Conductometric Studies on the Interaction of Some of the Lanthanon Nitrates with Monofunctional Bidentate Schiff Bases

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Conductometric titrations of some of the lanthanon nitrates with monofunctional bidentate Schiff bases in the ethanolic medium reveal the formation of Ln(NO$_3$)$_3$·3 SBH and Ln'(NO$_3$)$_3$·2 SBH (where, Ln = La(III), Pr(III) or Sm(III); Ln' = Yb(III) and SBH = 2,4-pentanedionebenzylimine or o-hydroxyacetophenoneanil) type of derivatives. Preparative studies also support these results.

A few references pertaining to the synthesis of lanthanon(III) derivatives of monofunctional bidentate Schiff bases in the aqueous medium have so far been described in the literature. Attempts to prepare 2,4-pentanedioneimine derivatives by the aqueous method, resulted in the isolation of lanthanon tris-2,4-pentanedionate hydrate, where as the preparation of lanthanon tris-2,4-pentanedionate by ammonia method yielded lanthanon hydroxide as the final product.

Recently, Yamada et al., have reported the synthesis of lanthanon salicylideneamine derivatives by grinding lanthanon chloride hexahydrate with the ligand. However, preparation of 2,4-pentanedioneimine derivatives of the lanthanons, using this method, resulted in the isolation of tris-2,4-pentanedionates.

The ion exchange, solvent extraction and the kinetic studies indicate that the ligand exchange reactions involving the lanthanon species in solution are extremely rapid. It was, therefore, considered of interest to undertake conductometric studies of these systems and as a result of these investigations the formation Ln(NO$_3$)$_3$·3 SBH and Ln'(NO$_3$)$_3$·2 SBH (where, Ln = La(III), Pr(III) or Sm(III); Ln' = Yb(III) and SBH = 2,4-pentanedionebenzylimine or o-hydroxyacetophenoneanil) type of derivatives have been shown by the conductometric titrations in the alcoholic medium. The present paper deals with such studies.

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**Experimental**

**Materials**

The rare earth nitrates (Schuchardt, Germany) were used and their solutions prepared in doubly distilled ethanol.

**Preparation of Schiff bases**

(i) o-Hydroxyacetophenoneanil $C_{13}H_{13}ON$: o-Hydroxyacetophenoneanil was prepared by the condensation of o-hydroxyacetophenone (Riedel) with an equimolar amount of aniline (B.D.H.) in benzene and refluxing for 3–4 h; the water formed in the reaction was removed azeotropically with benzene. The excess of solvent was removed under reduced pressure and the o-hydroxyacetophenoneanil so obtained was finally distilled at 135–137°C/0.2–0.3 mm to give a yellow solid (m.p. 79.8°C).

Found C 79.52 N 6.49 H 6.18,
Caled C 79.60 N 6.63 H 6.21.

(ii) 2,4-Pentanedionebenzylimine $C_{12}H_{15}ON$: 2,4-Pentanedionebenzylimine was prepared as described earlier by refluxing equimolar amount of the reactants in benzene and distilled at 110–111°C/0.1 mm to give a yellow liquid. This was analysed before use.

Found C 76.01 N 7.48 H 7.84,
Caled C 76.15 N 7.40 H 7.92.

**Conductometric titrations**

Conductometric titrations were carried out at 25 ± 1°C with Tesla RLC bridge having a cell constant 0.74 cm$^{-1}$. All the systems were titrated against 0.5 M lanthanon nitrate solutions and the volume of 0.025 M Schiff base solution to be titrated was always kept constant (25 ml). All the solutions were prepared in distilled ethanol.

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Results and Discussion

Curve a represents the conductometric titration of 0.025 M 2,4-pentanedionebenzylimine (Fig. 1) or o-hydroxyacetophenoneanil (Fig. 2) with 0.5 M lanthanum nitrate solution. In these cases, the conductance increases steadily as the amount of lanthanum nitrate increases, till the molar ratio of La(NO$_3$)$_3$:SBH (where SBH = 2,4-pentanedionebenzylimine or o-hydroxyacetophenoneanil) reaches 0.33, showing the presence of La(NO$_3$)$_3$·3 SBH species. Beyond this point, the conductance increases slowly without any inflection in the curve.

The formation of similar type of derivatives is indicated by the curves b and c (Figs. 1 and 2), which represent the conductometric titrations of 0.025 M 2,4-pentanedionebenzylimine and o-hydroxyacetophenoneanil respectively with 0.5 M praseodymium and samarium nitrate solutions. Only one sharp break at the molar ratio, 0.33 corresponds to the formation of Pr(NO$_3$)$_3$·3 SBH and Sm(NO$_3$)$_3$·3 SBH derivatives. These reactions may be exemplified as follows:

Fig. 1. Conductometric titrations of 2,4-pentanedionebenzylimine (0.025 M) with (i) La(NO$_3$)$_3$ 0.5 M (curve a), (ii) Pr(NO$_3$)$_3$ 0.5 M (curve b), (iii) Sm(NO$_3$)$_3$ 0.5 M (Curve, c) and (iv) Yb(NO$_3$)$_3$ 0.5 M (Curve, d) in the ethanolic medium.

Fig. 2. Conductometric titrations of o-hydroxyacetophenoneanil (0.025 M) with (i) La(NO$_3$)$_3$ 0.5 M (Curve, a), (ii) Pr(NO$_3$)$_3$ 0.5 M (Curve, b), (iii) Sm(NO$_3$)$_3$ 0.5 M (curve c) and (iv) Yb(NO$_3$)$_3$ 0.5 M (curve d) in the ethanolic medium.
The formation of the above two different type of derivatives, \( \text{Ln(NO}_3\text{)}_3 \cdot 3 \text{SBH} \) and \( \text{Yb(NO}_3\text{)}_3 \cdot 2 \text{SBH} \) (where, \( \text{Ln} = \text{La(III)}, \text{Pr(III)} \) or \( \text{Sm(III)} \)), in the case of lighter and heavier lanthanons may be attributed to the decrease in the ionic radii with the increase in atomic number. This is in accordance with the previously reported rare earth complexes of ethylenediamine, bis-2,4-pentanedione\(^6\), ethylenediamine tetraacetic acid\(^7\), dimethylformamide\(^8\), dimethylsulphoxide\(^9\) and dimethylacetamide\(^10\).

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\(^7\) J. L. Hoard, M. D. Lind, and B. Kocklee, Proc. 4th Rare Earth Research Conference, Arizona, April 1964.