398. *Lanthanon Complexes with Ethylenediaminetetra-acetic Acid. Part I.*

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Marsh's work (*J.*, 1950, 1819) on ethylenediaminetetra-acetic acid (" enta ") complexes of the heavy lanthanons has been supplemented by investigations on the use of this reagent in separating the lighter earths. Excellent separation of lanthanum and good concentration of samarium have been obtained, together with a certain degree of differentiation between neodymium and praseodymium. Various modifications have been examined and some crystalline complexes prepared and analysed. Further evidence has been obtained of two-stage co-ordination (Vickery, *J.*, 1950, 2058), and some preliminary titration studies have been made.

Much attention has lately been paid to the function of complex formation in lanthanon fractionation, and Marsh (*J.*, 1950, 1819) recently followed up the work of Schwarzenbach *et al.* (*Helv. Chim. Acta*, 1945, **28**, 828 *et* seq.) on the separation of the rare earths with the aid of " enta " (ethylenediamine-*NNN'N'*-tetra-acetic acid). Marsh, however, studied the separation of heavy lanthanons, although it was indicated that similar rapid separations might be obtainable in the case of the lighter earths.

Owing to their relatively higher basicity, the lighter lanthanons form complexes slightly less easily than do the heavier earths, in that they require somewhat longer digestion for complete reaction. It was considered that this difference in reaction velocity might provide the basis of a separation, but satisfactory results by this method have yet to be obtained.

Formation of complexes from light lanthanon oxalates in ammonium " enta " solution, followed by fractional acidification, gave excellent separation of lanthanum and good concentration of samarium (Table I); praseodymium and neodymium were resolved to a certain extent. Precipitation by excess of oxalic acid did not yield such good results (Table II), even in the presence of excess of " enta " (Table III).

It has been shown (*e.g.*, Maley and Mellor, *Nature*, 1948, **161**, 437; 1950, **165**, 453; *Austral. J. Sci. Res.*, 1949, **2**, *A*, 92) that the use of non-aqueous solvents increases the stability constants of metal co-ordination compounds. In lanthanon–enta systems, the use of dioxan did indeed render necessary lower pH values for precipitation, but advantage in the use of such organic solvents appears restricted to the ultimate concentration of samarium (Table IV). Possibly, however, in the heavy lanthanon group this modification might be more useful.

Table I.

Fraction.	Wt. (g.).	Pr (%).	Nd (%).	Sm (%).	Fraction.	Wt (g.).	Pr (%).	Nd (%).	Sm (%).
1	10		0·5 *		8	3	17	50	17
2	12	9·2	3·3	—	9	6	—	—	—
3	16	10	3·8	—	10	9	—	87·5	10
4	8	—	—	—	11	7	—	—	—
5	5	44	10	6	12	4	—	87	8
6	7	—	—	—	13	4	—	50	6
7	5	64	30	6					

* Indicates total of Pr, Nd, and Sm.

Table II.

Fraction.	Wt (g.).	Pr (%).	Nd (%).	Sm (%).	Fraction.	Wt. (g.).	Pr (%).	Nd (%).	Sm (%).
1	8	13·7	5·0	—	6	15	33·0	40·0	6·5
2	12	16·5	8·5	—	7	16	—	—	—
3	9	—	—	—	8	6	5·0	81·5	8·0
4	10	18·5	5·0	1·0	9	7	1·0	79·0	10·0
5	7	—	—	—					

Table III.

Fraction.	Wt (g.).	Pr (%).	Nd (%).	Sm (%).	Fraction.	Wt (g.).	Pr (%).	Nd (%).	Sm (%).
1	5	12·0	6·0	—	6	18	17·2	44·5	5·0
2	12	17·5	6·5	0·8	7	13	—	—	—
3	10	—	—	—	8	6	—	91·5	7·5
4	15	19·5	6·0	1·3	9	5	—	89·9	7·0
5	7	—	—	—					

Table IV.

Fraction.	Wt. (g.).	Pr (%).	Nd (%).	Sm (%).	Fraction.	Wt. (g.).	Pr (%).	Nd (%).	Sm (%).
1	0·75	6	13	5	6	2·5	15	56	13
2	3·0	7	12	2	7	0·5	13	56	18
3	1·1	10	16	5	8	0·6	10	50	23
4	4·1	15	30	5	9	0·5	10	26	26
5	4·1	17	51	8					

Complex formation from sulphates and alkali double sulphates, followed by fractional acidification, yielded only mediocre separation—in the case of the double sulphates no separation was obtained better than that reported earlier (*J.*, 1950, 1101) with the use of ammonium acetate.

Lanthanon phosphates and fluorides yield complexes with " ammonium enta," but reduction of the pH of such solutions yields unfilterable precipitates. Tungstates, molybdates, chromates, vanadates, and complex cyanides all enter into complexes with " enta," but in such cases there appear to be formed also anionic complexes of the metallic ion, with disruption of the lanthanon salt; this was indicated by the colour change of the solutions and the impossibility of reprecipitating the lanthanons as the original salt either by acidification or by addition of more precipitant.

It was considered that formation of an " enta " complex from an insoluble lanthanon chelate compound might yield an interesting fractionation, as the result of the tendencies of the two reagents to act in opposite directions, one towards precipitation and the other towards solvation. Oxalate solvation–precipitation might be considered a mild example of this, but the 8-hydroxyquinoline inner lanthanon complexes are very stable and their use should provide more definite data.

Lanthanon–8-hydroxyquinoline complexes were dissolved in ammonium " enta " solution, to yield a red solution which would not yield precipitates with either oxalic or mineral acid until a pH of *ca.* 4·5 was reached. On decomposition by mineral acid, mixed precipitates were obtained of free hydroxyquinoline, " H_4-enta," and lanthanon " enta " : oxalic acid merely precipitated lanthanon oxalates. It appears therefore that the stability of these insoluble complexes is comparable with the tendency to form soluble stable complexes. The possibility of two or more solvating chelate compounds in the same system providing additive stability for lanthanon complexes has yet to be determined.

After forming complexes with ammonium " enta," lanthanon oxalates, sulphates, and hydroxides did not divide between the aqueous phase and chloroform at various concentrations and at pH values from 4 to 10.

On the basis of Brintzinger's preparation of simple lanthanon " enta " salts (*Z. anorg. Chem.*, 1943, **251**, 285), Marsh (*loc. cit.*) suggested the formula $(NH_4)_3[(enta)Ln(C_2O_4)]$ for the ammonium oxalate complexes. These salts of lanthanum and samarium have been prepared and shown by analysis to conform to the above formula in both cases. In the case of lanthanum, however, two forms are obtainable : an α-form obtained from solutions where complex formation and crystallisation occurred below *ca.* 50°; and a β-form which is formed at higher temperatures. The β-form is the more stable and soluble. On dissolution of the α-modification in water, boiling, and recrystallisation, the β-modification is obtained. The α-complex also differs in that its lanthanum is precipitated at pH *ca.* 6·5, whereas the more stable form decomposes only at pH *ca.* 5·0.

This two-phase, or two-stage, complex formation was not observed with cerium and is probably caused essentially by the high basicity of lanthanum; it is unlikely to be caused primarily by ionic size, as the difference between the ionic radii of La^{3+} and Ce^{3+} is hardly sufficient to account for such a difference. Preparation of the cerium α-complex was attempted at 40°, 30°, 20°, and 10° without success, hexagonal needles being obtained at all temperatures with no indication of prism formation.

FIG. 1.

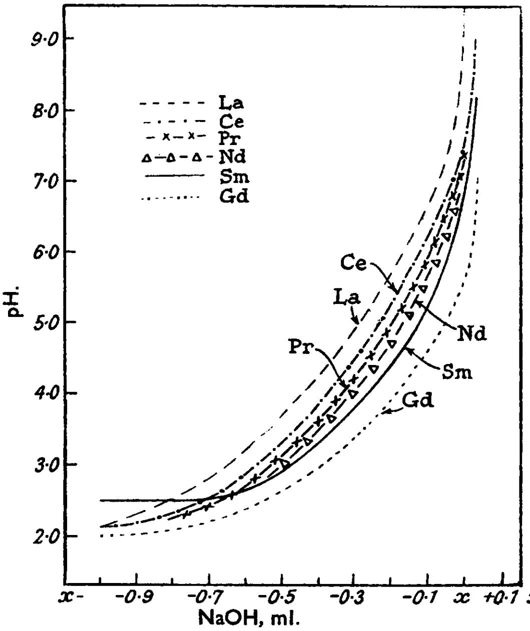
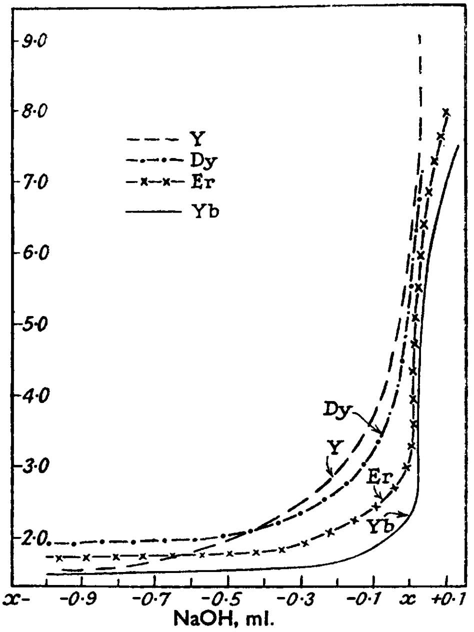


FIG. 2.



Moeller and Brantley (Univ. Illinois, Chem. Task VII, N6OR1—71) observed the possible formation of two complexes of Nd-enta but ascribed this to dilution effects involving varying Nd : enta ratios. Since cerium does not take part in this two-stage complex formation it is doubtful whether neodymium would do so; thus it is unlikely that the variation observed by these workers was due to this dual-stage effect. A similar variation in complex formation was observed by the author (*loc. cit.*) in studying lanthanon–amino-acid co-ordination, and in this instance, as earlier, the effect is probably one of ionisation isomerism, some of the " enta " and ammonium, and possibly oxalate, ions being interchangeable.

Titration Curves.—As a preliminary to a more complete determination of the stability constants of the lanthanon–" enta " complexes, solutions of lanthanon nitrates and enta were titrated with standard alkali. Insufficient results were obtained to enable the full calculation of stability constants, but the individual titration curves obtained for both light and heavy earths (Figs. 1 and 2) show much agreement with separational practise, *viz.*, yttrium close to dysprosium; ease of concentration of lanthanum and samarium; greater complex formation in the heavier than lighter earths, confirming the rapid separation of erbium and ytterbium at the tail of a series. The difference in curve slope between, *e.g.*, yttrium and gadolinium is striking. Although only four members of the heavy group are given, as compared with six of the lighter earths, the difference in behaviour of the two groups is well evident.

The curves for samarium and yttrium appear anomalous towards the lower pH values but this may be due to impurities in each case. On the basis of the curves given, gadolinium should be separated readily from samarium at pH values between 6·0 and 3·0, whilst lanthanum should most easily be separated at pH 3·0—4·5. Any separation of praseodymium and neodymium should be most marked at pH 4—5·5, whilst the purification of yttrium and erbium from each other should proceed best at pH 2·0—3·0.

EXPERIMENTAL.

The solution subsequently referred to as " stock enta " was a 25% solution of the ammonium salt prepared by suspending 250 g. of " enta " in 500 ml. of water and adding aqueous ammonia (*d* 0·880) with stirring at *ca.* 60° to give a clear solution. This solution was cooled, diluted to 1 l., kept for 48 hours, and filtered through a fluted paper before use.

The mixed lanthanon salts employed were all derived from monazite sources less cerium, and had been subjected to one alkali double sulphate fractionation for removal of the heavy earths.

The lanthanum and samarium oxalates employed for preparation of the crystalline complexes were both of 99% purity, and the salts employed for the titration studies were of similar purity, except that for dysprosium 96% purity only was claimed.

Analyses of fractions are derived directly from spectrophotometric readings without correction for the presence of other lanthanons. There should, however, be little interference between praseodymium and neodymium which were determined at 444 and 522 mμ., respectively. Results for samarium, obtained at 402 mμ., may be a little high owing to traces of iron and cerium, as well as to any turbidity, although the chloride solutions were reduced with one drop of 2% oxalic acid and centrifuged before examination in order to reduce these effects.

Oxalate Complexes.—(*a*) Lanthanon oxalates (200 g.) were dissolved in boiling stock enta (850 ml.). To the boiling solution, with vigorous mechanical agitation, 6N-hydrochloric acid was added dropwise and very slowly (1 drop in 2 seconds) until a trace of permanent cloud appeared. Digestion was then carried out for 10—15 minutes without further addition of acid, and fractionation then continued by the slow dropwise addition of acid. This slow-digestion method was employed for each fraction. Subsequent studies appear to indicate a relation between the purity of the fractions and the speed of addition of acid (Table I).

(*b*) As in (*a*), but precipitation was effected with saturated aqueous oxalic acid (Table II).

(*c*) Complexes were formed from oxalates (200 g.), and excess (300 g.) of oxalic acid was added; the precipitate was taken up again in further enta solution (600 ml.), and fractionation by acidification with hydrochloric acid carried out at 90—95° (Table III).

(*d*) Complexes were formed from oxalates (35 g.) with 150 ml. of stock enta, and 150 ml. of redistilled dioxan were added. Some white crystals separated which were filtered off, but contained no lanthanon. Saturated oxalic acid solution (300 ml.) was added without producing a precipitate, the pH then being 8·3. A further 150 ml. of dioxan were added and fractional precipitation by the addition of 6N-hydrochloric acid was carried out at 80°. Seven fractions were taken off at pH values of 7·0, 6·1, 5·2, 4·5, 4·0, 3·5, and 2·5. Each fraction was reconverted into complex and refractionated, the series being extended to nine fractions (Table IV).

(*e*) Samarium oxalate was converted into complex in the minimum of stock enta at the b. p. and carefully evaporated until crystallisation occurred. Owing to the great solubility of the salt, excessive care and two or three recrystallisations from water were necessary in order to obtain good crystals rather than a solidus mixture.

(*f*) The lanthanum oxalate complex was similarly prepared and also obtained by shaking of an excess of the oxalate with stock enta for several hours at 30°, followed by filtration and spontaneous crystallisation of the filtrate.

The β-lanthanum and samarium salts, prepared and crystallised with heat, adopted hexagonal, needle-like shapes, sometimes forming rosettes. The low-temperature α-lanthanum salt gave, however, rather stubby hexagonal prisms which, on redissolution in a little boiling water, yielded the hexagonal needles of the β-form. Precise solubility measurements could not be made, but small volumes of the mother-liquors above the crystals were pipetted off, weighed, evaporated to dryness in platinum, and finally ignited, the weights of residual oxide being calculated back on the basis of analyses of the crystals. The degree of hydration of these salts appears complicated, no definite hydration levels being determinable by desiccation over sulphuric acid or magnesium perchlorate or by drying at 110°. The water content of salts prepared at various times varied from 0 to 12·5%. The following data, based on the anhydrous compounds, were obtained. α-Lanthanum ammonium enta-oxalate: La_2O_3, 29·0; total N, 10·1; NH_3, 9·0; C, 25·2%. {Calc. for $(NH_4)_3[(C_{10}H_{12}O_8N_2)La(C_2O_4)]$: La_2O_3, 28·6; N, 9·84; NH_3, 8·96; C, 25·3%}; stubby hexagonal prisms; 3·2 g. of saturated solution at 20° contained 0·42 g. of La_2O_3; 1·45 g. of complex.

β-Lanthanum ammonium enta-oxalate: La_2O_3, 28·9; total N, 9·9; NH_3, 9·1; C, 25·4%; hexagonal needles; 4·3 g. of saturated solution at 20° contained 0·90 g. of $La_2O_3 \equiv$ 3·12 g. of complex.

Samarium ammonium enta-oxalate: Sm_2O_3, 30·2; total N, 9·55; NH_3, 8·85; C, 24·7% {Calc. for $(NH_4)_3 [(C_{10}H_{12}O_8N_2)La(C_2O_4)]$: Sm_2O_3, 30·0; N, 9·65; NH_3, 8·79; C, 24·8%}; hexagonal needles; 4·1 g. of saturated solution at 20° contained 0·97 g. of $Sm_2O_3 \equiv$ 3·24 g. of complex.

Sulphate Complexes.—(*a*) From a chloride solution, $Ln_2(SO_4)_3,8H_2O$ was precipitated by addition of concentrated sulphuric acid. Complexes were formed from the moist sulphates (75 g., equiv. to 31·2 g. of Ln_2O_3) with stock enta (260 ml.), a little additional ammonia being necessary to obtain a clear solution at the b. p. From this solution, a small fraction crystallised as stubby hexagonal prisms containing 23·2% of Ln_2O_3. The remainder of the solution was fractionally precipitated by 50% sulphuric acid at 90° (Table V).

TABLE V.

Fraction.	Wt. (g.).	Pr (%).	Nd (%).	Sm (%).
1	6	12	20	8
2	16	18	36	8
3	1	12	36	16
4	5	10	32	12
5	4	12	34	14

TABLE VI.

Fraction.	Wt. (g.).	Pr (%).	Nd (%).	Sm (%).
1	3	13·0	15	6·0
2	8	22·5	15	6·5
3	5	—	—	—
4	10	2·5	28	3·0
5	4	—	—	—
6	7	1·4	58	7·1
7	6	—	66	8·3

(*b*) Complex was formed from the sodium double sulphate dihydrate (100 g.) with stock enta (480 ml.). Crystallisation of a small portion of the solution yielded no solids of definite composition. The major portion of the solution was fractionally precipitated by 50% sulphuric acid at 90° (Table VI).

Various Experiments.—Lanthanon–8-hydroxyquinoline complexes were dissolved in stock enta with a slight excess of ammonia. The addition of oxalic acid to this solution yielded no precipitate; neither did hydrochloric acid until a pH of 4·5 was reached. The solution initially obtained was red and this was intensified with lowering of the pH. Owing to the acidity at the initial precipitation, only a few fractions could be collected before final complete precipitation—on ignition, the colours of the oxides of the five fractions showed no variation, and visual observation of the absorption spectra did not indicate any appreciable separation.

Attempts to form enta complexes with single and double lanthanon nitrates, with a view to fractional crystallisation, led to no useful results, the solutions requiring evaporation nearly to dryness before any indications of solidus formation occurred.

After complex formation with stock enta, lanthanon oxalates, sulphates, and hydroxides in solution at pH values between 10 and 4 (the latter in presence of excess of enta) were shaken with chloroform for several hours. Emulsions were obtained at the liquid–liquid interface, but no extraction into the chloroform occurred. Excessive concentration or dilution of the lanthanon solutions had no effect.

Alkali-titration Curves.—M/500-Lanthanon nitrate and M/1000-ammonium enta were mixed, to give a Ln : enta ratio of 1 : 2. Sufficient N-nitric acid was added to give a pH of 1·5—2·5, and 10 ml. of the mixed solutions were titrated with N-sodium hydroxide. Figs. 1 and 2 give results of alkali titration. The readings were obtained on a Marconi-Ekco pH meter with glass and calomel electrodes. Insufficient data were obtained for the determination of full stability constants but this will form the subject of further work.

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