348. *Lanthanon Complexes with Ethylenediamine-*NNN'N'*-tetra-acetic Acid.   Part III.**
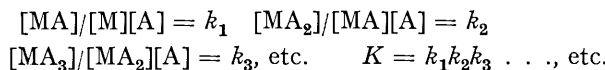
By R. C. VICKERY.

Stability constants have been derived for complexes of some lanthanons with ethylenediaminetetra-acetic acid. They increase from 15·3 for the lanthanum complex to 18·7 for the ytterbium complex, the constant of 18·0 for the yttrium complex being between those for dysprosium and erbium. Values for the free energies of formation of these complexes have been derived, and some conclusions drawn on the probable structure of the complexed molecules.

STABILITY constants for several bivalent-ion chelate systems have been given by various workers (*e.g.*, Schwarzenbach *et al.*, *Helv. Chim. Acta*, 1945, **28**, 828, *et seq.*; Maley and Mellor, *Aust. J. Sci. Res.*, 1949, **2**, 92, 579) but few determinations have been made of the constants of the various tervalent lanthanon chelate systems. A knowledge of these constants is of considerable value in separations of the lanthanons based on their ethylene-diaminetetra-acetic acid (" enta ") complexes, and it was for this reason that the determinations were made.
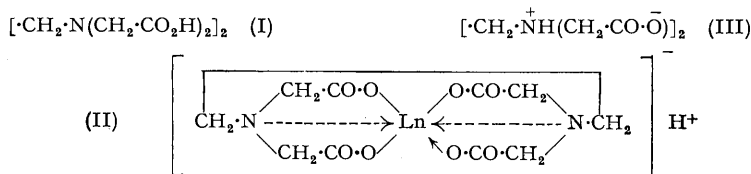
Adaptation of Bjerrum's theory of step equilibria (" Metal Ammine Formation in Aqueous Solutions," Copenhagen, 1941) to the derivation of stability constants of complex cations requires the solution of expressions for n (the average number of ligands, A, attached to the metal, M) and $\log 1/[\text{A}]$. Maley and Mellor (*loc. cit.*) have generalised the form of derivation of these expressions from which are constructed the formation curves of the systems (the plot of n against $\log 1/[\text{A}]$). From these curves the step-equilibria constants can be obtained and may be combined to yield the overall stability constant K.

The step equilibria normally involved in complex systems are

$$[\text{MA}]/[\text{M}][\text{A}] = k_1 \quad [\text{MA}_2]/[\text{MA}][\text{A}] = k_2$$
$$[\text{MA}_3]/[\text{MA}_2][\text{A}] = k_3, \text{ etc.} \qquad K = k_1 k_2 k_3 \ldots, \text{ etc.}$$

but Schwarzenbach has pointed out (*Nature*, 1951, **167**, 434) that bonds between a polydentate ligand and a metal are formed simultaneously and that only complexes involving more than one ligand mole per metal ion are formed stepwise. In the lanthanon–" enta " systems therefore the reaction is $\text{Ln}^{3+} + \text{H}_4\text{A} \longrightarrow \text{LnHA} + 3\text{H}^+$ giving $K = [\text{LnHA}]/[\text{Ln}^{3+}][\text{HA}^{3-}]$.

" Enta " (I) forms complexes with the lanthanons as in (II). Zwitterion characteristics

$$[\cdot\text{CH}_2\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{H})_2]_2 \quad \text{(I)} \qquad\qquad [\cdot\text{CH}_2\cdot\overset{+}{\text{N}}\text{H}(\text{CH}_2\cdot\text{CO}\cdot\bar{\text{O}})]_2 \quad \text{(III)}$$

have been attributed to " enta," for Long, Jones, and Burke (Brookhaven Chemical Conf., No. 2, 1948, 106) and Schwarzenbach (*loc. cit.*) have represented it as (III), but the zwitterion would not be expected to promote complex formation because of the positive charge on the nitrogen atom. An equilibrium would exist between the zwitterion and " enta " and the effect of zwitterion formation would be to reduce the rate of complex formation. However, since " enta " may be titrated as a tetrabasic acid, Schwarzenbach claims that the zwitterion effect may be disregarded in calculations of stability constants. The pK_a values for " enta " (Schwarzenbach, *loc. cit.*) would appear to confirm this, *viz.*, pK_1, 1·996; pK_2, 2·672; pK_3, 6·161; pK_4, 10·262. Joy, however (private communication), considers that this zwitterion effect cannot be so disregarded, for it

* Part II, *J.*, 1952 421.

becomes of increasing importance with increase in pH of the system above *ca.* 6·0. Since it is now found that in dilute solutions some 90% of the lanthanon–" enta " chelation occurs below pH 6·0, for the purpose of this work we may disregard the zwitterion characteristics of " enta " and be concerned only with the relationships between (I) and (II).

Conventions and Derivations (all concentrations in moles/litre).

T_{Ln} = Concentration of total lanthanons in system.

T_A = Concentration of total " enta " in all forms in system.

T_H = Concentration of total ionised and potentially ionisable hydrogen in system.

n_A = (Total potentially ionisable hydrogen bound to " enta ")/(Total " enta " unattached to lanthanons).

α = (" Enta " unattached to lanthanons or hydrogen)/(Total " enta " unattached to lanthanons).

n = (" Enta " attached to lanthanons)/T_{Ln}.

E = Initial concentration of strong acid (normality).

Q = Added strong alkali.

The four dissociation constants of " enta," K_1, K_2, K_3, K_4, follow from Schwarzenbach's pK values (above), and, on introduction of the various species concerned, we have :

$$T_{Ln} = [Ln^{3+}] + [LnHA]$$

$$T_A = [A^{4-}] + [HA^{3-}] + [H_2A^{2-}] + [H_3A^-] + [H_4A] + nT_{Ln}$$

$$T_H = [H^+] + [HA^{3-}] + 2[H_2A^{-2}] + 3[H_3A^-] + 4[H_4A] + nT_{Ln}$$

$$n_A = \frac{[HA^{3-}] + 2[H_2A^{2-}] + 3[H_3A^-] + 4[H_4A]}{[A^{4-}] + [HA^{3-}] + [H_2A^{2-}] + [H_3A^-] + [H_4A]}$$

$$\alpha = [A^{4-}]/([A^{4-}] + [HA^{3-}] + [H_2A^{2-}] + [H_3A^-] + [H_4A])$$

$$n = T_A - ([A^{4-}] + [HA^{3-}] + [H_2A^{2-}] + [H_3A^-] + [H_4A])/T_{Ln}$$

$$T_A = (T_H - [H^+] - nT_{Ln})/n_A + nT_{Ln}$$

Since " enta " has four dissociable hydrogens, we have $T_H = (E - Q) + K_w/[H^+] + 4T_A$ and substitution of dissociation constants for " enta " in n_A gives

$$n_A = \frac{[A^{4-}][H^+]/K_4 + 2[HA^{3-}][H^+]/K_3 + 3[H_2A^{2-}][H^+]/K_2 + 4[H_3A^-][H^+]/K_1}{K_4[HA^{3-}]/[H^+] + [A^{4-}][H^+]/K_4 + [HA^{3-}][H^+]/K_3 + [H_2A^{2-}][H^+]/K_2 + [H_3AH^+]/K_1^-][}$$

Dividing through by $[HA^{3-}]$, we have

$$n_A = \frac{1 + 2[H^+]/K_3 + 3[H^+]^2/K_2K_3 + 4[H^+]^3/K_1K_2K_3}{1 + K_4/[H^+] + [H^+]/K_3 + [H^+]^2/K_2K_3 + [H^+]^3/K_1K_2K_3}$$

Similarly

$$\alpha = \frac{K_4/[H^+]}{1 + K_4/[H^+] + [H^+]/K_3 + [H^+]^2/K_2K_3 + [H^+]^3/K_1K_2K_3}$$

$$n = T_A - \frac{\left(\dfrac{(E - Q) + K_w/[H^+] + 4T_A - [H^+] - nT_{Ln}}{n_A}\right)}{T_{Ln}}$$

$$= \frac{T_A\left(1 - \dfrac{4}{n_A}\right) - \dfrac{(E - Q) + K_w/[H^+] - [H^+] - nT_{Ln}}{n_A}}{T_{Ln}}$$

$$[A] = \alpha(T_H - [H^+])/n_A - nT_{Ln} = \alpha\{(E - Q) + K_w/[H^+] + 4T_A - [H^+] - nT_{Ln}\}/n_A$$

Values thus obtained for n and log 1/[A] are plotted against each other to give the formation curve, and $K = [\text{LnHA}]/[\text{Ln}^{3+}][\text{HA}^{3+}]$ is extracted, as the value when $n = 0.5$, *i.e.*, when there are equal amounts of LnHA_{x-1} and LnHA_x present (Bjerrum, *loc. cit.*).

Fig. 1 shows the pH curves for titration of lanthanon–" enta " systems with standard alkali, and Fig. 2 the formation curves obtained from data yielded by the titrations. The table records the K values extracted from the formation curves at $n = 0.5$. Titration and formation curves and K values are also included for the yttrium–" enta " system. The gadolinium–" enta " system gave a titration curve identical with that of the samarium–" enta " system and is not therefore shown, nor is its formation curve plotted. Within experimental error, the constant K for gadolinium is considered to be identical with that for samarium.

The increase in K values for the lanthanon–" enta " systems parallels the increase in atomic number through the lanthanon series, with yttrium coming between dysprosium

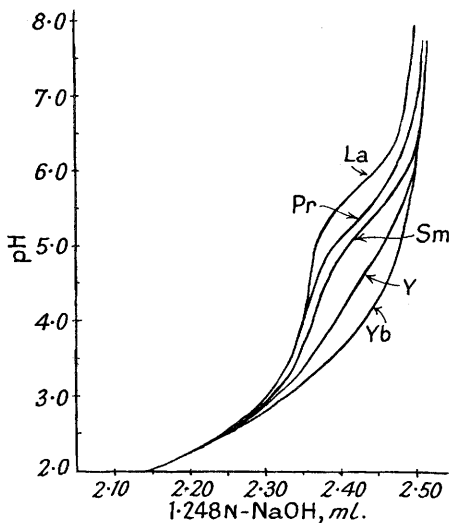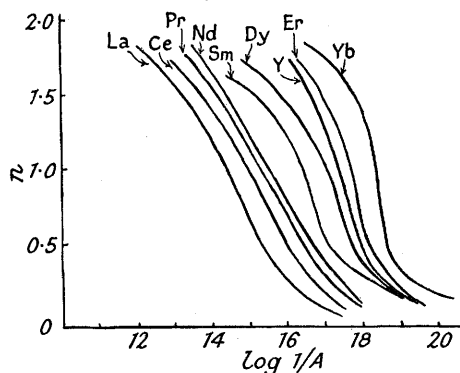FIG. 1. *Titration curves for lanthanon–enta systems.*

FIG. 2. *Formation curves for lanthanon–enta systems.*

and erbium at about the position of holmium. The value for lanthanum is in good agreement with Schwarzenbach's value (*Helv. Chim. Acta*, 1951, **34**, 1503) of 15.4 ± 0.05, and the situation of yttrium between dysprosium and erbium is in keeping with the sequence obtained during separation of the lanthanons by decomposition of their " enta " complexes (Marsh, *J.*, 1950, 1819).

Since the ligand–metal reaction is in this instance one-step and the ligand sexadentate, the " characteristic co-ordination number " Z (Bjerrum) is 6. We may therefore expect the complex to have an octahedral configuration with the ligand bound exclusively in the form of five-membered chelate rings (Bjerrum, *Chem. Reviews*, 1950, **46**, 381).

Employing Bjerrum's quantity (*loc. cit.*) $(N/Z)\log K + \log 55$, we may easily derive the free energies of complex formation of the lanthanon–" enta " chelates. These are given also in the table. The only data available for comparison are those given by Bjerrum for

Overall stability constants and free energies of formation of lanthanon–enta complexes.

Lanthanon	log K	(N/Z) log K + log 55	Lanthanon	log K	(N/Z) log K + log 55	Lanthanon	log K	(N/Z) log K + log 55
La	15.30	4.29	Sm ......}	17.2	4.61	Er	18.15	4.77
Ce	16.05	4.41	Gd ......}			Yb	18.70	4.85
Pr	16.55	4.50	Dy	17.75	4.70	Y	18.0	4.74
Nd	16.75	4.53						

La–OH and La–SO$_4$ systems which are ~5 and 3.7, respectively. The values given represent only measures of the change in free energy on complex formation and must be multiplied

6 F

by 1·362 to give the results in kcals. at 25°. Values of K or of free-energy change for lanthanon complexes with ethylenediamine, ammonia, or acetates are not known, and it is not therefore possible to derive information concerning the increase of stability arising from chelation in the lanthanon–" enta " system as compared with other lanthanon systems.

Plumb, Martell, and Bersworth (*J. Phys. Coll. Chem.*, 1950, **54**, 1208), employing spectrophotometry, derived values for the relative strengths of " enta " complex formation with metal ions. The values they obtained were, however, somewhat empirical and took Cu = 100 as the standard : this gave a value of 300 for Cr and 39 for Ni at pH 4·00. Such values are much distorted in comparison with those obtained titrimetrically, but the data given by these workers do show clearly the effect of pH on the location of a metal ion in the stability series, thus affording confirmation of the zwitterion effect noted above.

EXPERIMENTAL

The lanthanons employed were of the purities indicated in Part II of this series (*loc. cit.*) and the " enta " employed was the analytical " Sequestrene " AA grade of the Alrose Chemical Co., Providence, U.S.A. This " enta " was further purified before use by two crystallisations from water and a final precipitation from ammoniacal solution by acidification. The " enta " was prepared as M/1000-aqueous solution and the lanthanons as M/100-nitrate solutions.

Titrations were carried out at 20° with 1·248N-sodium hydroxide (carbonate free) against 100 ml. of solution 0·98 × 10⁻³M with regard to " enta," 0·2 × 10⁻⁵M to lanthanon ion, and 2·563 × 10⁻³N to nitric acid, the ionic concentrations of the system being maintained at 0·1M by addition of potassium chloride.

Moeller and Brantley (Univ. Illinois N6OR-71 Chem. Task 7, Sept. 1949), in titration studies of neodymium–" enta " complexes, employed higher concentration of neodymium than used in the present work, and what were considered correspondingly higher effective concentrations of " enta " by suspending the latter in the neodymium solution and stirring mechanically for several minutes before taking pH readings. This method is insufficiently accurate, however, when stability constants are to be computed, because of the possibility of non-attainment of equilibrium between the solid and the liquid phase of the system. Further, the presence in solution of insufficient " enta " to convert the lanthanon fully into complex could lead to titration of the lanthanon itself (as distinct from the complex) thereby precipitating lanthanon hydroxide, which would extend the time required for attainment of equilibrium in the system. In this work it was considered preferable to employ fully solvated " enta " even though higher dilutions of lanthanon ions had to be employed.

pH measurements obtained on a Cambridge pH meter were taken as measurements of hydrogen-ion concentrations in the system, no account being taken of activity coefficients. A simple calculation showed that this did not lead to an appreciable variation in the formation curve functions.

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