AUGMENTING THE SEPARATION OF GADOLINIUM AND EUROPIUM AND EUROPIUM AND SAMARIUM MIXTURES IN ION EXCHANGE ELUTIONS WITH EDTA[*]

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(Received December 27th, 1966)

INTRODUCTION

The major difficulty encountered in resolving mixtures of europium and gadolinium by ion exchange has been the small magnitude of the separation factor afforded by difference in stabilities of europium and gadolinium chelates[1,2] (see upper curve in Fig. 1). When EDTA is employed as the eluant at 25° for example, $\alpha\dfrac{Gd}{Eu} = K_{Gdch}/K_{Euch} \cong 1.1$ (ref. 2); and it is necessary to elute a band of sorbed Eu–Gd mixture approximately 10 times its length down an ion exchange system to attain the steady state. At this point the inherent overlap between 99.9 % pure, 99.99 % pure, etc., Gd and Eu products is $L = 6h/\log \alpha \dfrac{Gd}{Eu}$, $L = 8h/\log \alpha \dfrac{Gd}{Eu}$, etc., where h is the height equivalent to a theoretical plate (usually 1 cm or more)[1,2]. Obviously the length of the sorbed band must exceed L if any "pure" product is to be had. The purpose of this work is first to examine the theories regarding chelate stabilities in order to decide whether or not it is feasible to improve the Gd–Eu and Eu–Sm separation factors, and then to perform confirmatory experiments.

It has been suggested by some on the basis of stability constant data[3] that the ligand in ethylenediamine-N,N,N',N'-tetraacetato complexes of the trivalent rare earths behaves hexadentately in combining with the lighter rare earth cations but only pentadentately when bonding to the heavier, but smaller, rare earth cations and to yttrium. Others[4] have speculated that the EDTA anion is pentadentate in its chelates with the lighter rare earth cations but only tetradentate in its association with the heavier lanthanons. These arguments were advanced to account for the non-monotonic behavior of $\Delta F°$, $\Delta H°$ and $\Delta S°$ for the reaction:

$$R(OH_2)_n{}^{3+} + Ch^{4-} \longrightarrow [R(OH_2)_{n-m}Ch]^- + mH_2O$$
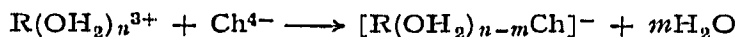
across the rare earth series[5]. (See Fig. 2.) Both of these views have been nullified by recent precision X-ray diffraction data[6].

From lanthanum through terbium (at least) the $[Ln(OH_2)_3Ch]^-$ anion is the dominant species in crystalline salts having the stoichiometry $MLnCh \cdot 8H_2O$, where M
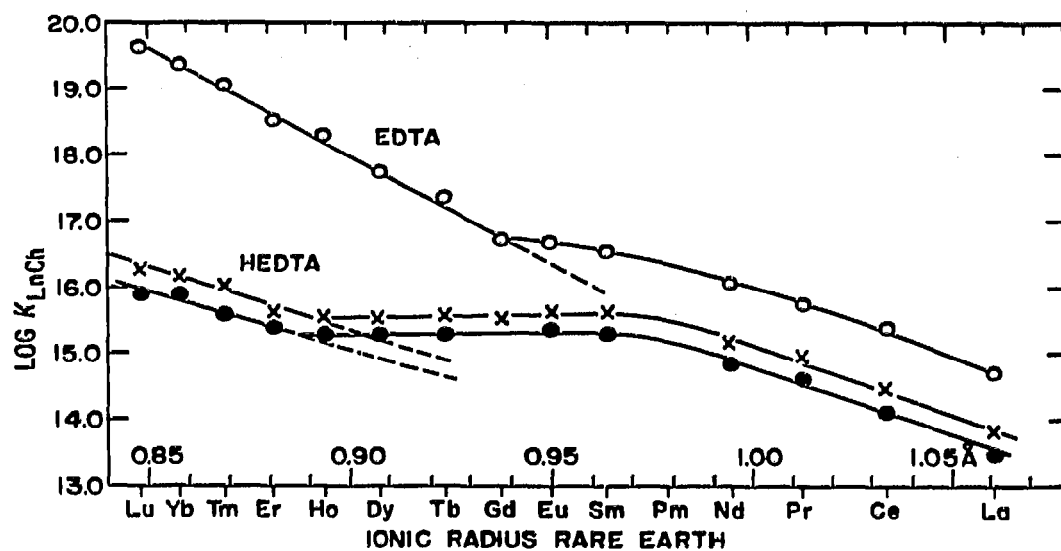

Fig. 1. Stabilities of rare earth EDTA and HEDTA chelates as a function of cationic radius: (O) WHEELWRIGHT, SPEDDING AND SCHWARZENBACH[3]; (×) MACKEY, HILLER AND POWELL[10]; (●) MOELLER AND FERRÚS[11].
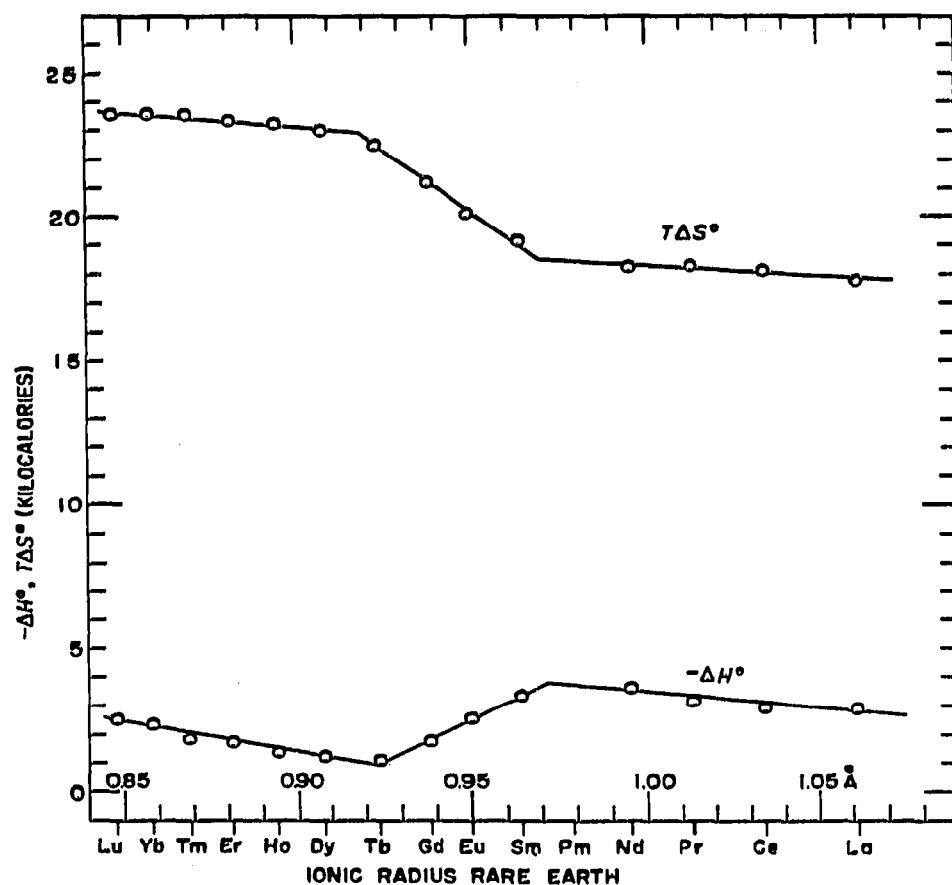

Fig. 2. Enthalpy and entropy contributions to $RT \ln K_{Ln(EDTA)}$ ($-\Delta F^{\circ}$) as a function of cationic radius.

is ammonium, sodium or potassium, Ln is a rare earth and Ch designates EDTA. This nine-coordinated configuration is believed to persist on through lutetium. The lanthanum and terbium compounds have been found to be completely isostructural so that the anomaly occurring between Sm and Gd can no longer be attributed to a change in the basic dentate character of the EDTA anion or to a change in the coordination number of the chelated rare earth ion.

It is possible, however, that part of the over-all bond energy of the lighter rare earth chelates is derived in a more subtle manner through a type of internal bonding in which the four uncomplexed carboxyl oxygen atoms augment the negativity of the electron donating oxygen atoms of the three adjacent coordinated water molecules. It is not implied that quasi-chelate rings form directly from carboxyl oxygen atoms to hydrogen atoms of the coordinately bound water molecules but circuitously through other water molecules located just outside the primary coordination sphere. Such an effect would impart a dentate character to the EDTA anion nominally greater than six in the case of the larger rare earth cations. Decreasing radius might produce such a strain that the quasi-chelate structure would gradually diminish and perhaps fail to exist at all with Ln^{3+} cations having radii less than about 0.93 Å. A regular decrease in stability with increased radius is consistent with an unvarying bonding mode, and the stability would be expected to continue decreasing along the dashed extension of the straight line through the Lu–Gd data in Fig. 1 if the Ln–EDTA bond strengths were not enhanced in some way from samarium through lanthanum.

An even greater anomaly, of the type observed near the middle of the rare-earth EDTA chelate stability sequence, occurs in the case of β-hydroxyethylethylenediaminetriacetato (HEDTA) chelates, but the transition occurring is more drastic, being manifested from neodymium through holmium rather than reaching completion at gadolinium (see lower curves of Fig. 1). The stability defect in the case of the heavier rare earth chelate species is much more obvious with HEDTA than with EDTA. Log $K_{Ln(EDTA)}$ — log $K_{Ln(HEDTA)}$ from Ln = La to Ln = Pm is remarkably constant and less than one log unit. This constant small depression of the log $K_{Ln(HEDTA)}$ values relative to log $K_{Ln(EDTA)}$ reflects the difference in bonding potential of the CH_2CH_2OH and CH_2COO^- groups; plus, of course, any related difference in hydrogen bonding. It would not be amiss then to suggest that HEDTA, as well as EDTA, behaves hexadentately in coupling to the lighter rare earths. From Nd through Gd, in both cases, one can envisage a progressive rupture of hydrogen bonds between carboxyl oxygen atoms and water molecules. The rapid divergence of the stability curves from Gd through Ho heralds a marked deviation in the bonding characters of HEDTA and EDTA. While increased nuclear charge draws both nitrogen atoms and four carboxyl oxygen atoms of EDTA ever closer, the effect on HEDTA is to pull the two nitrogen atoms and three carboxyl oxygen atoms closer in such a way that a strain results which tends to prevent the hydroxyl oxygen atom from freely occupying a coordination site. Probably a water molecule enters the equatorial site in an increasing percentage of cases, and the change in dentate character is gradual rather than abrupt. One would judge then that the straight line through the (Lu–Gd) EDTA data and its dashed extension represents the stability curve for an uncomplicated $[Ln(OH_2)_3 (EDTA)]^-$ anion in which EDTA is hexadentate and, likewise, that the straight line through the (Lu–Ho) HEDTA data represents the stability curve for a simple $[Ln(OH_2)_4(HEDTA)]^-$ anion in which HEDTA is pentadentate.

The models suggested then for EDTA chelate formation are: (1) at least enneahydrated rare earth cations initially in all cases, since X-ray diffraction studies indicate 9 moles of water in coordination sites about the cations in lanthanum, praseodymium, erbium, and yttrium ethylsulfates[7,8]; (2) a nine-coordinated chelate species $[Ln(OH_2)_3Ch]^-$ from lanthanum through neodymium (perhaps promethium) in which a number of hydrogen bonds form between uncoordinated carboxyl oxygen atoms and coordinated water molecules, and tend to enhance the chelate stability above that expected to be due to a simple hexadentate attachment; (3) a gradual change in the number of existing hydrogen bonds, due to strains introduced as Ln decreases in radius from Sm to Eu to Gd, accompanied by progressive reduction in the nominal dentate character of the ligand anion to a minimum value of six; (4) an uncomplicated nine-coordinated chelate species $[Ln(OH_2)_3Ch]^-$ with Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y, which receives no stability contribution at all from hydrogen bonding.

Now it is immediately apparent that, if something were done to cause Eu^{3+}, Sm^{3+}, etc., to form lesser hydrogen bonded chelate species, the stability constants of the EDTA chelates of these lanthanons would drop to values represented by the extension of a straight line through the Lu–Gd data in Fig. 1. The formation reaction would become less exothermic and the entropy would increase (Fig. 2). It is also apparent that a rise in temperature would accomplish this end since temperature elevation would tend to increase the entropy of the system by destroying the tenuous hydrogen bonded structure between the uncoordinated carboxyl oxygen atoms and the coordinated water molecules.

One way to test the above hypothesis is, of course, to determine painstakingly the temperature dependence of individual Ln–EDTA stability constants; but a simpler test can be made by taking advantage of the fact that the minimum number of band displacements required to resolve a mixture by displacement chromatography depends solely on the mole fraction of the component which elutes first in the original mixture and the separation factor[1,2], that is:

$$\nu = \frac{1 + (\alpha - 1)N_0}{(\alpha - 1)} \tag{1}$$

Another convenient means of ascertaining the separation factor at 92° is to prepare an excess of a known mixture of two dilute pure rare earth EDTA solutions, heat it, and pass it slowly through a section of H^+-form resin bed maintained at 92° until the composition of the effluent solution coincides with that of the feed solution. Then the rare earth mixture is stripped from the resin bed to determine the molar ratio of the components sorbed.

$$\alpha\frac{A}{B} = \frac{\text{ratio of A to B in solution}}{\text{ratio of A to B in resin bed}} \tag{2}$$

Actually when the value of $\alpha - 1 = \varepsilon$ is small, it is more precise in view of analytical considerations to compute ε directly[9] instead of α. This is possible from material balance data obtained from such an experiment since

$$\varepsilon = \frac{\Delta n}{X_0 Q(1 - X_0 - \Delta n/Q)} \tag{3}$$

where Δn is the total number of moles of component B missing from a series of weighed rare earth oxide samples derived from individual fractions of the effluent solution collected prior to achieving equilibrium (*i.e.*, sorbed on the resin bed in excess of what would have resulted had no separation of components occurred), X_0 is the original mole fraction of B in the aqueous solution, and Q is the total capacity of the resin bed (total number of moles of rare earth mixture sorbed).

EXPERIMENTAL

The experimental set-up consisted of a number of identical ion exchange columns constructed of standard, 2-in. I.D., flanged Pyrex pipe, 5 ft. long, fitted with Teflon resin-bed supports and gaskets, and Plexiglas end closures (reinforced externally by steel plates). The columns were interconnected when it was so desired by means of 6-mm Pyrex tubing and Beckman Teflon fittings. Each column unit was mounted on a rack in a steam heated, thermostated, 10 × 10 × 8 ft., insulated room and filled to a height of 45 in. with 40–50 mesh spheres of Dowex 50-X8 cation-exchange resin in the H^+-cycle.

In the first experiment, the columns were backwashed with de-aerated distilled water, and two columns of the set were charged with an excess of dilute (Eu–Gd) chloride solution applied by back flow to obtain a uniform band of sorbed Eu–Gd mixture. The excess chlorides were removed by further backwashing with de-aerated distilled water, and the rare earth saturated resin beds were allowed to settle.

In the second experiment, two columns were saturated with an excess of (Sm–Eu) chloride mixture and the excess rare earths were removed as described above.

In both cases, the charged columns were connected in series and the sorbed band of binary rare earth mixture (two columns in length) was eluted down a series of additional resin beds at a flow rate of 65 ml/min with 0.01 M ammonium EDTA at pH 8.32 (originally made up at 25°), with the enclosure temperature maintained at 92°. The ammonium EDTA solution was heated to 90° before entering the 92° enclosure and fed through a column containing moist ammonium-form resin beads and air. The top of the resin bed in this column was maintained slightly above ambient temperature by means of an external heating tape. A venting system at the top of the first column of the experimental series allowed air bubbles issuing from the de-aerator to be discharged from the system. The eluant was forced through the system by a pump located outside the heat shield, and the eluate was discharged from the system at a point higher than the top of the last column to ensure that further degassing would not occur in the experimental columns due to a pressure drop. The Gd–Eu and Eu–Sm bands moved down the resin bed system at a rate of about 19 in. per day in both experiments and analytical profiles of the developing chromatograms were obtained by periodically analyzing small portions of solution as the bands passed between adjacent columns of the system, *i.e.*, a complete profile of each developing chromatogram was obtained approximately every half band length of travel. In this way it was possible to estimate the minimum displacement distances required to achieve steady state conditions to about a fifth of a band length (steady state is approached at a constant rate and achieved when the constant composition plateau of a developing chromatogram disappears).

The separation factors α^{Gd}_{Eu} and α^{Eu}_{Sm} were calculated by means of eqn. (1) and are given in Table I. The theoretical plate height, in each case, was calculated from a plot of the log of the ratio of the two components involved as a function of the distance from the front of the chromatogram after steady state conditions were achieved through the relationship

$$h = \Delta L \cdot \log \alpha^A_B / \Delta \log r \qquad (4)$$

where $r = [A]/[B]$.

TABLE I

SEPARATION FACTORS AND PLATE HEIGHTS CALCULATED FROM THE ELUTION OF Gd–Eu AND Eu–Sm MIXTURES WITH EDTA AT 92°

Mixture (A–B)	N_0	v	$\alpha - 1$	α^A_B	h (cm)
Gd–Eu	0.610	3.04 ± 0.2	0.41 ± 0.04	1.4 ± 0.05	0.7 ± 0.1
Eu–Sm	0.396	1.85 ± 0.2	0.68 ± 0.10	1.7 ± 0.1	0.7 ± 0.1

The values of α^A_B and ε (see Table II) were also evaluated by the alternate method outlined briefly above.

TABLE II

SEPARATION FACTOR DATA OBTAINED AT 92° IN THE PRESENCE OF EDTA BY AN ALTERNATE PROCEDURE

Mixture (A–B)	α^A_B	ε	$1 + \varepsilon$	α^A_B (av.)
Gd–Eu	1.53	0.478	1.478	1.5
Eu–Sm	1.77	0.82	1.82	1.8

It is of interest that the latter values are a bit higher than those observed in the elution experiments. It is likely that complete equilibrium was not achieved at the flow rate used in the elution experiments. If such were the case, the transport rate would be affected, a greater than the minimum number of band displacements would be required, and $\alpha - 1$ and α calculated would be low. The figures reported for α^{Gd}_{Eu} and α^{Eu}_{Sm} in Table I, therefore, probably represent minimum rather than true values.

CONCLUSIONS

The observed separation factors in these systems represent a substantial improvement over those reported previously for elution with EDTA at room temperature ($\alpha^{Gd}_{Eu} = 1.1$ and $\alpha^{Eu}_{Sm} = 1.4$)[1]. From this fact it may be inferred that the models

proposed herein are substantially correct. Although the factors were smaller than projected purely on the basis of an extension of the straight line plot through the Lu–Gd data[10] of the upper curve of Fig. 1, they are sufficiently large that elution with EDTA above 90° becomes competitive with other techniques for isolating pure europium from its concentrates. Additional benefits stemming from the application of heat are: (1) substantial improvement in theoretical plate height, allowing faster flow rates to be used; and (2) increased solubility of the H_4Ch species of EDTA, allowing H^+ retaining ion to be used in place of Cu^{2+} or Zn^{2+}, so that recycling of both eluting agent and water becomes economically attractive.

Similar enhancement of separation factors through temperature elevation should occur in the cases of Ho–Dy and Dy–Tb pairs when HEDTA rather than EDTA is the eluant, but it is by no means clear what will occur with pairs of elements from Gd through Nd in the more complex HEDTA system. That the HEDTA Ho–Dy and Dy–Tb separation factors do actually improve with elevated temperature is obvious from data published by MOELLER AND FERRÚS[11] (see Fig. 3). One can only conclude from the observed trend over a 25° temperature range that continued elevation of temperature would depress log $K_{Ln(HEDTA)}$ still further in the cases of terbium, dysprosium and holmium, yet not much affect the stabilities of the erbium, thulium and ytterbium chelates. Consequently, the Tb–Ho chelate stabilities would finally drop to levels corresponding to points lying on an extension of a straight line through the Er–Yb data.
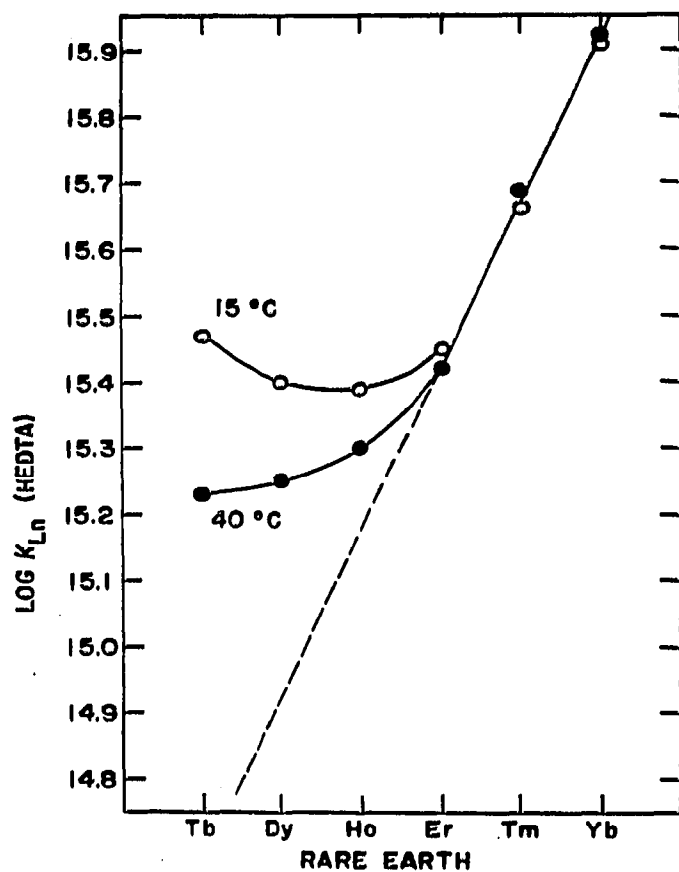

Fig. 3. The effect of increased temperature on the Tb–Yb HEDTA stability constants.

SUMMARY

        Scrutiny of thermodynamic data and proposed models for the hydrated ethylene-diaminetetraacetato (EDTA) chelates of the rare earths has suggested a rather obvious means of improving displacement chromatographic separations of Gd–Eu and Eu–Sm mixtures on cation exchange columns. Increasing the operating temperature from 25 to 92° was found to effect an increase in the Gd–Eu separation factor from a skimpy 1.1 to a robust 1.47 ± 0.07 and the Eu–Sm separation factor from 1.4 to 1.8, presumably by destroying a degree of internal hydrogen bonding which occurs to a varying extent in the case of the less constrained lighter rare earth EDTA chelates at room temperature. Apparently this type of internal hydrogen bonding is not possible in the case of the smaller heavier rare earth EDTA chelates (Gd through Lu). This interesting and important effect has been correlated with a similar trend noted in the stability behavior of terbium, dysprosium and holmium β-hydroxy-ethylethylenediaminetriacetates with increased temperature.

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