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Some properties of yttrium and rare-earth N'-methylethylene-diamine-N', N,N-triacetate complexes

Donald Austin Johnson
Iowa State University

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N'-METHYLETHYLENEDIAMINE-N',N,N-TRIACETATE
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Some properties of yttrium and rare-earth
N'-methylethylenediamine-N',N,N-triacetate complexes

by

Donald Austin Johnson

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

Department: Chemistry
Major: Physical Chemistry

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In Charge of Major Work

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Ames, Iowa

1973

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I. INTRODUCTION

This dissertation is concerned with the measurement of the stability constants and certain ion-exchange parameters of rare-earth and certain transition metal cations with an aminopolyacetic acid ligand. These measurements provide an evaluation of this ligand as a reagent for the ion-exchange separation of these metals. These data also provide insight into the type of bonding which occurs in this system and fill a large gap in the literature concerning rare-earth complexes.

Many substances have been used as chelating agents. They have been used in many areas of chemistry for a wide variety of purposes. A much sought-after property in these ligands is their selectivity in complexation of different metal ions. Also desirable for many uses is high stability of complexation. The aminopolycarboxylic acids have found wide acceptance as reagents where these properties are required.

The ion-exchange method of separating large amounts of very pure rare earths is an example of an application where selectivity is of great importance. Evaluation of the rare-earth complex stability constants is one way to determine the suitability of a new ligand as a reagent for ion-exchange rare-earth separations. This is, however, not the only cri-

terion for a satisfactory ion-exchange eluant. The speed of the ion-exchange separation process as represented by the theoretical plate distance for a given set of ion-exchange conditions is also important. This value may be measured by ion-exchange experiments.

The rare-earth series of cations provides an excellent system on which to study the factors which effect the chelation of metal ions. This series offers a group of fourteen metal ions which differ from each other with respect to ionic radius in a regular manner. The electronic differences between these elements occur in the inner 4f orbital and exhibit only a small effect on the properties of the series in solution. There is a large amount of literature on the complexes of this series, so it is possible to compare many ligands as to their complexation of a series of similar ions of regularly varying radius.

The research described in this dissertation concerns the potentiometric and polarographic measurements of rare-earth complex stability constants with one ligand, and some ion-exchange experiments with this same ligand.

II. REVIEW OF PREVIOUS WORK

A. Preparation of Aminopolycarboxylic Acids

A large number of aminopolycarboxylic acids have been synthesized. Dwyer and Mellor (1), Debbrecht (2), and Smith (3) have given historical reviews on the preparation of these compounds. In addition, Smith (3) gives a listing of compounds of this type which are under patents. Some of these compounds are commercially available. Since 1964 activity in this area has tapered off somewhat and information about the organic chemistry of these ligands is very sparse and limited almost exclusively to their synthesis. This is probably due to the fact that the metal ion complex chemistry of these compounds is extensively studied at the expense of their organic chemistry.

The methods of aminopolycarboxylic acid synthesis fall roughly into seven categories which are summarized in Table 1 (1). These synthetic routes are fairly flexible; and, within the limitations of steric hindrance, one may obtain a wide variety of aminopolycarboxylic acids by varying the reactants used.

Isolation of the aminopolycarboxylic acid from the reaction mixture has, in some cases, proven to be far more difficult than the actual synthesis. In the case of ethylenedi-

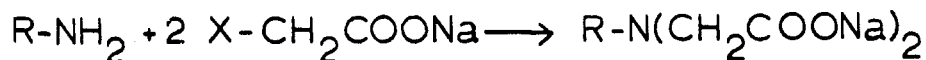
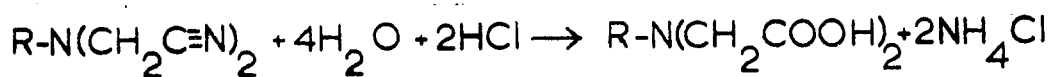
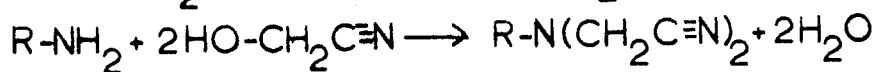
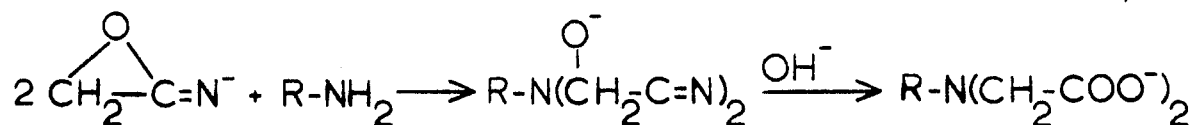
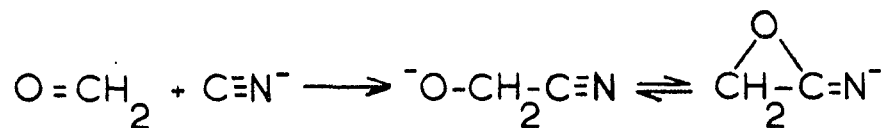
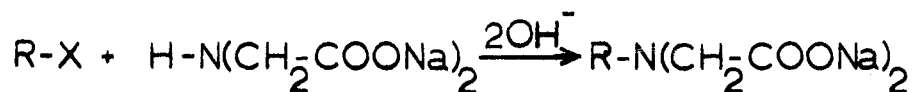
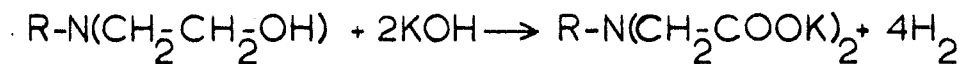
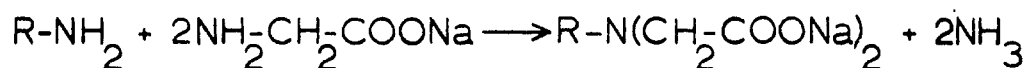
Table 1. Methods of synthesis**1. Condensation of an amine with a monohalogenated carboxylic acid****2. Strecker synthesis****3. Carboxymethylation of amines****4. Condensation of an alkyl halide with an amino acid**

Table 1. (Continued)

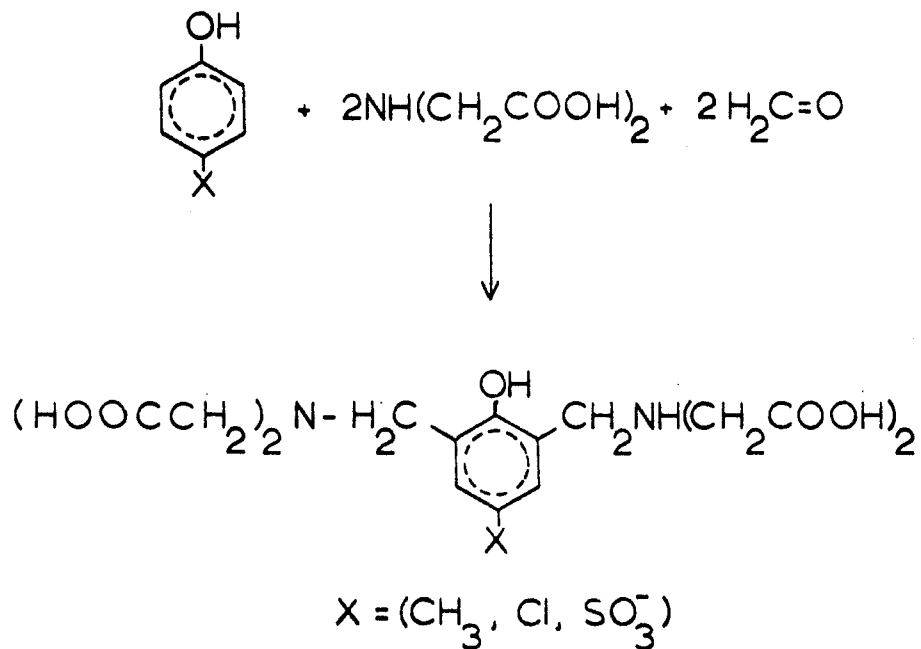
5. Oxidation of polyethanolamines



6. Condensation of an amine with two or more moles of an amino acid



7. Condensation of an aromatic compound with formaldehyde and iminodiacetic acid



amine-*N,N,N',N'*-tetraacetic acid (EDTA) and other relatively insoluble acids, this was accomplished by increasing the acidity of the reaction mixture, causing the insoluble acid to precipitate. More soluble acids, however, can be more difficult to isolate.

Ion-exchange methods have been used to isolate ligands (4, 5), and complexes (6, 7), from multicomponent reaction mixtures. Blackmer et al. (7) used the method of Dwyer and Garvan (4) to isolate the cobalt(III) complex of ethylenediamine-*N,N,N'*-triacetic acid (ED3A) from a reaction mixture containing a variety of ligands. They were unable to obtain the acid form of this ligand. Similarly, Van Saun and Douglas (6) prepared the cobalt (III) complex of *N'*-methyl-ethylenediamine-*N,N,N'*-triacetic acid (MEDTA). In this case too, the free acid was not prepared.

Bruno, Chaberek, and Martell (8) reported the synthesis of *N'*-substituted ethylenediaminetriacetic acids by the method of carboxymethylation of *N*-alkylated ethylenediamines. They prepared the *N'*-*n*-butyl, *N'*-*n*-octyl, *N'*-*n*-dodecyl, *N'*-cyclohexyl, and *N'*-benzyl compounds of this type. They found increased water solubility and decreased yield as the *N'*-alkyl substituent decreased in bulk from *n*-octyl to *n*-butyl. The yields of recovered product were 15% and 3% respectively. Bruno et al. reported that the carboxymethylation reaction was complicated by evolution of ammonia which is

subsequently converted into the relatively insoluble product nitrilotriacetic acid (NTA). Also causing difficulty in this work was the large amount of sodium sulfate produced in the reaction. They desalted the mixture by fractional crystallization from an ethanol-water solution until a negative sulfate test was obtained. It was this procedure which apparently caused the low yields of the more soluble members of the series.

Powell and Johnson (9) used a displacement ion-exchange chromatographic technique, which will be described later in this dissertation, to isolate the extremely water-soluble compound MEDTA from the carboxymethylation reaction mixture. This method seems to offer a considerable advantage in syntheses of this type, as the yield of purified product was reported at 71%.

In summation, a number of aminopolycarboxylic acids have been prepared and studied. It is practical to use a small group of extensively studied reactions which may be found in many organic textbooks to prepare almost any ligand of this type. The real problem in many cases is the isolation and purification of the desired ligand.

B. Rare-Earth Aminopolycarboxylates

Many rare earth aminopolycarboxylate complexes have been studied using various techniques. Dwyer and Mellor (1), Sinha (10) and Mackey (11) have reviewed much of this work. Sillen and Martell (12) have published an extensive compilation of stability data which includes much of the information on rare-earth stability constants.

Since its introduction by Schwarzenbach and Ackermann (13) in the 1940s, EDTA has been extensively studied for its metal ion chelating properties, and a large amount of data has been gathered on rare earth-EDTA complexes. The formation constants of these complexes have been determined several times under various conditions by different methods. Some of these data are summarized in Table 2. These data tend to parallel each other, with the main difference being in the absolute magnitudes of the stability constants for the series. Figure 1 shows a plot of the data of Betts and Dahlinger (15) and Wheelwright and Spedding (14) versus ionic radius (19). Figure 1 shows the characteristic "gadolinium break" which is associated with data of this sort.

Much of the literature on rare-earth complexes is concerned with their structure and bonding. Figure 1 shows the nearly linear relationship of the logarithm of the complex formation constant vs. ionic radius. Except for the dip in

Figure 1. Formation constants of EDTA complexes of the rare earths vs ionic radius

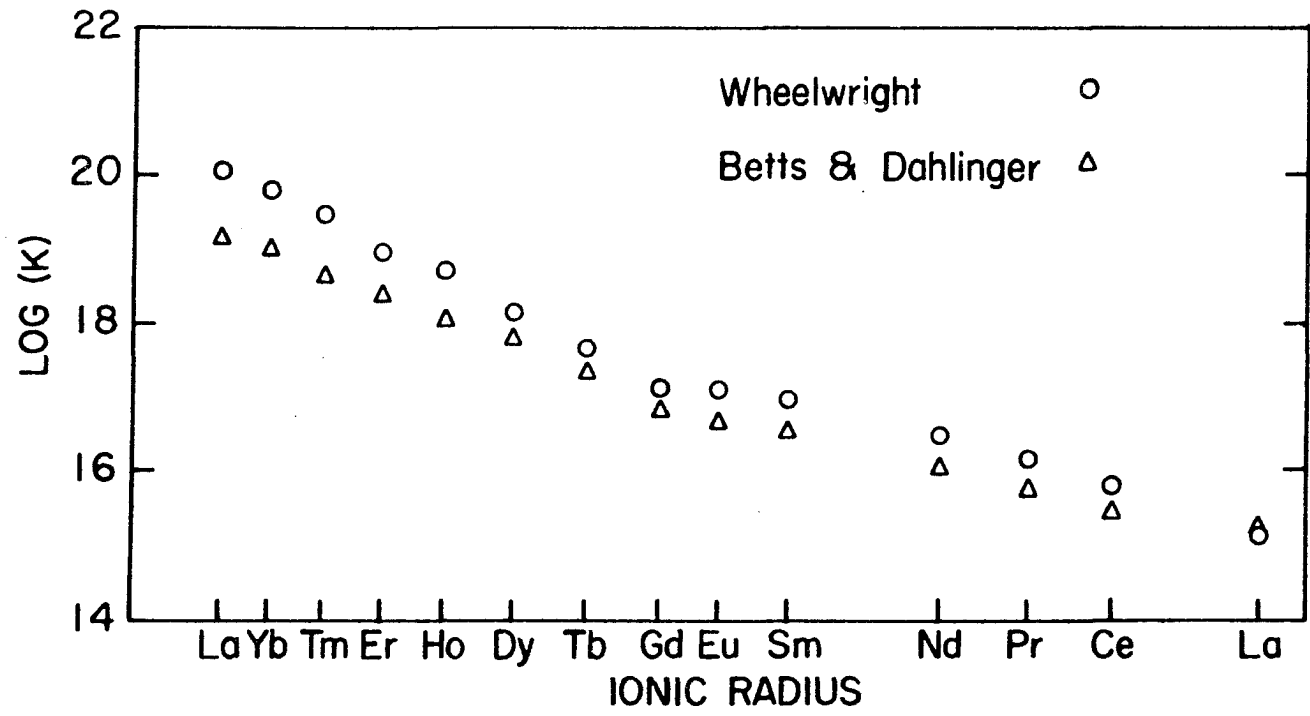


Table 2. Rare earth-EDTA complex formation constants

METAL	LOG (K)				
	(14)	(15)	(16)	(17)	(18)
La	15.14	15.19	15.30	15.13 15.50	14.72
Ce	15.81	15.45	16.05	15.80 16.01 15.98	15.39 15.6
Pr	16.17	15.76	16.55	16.16 16.21 16.40	15.75 15.8
Nd	16.48	16.05	16.75	16.47 16.61	16.06 16.0
Sm	16.97	16.53	17.2	16.9 16.7 17.14	16.55 16.3
Eu	17.11	16.66		17.35	16.69 16.5
Gd	17.12	16.82	17.2	17.10 17.0 17.37	16.7 17.0 16.6
Tb	17.67	17.32		17.6 17.81 17.93	17.4 17.25 17.38
Dy	18.17	17.78	17.75	18.00 18.18 18.30	17.75 17.57
Ho	18.73	18.04		18.1 18.74	17.67 18.05 18.31
Er	18.97	18.37	18.15	18.98 18.85	17.98 18.38 18.55
Tm	19.49	19.64		19.32	18.59 18.62 19.07

Table 2. (continued)

METAL	LOG (K)				
	(14)	(15)	(16)	(17)	(18)
Yb	19.81	18.99	18.70	19.82	18.68
				19.51	18.88
					19.82
					19.39
Lu	20.07	19.14		19.83	19.07
					19.06
					19.65
Y	17.98		18.0	17.8	17.8
				17.38	
				18.08	
				18.09	

the curve in the region of gadolinium, the relationship is fairly linear. Many workers have tried to explain this "gadolinium break", with a change of coordination being the most frequent conclusion.

Wheelwright et al. (18) suggested that the plateau is caused by increasing steric hindrance due to the progressively smaller ionic radii of the series from La to Lu. These authors also suggested that from La to Gd, EDTA acts as a six coordinate ligand, but that after Gd it is restricted by size limitations to five coordination.

Moeller et al. (20) studied the absorption spectra of protonated Nd and Y-EDTA complexes. They observed two carbonyl peaks and concluded that one of the acid groups of EDTA is not bonded to the metal ion. They also studied the sodium salts of these complexes, but were unable to find a similar effect.

Table 3. Thermodynamic quantities for the formation of rare-earth-EDTA complexes at 25°C.

M	ΔG°	ΔH°	ΔS°	M	ΔG°	ΔH°	ΔS°
La	-20.72a	-.80a	66.0b	Tb	-23.62	1.50	84.3
Ce	-21.07	-.47	69.1	Dy	-24.25	1.50	86.3
Pr	-21.49	-.80	69.4	Ho	-24.61	1.25	86.7
Nd	-21.89	-.80	70.7	Er	-25.06	1.50	89.1
Sm	-22.54	-.80	72.9	Tm	-25.44	1.58	90.6
Eu	-22.72	-.16	75.7	Yb	-25.91	1.32	91.3
Gd	-22.94	+.43	78.4	Lu	-26.11	0.64	89.7

a Kcal./mole

b e. u./mole

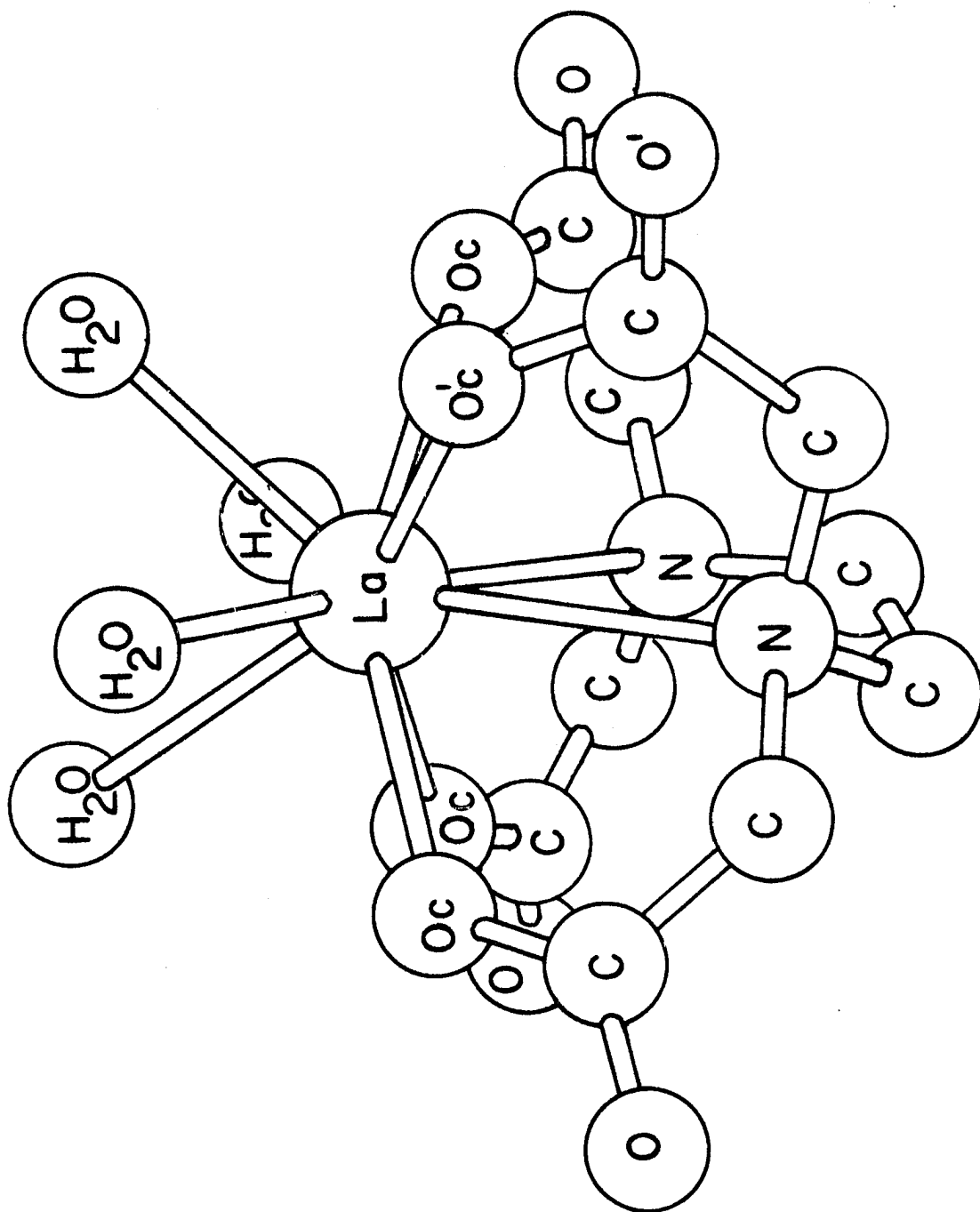
Kolat and Powell (21) extended the work done by Moeller et al. over the rare-earth series. Kolat and Powell found that the solid protonated chelates of EDTA from Ce through Sm exhibit somewhat different properties than do those from Eu through Ho. The former group had one tightly held water of hydration and exhibited infrared spectra indicative of an uncomplexed acid group in the ligand. The latter group showed none of these characteristics. These authors state that their data is suggestive, but far from conclusive, of five coordination by EDTA of the light rare earths.

Mackey et al. (22) studied the solid hydrates of EDTA complexes of La, Sm and Eu. They found that the multihydrate $HLnEDTA$ compounds convert irreversibly in the presence of water to the monohydrate or anhydrous compounds at temperatures well below 100° C. Thermogravimetric analysis, however, showed the hydrated chelates holding water to well above 100° C.

Betts and Dahlinger (15) studied the standard entropies, enthalpies and free energies of association for EDTA with the rare earths (Table 3). From this work, they concluded that the coordination shift causing the "gadolinium break" is from five to four coordinate. From these data and calculated partial molal entropies for the rare-earth ions, they were able to calculate the partial molal entropies for the lanthanide-EDTA complexes. It may be seen that these data fall into two groups. From La to Gd, the sum of the partial molal entropy for the complex and that for the ligand (presumably a constant) is 33.3 ± 1.4 or $27.1 \pm .09$ e. u. depending on the method of calculation. These quantities for the lanthanides from Tb to Lu are $43.1 \pm .11$ and $33.3 \pm .7$ e. u. respectively. The authors attribute this grouping to a change in the configuration of the complex, such as the opening of one of the chelate rings. It must be noted, however, that the calculated partial molal entropies for the hydrated ions did not take into account the entropy term which is due to the multiplicity of the electronic ground state of the ions. The authors used the empirical entropy calculation of Cobble (23) to suggest a change in ligand chelate character from four with the smaller ions to five with the larger lanthanides.

Structural determinations of rare-earth-EDTA complexes were done by Hoard, Lee and Lind (24,25,26) in 1965. The crystal structure of HLaEDTA is shown in Figure 2. The

Figure 2. Structure of the protonated EDTA complex of lanthanum



protonated acid group is labeled by O' and C'. Although it can be misleading to infer too much about structures in solution from crystallographic data, this work seems to clear up some questions. It was shown by these workers that EDTA is six coordinate in its chelates throughout the entire lanthanide series. The removal of the proton from the complex causes tightening of all chelate linkages and the ejection of one water molecule. The average oxygen to metal distance in the neutral molecule is 2.555 Å compared to 2.507 Å for the anion. The average metal to nitrogen distance is decreased by .110 Å. These compounds are distorted somewhat from the tricapped trigonal prism found by Fitzwater and Rundle (27) and Hubbard et al. (28) in the nine-hydrated rare-earth ethylsulfates. The configuration of the ligand is thought to be the cause of this distortion.

Martyenko et al. (29) determined the infrared spectrum of solid rare-earth chelates of the type HLnEDTA. According to them, the covalency of the Ln-O bond increases through the series from La to Yb. Also, a decrease in the covalency of the Ln-N bond for this series was noted. The authors compared their data with similar work on iminodiacetic acid and NTA complexes and conclude that EDTA is in a relatively strained configuration in rare-earth complexes.

The ion-exchange data of Powell and Burkholder (30) shows an increase in the ion-exchange separation factors be-

tween Gd, Eu and Sm at elevated temperatures. This is thought to be caused by a temperature dependent reduction in the stabilities of the EDTA chelates of Sm and Eu. The authors state that this phenomenon may be caused by lessening at high temperature of the hydrogen bonding between uncoordinated carbonyl oxygen atoms on the ligands and water molecules which are coordinated to the metal ion. This subject will be discussed more extensively in a later section.

Geier et al. (31) observed the absorption at 395 nm. of solid rare-earth-EDTA complexes at several temperatures. They found that Eu-EDTA exhibits a strongly temperature dependent shift of this peak. Similar but weaker temperature effects were observed with Sm and Gd-EDTA. The other members of the series showed no effect of this type. The authors interpreted these data as being indicative of a temperature dependent change in the mode of bonding.

An alternative explanation for the gadolinium anomaly was proposed by Stavely and Randall (32). They suggested that it is unlikely that, when a critical size of cation is reached, a sudden change of coordination occurs. They proposed ligand field stabilization of the 4f electrons as a possible cause of the gadolinium break.

A number of aminopolycarboxylic acids have been studied with similarities to EDTA, but which have various structural differences. These EDTA derivatives sometimes exhibit dif-

Table 4. Thermodynamic functions of chelation of rare-earth ions with t-DCTA at 25° C.

M	log(K)	ΔH°	ΔS°	M	log(K)	ΔH°	ΔS°
La	16.35	+3.6a	87b	Tb	19.30	+5.0	105
Ce	16.76			Dy	19.69	+3.1	100
Pr	17.23	+5.0	96	Ho	19.89	+1.2	95
Nd	17.69	+5.0	98	Er	20.20	+0.1	93
Sm	18.63	+5.0	102	Tm	20.46	-1.6	88
Eu	18.77			Yb	20.80	-4.5	80
Gd	18.80	+5.8	105	Lu	20.91	-4.9	79
				Y	19.41	+4.2	103

a Kcal./mole

b e. u./mole

ferent complexing behavior than does EDTA. One class of ligands of this sort is sometimes referred to as "C-substituted" EDTA derivatives. These ligands consist of the EDTA framework with various addenda on the methylene (between the nitrogen atoms) carbon chain. Simeon (33) has reviewed the alkaline-earth and rare-earth complex chemistry of some of these ligands.

Some properties of trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (t-DCTA) complexes with the rare earths have been observed. Schwarzenbach *et al.* (17), and Karraker (34) measured the formation constants of t-DCTA complexes of the rare earths. Moeller and Hseu (35) measured the standard enthalpies, entropies and free energies of chelation for the rare-earth series at 25° C. The data from these two studies are summarized in Table 4.

Moeller and Horwitz (36) measured the magnetic susceptibilities, infrared spectra, X-ray powder patterns, and dehyd-

Table 5. Stability constants, in log. units, of rare-earth complexes with C-substituted EDTA ligands

M	log(K)					
	PDTA	PhEDTA	±DiMEDTA	m-DiMEDTA	DCPTA	DCTA
La	16.42	15.49	16.68	14.60	17.01	16.26
Ce	16.79	15.96	17.21	15.48	17.28	16.76
Pr	17.17	16.29	17.49	15.81	17.47	17.31
Nd	17.54	16.56	17.70	16.06	17.72	17.68
Sm	17.97	17.09	18.32	16.47	18.11	18.38
Eu	18.26	17.25	18.61	16.57	18.21	18.62
Gd	18.21	17.40	18.84	16.51	18.24	18.77
Tb	18.64	17.96	19.45	16.72	18.64	19.50
Dy	19.05	18.42	19.93	17.01	18.94	19.69
Ho	19.30	18.69	20.27	17.25	19.24	
Er	19.61	19.01	20.68	17.55	19.49	20.68
Tm	20.08	19.34	20.96	17.87	19.71	20.96
Yb	20.25	19.68	21.29	18.15	19.95	21.12
Lu	20.56	19.83	21.33	18.11	20.20	21.51

ration temperatures of solid rare-earth-t-DCTA chelates.

Data from this work indicate that 4f electrons are not appreciably involved in metal-ligand bonding. The barium salt of the Nd complex was found to begin dehydration at 50° C. and to decompose at 200° C. X-ray powder patterns indicated that the series is isomorphous.

Irving et al. (37,38), Dvorakova et al. (39), Novak et al. (40, 41), and Vloder et al. (42) have measured the rare earth complex stability constants with several C-substituted polyaminocarboxylic acids. Results of this work are summarized in Table 5. These include 1,2-diaminopropane-N,N,N',N'-tetraacetic acid (PDTA), racemic and meso 2,3-diaminobutane-N,N,N',N'-tetraacetic acid (DiMEDTA), 1-phenyl-1,2-diaminoethane-N,N,N',N'-tetraacetic acid

(PhEDTA) and 1,2-diaminocyclopentane-N,N,N',N'-tetraacetic acid (DCPTA).

It may be seen (Figure 3) that the stability constants of the C-substituted EDTA derivatives with the rare earths tend to parallel those of EDTA. With the exception of *m*-DiMEDTA, the derivatives all form more stable complexes with the rare earths than does EDTA. This is probably due to a combination of inductance and steric effects. Spectroscopic data (29) show that EDTA is in a rather strained configuration when complexing rare earths. It may be that more hindered derivatives are forced into a relatively favorable configuration for complex formation by the organic groups on the skeleton of the ligand.

Table 6. Stability constants, in log. units, of rare-earth complexes with 2-substituted EDTA ligands

M	log(K)					
	EDDPDA	EDDBDA	EDDVDA	EDDIVDA	EDDNA	EDDSA
La	14.70	14.13	14.12	10.78	9.8	11.98
Ce	15.35	14.77	14.77	11.54	10.42	12.67
Pr	15.76	15.09	15.11	11.93	10.50	12.96
Nd	16.00	15.35	15.38	12.09	10.71	13.03
Sm	16.59	16.00	16.07	12.87	11.00	13.46
Eu	16.78	16.31	16.39	13.23	11.04	13.54
Gd	16.96	16.48	16.60	13.39	10.83	13.45
Tb	17.57	17.13	17.16	14.07	11.19	13.51
Dy	17.98	17.58	17.63	14.41	11.08	13.59
Ho	18.27	17.85	17.83	14.70	11.04	13.60
Er	18.51	18.19	18.16	14.91	11.05	13.63
Tm	18.91	18.45	18.45	15.20	11.04	14.00
Yb	19.21	18.70	18.75	15.38	10.96	14.13
Lu	19.41	18.92	18.92	15.50	11.21	14.32

Figure 3. Formation constants of rare-earth complexes with EDTA homologues

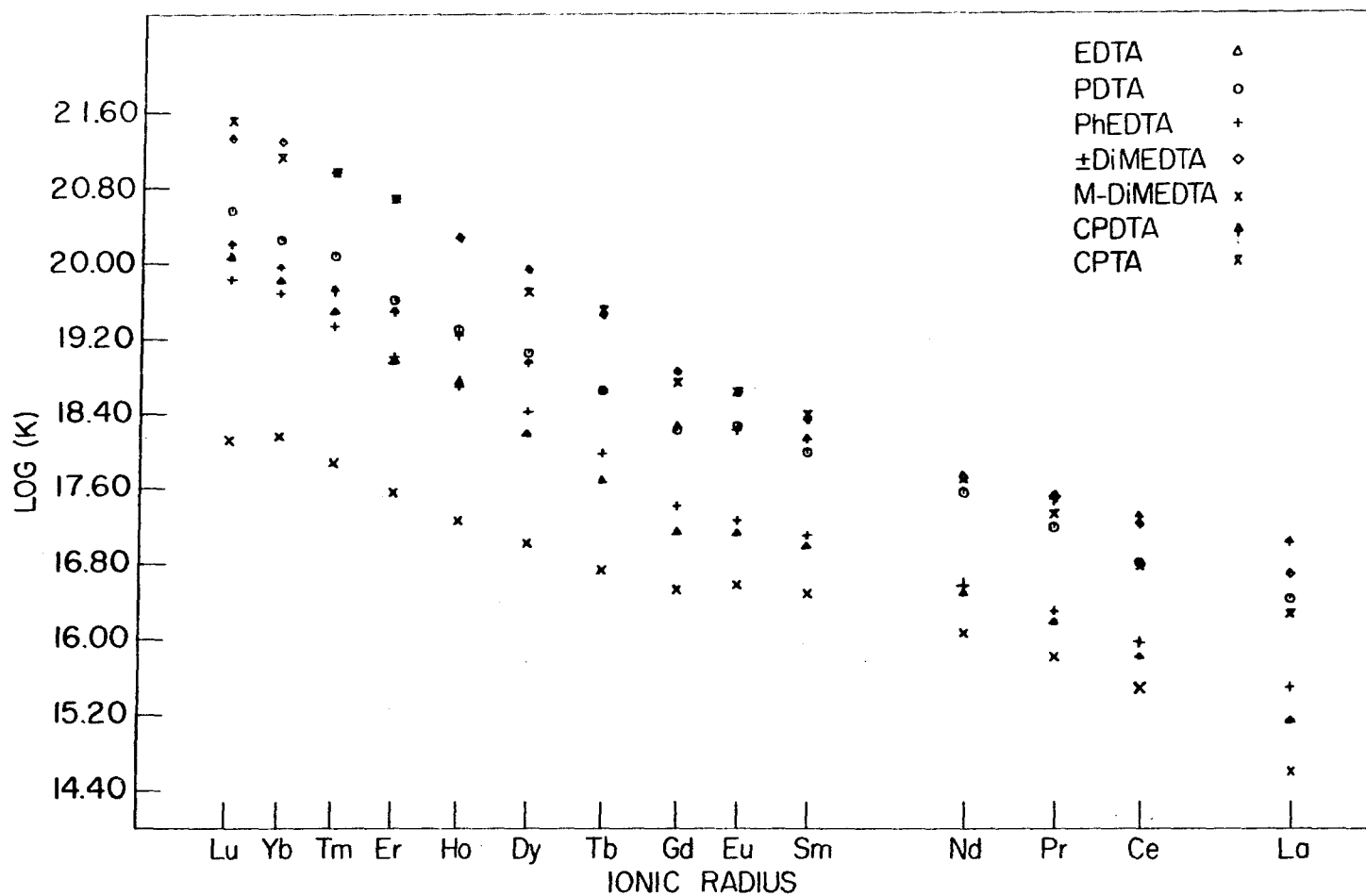
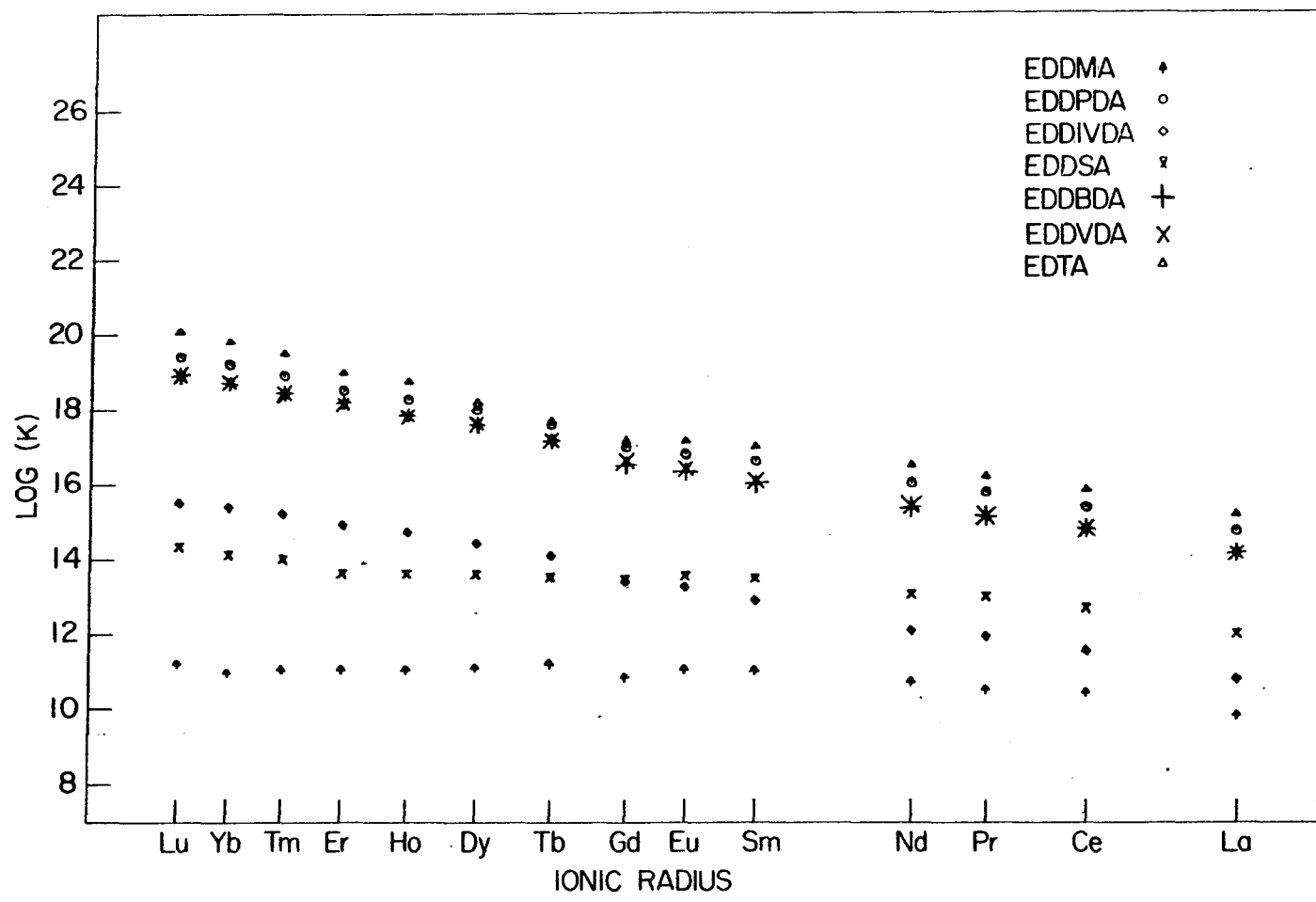


Figure 4. Formation constants of rare-earth complexes with EDTA homologues



Dvorakova et al. (43) and Novak et al. (44) determined the rare-earth complex stability constants for a group of ethylenediamine tetraacids which have different organic groups at the 2-carbon position of two of the acid groups. Included in this group are ethylenediamine-*N,N'*-diacetic-*N,N'*-(2,2'-dipropionic) acid (EDDPDA), ethylenediamine-*N,N'*-diacetic-*N,N'*-(2,2'-dibutyric) acid (EDDBDA), ethylenediamine-*N,N'*-diacetic-*N,N'*-(2,2'-divaleric) acid (EDDVDA) and ethylenediamine-*N,N'*-diacetic-*N,N'*-(2,2'-diisovaleric) acid (EDIDVDA). These ligands will be referred to in this work as 2-substituted EDTA derivatives. Babich and Gorelov (45, 46) have studied the stabilities of rare-earth complexes with ethylenediamine-*N,N'*-dimalonic acid (EDDMA) and ethylenediamine-*N,N'*-disuccinic acid (EDDSA). Results of their work are included with those on the 2-substituted ligands. Data on these compounds are summarized in Table 6 and Figure 4.

Comparison of the stability constants of the complexes formed by the rare earths with these compounds with those formed by EDTA shows that except for EDDSA and EDDMA, they show patterns of chelation similar to that of EDTA. As a group, the stabilities of their complexes are lower than are those of EDTA. The derivatives with the smaller groups on the 2-carbon atoms of the acid "arms" of the ligands, show the greatest complex stabilities. It is interesting that the

stability curves of EDDBDA and EDDVDA are almost identical, while the curve of EDDIVDA is considerably different. The structural difference of the three ligands is that of an ethyl, propyl, and isopropyl group respectively on the 2-carbon atom of two acid arms of the ligands. EDDSA exhibits EDTA-like complexing behavior, with lower overall complex stabilities than those of EDTA. EDDMA however has complexing characteristics unlike any of the other ethylenediamine tetraacids. EDDMA greatly resembles, in the shape of its rare-earth complexation curve, some of the ligands to be discussed later in this section.

Work on the C-substituted and 2-substituted EDTA derivatives is, for the most part, fairly recent and few data on their complexes, other than stability constants are currently available.

A few ligands of potentially higher coordination number than the 5 (or 6) of EDTA have been studied. Harder and Chaberek (47) first determined the stabilities of rare-earth diethylenetriamine-N,N,N',N'',N'''-pentaacetic acid (DTPA) complexes. Moeller and Thompson (48) determined the standard enthalpies, entropies, and free energies of chelation for DTPA-rare-earth complexes (Table 7). DTPA has been shown by Holleck and Liebold (49) to form a binuclear complex with the rare earths above pH 8. Hiller (50) and Mackey et al. (11,51) determined the rare-earth complex stability constants with

Figure 5. Formation constants of rare-earth complexes with DTPA,
ME and DE

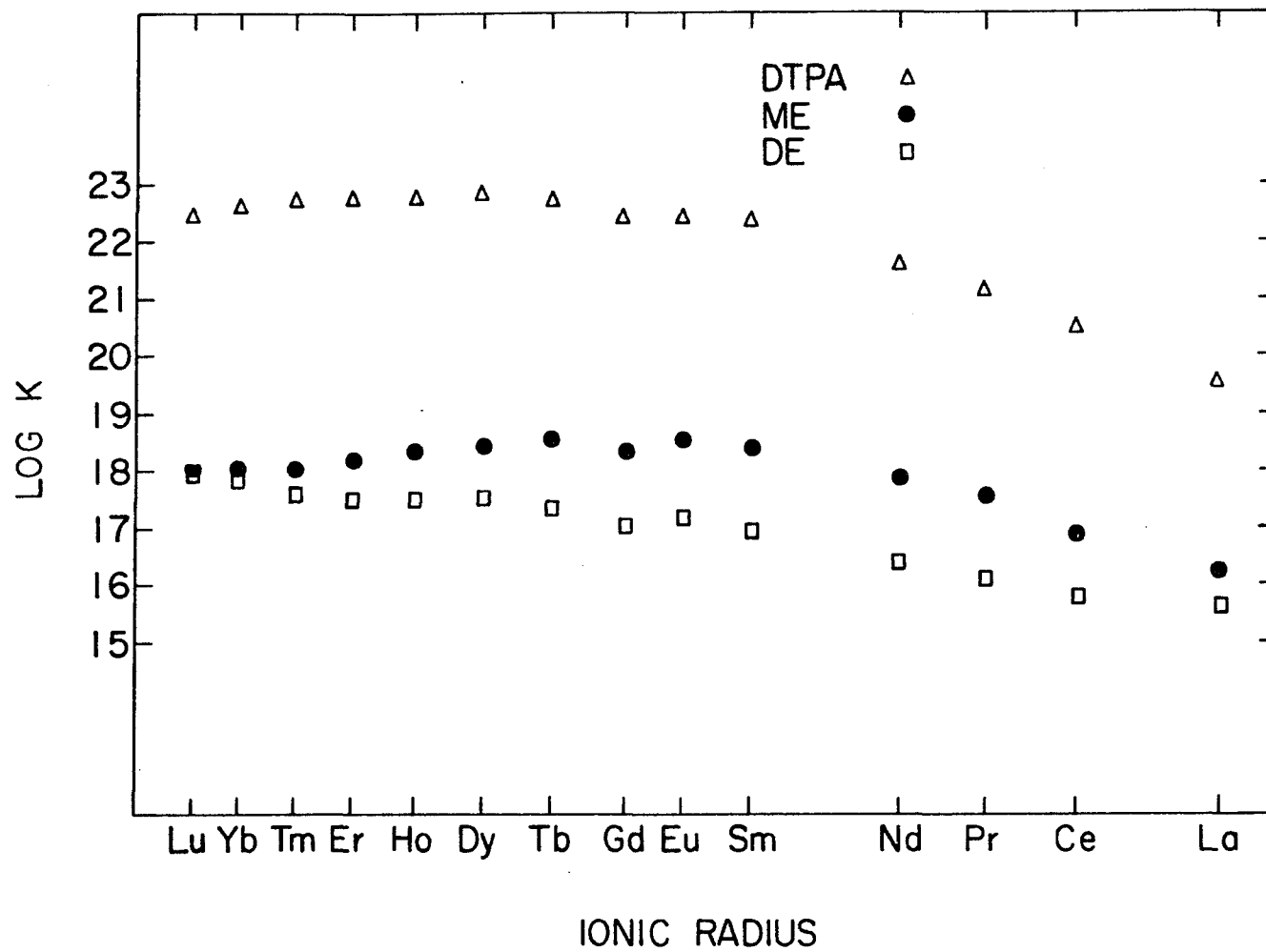


Table 7. Thermodynamic functions of formation of rare-earth-DTPA complexes

M	log(K)	ΔH°	ΔS°	M	log(K)	ΔH°	ΔS°
La	19.48	-5.7a	70.0b	Tb	22.71	-7.7	78.1
Ce	20.40			Dy	22.82	-8.0	77.6
Pr	21.07	-7.1	72.0	Ho	22.78	-7.6	78.7
Nd	21.60	-5.8	79.4	Er	22.74	-7.3	79.6
Sm	22.34	-8.2	74.7	Tm	22.72	-5.5	85.5
Eu	22.39	-8.1	75.3	Yb	22.62	-5.5	85.1
Gd	22.46	-7.5	77.6	Lu	22.44	-4.6	87.2
Y	22.05	-5.2	83.4				

a Kcal/mole

b e. u./mole

Table 8. Stability constants of rare-earth DE and ME chelates at 25°C.

M	log(K)			
	ME(11)	ME(50)	DE(11)	DE(50)
La	16.21	15.92	15.63	15.87
Ce	16.90	16.76	15.78	16.09
Pr	17.57	17.24	16.13	16.20
Nd	17.88	17.44	16.36	16.62
Sm	18.40	17.88	16.96	17.28
Eu	18.52	18.04	17.18	17.80
Gd	18.34	17.84	17.02	17.53
Tb	18.52	17.94	17.35	17.83
Dy	18.42	17.92	17.50	17.87
Ho	18.34	17.80	17.46	17.93
Er	18.20	17.81	17.48	18.03
Tm	18.04	17.64	17.56	17.99
Yb	18.06	17.69	17.86	18.25
Lu	17.96	17.55	17.89	19.51
Y	17.65	17.42	16.90	17.19

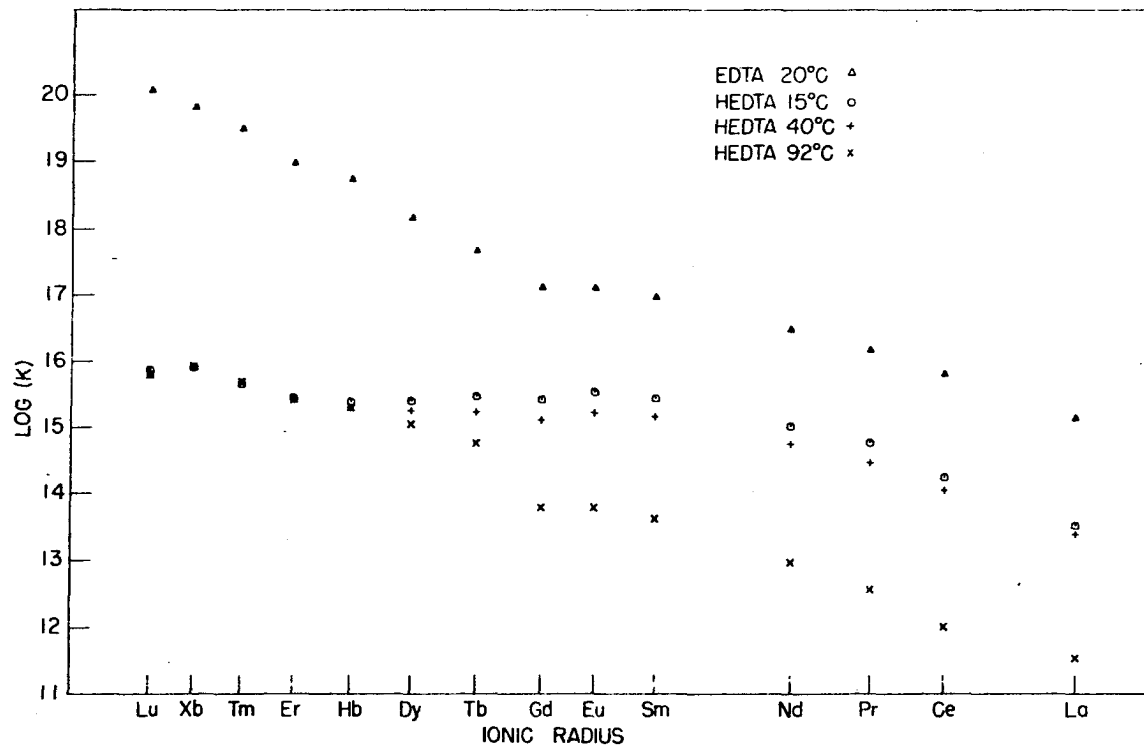
1,2-bis[2-di(carboxymethyl)-aminoethoxy ethane (ME) and 2,2'-bis-[di(carboxymethyl)-amino-diethyl ether (DE). Data from these papers are summarized in Table 8.

It may be seen (Figure 5) that the large ligands described in the above paragraph, complex the rare earths in rather different fashion than does EDTA. These results cannot easily be explained by an electrostatic model. It seems quite apparent that steric effects are exerting a rather strong influence on chelation with these ligands.

Aminopolycarboxylate ligands of smaller coordination number than that of EDTA have been prepared and the rare earth complex chemistry of some of them has been studied. Of these, the one most resembling EDTA structurally is N'-(2-hydroxyethyl)-ethylenediamine-N',N,N-triacetic acid (HEDTA). While not so extensively studied or widely used as EDTA, HEDTA has some rather interesting solution chemistry and has been adopted for use in ion-exchange separation processes for the rare earths. HEDTA has a number of advantageous properties in separations of this sort, which will be discussed in a later section.

The rare-earth-HEDTA chelate stability constants were first determined by Spedding et al. (52), and later by Powell and Mackey (53) using a mercury electrode method. Moeller and Ferrus (54) observed the variation of the chelate stability constants from 15° C. to 40° C. and calculated the stan-

Figure 6. The effect of temperature on the stability constants of rare-earth-HEDTA complexes



dard entropy and enthalpy changes at 25° C. Their results are summarized in Tables 9 and 10. Comparison of the rare earth complex stability curves of EDTA and HEDTA (Figure 6) shows their considerably different behavior. If the gadolinium break of EDTA is caused by a change in the mode of coordination, the behavior of HEDTA in that region must be caused by a much more drastic change. Also of interest is the rather large variation of the stability constants of the light-rare-earth-HEDTA chelates with temperature, compared to the relatively small variation of the heavy members of the series. Moeller and Ferrus interpret their data as being indicative of a gradual loosening of one of the chelate linkages as a result of increasing steric hindrance which parallels the decrease in ionic radius across the series. This steric hindrance apparently becomes operative only after Gd in the rare-earth series.

Powell and Burkholder (55) measured the ion-exchange separation factors for the rare earths with HEDTA as the eluant at 92° C. From these data and the assumption that the stability constants of the heavy rare-earth-HEDTA chelates continue to remain constant from 40° C to 90° C., Powell and Burkholder calculated the stability constants for the series at 92° C. As may be seen from Figure 6, this curve is quite markedly different from the stability curves obtained at lower temperatures. Indeed, at 92° C, the stability constant

Table 9. Thermodynamic functions of chelation of rare earth-HEDTA complexes at 25° C.

M	ΔH°	ΔS°	M	ΔH°	ΔS°
La	-2.20a	54.2b	Tb	-3.39	58.8
Ce	-3.06	54.4	Dy	-2.12	62.8
Pr	-4.45	52.0	Ho	-1.14	66.3
Nd	-4.25	53.8	Er	-0.32	69.4
Sm	-4.05	54.4	Tm	+0.92	74.5
Eu	-4.81	54.1	Yb	+0.36	74.0
Gd	-4.66	54.1	Lu	+0.22	73.4
			Y	-0.29	66.1

a Kcal./mole
b e.u./mole

Table 10. Stability constants of rare-earth-HEDTA chelates at various temperatures

M	15° C.	20° C.	25° C.	30° C.	35° C.	40° C.
La	13.52a	13.49	13.46	13.40	13.43	13.39
Ce	14.25	14.19	14.11	14.07	14.12	14.05
Pr	14.77	14.68	14.61	14.54	14.58	14.47
Nd	15.02	14.94	14.86	14.78	14.83	14.75
Sm	15.44	15.39	15.28	15.21	15.23	15.16
Eu	15.54	15.44	15.35	15.30	15.32	15.22
Tb	15.47	15.41	15.32	15.28	15.34	15.23
Dy	15.40	15.34	15.30	15.26	15.31	15.25
Ho	15.39	15.34	15.32	15.27	15.35	15.30
Er	15.45	15.45	15.42	15.41	15.46	15.42
Tm	15.66	15.64	15.59	15.62	15.72	15.69
Yb	15.91	15.93	15.88	15.86	15.95	15.92

a log (K)

curve of HEDTA with the rare earths greatly resembles that of EDTA although its overall magnitude is smaller. EDTA also shows some temperature dependent behavior in the region of Sm and Eu, but the effect of temperature on the HEDTA curve is much greater. In view of the great structural similarities between EDTA and HEDTA, such marked differences are somewhat surprising.

Powell and Burkholder concur with Moeller and Ferrus that the behavior of the rare-earth-HEDTA system is indicative of a gradual change in coordination number at room temperature. At 92° C, they suggest that HEDTA bonds to the metal ion through two nitrogen atoms and three carboxyl oxygens, regardless of the size of the metal ion. A small gadolinium anomaly persists, which is thought to be caused by some phenomenon other than that which causes the large HEDTA anomaly at room temperature. Two possible explanations which have been advanced are, coordination of an uncomplexed carbonyl oxygen to a water of hydration on the metal ion, and an overall change in the coordination number of the metal ion.

Data of Spedding et al. (56-59) suggest that the coordination number of the rare earths does indeed increase by one unit as the ionic radius changes from that of Dy to that of Nd.

Gupta and Powell (60) determined the step formation constants for the LnHEDTA(OH) species for the rare-earth series.

These data fit the hypothesis of Powell and Burkholder (30) in that the formation constant for the addition of a hydroxide to the complex shows a sharp decrease in magnitude from Ho to Sm. This is what one would expect if the chelate coordination character is changing from a smaller to a larger value.

Moeller and Horwitz (36) studied the X-ray powder patterns, infrared spectra, magnetic susceptibilities, and dehydration characteristics of some solid rare-earth-HEDTA chelates. They found the 4f electrons to be uninvolved in the bonding with the ligand. One water of hydration was found to be much more strongly attached to the complex than the others. This is thought to indicate that, if the rare earths are six coordinate, HEDTA is functioning as a five coordinate ligand. The authors suggest that, in view of its generally poor bonding ability, the hydroxyethyl group is probably not involved in ligand to metal bonding. A water molecule is thought to occupy the sixth metal coordination site.

Merciny and Duyckaerts (61) determined the solubilities at 50° and 100° C, the hydration numbers, and the dehydration and decomposition temperatures of solid HEDTA chelates of the rare earths. They found identical dehydration behavior in three groups of rare earths. La and Pr were found to lose waters of hydration at 190° C. and 285° C. These tempera-

tures in the cases of Er and Yb were reported at 105° C. and 169° C. respectively. These chelates were all reported as having two waters of hydration. The rare-earth chelates from Nd to Ho were found to form five-hydrate species which dehydrate at 128° C. They also determined the molecular weight of the Er and Dy compounds in concentrated solution from colligative properties. This revealed the Er chelate to be monomeric and the Dy chelate to be partially dimeric.

Merciny et al. (62) compared the infrared spectra of EDTA, HEDTA and some hydrated, anhydrous and deuterated HEDTA chelates of the rare earths. From this information, they conclude that the alcoholic group of HEDTA is bonded to the metal ion in the case of the light rare-earth complexes and is not in the heavy rare-earth complexes, in agreement with the conclusions of Powell and Burkholder (55).

Recent single-crystal X-ray diffraction data (63) indicate that in the solid state, the LaHEDTA complex forms a dimer, not unlike that formed by the solid NTA complexes of the rare earths. This data also indicate that the hydroxyethyl group of the HEDTA ligand forms a chelate linkage with the lanthanum ion.

Thompson (64) determined the first and second step formation constants of the rare-earth chelates of symmetrical ethylenediaminediacetic acid (EDDA). Powell and Swaminathan (65) report values for the ligand N,N'-diethylethylene-

Table 11. Formation constants of ethylenediaminediacetate complexes of the rare earths at 25° C.

M	DEEDA log(K ₁)	EDDA log(K ₁)	EDDA log(K ₁₂)
La		7.04	4.73
Ce		7.48	4.92
Pr		7.84	5.23
Nd		8.06	5.63
Sm		8.28	6.07
Eu	7.0	8.38	6.35
Gd	6.9	8.13	6.08
Tb	7.0	8.18	6.52
Dy	7.0	8.31	6.78
Ho	6.9	8.42	7.00
Er	7.0	8.59	7.45
Tm	7.1		
Yb	7.1	8.93	7.92
Lu	7.1	9.09	8.48
Y	6.8	7.78	6.34

diamine-N,N'-diacetic acid (DEEDA) with part of the rare-earth series. Data of Thompson and Powell and Swaminathan are shown in Table 11. It is rather difficult to obtain reliable stability constants for complexes of the rare earths with ligands such as EDDA which, while very weak acids, exhibit low complexing affinities for the rare earths (65). These conditions require high pH values to be used in order to achieve an anion concentration which will cause appreciable amounts of complex to form. Rare-earth ions and complexes have considerable tendencies to form hydroxide species. These hydroxide species cause considerable difficulty in obtaining reliable data.

The properties of the rare-earth chelates of NTA and its derivatives have been investigated by several workers.

Figure 7. First step-formation constants of rare-earth complexes of glycine derivatives

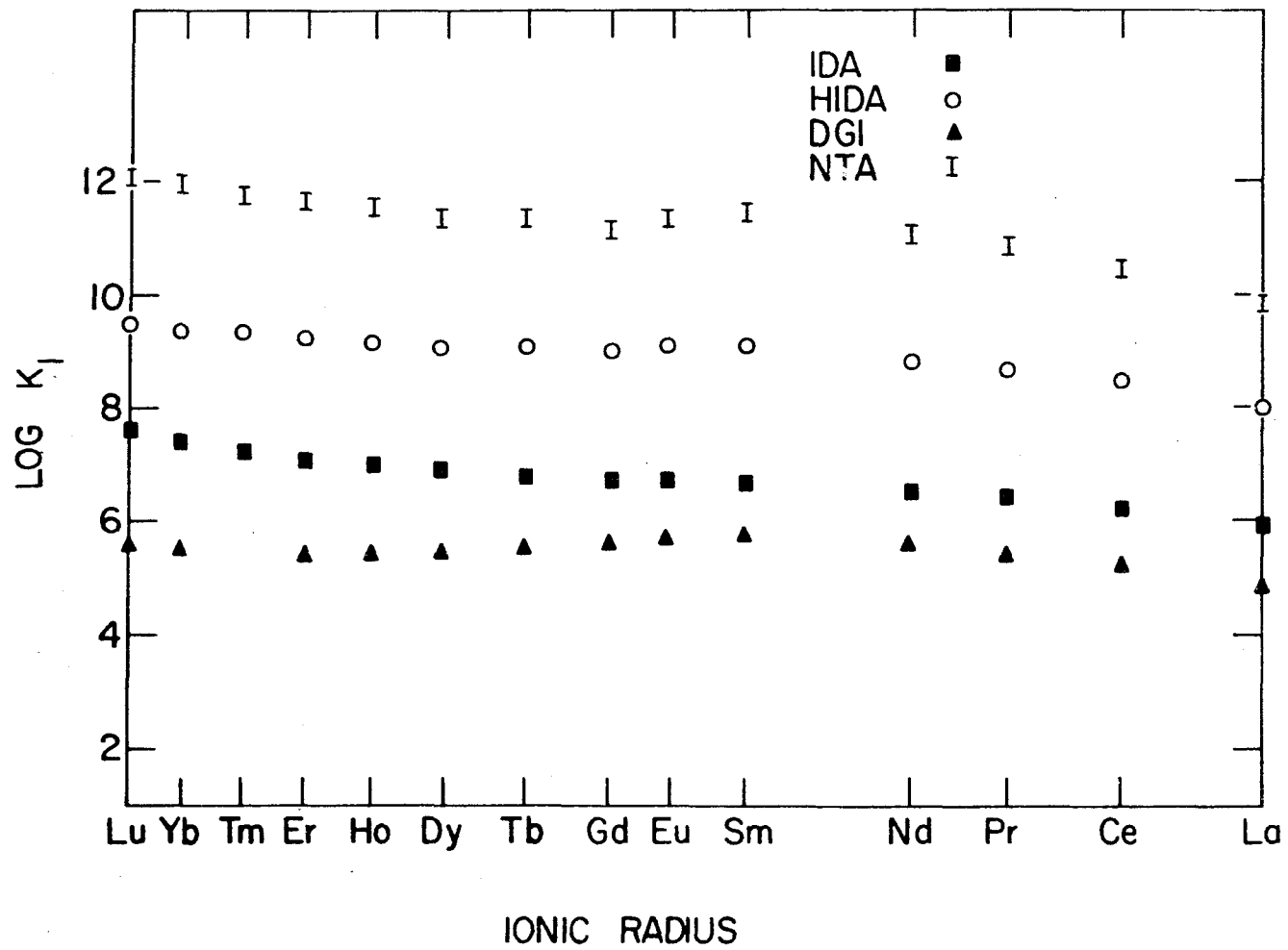


Figure 8. Second step-formation constants of rare-earth complexes of glycine derivatives

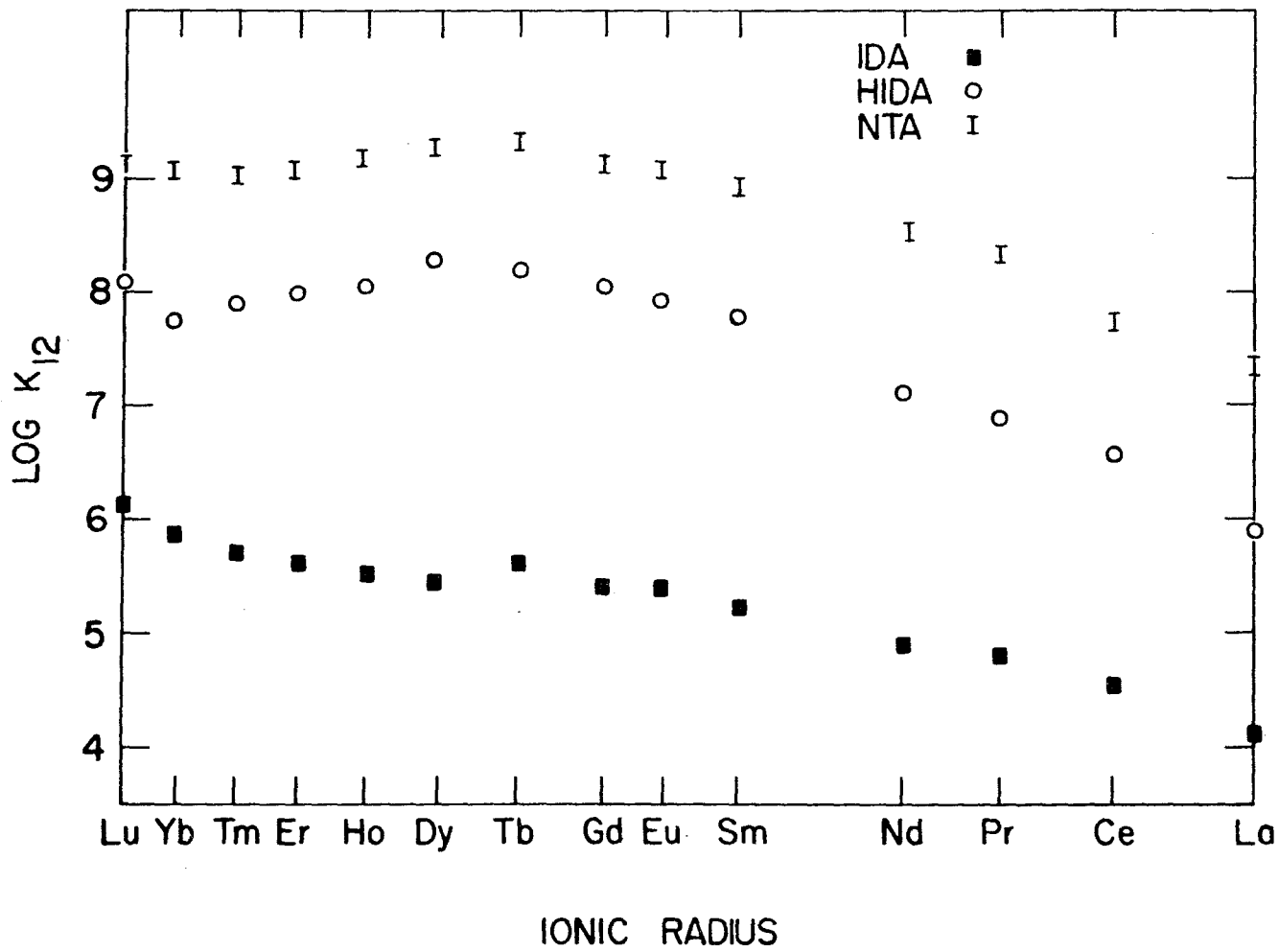


Table 12. Standard entropies, enthalpies and free energies of formation of 1-1 and 1-2 rare-earth complexes with NTA at 20° C.

M	ΔG°_1	ΔG°_2	ΔH°_1	ΔH°_2	ΔS°_1	ΔS°_2
La	-13.24a	-9.91a	8.23a	-0.32a	73.2b	32.7b
Ce	-13.99	-10.40	5.33	-0.93	65.9	32.3
Pr	-14.66	-11.15	3.40	-1.25	61.6	33.8
Nd	-14.93	-11.43	3.97	-1.91	64.5	32.5
Sm	-15.27	-12.02	4.41	-2.98	67.1	30.8
Eu	-15.23	-12.30	5.25	-3.62	69.9	29.6
Gd	-14.98	-12.35	7.03	-4.05	75.1	28.3
Tb	-15.17	-12.53	8.31	-3.76	80.1	29.9
Dy	-15.27	-12.44	7.31	-4.25	77.0	27.9
Ho	-15.47	-12.38	6.54	-4.55	75.1	26.7
Er	-15.64	-12.22	7.31	-2.21	78.3	34.1
Tm	-15.81	-12.14	7.31	-0.99	78.9	38.0
Yb	-16.07	-12.17	5.96	-0.85	75.1	38.6
Lu	-16.23	-12.29	6.88	-2.07	78.8	34.9
Y	-15.06	-12.06	10.29	-1.49	86.5	36.1

a. Kcal./mole

b. e. u./mole

Table 13. Formation constants of NTA complexes of the rare earths at 10° C. and 40° C.

M	log (K ₁)		log (K ₁₂)	
	10°C.	40°C.	10°C.	40°C.
La	9.86	10.41	7.68	7.67
Ce	10.18	10.61	8.17	8.11
Pr	10.67	10.98	8.38	8.26
Nd	10.94	11.32	8.60	8.42
Sm	11.05	11.67	9.07	8.81
Eu	11.20	11.62	9.34	9.03
Gd	11.03	11.61	9.33	9.00
Tb	11.03	11.70	9.45	9.13
Dy	11.22	11.83	9.43	9.03
Ho	11.33	11.87	9.34	8.97
Er	11.44	12.03	9.14	8.97
Tm	11.67	12.25	9.03	8.93
Yb	11.82	12.29	9.04	8.95
Lu	11.86	12.43	9.18	8.99
Y	10.89	11.71	8.93	8.80

Anderegg (66), Levy and Powell (67), and Astakhov et al. (68) determined the first step formation constants of the rare-earth-NTA complexes more or less concurrently.

Anderegg, and Levy and Powell also determined the second step formation constants of these complexes. Levy and Powell, and Moeller and Ferrus (69) determined the standard enthalpies and entropies of chelation for the rare earth 1-1 and 1-2 NTA complexes. The data of Levy and Powell are shown in tables 12 and 13, and Figures 7 and 8.

Levy and Powell (67) prepared various hydrates of the solid rare-earth-NTA chelates. They determined the solubilities and dehydration temperatures of these substances.

Table 14. Formation constants of rare-earth complexes with glycine derivatives.

M	IDA		HIDA		DGI
	$\log(K_1)$	$\log(K_{12})$	$\log(K_1)$	$\log(K_{12})$	$\log(K_1)$
La	5.88	4.09	8.00	5.98	4.84
Ce	6.18	4.53	8.46	6.56	5.22
Pr	6.44	4.78	8.64	6.86	5.44
Nd	6.50	4.89	8.80	7.13	5.57
Sm	6.64	5.24	9.10	7.77	5.74
Eu	6.73	5.38	9.10	7.91	5.70
Gd	6.68	5.39	9.01	8.04	5.59
Tb	6.78	5.46	9.08	8.19	5.53
Dy	6.88	5.43	9.08	8.30	5.49
Ho	6.97	5.50	9.18	8.13	5.43
Er	7.09	5.59	9.24	7.98	5.39
Tm	7.22	5.68	9.35	7.88	
Yb	7.42	5.85	9.38	7.74	5.45
Lu	7.61	6.12	9.50	8.02	5.46
Y	6.78	5.25	9.22	7.61	

Martin and Jacobson (70, 71) determined the crystal structure of Pr and Dy NTA chelates. These were both dimeric in the solid state with a decrease in metal coordination number from nine in the Pr complex to eight in the Dy compound. The geometry of the complexes was described as a distorted, tricapped trigonal prism for the nine coordinate Pr complex and as a distorted dodecahedron in the case of the eight coordinate Dy compound.

A number of ligands which have the same fundamental structure as does NTA have been studied. Thompson and Loraas (72) determined the first and second formation constants of rare-earth complexes with HIMDA. Kostrominia and Romanenko (73) determined the 1-1 complex formation constants of the rare earths with DGL. Thompson (74) determined the first and second formation constants for IDA complexes of the rare earths. Results of these studies are shown in Table 14 and Figures 7 and 8.

C. Ion-exchange Processes

Aminopolycarboxylic acids have been extensively used in ion-exchange separations of the rare earths. It is far beyond the scope of this dissertation to review the entire literature on this subject. The body of literature on ion-exchange separations of the rare earths using aminopolycar-

boxylic acids is huge and includes much material which is not very comparable to the results of this work. It is, for example, quite difficult to compare tracer-scale cation-exchange elution chromatography to macro-scale anion-exchange displacement chromatography. For this reason and because of the bulk of the work done in this area, the scope of this review will be sharply limited to the more comparable portion of the literature, that is, to work on displacement, cation-exchange chromatography done on strong-acid resins. The main purpose of this section is to show some of the strengths and shortcomings of the aminopolycarboxylic acids which are widely used as ion-exchange eluants for rare-earth separations.

Powell (75), Sinha (10) and Moeller et al. (76) have reviewed the literature on ion-exchange separations of the rare earths using aminopolycarboxylate eluants.

A quantitative basis for discussion of displacement ion-exchange chromatography has evolved over the years. Sillen (77), Powell and Spedding (78) and others (75, 79, 80, 81) have developed quantitative methods of sufficient scope as to be able to accurately predict the performance of an ion-exchange system, provided certain parameters are known. Two of the important terms relevant to these methods are the binary separation factor and the height equivalent to a theoretical plate (HETP), h .

The separation factor between two species, B and C is defined by Powell (75) as the ratio of the distribution of B and C between the resin and solution phases, that is:

$$\alpha = K_c/K_b = \frac{[B] [\bar{C}]}{[\bar{B}] [C]} \quad (1)$$

Where K_b and K_c are the distribution coefficients and $[B]$, $[C]$, $[\bar{B}]$, and $[\bar{C}]$ refer to the total concentrations of B and C in the solution and resin phases respectively. The HETP is the distance along a column of resin over which a redistribution of B and C in the resin and solution phases equivalent to one separation factor occurs, that is, the distance along the ion-exchange bed between points at which the ratio of $[B]$ to $[C]$ in the solution and the ratio of $[\bar{B}]$ to $[\bar{C}]$ in the resin both differ by one separation factor. Although the separation factor for a given set of rare earths depends mostly on the nature of the eluant, h is a function of both the eluant and the experimental conditions. Such things as flow rate, resin size and permeability, temperature, pH and concentration all exert rather strong effects on the value of h .

Powell and Spedding (78) derived the following equations which define the separation of binary mixtures by displacement chromatography.

$$v = l/\epsilon + N_0 \quad (2)$$

$$\log \frac{(B/C)_m}{(B/C)_0} = m \log \alpha = \frac{\log \alpha}{h} L \quad (3)$$

v = the number of band lengths the mixture must be displaced to attain complete separation.

ϵ = $\alpha - 1$.

N_0 = mole fraction of the leading element.

$(B/C)_0$ = ratio of B to C at a reference point in the band

$(B/C)_m$ = ratio of B to C at a point m theoretical plates down the band.

m = number of theoretical plates between points where $(B/C)_0$ and $(B/C)_m$ are observed.

L = distance in centimeters corresponding to m .

h = HETP.

Equation 1 defines the number of band lengths a binary mixture must be displaced in order to completely resolve its two components. In order for Equation 1 to be valid, the HETP of the system must be small compared to the band length, and the separation factor must be sufficiently different from one so that the region of overlap between the bands at equilibrium is small compared to the length of the separated bands. These conditions may be verified using Equation 2 which defines the composition of the band in terms of the

HETP and the separation factor.

When evaluating an ion-exchange separation process of this type, the separation factor and HETP are good indices as to the economy of the proposed process. Simple displacement of the ions, however, is generally not a feasible process for the separation of adjacent rare earths. The rare-earth cations exhibit very similar affinities for most ion-exchange resins. In order to enhance the separation factors for adjacent rare earths, chelating agents have come into extensive use.

Powell (75) defined the following characteristics as necessary for a chelating agent to be useful in ion-exchange separations of the rare earths.

1. The reagent and its metal chelates must be soluble in some inexpensive solvent (preferably water).
2. The reagent must have selectivity in its chelating action.
3. The reagent must form chelates of sufficient stability to promote displacement of the metal ions from the resin by alkali-metal or ammonium ions.
4. The reagent must not form chelates of such great stability as to hamper the ion-exchange process.

As a group, aminopolycarboxylic acids have been widely studied as ion-exchange eluants for rare-earth separations. To greater or lesser extents, they fit the four criteria of Powell more closely than any other group of compounds. Although a great number of studies have been made as to the stabilities of rare-earth complexes of this class of compounds, a smaller number have been used for rare-earth separations. Of those which have been studied for this purpose, each has strengths and shortcomings. The ideal ligand for this purpose has not been found.

EDTA has been extensively used as an ion-exchange eluant (75, 76). It shows a steady increase in its complexing tendency across the rare-earth series (Figure 1), and forms only 1:1 complexes with the rare earths. The theoretical plate heights for rare-earth displacement chromatography with EDTA as the eluant are not excessive under reasonable experimental conditions. The insolubility of the acid form of EDTA does, however, cause some problems.

Displacement chromatography requires the use of a retaining ion. This is an ion, loaded on the resin bed previous to the separation, which causes the rare-earth ions to be reabsorbed by the resin. The use of a retaining ion causes the rare-earth bands to remain compact, a condition necessary for displacement chromatography to occur. H^+ is commonly used as a retaining ion for rare-earth separations when the

anion of a weak acid is used as the eluant. The acid form of EDTA is quite insoluble, and as a result precipitation occurs upon contact of EDTA-containing solutions with H^+ -containing resin.

Spedding, Powell and Wheelwright (82) proposed the use of Fe^{+3} , Cu^{+2} and Ni^{+2} as retaining ions for separations involving EDTA. These ions form very stable complexes with EDTA which are more soluble than the acid form of EDTA. Cu^{+2} forms an insoluble compound with EDTA having a copper to EDTA ratio of 2:1 which limits the usefulness of Cu^{+2} as a retaining ion. Furthermore, Cu^{+2} does not completely retain Lu^{+3} or Yb^{+3} . Marsh (83) reported successful elutions using a mixed retaining bed of H^+ and Cu^{+2} . Separations of rare-earth mixtures containing La^{+3} and Ce^{+3} are hampered by the low solubilities of hydrated $HLaEDTA$ and $HCeEDTA$ species (22).

Considerable improvement in ion-exchange separations of the rare earths with EDTA was reported by Powell and Burkholder (30). At 25° C. the separation factors between Sm^{+3} , Eu^{+3} and Gd^{+3} are unfavorable due to the gadolinium break in the stability constant sequence of the EDTA complexes of the rare earths (Figure 1). Increasing the operating temperature of the system greatly enhanced the separation of these elements. The Gd^{+3} - Eu^{+3} separation factor was found to increase from 1.1 at 25°C. to 1.47 at 92°C.. Similarly, the Eu^{+3} - Sm^{+3}

separation factor was found to increase from 1.4 to 1.8.

Further advantages of high temperature operation are substantial reduction of the theoretical plate distance, allowing faster flow rates to be used, and increased solubility of acid EDTA, allowing H^+ to be used as a retaining ion, considerably facilitating reuse of reagents. A drawback of this method, other than the the obviously greater experimental difficulty is the reduced solubility of some protonated EDTA chelates at high temperature (22).

Table 15. Ion-exchange separation factors for the rare-earths with EDTA and HEDTA eluants

	EDTA	HEDTA			EDTA	HEDTA	
Lu-Yb	1.9a	1.3a	1.5b	Gd-Eu	1.05	0.7	1.0
Yb-Tm	1.8	1.6	1.7	Eu-Sm	1.5	1.0	1.5
Tm-Er	3.1	2.0	1.5	Sm-Nd	3.2	2.6	3.1
Er-Ho	1.8	1.2	1.7	Nd-Pr	1.8	1.8	2.1
Ho-Dy	2.6	1.0	1.8	Pr-Ce	2.5	2.8	
Dy-Tb	2.3	1.0	1.9	Ce-La	3.7	5.0	
Tb-Gd	4.2	1.0	2.0	Dy-Y	1.6		
				Y-Tb	1.5		

a. 25° C.

b. 92° C.

Although not as selective in separating the middle rare earths, HEDTA offers some advantages over EDTA as an ion-exchange eluant. The acid form of HEDTA is more soluble in cold water than is that of EDTA (78). This fact permits use of hydrogen ion retaining beds. HEDTA forms an ammonium-type cation which is retained on acid-form ion-exchange resin, greatly simplifying its recovery and reuse. HEDTA also gives

better (smaller) values of the theoretical plate distance than does EDTA under similar conditions (84, 85). Powell and Burkholder (55) found that a drastic drop in the stabilities of the light members of the rare-earth series occurs when the temperature is elevated to near the boiling point of water. Their observations confirmed the tendency noted by Moeller and Ferrus (54) over a smaller temperature range. Table 15 shows that quite adequate separation factors for the middle rare earths may be obtained with HEDTA at 92°C. The limited solubility of some of the HEDTA chelates of the heavy rare earths requires that eluant concentrations be kept below 0.018 M at room temperature, but at temperatures above 90°C., concentrations of up to 0.072M have been successfully used (75).

Depending on the set of results chosen, DCTA appears to be at least as selective across the rare-earth series as is EDTA and is possibly considerably more selective. This consideration would appear to make DCTA the reagent of choice for rare-earth separations. This is, however, not the case. Holleck and Hartinger (86) found that the boundaries between rare-earth bands at steady-state are very diffuse for elutions with DCTA at room temperature. As this was certainly not caused by unfavorable separation factors, it was decided that the very high overall stability of the complexes introduces an unfavorable kinetic factor into the exchange

process, causing the HETP to be excessively large. Lindstrom and Winget (87) reported considerable difficulty with leakage of the rare-earth band through all the commonly used retaining ions at room temperature using DCTA. Increasing the temperature to 200° F. and 250° F. improved the process considerably, but not enough to make DCTA competitive with EDTA as a reagent for rare-earth separations (87). The data of Schwarzenbach, Gut and Anderegg (17) predicts that Cu^{+2} should retain the rare earths with DCTA as the eluant, but it does so only poorly.

DTPA is not particularly well suited for use in rare-earth separations (75). It shares the problem of poor kinetics with DCTA. Furthermore, DTPA is not as selective as EDTA and DCTA for the heavy rare earths. Orr (88) reported successful separations of the light rare earths (including promethium) with DTPA using H^{+} as the retaining ion. Wheelwright (89) studied EDTA, HEDTA, DTPA and NTA as eluants for the separation of fission-produced mixtures, consisting mainly of the light rare earths. He found NTA to be the best of the four, due mainly to its superior exchange kinetics.

Substituted glycine derivatives have been widely used in rare-earth separations. Due to the comparatively low stabilities of rare-earth complexes of some of these ligands, many of the reported separations were at least partially elution-chromatographic in nature. NTA has been extensively used in

rare-earth separations (75, 90, 91, 89), and is quite good for separations involving the light rare earths.

III. EXPERIMENTAL PROCEDURES

A. Preparation of MEDTA

As MEDTA was not commercially available and had been reported only as the cobalt complex (6), a method was developed to prepare the free acid form of MEDTA economically and in good yield.

The method of Bruno et al. (8) was adapted to accomplish the synthesis of MEDTA. Their method was used in the preparation of a number of N'-substituted ethylenediamine-triacetic acids by the method of carboxymethylation of amines. In general, yields of purified acid from the method of Bruno, et al. were rather poor. Only in the case of N'-benzyl-ethylenediamine-N',N,N,-triacetic acid was the reported yield over 50%. Bruno et al. report considerable difficulty in isolating the relatively soluble (in water) butyl derivative, and the reported yield of this compound was 1%. The authors attempted to recover the amino acid products from the reaction mixture by crystallization from mixed solvents.

It was decided to adopt an ion-exchange method to the isolation of MEDTA. NTA, which is the main organic by-product of the carboxymethylation reaction, does not form sufficient concentrations of ammonium-type cations in acidic solution to be retained on strongly acidic ion-exchange resin (92). HEDTA, a compound similar in structure to MEDTA, is retained on resin of this type. The carboxymethylation reac-

tion mixture contains sodium sulfate, NTA, and the desired amino acid as its major components. If one loads a mixture of this type onto a strong acid cation-exchange column, the sodium sulfate is converted to sulfuric acid which is easily washed off the column, as is NTA. MEDTA, as it forms the ammonium-type ion, forms a compact band on the column. This band may be displaced off the column by base.

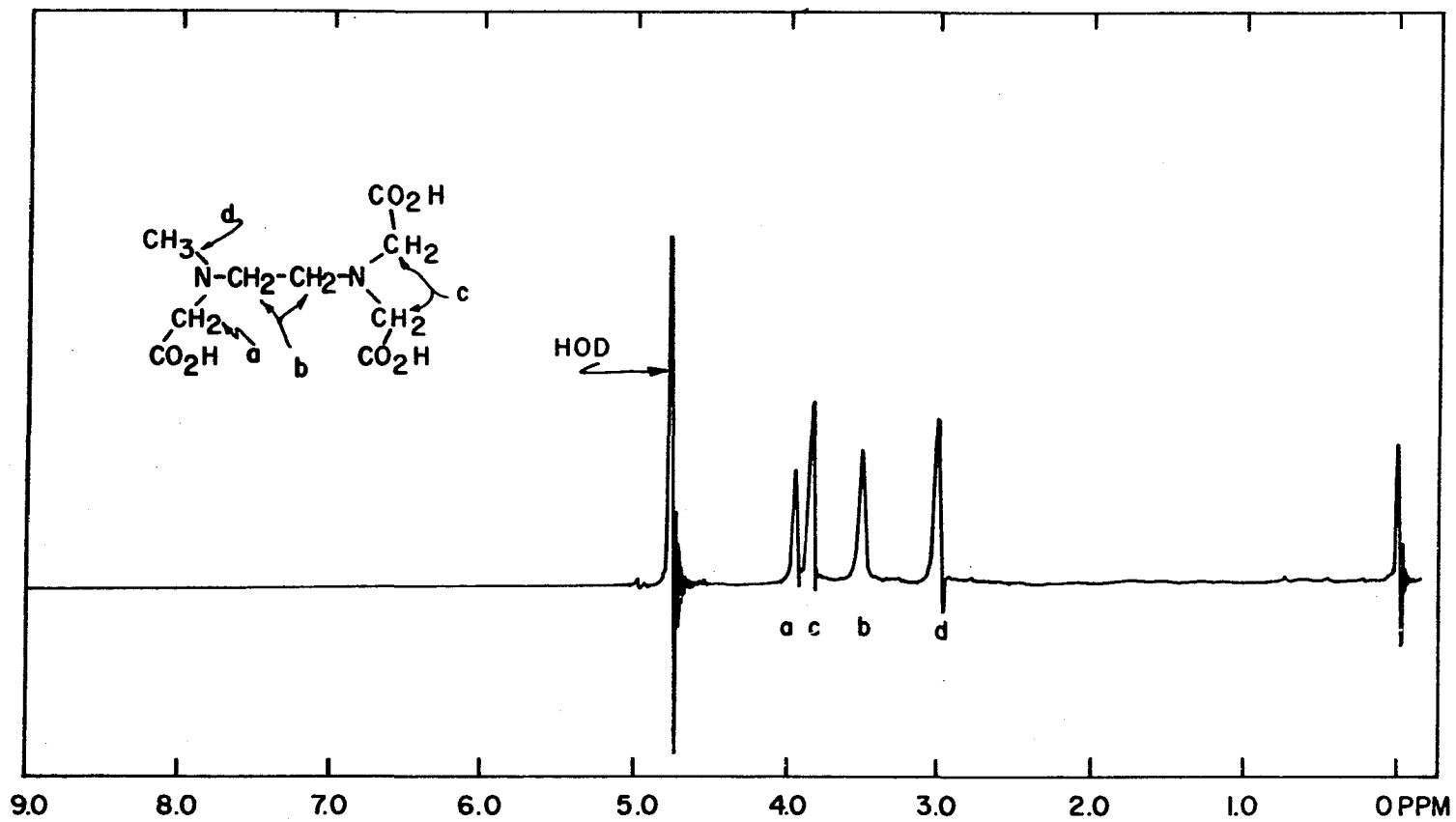
1. Experimental procedures

One mole (74 g.) of N-methylethylenediamine, purchased from Ames Laboratories, Inc., 250 ml. of t-butanol and 250 ml. of water were heated to the boiling point in a 3-liter, 3-necked round-bottom flask equipped with two 500-ml. addition funnels, a reflux condenser and a magnetic stirrer. One funnel was filled with 500 ml. of a water solution containing 3.5 moles (171 g.) of sodium cyanide and 10 g. of sodium hydroxide; and the other was filled with 500 ml. of a solution prepared by diluting 296 ml. (3.7 moles) of 37% formaldehyde to volume. The mixture in the flask was heated under reflux while the cyanide and formaldehyde were added slowly. At the completion of the addition, reflux was continued and the system was swept with air in order to aid the evolution of ammonia. The reflux and sweeping operations were continued for 24 hours until the evolution of ammonia ceased. The t-butanol was distilled off, the pH was adjusted to 1.2 with

sulfuric acid, and the mixture was again refluxed for 3 more hours. After cooling, the contents of the flask were passed through a series of columns comprised of three, 2-in.-diameter by 4-ft.-length cation-exchange beds containing 40-50 mesh, acid-form, Dowex 50W-X8 resin; and the system was rinsed with distilled water to eliminate sulfuric acid and NTA. The system was then eluted with .1 N sodium hydroxide. During elution, a 2-ft. light-colored band formed and progressed down the columns ahead of the lengthening sodium band.

The light-colored band was collected as it passed off the system in a total of twenty 900-ml. fractions. Fractions 1-15 (being colorless and giving similar titration curves) were combined and evaporated to a volume of approximately 400 ml. and cooled to room temperature. Addition of 200 ml. of absolute ethanol induced turbidity which disappeared as the solution was warmed. More alcohol was added and heating was continued until a total of 800 ml. of ethanol had been incorporated and the solution was at its boiling point and permanently turbid. At this point, a further 800 ml. of ethanol was added with stirring and the solution was allowed to cool. The precipitate was recovered by filtration, recrystallized from an ethanol-water solution, and dried under vacuum, yielding 160 g. of product (melting point, 204°-206° C. with decomposition. Elemental analysis of the

Figure 9. NMR spectrum of MEDTA in deuterated water



product gave 43.4% carbon, 6.8% hydrogen, and 11.32% nitrogen (theoretical: 43.55% carbon, 6.45% hydrogen, and 11.29% nitrogen). The formula weight was ascertained to be 250.2 g./mole (theoretical: 248.24) by titration. The NMR spectrum was taken in deuterated water (Figure 9) and consists of singlets 3.0, 3.5, 3.8, and 3.9 ppm. downfield from Tiers salt. The peaks integrate in ratios of 3:4:4:2 respectively. Assignment of these peaks is shown in Figure 9. An additional yield of 18 g. of product was recovered from fractions 16-19, increasing the overall yield to 71%.

B. Determination of Formation Constants

1. Potentiometric method

The experiments done in order to determine the acid-ionization and metal-complex-formation constants of MEDTA were basically high-precision acid-base titrations of the ligand done in the absence and presence of an equivalent quantity of metal ions with which the acid anion forms a strong complex. The temperature and ionic strength of the solutions were regulated at 25° and .1 M respectively. The stock solutions prepared and used in this research are as follow.

a. Rare-earth nitrate solutions Rare-earth nitrate solutions with a concentration of approximately .1M were pre-

pared by dilution of concentrated stock solutions of rare-earth nitrates prepared by Mr. James Farrell. These solutions were in turn prepared from rare-earth oxides of at least 99.9% purity supplied by the rare-earth separation group at the Ames Laboratory of the U. S. Atomic Energy Commission. The concentrated rare-earth nitrate solutions were prepared by the method described by Adolphson (93). They were found to have a 3:1 anion to cation ratio, within experimental error.

The diluted solutions were standardized by precipitation of aliquots with oxalic acid and ignition of the rare-earth oxalates to their corresponding oxides. As a check of these standardizations, complexometric EDTA titrations of the type described by Fritz and Schenk (94) were used.

b. Potassium hydroxide solution .1 M potassium hydroxide was prepared by diluting concentrated, carbonate-free potassium hydroxide purchased from Anchemia Chemicals Ltd. in boiled, deionized water. The resulting solution was kept in a large container and protected from carbonate contamination by a carbon dioxide trap. The solution was standardized by titration against primary standard grade potassium acid phthalate.

c. Nitric acid solution Approximately .1 M nitric acid solution was prepared from concentrated, reagent-grade acid. The solution was standardized by titration against

standard potassium hydroxide solution.

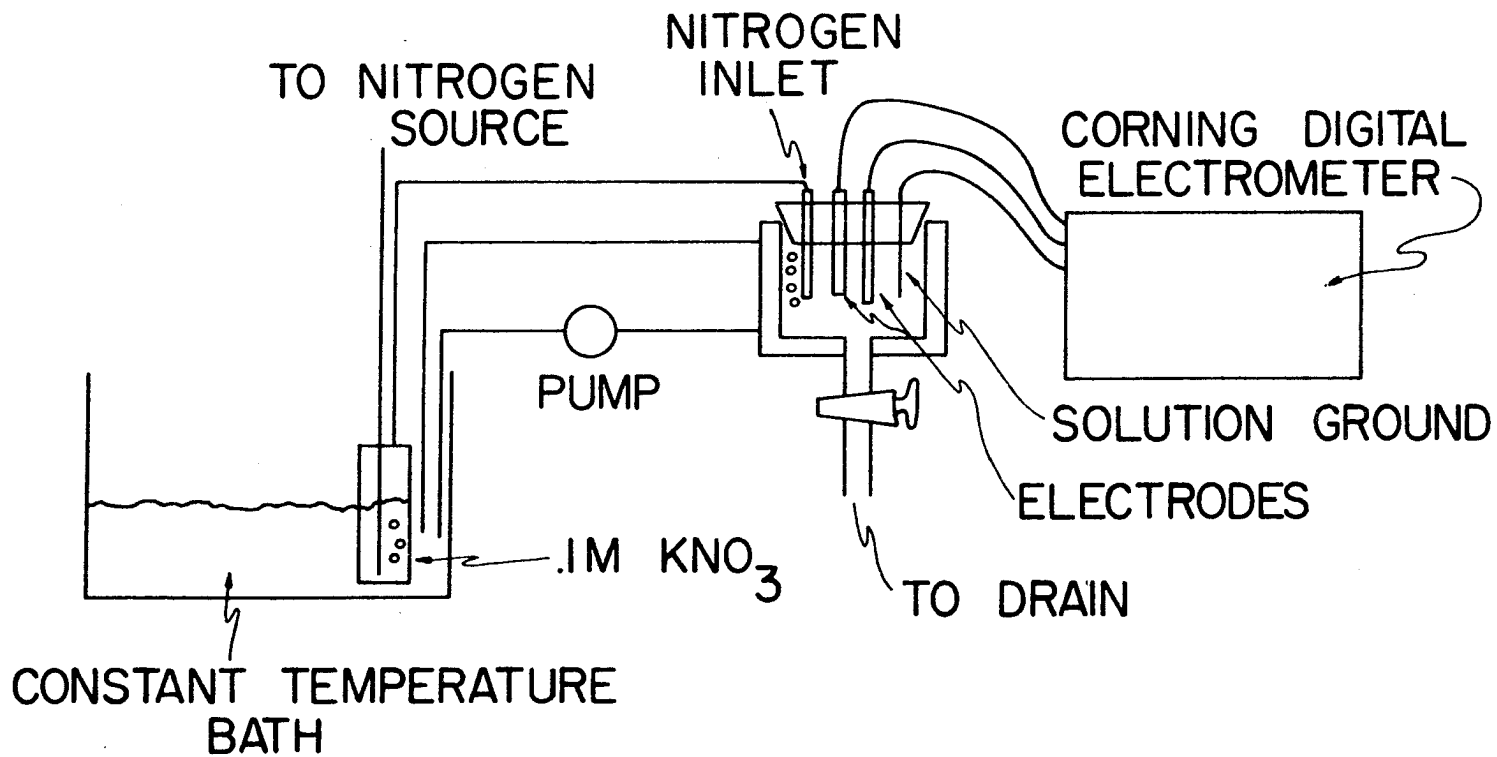
d. Potassium nitrate solution Approximately 2 M potassium nitrate was prepared from J. T. Baker reagent-grade potassium nitrate, dissolved in boiled, deionized water. The resulting solution was standardized by passing aliquots through a bed of Dowex-50 strong acid ion-exchange resin in the H⁺ form and titration of the displaced acid with potassium hydroxide.

e. MEDTA solution A solution containing approximately .1 M MEDTA was prepared by dissolution of recrystallized MEDTA, prepared by the method described earlier. The solution was standardized by titration with standard potassium hydroxide.

f. Experimental apparatus The apparatus for the potentiometric experiments included a pair of constant temperature water baths, equipped to circulate through a jacketed titration cell. The temperature of these baths was maintained at 25.00° ± .02° by a Philadelphia Micro-set thermoregulator and a Precision Scientific electronic relay, which switched a heating element.

The titration cell was prepared by the Ames Laboratory glass shop and is shown in Figure 10. The cell is equipped with a Beckman sleeve-type calomel reference electrode, a Beckman (or Corning) glass electrode, a solution ground, a tube for bubbling nitrogen through the solution, a filling

Figure 10. Apparatus for pH measurements .



funnel and a drain. Since a separate solution was prepared for each experimental point, this cell was not a titration cell in the true sense of the word, but was rather designed to make highly reproducible pH determinations of successive prepared solutions of known stoichiometry. The solution ground was simply a platinum wire, immersed in the solution and connected electrically to the ground terminal of the potentiometer. The solution ground and the sleeve-type reference electrode were incorporated into the system in order to alleviate some rather persistent problems of instability and irreproducibility. They did, in fact, solve the problem rather well. It was also found that the stability of the glass electrode was improved substantially by storing it in strong acid solutions during periods of disuse.

The potentiometer used in this research was a Corning Model 101 Digital Electrometer. This instrument has a number of modes of operation, including direct pH readout which was used in this research. This instrument was better than the currently available electrodes in terms of accuracy, stability, and reproducibility. The 101 Electrometer will read pH values to within ± 0.001 pH units with comparable linearity and repeatability. High quality glass and reference electrodes will deliver comparable performance only when in perfect operating condition, a state much more easily discussed than attained.

g. Experimental procedure The pH measuring equipment was standardized in the following manner in order to yield readings in terms of H^+ concentration rather than activity.

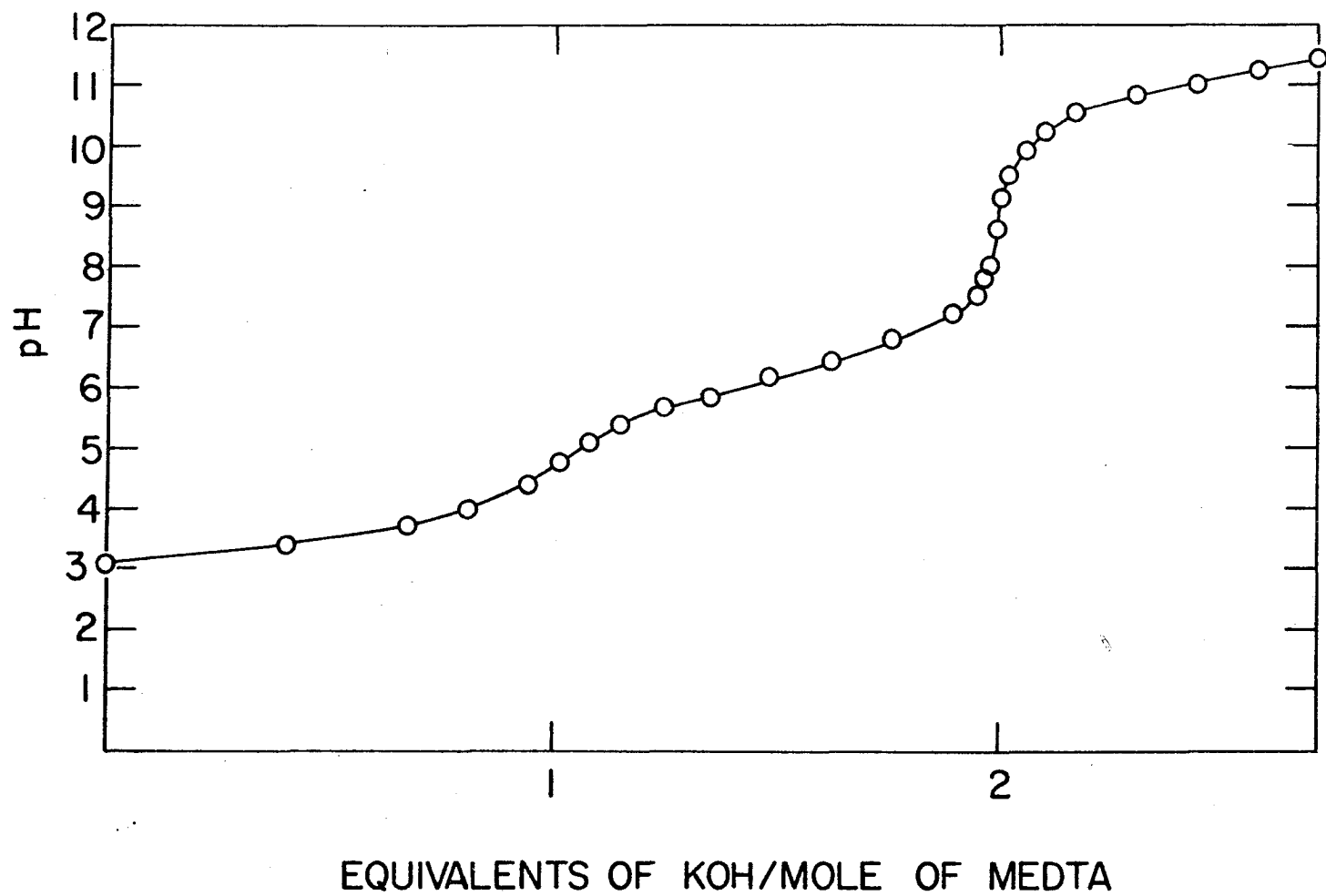
The Corning Electrometer has controls for standardization of the instrument on a given value for a standard solution, and for compensation for deviations from the theoretical value of the Nernst slope of the electrodes. Standardization of the slope requires the use of two standard solutions, one of which must have a pH of greater than 3.5. For best accuracy of standardization, the nominal pH values of these standards should be separated by at least one full pH unit. As the correction between the activity (pH) scale and the concentration scale at a given temperature and ionic strength is an additive constant (95), the slopes of the activity and concentration scales, for a given set of electrodes are equal. Standard pH buffers, purchased from Beckman Inc. with pH values of 4.008 and 7.00 were used to standardize the slope of the pH measuring apparatus. After adjusting the slope in this manner, the instrument was standardized to read 3.000 as the pH of a 10^{-3} M nitric acid solution with its ionic strength adjusted to .100 M. For measurements made in the basic range, the instrument was standardized using 10^{-3} M potassium hydroxide solution, the hydrogen ion concentration of which was calculated from the

value of the water constant at $.100M$ ionic strength at $25^{\circ}C$. given by Harned and Owen (95). The validity of this standardization procedure was checked by measurement of $.100 M$ ionic strength solutions of varying H^+ concentrations. Agreement was found to be excellent up to a pH of 4, above which it becomes difficult to prepare accurate strong acid concentration standards.

The ionization constants of MEDTA were determined by two experiments. MEDTA exhibits three buffer ranges in its titration curve, one of which occurs at a considerably higher pH range than do the other two (Figure 11). The value of K is determined by points from the titration curve at which MEDTA is between $2/3$ and completely neutralized by potassium hydroxide, that is, for points on the curve which give \bar{p} between 0 and 1. The other ionization constants are determined from points on the curve which correspond to MEDTA being less than two-thirds neutralized. Since the values of the second, third, and fourth ionization constants are relatively similar, they must be determined simultaneously, by the method discussed in the calculations section of this dissertation.

In order to closely control the ionic strength of the system, a separate solution was prepared for each experimental point. The amount of potassium nitrate needed to raise the total ionic strength to $.1M$ was calculated and added.

Figure 11. Titration curve of MEDTA



The individual solutions were prepared in 200-ml. volumetric flasks. They were approximately .002 M in MEDTA and contained varying amounts of potassium nitrate or nitric acid. Sufficient potassium nitrate was added to raise the ionic strength to .1 M. The solutions were equilibrated at 25° C. for at least 12 hours. The pH measuring apparatus was then standardized and the concentration pH values were measured. At the completion of the measurements, the standardization was checked for drift. The variation was typically less than .002 pH units.

Data for the determination of the rare-earth-MEDTA complex formation constants were obtained in much the same manner as those for the ionization constants. Solutions containing .002 M MEDTA and rare earth and varying amounts of base and salt were prepared, equilibrated, and their pH measured. All pH measurements were made in a buffer range of the particular system. Measurements made in the region of an inflection point injected considerable error into the curve fit.

2. Polarographic method

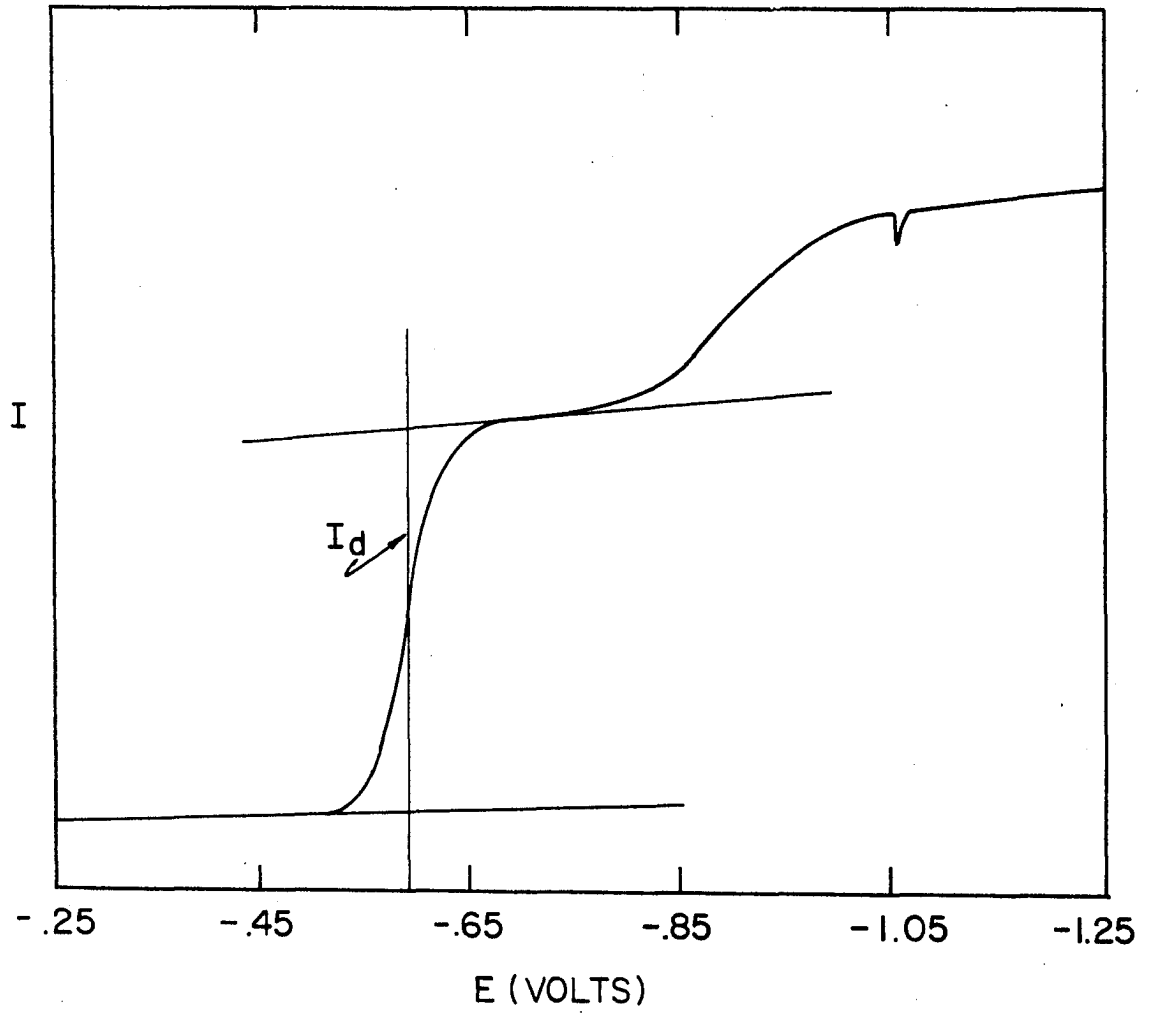
a. Reagents The same stock solutions as described in the potentiometric procedure were used in the polarographic determination of the rare-earth-MEDTA complex stability constants. In addition, standard zinc and cadmium solutions

were prepared. Standard zinc and cadmium solutions were prepared by the dissolution of reagent-grade zinc and cadmium nitrates in sufficient water to cause the solution to be 0.1 M in zinc or cadmium. The solutions were then standardized by titration with EDTA.

b. Apparatus The apparatus used for the polarographic determination of the rare-earth--MEDTA complex stability constants consisted of a Metrohm model 12 polarograph, equipped with a jacketed electrolysis cell, a dropping mercury electrode and a Sargent rapid drop apparatus. The electrolysis cell was connected to a constant (25° C.) temperature bath and was equipped to bubble nitrogen through the test solution. For the determination of the cadmium-MEDTA complex stability constant, it was necessary to measure the hydrogen ion concentration of each solution. The apparatus described in the previous section was used to do so.

c. Experimental procedure The determination of the cadmium-rare-earth ligand exchange constant requires only knowledge of the free cadmium diffusion current and the initial concentrations of all species, if the pH is kept in a range which precludes the formation of protonated or hydroxide species. A series of solutions were prepared, containing .001 M cadmium nitrate, rare-earth nitrate and MEDTA. Sufficient base was added to bring the pH to approximately 5.0. The solutions were equilibrated at least 12 hours in a con-

Figure 12. Polarogram of Cd^{+2} in the presence of CdMEDTA



stant temperature bath at 25°C. The pH of the solutions was measured as described in the previous section. The polarographic cell was then rinsed several times and filled with each solution in turn. One drop of .2% basic fuchsin solution was added in order to suppress the polarographic maxima. Purified nitrogen was bubbled through the solution for 10 minutes to remove dissolved oxygen. The polarogram was then taken. A typical cadmium polarogram, obtained from equivalent amounts of rare-earth, cadmium and MEDTA is shown in Figure 12.

Considerable variation was observed in the exchange constants of cadmium and the heavy rare earths. It was decided that, since this scatter rendered data on complexes of the rare earths beyond erbium practically worthless, it would be worthwhile to determine the exchange constants between the heavy rare earths and a metal which forms MEDTA complexes of greater stability than does cadmium. For this purpose, zinc was chosen. The exchange constants between zinc and the heavy rare earths were determined by the same procedure as were those of cadmium. The starting voltage of the polarograph was increased in order to accommodate the increased reduction potential of zinc with respect to cadmium. Data taken on the zinc-rare-earth exchange constants proved to be quite self-consistent as far down the series as dysprosium.

C. Ion-exchange Experiments

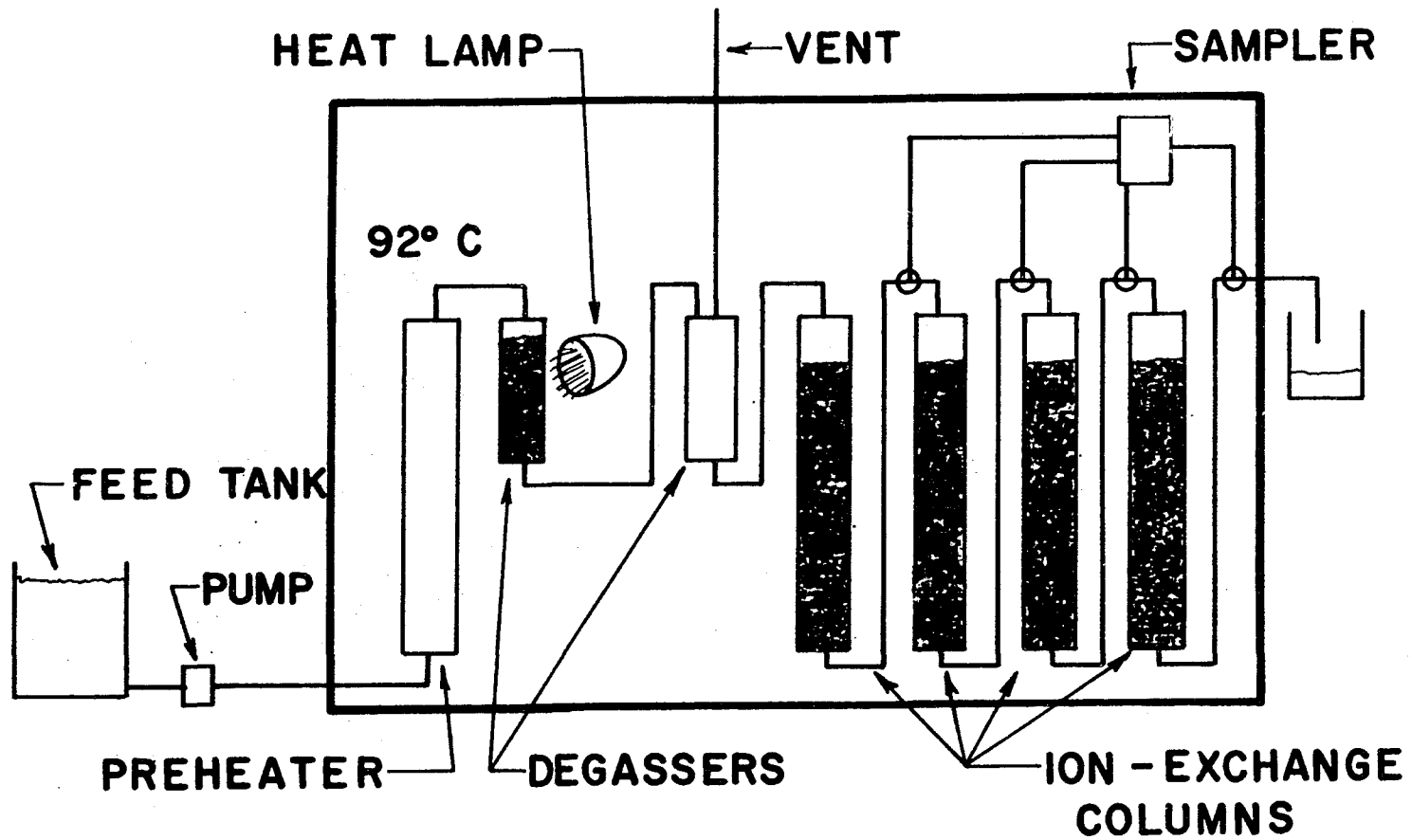
Ion-exchange experiments were done using the anion of MEDTA as the eluant. The experiments were done at room temperature and at 92°C. in a specially designed hot room. The purpose of the experiments was to obtain steady-state profiles of the area of overlap between bands of individual rare earths. From this information, one may calculate the ratio of the logarithm of the separation factor to the HETP.

1. Apparatus

The same set of ion-exchange columns was used for the boundary experiments at both room and high temperature. It consisted of five 1-inch diameter by 4-foot length Pyrex columns equipped with heat resistant fittings made of teflon. They contained Dowex 50W-X8 cation-exchange resin. For the room temperature experiments, the only ancillary equipment needed was a variable-speed pump, an eluant feed tank and a sample collector.

Operation at near the boiling point of water required some additional equipment. The high temperature apparatus shown in Figure 13 incorporated an empty 1-inch column as a preheater and a column filled with unbackwashed ammonium-form cation-exchange resin with a heat lamp mounted as an additional heat source. These columns, in addition to a short empty column with a long vent pipe, served to degas the solution and prevent disruption of the resin beds by gas

Figure 13. Experimental apparatus for ion-exchange boundary determinations



desorption. The degassed eluant then passed into the ion-exchange system. Provision for sample collection was made between the columns where an electrically controlled 3-way valve was inserted. This valve and the thermally insulated fraction collector were controlled by an electronic timer.

Most of the equipment described in this section was built or adapted by Ames Laboratory personnel.

2. Procedures

The steady-state boundary concentration gradients at both room temperature and 92° C. were determined by the following procedure.

Portions of 40-50 mesh Dowex 50W-X8 cation-exchange resin, each saturated with a different pure rare-earth cation were sequentially introduced, in the predicted order of elution, into the 1-inch diameter column system. The system, comprised of 24 inches each of from 4 to 6 bands of rare-earth resin, was eluted two band lengths down additional 1-inch columns of the same resin in the H⁺ form with pH 8.0, .01M MEDTA solution at a flow rate of 6.5 ml./minute. This rate of elution caused the visible band boundaries to advance at a rate of about 0.5 inches per hour down the resin bed. After equilibrium was attained, the solution was sampled across the band boundaries as each passed from one column to the next, and was analyzed to obtain ratios of rare earth

concentrations as a function of distance along the band.

After data at 25° C was obtained, the system was moved into a room heated to 92° C., and the procedure was repeated.

The samples were analyzed spectrographically for their rare-earth concentrations. Depending on the rare earths involved, visible, ultraviolet, atomic-absorption or emission spectroscopy were used. In the process of elution, a band of MEDTA formed between the leading rare-earth band and the H⁺ form resin. This phenomenon provided an excellent procedure for recycling the MEDTA. The MEDTA band was simply collected as it came off the end column, diluted, buffered with ammonia and reused.

IV. CALCULATIONS

A. Acid Ionization Constants

Because of the large number of species in the solutions dealt with in this work and the highly charged nature of some of these species, it is rather difficult to calculate thermodynamic equilibrium constants. For this reason, all equilibrium constants referred to in this work are stoichiometric. The measures necessary to determine stoichiometric equilibrium constants are discussed in the experimental section of this dissertation.

The acid ionization constants of MEDTA were calculated by a computer program which used the algorithm described in this section (96, 97).

The N ionization constants of a polybasic acid may be described by N equations of the following form.

$$\chi_n = \frac{[H_n A^{n-3}]}{[H^+]^n [A^{-3}]} \quad (4)$$

$$n = 1, 2, 3, 4$$

Expression of the ionization constants in this form makes them somewhat more amenable to the sort of calculations in which they must be used. The ionization constants in this form may be related to the individual step-protonation con-

starts by equation 5.

$$\log \chi_n = \log K_1 + \log K_{12} + \log K_{13} + \log K_{14} \quad (5)$$

In order to calculate the ionization constants of a weak acid, one needs to know the following experimentally determined quantities.

H_t = total acid concentration

A_t = total ligand concentration

$[H^+]$ = hydrogen ion concentration

The quantity \bar{p} , the average protonation number of the ligand is given by equation 6.

$$\bar{p} = \frac{H_t - [H^+]}{A_t} \quad (6)$$

\bar{p} may also be defined in terms of the formation constants for acidic species.

$$\bar{p} = \frac{\sum_{n=1}^N n \chi_n [H^+]^n}{1 + \sum_{n=1}^N \chi_n [H^+]^n} \quad (7)$$

Equations 6 and 7 may be combined to give equation 8.

$$\sum_{n=1}^N (H_t - [H^+] - nA_t) [H^+]^n \chi_n = [H^+] - H_t \quad (8)$$

This is an equation in which the only unknown quantities are the N acid formation constants. Each alteration of the stoichiometry of the system gives an independent equation of the form of equation 8, so if one has N data points, the N values of the acid formation constants may be calculated algebraically. It leads to more reliable results if a large number of data points (M) are taken. This, however, causes the system to be overspecified. One now has the options of taking the points N at a time and calculating the N acid formation constants using the N simultaneous equations, or using regression techniques. The use of multiple linear regression is advantageous because it allows one to evaluate the entire data set, regardless of how many data points are involved.

The matrix linear regression method, described by Draper and Smith (98) was incorporated into a Fortran subroutine called WLSQ. WLSQ is a weighted, double precision multiple linear regression routine. WLSQ uses the doubly pivoted Gaussian elimination routine DGELG, described in the IBM scientific Subroutine Package Manual (99) to solve the normal equations of the linear regression. Sample data from Draper and Smith (98) were fed into WLSQ. The regression coeffi-

coefficients calculated by WLSQ were found to be in excellent agreement with previously calculated regression coefficients for the data.

It is necessary to weight the regression, as some data points for this system inherently contain greater relative error than do others. The expression for the residual formed by the regression is of the form;

$$S = \sum_{i=1}^N \omega_i v_i^2 \quad (9)$$

where v_i is defined as;

$$v_i = H_t - [H^+] - \sum_{n=1}^N (\{H_t - [H^+] - nA_t\} [H^+]^n \chi_n) \quad (10)$$

The standard deviation for each v_i is given by the law of propagation of errors (equation 11).

$$s_i = (\partial v_i / \partial H_t)^2 s_{H_t}^2 + (\partial v_i / \partial [H^+])^2 s_{[H^+]}^2 + (\partial v_i / \partial A_t)^2 s_{A_t}^2 \quad (11)$$

This gives an expression for the standard deviation of the residual corresponding to each point in terms of the estimated standard deviation of each experimental quantity, the

regression coefficients, and the value of the experimental quantities. The weight of each point i is given by:

$$\omega_i = 1/s_i^2 \quad (12)$$

Since it is necessary to have values for the regression coefficients in order to calculate the weights, an iterative procedure is required.

During the solution of the regression problem, a set of normal equations are generated (equation 13).

$$|C| |E| = |D| \quad (13)$$

$|C|$ is the matrix of the coefficients of X , $|E|$ is the column vector of regression coefficients, and $|D|$ is a column vector of constants. The standard deviation of X_i is given by equation 14.

$$s_{\chi_i} = (c_{ii} \sigma^2)^{1/2} \quad (14)$$

The linear regression treatment is needed (and applicable) only when two or more buffer ranges of the acid in question overlap. If the ratio of the two ionization constants

is greater than approximately 1000, they may be determined independently. In the case of MEDTA, χ_1 was determined by one set of experiments and calculations. χ_1 , χ_2 and χ_3 were determined simultaneously, using the procedure described in this section.

B. Rare-Earth and Yttrium Complex Formation Constants

Several methods exist for the elucidation of metal complex formation constants. Since many reviews (93, 11, 4, 97) have been written on this topic would serve little purpose to discuss all the commonly used methods in this section. This discussion will be restricted to methods used in this research. Two methods were used to determine the formation constants of MEDTA complexes of yttrium and the rare earths, the first was a polarographic method, using the limiting current as a measure of free reducible ion concentration and the second made use of the potential of a glass electrode in the determination of hydrogen ion concentration.

1. Polarographic method

Determination of the polarographic diffusion current is a convenient method for the determination of the concentration of certain metal ions in solution. The diffusion current is directly proportional to the concentration of the ion

causing the polarographic wave over a rather large range of concentrations. Since most stable complexes reduce at an appreciably different potential than do their free metal ions, it is possible to determine the free metal ion concentration in the presence of stable complexes of this metal.

As it is not feasible to polarographically determine rare-earth ion concentrations (with the exception of trivalent Eu), it was decided to use divalent Cd as an "indicator ion", that is to compete cadmium with rare earths for a limited amount of ligand anion.

The formation constant of the cadmium complex of MEDTA was calculated from titrations of MEDTA in the presence of equivalent and 10-fold excess concentrations of cadmium. The protonation constant of the Cd-MEDTA complex was determined from the excess metal titration curve and the formation constant of the anionic complex was determined from the equivalent curve.

In a system comprised of MEDTA and a 10-fold excess of cadmium, the equilibrium is shifted toward formation of the protonated and anionic complexes. If it is assumed that all the ligand is in the form of one of these complexes (as is the case above pH 3), it is not difficult to calculate the protonation constant (equation 15) from a titration of the acidic complex.

$$\beta_H = \frac{[\text{HCdA}]}{[\text{H}^+][\text{CdA}^-]} \quad (15)$$

The average protonation number \bar{p} of the complex is given by equation 6. From this information one may calculate β_H .

$$\beta_H = \frac{\bar{p}}{(1-\bar{p})[\text{H}^+]} \quad (16)$$

In order to calculate the formation constant of the anionic MEDTA complex of cadmium from an equivalent titration curve, the following data must be known.

H_t = Total acid concentration.

A_t = Total ligand concentration.

M_t = Total cadmium concentration.

$[\text{H}^+]$ = Hydrogen ion concentration.

β_H = Complex protonation constant.

The material balance equations of the system are given by equations 17-19.

$$H_t = [\text{HCdA}] + [\text{A}^{-3}]\psi \quad (17)$$

$$A_t = [\text{HCdA}] + [\text{CdA}^-] + [\text{A}^{-3}]\phi \quad (18)$$

$$M_t = [\text{Cd}^{+2}] + [\text{CdA}^-] + [\text{HCdA}] \quad (19)$$

ψ and ϕ are functions defining the concentrations of protonated acid species (equations 20 and 21).

$$\psi = \sum_{i=1}^4 \chi_i [\text{H}^+]^i \quad (20)$$

$$\phi = 1 + \sum_{i=1}^4 \chi_i [\text{H}^+]^i \quad (21)$$

combining equations 6, 17 and 18 and solving for the ligand anion concentration gives equation 22.

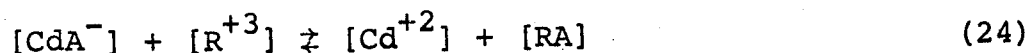
$$[\text{A}^{-3}] = \frac{\frac{H_t - [\text{H}^+]}{\beta_H [\text{H}^+]} - \frac{A_t}{1 + \beta_H [\text{H}^+]}}{\frac{\phi}{\beta_H [\text{H}^+]} - \frac{\psi}{1 + \beta_H [\text{H}^+]}} \quad (22)$$

Equation 17 may now be solved for the protonated complex concentration which may in turn be used with equation 18 to find the complex anion concentration. The free metal concentra-

tion may then be found from equation 19. With these quantities at hand, one may calculate the formation constant of the cadmium-MEDTA complex from equation 23.

$$\beta_{\text{Cd}} = \frac{[\text{CdA}^-]}{[\text{Cd}^{+2}][\text{CdA}^-]} \quad (23)$$

A solution containing approximately equimolar amounts of rare earth, cadmium and ligand at a sufficiently high pH as to minimize formation of acid species will attain the following equilibrium.



The equilibrium constant for this reaction is called the exchange constant, and consists of the ratio between the formation constant of the lanthanide complex and that of cadmium.

$$K_e = \beta_{\text{R}}/\beta_{\text{Cd}} = \frac{[\text{Cd}^{+2}][\text{RA}]}{[\text{R}^{+3}][\text{CdA}^-]} \quad (25)$$

The experimental quantities needed to calculate the exchange constant are;

$$A_t = \text{total ligand concentration}$$

R_t = total lanthanide concentration

Cd_t = total cadmium concentration

$[Cd^{+2}]$ = free cadmium concentration

If the pH is kept in a region (4-5) which minimizes the formation of acid or hydroxy species, the material balance equations become;

$$R_t = [R^{+3}] + [RA] \quad (26)$$

$$Cd_t = [Cd^{+2}] + [CdA^-] \quad (27)$$

$$A_t = [RA] + [CdA^-] \quad (28)$$

With the knowledge of each of the total quantities and the free cadmium concentration, it becomes a simple matter to calculate the exchange constants.

In practice, the stabilities of the complexes of the rare earths must be comparable to that of the polarographically reducible ion. If this is not the case, the exchange equilibrium will be shifted excessively. This is particularly troublesome if the inert complex is greatly more stable than that of the polarographically reducible ion. The problem in either case is that the concentrations of some species become so small as to become comparable with experimental error. This situation, of course, causes extremely large errors in the calculated exchange constant.

In order to minimize the effect of the above mentioned problem, the heavy-rare-earth exchange constants were obtained for zinc. The zinc-MEDTA complex is slightly more stable than is that of Lu. In order to obtain the most self consistent set of rare earth data possible, the zinc-MEDTA stability constant was determined from the previously determined stability constants of the middle rare earths and the exchange constants between these metals and zinc.

2. Potentiometric method

In hope of improving the precision of the data on the stability constants of the rare earth complexes of MEDTA and to provide a check of the polarographic method, the stability constants of the rare earth and yttrium complexes were determined by a potentiometric method. This was accomplished by the use of a glass electrode to measure the hydrogen ion concentration of equilibrium solutions containing approximately equal amounts of metal ion and ligand with varying amounts of base. Data from polarographic studies indicated that significant breakdown of rare-earth-MEDTA complexes into metal ions and protonated ligand species would occur in the pH range of 2 to 3. This method is similar to the polarographic method in that two species are competing for a limited amount of ligand.

The material balance equations for a solution containing nearly equimolar amounts of a weak, polybasic acid and a metal ion with which it forms a 1-1 complex are as follow.

$$H_t = [A^{-3}]\psi + [H^+] \quad (29)$$

$$A_t = [RA] + [A^{-3}]\phi \quad (30)$$

$$R_t = [R^{+3}] + [RA] \quad (31)$$

The experimentally known quantities are:

M_t = total metal in the system

A_t = total ligand in the system

H_t = total acid in the system

$[H^+]$ = hydrogen ion concentration

As the protonation constants of the MEDTA anion are known, equation 29 may be solved for the ligand anion concentration (equation 32).

$$[A^{-3}] = \frac{H_t - [H^+]}{\psi} \quad (32)$$

Equation 30 may be arranged in the following fashion:

$$[MA] = A_t - [A^{-3}]\phi \quad (33)$$

and solved for the concentration of complex. The metal ion concentration may be determined from equation 33. As the concentrations of metal ion, metal complex and ligand anion have been found, the stability constant of the complex may be calculated using equation 15.

C. Ion-Exchange Parameters

The two parameters obtained from the ion-exchange experiments are the HETP and the ion-exchange separation factor. The significance of these two parameters is discussed in Section I.

In a cation-exchange system in which two metal ions B^{+3} and C^{+3} are loaded upon the resin, the separation factor for elution with a chelating agent (A^{-3}) may be calculated from stability constant data as follows.

The definition of the ion-exchange separation factor for B and C is

$$\alpha = \frac{[B][\bar{C}]}{[\bar{B}][C]} \quad (34)$$

where $[B]$, $[C]$, $[\bar{B}]$ and $[\bar{C}]$ refer to the concentrations of all species containing B or C in the solution and resin phases, respectively. If A^{-3} is a ligand which forms only simple neutral or anionic complexes with B and C cations at

the experimental conditions, one may write the following material balance equations:

$$[B] = [B^{+3}] + [BA] \quad (35)$$

$$[C] = [C^{+3}] + [CA] \quad (36)$$

If the stabilities of the BA and CA species are sufficiently large (as in the case of most rare-earth aminopolycarboxylates) the concentrations of the complexes will be large compared to the concentrations of metal cations. One may then simplify the solution-phase material balance equations to:

$$[B] \approx [BA] \quad (37)$$

$$[C] \approx [CA] \quad (38)$$

The separation factor then becomes:

$$\alpha = \frac{[BA][\bar{C}]}{[CA][\bar{B}]} \quad (39)$$

This may be expressed in terms of complex formation constants.

$$\alpha = \frac{\beta_B [B^{+3}] [\bar{C}]}{\beta_C [C^{+3}] [\bar{B}]} \quad (40)$$

Most ion-exchange resins (Dowex 50W-X8 included) are virtually nonselective toward rare-earth cations, so:

$$1 \approx \frac{[B^{+3}] [\bar{C}]}{[C^{+3}] [\bar{B}]} \quad (41)$$

Equation 40 then simplifies to the ratio of the two complex stability constants.

$$\alpha = \frac{\beta_B}{\beta_C} \quad (42)$$

Knowing the stability constants of the two complexes, one may, to a good approximation, calculate the separation factor.

Once the separation factor is known, one may calculate the HETP from the steady-state concentration gradient at the boundary between the B and C bands.

Equation 3 applies to the area of overlap at equilibrium, and may be rearranged to give equation 43.

$$\log (B/C)_m = \frac{\log \alpha}{h} L + \log (B/C)_0 \quad (43)$$

it may be seen that the slope of a plot of the logarithm of the ratio of B to C vs. distance along the band (L) will be $(\log \alpha)/h$, so, if the separation factor is known, one may evaluate the HETP using graphical or least squares techniques.

Methods for the calculation of separation factors and plate distances in nonequilibrium systems using rates of boundary movement in displacement chromatographic systems are known (77, 24, 100). This method, however, requires far more samples to be taken and analyzed. The steady state approach was deemed to be more suitable for the MEDTA-rare-earth system.

V. RESULTS

All the equilibrium constants reported in this dissertation are stoichiometric values at an ionic strength of 0.1 M and a temperature of 25° C. The ion-exchange results were not obtained at a controlled ionic strength and were subject to greater temperature fluctuations than were the equilibrium measurements.

A. Protonation Constants of the MEDTA Anion

The protonation constants of the MEDTA anion were calculated from the data in Appendix A. and are shown in Table 16. The titration curve of MEDTA (Figure 11) shows the three distinct buffer ranges exhibited by MEDTA. The buffer range corresponding to the singly protonated MEDTA species occurs at significantly higher pH values than do any of the others. This fact allows the independent calculation of the first protonation constant of the MEDTA anion. The step-formation constants corresponding to the formation of more extensively protonated species are of sufficiently similar magnitude to necessitate their simultaneous calculation.

The indicated standard deviation for the first protonation constant was calculated from the distribution of the experimental formation constants calculated from the experi-

Table 16. Step-protonation constants of the MEDTA anion

		σ
K ₁	2.036 X 10 ¹⁰	1.4%
K ₁₂	2.612 X 10 ⁵	1.4%
K ₁₃	2.84 X 10 ²	8.3%
K ₁₄	84	17.7%

mental points. The standard deviations of the other step-formation constants were calculated by the regression procedure. Errors in standardization of the stock solutions are reflected in these standard deviations as lack of fit in the regression model.

B. Formation Constants of MEDTA Complexes

1. Potentiometric method

The formation constants of MEDTA complexes of the rare earths were determined by measurement of the pH of solutions containing various proportions of MEDTA and rare-earth cations (Appendix A). Results of this work are shown in Table 17. The indicated standard deviations were obtained from the distribution of experimental formation constants. The various input data were varied over the range of their expected experimental errors in order to determine the effect of these errors on the calculated formation constants. This caused a variation of the formation constants of approximately 0.1 log. units. This figure is probably a good indication

of the overall precision of the data. The standard deviations indicated in Table 17 are indicative of the self-consistency of the series.

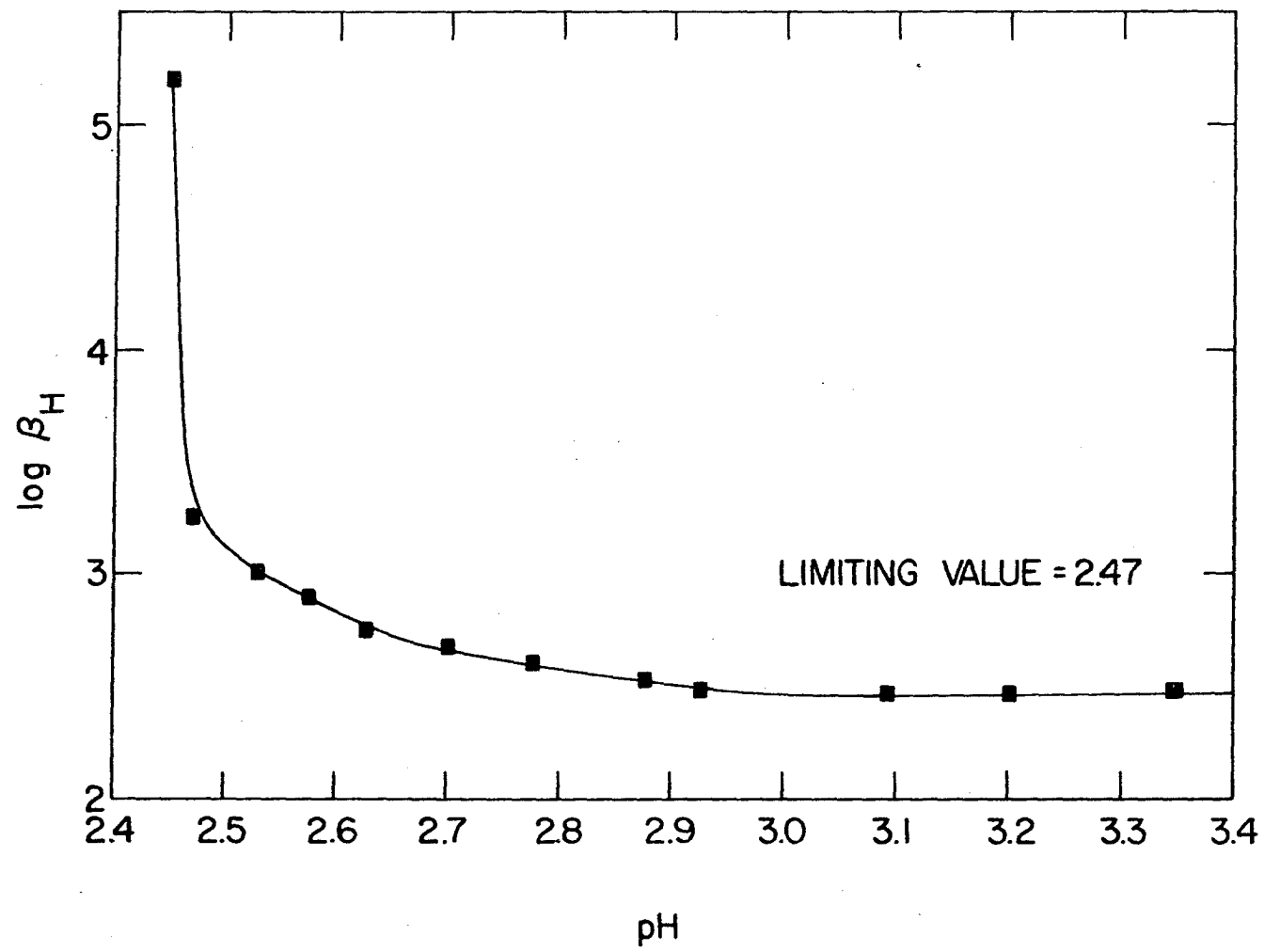
Table 17. Formation constants of rare-earth complexes of MEDTA as determined by the potentiometric method

M	log K	σ	M	log K	σ
La	11.50	.01	Tb	13.35	.03
Ce	11.87	.01	Dy	13.61	.02
Pr	12.33	.01	Ho	13.81	.01
Nd	12.51	.02	Er	14.04	.01
Sm	12.86	.02	Tm	14.31	.01
Eu	12.96	.02	Y	14.43	.01
Gd	12.98	.03	Lu	14.51	.02
			Y	13.35	.01

In order to calculate the formation constant of the anionic MEDTA-cadmium complex, it was necessary to determine the protonation constant of the complex. This was done by swamping the system with cadmium and titrating the resulting acidic cadmium complex. Some dissociation of the complex into Cd^{+2} ions and protonated MEDTA species was indicated at low pH values. This caused the calculated value of the formation constant to be erroneously high at low pH values. A plot of the logarithm of the protonation constant vs. pH (Figure 14) shows an initially high value, which approaches a limit with increasing pH. This limiting value was determined to be $2.47 \pm .01$ log. units.

The formation constant of the anionic MEDTA complex was determined from a titration of MEDTA in the presence of an equivalent amount of Cd^{+2} . This quantity was found to be

Figure 14. Results from the excess cadmium titration curve



13.02± .01 log. units.

2. Polarographic method

The ligand-exchange constants for MEDTA with Cd⁺² and the trivalent rare-earth cations were polarographically determined. In addition, the exchange constants for MEDTA with Zn⁺² and the heavy rare-earths were found. Results of this work are shown in Table 18.

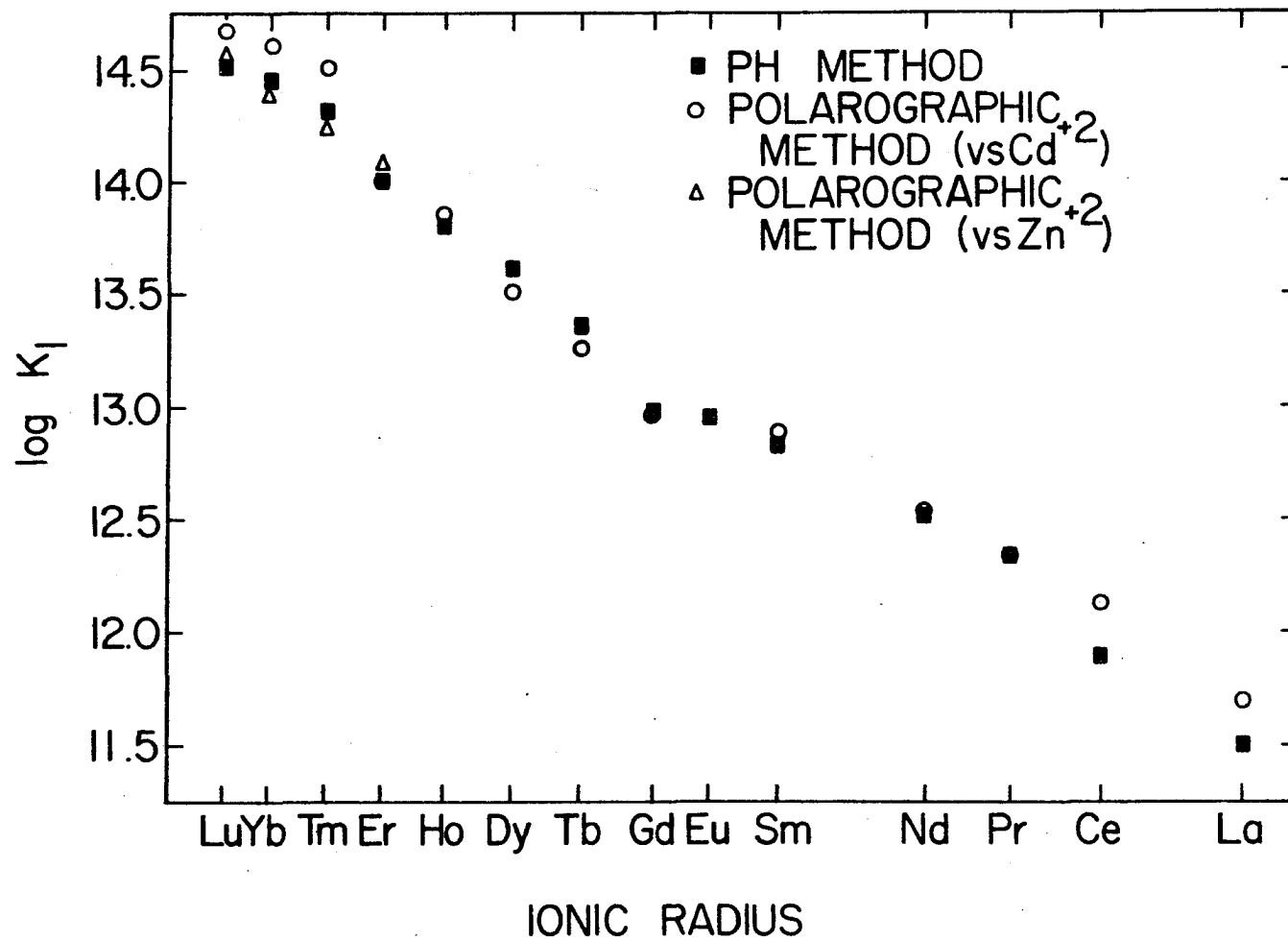
Table 18. Formation constants of rare-earth complexes with MEDTA as determined polarographically

M	log K	σ	M	log K	σ	log K	σ
La	11.71	.07	Tb	13.24	.06		
Ce	12.13	.03	Dy	13.51	.04		
Pr	12.34	.02	Ho	13.84	.16		
Nd	12.53	.03	Er	14.09	.15	14.10a	.04
Sm	12.90	.06	Tm	14.50	.02	14.28	.01
Gd	12.95	.03	Yb	14.61	.10	14.45	.05
Y	13.36	.06	Lu	14.69	.20	14.57	.01

a. vs. zinc

These results were not as reproducible as were the potentiometrically determined formation constants. The exchange constants for cadmium with the heavy rare-earths exhibited a particularly large amount of scatter. The formation constants of the heavy rare-earth complexes are considerably greater than that of the cadmium complex. This causes the difference between the total and uncomplexed cadmium to become so small as to be comparable to the experimental error

Figure 15. Formation constants of rare-earth-MEDTA complexes



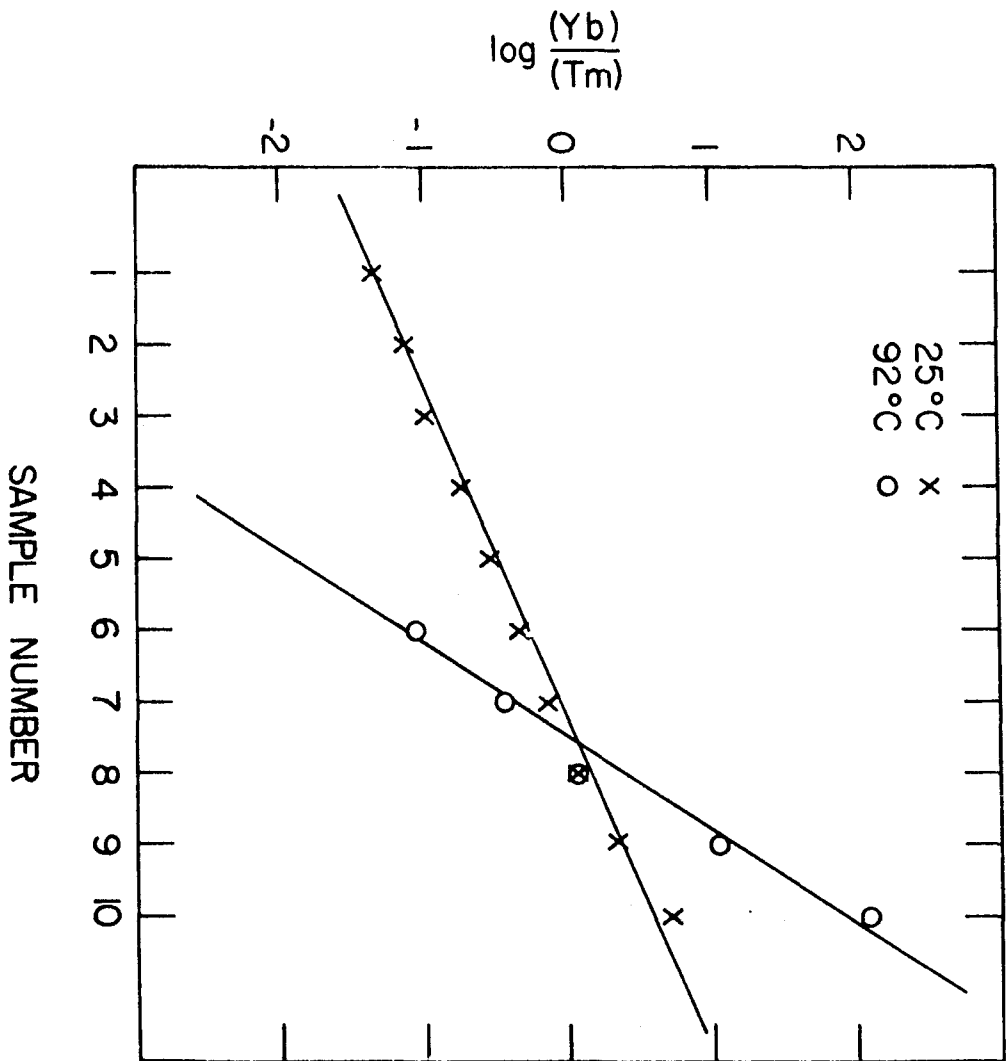
of the polarographic determination of the cadmium ion concentration, causing excessive indeterminate error in the results. The zinc complex exhibits a formation constant which is more comparable to that of these elements, causing smaller amounts of scatter to be observed.

Figure 15 shows the formation constants of the rare-earth-MEDTA complexes as given by the two experimental methods. The data given by the pH method show less experimental scatter than do those provided by the polarograph. The heavy-rare-earth formation constants obtained from ligand exchange data vs. cadmium were extremely imprecise. The same quantities, when obtained vs. zinc, were not only more internally consistent, but fitted the trend of the rare-earth stabilities more closely.

C. Ion-Exchange Results

The ion-exchange boundary gradients were determined for adjacent rare-earth pairs from Lu through Tb. Data was taken at both room temperature and 92° C. Using the previously determined formation constants for MEDTA complexes of these elements, the separation factors shown in Table 19 were calculated. With these separation factors, the HETP values for the individual boundaries may be calculated. Results of such calculations are shown in Table 20. The concentration gradient of a typical boundary in this system is shown

Figure 16. Typical ion-exchange boundary gradient



in Figure 15.

Table 19. Calculated separation factors for ion-exchange separations of the rare earths with MEDTA

	a	b		a	b
La-Ce	2.34	2.63	Tb-Y	1.0	1.32
Ce-Pr	2.88	1.62	Tb-Dy	1.82	1.86
Pr-Nd	1.51	1.55	Y-Dy	1.82	1.86
Nd-Sm	2.24	2.34	Dy-Ho	1.58	2.14
Sm-Eu	1.26		Ho-Er	1.70	1.78
Eu-Gd	1.05		Er-Tm	1.86	2.57
Gd-Tb	2.34	1.95	Tm-Yb	1.32	1.29
			Yb-Lu	1.20	1.20

a. potentiometric data

b. polarographic data

Table 20. Ion-exchange boundary concentration gradients and HETP values at 25° and 92° C.

R - R'	slope	h (cm.)	slope	h (cm.)
Lu-Yb	.064a	1.25a	.217b	.308b
Yb-Tm	.103	1.16	.303	.396
Tm-Er	.101	1.88	.244	.778
Er-Ho	.221	1.04	.562	.409
Ho-Dy	.205	1.58	.472	.423
Dy-Tb	.210	1.23	.507	.512

a. 25° C

b. 92° C.

The concentration gradients were obtained from least-squares fits of the logarithm of the concentration ratio vs. distance along the band. For this particular system, one sample corresponded to 2.54 cm. The experimental curves typically fit a straight line with a standard deviation of from 5% to 10%.

VI. DISCUSSION AND CONCLUSIONS

At the outset, the goals of this research were twofold. Studies of HEDTA complexes of the rare earths (54, 55) revealed some unusual properties. It was thought that a study of the MEDTA complexes of the rare earths might provide some insight into these properties. Second, it was hoped that MEDTA might prove to be a superior reagent for displacement ion-exchange separations of the rare-earth elements.

A. Trends in Rare-Earth Complex Stabilities

The high stabilities of multidentate chelate complexes of the rare-earth cations are largely attributed by Betts and Dahlinger (15) to a large entropy increase upon disruption of the highly ordered hydration sphere of the cations by the multidentate ligand. It has been well established (24, 25, 28) that rare-earth cations have large coordination numbers (Figure 2). The number of chelate rings which may be formed is then chiefly limited by the restrictions of the ligand, with respect to functionality and configuration. Each additional chelate linkage which can be formed causes further disruption of the hydration sphere of the rare-earth cation, resulting in greater entropy of formation and correspondingly greater complex stability.

The rare-earth cations show a regular decrease in ionic radius across the series from La^{+3} to Lu^{+3} with atomic number. This is indicative of the increasing electrostatic forces exerted by the ion on its coordination sphere. While, in general, an increase in electrostatic attraction between metal and ligand is paralleled by an increase in complex stability, some ligands do not show a regular increase in stability with atomic number. HEDTA, DTPA, ME and DE are ligands of this type (Figures 5, 6). This behavior is thought to be caused by a change in the dentate character of the ligand as a function of ionic radius. Some ligands appear to be sufficiently strained when complexing the smaller members of the rare-earth series that all the potential chelate linkages cannot form.

EDTA and HEDTA are extremely similar in structure, differing only in the substitution of a hydroxyethyl group for one of the acetic acid groups of EDTA. This small change in structure causes quite radical changes in properties. For example, the solubilities of HEDTA and its rare-earth complexes in water are considerably higher than are those of EDTA and its complexes.

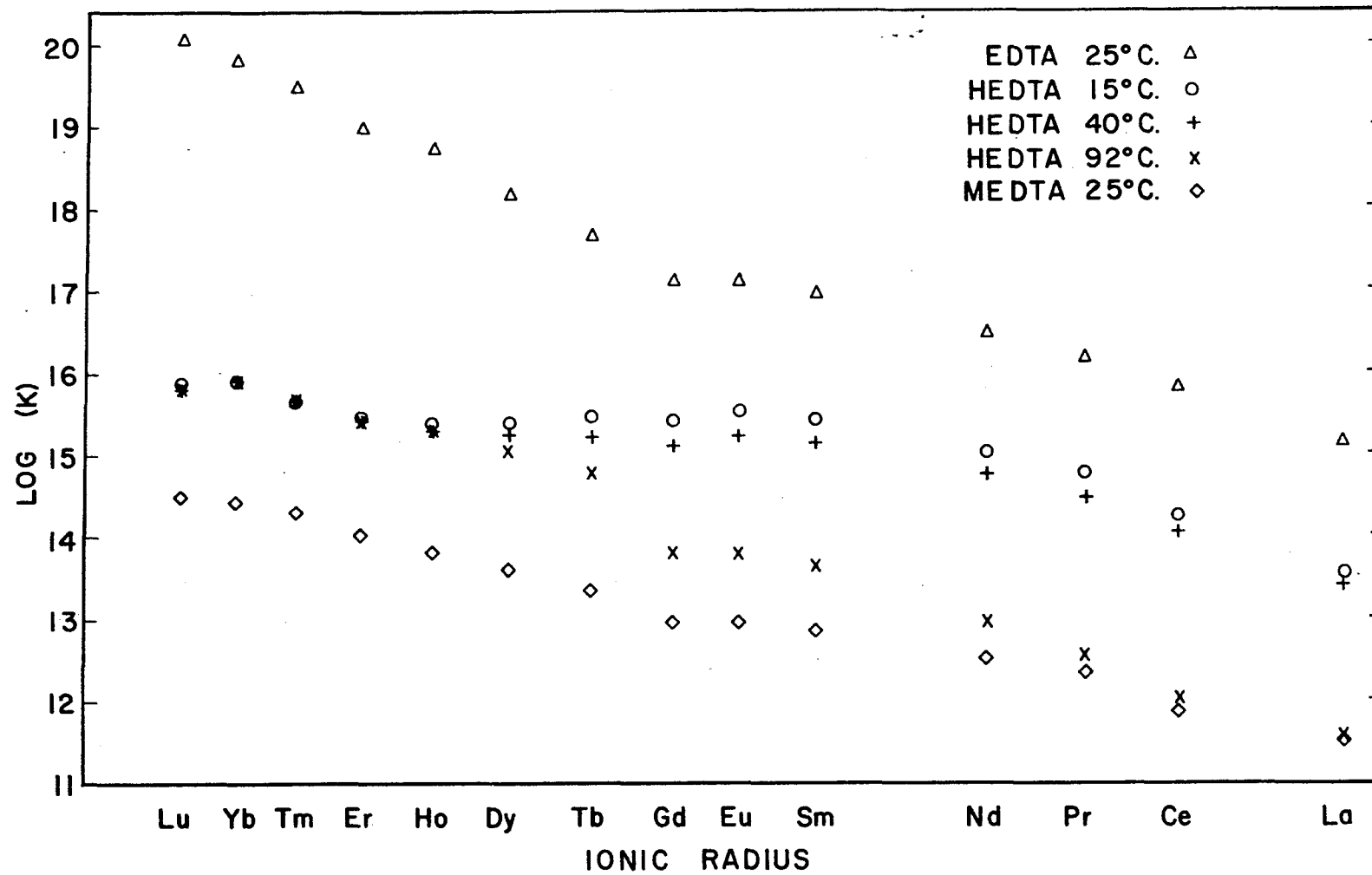
The stabilities of HEDTA and EDTA complexes of the rare earths do not follow similar patterns. Figure 6 clearly reveals that, while EDTA chelates show a regular stability increase across the series, HEDTA chelates exhibit a leveling

out of complex stability across the middle of the series with an increase from Tm to Lu. A change in the dentate character of the ligand from 6 with the light rare earths to 5 with the heavy members of the series has been proposed (54). As the only structural difference between EDTA and HEDTA is the substitution of a hydroxide for a carboxylate group, the hydroxyethyl chelate linkage is thought to be unable to form with the smaller rare-earth ions.

The change in the complexation of the rare earths by HEDTA with increased temperature has been explained by a similar mechanism. It may be seen (Figure 17) that, at 92° C., HEDTA complexes the rare earths in much the same manner as does EDTA, although the overall stability of the series is lower. It has been proposed (55) that, at 92° C., the hydroxyethyl chelate linkage does not form in any of the rare-earth complexes. This would cause HEDTA to act as a purely 5-coordinate ligand across the series, much as EDTA is thought to be purely 6-coordinate.

One of the objectives of this research was to provide a chemical test for the validity of this hypothesis. MEDTA is restricted by functionality to the formation of five chelate linkages. It should then, be quite similar in this respect, to HEDTA with the effect of the hydroxyethyl group removed. This would imply that the formation constant curve of HEDTA at high temperature should resemble the MEDTA curve at room

Figure 17. Comparison of MEDTA to other chelating agents



temperature

Examination of Figure 16 shows that the complexes of MEDTA do indeed exhibit a regular increase in stability across the series. MEDTA does appear to be acting as a 5-dentate ligand across the series. The stabilities of light-rare-earth complexes of MEDTA at 25° C. and HEDTA at 92° C. are indeed quite similar. As the ionic radius decreases, however, the MEDTA curve falls considerably below that of HEDTA. Two possible explanations for this discrepancy are as follow.

The hydroxyethyl group of HEDTA may contribute to the bonding of the complex in an indirect manner, such as a hydrogen bond through a coordinated water molecule. This type of bond might be strengthened by the increasing electrostatic attraction of the smaller heavy-lanthanide ions. This would account for the increasing difference between HEDTA and MEDTA stabilities with decreasing ionic radius.

An alternative explanation takes the effect of the hydroxyethyl and methyl groups on the configuration of the ligand into account. Spectral evidence (29) has indicated that EDTA is in a relatively strained configuration when complexing the rare earths. The hydroxyethyl group is rather bulky compared to the methyl group and may force the HEDTA molecule into a relatively favorable configuration for complexation of the smaller rare-earth ions. In this way,

the presence of the hydroxyethyl group would increase the stability of the complexes of the smaller ions without being involved in the bonding. Studies of EDTA homologues have indicated that often the addition of a nonbonding functional group causes increases in complex stabilities. The stability curves of HEDTA complexes at 92° C. and MEDTA complexes at room temperature are quite similar for the larger, light rare earths, but steadily diverge with decreasing ionic radius. This fact fits the above hypothesis that the ligand is more strained when complexing the smaller ions.

A test of this hypothesis would be a study of the formation constants of rare-earth complexes with an ethylenediaminetriacetic acid which has an N'-alkyl group of comparable bulk to the hydroxyethyl group. The synthetic methods outlined in this dissertation should permit the synthesis of ligands of this type from commercially available substituted ethylenediamines.

B. Ion-Exchange Separations

The second goal of this research was the investigation of MEDTA as a potentially superior reagent for ion-exchange separations of the rare-earth elements.

Considerable improvement in ion-exchange separations of the rare earths with HEDTA was realized by elevation of the

operating temperature to 92° C. For reasons discussed previously, the stabilities of MEDTA complexes of the rare earths were expected to be similar to those of HEDTA at 92° C. For this reason, it was expected that MEDTA would provide ion-exchange separations of the rare earths at room temperature similar to those of HEDTA at 92° C. It was also thought that since the overall stability of MEDTA complexes of the rare earths is smaller than HEDTA complexes, the kinetics of ion-exchange separation, as represented by the HETP would be superior to those of HEDTA at room temperature.

The results were not as favorable as had been hoped. Tables 15 and 19 show that the separation factors for separations with MEDTA are generally lower than are those involving HEDTA at 92° C.

Sellers and Powell (101) reported values for the HETP of ion-exchange separations with HEDTA at various temperatures under conditions similar to those of this work. They found HETP values of .28 cm. at 80° C and 8.5 cm. at 20°C. Values reported in this work are typically .4 cm. at 92° C. and 1.2 cm. at room temperature. Thus it may be seen that while MEDTA offers some improvement in room-temperature kinetics, the gain is offset by smaller separation factors.

Both HEDTA and MEDTA may be used in separations with H⁺ retaining ions. They are both absorbed on acid-form resin.

The primary advantage of MEDTA over HEDTA in rare-earth separations is that MEDTA may be used to separate the middle rare earths without the use of high-temperature apparatus. A ligand of this type which has room-temperature separation factors which are the equivalent of those of HEDTA at high temperature, would probably supplant HEDTA for certain rare-earth separations if its cost were not excessive. While EDTA has separation factors which are quite favorable, its use has other drawbacks which limit its usefulness. For this reason, it would seem that further investigations into the properties of rare-earth complexes of ethylenediaminetriacetic acids are warranted.

VII. SUMMARY

The synthesis of MEDTA is complicated by its high solubility in water. It is, however, retained on acid-form ion-exchange resin, allowing ion-exchange chromatography to be useful in isolation of this compound from the reaction mixture. The overall yield was observed to be 71%.

The complexes of MEDTA with the rare earths appear to be five-dentate across the series. The formation constants of MEDTA complexes of the heavy rare earths are somewhat lower than those of HEDTA at high temperature, possibly due to steric effects.

Ion-exchange separations of the heavy rare earths with MEDTA show that the elution order is as predicted by the formation constants of the complexes. The HETP values for these separations at room temperature are somewhat smaller than those for separations with HEDTA under similar conditions. The HETP values for the two ligands at high temperature are quite similar.

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X. APPENDIX A. POTENTIOMETRIC DATA

Ionization constants of MEDTA

MEDTA stock concentration .04866
 MEDTA volume = 10.00
 Nitric acid stock concentration = .15240
 KOH stock concentration = .11796
 Final volume = 200.0

#	KOH vol.	pH	\bar{p}	Salt vol.
1	14.0	10.951	.178	10.20
2	13.5	10.876	.210	10.28
3	13.0	10.799	.252	10.32
4	12.5	10.698	.290	10.38
5	12.0	10.610	.352	10.45
6	11.5	10.502	.416	10.52
7	11.0	10.384	.489	10.60
8	10.5	10.220	.561	10.68
9	10.0	10.047	.647	10.76
10	9.5	9.800	.737	10.84
11	9.0	9.456	.837	10.93
12	8.8	9.227	.878	10.95
13	8.7	9.036	.898	10.97
14	8.6	8.846	.920	10.99
15	8.5	8.524	.942	11.01
16	8.4	7.864	.964	11.03

MEDTA VOLUME = 5.0

#	KOH vol.	Acid vol.	pH	\bar{p}	Salt vol.
1	10.0		2.280	1.881	12.61
2	9.0		2.315	1.839	12.69
3	8.0		2.351	1.787	12.75
4	7.0		2.393	1.746	12.81
5	6.0		2.439	1.704	12.85
6	5.0		2.487	1.649	12.91
7	4.0		2.542	1.598	13.06
8	3.0		2.602	1.539	13.02
9	2.0		2.673	1.483	13.07
10	1.0		2.755	1.422	13.10
11			2.851	1.353	13.08
12		1.0	2.965	1.278	13.05
13		2.0	3.117	1.200	13.02
14		3.0	3.360	1.114	12.90
15		5.0	4.582	.865	12.86
16		5.5	4.904	.759	12.80
17		6.0	5.156	.649	12.74
18		6.5	5.363	.538	12.67
19		7.0	5.690	.426	12.60
20		7.5	5.781	.314	12.53
21		8.0	6.031	.202	12.49

MEDTA formation constant data

Ligand volume = 5.0
 Base concentration = .10549
 Salt concentration = 1.888
 Rare-earth volume = 4.0
 Final volume = 200.0

La-Eu, Tb, Y, Tm
 Ligand concentration = .08202

Gd, Tb, Dy, Ho, Er, Yb, Lu
 Ligand concentration = .08708

Vbase	pH	Vsalt	Vbase	pH	Vsalt
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 Lanthanum concentration = .10061

3.00	3.138	9.31	7.00	3.606	9.69
4.00	3.252	9.39	8.00	3.746	9.79
5.00	3.369	9.49	9.00	3.912	9.86
6.00	3.484	9.59			

Cerium concentration = .10150

0.0	2.796	9.27	5.00	3.242	9.60
1.00	2.884	9.31	6.00	3.343	9.69
2.00	2.970	9.37	7.00	3.456	9.77
3.00	3.058	9.44	8.00	3.591	9.85
4.00	3.149	9.52	9.00	3.761	9.90

Praseodymium concentration = .10012

3.00	2.947	9.57			
4.00	3.027	9.66	4.00	3.024	9.65
5.00	3.110	9.73	5.00	3.107	9.72
6.00	3.200	9.79	6.00	3.198	9.79
7.00	3.303	9.85	7.00	3.301	9.85
8.00	3.425	9.90	8.00	3.413	9.89
9.00	3.581	9.93	9.00	3.590	9.93

Neodymium concentration = .10011

0.0	2.714	9.41	5.00	3.055	9.72
1.00	2.778	9.47	6.00	3.149	9.79
2.00	2.843	9.53	7.00	3.246	9.84
3.00	2.911	9.59	8.00	3.365	9.89
4.00	2.985	9.67	9.00	3.513	9.92

Vbase	pH	Vsalt	Vbase	pH	Vsalt
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Samarium concentration = .10060

0.0	2.664	9.51	0.0	2.664	9.51
1.00	2.717	9.56	1.00	2.717	9.56
2.00	2.772	9.62	2.00	2.775	9.62
3.00	2.834	9.68	3.00	2.836	9.68
4.00	2.896	9.73	4.00	2.898	9.73
5.00	2.975	9.79	5.00	2.970	9.78
6.00	3.047	9.83	6.00	3.053	9.84
7.00	3.137	9.87	7.00	3.143	9.87
8.00	3.252	9.91	8.00	3.257	9.91
9.00	3.405	9.94	9.00	3.407	9.94

Europium concentration = .10104

0.0	2.646	9.53	5.00	2.945	9.80
1.00	2.699	9.59	6.00	3.021	9.84
2.00	2.752	9.64	7.00	3.113	9.88
3.00	2.810	9.69	8.00	3.224	9.91
4.00	2.872	9.74	9.00	3.370	9.94

Gadolinium concentration = .08388

0.0	2.628	9.49	4.00	2.843	9.70
1.10	2.678	9.54	5.00	2.907	9.75
2.00	2.728	9.59	6.00	2.983	9.81
3.00	2.783	9.65	7.00	3.071	9.85

Terbium concentration = .09929

0.0	2.580	9.66	5.00	2.849	9.87
1.00	2.625	9.70	6.00	2.923	9.90
2.00	2.676	9.75	7.00	3.010	9.92
3.00	2.727	9.79	8.00	3.119	9.94
4.00	2.788	9.84	9.00	3.269	9.96

Yttrium concentration = .09698

0.0	2.594	9.68	5.00	2.864	9.88
1.00	2.639	9.73	6.00	2.937	9.91
2.00	2.689	9.77	7.00	3.023	9.93
3.00	2.742	9.81	8.00	3.131	9.95
4.00	2.799	9.85	9.00	3.273	9.96

Vbase	pH	Vsalt	Vbase	pH	Vsalt
Dysprosium concentration = .10177					
0.0	2.534	9.69	4.00	2.719	9.83
1.00	2.574	9.72	5.00	2.777	9.86
2.00	2.619	9.76	6.00	2.845	9.89
3.00	2.665	9.80	8.00	3.021	9.93
Holmium concentration = .09840					
0.0	2.506	9.77	5.00	2.744	9.91
1.00	2.547	9.81	6.00	2.808	9.93
2.00	2.593	9.85	7.00	2.888	9.94
3.00	2.635	9.87	8.00	2.982	9.95
4.00	2.686	9.89	9.00	3.104	9.95
Erbium concentration = .10546					
0.0	2.468	9.77	8.00	2.852	9.91
2.00	2.537	9.82	9.00	2.942	9.92
4.00	2.618	9.86	10.0	3.054	9.92
6.00	2.720	9.89	11.0	3.204	9.92
7.00	2.779	9.90	12.0	3.466	9.92
Thulium concentration = .09901					
0.0	2.445	9.87	5.00	2.679	9.95
1.00	2.484	9.89	6.00	2.747	9.96
2.00	2.524	9.91	7.00	2.829	9.96
3.00	2.571	9.92	8.00	2.931	9.96
4.00	2.621	9.94	9.00	3.068	9.96
Ytterbium concentration = .10012					
0.0	2.420	10.04	7.00	2.732	9.98
2.00	2.487	10.02	8.00	2.810	9.97
4.00	2.568	10.00	9.00	2.903	9.96
6.00	2.670	9.99	10.0	3.022	9.95
Lutetium concentration = .10210					
0.0	2.410	9.89	7.00	2.716	9.94
2.00	2.475	9.91	8.00	2.788	9.94
4.00	2.555	9.93	9.00	2.877	9.94
6.00	2.655	9.94	10.0	2.995	9.94

Excess cadmium titration curve of MEDTA

Ligand concentration = 0.10076

Ligand volume = 4.0

Metal concentration = 0.100

Metal volume = 40.0

KOH concentration = 0.10204

Final volume = 200.0

#	Vbase	pH	\bar{p}
1	1.0	2.453	.998
2	2.0	2.484	.866
3	3.0	2.527	.766
4	4.0	2.579	.679
5	5.0	2.632	.576
6	6.0	2.699	.489
7	7.0	2.777	3.98
8	8.0	2.874	.312
9	8.5	2.982	.262
10	9.5	3.092	.193
11	10.	3.201	.156
12	10.	3.350	.120
13	11.	3.562	.079

Cadmium-MEDTA formation constant

Cadmium concentration = .1000

Cadmium volume = 5.0

Ligand concentration = .04866

Ligand volume = 15.0

Base concentration = .11796

Final volume = 500.0

0.0	2.762
5.0	2.962
5.0	2.958
7.0	3.060
10.0	3.262
10.0	3.262
12.0	3.466
12.0	3.464
14.0	3.883
14.0	3.878

XI. APPENDIX B. POLAROGRAPHIC DATA

Rare earth vs. cadmium exchange constant-----
All quantities expressed in millimoles

Total cadmium = .5056

Total ligand (1,4) = .5013

Total ligand (2,3) = .50045

R	Total R	Cd(1)	Cd(2)	Cd(3)	Cd(4)
La	.5030	.172	.083	.086	.100
Ce	.5075	.197	.130	.128	.140
Pr	.5104	.225	.165	.164	.146
Nd	.5055	.243	.179	.177	.191
Sm	.5061	.275	.225	.226	.208
Gd	.5084	.310	.243	.239	.238
Tb	.4964	.341	.285	.284	.272
Dy	.5058	.377	.381	.393	.367
Tm	.4890	.427	.417	.416	.421
Yb	.4994	.427	.425	.433	.429
Lu	.5217	.441	.434	.431	.407
Y	.4849	.345	.294	.292	.286

Data for rare earth vs. zinc ligand exchange constant-----
Total zinc = .5038

Total ligand (1) = .5013

Total ligand (2) = .5094

R	Total R	Zn(1)	Zn(2)
Tb	.4694	.072	.072
Dy	.5088	.091	.093
Ho	.5020	.108	.119
Er	.5058	.142	.133
Tm	.4890	.159	.165
Yb	.4494	.179	.181
Lu	.5217	.214	.199