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Potentiometric Studies on the Chelation Behaviour of ω-Benzoyl-2-hydroxy-4-methoxy-3-methyl-acetophenone (*BHMMA*) 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 ω-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_{min} have been calculated. The order of stability constants was found to be: La < Pr < Nd < Sm < Y < Tb < Dy < Ho.

(Keywords: Potentiometry; Stability constant; ω-Benzoyl-2-hydroxy-4-methoxy-3-methyl-acetophenone; Lanthanons)

Potentiometrische Untersuchungen zum Komplexierungsverhalten von ω-Benzoyl-2-hydroxy-4-methoxy-3-methyl-acetophenon (BHMMA) mit Lanthanoiden

Das Chelationsverhalten von La(III), Pr(III), Nd(III), Sm(III), Y(III), Tb(III), Dy(III) und Ho(III) mit ω-Benzoyl-2-hydroxy-4-methoxy-3-methyl-acetophenon wurde in 75% (*v*/*v*) wäßrigem Alkohol bei verschiedenen Ionenstärken potentiometrisch untersucht. Mittels der Methode von *Bjerrum* und *Calvin*, in der Modifikation nach *Irving* und *Rossotti*, wurden Werte für $\bar{n}$ und pL bestimmt. Die Stabilitätskonstanten und die Werte für S_{min} wurden berechnet. Die Ordnung der Stabilitätskonstante war: La < Pr < Nd < Sm < Y < Tb < Dy < Ho.

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 ω-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 throughly 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 $\bar{n}$ 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 $\bar{n}$ and pL values of the complexes.

(i) 3 ml $HClO_4$ (0.02 *M*) + 1 ml $NaClO_4$ (2 *M*) + 1 ml H_2O + 15 ml alcohol.

(ii) 3 ml $HClO_4$ (0.02 *M*) + 1 ml $NaClO_4$ (2 *M*) + 1 ml H_2O + 10 ml ligand (0.01 *M*) + 5 ml alcohol.

(iii) 3 ml $HClO_4$ (0.02 *M*) + 1 ml $NaClO_4$ (2 *M*) + 0.5 ml H_2O + 0.5 ml metal soln. (0.02 *M*) + 10 ml ligand (0.01 *M*) + 5 ml alcohol.

In other sets a requisite amount of $NaClO_4$ was added to maintain the ionic strength at $\mu = 0.15\,M$, $0.05\,M$ and $0.02\,M$. From the above titration curves of solutions (i), (ii) and (iii) the values of $\bar{n}$ 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 β_n values which makes the function

$$U\left[U = \sum_{n=0}^{N} (y - x - \mathrm{n}z)\,\beta^n x^n\right]$$

nearest to zero by minimizing

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

with respect to the variation in β_n.

We report the $S_{\min}$ values for the different metal complexes. $S_{\min}$ has the same statistical distribution as χ^2 with K degrees of freedom and with weights defined in accordance with *Sullivan* et al. [3]. $S_{\min}$ can be equated to χ^2. The stability constants thus calculated are given in Tables 1–4.

Results and Discussion

Complexes of lanthanon ions with *BHMMA* show an increase in stability from La(III) to Ho(III) in agreement with increasing acidity of the metal ion. The order of stability constants for the first and second steps in the formation of lanthanide complexes with *BHMMA* is found to be: La < Pr < Nd < Sm < Y < Tb < Dy < Ho.

Table 1. *Stability constants of lanthanon complexes with BHMMA in 75% (v/v) alcohol-water media at* $\mu = 0.15\,M$ $NaClO_4$ *and* $t = 30 \pm 0.5\,°C$

Metal ion	Weighted least-squares method			$S_{\min}$
	$\log K_1$	$\log K_2$	$\log \beta_2$	
H^+	9.14	—	—	—
La(III)	5.51	4.41	9.92	0.0038
Pr(III)	6.29	5.12	11.41	0.0008
Nd(III)	6.36	5.66	12.02	0.0011
Sm(III)	6.43	6.01	12.44	0.0230
Y(III)	6.70	6.12	12.82	0.0074
Tb(III)	6.72	6.56	13.28	0.0392
Dy(III)	6.86	6.57	13.43	0.0187
Ho(III)	7.38	6.67	14.05	0.0113

Table 2. *Stability constants of lanthanon complexes with BHMMA in 75% (v/v) alcohol-water media at* $\mu = 0.1\,M$ $NaClO_4$ *and* $t = 30 \pm 0.5\,°C$

Metal ion	Weighted least-squares method			$S_{\min}$
	$\log K_1$	$\log K_2$	$\log \beta_2$	
H^+	9.38	—	—	—
La(III)	6.33	5.64	11.97	0.0225
Pr(III)	6.55	5.80	12.35	0.0517
Nd(III)	6.99	6.23	13.22	0.0251
Sm(III)	7.05	6.41	13.46	0.0278
Y(III)	7.38	6.62	14.00	0.0466
Tb(III)	7.57	6.64	14.21	0.0723
Dy(III)	7.72	6.73	14.45	0.1440
Ho(III)	8.13	6.31	14.44	0.0250

Table 3. *Stability constants of lanthanon complexes with BHMMA in 75% (v/v) alcohol-water media at* $\mu = 0.05\,M$ $NaClO_4$ *and* $t = 30 \pm 0.5\,°C$

Metal ion	Weighted least-squares method			S_{min}
	$\log K_1$	$\log K_2$	$\log \beta_2$	
H^+	9.54	—	—	—
La(III)	6.92	6.01	12.92	0.0093
Pr(III)	7.12	6.26	13.38	0.0405
Nd(III)	7.16	6.87	14.03	0.1361
Sm(III)	7.37	6.73	14.10	0.1328
Y(III)	7.59	7.23	14.82	0.0416
Tb(III)	7.84	6.98	14.82	0.0175
Dy(III)	7.94	7.25	15.19	0.0672
Ho(III)	8.11	7.63	15.74	0.0323

Table 4. *Stability constants of lanthanon complexes with BHMMA in 75% (v/v) alcohol-water media at* $\mu = 0.02\,M$ $NaClO_4$ *and* $t = 30 \pm 0.5\,°C$

Metal ion	Weighted least-squares method			S_{min}
	$\log K_1$	$\log K_2$	$\log \beta_2$	
H^+	9.84	—	—	—
La(III)	7.49	6.69	14.18	0.0300
Pr(III)	7.52	6.99	14.51	0.2742
Nd(III)	7.97	7.39	15.36	0.1369
Sm(III)	8.43	7.49	15.92	0.0090
Y(III)	8.49	7.55	16.04	0.0121
Tb(III)	8.57	7.65	16.22	0.0203
Dy(III)	8.60	7.92	16.52	0.1949
Ho(III)	8.99	8.21	17.20	0.0094

The same trend has also been noticed in the complexes of α-iminodiacetic acid, α-hydroxy-isobutyric acid, nitrilotriacetic acid, ethylene-diamine-N,N,N′,N′-tetraacetic acid, tropolone, β-isopropyltropolone [4] and *cis*-1,2,3,4-cyclopentane-tetracarboxylic acid [5].

The $\log K_1$ values for yttrium lie near terbium because of the lack of ligand field stabilization. The stability constants of the complexes are found to decrease with increasing ionic strengths of the medium which is in agreement with the *Debye-Hückel* equation [6].

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