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**AMES
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COLLEGE**

THE STABILITY OF THE RARE EARTH COMPLEXES WITH
N-HYDROXYETHYLETHYLENEDIAMINETRIACETIC ACID.

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U N C L A S S I F I E D

ISC-604

U N I T E D S T A T E S A T O M I C E N E R G Y C O M M I S S I O N

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THE STABILITY OF THE RARE EARTH COMPLEXES WITH
N-HYDROXYETHYLETHYLENEDIAMINETRIACETIC ACID

by

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U N C L A S S I F I E D

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THE STABILITY OF THE RARE EARTH COMPLEXES WITH
N-HYDROXYETHYLETHYLENEDIAMINETRIACETIC ACID

F. H. Spedding, J. E. Powell, and E. J. Wheelwright

~~ABSTRACT~~

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°C and an ionic strength of $\mu = 0.1$ 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. The equilibrium constants were calculated from pH 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. (auth)

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 Martell¹. The complexes are all

(1) S. Chaberek Jr., and A. E. Martell, J. Am. Chem. Soc., 77, 1477 (1955).

about 1 log unit 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^{2,3,4} and are quite large. In addi-

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- (2) R. C. Vickery, J. Chem. Soc., 1952, 1895.
(3) E. J. Wheelwright, F. H. Spedding, and G. Schwarzenbach, J. Am. Chem. Soc., 75, 4196 (1953).
(4) G. Schwarzenbach, R. Gut, and G. Anderegg, Helv. Chim. Acta, 37, 937 (1954).
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tion, EDTA has been used successfully to separate macro quantities of individual pure rare earths from each other by ion-exchange methods⁵. Because of the similarity in the structures of EDTA and

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- (5) F. H. Spedding, J. E. Powell, and E. J. Wheelwright, J. Am. Chem. Soc., 76, 2557 (1954).
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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 eluant 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

$$K_{MV} = \frac{[MV]}{[M][V]}.$$

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

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 pH measurements of such a solution.

The indirect potentiometric method used in this research was first used by Schwarzenbach and Freitag⁶ to measure some very stable

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

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, $N(CH_2-CH_2-NH_2)_3$, designated as "tren", are mixed together, reaction I takes place.

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

The tri-(β -aminoethyl)-amine, "tren", is a strong triprotonic base with pK values of 10.29, 9.59, and 8.56⁷. These constants can

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- (7) H. Ackermann and G. Schwarzenbach, Helv. Chim. Acta, 32, 1543 (1949).
-

be expressed as follows:

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

The amine, "tren", forms a very stable complex with the copper II ion^{8,9}.

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- (8) J. E. Prue and G. Schwarzenbach, Helv. Chim. Acta, 33, 963 (1950).
- (9) T. C. Loomis, "Metal Chelates of Cyclohexenediaminetetraacetic Acid", Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa, 1953.
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$$K_{Cutren} = \frac{[Cutren]}{[Cu][tren]} = 10^{19.1}$$

The equilibrium constant for reaction I can be expressed as follows:

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

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 follows:

$$\begin{array}{rcl}
 \overline{[Cu]}_t = c = \overline{[CuV]} + \alpha \overline{[Cutren]} & a) \\
 \overline{[M]}_t = c = \overline{[MV]} + \overline{[M]} & b) \\
 \overline{[V]}_t = c = \overline{[CuV]} + \overline{[MV]} & c) \\
 \overline{[tren]}_t = c = \overline{[Cutren]} + \overline{[H_3tren]} & d) \\
 \overline{[H]}_t = c(3-a) = \overline{[H]} + 3\overline{[H_3tren]} & e)
 \end{array} \quad (2)$$

The term "c" is used to indicate the initial concentration of the reacting species and "a" denotes the number of equivalents of 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. Since "tren" is tetradentate and "V" is probably pentadentate, each is capable of individually satisfying the coordination number of copper and it is unlikely that mixed complexes would form. The last term in equation (1a) represents the concentration of $Cutren^{+2}$ as well as Cu^{+2} since

$$\alpha \overline{[Cutren]} = \overline{[Cutren]} + \overline{[Cu]}.$$

and

$$\alpha = 1 + \frac{\overline{[H]}^3 \overline{K}_{H_3tren}}{\overline{[H_3tren]} \overline{K}_{Cutren}}. \quad (3)$$

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 M_t .

Equations (2c) and (2d) are valid because the term H_3V , H_2V , HV , V , H_2tren , Htren , and tren are so small that they can be neglected in the pH range concerned. This is easily shown from the known ionization constants of $\text{H}_3\text{tren}^{+3}$, the dissociation constants of 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. 0.01M $\text{H}_3\text{tren}^{+3}$. 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. The crystals were filtered each time in a sintered glass crucible and washed repeatedly with cold absolute ethanol. Finally, the crystals were dried at 100°C under a reduced pressure for 24 hours. A two-liter 0.0100 molar solution of the amine was prepared by dissolving 5.1126 grams of the dried crystals in pure water and diluting to 2000 ml.

B. 0.01M 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°C 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 ppm of sodium.

A two-liter solution of HEDTA was prepared by dissolving 55.652 grams of the solid in water and diluting to 2 liters. The acid solution was 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. 0.01M NaCuV. A copper II chloride solution was prepared by dissolving $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in water. Electrolytic analysis of the solution showed its concentration to be 0.1001 molar. Therefore, 199.8 ml of the copper solution were 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. 0.01M MCl_3 . Sufficient freshly ignited pure rare earth oxide* was dissolved in a slight excess of HCl to give a solution

* 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. J. Am. Chem. Soc. 69, 2786 (1947); 72, 2354 (1950).

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 pH of a neutral rare earth solution was then located from a graph of $\Delta pH / ml$ against ml of base added to the solution. These pH values ranged from 5.2 to 4.8. After titration, the two solutions were recombined, adjusted to the equivalence point pH 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 $900^{\circ}C$ 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 cerium 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 by withdrawing an aliquot, precipitating the cerium with oxalic acid, igniting, and weighing the ignited oxide. 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 $NaCuV$, MCl_3 , and 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 pH 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 pH 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 pH 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, MCl_3 , and $\text{H}_3\text{tren}^{+3}$, 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 0.1N 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 $25.00 \pm 0.02^\circ\text{C}$. At the end of that period, the pH of each solution was measured with a Beckman Model GS pH meter using a fiber type saturated calomel electrode and a "General Purpose" glass electrode. The pH meter was standardized with Beckman pH 4 buffer before each set of determinations. Since the pH 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 pH meter reading. Three solutions were

independently prepared, each containing 0.000802 M HCl and 0.100 M KCl. These solutions should have pH values of 3.096 based upon concentrations at an ionic strength of $\mu = 0.10$. The pH meter was standardized in the conventional manner using Beckman pH 4 buffer and then two separate determinations were made upon the three solutions. The pH 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 pH and "a" values by use of equations (1), (2), and (3). An average value was then used to calculate K_{MY} . 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 1.

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, $\text{M}(\text{NO}_3)_3$, are allowed to equilibrate, the rare earth ion competes with the copper ion for the complexing agent.

In such a solution, two separate individual polarographic waves are produced by the reduction of Cu^{+2} and of CuV^- . The first

Table 1

Results for the Potentiometric Determination of the
Rare Earth-HEDTA Stability Constants*

Rare Earth	"a"	Corrected pH	-log K _{IV}	Ave. -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		

* Supporting electrolyte = KCl; temperature = 25.00 ± 0.02°C;
ionic strength = 0.10.

Table 1 (Continued)

Rare Earth	"a"	Corrected pH	-log K _{IV}	Ave. -log K _{IV}	log K _{MV}
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		

has the shape of a two-electron wave with $E_{1/2} = -0.04$ V vs sat. 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

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

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).

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

Preparation of Solutions

Previous measurements (3) indicated that chloride ions may interfere with the polarographic measurements. Therefore, 0.0100 molar solutions of NaCuV and $\text{M}(\text{NO}_3)_3$ 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 $\text{M}(\text{NO}_3)_3$, 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 $25.00 \pm 0.02^\circ\text{C}$. 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 $\text{Cu}(\text{NO}_3)_2$ 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 2.

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°C . However, its magnitude would probably not be changed much more than the experimental error with a temperature change of only 4.6°C . Schwarzenbach and his co-workers (4) report a value of $10^{18.8}$ for the copper-ethylenediaminetetraacetate stability constant, measured at 20°C , while Loomis (9) gives a value of $10^{18.6}$ for the same constant at 25°C .

The pH values obtained with the Beckman Model GS pH meter are more accurate than the buffer used to standardize the meter.

Table 2
Polarographic Determination of the Rare
Earth-HEDTA Stability Constants*

| Rare Earth | Per Cent
Uncomplexed Copper | log K_{MV} |
|------------------|--------------------------------|--------------|
| Sm ⁺³ | 7.7 | 15.3 |
| Gd ⁺³ | 9.0 | 15.4 |
| Dy ⁺³ | 8.1 | 15.3 |
| Ho ⁺³ | 8.6 | 15.4 |
| Er ⁺³ | 9.5 | 15.4 |
| Tm ⁺³ | 10.5 | 15.5 |
| Yb ⁺³ | 14.4 | 15.8 |
| Lu ⁺³ | 17.2 | 16.0 |
| Y ⁺³ | 4.8 | 14.8 |

*Temperature = $25.00 \pm 0.02^\circ\text{C}$; ionic strength = 0.10; supporting electrolyte = KNO_3 .

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 units, but have a relative accuracy of ± 0.0025 units, 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 units. Because of the uncertainty of the values of the other constants, $\bar{K}_{\text{H}_3\text{tren}}$, K_{CuV} , and K_{Cutren} , the values of log K_{MV} reported in Table 1, probably have an absolute uncertainty of about ± 0.2 units. The relative values within the rare earth series are probably of the order of ± 0.06 units 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 predominately toward the left. As a result, less than 20% of the total copper is uncomplexed. Since an error of $\pm 2\%$ is committed in measuring the copper, the constant K_{MV} is accurate to only ± 0.2 to ± 0.4 units. With errors of this magnitude, a comparison of the values as shown in Figure 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 1 and Figure 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 grams 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 eluant containing 5 grams of HEDTA per liter, buffered to pH 8.68 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.