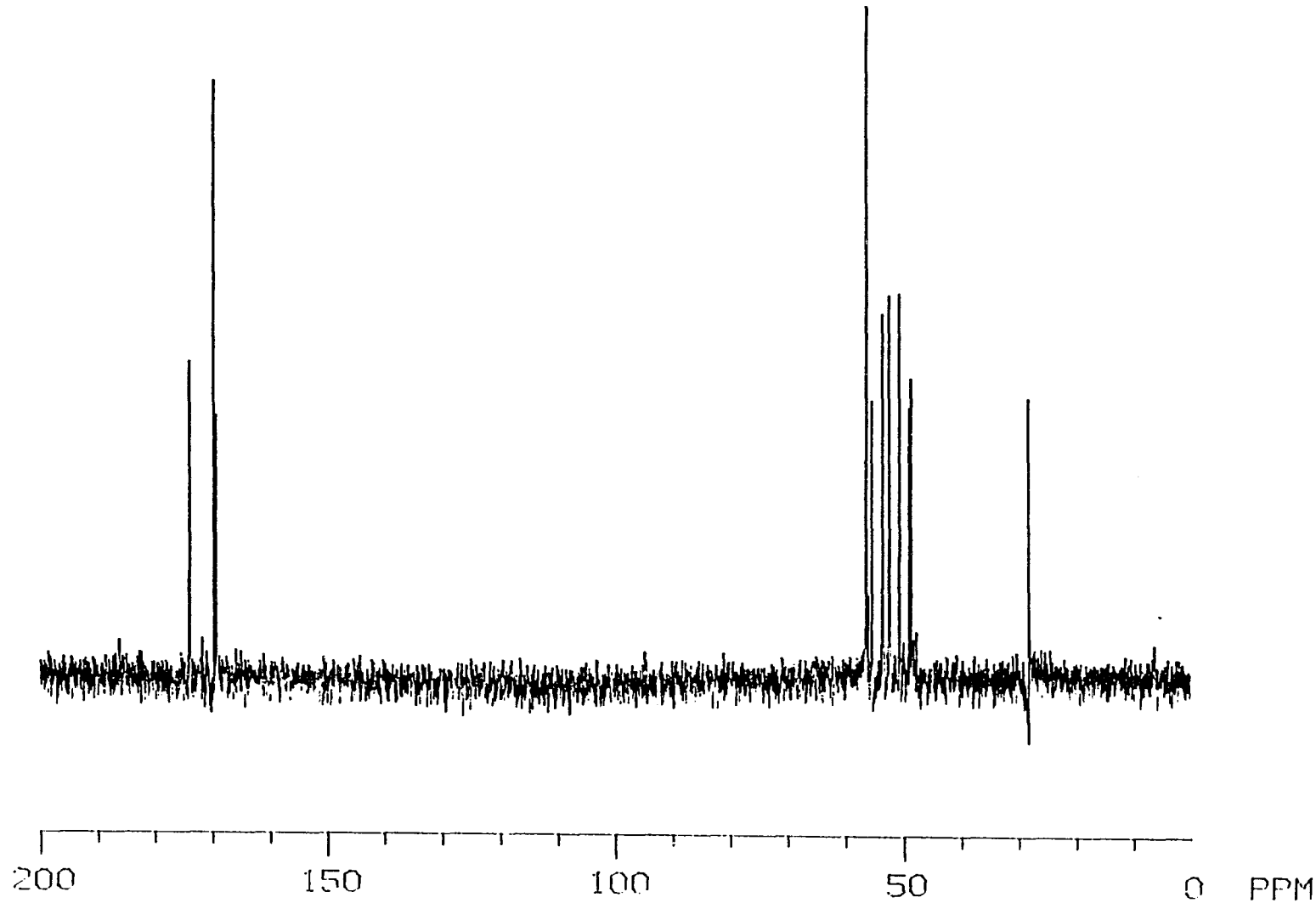
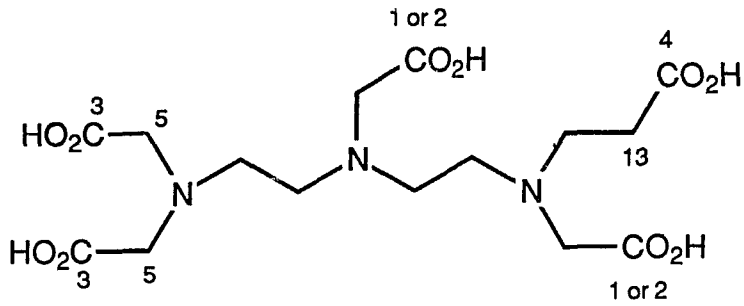


Figure 8. ^{13}C NMR spectrum of Cl^--free DTTAP



Peak #	Shift (ppm)
1	173.78
2	173.71
3	169.54
4	169.22
5	56.21
6	55.31
7	53.43
8	52.31
9	52.27
10	50.54
11	48.88
12	48.50
13	28.17

Figure 9. ^{13}C chemical shifts of DTTAP

assigned to the carboxylic acid carbon of the propionate group. This carbon is expected to resonate upfield relative to the other carboxylic acid carbons [33]. The peaks at 173.78 and 173.71 ppm have been assigned to the carboxylic acid carbons labeled 1 or 2 in Figure 9. Distinguishing which of these two nearly coincident peaks belongs to which of these carbonyl carbons is not possible without further experimentation. The peak at 28.17 ppm is assigned to the carbon atom labeled "13" in Figure 9. This is the only carbon atom adjacent to a carboxylic acid carbon and a CH_2 group and corresponds to the only reasonable resonance for that chemical environment. The remaining seven peaks in the ^{13}C NMR spectrum for this compound are currently unassigned. Further experiments would be necessary in order to assign each peak to the individual carbon atom which corresponds to it. The chemical shifts of these remaining peaks are, however, in the range one would expect for the remaining carbon atoms of DTTAP.

Titration data

An aqueous sample of the substance showing the ^{13}C NMR spectrum described above was further characterized by two potentiometric titrations with standard KOH solution.

A 1.00 ml aliquot of an aqueous solution believed to contain pure DTTAP was titrated potentiometrically with 0.0610M KOH solution. An additional 1.00 ml aliquot was titrated potentiometrically with the same KOH solution in the presence of 1.00 equivalent of Sm^{3+}. A plot of pH vs. ml OH^- added can be seen in Figure 10. In the plot of the

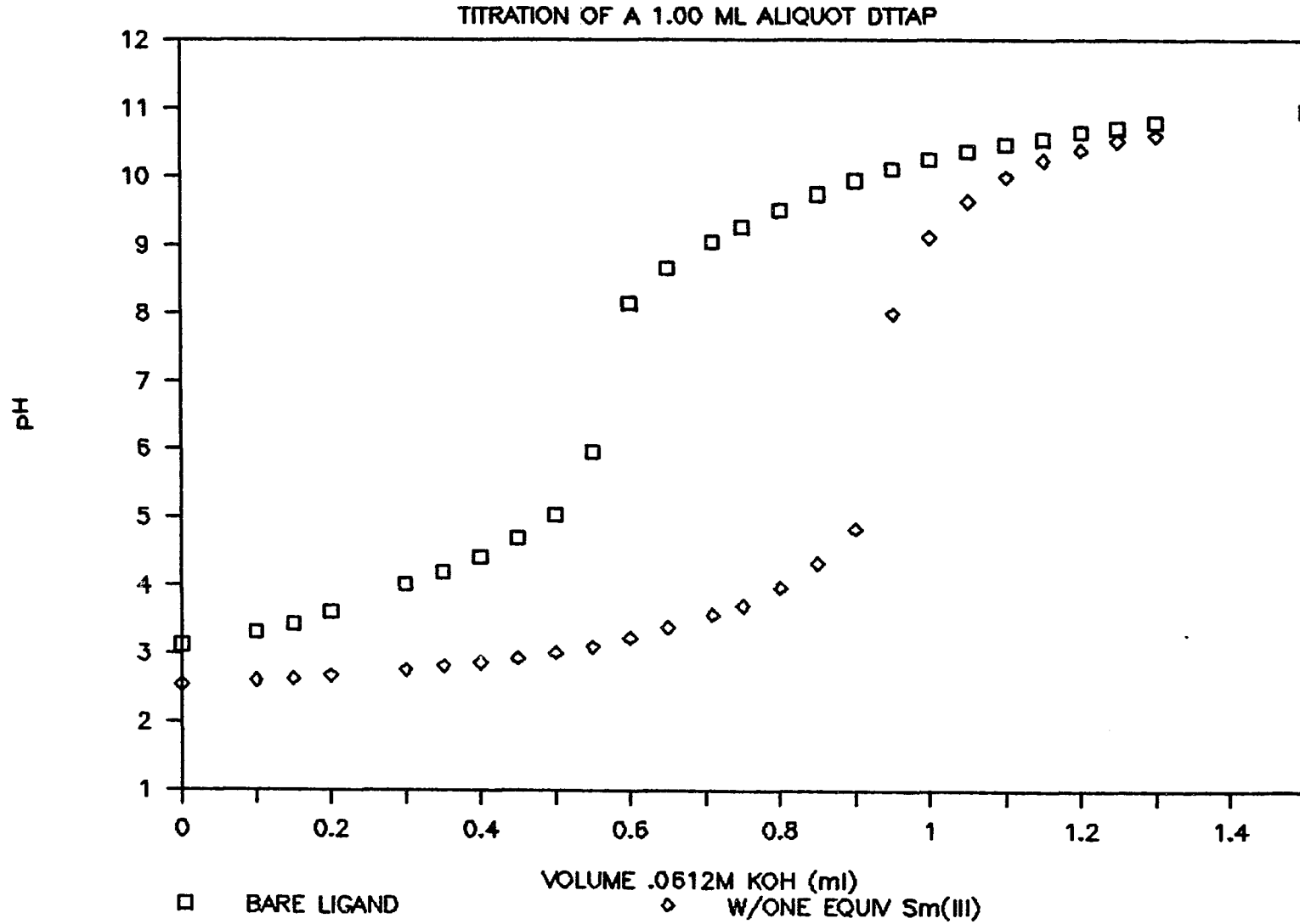


Figure 10. pH titrations of DTTAP

bare acid titration, an equivalence point at 0.57 ml of KOH solution is observed. This volume was assumed to correspond to the neutralization of three protons of DTTAP. Based on this assumption, 1.00 equivalents of Sm^{3+} were added to a second 1.00 ml aliquot of the sample. In the plot of the titration of this solution, an equivalence point at 0.95 ml of KOH solution is observed. The ratio of KOH volumes for the two titrations is 3.0:5.0. The second titration is a titration of the protons liberated when the ligand complexes the Sm^{3+} metal ion. The data support the existence of a ligand which strongly complexes Sm^{3+}, such as a polyaminopolycarboxylate. The ratio of volumes observed at each equivalence point provides convincing evidence that the ligand contains five carboxylic acid groups [36].

Mass spectrometry

Fast-atom-bombardment (FAB) mass spectrometry was utilized in order to determine the molecular weight and/or partial structural makeup of the compound. The compound was dissolved in a water-glycerol matrix. The mass spectral analysis was performed with a Kratos MS-50 mass spectrometer.

The matrix-subtracted mass spectrum can be seen in Figure 11. The M+1 peak observed at 408.1 ($\frac{\text{mass}}{\text{charge}}$) provides further convincing evidence that the desired DTTAP has been formed:

	Molecular formula	Molecular weight
DTTAP	$C_{15}H_{25}N_3O_{10}$	407.1 amu

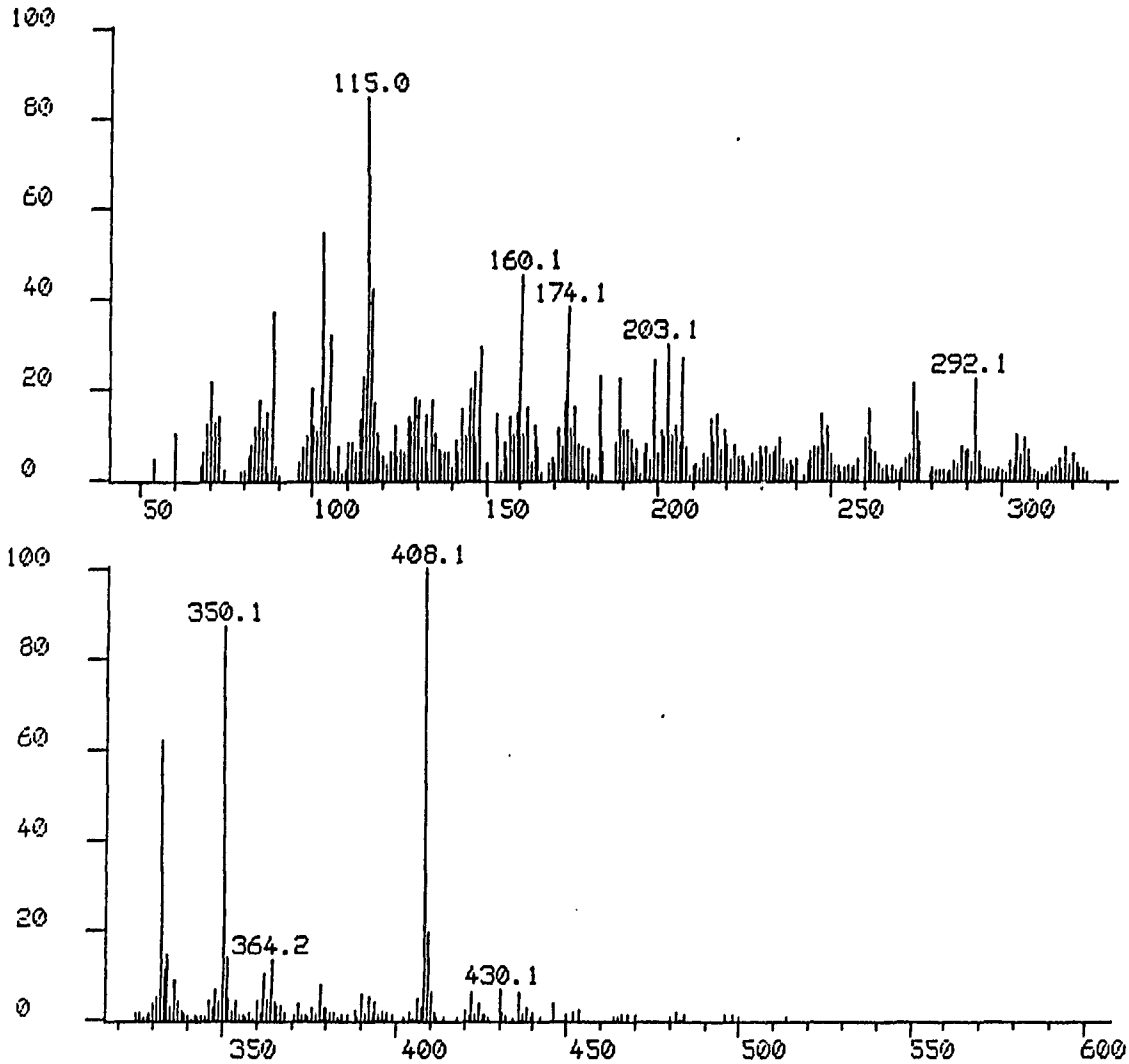


Figure 11. Fast-atom-bombardment mass spectrum of DTTAP

Other major peaks in the mass spectrum are due to fragments of the original DTTAP molecule. A list of fragments possessing the masses corresponding to these peaks is shown in Figure 12. The peak at 115.0 ($\frac{\text{mass}}{\text{charge}}$) is believed to be due to a species formed by glycerol (mwt = 92.1 amu) and sodium (mwt 22.99 amu) [37, 38].

Elemental analysis

A solid sample of the compound believed to be DTTAP was isolated for further characterization. An aqueous solution containing the ligand was evaporated to a syrup consistency at 50°C under a vacuum. The concentrated solution was then slowly added to a large volume of boiling ethanol until the solution began to get cloudy. The ethanol solution was cooled to room temperature. Overnight, a white precipitate formed which was isolated by suction filtration and dried at 70°C for eight hours:

mp = 159-162°C.

The dried solid was submitted to Desert Analytics for elemental analysis. The results are seen in Table 9.

The results show that the compound was isolated as the monohydrate.

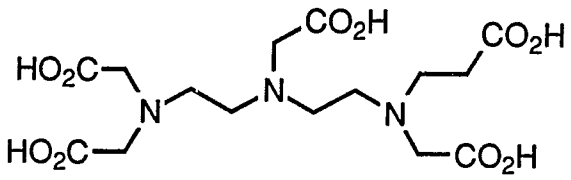
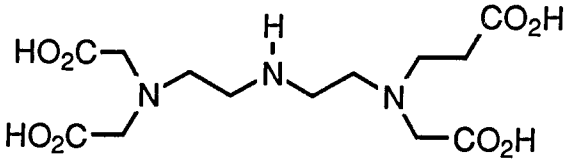
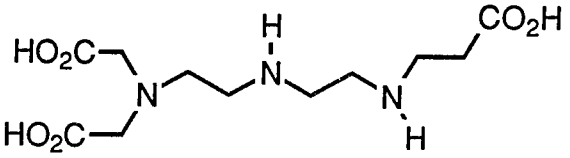
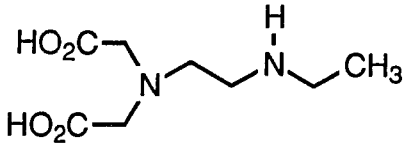
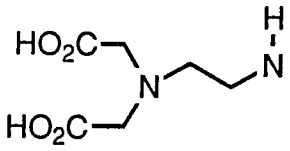
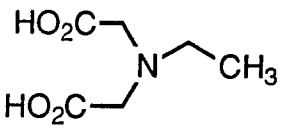
	Mass	Observed M+1
	407.1	408.1
	349.1	350.1
	291.1	292.1
	202.1	203.1
	173.1	174.1
	159.1	160.1

Figure 12. Possible fragments of DTTAP

Table 9. Elemental analysis for DTTAP

	Found	Calculated for $C_{15}H_{25}N_3O_{10}\cdot H_2O$
%C	42.09	42.35
%H	6.13	6.35
%N	9.44	9.88

DISCUSSION

The desired chelating agent, diethylenetriamine-N, N, N', N"-tetraacetic acid-N"-monopropionic acid (DTTAP) has been successfully prepared and extensively characterized. Successful synthesis of this compound requires two steps, and was achieved with some difficulty. The purification of DTTAP was achieved using a somewhat rare technique, anion-exchange displacement chromatography.

In the first step of the DTTAP synthesis, a 3.00 molar ratio of diethylenetriamine to 3-choloropropionate was used in order to maximize the formation of the two monopropionate products and minimize the formation of any dipropionate products or more highly substituted species. For both steps of the synthesis, the pH must be kept between 8 and 10. If the pH falls below 8, the reaction rate is slowed significantly because lower pH values are not adequate for efficient consumption of the HCl produced. If the pH is allowed to exceed 10, hydrolysis of the chloro-acids will occur. This would result in the formation of 3-hydroxypropionic acid and glycolic acid in the first and second steps, respectively. The ice-water baths were also used in the neutralization of these acids in order to prevent hydrolysis. The 24-hour reaction time reported for the first step of this synthesis represents the point at which the pH stayed above 8 for three hours without the addition of NaOH solution.

The end-substituted monopropionic acid intermediate species must be isolated in >99% purity. If, for example, the middle-substituted monopropionate or some dipropionate species were present upon treatment

with chloroacetic acid, several different triamino-pentacarboxylate products would result. The separation of these products would be extremely difficult. This situation is successfully avoided by using cation-exchange chromatography to isolate the pure end-substituted monopropionate from the other species produced in the first step.

A chloroacetate:monopropionate ratio of 4.4 is necessary for the second step of the DTTAP synthesis. Lower ratios result in incomplete substitution at the nitrogen atoms. Higher chloroacetate:monopropionate ratios result in the formation of DTPA. Isolation of pure DTTAP in the presence of DTPA was unsuccessful using fractional crystallization, cation-exchange chromatography, and other common chromatographic techniques.

Although cation-exchange displacement chromatography was successfully used to isolate the intermediate of this synthesis, this technique proved unsuccessful when used to isolate the final product. The major impurities of the second step are believed to be incompletely substituted tri- and tetra-carboxylic acids. DTTAP was isolated from these impurities using anion-exchange displacement chromatography.

Few examples of anion-exchange displacement chromatography have been reported in the literature. In 1952, Partridge and Brimley [39] reported the use of this technique for the separation of several mixtures of amino acids. This work demonstrates the tremendous value of this technique for resolving mixtures of aminocarboxylic acids possessing very similar pK values. Peterson and Torres [40] and Peterson [41] have reported the use of carboxymethyldextrans as spacers

and displacers in anion-exchange displacement chromatography. In these reports, dextran was carboxymethylated to varying degrees with chloroacetate. The derivatives containing the largest number of carboxylate groups (~400) were used as displacers, and the intermediately substituted derivatives were used as spacers in an anion-exchange separation of various proteins. Guéron et al. [42] reported the separation of mixtures of acrylic and methacrylic acids using anion-exchange displacement chromatography. In 1968, Coleman and Gilbert [43] showed that chromium (III) thiocyanate complexes can also be separated using this technique.

In this work, clean separation of compounds containing different numbers of carboxylate groups is achieved. The result is not surprising after reviewing the work of Peterson and Partridge.

The infrequent use of anion-exchange displacement chromatography is surprising. This work and the few examples that can be found in the literature illustrate that this technique deserves wider application for the large-scale separation of anionic species.

PART III. MATHEMATICS USED TO CALCULATE THE PROTONATION CONSTANTS OF DIETHYLENETRIAMINE-N, N, N', N"-TETRAACETIC ACID-N"-MONOPROPIONIC ACID AND THE FORMATION CONSTANTS OF THE COMPLEXES ITS ANIONS FORM WITH THE TRIVALENT LANTHANIDES

INTRODUCTION

The mathematical calculations used to determine the protonation constants of diethylenetriamine-N, N, N', N"-tetraacetic acid-N"-monopropionic acid are performed using a computer program developed by previous members of this research group [23, 44, 45].

The mathematical methods used to calculate the formation constants of the species formed by this ligand's anions with the lanthanide ions are also performed using a computer program designed by these individuals.

In both cases, slight modifications of these computer programs were incorporated in order to accommodate the properties of the pentaprotic acid.

PROTONATION CONSTANTS CALCULATION

The protonation of a pentacarboxylate anion (L) can be described by the following five equilibria:

$$L + H = HL$$

$$L + 2H = H_2L$$

$$L + 3H = H_3L$$

$$L + 4H = H_4L$$

$$L + 5H = H_5L \quad .$$

The equilibrium constants associated with these equilibria are commonly designated as alpha (α_N). Specifically, they are defined as:

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

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

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

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

$$\alpha_5 = \frac{[H_5L]}{[H]^5[L]} \quad .$$

The total proton concentration, H_t, may be expressed in terms of the alphas, free ligand concentration [L], and hydrogen ion concentration [H]:

$$H_t = [H] + [HL] + 2[H_2L] + 3[H_3L] + 4[H_4L] + 5[H_5L]$$

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

$$+ 4\,\alpha_4[H]^4[L] + 5\,\alpha_5[H]^5[L]$$

$$H_t - [H] = [L] \sum_1^5 N\,\alpha_N[H]^N \quad .$$

The total ligand concentration, L_t, can also be expressed in terms of the alphas, free ligand concentration [L], and hydrogen ion concentration [H]:

$$L_t = [L] + [HL] + [H_2L] + [H_3L] + [H_4L] + [H_5L]$$

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

$$+ \alpha_4[H]^4[L] + \alpha_5[H]^5[L]$$

$$= [L]\,(1 + \sum_1^5 \alpha_N\,[H]^N) \quad .$$

Taking the ratio $\{H_t - [H]\}/L_t$ eliminates [L] as shown:

$$\frac{H_t - [H]}{L_t} = \frac{\sum_{1}^{5} N \alpha_N [H]^N}{1 + \sum_{1}^{5} \alpha_N [H]^N} \quad .$$

Cross multiplication and rearrangement gives:

$$[H] - H_t = \sum_{1}^{5} (H_t - [H] - N L_t)\alpha_N [H]^N \quad .$$

The values of H_t and L_t are known for each ligand titration point and [H] is obtained from experimental measurement so that the only unknowns are α_1, α_2, α_3, α_4, and α_5.

In theory, these values can be solved by measuring a set of five solutions. In practice, however, more than five (in fact 10-20) sets are measured and the equations are solved using a least-squares multiple linear regression.

The computer program OMEGA, developed by Johnson [44] and Miller [45], was used to determine the five alpha values of the pentacarboxylate (see Appendix C). The least-squares analysis employed by this program has been described in detail by Tse [24].

The mathematical treatment of the data carried out by the computer program OMEGA will only be valid when two or more buffer regions of the ligand overlap. For diethylenetriamine-N, N, N', N"-tetraacetic acid-N"-monopropionic acid, however, there are two separate pH regions where there is adequate overlap of the individual buffer regions. In

the low pH region, the third, fourth, and fifth protonations overlap. In the high pH region, the first and second protonations overlap. The large difference in pH of the two buffer regions requires that the five α values be solved in two separate runs; one yielding values of α_3, α_4 and α_5, and the other yielding values for α_1 and α_2.

METAL-ANION STABILITY CONSTANTS CALCULATION

The equilibria between the trivalent lanthanide ions (M) and diethylenetriamine-N, N, N', N"-tetraacetate-N"-monopropionate pentaanion (L) and its protonated tetraanion (HL) are described as follows:

$$M + L = ML$$

$$M + HL = MHL \quad .$$

The equilibrium constants associated with these equilibria are commonly referred to as betas (e.g., β_{ML}). Specifically, they are defined as:

$$\beta_{ML} = K_{ML} = \frac{[ML]}{[M][L]}$$

$$\beta_{MHL} = K_{MHL} = \frac{[MHL]}{[M][HL]} \quad .$$

The values of K_{ML} and K_{MHL} can be determined using a complicated mathematical treatment developed by Potter [23], described in some detail by Tse [24]. The beta values are determined by equating two quadratic equations containing these unknowns, and arriving at one of many mathematical solutions by iteration.

The computer program HCMPLX, developed in this laboratory, was used to determine the stability constants of the diethylenetriamine-N, N, N', N"-tetraacetate-N"-monopropionate complexes with the lanthanide ions [23]. Slight modifications were incorporated into the HCMPLX program

in order to accommodate a pentaprotic acid ligand. The revised version of HCMPLX is listed in Appendix D.

This program makes use of the IMSL subroutine ZXSSQ, available at the Iowa State University Computation Center. The ZXSSQ subroutine requires an initial guess of the values of K_{ML} and K_{MHL} in order for the iteration to be initiated. The initial guess of beta values determines which mathematical solution is arrived upon by the ZXSSQ subroutine. Only one of the several possible mathematical solutions is acceptable and readily recognized. Other possible solutions may give negative beta values or values with negative exponents. If the initial values are too small, ZXSSQ usually converges to the trivial solution $K_{ML} = 0$, $K_{MHL} = 0$. The subroutine, in some cases, was found to converge to unacceptable solutions even with small deviations, less than a factor of ten, from the actual beta values.

The ZXSSQ subroutine gives K_{ML} and K_{MHL} values for each pair of data points and will handle up to ten data points or forty-three values of each beta. The averages of all acceptable K_{ML} and K_{MHL} values for each lanthanide-anion complex were calculated and reported as the calculated beta values.

PART IV. DETERMINATION OF THE PROTONATION CONSTANTS OF DIETHYLENE-TRIAMINE-N, N, N', N"-TETRAACETATE-N"-MONOPROPIONATE AND OF THE STABILITY CONSTANTS OF ITS COMPLEXES WITH THE TRIVALENT LANTHANIDES

INTRODUCTION

This section describes the experimental conditions employed for the determination of the protonation constants (α's) and the stability constants (K's) of diethylenetriamine-N, N, N', N"-tetracetate-N"-monopropionate and its anion-lanthanide complexes, respectively.

The calculated α and K values are reported and discussed extensively. It will be shown that the results obtained from this work are not unexpected.

A discussion of the possible role this ligand could play in the separation of Am from nuclear waste mixtures will also be presented.

EXPERIMENTAL

This section describes the materials and experimental procedures used to determine the alphas and betas for diethylenetriamine-N, N, N', N"-tetraacetate-N"-monopropionate and its anion-lanthanide complexes, respectively.

Determination of Protonation Constants

Reagents

Potassium hydroxide solution A standard potassium hydroxide solution was prepared by dilution of a carbonate-free KOH ampoule obtained from J. T. Baker Chemical Company. The ampoule was diluted with deionized condensed steam. Deionization of the condensed steam was achieved by passing it through a mixed bed of cation- and anion-exchange resins. The carbonate-free KOH solution was protected from atmospheric moisture and carbon dioxide with a Drierite/Ascarite trap. The KOH solution was standardized by pH titration with carefully measured masses of dry primary-standard-grade potassium hydrogen phthalate.

Concentration KOH = .0610M

Potassium nitrate solution A 1.002M KNO_3 solution was prepared by dissolving a carefully measured mass of analytical-grade KNO_3 into deionized condensed steam. Deionization is achieved by passing the condensed steam through a mixed bed of cation and anion-exchange resins. Dilution to the mark on a clean 2000-ml volumetric

flask provided an accurate volume measurement.

Standard HNO_3 solution, pH_c = 2.740 A nitric acid solution was prepared by dilution of concentrated reagent grade HNO_3 with deionized condensed steam and was standardized by titration with standard KOH solution. An appropriate amount of KNO_3 solution was added to provide an ionic strength of .100 ± .002 M.

Standard KOH solution, pH_c = 10.881 A KOH solution was prepared by dilution of a carbonate-free KOH solution with deionized condensed steam. The solution was standardized by titration with standard HNO_3 solution. An appropriate amount of KNO_3 solution was added to provide an ionic strength of .100 ± .002 M. The hydrogen-ion concentration of this solution was calculated using the value of the water constant at μ = .100 M ionic strength at 25°C given by Harned and Owen [46].

Ligand solution A 0.01110M solution of diethylenetriamine-N, N, N', N"-tetraacetic acid-N"-monopropionic acid was prepared by dilution with deionized condensed steam of the pure concentrated solution which was prepared as described in Part II of this dissertation. The solution was standardized by several potentiometric titrations with standard KOH solution.

Experimental procedure

The five alpha values for diethylenetriamine-N, N, N', N"-tetraacetic acid-N"-monopropionic acid (DTTAP) were determined using two separate sets of DTTAP solutions. Solutions prepared at high pH

(8.7-10) were used to determine α_1 and α_2, and solutions prepared at low pH (2.8-6) were used to determine α_3, α_4, and α_5. Nineteen solutions were prepared in all; twelve of which were low pH solutions, and seven of which were high pH solutions.

Each of the nineteen solutions was prepared by combining 4.00 ml of ligand solution, a measured amount of standard KOH solution, and an appropriate amount of KNO_3 solution to produce a .100 M ionic strength. The required amount of KNO_3 was calculated for each solution using the computer program ALPHA, developed in this laboratory (see Appendix A). The solutions were all diluted to 25.00 $\pm$ .01 ml with deionized condensed steam. The specific content of each solution may be seen in Appendix E.

After preparation, the solutions were equilibrated for eight hours in a constant temperature water bath at 25.00 $\pm$ .05°C, prior to measurement of pH_c.

The pH_c of each solution was measured using a Beckman model 1019 research pH meter equipped with a Phoenix model 5733928 sealed calomel electrode. The meter was standardized to measure pH_c directly with standard HNO_3 solution (pH_c = 2.740) and standard KOH solution (pH_c = 10.881), each adjusted to .10 M ionic strength.

The five alpha values were calculated from the solution data using the computer program OMEGA, described in Part III.

Determination of Lanthanide-Anion Stability Constants

Reagents

Potassium hydroxide solution The standard potassium hydroxide solution described in the previous section was used for the determination of the metal-anion stability constants.

Potassium nitrate solution The potassium nitrate solution described in the previous section was used for the determination of the metal-anion stability constants.

Standard HNO_3 solution, $pH_c = 2.740$ The standard HNO_3 solution described in the previous section was used for the determination of the metal-anion stability constants.

Ligand solution The 0.01110M DTTAP solution described in the previous section was used for the determination of the metal-anion stability constants.

Trivalent lanthanide nitrate solutions Approximately 0.1 M lanthanide nitrate solutions were prepared by dilution of concentrated stock solutions. These solutions were prepared from Ln_2O_3 samples of 99.999% purity using the method described by Adolphson [47]. Solutions of all lanthanides were prepared, except promethium, all possessing a $3.000 \pm .05$ ratio of nitrate:metal. $Ce(NO_3)_3$ is the one exception where a slight excess of HNO_3 is present in order to prevent precipitation of Ce(IV) hydroxide. The stock metal solutions have been sealed and checked periodically over the years and were found to show no change in concentration [48]. The solutions for this work were the same solutions used by Powell and Ling [25]. The La, Nd and

Sm nitrate solution concentrations were rechecked using standard DTTAP solution and found to be unchanged from Ling's work.

Experimental procedure

The values of K_{ML} and K_{MHL} were determined for the complexes formed by DTTAP with the elements La-Lu, excluding Pm, using 8-10 carefully prepared solutions for each metal-DTTAP system.

Each of the solutions was prepared by combining 4.00 ml of ligand solution, a measured amount of standard KOH solution, a measured amount of metal nitrate solution, and an appropriate amount of KNO_3 solution to produce a .100 M ionic strength. The required amount of KNO_3 was calculated for each solution using the computer program BETA which was developed in this laboratory (see Appendix B). The volume of metal-nitrate solution was selected to provide an approximate one-to-one ratio of metal to ligand. The solutions were all diluted to 25.00 $\pm$ .01 ml with deionized condensed steam. The specific content of each solution may be seen in Appendix F.

After preparation, the solutions were equilibrated for 12-16 hours in a constant temperature water bath at 25.00 $\pm$ .05°C, prior to measurement of pH_c.

The pH_c of each solution was measured using a Beckman model 1019 research pH meter equipped with a Phoenix model 5733928 sealed calomel electrode. The meter was standardized to measure pH_c directly with the standard HNO_3 solution (pH_c = 2.740) described previously.

The values of K_{ML} and K_{MHL} for each lanthanide-DTTAP system were calculated from the solution data using the computer program HCMPLX, described in Part III.

RESULTS AND DISCUSSION

Protonation Constants

The protonation constants for diethylenetriamine-N, N, N', N"-tetraacetic acid-N" monopropionic acid (DTTAP) have been determined experimentally for the first time in this work. The alpha values are displayed in Table 10 along with the logarithms of the five stepwise protonation constants (pK_a values).

The values of the fourth and fifth stepwise protonation constants indicate that DTTAP is a weaker acid than DTPA in the lower pH region. The values of the logarithms of the stepwise protonation constants of DTPA are shown in Table 11, as reported by Smith and Martell [26]. These results are expected, when considering that the only difference between the two ligands is that in DTTAP a propionate group has replaced one acetate group on one end of the DTPA ligand. The propionate group, being less acidic, retains a proton at higher pH values than the acetate group. It is also observed that three protons are dissociated at low pH and the two remaining protons are dissociated at high pH. These two most tightly bound protons are each stabilized by association with two carboxylate groups and one nitrogen atom, at opposite ends of the molecule. Keeping in mind the relative acidities of propionic and acetic acid groups, and the stabilities associated with five and six membered chelate rings, the following order of proton dissociation is proposed:

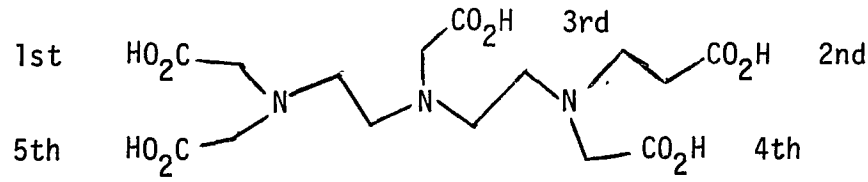
Table 10. Protonation constants for the DTTAP anion at 25.00 ± .05°C (μ=.10)

α_N	log K	K
$\alpha_1 = \frac{[HL]}{[H][L]} = 4.35\times10^{9}$	9.64	$\frac{[HL]}{[H][L]}$
$\alpha_2 = \frac{[H_2L]}{[H]^2[L]} = 3.18\times10^{18}$	8.86	$\frac{[H_2L]}{[H][HL]}$
$\alpha_3 = \frac{[H_3L]}{[H]^3[L]} = 1.05\times10^{23}$	4.52	$\frac{[H_3L]}{[H][H_2L]}$
$\alpha_4 = \frac{[H_4L]}{[H]^4[L]} = 3.69\times10^{26}$	3.54	$\frac{[H_4L]}{[H][H_3L]}$
$\alpha_5 = \frac{[H_5L]}{[H]^5[L]} = 2.26\times10^{29}$	2.79	$\frac{[H_5L]}{[H][H_4L]}$

Table 11. Stepwise protonation constants for DTPA[a] at 25°C (μ=.10)

Equilibrium	log K
$\frac{[HL]}{[H][L]}$	10.45
$\frac{[H_2L]}{[H][HL]}$	8.53
$\frac{[H_3L]}{[H][H_2L]}$	4.28
$\frac{[H_4L]}{[H][H_3L]}$	2.65
$\frac{[H_5L]}{[H][H_4L]}$	1.82

[a]DTPA = diethylenetriaminepentaacetic acid.



Metal-Anion Stability Constants

The lanthanide-DTTAP stability constants have been determined experimentally for the first time in this work. The beta values are displayed in Table 12.

The stability of the ML complexes increases across the series from La to Eu. After reaching a maximum at Eu, a slight decrease in stability is observed until Tb, followed by some relatively small changes for the rest of the lanthanides. A plot of the log K_{ML} values vs. the metal-ionic radius is shown in Figure 13 for DTTAP and several other ligands [25, 26, 32]. The DTTAP ligand shows an overall stability with the lanthanides of about 10^3 times lower than that of DTPA. The maximum ligand affinity for DTTAP at Eu represents a shift of the maximum relative to that of DTPA.

The overall magnitude of the lanthanide-DTTAP complexes is expected. A 10^3-fold attenuation in overall magnitude of the stability constants is also observed when comparing the lanthanide-ligand stabilities of DETAP with EEDTA, as seen in Figure 13. The 10^3-fold attenuation in overall stability is explained in both cases by the

Table 12. Stability constants of trivalent lanthanide-DTTAP complexes at 25.00 ± .05°C (μ=.10)

M	K_{mHL}	log K_{mHL}	K_{ML}	log K_{ML}
La	0.2423×10^{12}	11.38	0.2434×10^{18}	17.39
Ce	0.1769×10^{13}	12.25	0.1772×10^{19}	18.25
Pr	0.6043×10^{13}	12.78	0.4392×10^{19}	18.64
Nd	0.9416×10^{13}	12.97	0.8623×10^{19}	18.94
Sm	0.2508×10^{14}	13.40	0.3815×10^{20}	19.58
Eu	0.2290×10^{14}	13.36	0.5592×10^{20}	19.75
Gd	0.2389×10^{14}	13.38	0.5515×10^{20}	19.74
Tb	0.3527×10^{14}	13.55	0.3308×10^{20}	19.52
Dy	0.3260×10^{14}	13.51	0.3477×10^{20}	19.54
Ho	0.2583×10^{14}	13.41	0.2805×10^{20}	19.45
Er	0.1914×10^{14}	13.28	0.2189×10^{20}	19.34
Tm	0.1300×10^{14}	13.11	0.2553×10^{20}	19.41
Yb	0.1461×10^{14}	13.16	0.3270×10^{20}	19.51
Lu	0.1224×10^{14}	13.09	0.2202×10^{20}	19.34

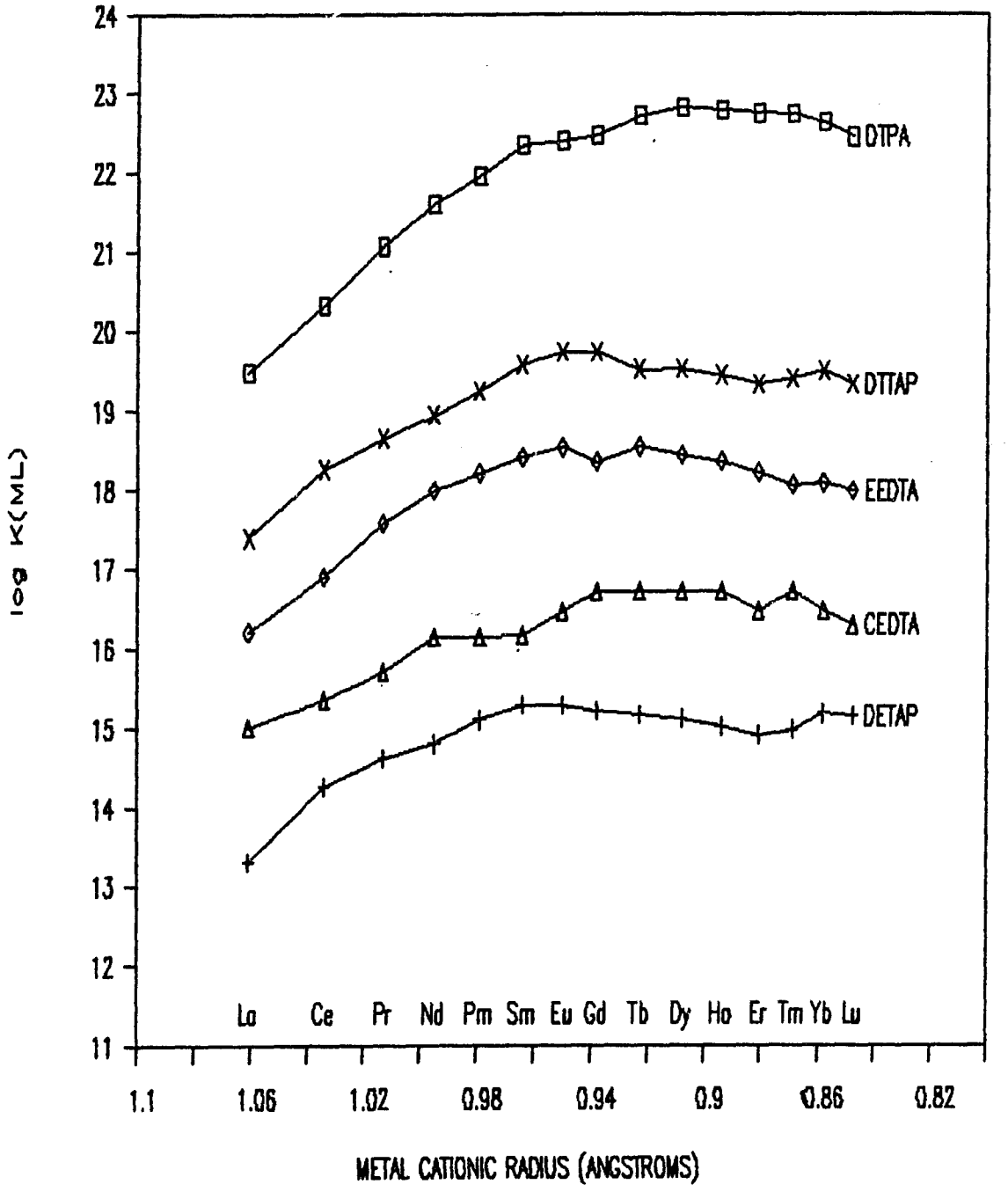
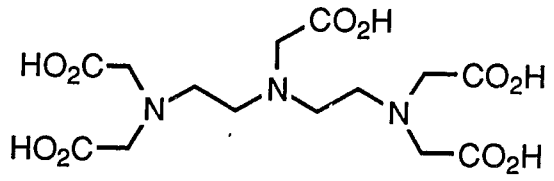


Figure 13. Stability constants of some lanthanide-anion complexes as a function of metal cationic radius

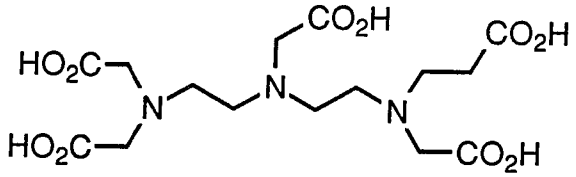
replacement of an acetate group, capable of forming stable 5-membered chelate rings, with a propionate group which would form less stable 6-membered rings upon chelation (see Figure 14). Furthermore, if the acetate group bonded to the middle nitrogen of DTPA is replaced with a propionate group, a more drastic 10^6-fold attenuation in overall stability is observed. This attenuation is shown by the comparison of the stabilities of the lanthanide-DTPA complexes with those of CEDTA [32]. A less drastic attenuation in overall stability is expected by the replacement of an acetate bonded to an end nitrogen of DTPA because a bulky chelate ring at the end nitrogen should not affect other chelate rings as much as a bulky chelate ring in the middle of the ligand.

The shift of the Ln-ligand stability maximum from right to left is also expected for the DTTAP function compared to the DTPA function. A similar shift of the Ln-ligand stability maximum is observed when considering the DETAP function compared to the EEDTA function. Both shifts are explained by a change in dentate character of the ligand across the lanthanide series. The size of the coordination sphere of the trivalent lanthanides diminishes significantly from La to Lu. It is reasonable to assume that a large ligand such as DTTAP or DTPA would coordinate in an octadentate fashion to the larger lanthanide ions and be forced to coordinate in a lower-dentate fashion to the smaller lanthanide ions. In progressing from La to Lu, the large polyaminopolycarboxylate ligands most likely experience a breaking of at least one of the chelate rings in order to coordinate the smaller

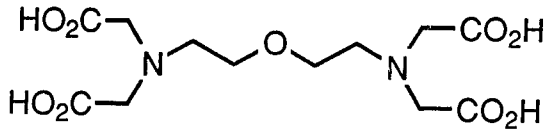
DTPA:



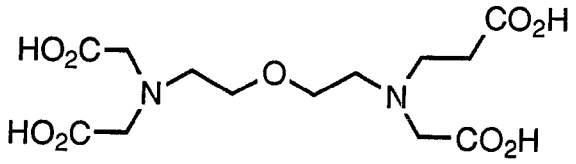
DTTAP:



EEDTA:



DETAP:



CEDTA:

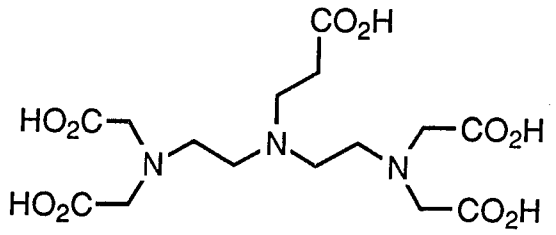


Figure 14. Key for identifying some polyaminopolycarboxylate ligands

ions with a minimum of steric hindrance. This decrease in coordination number of aqueous lanthanide ions across the series is generally agreed upon by experts in this field [49-51]. By replacement of an acetate group with a propionate group, a ligand will have a more strained 6-membered chelate ring that will be likely to "fail" faster than the more sterically-favored five-membered chelate ring offered by the acetate group. DTTAP, therefore, shows an earlier turnover in the log K_{ML} vs. ionic radius function due to an earlier failure of its octadentate character relative to that of DTPA. This premature failure of the octadentate character, caused by the strained ring, is apparently damaging enough to effect the rest of the series. This is illustrated by the fact that the stability constant values do not increase as much as those of DTPA when the heptadentate character takes over in the Gd-Tb range.

The minimum Am-Ln separation factor (α_{Ln}^{Am}) can be estimated by interpolation, as explained by Powell and Ling [25]. The Am-Nd separation factor (α_{Nd}^{Am}) varies with the value of K_{NdL} as shown in Figure 15.

Since the cationic radius of Am(III) is nearly identical to that of Nd(III), the difference in affinity of these ions for polyaminopoly-carboxylate ligands is explained mostly by the higher effective nuclear charge of Am(III). These largely electrostatic attractions are exemplified by the rapid exchange of lanthanide and actinide cations with polyaminopolycarboxylates and cation-exchange resin. Also, the K_{AmL} is always larger than K_{NdL} with these types of ligands, and the

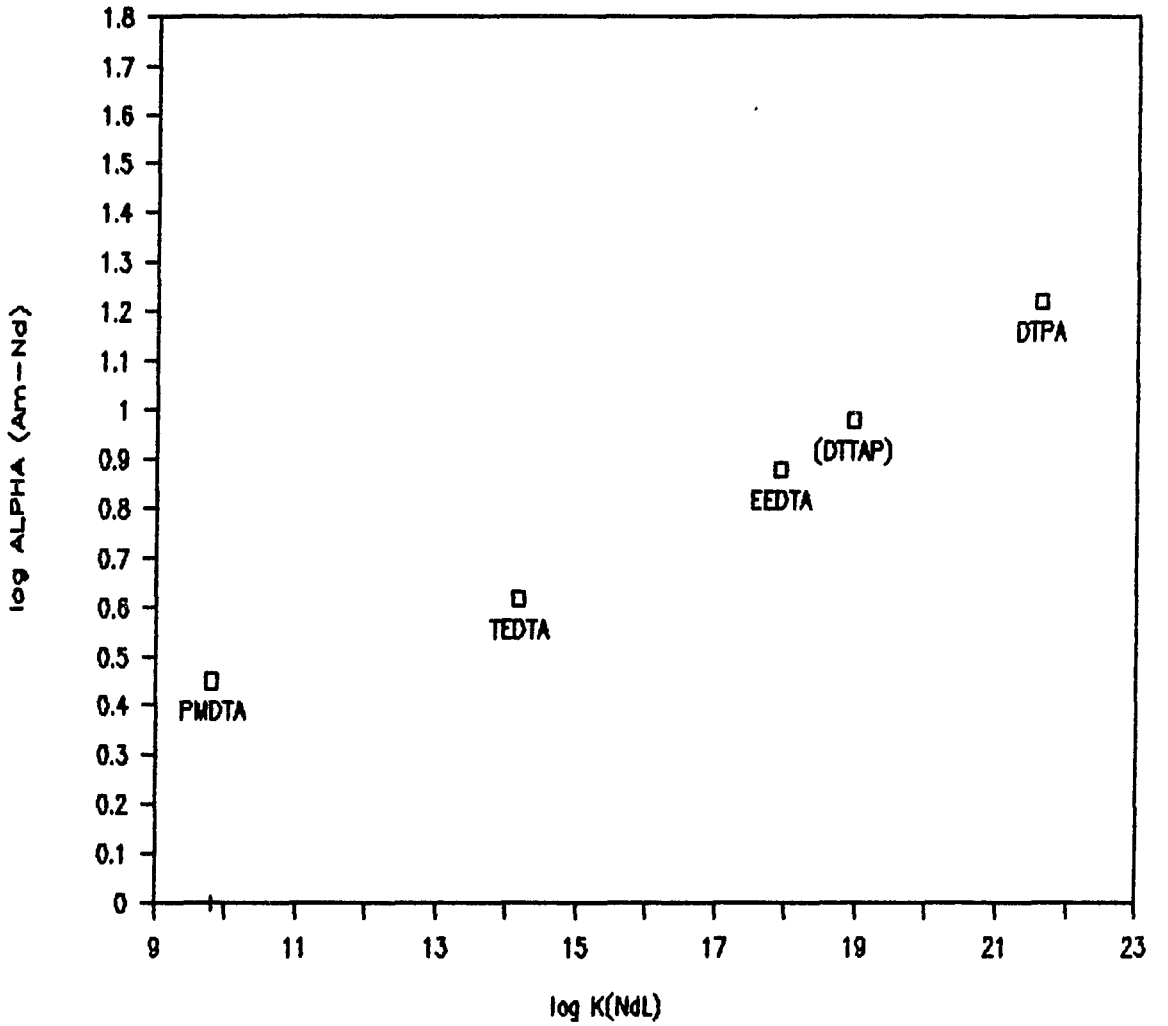


Figure 15. Am^{3+}-Nd^{3+} separation factors as a function of affinity [25]

difference between K_{AmL} and K_{NdL} has been shown to increase with the overall magnitudes of K_{NdL} [24, 31, 52, 53].

The estimated logarithm of the Am-Nd separation factor for DTTAP, by interpolation, is .98. If one subtracts the difference (log K_{EuL} - log K_{NdL}) from .98, the log α_{Eu}^{Am} value is estimated:

$$\log \alpha_{Eu}^{Am} = .17$$

$$\alpha_{Eu}^{Am} = 1.48 \quad .$$

The estimated minimum separation factor of 1.48 for Am and the strongest complexing lanthanide ion do not represent the largest separation factor known for these systems. EEDTA provides a known α_{Eu}^{Am} value of 1.7, which is the largest known to date.

The value of 1.48 for α_{Eu}^{Am} estimated in this work, suggests that DTTAP is a chelating agent capable of effecting a separation of Am from a mixture of the lanthanides, even though it may not be the most efficient ligand for this purpose.

Although the Am-Ln separation factor estimated for the DTTAP system is slightly less than the 1.7 value observed for EEDTA, one should keep in mind that 1.48 is the minimum estimated α_{Ln}^{Am} value, and that the actual value may be larger.

The value of log α_{Nd}^{Am} for DTTAP could be more on the order of 1.22. This would result in a value of 2.57 for α_{Eu}^{Am}.

There is some precedent for considering the higher value of α_{Nd}^{Am} for DTTAP. In 1985, Powell and Ling [25] reported a log α_{Y}^{Ho} value of .73 for the DETAP system. This value is very close to the log α_{Y}^{Ho} value observed for the EEDTA system, despite the considerable difference in overall stability of the HoL complexes (see Figure 16). While the replacement of an acetate ligand with a propionate resulted in a change in overall stability of HoL and YL complexes, the difference in stability between Ho-DETAP and Y-DETAP complexes was about the same as the difference in stabilities between Ho-EEDTA and Y-EEDTA complexes. The difference in electrostatic attractions was unchanged within the complexes by the replacement of acetate with propionate. Since the same type of electrostatic differences in Y(III) and Ho(III) are known for Nd(III) and Am(III), it is not unreasonable to consider the possibility of a log α_{Nd}^{Am} value for DTTAP close to that of DTPA. This consideration would result in a very attractive value for α_{Ln}^{Am} of 2.57; far superior to any separation factor observed to date for these systems.

DTTAP is very soluble in water. Once the ligand is in aqueous solution, it is impossible to isolate by evaporation of the water. A concentrated solution of syrup-consistency is observed.

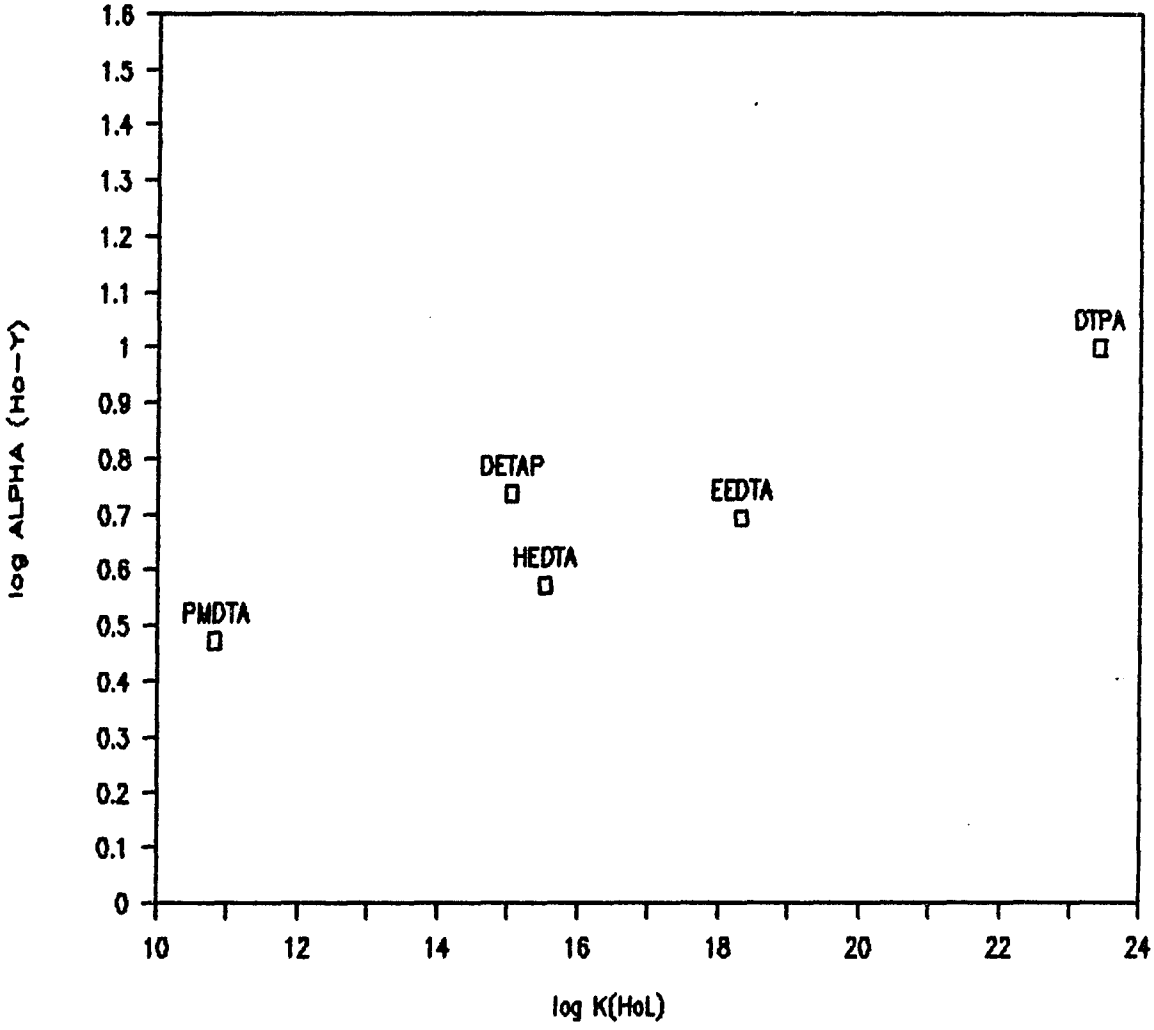


Figure 16. Ho^{3+}-Y^{3+} separation factors as a function of affinity [25]

CONCLUSIONS

A new polyaminopolycarboxylate ligand, DTTAP, has been synthesized, purified, and extensively characterized. The synthesis of this ligand is difficult and the yield obtained with the present procedure is very low. The purification of DTTAP was achieved using a relatively rarely-used technique: anion-exchange displacement chromatography. The new ligand was characterized using ^{13}C NMR spectroscopy, fast-atom bombardment mass spectrometry, elemental analysis, and potentiometric titration data.

The extensive characterization and purification of this ligand are both essential to the integrity of this work. The ligand must be >99.9% pure. If there were any impurities present, large errors in the computer-assisted calculations of the α and β values would result. Extensive characterization insures the purity of the ligand. ^{13}C NMR spectroscopy is a valuable tool for identifying these types of compounds, where the presence of isomers is possible and is undetectable by elemental analysis, mass spectrometry, or titration data.

The values of the stability constants of the lanthanide-DTTAP complexes have been calculated for the first time. This ligand shows an overall attenuation of about 10^3-fold for its Ln-ligand stability constant values relative to DTPA. A shift in the stability constant maximum, toward the lighter lanthanides, is also observed for this ligand relative to DTPA. These observations are not unexpected.

These data provide some information about the nature of chelation of these types of ligands across the lanthanide series. The results indicate that the dentate character of these polyaminopolycarboxylates is changing across the lanthanide series, and can be made to change earlier by weakening one of the chelate rings.

Future Work

This work with DTTAP represents a step in the right direction. Although this ligand shows much promise for use in Ln/An separations, there is still much more to investigate before a cost-efficient large-scale separation of Am and Cm from the lanthanides can be implemented.

The α_{Eu}^{Am} separation factor needs to be determined experimentally for DTTAP. If the α_{Eu}^{Am} is good enough to consider large-scale applications of this ligand, then the synthetic procedure should be re-examined. Presently, the yield of the pure DTTAP ligand is too low to provide for the cost-efficient use of this ligand on an industrial scale.

The syntheses and separation properties of other ligands need to be investigated before the decision can be made as to which ligand will be used for the large-scale Ln/An separations. Modifications of DTPA are the most promising, because of the attenuation in the overall stability constant values associated with weakening one of the chelate rings. It would be interesting to evaluate the stability constants of the complexes formed by the lanthanides with the end-end-dipropionate-triacetate derivative of DTPA. Replacing an acetate with bulky groups

other than the propionate group may also provide interesting properties that could improve the existing separation capabilities of these polyaminopolycarboxylate ligands. Such groups include 2-methylacetate, 2-phenylacetate, and 2, 2-dimethylacetate.

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APPENDIX A. COMPUTER PROGRAM ALPHA

```
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                .
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
CC          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),VHNO3(100),VBFR(50)
         INTEGER HTIT
         DOUBLE PRECISION BOT,TOP,OTHER,UA
        READ(5,1)(TITE(I),I=1,20)
       READ(5,2)N,NN,HTIT,CBFRAC,CBFRAN,CHNO3,FINV,CKNO3,US
       READ(5,3)(ALPHA(I),I=1,NN)
       READ(5,4)(VBFR(I),VBASE(I),VHNO3(I),I=1,N)
       ERR=0.001
       CACID=(CBFRAC+CBFRAN)*2.
       CBASE=CBFRAN*2.
       DO 5 I= 1,N
       VACID(I)=VBFR(I)/2.
       VBASE(I)=VACID(I)
    5  CONTINUE
        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
   10 HINC=HT/HFAC
   20 H=H+HINC
       HPH=-ALOG10(H)
       ANBAR=(HT-H+10**(-13.9069+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)CBFRAC,CBFRAN
      WRITE(6,203)CKNO3
       WRITE(6,204)FINV,US
      WRITE(6,205)
      WRITE(6,206)(L,VBFR(L),APH(L),CNBAR(L),VKNO3(L),L=1,N)
       WRITE(6,207)NN
      WRITE(6,208)(IW,ALPHA(IW),IW=1,NN)
 1     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,'BUFFER ACID CONCENTRATION = ',T40,F8.5,T55,'BUFFER ANION CONCEN
     1TRATION = ',T90,F8.5)
 203  FORMAT(T2,'POTASSIUM NITRATE CONCENTRATION = ',T40,F8.5)
 204  FORMAT(T2,'FINAL VOLUME =',T39,F7.3,T55,'IONIC STRENGTH =',T90,
     1F8.5/)
 205  FORMAT('   (I)',3X,'VBFR',6X,'PH',8X,'NBAR',6X,'VOL KNO3')
 206   FORMAT(3X,I2,4X,F8.3,2X,F8.4,2X,F8.3,2X,F8.3)
 207  FORMAT('0ASSUMED PROTONATION CONSTANTS  ALPHA(1)-ALPHA(',I2,')'/)
 208  FORMAT(6X,I2,6X,E12.5)
      RETURN
      END
$ENTRY
```

APPENDIX B. COMPUTER PROGRAM BETA

```
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               CKNO  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(M)=BNBAR
      APH(M)=-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(M)/FINV
      UC=0.5*10.0**(-APH(M))
      UD=0.5*10.0**(-13.8069+APH(M))
      UE=0.5*ZC*MT
      UF=0.5*MT*(ZC-BNBAR*ZA)**2
      UA=UA-UB+UC+UD+UE+UF
      VKNO(M)=((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)US
      WRITE(6,215)FINV
      WRITE(6,206)
      WRITE(6,207)(L,VBASE(L),APH(L),CNBAR(L),VKNO(L),L=1,NN)
      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)
  206 FORMAT(' (I)',T9,'VBASE',T19,'PH',T29,'NBAR',T39,'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)
```

```
  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/)
      RETURN
      END
$ENTRY
```

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,CKNO,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))
   60 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),
     1ETA(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)**M*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
$ENTRY
```

APPENDIX D. COMPUTER PROGRAM HCMPLX

```
C PROGRAM HCMPLX
C THIS PROGRAM CALCULATES BMHLAND BML FOR METAL ION AND ACIDS OF THE FORM H5L
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     ALPHA(5)
C     COL 61   E10.5     TBETA(1)  BETA(MHL)
C     COL 71   E10.5     TBETA(2)  BETA(ML)
C CARD 4  THROUGH N+3
C     COL  1   F10.5     LIGVOL(N)
C     COL 11   F10.5     BASVOL(N)
C     COL 21   F10.5     METVOL(N)
C     COL 31   F10.5         PH(N)
      IMPLICIT REAL*8 (A-H,O-Z),INTEGER(I-N)
      REAL*8 IONSTR,LIGCON,LIGVOL,METCON,METVOL,MTOT
      DIMENSION R(10),S(10),T(10),U(10),V(10),W(10),X(10),Y(10),Z(10),AL
     1PHA(5),TBETA(2),WA(20),TITLE(20),LIGVOL(10),BASVOL(10),MET
     2VOL(10),PH(10),PARM(4),FFF(2),XJAC(2,2),XJTJ(3),WORK(17)
      COMMON/XX/PAR(18)
      EXTERNAL FUNCT
C   TRAPS ALLOWS  THE PROGRAM TO CONTINUE AFTER AN EXPONENTIAL UNDERFLOW
      CALL TRAPS(0,0,32767,0,0)
  400 READ(5,10,END=2000)(TITLE(I),I=1,20)
      READ(5,20)LIGCON,BASCON,METCON,SLTCON,FINVOL,IONSTR
      READ(5,30)N,ALPHA(1),ALPHA(2),ALPHA(3),ALPHA(4),ALPHA(5),TBETA(1),
     1TBETA(2)
      READ(5,40)(LIGVOL(I),BASVOL(I),METVOL(I),PH(I),I=1,N)
      WRITE(6,50)
      WRITE(6,10)(TITLE(I),I=1,20)
      WRITE(6,60)LIGCON,BASCON,METCON
      WRITE(6,70)SLTCON,FINVOL,IONSTR
      WRITE(6,80)(I,ALPHA(I),I=1,5)
      WRITE(6,90)TBETA(1)
      WRITE(6,100)TBETA(2)
      WRITE(6,110)
      WRITE(6,120)(I,LIGVOL(I),BASVOL(I),METVOL(I),PH(I),I=1,N)
C  THIS DO LOOP CALCULATES COEFFICIENTS A-F
      DO 500 I=1,N
      H=10.0**(-PH(I))
      MTOT=METCON*METVOL(I)/FINVOL
      ATOT=LIGCON*LIGVOL(I)/FINVOL
      HTOT=(LIGCON*5.0*LIGVOL(I)/FINVOL)-(BASCON*BASVOL(I)/FINVOL)
      A=1.0+ALPHA(1)*H+ALPHA(2)*H**2.0+ALPHA(3)*H**3.0+ALPHA(4)*H**4.0+
     1ALPHA(5)*H**5.0
      B2=(MTOT-ATOT)
      C2=(-MTOT)
      D=ALPHA(1)*H+2.0*ALPHA(2)*H**2.0+3.0*ALPHA(3)*H**3.0+4.0*ALPHA(4)*
     1H**4.0+5.0*ALPHA(5)*H**5.0
```

```
      E1=ALPHA(1)*H*(MTOT-HTOT+H)
      E2=H-HTOT
      B3=-A
      B1=ALPHA(1)*H*B2
      C1= ALPHA(1)*H*C2
      E3=-D
      F=C1
      R(I)=A*C2*E2*E2-D*C2*E2*B2
      S(I)=B2*B2*D*F-A*F*E2*B2-D*C1*E2*B2-D*C2*E1*B2-D*C2*E2*B1+A*C1*E2*
     1E2+2.0*A*C2*E1*E2
      T(I)=C2*C2*D*D-D*C2*E2*B3-D*C2*B2*E3+2.0*A*C2*E2*E3
      U(I)=2.0*C1*C2*D*D-2.0*A*D*C2*F+2.0*B2*B3*D*F-A*F*B2*E3-A*F*E2*B3-
     1D*C1*E2*B3-D*C1*B2*E3-D*C2*E1*B3-D*C2*E3*B1+2.0*A*C1*E2*E3+2.0*A*C
     22*E1*E3
      V(I)=0.0
      W(I)=0.0
      X(I)=A*A*F*F-2.0*A*D*C1*F+C1*C1*D*D+2.0*B1*B3*D*F-A*F*E1*B3-A*F*E3
     1*B1-D*C1*E1*B3-D*C1*E3*B1+2.0*A*C1*E1*E3
      Y(I)=2.0*B1*B2*D*F-A*F*E1*B2-A*F*E2*B1-D*C1*E1*B2-D*C1*E2*B1-D*C2*
     1E1*B1+A*C2*E1*E1+2.0*A*C1*E1*E2
      Z(I)=B1*B1*D*F-A*B1*E1*F-E1*B1*C1*D+A*C1*E1*E1
  500 CONTINUE
      DO 81 I=1,N
      R(I)=R(I)*1.0D-50
      S(I)=S(I)*1.0D-50
      T(I)=T(I)*1.0D-50
      U(I)=U(I)*1.0D-50
      V(I)=V(I)*1.0D-50
      W(I)=W(I)*1.0D-50
      X(I)=X(I)*1.0D-50
      Y(I)=Y(I)*1.0D-50
      Z(I)=Z(I)*1.0D-50
   81 CONTINUE
C THIS SECTION NOW PICKS TWO POINTS AT A TIME AND CALCULATES BMHL AND BML
      IXJAC=2
      NN=2
      MM=2
      FBETA1=TBETA(1)
      FBETA2=TBETA(2)
      M=N-1
      DO 1000 I=1,M
      L=I+1
      DO 900 J=L,N
      WRITE(6,130)I,J
      PAR(1)=R(I)
      PAR(2)=S(I)
      PAR(3)=T(I)
      PAR(4)=U(I)
      PAR(5)=V(I)
      PAR(6)=W(I)
      PAR(7)=X(I)
      PAR(8)=Y(I)
      PAR(9)=Z(I)
      PAR(10)=R(J)
      PAR(11)=S(J)
      PAR(12)=T(J)
      PAR(13)=U(J)
      PAR(14)=V(J)
      PAR(15)=W(J)
      PAR(16)=X(J)
```

```
      PAR(17)=Y(J)
      PAR(18)=Z(J)
C     THIS SECTION NOW CALCULATES BMHL AND BML USING IMSL ROUTINE ZXSSQ
      EPS=1.0D-70
      IOPT=1
      MAXFN=500
      DELTA=0.0D0
      NSIG=4
      K=2
      ITMAX=20
      IXJAC=2
      CALL ZXSSQ (FUNCT,MM,NN,NSIG,EPS,DELTA,MAXFN,IOPT,PARM,TBETA,
     1SSQ,FFF,XJAC,IXJAC,XJTJ,WORK,INFER,IER)
      WRITE(6,140)ITMAX
      WRITE(6,160)TBETA(1)
      WRITE(6,170)TBETA(2)
      TBETA(1)=FBETA1
      TBETA(2)=FBETA2
      WRITE(6,180)SSQ
      WRITE(6,190)FF
      WRITE(6,200)INFER
      WRITE(6,210)IER
  900 CONTINUE
 1000 CONTINUE
      GO TO 400
 2000 STOP
   10 FORMAT(20A4)
   20 FORMAT(6F10.5)
   30 FORMAT(I2,8X,7D10.4)
   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)
  160 FORMAT(' BMHL = ',D28.16)
  170 FORMAT(' BML = ',D28.16)
  180 FORMAT('   SSQ= ',E12.4)
  190 FORMAT('    FF= ',9E12.4)
  200 FORMAT(' INFER= ',I2)
  210 FORMAT('   IER= ',I4)
      END
C     WHERE THE SUBROUTINE FUNCT HAS THE FOLLOWING CODE
      SUBROUTINE FUNCT(TBETA,M,N,AUX)
      INTEGER K
      REAL*8 TBETA(2),PAR,AUX(2)
      COMMON/XX/PAR(18)
      AUX(1)=PAR(1)*TBETA(2)**3+PAR(2)*(TBETA(2)**2)*TBETA(1)+PAR(3)*T
     2BETA(2)**2+PAR(4)*TBETA(2)*TBETA(1)+PAR(5)*TBETA(2)+PAR(6)*TBETA
     3(1)+PAR(7)*TBETA(1)**2+PAR(8)*(TBETA(1)**2)*TBETA(2)+PAR(9)*
     4TBETA(1)**3
      AUX(2)=PAR(10)*TBETA(2)**3+PAR(11)*(TBETA(2)**2)*TBETA(1)+PAR(12)
     2*TBETA(2)**2+PAR(13)*TBETA(2)*TBETA(1)+PAR(14)*TBETA(2)+PAR(15)*
     3TBETA(1)+PAR(16)*TBETA(1)**2+PAR(17)*(TBETA(1)**2)*TBETA(2)+PAR
     4(18)*TBETA(1)**3
      RETURN
      END
$ENTRY
```

APPENDIX E. PROTONATION CONSTANT DATA

Table 13. Protonation constant data[a]

Sample	Vol. ligand (ml)	Vol. KOH (ml)	Vol. KNO_3 (ml)	pH
1	4.00	0.00	2.50	2.878
2	4.00	0.20	2.46	2.996
3	4.00	0.40	2.45	3.117
4	4.00	0.60	2.45	3.284
5	4.00	0.80	2.43	3.436
6	4.00	1.00	2.42	3.605
7	4.00	1.20	2.40	3.790
8	4.00	1.40	2.37	4.038
9	4.00	1.60	2.33	4.220
10	4.00	1.80	2.30	4.663
11	4.00	2.00	2.26	5.008
12	4.00	2.10	2.24	5.966
13	4.00	2.44	2.50	8.768
14	4.00	2.60	2.50	8.783
15	4.00	2.80	2.46	9.060
16	4.00	3.00	2.44	9.378
17	4.00	3.20	2.42	9.666
18	4.00	3.40	2.40	9.919
19	4.00	3.50	2.40	10.043

[a]KOH concentration = .0610M; KNO_3 concentration = 1.002M; ligand concentration = .0111M.

APPENDIX F. STABILITY CONSTANT DATA

Table 14. Data for La-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.4260	0.00	2.22	2.634
2	4.00	0.4260	0.40	2.25	2.726
3	4.00	0.4260	0.80	2.28	2.820
4	4.00	0.4260	1.00	2.29	2.871
5	4.00	0.4260	1.40	2.32	2.980
6	4.00	0.4260	1.80	2.33	3.100
7	4.00	0.4260	2.20	2.34	3.236
8	4.00	0.4260	2.60	2.33	3.419
9	4.00	0.4260	3.00	2.30	3.712

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = 0.1042M.

Table 15. Data for Ce-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (mo)	pH
1	4.00	0.505	0.80	2.35	2.666
2	4.00	0.505	1.00	2.35	2.699
3	4.00	0.505	1.40	2.35	2.797
4	4.00	0.505	1.80	2.34	2.904
5	4.00	0.505	2.60	2.30	3.282
6	4.00	0.505	3.00	2.27	3.630
7	4.00	0.505	3.40	2.24	4.360

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = 0.08797M.

Table 16. Data for Pr-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.411	0.80	2.35	2.579
2	4.00	0.411	1.00	2.35	2.616
3	4.00	0.411	1.40	2.35	2.700
4	4.00	0.411	1.80	2.34	2.819
5	4.00	0.411	2.20	2.33	2.978
6	4.00	0.411	2.60	2.30	3.199
7	4.00	0.411	3.00	2.27	3.559
8	4.00	0.411	3.40	2.24	4.242

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = 0.1079M.

Table 17. Data for Nd-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.402	0.80	2.35	2.541
2	4.00	0.402	1.00	2.35	2.577
3	4.00	0.402	1.40	2.35	2.670
4	4.00	0.402	1.80	2.34	2.790
5	4.00	0.402	2.20	2.33	2.947
6	4.00	0.402	2.60	2.30	3.231
7	4.00	0.402	3.00	2.27	3.654
8	4.00	0.402	3.40	2.24	4.347

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = 0.1105M.

Table 18. Data for Sm-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.415	0.80	2.35	2.486
2	4.00	0.415	1.00	2.35	2.518
3	4.00	0.415	1.40	2.35	2.610
4	4.00	0.415	1.80	2.34	2.739
5	4.00	0.415	2.20	2.33	2.916
6	4.00	0.415	2.60	2.30	3.153
7	4.00	0.415	3.00	2.27	3.578
8	4.00	0.415	3.40	2.24	4.184

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = 0.1070M.

Table 19. Data for Eu-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.342	0.80	2.35	2.469
2	4.00	0.342	1.00	2.35	2.506
3	4.00	0.342	1.20	2.35	2.548
4	4.00	0.342	1.40	2.35	2.604
5	4.00	0.342	1.80	2.34	2.730
6	4.00	0.342	2.20	2.33	2.895
7	4.00	0.342	2.40	2.32	3.014
8	4.00	0.342	2.60	2.30	3.132
9	4.00	0.342	2.80	2.28	3.328
10	4.00	0.342	3.00	2.27	3.556
11	4.00	0.342	3.20	2.26	3.843
12	4.00	0.342	3.40	2.24	4.282

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = .1299M.

Table 20. Data for Gd-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.412	0.80	2.35	2.469
2	4.00	0.412	1.00	2.35	2.508
3	4.00	0.412	1.20	2.35	2.553
4	4.00	0.412	1.40	2.35	2.601
5	4.00	0.412	1.80	2.34	2.730
6	4.00	0.412	2.20	2.33	2.889
7	4.00	0.412	2.40	2.32	3.004
8	4.00	0.412	2.60	2.30	3.128
9	4.00	0.412	2.80	2.28	3.347
10	4.00	0.412	3.00	2.27	3.549
11	4.00	0.412	3.20	2.26	3.845
12	4.00	0.412	3.40	2.24	4.260

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = .1078M.

Table 21. Data for Tb-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.443	0.80	2.35	2.471
2	4.00	0.443	1.00	2.35	2.512
3	4.00	0.443	1.40	2.35	2.596
4	4.00	0.443	1.80	2.34	2.727
5	4.00	0.443	2.20	2.33	2.878
6	4.00	0.443	2.60	2.30	3.142
7	4.00	0.443	3.00	2.27	3.484
8	4.00	0.443	3.40	2.24	4.223

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = 0.1002M.

Table 22. Data for Dy-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.448	0.80	2.35	2.476
2	4.00	0.448	1.00	2.35	2.509
3	4.00	0.448	1.40	2.35	2.597
4	4.00	0.448	1.80	2.34	2.726
5	4.00	0.448	2.20	2.33	2.879
6	4.00	0.448	2.60	2.30	3.120
7	4.00	0.448	3.00	2.27	3.467
8	4.00	0.448	3.40	2.24	4.136

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = 0.09901M.

Table 23. Data for Ho-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.414	0.80	2.35	2.491
2	4.00	0.414	1.00	2.35	2.526
3	4.00	0.414	1.40	2.35	2.623
4	4.00	0.414	1.80	2.34	2.748
5	4.00	0.414	2.20	2.33	2.937
6	4.00	0.414	2.60	2.30	3.138
7	4.00	0.414	3.00	2.27	3.517
8	4.00	0.414	3.40	2.24	4.200

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = 0.1072M.

Table 24. Data for Er-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.447	0.80	2.35	2.520
2	4.00	0.447	1.00	2.35	2.553
3	4.00	0.447	1.40	2.35	2.653
4	4.00	0.447	1.80	2.34	2.790
5	4.00	0.447	2.20	2.33	2.954
6	4.00	0.447	2.60	2.30	3.212
7	4.00	0.447	3.00	2.27	3.563
8	4.00	0.447	3.40	2.24	4.734

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = 0.09930M.

Table 25. Data for Tm-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.418	0.80	2.35	2.507
2	4.00	0.418	1.00	2.35	2.552
3	4.00	0.418	1.40	2.35	2.650
4	4.00	0.418	1.80	2.34	2.762
5	4.00	0.418	2.20	2.33	2.924
6	4.00	0.418	2.60	2.30	3.140
7	4.00	0.418	3.00	2.27	3.464
8	4.00	0.418	3.40	2.24	4.190

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = 0.1063M.

Table 26. Data for Yb-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.458	0.80	2.35	2.501
2	4.00	0.458	1.00	2.35	2.540
3	4.00	0.458	1.40	2.35	2.636
4	4.00	0.458	1.80	2.34	2.747
5	4.00	0.458	2.20	2.33	2.895
6	4.00	0.458	2.60	2.30	3.076
7	4.00	0.458	3.00	2.27	3.357
8	4.00	0.458	3.40	2.24	4.049

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = 0.09684M.

Table 27. Data for Lu-DTTAP complexes[a]

Sample	Ligand vol. (ml)	Metal vol. (ml)	KOH vol. (ml)	KNO_3 vol. (ml)	pH
1	4.00	0.478	0.80	2.35	2.508
2	4.00	0.478	1.00	2.35	2.578
3	4.00	0.478	1.40	2.35	2.657
4	4.00	0.478	1.80	2.34	2.775
5	4.00	0.478	2.20	2.33	2.929
6	4.00	0.478	2.60	2.30	3.148
7	4.00	0.478	3.00	2.27	3.507
8	4.00	0.478	3.40	2.24	4.563

[a]Ligand concentration = 0.0111M; KOH concentration = 0.0610M; KNO_3 concentration = 1.002M; metal concentration = 0.09290M.