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The Stability of the Rare Earth Complexes with N-Hydroxyethylethylenediaminetriacetic Acid

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The stability constants of the complexes formed between the rare earth metal ions and the anion of N-hydroxyethylethylenediaminetriacetic acid, abbreviated HEDTA, have been measured at a temperature of 25° and an ionic strength of μ = 0.1 by two independent methods. In the first method, the rare earth–HEDTA stability constants were calculated from measurements of the equilibrium constants of reactions involving competition between HEDTA and a polyamine chelating agent, triaminotriethylamine, for the rare earth ions and cupric ions. The equilibrium constants were calculated from *p*H measurements of the various reaction mixtures. The second method involved the polarographic measurement of the amount of free copper ions liberated when equal molar quantities of the copper(II)–HEDTA complex and rare earth ions are mixed together.

Introduction

The stability constants of the complexes formed between N-hydroxyethylethylenediaminetriacetic acid, abbreviated HEDTA, and Cu^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}, Cd^{+2}, Fe^{+2} and Mn^{+2} have been measured by Chaberek and Martell.[1] The complexes are all about a factor of ten less stable than the complexes formed between the same metal ions and ethylenediaminetetraacetic acid. The stability constants of the rare earth–EDTA complexes have been measured by a number of people[2–4] and are quite large. In addition, EDTA has been used successfully to separate macro quantities of individual pure rare earths from each other by ion-exchange methods.[5] Because of the similarity in the structures of EDTA and HEDTA and because of the much greater solubility of the free acid form of HEDTA, it seemed desirable to measure the stability of the complexes formed between each of the rare earth metal ions and the anion of HEDTA. Such a series of constants would give a good indication of the effectiveness of HEDTA as an eluent in the ion-exchange separation of various adjacent rare earths.

The methods used to measure the rare earth–HEDTA stability constants are the same as those used by the authors to measure the rare earth–EDTA stability constants. The symbol H_3V is used in this paper to designate the organic acid HEDTA. The apparent stability constants of the rare earth complex is defined

$$K_{MV} = [MV]/[M][V]$$

The brackets denote concentrations and all data were obtained from aqueous salt solutions of ionic strength $\mu = 0.1$ and a temperature of 25°.

The Potentiometric Method

Because of the great stability of the rare earth–HEDTA complexes, a direct potentiometric titration method is not desirable. A mixture, containing equal molar amounts of rare earth salt and the acid H_3V, behaves very much like a strong acid. The hydrogen ion concentration of such a mixture is only slightly less than three times the total concentration of rare earth. Only very approximate values for the equilibrium concentrations of [MV] and [M] could be obtained from *p*H measurements of such a solution.

The indirect potentiometric method used in this research was first used by Schwarzenbach and Freitag[6] to measure some very stable ethylenediaminetetraacetate complexes. If equal molar quantities of the copper(II) complex of HEDTA, NaCuV, a rare earth salt, MCl_3, and the trihydrochloride of β,β',β''-triaminotriethylamine, $N(CH_2\text{-}CH_2\text{-}NH_2)_3$, designated as "tren," are mixed together, reaction I takes place.

$$M^{+3} + CuV^- + H_3tren^{+3} \rightleftharpoons MV + Cutren^{+2} + 3H^+ \qquad (I)$$

If such a mixture is titrated with NaOH, three formula weights of the base are used in a buffer region between *p*H 4 and 6.

The tri-(β-aminoethyl)-amine, "tren," is a strong triprotonic base with *pK* values of 10.29, 9.59 and 8.56.[7] These constants can be expressed as

$$\bar{K}_{H_3tren} = [H_3tren]/[H]^3[tren] = K_{Htren} \times K_{H_2tren} \times K_{H_3tren} = 10^{28.44}$$

The amine, "tren," forms a very stable complex with the copper(II) ion.[8,9]

$$K_{Cutren} = \frac{[Cutren]}{[Cu][tren]} = 10^{19.1}$$

The equilibrium constant for reaction I can be expressed as

$$K_I = \frac{[MV][Cutren][H]^3}{[CuV][H_3tren][M]} = \frac{K_{Cutren} \times K_{MV}}{\bar{K}_{H_3tren} \times K_{CuV}} \qquad (1)$$

Before K_I can be calculated, the equilibrium concentration of five of the six concentration terms expressed in equation 1 must be evaluated. The hydrogen ion concentration is measured directly.

Five material balance equations which describe the concentrations of all important species involved in the reaction I can be written as

$$[Cu]_t = c = [CuV] + \alpha[Cutren] \qquad (2a)$$

$$[M]_t = c = [MV] + [M] \qquad (2b)$$

$$[V]_t = c = [CuV] + [MV] \qquad (2c)$$

$$[tren]_t = c = [Cutren] + [H_3tren] \qquad (2d)$$

$$[H]_t = c(3 - a) = [H] + 3[H_3tren] \qquad (2e)$$

The term "*c*" is used to indicate the initial concentration of the reacting species and "*a*" denotes the number of equivalents of sodium hydroxide added to the reaction per mole of rare earth in solution. Equation 2a is valid if no complexes are formed in which both "tren" and "V" are bound to the same copper ion.

The last term in equation 1a represents the concentration of $Cutren^{+2}$ as well as Cu^{+2} since

$$\alpha[Cutren] = [Cutren] + [Cu]$$

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[1] S. Chaberek, Jr., and A. E. Martell, This Journal, **77**, 1477 (1955).

[2] R. C. Vickery, *J. Chem. Soc.*, 1895 (1952).

[3] E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, This Journal, **75**, 4196 (1953).

[4] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

[5] F. H. Spedding, J. E. Powell and E. J. Wheelwright, This Journal, **76**, 2557 (1954).

[6] G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1503 (1951).

[7] H. Ackermann and G. Schwarzenbach, *ibid.*, **32**, 1543 (1949).

[8] J. E. Prue and G. Schwarzenbach, *ibid.*, **33**, 963 (1950).

[9] T. C. Loomis, "Metal Chelates of Cyclohexenediaminetetraacetic Acid," unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa, 1953.

and

$$\alpha = 1 + \frac{[\mathrm{H}]^3\bar{K}_{\mathrm{H_3tren}}}{[\mathrm{H_3tren}]K_{\mathrm{Cutren}}} \qquad (3)$$

Equation 2b is true only if "tren" does not form a very stable complex with any of the rare earths. However, since no one has been able to measure any very stable rare earth–ammonium type complexes, it seems very unlikely that any rare earth–tren complexes that might exist would be more stable than the Mntren^{+2} or Fetren^{+2} complexes which have stability constants of $10^{5.8}$ and $10^{8.8}$, respectively. It can be shown that under the experimental conditions involved, K_{Mtren} would have to be larger than 10^{12} in order to make the concentration of the complex Mtren^{+3} exceed 10^{-5}, which is 1% of $[\mathrm{M}]_t$.

Equations 2c and 2d are valid because the term $[\mathrm{H_3V}]$, $[\mathrm{H_2V}]$, $[\mathrm{HV}]$, $[\mathrm{V}]$, $[\mathrm{H_2tren}]$, $[\mathrm{Htren}]$ and $[\mathrm{tren}]$ are so small that they can be neglected in the *p*H range concerned. This is easily shown from the known ionization constants of $\mathrm{H_3tren}^{+3}$, the dissociation constants of $\mathrm{H_3V}$, and the stability constant of the copper(II)–HEDTA complex.

The total amount of available acid hydrogen is summarized in equation 2e.

Preparation of Solutions. A. 0.01 *M* $\mathrm{H_3tren}^{+3}$.—A sample of triaminotriethylamine trihydrochloride, obtained from Chemicals Procurement Co., was carefully purified by a double recrystallization. The amine salt was first dissolved in a minimum amount of warm water and then crystallized from the water with 95% ethanol. Finally, the crystals were dried at 100° under a reduced pressure for 24 hours and a 0.0100 *M* aqueous solution of the amine was prepared.

B. 0.01 *M* $\mathrm{H_3V}$.—The HEDTA, secured from Geigy Chemical Co., was further purified by two operations. The acid was first dissolved in a small amount of warm water and filtered. Then 95% ethanol was added and the solution allowed to cool. The acid crystals were filtered on a sintered glass funnel, washed three times with cold absolute ethanol, then once again dissolved in warm water, recrystallized, filtered and washed. A triple leaching with cold water followed by drying at 100° under a reduced pressure for 24 hours completed the purification. A solution of the purified product was tested for sulfate with barium chloride and for sodium with a flame spectrophotometer. No barium sulfate precipitate could be detected. The flame test indicated 0.1 p.p.m. of sodium.

A 0.1 *M* aqueous solution of HEDTA was prepared and standardized by three independent methods: titration against a standard zinc(II) chloride solution using Eriochrome–Schwartz T as the indicator, titration against a standard copper chloride solution using Murexide as the indicator, and a potentiometric titration of the free acid with standard sodium hydroxide. The three methods gave values of 0.0992, 0.0989 and 0.0994 for the molar concentration of the HEDTA stock solution.

C. 0.01 *M* NaCuV.—A copper(II) chloride solution was prepared by dissolving $\mathrm{CuCl_2{\cdot}2H_2O}$ in water. Electrolytic analysis of the solution showed its concentration to be 0.1001 *M*. Therefore, 199.8 ml. of the copper solution was added to 201.82 ml. of the stock HEDTA solution and the resultant acid solution neutralized with sodium hydroxide. The neutral solution was then diluted to 2000 ml.

D. 0.01 *M* $\mathrm{MCl_3}$.—Sufficient freshly ignited pure rare earth oxide[10] was dissolved in a slight excess of HCl to give a solution containing 0.005 of a mole as M^{+3}. A part of this solution was then potentiometrically titrated with sodium hydroxide to a point just past the neutral equivalence point. The *p*H of a neutral rare earth solution was then located from a graph of $\Delta p\mathrm{H}/\Delta\mathrm{ml.}$ against ml. of base added to the solution. These *p*H values ranged from 5.2 to 4.8. After titration, the two solutions were recombined, adjusted to the equivalence point *p*H with sodium hydroxide, and diluted to 500 ml.

The composition of terbium oxide depends upon the ignition temperature. In order to correct this uncertainty, a sample of the oxide was reduced to the sesquioxide by heating it for 8 hours at 900° in a stream of hydrogen. The sesquioxide was then weighed out and dissolved in HCl as described above.

It is virtually impossible to dissolve quantitatively a small amount of ceric oxide, even with the help of hydrogen peroxide. Consequently, a larger amount of oxide was dissolved in acid, the solution filtered, and diluted to volume. Then the cerium stock solution was standardized. Once the concentration of the solution was known, 0.005 of a mole was removed and prepared in the same manner as the other rare earth salt solutions.

Experimental Procedure.—When equal molar quantities of NaCuV, $\mathrm{MCl_3}$ and $\mathrm{H_3tren}^{+3}$ are mixed together, reaction I takes place. If the reaction mixture is potentiometrically titrated with standard sodium hydroxide, a normal acid-base neutralization curve is obtained with a large *p*H increase occurring at "*a*" = 3. If the reaction proceeded as fast as the neutralization of a strong acid with a strong base, a direct potentiometric titration could be carried out. In such a case, the rare earth stability constants could be calculated from any value of "*a*" and *p*H picked from the buffer region of the neutralization curve (roughly from "*a*" = 0.4 to 1.9) by the use of equations 1, 2 and 3. Such a direct approach cannot be used because the reaction is slow. Usually, 25 to 30 minutes are required for the *p*H of the reaction mixture to reach a stationary value after each addition of base. It was found necessary to prepare five individual solutions, each one with the same equal molar amounts of NaCuV, $\mathrm{MCl_3}$ and $\mathrm{H_3tren}^{+3}$, enough KCl to adjust the ionic strength of the solution to $\mu = 0.1$, and different amounts of standard sodium hydroxide so as to correspond to five different positions across the buffer region of a normal neutralization curve. This was accomplished by pipeting 10 ml. of solution A, 10 ml. of solution C, 10 ml. of solution D, 9.10 ml. of 1.00 *M* KCl, and different predetermined amounts of 0.1 *N* NaOH into 100-ml. volumetric flasks and diluting to the mark. The five solutions were allowed to equilibrate for 24 hours in a constant temperature water-bath adjusted to 25.00 ± 0.02°. At the end of that period, the *p*H of each solution was measured with a Beckman Model GS *p*H meter using a fiber type saturated calomel electrode and a "General Purpose" glass electrode. The *p*H meter was standardized with Beckman *p*H 4 buffer before each set of determinations. Since the *p*H thus obtained is defined in terms of the hydrogen ion activity, while hydrogen ion concentrations are needed for the calculations, it was necessary to correct each *p*H meter reading. Three solutions were independently prepared, each containing 0.000802 *M* HCl and 0.100 *M* KCl. These solutions should have *p*H values of 3.096 based upon concentrations at an ionic strength of $\mu = 0.10$. The *p*H meter was standardized in the conventional manner using Beckman *p*H 4 buffer and then two separate determinations were made upon the three solutions. The *p*H was found to be 3.167 ± 0.001, indicating that a correction of −0.071 is necessary.

Five values for K_{I} were calculated for each rare earth from the five *p*H and "*a*" values by use of equations 1, 2 and 3. An average value was then used to calculate K_{MV}. Check determinations, allowing 48-hour equilibration, were made for dysprosium, gadolinium and ytterbium. Since the results were the same as those obtained with 24-hour equilibration, the practice was discontinued for the rest of the series. The experimental data and calculated results are presented in Table I.

Polarographic Method

This method is based upon the fact that it is possible to measure the concentration of free uncomplexed copper(II) ions in the presence of the copper complex CuV^-, by polarographic means. If equal molar amounts of NaCuV, and a rare earth nitrate, $\mathrm{M(NO_3)_3}$, are allowed to equilibrate, the rare earth ion competes with the copper ion for the complexing agent.

$$\mathrm{CuV^-} + \mathrm{M}^{+3} \rightleftarrows \mathrm{Cu}^{+2} + \mathrm{MV} \qquad (\mathrm{II})$$

In such a solution, two separate individual polarographic waves are produced by the reduction of Cu^{+2} and of CuV^-. The first has the shape of a two-electron wave with $E_{1/2} = -0.04$ v. *vs.* satd. calomel electrode. The second wave has an $E_{1/2}$ at about −0.2 v. *vs.* sat. calomel electrode. Between the two waves the diffusion current, i_{d}, remains constant and is proportional to the concentration of Cu^{+2} present in the solution.

The equilibrium constant for equation II can be written as

$$K_{\mathrm{II}} = \frac{[\mathrm{Cu}][\mathrm{MV}]}{[\mathrm{CuV}][\mathrm{M}]} = \frac{[\mathrm{Cu}]^2}{(c - [\mathrm{Cu}])^2} \qquad (4)$$

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[10] The rare earths used in this research were separated from each other on ion-exchange columns according to the method of Spedding, *et al.*, and each rare earth was spectrographically pure. F. H. Spedding, *et al.*, THIS JOURNAL, **69**, 2786 (1947); **72**, 2354 (1950).

TABLE I

RESULTS FOR THE POTENTIOMETRIC DETERMINATION OF THE RARE EARTH–HEDTA STABILITY CONSTANTS[a]

Rare earth	"a"	Cor. pH	$-\log K_{IV}$	Av. $-\log K_{IV}$	$\log K_{MV}$
La^{+3}	0.697	5.112	13.24		
	0.930	5.257	13.30		
	1.162	5.364	13.27	13.29	13.22
	1.394	5.482	13.29		
	1.627	5.611	13.34		
Ce^{+3}	0.697	4.847	12.44		
	0.930	4.970	12.42		
	1.162	5.087	12.43	12.43	14.08
	1.394	5.196	12.43		
	1.627	5.316	12.45		
Pr^{+3}	0.697	4.730	12.07		
	0.930	4.859	12.08		
	1.162	4.980	12.11	12.12	14.39
	1.394	5.097	12.13		
	1.627	5.226	12.18		
Nd^{+3}	0.697	4.637	11.78		
	0.930	4.762	11.78		
	1.162	4.876	11.79	11.80	14.71
	1.394	4.991	11.81		
	1.627	5.122	11.86		
Sm^{+3}	0.697	4.495	11.31		
	0.930	4.616	11.32		
	1.162	4.735	11.35	11.36	15.15
	1.394	4.850	11.38		
	1.627	4.977	11.42		
Eu^{+3}	0.697	4.480	11.26		
	0.930	4.600	11.27		
	1.162	4.718	11.30	11.30	15.21
	1.394	4.832	11.32		
	1.627	4.959	11.35		
Gd^{+3}	0.697	4.517	11.39		
	0.930	4.636	11.39		
	1.162	4.754	11.41	11.41	15.10
	1.394	4.885	11.38		
	1.627	4.998	11.47		
Tb^{+3}	0.697	4.517	11.39		
	0.930	4.637	11.39		
	1.162	4.755	11.41	11.41	15.10
	1.394	4.863	11.41		
	1.627	4.989	11.45		
Dy^{+3}	0.697	4.517	11.39		
	0.930	4.640	11.40		
	1.162	4.758	11.42	11.43	15.08
	1.394	4.873	11.44		
	1.627	5.001	11.49		
Ho^{+3}	0.697	4.524	11.41		
	0.930	4.645	11.41		
	1.162	4.764	11.44	11.45	15.06
	1.394	4.881	11.47		
	1.627	5.008	11.52		
Er^{+3}	0.697	4.489	11.29		
	0.930	4.608	11.30		
	1.162	4.729	11.33	11.33	15.17
	1.394	4.842	11.35		
	1.627	4.971	11.40		
Tm^{+3}	0.697	4.432	11.09		
	0.930	4.549	11.10		
	1.162	4.664	11.12	11.13	15.38
	1.394	4.778	11.15		
	1.627	4.903	11.19		
Yb^{+3}	0.697	4.358	10.81		
	0.930	4.474	10.84		
	1.162	4.584	10.86	10.87	15.64
	1.394	4.697	10.89		
	1.627	4.823	10.95		
Lu^{+3}	0.697	4.322	10.68		
	0.930	4.429	10.68		
	1.162	4.539	10.71	10.72	15.79
	1.394	4.652	10.75		
	1.627	4.775	10.80		
Y^{+3}	0.697	4.701	11.98		
	0.930	4.827	11.99		
	1.162	4.952	12.02	12.02	14.49
	1.394	5.066	12.03		
	1.627	5.194	12.08		

[a] Supporting electrolyte = KCl; temperature = 25.00 ± 0.02°; ionic strength = 0.10.

where "c" is the initial concentration of both reactants. Since $K_{II} = K_{MV}/K_{CuV}$, the desired stability constant can be calculated from equation 5.

$$K_{MV} = K_{CuV}\,\frac{(\%\ Cu^{+2})^2}{(100 - \%\ Cu^{+2})^2} \tag{5}$$

Preparation of Solutions.—Previous measurements[3] indicated that chloride ions may interfere with the polarographic measurements. Therefore, 0.0100 M solutions of NaCuV and $M(NO_3)_3$ were prepared with nitrate rather than chloride ions in the same manner as previously described.

Experimental Procedure.—The polarograms were taken from solutions prepared by mixing 10 ml. of 0.0100 M $M(NO_3)_3$, 10 ml. of 0.0100 M NaCuV, 10 ml. of 0.10 M acetic acid, 10 ml. of 0.10 M sodium acetate, and enough 1.00 M KNO_3 to adjust the final ionic strength to $\mu = 0.10$, and diluting the solution to 100 ml. in 100-ml. volumetric flasks. After mixing, the solutions were allowed to equilibrate for 24 hours in a constant temperature water-bath at 25.00 ± 0.02°. The acetic acid–sodium acetate buffer buffered the solutions to a pH of approximately 4.65.

The measurements were made with a Sargent Model XXI polarograph. An H type cell was used, with a dropping mercury electrode in one side and a saturated calomel electrode in the other side, contact being made through a porous plug. Two drops of basic fuchsin (0.2%) were added to the solutions in the electrolytic cell and pure nitrogen was bubbled through the solutions for 20 minutes before each polarogram was taken. Reference i_d values were obtained for 100% uncomplexed copper and for 100% complexed copper by obtaining polarograms from solutions containing $Cu(NO_3)_2$ and NaCuV, respectively, but no rare earth nitrate. The stability constants were calculated from the reference and experimental i_d values by use of equation 5. The results are given in Table II.

TABLE II

POLAROGRAPHIC DETERMINATION OF THE RARE EARTH-HEDTA STABILITY CONSTANTS[a]

Rare earth	Uncomplexed copper, %	log K_{MV}	Rare earth	Uncomplexed copper, %	log K_{MV}
Sm^{+3}	7.7	15.3	Tm^{+3}	10.5	15.5
Gd^{+3}	9.0	15.4	Yb^{+3}	14.4	15.8
Dy^{+3}	8.1	15.3	Lu^{+3}	17.2	16.0
Ho^{+3}	8.6	15.4	Y^{+3}	4.8	14.8
Er^{+3}	9.5	15.4			

[a] Temperature = 25.00 ± 0.02°; ionic strength = 0.10; supporting electrolyte = KNO_3.

Discussion of Results

The accuracy of the constants, K_{MV}, depends directly upon the accuracy of K_{CuV}. This constant was determined at 29.6° by Chaberek and Martell[1]. The constant was not re-evaluated at 25° since it was believed that its magnitude would probably not be changed much more than the experimental error with a temperature change of only 4.6°.

The pH values obtained with the Beckman Model GS pH meter are more accurate than the buffer used to standardize the meter. Since sufficient buffer solution was prepared at the beginning of the experiments to standardize the pH meter with the same buffer each time, the pH values have an absolute accuracy of only ±0.01 pH unit, but have a relative accuracy of ±0.0025 unit, the limit of the pH meter. The errors in determining the pH of the various solutions have an effect upon the stability constant of only ±0.03 log unit. Because of the uncertainty of the values of the other constants, $\bar{K}_{\mathrm{H_3tren}}$, K_{CuV} and K_{Cutren}, the values of log K_{MV} reported in Table I, probably have an absolute uncertainty of about ±0.2 unit. The relative values within the rare earth series are probably of the order of ±0.06 unit or better.

The uncertainty in the values of the polarographically determined stability constants is much larger. This is a direct result of the instability of K_{MV} compared to K_{CuV}. The equilibrium in equation II is shifted predominantly toward the left. As a result, less than 20% of the total copper is uncomplexed. Since an error of ±2% is committed in measuring the copper, the constant K_{MV} is accurate to only ±0.2 to ±0.4 unit. With errors of this magnitude, a comparison of the values as given in Fig. 1 shows that the values determined by the two independent methods do agree reasonably well. The errors are so great that the light rare earth constants could not be measured by polarography. Two important facts can be observed from Table I and Fig. 1. First, there is no significant variation in the magnitude of the stability of the rare earth–HEDTA constants from samarium to erbium. This means that little or no separation of these elements from one another could be obtained by an ion-exchange elution with HEDTA as the eluting agent. The second important fact to observe is the very dramatic shift of the yttrium constant from its usual holmium–dysprosium region to the neodymium–praseodymium region. Since the R_2O_3 leached from gadolinite ore contains 60% yttrium, 25% light rare earths and only 15% heavy rare earths, this shift presents the possibility of a very fast removal of yttrium from the more desirable heavy rare earth fraction of the ore. HEDTA has the advantage of being quite soluble in acid solutions, so it can be used to elute rare earth bands directly onto ion-exchange resin in the hydrogen cycle.

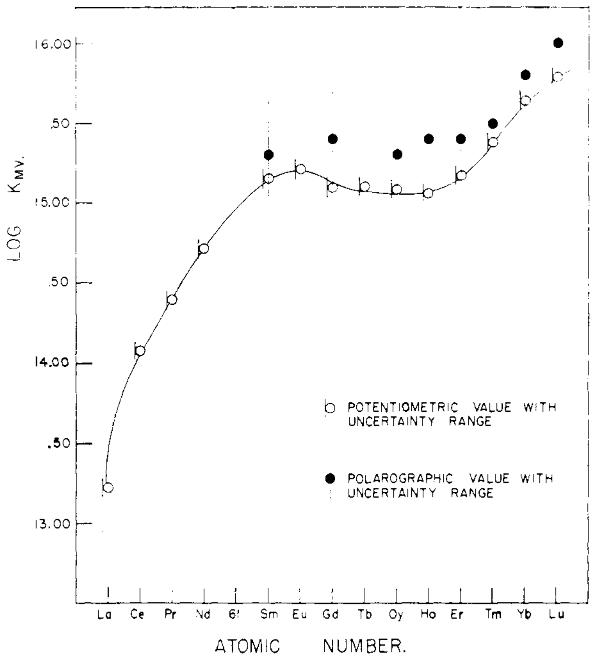

Fig. 1.—Rare earth–HEDTA stability constants.

An experiment was conducted in which a band containing 1223 g. of mixed rare earths (weighed as oxide) was eluted three times its length down a series of columns containing 100 to 200 mesh Dowex-50 resin with an eluent containing 5 g. of HEDTA per liter, buffered to pH 7.68 with ammonium hydroxide. An analysis of the 37 eluate fractions collected showed too much trailing of the heavy rare earths into the yttrium region, and no separation was obtained for any of the rare earths from samarium to lutetium. This separation is inferior to that which can be obtained by the copper–EDTA method.[5] The results did show that the yttrium was concentrated between samarium and neodymium, thus giving support to the correctness of the yttrium–HEDTA stability constant.

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