

was shown to be appreciably larger for the hydroxylated form of collagen than the unhydroxylated form from the same source. In the latter studies by Jiminez *et al.*<sup>4</sup>, the thermal stability of unhydroxylated collagen relative to hydroxylated collagen was investigated using pepsin digestion at various temperatures as an enzymatic probe of conformation. Their results also indicate that the unhydroxylated molecules have a denaturation temperature between 20° and 25°, while the hydroxylated molecules are stable beyond 35°. These studies can be taken to be very good evidence in support of the theoretical ideas put forward from our laboratory regarding the role played by hydroxyproline in the stability of the collagen molecule.

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1. Ramachandran, G. N., Bansal, M. and Bhatnagar, R. S., *Biochim. Biophys. Acta*, 1973, 322, 166.
2. Koetzle, T. F., Lehmann, M. S. and Hamilton, W. C., *Acta Cryst.*, 1973, 29 B, 231.
3. Berg, R. A. and Prockop, D. J., *Biochem. Biophys. Res. Commun.*, 1973, 52, 115.
4. Jiminez, S., Harsch, M. and Rosenbloom, J., *Ibid.*, 1973, 52, 106.

## AMPEROMETRIC, POTENTIOMETRIC AND MAGNETIC STUDIES OF SOME RARE EARTH KOJATES

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### ABSTRACT

The reactions of the rare earth elements ( $\text{La}^{+3}$ ,  $\text{Ce}^{+3}$ ,  $\text{Pr}^{+3}$ ,  $\text{Nd}^{+3}$ ,  $\text{Sm}^{+3}$  and  $\text{Gd}^{+3}$ ) with kojic acid have been studied by employing amperometric and potentiometric titrations. The results of these titrations reveal 1 : 3 (metal : ligand) stoichiometry for the complexes. The experimental magnetic moments are in agreement with those reported for typical lanthanide sulphates and other compounds, indicating that metal ion in these chelates acts as a free ion, as far as the *f*-electrons are concerned.

### INTRODUCTION

**R**ARE earth complexes of kojic acid of the general composition  $[\text{M}(\text{C}_6\text{H}_5\text{O}_4)_3(\text{H}_2\text{O})_2]$  (where  $\text{M} = \text{La}^{+3}$ ,  $\text{Ce}^{+3}$ ,  $\text{Pr}^{+3}$ ,  $\text{Nd}^{+3}$ ,  $\text{Sm}^{+3}$ ,  $\text{Gd}^{+3}$ ,  $\text{Dy}^{+3}$ ,  $\text{Ho}^{+3}$  and  $\text{Y}^{+3}$ ) were prepared recently by us<sup>1-3</sup> and characterised. Analytical data and IR spectra of complexes show kojic acid acting as bidentate ligand and two water molecules are also present in the coordination sphere. In this communication the reactions of rare earth elements ( $\text{La}^{+3}$ ,  $\text{Ce}^{+3}$ ,  $\text{Pr}^{+3}$ ,  $\text{Nd}^{+3}$ ,  $\text{Sm}^{+3}$  and  $\text{Gd}^{+3}$ ) have been studied by employing amperometric and potentiometric titrations. Magnetic susceptibility data on the complexes are also reported in this paper.

### MATERIALS AND METHODS

All chemicals were of BDH (AR) quality. Elico model LI-10 pH meter, in conjunction with a glass electrode and a SCE, was used for potentiometric titrations conducted at 30° C. Amperometric and magnetic measurements were made as reported in the earlier communication<sup>2</sup>.

### RESULTS AND DISCUSSION

**Amperometric titrations.**—The amperometric titrations, both direct and reverse, were carried out, using 2 M sodium nitrate as supporting electrolyte and 0.2% gelatine solution as maximum suppressor, at the plateau of the rare earth ion ( $-1.2 \text{ V}$ ) and the ligand ( $-0.95 \text{ V}$ ) respectively.

From the results of these titrations it is indicated that the mole ratio in which the metal and the ligand combine to form the respective complex is 1 : 3.

**Potentiometric titrations.**—The titrations were carried out with the solutions containing the metal and the ligand in the ratios of 1 : 0, 1 : 1, 1 : 2 and 1 : 3 against 0.1 M NaOH.

The solution containing lanthanum nitrate alone exhibits only one inflexion point (Fig. 1, curve A), corresponding to the interaction of 3 moles of NaOH with 1 mole of lanthanum to give 1 mole of lanthanum hydroxide.



On the addition of 1 mole of the ligand to the lanthanum nitrate solution, the pH of the solution is lowered (Fig. 1, curve B). This lowering of pH can be attributed to the release of protons during complex formation. The curve shows two inflexion points, one corresponding to 1 mole and the other to 3 moles of NaOH respectively. As the solution contains lanthanum and the ligand in 1:1 ratio, it is assumed that 1/3 of the metal reacts with the ligand to form 1:3 complex with the release of a proton which is neutralized by 1 mole of NaOH, while the remaining 2/3 of the metal is precipitated as hydroxide on the addition of another 2 moles of NaOH.

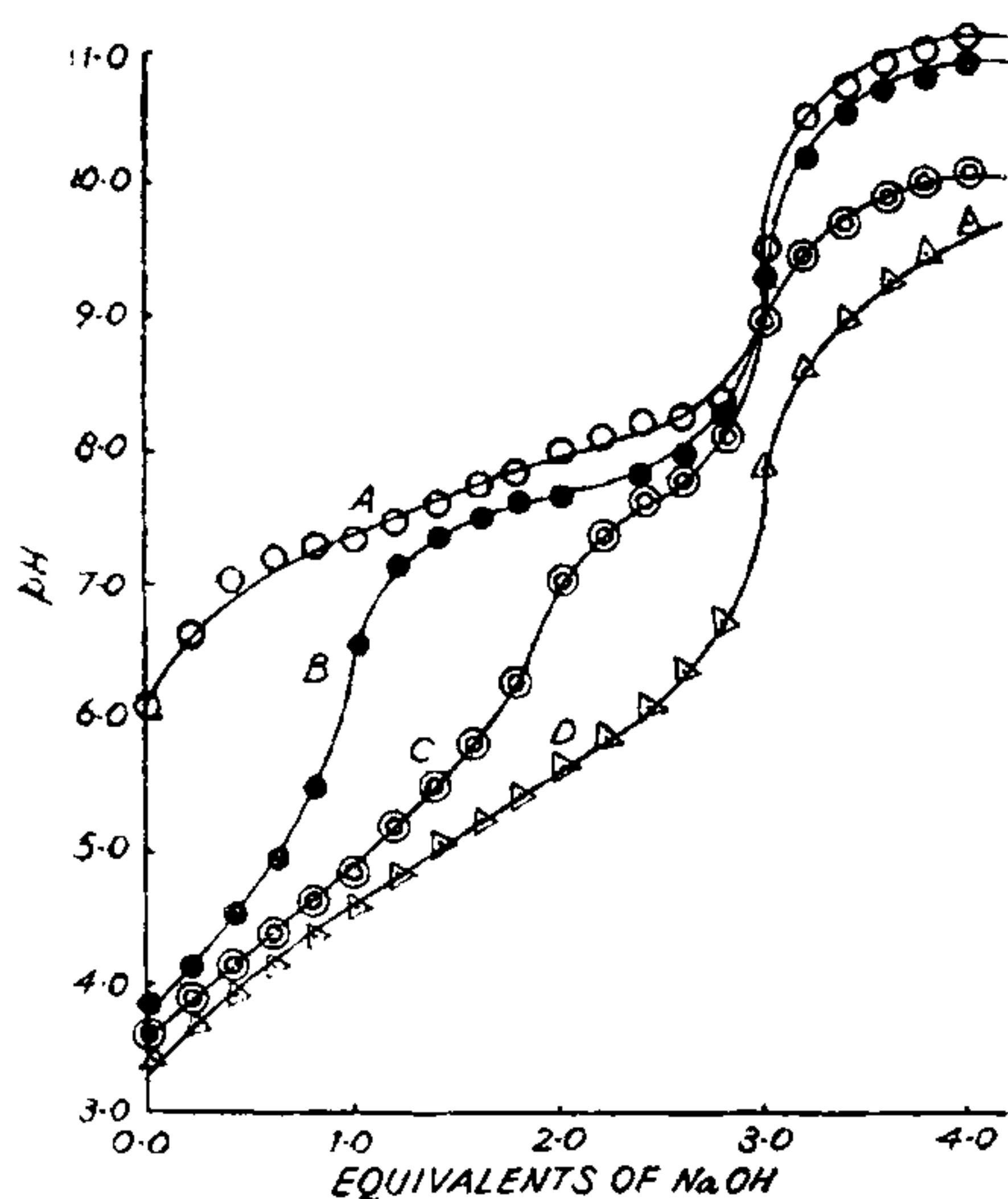


Fig. 1. pH-metric titration curves. A, 20 ml 0.005 M lanthanum nitrate + 30 ml  $H_2O$ ; B, 20 ml 0.005 M lanthanum nitrate + 5 ml 0.02 M kojic acid + 25 ml  $H_2O$ ; C, 20 ml 0.005 M lanthanum nitrate + 10 ml 0.02 M kojic acid + 20 ml  $H_2O$ ; D, 20 ml 0.005 M lanthanum nitrate + 15 ml 0.02 M kojic acid + 15 ml  $H_2O$ ; titrant, 0.1 M NaOH.

The titration of the solution containing metal and the ligand in 1:2 ratio (Fig. 1, curve C) shows two inflexion points, one corresponding to 2 moles and the other to 3 moles of NaOH respectively. This clearly indicates that at 2 equivalence the 2 protons were neutralized and other one equivalence of NaOH is required for the hydroxide formation.

Similarly with the solution containing metal and the ligand in 1:3 ratio (Fig. 1, curve D) shows only one inflexion point corresponding to 3 moles of NaOH, which are required to neutralize the 3 protons released during 1:3 complex formation.

Similar potentiometric behaviour was observed with the other rare earth ions ( $Ce^{+3}$ ,  $Pr^{+3}$ ,  $Nd^{+3}$ ,  $Sm^{+3}$  and  $Gd^{+3}$ ) showing thereby the existence of 1:3 complexes in these systems also.

**Magnetic measurements.**—Results of magnetic measurements at room temperature are presented in Table I. The effective magnetic moment has been calculated from corrected molar susceptibilities by Curie law.

$$\mu_{eff} = 2.84 \sqrt{\chi_M (corr.)^T}$$

TABLE I

Magnetic susceptibilities of rare earth kojates

Complex	Temp. $\times 10^3$ $^{\circ}K$	$\chi \times 10^6$	$\chi'_M \times 10^6$	$\mu_{eff}$ (BM)
$[Ce(C_6H_5O_4)_3(H_2O)]$	303.0	4.04	2020	2.33
$[Pr(C_6H_5O_4)_3(H_2O)]$	303.0	10.18	5907	3.69
$[Nd(C_6H_5O_4)_3(H_2O)]$	302.5	8.08	4908	3.46
$[Sm(C_6H_5O_4)_3(H_2O)]$	302.5	1.95	987	1.53
$[Gd(C_6H_5O_4)_3(H_2O)]$	302.5	43.14	26390	7.90

$\chi$  = Magnetic susceptibility per g of material,  
 $\chi'_M$  = Corrected magnetic susceptibility per g mole.

The  $La^{+3}$  chelate under examination was found to be diamagnetic. The magnetic moments obtained experimentally for the remaining rare earth chelates are in good agreement with the values for typical lanthanide sulphates<sup>4</sup>. These values suggest that the lanthanide ion acts approximately as free ion, as far as the *f*-electrons are concerned.

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1. Agarwala, R. C., Gupta, S. P. and Rastogi, D. K., *J. Inorg. Nucl. Chem.*, 1974, **36**, 208.
2. — and —, *Curr. Sci.*, 1974, **43**, 263.
3. — and —, *J. Acta Ciencia Indica*, 1974, **1**, 31.
4. Figgis, B. N. and Lewis, J., *Techniques of Inorganic Chemistry*, Interscience, N.Y., 1965, **4**, 137.