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Formation Constants of the Complex Species Formed by Interaction of Rare-Earth Nitrilotriacetate Complexes with an Equivalent Amount of Base[1]

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Abstract--The formation constants of the $RChOH^-$ species, formed by interaction of individual rare-earth nitrilotriacetate species and KOH at 25°C and an ionic strength of 0.1, have been determined by the potentiometric method, i.e., computed from the pH values of equilibrium mixtures containing varying proportions of rare-earth complex and base. The relationship of these constants to the ion-exchange separation of rare earths at high pH has been discussed.

Introduction

From the pH buffering properties and the solubility of rare-earth nitrilotriacetate (NTA) complexes in base, as well as from the results of a previous investigation of the reaction of rare-earth HEDTA complexes with base,[2] it has been assumed tentatively that very sparingly soluble neutral RCh species combine with an equivalent amount of base to form

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new complex species of the type $RChOH^-$. That is,

$$RCh + OH^- \rightleftarrows RChOH^- \; ; \; K_{RChOH} = \frac{a_{RChOH^-}}{a_{RCh} \cdot a_{OH^-}} \qquad (1)$$

where R^{+3} and Ch^{-3} denote the rare-earth cation and the nitrilotriacetate (NTA) anion, respectively. Available data are in good agreement with this association mechanism.

At a fixed ionic strength an apparent formation constant, based on concentrations, can be defined as follows:

$$K'_{RChOH} = \frac{[RChOH^-]}{[RCh]\;[OH^-]} = \frac{\gamma RCh \cdot \gamma OH^-}{\gamma RChOH^-} \cdot K_{RChOH} . \qquad (2)$$

Such constants are valuable in predicting what separations may be achieved when binary rare-earth mixtures are eluted down cation-exchange systems with NTA under alkaline conditions. Consequently, it was decided to study these apparent formation constants as a function of the atomic number of the central rare-earth ion.

Experimental

Preparation of the Reagents. -All the rare-earth nitrilotriacetates, except the yttrium compound, were supplied by Dr. S. C. Levy, formerly of this laboratory.[3] The complexes were recrystallized by the following method. The complex compound was combined with distilled water and heated as a minimum amount of alkali was added, drop by drop, until dissolution was complete. The solution was then filtered, acidified to a pH between 5 and 6 by addition of HCl, and heated. The neutral 1:1

rare-earth NTA complex immediately reprecipitated and was filtered off and dried in the air. After several days weighed specimens were assayed for rare-earth content by ashing to R_2O_3 at 900°C and weighing.

The yttrium complex species was prepared by the direct reaction of yttrium chloride with an equivalent amount of trisodium nitrilotriacetate. The precipitate of yttrium nitrilotriacetate was then purified by several recrystallizations of the type described above and assayed for rare-earth content.

A 0.002M stock solution of each rare-earth chelate (except La, Ce, Sm, and Eu chelates) was prepared by dissolving the required amount of solid chelate in boiling conductivity water. In the cases of the La, Ce, Sm, and Eu chelates, 0.0002M solutions were prepared, due to the low solubility and slow rate of dissolution of these compounds. Each solution was standardized by determining the equivalent rare-earth oxide content by the usual gravimetric procedure, i.e., precipitation as the oxalate followed by thermal decomposition to the oxide at 900°C.

A 0.01M solution of carbonate-free KOH was prepared by the method of Powell and Hiller[4] and was standardized against HCd (HEDTA) by the method of Powell, Fritz, and James.[5]

A 1M solution of KNO_3 was prepared by dissolving a mole of KNO_3 in conductivity water in a 1-liter volumetric flask.

Experimental Procedure.-Fifty ml of RCh stock solution and ten ml of 1M KNO_3 solution were introduced into each of ten calibrated 150-ml volumetric flasks. Varying amounts (one to ten ml generally and one tenth to one ml in the cases of La, Ce, Sm, and Eu) of 0.01M KOH were added to each flask. The solutions were next diluted so that they were 0.1M with respect to KNO_3 and 0.001M with respect to total rare-earth species (0.0001M in the case of La, Ce, Sm, and Eu) and were allowed to equilibrate in a 25° water bath for 100 hr. Then the pH of each solution was read by means of a Beckman Zeromatic pH meter standardized against pH-7 buffer. From the pH values of the various solutions and the mean activity coefficient of the hydroxyl ion at 25° and ionic strength 0.1, the concentration of the hydroxyl ion was computed and used as the basis for calculation K'_{RChOH} from material balances and equation 2. That is, K'_{RChOH} was redefined as

$$K'_{RChOH} = \frac{\{(OH_t) - [OH^-]\}}{\{1.00 \times 10^{-3} - (OH_t) + [OH^-]\} \; [OH^-]} \qquad (3)$$

where (OH_t) represents the concentration of hydroxyl ion that would have resulted from the amount of base added, had no association occurred. In those cases where 10^{-4} concentrations of RCh were employed instead of 10^{-3}, equation 3 was altered properly.

The log K'_{RChOH} values for individual rare earths given in Table I are average values, each computed from seven random points taken from the plot of pH vs. milliliters of base added between the limits $a = 0.25$ and $a = 0.85$ (a is the ratio of moles of base added to moles of RCh originally present). The data were treated statistically so that the limits given in Table I define the interval of 90% confidence.

Table I

FORMATION CONSTANTS OF THE MONOHYDROXO RARE-EARTH CHELATES

$t = 25°$, $\mu = 0.1$ (KNO_3)

rare earth	atomic no.	log K'_{RChOH}
La	57	5.89 ±.11
Ce[a]	58	--
Pr	59	5.72 ±.05
Nd	60	5.86 ±.05
Pm	61	--
Sm	62	6.59 ±.05
Eu	63	6.84 ±.08
Gd	64	6.54 ±.05
Tb	65	6.67 ±.05
Dy	66	6.84 ±.10
Ho	67	6.66 ±.09
Er	68	6.56 ±.05
Tm	69	6.24 ±.11
Yb	70	6.29 ±.12
Lu	71	6.30 ±.10
Y	39	6.39 ±.04

[a] The K'_{RChOH} data for cerium drifted upward one log unit between $\underline{a} = 0.25$ and $\underline{a} = 0.85$. Apparently cerium (III) tends to be oxidized to cerium (IV) as base is added to chelate solutions.

Discussion

The value of log K'_{RChOH} is relatively constant from lanthanum through neodymium but rises steadily thereafter to a maximum of 6.84 at europium. A sharp drop occurs at gadolinium and is followed by a rise in stability through dysprosium. After dysprosium the stability declines gradually to a relatively constant level again for the last three elements, thulium, ytterbium, and lutetium.

A comparison of the behavior of R(NTA) chelates with that of R(HEDTA) chelates in the presence of base (Figure 1) reveals that the affinity of the R(NTA) species for the hydroxyl ion is greater than the affinity of the corresponding R(HEDTA) compound for OH^- in every case. Although the ratio of $K'_{R(NTA)OH}$ to $K'_{R(HEDTA)OH}$ is about 270 in the case of R equal to lanthanum, it is only 15 when R equals lutetium.

The behavior of rare earths in ion-exchange systems in the presence of NTA is complicated by the tendency of R(NTA) species to associate with additional NTA anion to form $R(NTA)_2$ species, the formation constants of which can be expressed as follows:

$$K'_2 = \frac{[RCh_2^{3-}]}{[RCh]\,[Ch^{=}]}\,. \qquad (4)$$

It can be ascertained by means of Figure 2 that K'_2 is of the order of 10^2 times the magnitude of K'_{RChOH}. Consequently, in situations where excess NTA anion is available, RCh_2^{3-} species form in preference to $RChOH^-$ species. That is why, when rare earths are eluted with 0.026M NTA eluant, even at pH 9, the ratio of total NTA to R in the eluate never falls much below two. Presumably, at sufficiently high pH values, $RChOH^-$ could become the predominant complex species in an ion-exchange system, but a comparison of the plots of log $K'_1K'_2$ and log K'_1K_{RChOH} vs. atomic number (Figure 2) reveals that, in general, poorer separations would result (except in the limited region from Nd to Eu).

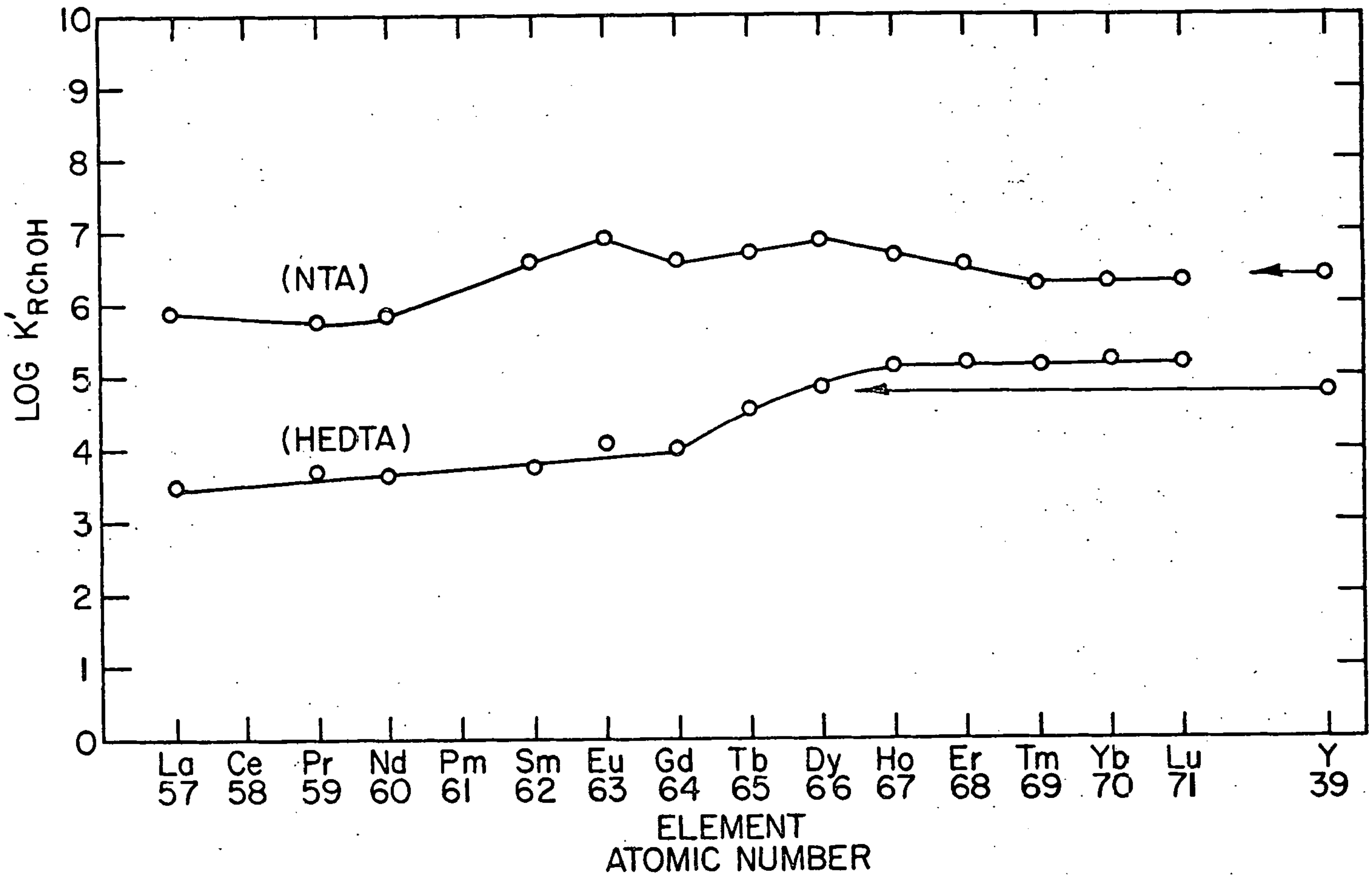

Fig. 1. A comparison of the stability constants of the complexes formed between rare-earth NTA and rare-earth HEDTA and the hydroxyl ion.

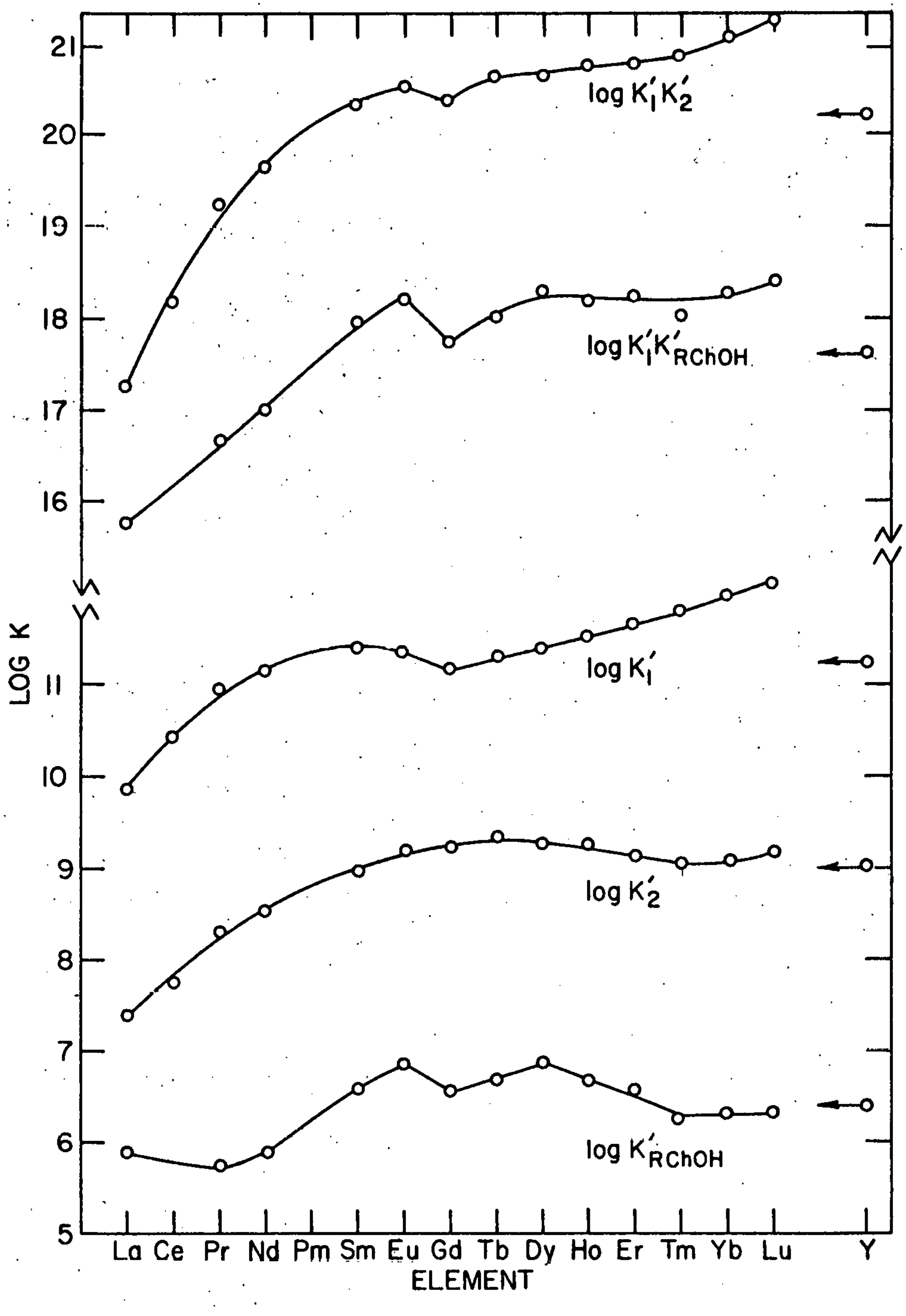

Fig. 2. A comparison of the various primary stability constants observed in the rare-earth NTA system, as well as logical combinations of these constants.

References

(1) Contribution No. 1154. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) A. K. Gupta and J. E. Powell, submitted for publication.

(3) S. C. Levy, doctoral dissertation, Iowa State University, Ames, Iowa, 1961. Present address: Sandia Corp., Albuquerque, New Mexico.

(4) J. E. Powell and M. A. Hiller, J. Chem. Ed., 34, 330 (1957).

(5) J. E. Powell, J. S. Fritz, and D. B. James, Anal. Chem., 32, 954 (1960).

Figure Captions

Fig. 1. A comparison of the stability constants of the complexes formed between rare-earth NTA and rare-earth HEDTA and the hydroxyl ion.

Fig. 2. A comparison of the various primary stability constants observed in the rare-earth NTA system, as well as logical combinations of these constants.