

NOTES

Spectrophotometric Studies on Th(IV) Complex of 4-Methoxy-2'-Chlorodibenzoylmethane

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4-Methoxy-2'-chlorodibenzoylmethane forms 1, 2 greenish yellow complex with Th(IV) at pH 2.5 to 3.5 with working wavelength 395 nm and gives absorption maxima at 390 nm. Values of molar absorptivity, Sandell's sensitivity, stability constant (log K) and free energy of formation were found to be $15,000 \text{ cm}^{-1} \text{ mol}^{-1}$, $0.015 \mu\text{g cm}^{-2}$, 9.0526 and -12.428 kcal per mole respectively. Beer's law is valid in the concentration range $1 \times 10^{-5} \text{ M}$ to $6 \times 10^{-5} \text{ M}$.

Some of the reagents recently used for the spectrophotometric determination of Th(IV) are 4-(2-pyridylazo)-resorcinol¹; thenoyl trifluoroacetone²; arsenazo-III²; 1-(2-thiazolylazo)-2-naphthol⁴; 3-nitro- α -methyl dibenzoylmethane⁵; chlorophosphonazo p- β in presence of hexadecyl trimethyl ammonium bromide⁶; semixylenol orange-hexadecyl trimethyl ammonium bromide⁷; N-phenyl benzohydroxamic acid⁸; 3-anti-pyrynylazo-6-(4-arsenophenylazo)-chromotropic acid⁹ and [3-(4-acetyl phenylazo)-6-(4-carboxyphenylazo)-chromotropic acid]¹⁰. In the present communication the use of 4-methoxy-2'-chloro-dibenzoylmethane as a spectrophotometric reagent for the determination of Th(IV) is described.

4-methoxy-2'-chloro DBM was synthesised by following the general method reported in organic syntheses¹¹ as a light yellow silky compound, m.pt; $79-80^\circ\text{C}$, molecular formula $\text{C}_{16}\text{H}_{13}\text{O}_3\text{Cl}$. Elemental analysis C% found 66.54 calc. 66.55. H% found 4.55 calc. 4.53 and Cl% found 12.31 calc. 12.28, yield ca. 21.3%. 4-methoxy-2'-chloro DBM solution ($5 \times 10^{-3} \text{ M}$) was always freshly prepared by dissolving the requisite quantity of the compound in ethanol. Weaker solutions were prepared by dilution with ethanol. A $1 \times 10^{-2} \text{ M}$ stock solution of A.R. $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ was prepared by dissolving the requisite quantity in distilled water and the solution was standardised in usual manner.¹² Desired volumes were taken from this solution with the help of micropipette. For complex studies ethanol was used as a solvent. Absorbance measurements were made on Beckman DU-2 spectrophotometer. Systronics pH meter-324 was used for pH measurements.

Spectrophotometric studies of Th(IV) complex with 4-methoxy-2'-chloro DBM was made at 395 nm and full colour development was

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obtained at pH 2.5 to 3.5 and Th(IV) to reagent ratio was kept 1 : 8 for determining maxima and working wavelength. Job's method¹³, mole ratio method¹⁴ and slope ratio method¹⁵ were employed to determine the composition of the complex as M : R = 1 : 2. Beer's law is obeyed for Th(IV) concentration of 1×10^{-5} M to 6×10^{-5} M. The molar absorptivity of the complex was found as $15,000 \text{ cm}^{-1} \text{ mol}^{-1}$ and Sandell's sensitivity as $0.015 \mu\text{g cm}^{-2}$. The standard deviation ' σ ' was obtained as 0.078 ppm by measuring the absorbance of ten solutions containing 11.60 ppm of Th(IV). A comparison of the values of Sandell's sensitivity of the reagents commonly used for Th(IV) are given in Table 1.

TABLE I
SENSITIVITIES OF SOME SPECTROPHOTOMETRIC REAGENTS FOR Th(IV)

Sl. No.	Reagent	Sandell's sensitivity in $\mu\text{g cm}^{-2}$	Wavelength used in nm
1.	Solochrome azurine-BS (C.I. Mordant blue-1) ¹⁶	0.120	600
2.	Lawsone [2-hydroxy-1,4-naphthaquinone semicarbazone (LSC)] ¹⁷	0.061	560
3.	3-(4-Bromo) chromotropic acid ¹⁸	0.038	585
4.	Aniline blue	0.073	660
5.	3-Nitro- α -methyl DBM ⁵	0.023	390
6.	4-(2, 3, 4-trihydroxy-phenylazo) benzene sulphonic acid ¹⁹	0.0027	420
7.	4-methoxy-2'-chlorodibenzoylmethane	0.015	395

The data reveals that 4-methoxy-2'-chloro DBM has sensitivity more than solochrome azurine-BS (C.I. Mordant blue-1), Lawsone [2-hydroxy 1,4-naphtha-quinone] semicarbazone (LSC); 3-(4-bromo) chromotropic acid; aniline blue and 3-nitro- α -methyl DBM. Hence, this seems to be one of the sensitive reagents suitable for spectrophotometric determination of Th(IV).

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[Received : 11 April 1989; Accepted : 30 August 1989]

AJC-98