SPECTROPHOTOMETRIC INVESTIGATION OF BERYLLIUM-2′-HYDROXY CHALCONE COMPLEX

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Abstract

2′-Hydroxy chalcone gave an intense orange-yellow color with beryllium in the pH range 5·5–6·2. The limits of identification and dilution were 0·125 γ and $1:4 \times 10^5$ respectively. A detailed spectrophotometric investigation of the color reaction was carried out. The complex obeyed Beer's Law in the concentration range of 0·5–6·0 p.p.m. at 460 nm. In the complex the ratio of metal to ligand is 1:2. The instability constant of the complex was $2{\cdot}176 \times 10^{-6}$ at 28°. Oxalate, tartrate, citrate and fluoride interfered. The tolerance limits of iron, aluminium, chromium, uranium, thorium and vanadium are reported.

Introduction

Snell[6, 7] described several organic reagents for the colorimetric determination of beryllium. Spectrophotometric data on the complexes of beryllium are also reported.[9] The orthohydroxy chalcones, however, have not been examined as colorimetric reagents for this metal. Lense *et al.*,[3] reported that these are much more reactive with metal ions than the ketones and aldehydes from which tney are synthesised. In the course of systematic investigations, the present author found that 2′-hydroxy chalcone gave an intense orange-yellow color with beryllium in the pH range 5·5–6·2 and the reaction was highly sensitive. The limits of identification and dilution were 0·125 γ and $1:4 \times 10^5$ respectively. A detailed spectrophotometric investigation of the color reaction was carried out.

Experimental

Reagents

2′-Hydroxy chalcone.—(Asahina[4])–*o*–Hydroxyacetophenone (2·5 g) and benzaldehyde (2·5 g) were dissolved in alcohol (20 ml). This solution was

treated gradually with 4 ml of 50 per cent solution of potassium hydroxide. The mixture first turned yellow and then became orange-red. After leaving overnight the reaction mixture was poured into cold dilute hydrochloric acid. The precipitate was filtered and recrystallized from alcohol, yellow needles, m.p. 88–89°, yield 2·0 g (Asahina, m.p. 88–89°). Alcoholic solutions were light yellow in color and quite stable.

Beryllium solution.—Beryllium sulphate (8·857 g; BDH, A.R.) was dissolved in distilled water and the solution made up to 500 ml with water in a volumetric flask. The beryllium content was determined by the oxide method.[8] The solution contained 0·9001 mg per ml of beryllium. Lower concentrations were prepared by dilution.

Buffer solution.—Buffer solutions in the pH range 4·5 to 6·5 were prepared from 0·5 M acetic acid and 15 per cent ammonium acetate solutions.

Apparatus.—A Hilger Uvispek Spectrophotometer with 1 cm glass absorption cells and the Elico (L1–10A) pH meter with a Beckman Glass Electrode were used for optical density measurements and pH determinations respectively.

Absorption Spectra

The optical density of the chlacone in 50 per cent alcohol (0·001 M) was measured at different wavelengths (Fig. 1). It showed a maximum absorption at 370 nm.

Beryllium solution (3 ml; 0·01 M) was treated with an excess of chalcone solution (8 ml; 0·01 M) and made up to 25 ml with 50 per cent aqueous alcohol. The optical density was measured at different wavelengths with the reagent solution of the same final concentration as blank (Fig. 2). The absorption maximum for the complex was at 460 nm.

Influence of pH

A measured volume of beryllium sulphate solution (3 ml; 0·01 M) was treated with an excess of chalcone solution (8 ml; 0·01 M) and the pH adjusted to a desired value with ammonium acetate and acetic acid buffer. The solution was made up to 25 ml in each case and the optical density measured at 460 nm. The maximum absorption was obtained at pH 5·5–6·2 (Fig. 3) and all the investigations were carried in this range.

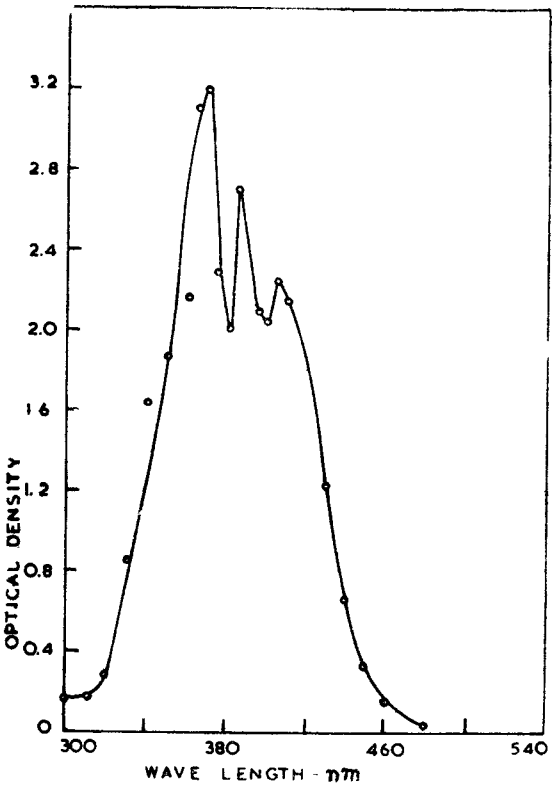

3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0
OPTICAL DENSITY
300
380
460
540
WAVE LENGTH - mm

FIG. 1

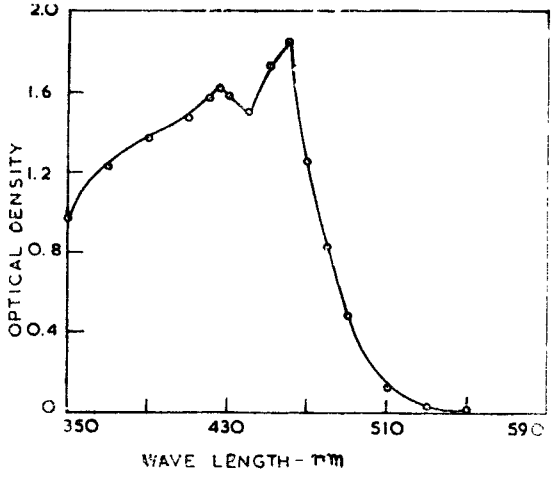

2.0
1.6
1.2
0.8
0.4
0
OPTICAL DENSITY
350
430
510
590
WAVE LENGTH - mm

FIG. 2

Applicability of Beer's Law

Known amounts of beryllium (1·0 to 12·0 p.p.m.) were treated with excess (8 ml) of 0·01 M chalcone solution. The pH was adjusted, the solution made up to 25 ml and the optical densities measured at 460 nm. The optical density values were plotted against p.p.m. of beryllium (Fig. 4).

The relationship between concentration and optical density was linear in the range 0·5–6·0 p.p.m.

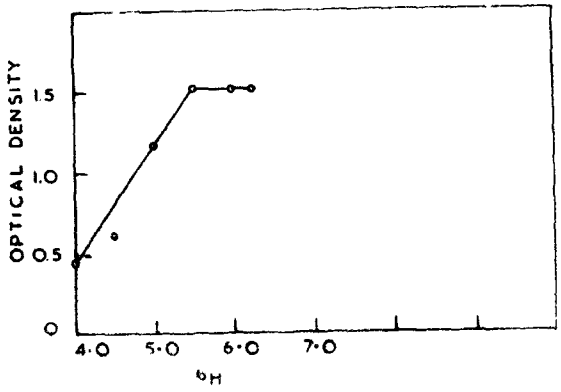


FIG. 3

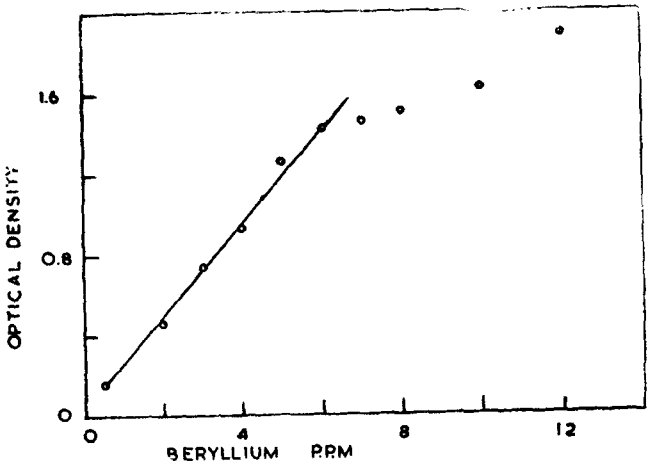


FIG. 4

Molar Composition of the Complex

Job's method of continuous variations[1].—The molar composition of the complex was determined by Job's method of continuous variations using

beryllium solution (0·005 M) and the chalcone solution (0·005 M). The solutions were mixed in different proportions to yield 10 ml. The pH was adjusted, the volume made up to 25 ml and the optical densities measured at 460 nm. The results (Fig. 5) showed that the reagent formed a 1 : 2 complex with beryllium.

Slope ratio method.[5]—Two series of solutions were prepared using 5×10^{-3} M solutions of the reagent and beryllium ion. In the first series the metal ion solution in large excess (5·0 ml) was treated with 0·2, 0·4, 0·8, 1·0 and 1·2 ml of reagent solution, the pH adjusted and the solution made up to 25 ml.

In the second series the reagent was in large excess (5·0 ml) and to it 0·2, 0·4, 0·6, 0·8, 1·0 and 1·2 ml of the metal ion was added, the pH adjusted and the solution made up to 25 ml.

The optical densities were measured at 460 nm, the values plotted (Fig. 6) and the slopes calculated by measuring the angles. The molar ratio of the complex was found to be metal to reagent as 1 : 1·974 (2·0 approx.).

Instability Constant of the Complex[2]

Optical densities of two solutions containing the same amount of beryllium (1·0 ml of 0·005 M) but different amounts of reagent (excess) were measured after adjusting the pH and making up the volume to 25 ml. The data are given in Table I. The instability constants were calculated in pairs of cases. The average value was $2{\cdot}176 \times 10^{-6}$ at 28°.

TABLE I

Reagent (ml)	Optical Density
4·0	0·140
6·0	0·245
8·0	0·330
10·0	0·395
12·0	0·460

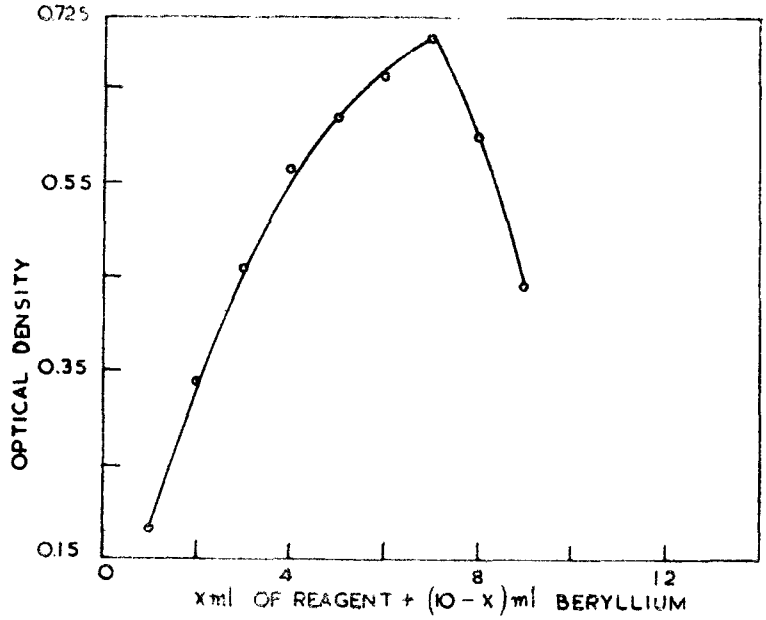

0.725
0.55
0.35
0.15
OPTICAL DENSITY
0
4
8
12
x ml OF REAGENT + (10 – x) ml BERYLLIUM

FIG. 5

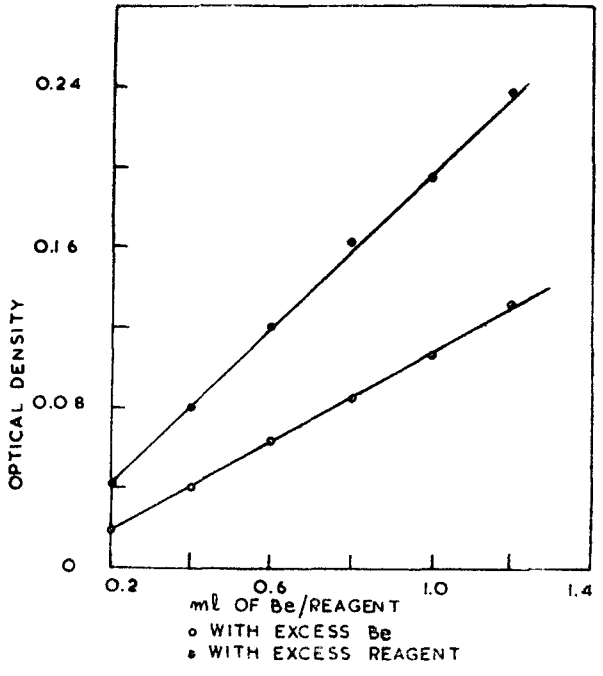

0.24
0.16
0.08
0
OPTICAL DENSITY
0.2
0.6
1.0
1.4
ml OF Be/REAGENT
o WITH EXCESS Be
• WITH EXCESS REAGENT

FIG. 6

Interference

The effect of cations and anions on the determination of beryllium with the reagent was investigated. 0·1 mg/25 ml of beryllium in each case was treated with reagent (3 ml, 0·01 M) and known variable amounts of other ion. The pH was adjusted and the optical densities were measured. Added metal ion and the tolerance limits are given in Table II.

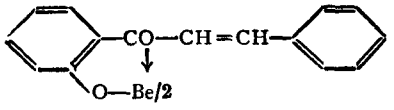
TABLE II

Metalion added	Tolerance limit in γ/25 ml
Fe^{3+}	100
Al^{3+}	2,000
Cr^{3+}	50
UO_2^{+2}	3,000
Th^{4+}	10,000
VO_3^-	1,500

Oxalate, tartrate, citrate and fluoride caused interference by inhibiting the development of color.

CONCLUSION

2′-Hydroxy chalcone is a sensitive reagent for beryllium. The limits of identification and dilution are 0·125 γ and $1:4 \times 10^5$ respectively at pH 5·5–6·2 and the absorption maximum is at 460 nm. Beer's Law is obeyed in the range of 0·5–6·0 p.p.m. of beryllium. Job's method of continuous variations and Slope ratio method showed that the ratio of metal to ligand is 1:2. The probable structure of the complex is given below.



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