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FORMATION CONSTANTS OF PROTONATED AND LANTHANON N′-METHYLETHYLENEDIAMINE-N,N,N′-TRIACETATE SPECIES

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SUMMARY

Formation constants of protonated and chelate species formed between hydrogen ion and rare-earth cations and the anion of the recently synthesized N′-methylethylenediamine-N,N,N′-triacetic acid were determined at an ionic strength of 0.100 *M* (KNO_3) and 25° by a potentiometric method.

INTRODUCTION

N′-Methylethylenediamine-N,N,N′-triacetic acid is a newly synthesized reagent[1] whose anion (MEDTA) may prove useful in the ion-exchange separation of the lanthanons, because the acid itself, H_3(MEDTA), is substantially more water-soluble than the ubiquitous complexant ethylenediamine-N,N,N′,N′-tetraacetic acid, H_4(EDTA). Use of EDTA anion in classical ion-exchange separations of individual lanthanide rare earths[2] lacks efficiency because a low eluant concentration is required to avoid precipitation of certain hydrated HLn(EDTA) species[3] and a retaining ion other than hydrogen ion (generally Cu^{2+}) is necessitated by the extremely low solubility of H_4(EDTA)[3] (*ca.* 0.2 g/l at 25°). Although the solubility of H_4(EDTA) increases to *ca.* 5 g/l at 90–95°, the solubilities of the hydrated lighter rare-earth EDTA species (*e.g.*, HLa(EDTA), HCe(EDTA) and HPr(EDTA)) decrease substantially with increased temperature. Mackey *et al.*[4] have shown that HLa(EDTA)$\cdot 7H_2O$, which is soluble to the extent of 1.1×10^{-3} moles/l at 25°, dehydrates irreversibly above 45° to HLa(EDTA)$\cdot 1H_2O$, which is appreciably less soluble than the heptahydrate. In the absence of lanthanum, cerium, praseodymium and neodymium, ammonium EDTA concentrations up to 0.01 *M* may be employed at 92° (ref. 5). In their presence an eluant concentration less than 0.005 *M* is mandatory.

At the outset of this investigation, it was clear that the MEDTA anion and its lanthanide chelate species might have solubility characteristics akin to those of N′-hydroxyethylethylenediamine-N,N,N′-triacetate (HEDTA) anion, but that MEDTA should lack the proclivity of HEDTA to bond hexadentately to some (the larger) lanthanons, but not to others[6]. A gradual change in bonding character of the HEDTA anion from hexadentate to pentadentate accounts for the anomalous trend in the lanthanide-HEDTA stability constant sequence and the resulting insignificant ion-exchange separation obtained with the intermediate rare earths (Sm through Ho) when HEDTA is employed as the eluant at 25° (refs. 3 and 6). Because MEDTA lacks the weak sixth donor atom possessed by HEDTA, MEDTA should exhibit a more uniform increase in lanthanon-chelate stability across the entire rare-earth sequence than is observed in the case of HEDTA.

In theory at least, MEDTA should hold rare-earth cations less tenaciously, but the lanthanon-chelate stability constant sequence ought to roughly parallel the lanthanon-EDTA sequence and furnish substantial (if not comparable) ion-exchange separation factors for adjacent pairs of lanthanons. Note that, although individual rare-earth chelate stabilities should be less in the case of (pentadentate)MEDTA than in the case of (hexadentate)EDTA, the ion-exchange separation factors

$$\alpha_{\mathrm{B}}^{\mathrm{A}} \simeq \frac{K_{\mathrm{ACh}}}{K_{\mathrm{BCh}}} = \frac{K_{\mathrm{A\ (MEDTA)}}}{K_{\mathrm{B\ (MEDTA)}}} = \frac{K_{\mathrm{A\ (EDTA)}}}{K_{\mathrm{B\ (EDTA)}}}$$

depend only upon ratios of respective individual chelate stability constants of the species ACh and BCh —not upon the over-all magnitude of the stabilities in the particular sequence under consideration.

EXPERIMENTAL AND RESULTS

Rare-earth nitrate solutions

Individual rare-earth nitrate solutions, having a concentration of *ca.* 0.1 *M*, were prepared by dilution from more concentrated stock solutions of rare-earth nitrates prepared by the method described by Adolphson[7], from Ames Laboratory rare-earth oxides exceeding 99.9% purity. Prior to dilution the concentrated stock solutions were analyzed and found to have an anion to cation ratio of 3.00:1.00. The diluted solutions were standardized both gravimetrically (oxalate precipitation plus ignition) and compleximetrically (by the method of Fritz and Schenk[8]).

Potassium hydroxide solution

A 0.1 *M* KOH solution was prepared by diluting concentrated carbonate-free KOH, purchased in sealed ampoules from Anachemia (Montreal Canada), in boiled deionized water. This solution was stored in a large Pyrex bottle and protected from contamination by an Ascarite trap. It was standardized by repeated titrations *versus* primary standard grade potassium acid phthalate.

Nitric acid solution

A 0.1 *M* HNO_3 solution was prepared from concentrated reagent grade nitric acid by dilution and was standardized against the standard KOH solution.

Potassium nitrate solution

A 2 *M* potassium nitrate solution was prepared from neutral reagent grade potassium nitrate, dissolved in boiled deionized water. This solution was standardized by passing aliquots through a bed of Dowex 50W (H^+) cation-exchange resin and titrating the effluent solutions with standard KOH.

Apparatus

The apparatus for potentiometric determinations included a pair of constant temperature water-baths, equipped to store the various solutions of known stoichiometry and to circulate water through a jacketed electrode compartment. The temperature of each bath was maintained at 25.0° by a Philadelphia micro-set thermoregulator (Precision Scientific Co., Chicago, Ill., U.S.A.) and a Precision electronic relay (Precision Scientific Co.)

The titration cell was a double-walled container, fitted with a large neoprene stopper. A Beckman (Fullerton, Calif., U.S.A.) sleeve-type electrode, a stiff platinum ground wire, a Pyrex tube to permit flushing with nitrogen gas and a small filling funnel were inserted through the stopper. The inner chamber had a capacity of about 100 ml in all and was fitted with a drain tube passing out through the bottom of the outer chamber, so that it could be emptied and flushed conveniently. The glass electrode was stored in a strong acid solution during periods of disuse.

The potentiometer was a Corning Model 101 digital electrometer (Corning Glass, Corning, N.Y., U.S.A.) capable of reading linearly and repeatably to ±0.001 pH unit. It was calibrated to read in units of pH_c against dilute HNO_3 solutions of known stoichiometry, adjusted to ionic strength 0.100 *M* (KNO_3). In this case conversion of pOH_c to pH_c was made via data on K_w at 25° and ionic strength 0.100 reported by Harned and Owen[9].

MEDTA anion protonation constants

The successive formation constants of the protonated ligand species H_n-(MEDTA), K_1, K_{12}, K_{13}, K_{14} (convention of Sillén and Martell[10]), were determined by pH_c measurements performed on series of independently prepared solutions at 25.0° and ionic strength 0.100 *M* (KNO_3). K_1 was determined from a series in which the (0.0022 *M*) MEDTA solution was from 0.7 to 0.9 neutralized with KOH. K_{12}, K_{13} and K_{14} were determined in the broad pH range 2.28–6.03 obtained in 0.0022 *M* MEDTA solutions by addition of standard HNO_3 or by neutralization with KOH. The constants are tabulated in Table I.

TABLE I

CONSECUTIVE FORMATION CONSTANTS OF H_n(MEDTA) SPECIES AT 25° AND I = 0.100 *M* (KNO_3)

$K_1 = 2.04 \times 10^{10}$	$\alpha_1 = K_1 = 2.04 \times 10^{10}$
$K_{12} = 2.61 \times 10^{5}$	$\alpha_2 = K_1K_{12} = 5.32 \times 10^{15}$
$K_{13} = 2.84 \times 10^{2}$	$\alpha_3 = K_1K_{12}K_{13} = 1.51 \times 10^{18}$
$K_{14} = 8.5 \times 10^{1}$	$\alpha_4 = K_1K_{12}K_{13}K_{14} = 1.28 \times 10^{20}$
K_{15} = not determined	α_5 = not determined

Rare-earth MEDTA chelate formation constants

In the case of each lanthanon and yttrium, a series of buffer solutions was prepared in the pH range 2–4, wherein the total rare-earth and total MEDTA concentrations were each 0.002 *M*. Within each series, the pH was altered prior to final dilution by adding from 1.00 to 12.00 ml of carbonate-free standard 0.1 *M* KOH to each 200-ml volumetric flask. A volume of 2 *M* KNO_3 calculated to adjust the ionic strength

TABLE II

FORMATION CONSTANTS OF THE 1:1 CHELATE SPECIES FORMED BY RARE-EARTH CATIONS AND THE MEDTA ANION AT 25.0° AND $I = 0.100\ M$ (KNO_3)

Cation	*log* K_{LnCh}	*Cation*	*log* K_{LnCh}
La^{3+}	11.50 ± 0.02	Tb^{3+}	13.35 ± 0.03
Ce^{3+}	11.87 ± 0.02	Dy^{3+}	13.61 ± 0.02
Pr^{3+}	12.33 ± 0.02	Ho^{3+}	13.81 ± 0.01
Nd^{3+}	12.51 ± 0.02	Er^{3+}	14.04 ± 0.01
Sm^{3+}	12.86 ± 0.02	Tm^{3+}	14.31 ± 0.01
Eu^{3+}	12.96 ± 0.02	Yb^{3+}	14.43 ± 0.01
Gd^{3+}	12.98 ± 0.03	Lu^{3+}	14.51 ± 0.02
Y^{3+}	13.35 ± 0.01		

to 0.100 M was also added in each instance before diluting to volume. After equilibrating overnight at 25.0°, the pH of each solution was read to 0.001 pH unit and the chelate formation constants were computed from the known stoichiometry and the previously determined MEDTA protonation constants. The average value for each series of determinations is reported in Table II.

Cation-exchange-elution separation factors

Practical ion-exchange separation factors[3] for adjacent lanthanons were computed from the data in Table II and are compared to separation factors of the eluants EDTA and HEDTA in Table III.

TABLE III

CATION-EXCHANGE SEPARATION FACTORS FOR ADJACENT PAIRS OF LANTHANONS AT 25°

Pair A–B	α_B^A *(EDTA)*[3]	α_B^A *(MEDTA)*	α_B^A *(HEDTA)*[3]
Lu–Yb	1.9	1.2	1.3
Yb–Tm	1.8	1.3	1.6
Tm–Er	3.1*	1.5	2.0
Er–Ho	1.8	1.7	1.2
Ho–Dy	2.6	1.6	*ca.* 1.0
Dy–Tb	2.3	1.8	*ca.* 1.0
Tb–Gd	4.2*	2.3	*ca.* 1.0
Gd–Eu	1.05	1.05	0.7
Eu–Sm	1.5	1.3	*ca.* 1.0
Sm–Nd**	3.2**	2.2**	2.6**
Nd–Pr	1.8	1.5	1.8
Pr–Ce	2.5	2.9*	2.8
Ce–La	3.7	2.3	5.0*

* Somewhat questionable values.

** The lanthanon Pm, which is not found in natural sources, is missing, so that the Sm–Nd factor is equal to the product of the Sm–Pm and Pm–Nd factors.

Actual cation-exchange elutions were performed at 25 and 92° to obtain linear plots of log [A]/[B] *vs.* distance along the sorbed band under steady-state conditions. From these data (log α_B^A)/h values could be determined in order to ascertain

TABLE IV

STEADY-STATE VALUES OF (log α_B^A)/h FOR SOME PAIRS OF ADJACENT RARE EARTHS OBTAINED AT 25 AND 92°

Column: 1-in., 40–50 mesh Dowex 50W-X8 resin beds; 0.01 *M* MEDTA of pH 8.0; flow-rate, 6.5 ml/min.

Pair A–B	*log α_B^A (25°)*	*(log α)/h (cm^{-1})*		*h (cm)*	
		25°	*92°*	*25°*	*92°*
Er–Ho	0.23	0.221	0.562	1.04	(0.41)
Ho–Dy	0.20	0.205	0.472	0.98	(0.42)
Dy–Tb	0.26	0.210	0.507	1.25	(0.51)
Tb–Y	(0.03)	0.027	0.014	av. (1.08)	

the theoretical plate height, *h*, under the prevailing conditions[3] (see Table IV). Experimentally segments of 40–50 mesh Dowex 50W-X8 cation-exchange resin, each saturated with a different pure rare-earth cation, were introduced sequentially into a 1-in.-diameter column system. The banded system, comprised of 24 in. each of Er^{3+}, Ho^{3+}, Dy^{3+}, Tb^{3+} and Y^{3+} resin (from front to rear), was eluted two band lengths (240 in.) down additional 1-in. columns of 40–50 mesh Dowex 50W-X8 (H^+) with 0.01 *M* MEDTA of pH 8.0 (*ca.* $(NH_4)_2H(MEDTA)$ stoichiometry) at a flow-rate of 6.5 ml/min. This rate of elution caused the visible band boundaries to advance about 0.5 in./h down the resin bed. The solution was sampled intermittently across the band boundaries, as each passed from one column to the next, and was analyzed to obtain [A]/[B] ratios as a function of distance along the resin bed. After obtaining data at 25°, the system was moved into an enclosure heated to 92°, and the banded system was eluted an additional 240 in. with the same eluant. Samples were withdrawn as before and analyzed to obtain the new [A]/[B] ratios as a function of distance.

CONCLUSIONS

It is clear from the data in Table II that the stability of the complexes formed between lanthanons and the MEDTA anion increases in a fairly regular manner from lanthanum through lutetium, although the difference in stability between Eu(MEDTA) and Gd(MEDTA) is small. The stability increases by a factor of 10^3 from La(MEDTA) to Lu(MEDTA); whereas, with EDTA the stability increases by a factor of 10^5. Thus, it can be seen that MEDTA is appreciably less selective than EDTA. Table III reveals the same fact, but also shows that MEDTA is much superior to HEDTA in the case of the middle rare earths, Sm–Er.

Since the values of K_{TbCh} and K_{YCh} obtained were identical within experimental error, it was not possible to assess the actual Tb–Y separation factor accurately from the measured stability constants. It was possible, nevertheless, to estimate the value of log α_Y^{Tb} from (log α_Y^{Tb})/h, using the average value of h computed at 25° for the other rare-earth pairs. If (log α_Y^{Tb})/h = 0.027 cm^{-1} and h = 1.08 cm at 25°, then log α_Y^{Tb} = 0.03 and α_Y^{Tb} = 1.07. If one makes the tacit assumption that (as Moeller and Ferrús[11] found in the cases of Er(HEDTA), Tm(HEDTA), Yb(HEDTA) and Lu(HEDTA)) the stabilities of Tb(MEDTA), Dy(MEDTA), Ho(MEDTA) and Er(MEDTA) are essentially independent of temperature, the value of h at 92° can also be estimated.

Values estimated at 92° from the Er–Ho, Ho–Dy and Dy–Tb data are included in parentheses in Table IV. Since the average value of h at 92° (0.45) times 0.014 gives 0.007 instead of 0.03, it appears that either K_{TbCh} or K_{YCh} is not completely independent of temperature. Note that the rare earth yttrium is not a lanthanide rare earth. Nevertheless, it is quite clear that MEDTA eluant cannot be used to isolate pure yttrium from lanthanide mixtures which contain terbium.

Qualitatively, at least, the elution experiments showed that ion-exchange kinetics were improved but little by substituting MEDTA for EDTA. In fact, the only advantages in using MEDTA in lieu of EDTA appear to lie in the appreciably greater solubility of H_3(MEDTA) compared to H_4(EDTA), which permits H^+ to serve as an adequate retaining ion, and the fact that all Ln(MEDTA) species are much more soluble than the corresponding HLn(EDTA) species. As in the case of HEDTA, MEDTA forms a cationic species $H_5(\mathrm{MEDTA})^{2+}$, so that a band of H_3(MEDTA) forms on the H^+-resin ahead of the sorbed lanthanons as the elution progresses, where it can easily be recovered in highly pure form and recycled. As the H_3(MEDTA) is eluted, the solution needs only to be diluted about twofold, adjusted to pH 8.0 with NH_4OH and re-used.

REFERENCES

1 J. E. Powell and D. A. Johnson, *J. Chromatogr.*, 74 (1972) 269.
2 J. E. Powell and F. H. Spedding, *Chem. Eng. Prog. Symp. Ser.*, 55 (1959) 101.
3 J. E. Powell, in L. Eyring (Editor), *Progress in the Science and Technology of the Rare Earths*, Pergamon, New York, 1964, p. 75.
4 J. L. Mackey, D. E. Goodney and J. R. Cast, *Proc. Rare Earth Res. Conf., 8th, Reno, Nev., 1970*, p. 277.
5 J. E. Powell and H. R. Burkholder, *J. Chromatogr.*, 29 (1967) 210.
6 J. E. Powell and H. R. Burkholder, *J. Chromatogr.*, 36 (1968) 99.
7 M. L. Adolphson, *Ph. D. Thesis*, Iowa State University of Science and Technology, Ames, Iowa, 1969.
8 J. S. Fritz and G. H. Schenk, *Quantitative Analytical Chemistry*, Allyn & Bacon, Boston, Mass., 1969, p. 234.
9 H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 1958, p. 639.
10 L. G. Sillén and A. E. Martell, *Stability Constants of Metal Ion Complexes*, The Chemical Society, Burlington, London, 1964, p. xi
11 T. Moeller and R. Ferrús, *J. Inorg. Nucl. Chem.*, 20 (1962) 261.