The Separation of the Lanthanons with the Aid of Ethylenediaminetetra-acetic Acid ("Enta Acid"). Part V. The Solubilities of Some Alkali Lanthanon Enta Salts.*

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Sodium lanthanon enta salts show a range of solubilities increasing by up to 18-fold from gadolinium to erbium. The behaviour of the potassium salts is similar but the range is smaller. Both series are readily crystallised. In the cerium group the solubility differences are small.

The probability that the sodium lanthanon ethylenediaminetetra-acetates would prove useful for fractional crystallisation purposes was indicated in Part III (*J.*, 1951, 3057). Solubilities of even-numbered elements have now been determined and indicate that, of all known salts of the group gadolinium to erbium (atomic nos. 64—68), these are much the most favourable for separational purposes by fractional crystallisation.

Experimental

Oxides of over 99% purity were used in all cases except dysprosium. Salts were prepared according to the equation, $Ln_2O_3 + 2NaOH + 2H_4$ enta = 2NaLn enta + $5H_2O$, by warming the ingredients together till dissolution occurred. The salts were recrystallised from slightly alkaline solution. It was found possible to prepare sodium salts of an isomorphous series (Moeller, *Record Chem. Prog.*, 1953, **14**, 69, quoting Moss, Thesis, Univ. of Illinois, 1952) over the range cerium to erbium (atomic nos. 58—68) but lanthanum gave a different salt, and the ytterbium product dried to a gum or glass. The potassium salts were prepared for the members from lanthanum to ytterbium (atomic nos. 57—70), but yttrium, erbium, and ytterbium salts occurred in two forms, one nearly square tablets, the other pyramidal and inclined to effloresce. There seemed little difference in solubility between the two forms.

The sodium and potassium series are both unstable in hot concentrated solution, passing into a less soluble lower hydrate. Reversion takes place in cold dilute solution. The stability of lower hydrates increases, however, with increasing atomic weight. It does not cause trouble in fractionating sodium salts of gadolinium and dysprosium; with erbium it is necessary to warm the solution very cautiously and to crystallise it near 0°. Rest periods for reversion, or restriction of crystallisation to thrice weekly, may be necessary. The freshly prepared erbium salts may require to be kept for a week or two in cold dilute solution before being concentrated at 30—40°. The solubility of the sodium ytterbium salt appears to be infinite, but it readily gives rise to the amorphous lower hydrate which is less soluble. All the lower hydrates are bulky solids useless for fractionation. Attempts to prepare lithium salts resulted in products physically similar to the sodium salt lower hydrates.

The solubilities were determined by preparing warm solutions of the salts with some remaining solid phase in small test-tubes. These were stoppered and placed in a thermostat at 25° or 35°, or a refrigerator at 2°. Equilibrium was attained after 40 hr., as shown by duplicate results. 1-ml. portions were removed, placed on watch-glasses, and dried *in vacuo*. Constant weights were obtained in 4—5 hr., though further very gradual loss of combined water might occur with prolonged desiccation. Accuracy within 2% was considered sufficient for the purpose of this study, and a few results seen to fit well into the expected trend were not duplicated.

In the Table the solubilities are given in terms of g. of hydrated salt per l. and for gadolinium and erbium also in terms of g./100 g. of water. The latter have been calculated in an approximate manner following determinations of the salt densities by flotation in alcohol–bromoform mixtures. The densities found for the hydrated enta salts were: K Er, 2·00; K Dy, 1·95; Na Dy, 1·94; Na Gd, 1·94. The factor for the increase in solubility in passing from Gd to Er is also indicated.

Discussion.—The phenomenal range of solubility between sodium gadolinium enta and sodium ytterbium enta is at once apparent from the Table. This, coupled with the ease of

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preparation and crystallisation of salts at least as far down the series as erbium, raises fractional crystallisation to a new level of efficiency for the middle range of the lanthanons.

Solubilities of alkali lanthanon enta salts (g./l.).

Alkali	Temp.	La	Ce	Pr	Nd	Sm	Gd	Dy	Y	Er	Yb
Na	2°	120	28	18	11·8	10·6	11·7	46	97	196	∞
,, ...	25	139	70	42	31	29	36	133	260	450	∞
,, ...	35	—	—	—	49	43	56	199	342	589	∞
K	2	58	—	19·6	17·6	17·9	26	86	220	207	167
,, ...	25	182	—	66	53	54	81	273	443	435	—
,, ...	35	292	—	—	90	96	126	403	523	550	—
* Na	2	—	—	—	—	—	1·18	(— × 18·5	⟶)	21·8	—
* ,, ...	35	—	—	—	—	—	5·7	(— × 14·8	⟶)	84·3	—
* K	2	—	—	—	—	—	2·64	(— × 8·8	⟶)	23·2	—
* ,, ...	35	—	—	—	—	—	13·5	(— × 5·6	⟶)	76·5	—

Also NH_4 Gd enta hydrate at 2° 86 g./l.; at 25° 240 g./l.
* In g./100 g. of water.

The much used bromate fractionation depends on an increase of solubilities from gadolinium to ytterbium from 110·5 to 351 g./100 g. of water at 25°, a factor of only 3·17. On a molecular solubility basis the increase from gadolinium to yttrium by bromates is a factor of 1·57 at 25°, by sodium enta salt it is 8·0. The dimethyl phosphates have hitherto been the salts with the greatest known range of solubility, amounting to 5·36-fold at 0° or 7·75-fold at 50° for gadolinium over erbium (Marsh, *J.*, 1939, 554), but their use is not practicable on a large scale.

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