Potentiometric Studies on the Chelation Behaviour of \( \omega \)-Benzoyl-2-hydroxy-4-methoxy-3-methyl-acetophenone (BHMMMA) with Lanthanons

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The chelation behaviour of complexes of La(III), Pr(III), Nd(III), Sm(III), Y(III), Tb(III), Dy(III), Ho(III) with \( \omega \)-benzoyl-2-hydroxy-4-methoxy-3-methyl-acetophenone has been studied potentiometrically in 75\% (v/v) aqueous alcohol medium at various ionic strengths. The method of Bjerrum and Calvin, as modified by Irving and Rossotti, has been used to find values of \( \bar{n} \) and \( pL \). The stability constants and the values of \( S_{\text{min}} \) have been calculated. The order of stability constants was found to be: \( \text{La} < \text{Pr} < \text{Nd} < \text{Sm} < \text{Y} < \text{Tb} < \text{Dy} < \text{Ho} \).

(Keywords: Potentiometry; Stability constant; \( \omega \)-Benzoyl-2-hydroxy-4-methoxy-3-methyl-acetophenone; Lanthanoids)

Introduction

Hydroxy acetophenone and its derivatives are well known for their chelating and biological properties. Lot of studies have been done on the complexation behaviour of substituted hydroxy acetophenones and their derivatives. Literature survey reveals that no work has been done on the lanthanon complexes of \( \omega \)-benzoyl-2-hydroxy-4-methoxy-3-methyl-acetophenone. So the present study was undertaken to determine the
stability constants of lanthanons with BHMMA at various ionic strengths in 75% alcohol medium.

Materials and Methods

A digital pH-meter (ECIL model PH 5652) with a glass electrode (0–14 pH range) was used for pH-measurements. The pH-meter was standardised with potassium hydrogen phthalate and phosphate buffers before performing the titrations.

Preparation of the Ligand. A solution of the 2-benzoyloxy-4-methoxy-3-methyl-acetophenone (2 g) in dry pyridine (15 ml) was treated with powdered potassium hydroxide (1 g) and the resulting mixture was thoroughly stirred at 45°. In about 45 minutes the solution became semi-solid due to the formation of potassium salt of β-diketone. The mixture was cooled and then treated with ice and dilute hydrochloric acid which gave benzoyl-2-hydroxy-4-methoxy-3-methylacetophenone. It was recrystallized from ethanol and its purity was checked by elemental analysis and TLC.

The solution of ligand (BHMMA) was prepared in 75% (v/v) aqueous alcohol. All the metal ion solutions were prepared and standardised by conventional procedures. Sodium perchlorate (Riedel) was used to keep the ionic strength constant for different sets. A solution of tetramethyl ammonium hydroxide (TMAH) (Merck) in 75% aqueous alcohol was used as the titrant. It was standardised with oxalic acid. All other chemicals used were of reagent grade. The titrations were carried out in an atmosphere of nitrogen, which was presaturated with 75% (v/v) aqueous alcohol. All measurements were made at a definite temperature which was kept constant by using a MLW (Federal Republic of Germany) (NBE type) thermostat.

The method of Bjerrum and Calvin as modified by Irving and Rossotti [1], has been used to determine n and pL values. The following solutions (total volume = 19.40 ml instead of 20 ml, due to contraction in volume on mixing alcohol and water) were titrated potentiometrically against standard 0.04 M TMAH, in 75% aqueous alcohol (v/v) to determine n and pL values of the complexes.

(i) 3 ml HClO4 (0.02 M) + 1 ml NaClO4 (2 M) + 1 ml H2O + 15 ml alcohol.
(ii) 3 ml HClO4 (0.02 M) + 1 ml NaClO4 (2 M) + 1 ml H2O + 10 ml ligand (0.01 M) + 5 ml alcohol.
(iii) 3 ml HClO4 (0.02 M) + 1 ml NaClO4 (2 M) + 0.5 ml H2O + 0.5 ml metal soln. (0.02 M) + 10 ml ligand (0.01 M) + 5 ml alcohol.

In other sets a requisite amount of NaClO4 was added to maintain the ionic strength at μ = 0.15 M, 0.05 M and 0.02 M. From the above titration curves of solutions (i), (ii) and (iii) the values of n and pL have been calculated using an IBM 360 computer (Fortran-IV). The corresponding values of stability constants have been calculated using the weighted least-squares method of Sullivan et al. [2]. The weighted least-squares treatment determines that the set of βn values which makes the function

\[ U = \sum_{n=0}^{N} (y - x - nz)^2 \beta^n \]

nearest to zero by minimizing

\[ S = \sum_{i=1}^{I} U^2 (x_i, y_i, z_i) \]

with respect to the variation in βn.