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AUGMENTING THE SEPARATION OF ADJACENT PAIRS OF RARE EARTHS IN ELUTIONS WITH HYDROXYETHYLETHYLENEDIAMINETRIACETATE (HEDTA)*

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SUMMARY

Rare-earth mixtures have been eluted with ammonium HEDTA at 92° with substantial gains in the separation of Er–Ho, Ho–Dy, Dy–Tb and Tb–Gd pairs. Individual stability constants at 92° have been derived from the observed separation factors, and a simple mechanism has been proposed to account for a drastic drop in chelate stability which occurs when only the lighter rare-earth chelate species are heated from 15° to 92°. A scheme for economical recovery of pure yttrium from yttrium–lanthanide mixtures is discussed.

INTRODUCTION

It has been demonstrated recently[1] that the Gd–Eu and Eu–Sm separation factors in cation-exchange elution with ammonium ethylenediaminetetraacetate (EDTA) can be augmented substantially by increasing the operating temperature from 25° to 92°. The authors suggested that similar enhancements should occur in the cases of Ho–Dy and Dy–Tb pairs when HEDTA (hydroxyethylethylenediaminetriacetate) rather than EDTA is the eluant. The following represents an experimental verification of this prediction, as well as a general discussion of the mechanism most likely responsible for the improvement in separation observed in the case of the middle rare earths Ho, Dy, Tb and Gd.

EXPERIMENTAL

To establish working stability constants for Ln(HEDTA) species at 92° the following experiments were performed. First of all, a 50:50, Nd–Pr mixture was sorbed on a uniform series of 2-in., 40–50 mesh, H+-form, Dowex 50W-X8 resin beds, maintained at 92°, and eluted at a constant flow rate of 40 ml/min with pH 7.5, 0.018 M ammonium HEDTA eluant until a series of analytical profiles of the sorbed band showed

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that the steady state was achieved. The separation factor for this pair of elements, α_{NdPr}, was then computed from the minimum number of band displacements required to achieve the steady state from the relationship $v = 1/(\alpha - 1) + N_0$. Next, the height equivalent to a theoretical plate was computed from the slope of a plot of log [Pr]/[Nd] vs. L, the distance along the band. The slope of such a plot equals (log α_{NdPr})/h. Thus it was determined (after several repetitions) that $h = 0.65$ cm under the conditions described above. Finally, a mixture of all the rare earths and yttrium was sorbed on the same system and eluted under identical conditions until the steady state was achieved. When the sorbed band reached the end of the bed system, the effluent solution was collected in small measured volumes and the composition of each fraction was determined. Values of (log α_{AB})/h were obtained from individual plots of log [B]/[A] vs. L (as in the case of neodymium and praseodymium); from these values α_{AB} values were computed, assuming h to be constant (i.e. 0.65 cm) across the entire sorbed band.

Data of MOELLER AND FERRÚS[2] indicate that the stabilities of the heavier rare-earth (Tm–Lu) HEDTA chelate species vary inappreciably over a 25° temperature range (from 15–40°). Therefore, one can assume arbitrarily that log $K^{92°}_{Yb(HEDTA)} \cong$ log $K^{40°}_{Yb(HEDTA)}$, for example, and obtain estimates of stability constants for all other lanthanide-HEDTA species at 92° from the individual separation factors observed at that temperature, using the approximation of SPEDDING AND POWELL[3,4]: log $K_{BCh} \cong$ log $K_{ACh} - $ log α_{AB}. The estimated individual $K^{92°}_{LnCh}$ values derived in this way are plotted vs. cationic radius[5] and compared to MOELLER's 15° and 40° data[2] in Fig. 1.
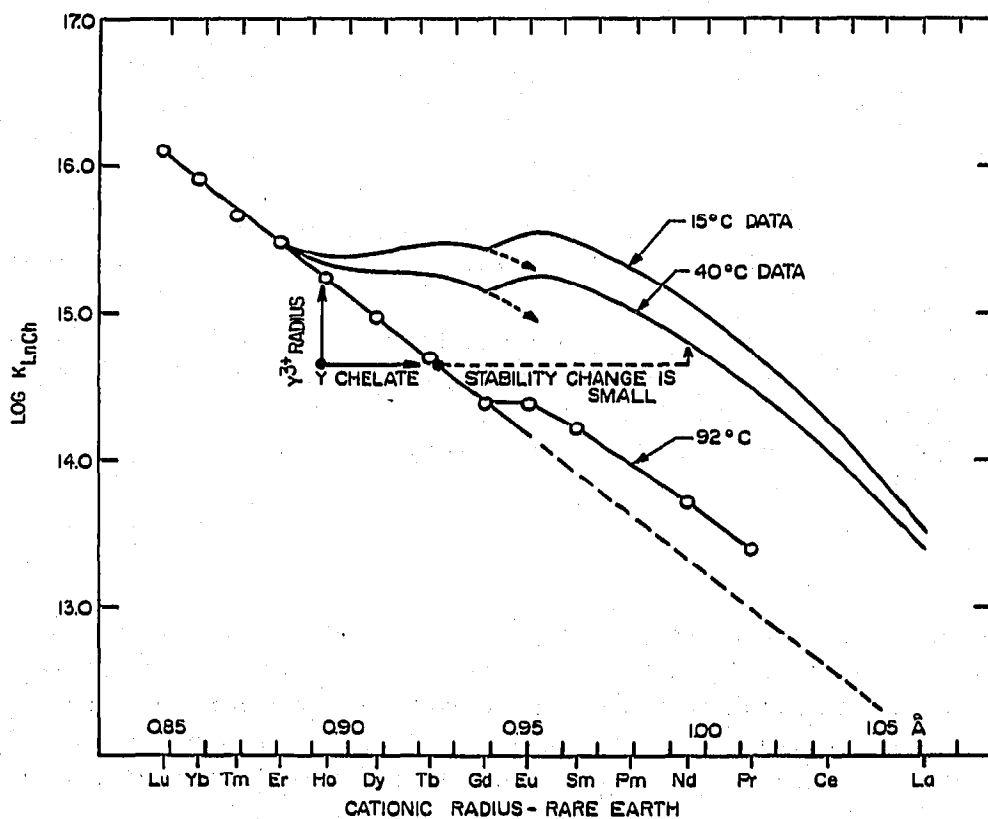

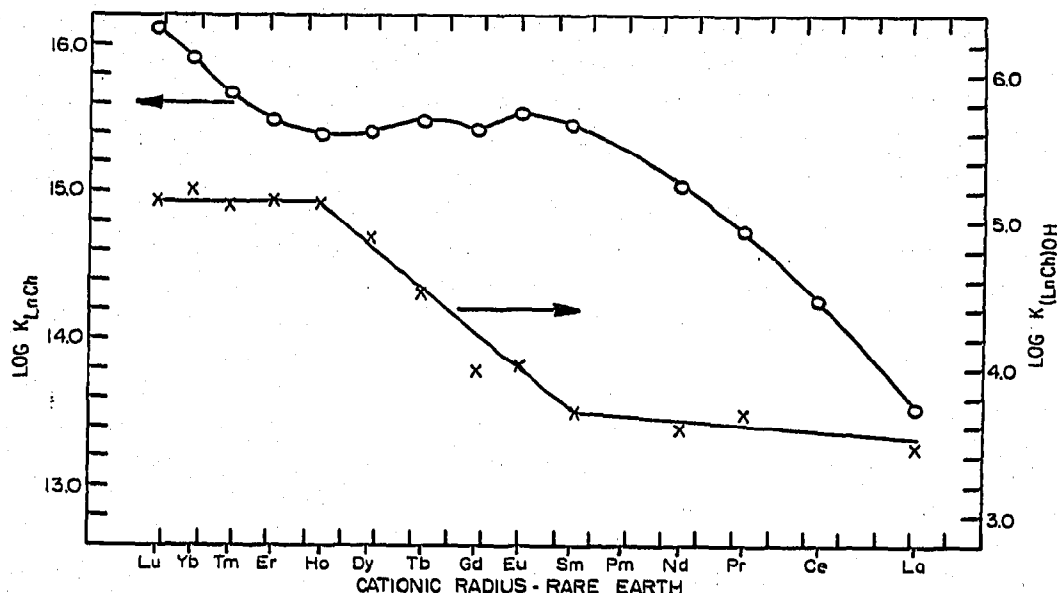Fig. 1. Stability constant trends at various temperatures.

Fig. 2. A comparison of the successive formation constants for Ln(HEDTA) and Ln(HEDTA)(OH)⁻ species at room temperature.

DISCUSSION

The different trends observed at the three temperatures may be explained by assuming that the HEDTA ligand always bonds pentadentately to the four smaller lanthanons (Lu^{3+}, Yb^{3+}, Tm^{3+}, Er^{3+}) but that it attaches hexadentately to all lighter lanthanons larger than Eu^{3+} (Sm^{3+}, Nd^{3+}, Pr^{3+}, Ce^{3+}, La^{3+}) at temperatures approaching 0°. The intermediate lanthanon chelates comprise a transitional set in which the character of the HEDTA anion increases gradually from pentadentate to hexandentate. These assumptions are verified by data of GUPTA AND POWELL[6] obtained for the following reaction which occurs in the presence of base.

$$RCh + OH^- \rightleftharpoons RCh(OH)^-$$
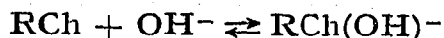
Data for the second step formation constant for the RCh(OH)⁻ species clearly complement the observed trend of the primary chelate formation constants at about room temperature. (See Fig. 2.) It is axiomatic that the heavier rare-earth chelates (in which HEDTA manifests the lower dentate character) should show substantially greater affinity for the auxiliary ligand (OH⁻).

As the temperature of the (La–Sm)HEDTA system is increased from 15° to 40°, thermal agitation causes the 6th donor atom of HEDTA (the oxygen of the hydroxyethyl group) to detach from the metal cation with increased frequency, reducing the average dentate character of the ligand to something between penta- and hexadentate. At 92° it may be presumed that HEDTA bonds only through the two nitrogen atoms and three carboxyl groups regardless of the radius of the rare-earth cation.

The small anomaly which persists at 92° (in proceeding from Gd^{3+} to Eu^{3+}) is apparent at all temperatures and must be attributed to something other than the hydroxyethyl donor group. This discontinuity is most likely traceable to (or at least related to) a change in coordination number of the hydrated lanthanide cation which occurs at this point in the sequence. Studies of the properties of dilute aqueous solutions

of ordinary rare-earth electrolytes by SPEDDING et al.[7-10] strongly suggest that the basic coordination number (C.N.) of the lanthanide cation does increase by one unit as the radius of the cation increases from that of Dy^{3+} to that of Nd^{3+}. SPEDDING has suggested that the smaller cations ($Dy^{3+}-Lu^{3+}$) exhibit a C.N. of 8, and that larger cations ($La^{3+}-Nd^{3+}$) have a C.N. of 9. The X-ray crystallographic data of FITZWATER AND RUNDLE[11], however, reveal 9 nearest-neighbor oxygen atoms (all donated by water molecules) about the lanthanon in crystalline $Er(C_2H_5OSO_3)_3 \cdot 9H_2O$, as well as in $Y(C_2H_5OSO_3)_3 \cdot 9H_2O$, $Pr(C_2H_5OSO_3)_3 \cdot 9H_2O$, and $La(C_2H_5OSO_3)_3 \cdot 9H_2O$. This leads one to propose that the change in C.N. of the freely hydrated rare-earth cation with radius is more likely to be from 9 to 10 than from 8 to 9. It is deemed unlikely that the freely aquated Er^{3+} cation (or any larger Ln^{3+} cation) would surround itself with *less* water of hydration than the number observed in the restricted environment of a crystalline solid; whereas, it is quite conceivable that the larger cations ($La^{3+}-Nd^{3+}$) might associate with *more* water in dilute solution than the maximum number observed in their crystalline salts.

Our data indicate that, whatever the individual C.N. values of the rare-earth cations at room temperature may be, elevating the temperature to 92° does not effect a drastic change in the inner hydration sphere; otherwise, the discontinuity apparent at the Gd-Eu interval in the 15° data would shift in the direction of larger radii as the temperature increased.

The stabilities of the (Eu-La)HEDTA chelates are seen to exceed the pentadentate ligandcy predictions obtained by extending a line drawn through the 92° (Lu-Gd)HEDTA data in Fig. 1. With the 92° data one might argue that the apparent affinity enhancement is spurious—that it merely reflects the decreased affinity of a physically larger 10-hydrated (compared to a 9-hydrated) cation for the cation-exchange medium present in this particular set of experiments—if it were not for the fact that the same anomaly is also clearly present in the 15-40° data, *which were obtained in the absence of ion-exchange materials*. This small temperature-independent enhancement in cation-ligand affinity may result then simply from a diminution in strain to which the HEDTA anion is subjected in assuming a nominally pentadentate configuration, arising from a more favorable array of coordination sites afforded by the larger C.N. Since a quite similar phenomenon occurs at the Gd-Eu interval in many systems involving ostensibly simpler ligands (*e.g.*, acetate[12], glycolate[13] and the 1-hydroxycyclopentanecarboxylic acid anion[14], and since b_1/b_2 ratio changes which occur in such systems imply that the carboxyl group (common to these ligands) can in certain instances (*i.e.* with the larger lanthanons) utilize both oxygen atoms in bonding to cations of proper dimensions, we must surmise that at least one carboxyl group (out of the three available with HEDTA) behaves in an effectively bidentate fashion. Probably what occurs is that one oxygen atom of a carboxyl group replaces a water molecule in the coordination sphere, and the other, due to its proximity to several water molecules in the coordination sphere, couples to one of them by bonding *via* a hydrogen atom. Such an alliance, resulting in pseudo hexadentate ligandcy at elevated temperatures and pseudo heptadentate ligandcy around room temperature, would be reflected undoubtedly by increased cation-ligand affinity.

The fact that the Gd-Eu and Eu-Sm separation factors improve from 1.1 to 1.5 and from 1.4 to 1.8, respectively, upon increasing the operating temperature from 25° to 92° in elutions with EDTA (ethylenediaminetetraacetate)[1], suggests that perhaps

more than one carboxyl group forms such an alliance with the hydrogen atoms of co-ordinated water in the case of (Eu–La) EDTA species, wherein the opportunity to do so is even greater than with corresponding HEDTA species. It should be noted that with EDTA a vestige of the Gd–Eu discontinuity persists at 92°, just as in the case of HEDTA. It appears then that EDTA, as well as HEDTA, couples to the larger lanthanons (Eu^{3+}–La^{3+}) with an effective dentate character greater than normally predicted (even at temperatures approaching the boiling point of water) by forming at least one hydrogen bond between an otherwise uncoordinated carboxyl oxygen and the hydrogen atom of coordinated water.

A SCHEME FOR ISOLATING YTTRIUM FROM MIXTURES

It is clear from the elution curves of MORTON AND JAMES[15] and Fig. 1 above that, if one wishes to isolate the non-lanthanide rare-earth yttrium from rare-earth mixtures, all that needs to be done is first to eliminate the heavy lanthanide elements (Sm–Lu) by eluting a band of sorbed yttrium–lanthanide mixture a short distance down an appropriate cation-exchange bed with ammonium HEDTA at 25° and then to separate yttrium from its low-temperature companion, neodymium, by further elution with the same eluant at 92°.

Yttrium-rich concentrates obtained from minerals such as xenotime and gadolinite are comprised roughly as given in Table I.

TABLE I

TYPICAL COMPOSITION OF CATIONIC MIXTURE OBTAINED FROM XENOTIME AND GADOLINITE

Element	Mole %	Element	Mole %
La	2.6	Gd	2.0
Ce	3.5	Tb	0.7
Pr	0.7	Dy	5.3
Nd	2.2	Ho	1.2
Y	71.9	Er	4.0
Pm	0.0	Tm	0.6
Sm	0.9	Yb	3.9
Eu	0.1	Lu	0.4

For computational purposes such a mixture can be considered equivalent (approximately) to a simple binary mixture[3,4], composed of 19.1 mole % HRE (Sm–Lu) and 80.9 mole % yttrium plus LRE (La–Nd) in elutions with ammonium HEDTA at 25°. The minimum separation factor between the HRE and Y-LRE groups is 2.65 at 25° by actual measurement. Consequently, if a band of mixture is sorbed on a system of columns of cation-exchange resin and eluted with HEDTA eluant down additional H^+-form cation-exchange beds equal to $1/(2.65 - 1.0) = 0.6$ lengths of the sorbed band, until slightly more than 19.1 % (say 25 % as a conservative estimate) of the band has progressed off the system, only yttrium, neodymium, praseodymium, cerium and lanthanum (incompletely resolved) will remain. This material will comprise a band 3/4 the length of the original (*i.e.* 0.75L) and should consist of 88 % yttrium and 12 % LRE (La–Nd). The separation factor between yttrium and the LRE group at 92° is

estimated to equal 8.5; therefore, a second retaining section comprised of H^+-form resin, at least $0.75L/(8.5 - 1.0) = 0.1L$ long, must be appended to provide for the elevated temperature phase of the separation. The length of the entire system required is thus *ca.* $1.7L$ compared to a length equal to $L + L/(1.5 - 1.0) = 3.0L$ computed for room temperature resolution of the same mixture with EDTA.

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