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Studies in Complex Formation of Metal Ions with Tropolones. Part III. Spectrophotometric Studies on Complexes of Molybdenum(VI), Thorium(IV), and Zirconium(IV) with ∝-Carboxy-β-methyltropolone

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A study of the composition of zirconium, thorium, and molybdenum complexes with ∝-carboxy-β-methyltropolone at different *p*H values has been made using Job's method of continued variations at different wave lengths. Both zirconium and molybdenum form 1 : 1 and 1:2 complexes, whereas thorium forms 1:1, 1:2, and 1:3 complexes with the above reagent with increasing *p*H values.

Very few studies on tropolone complexes with zirconium, thorium, and molybdenum have been reported. Tropolone-5-sulphonic acid has been reported to form 1 : 1 and 1 : 2 complexes with thorium[1]. Also the stepwise stability constants of thorium complexes with β-isopropyltropolone have been determined, using solvent extraction technique[2]. No work has been reported on tropolone complexes with molybdenum and zirconium. The present investigations have been carried out to determine the stoichiometry of the complexes of the above metal ions with ∝-carboxy-β-methyltropolone.

EXPERIMENTAL

A Unicam spectrophotometer, model SP 600, was used for taking all spectrophotometric measurements. All measurements of *p*H were carried out with the help of a Swiss Metrohm *p*H-meter, model E-350. Standard solutions of molybdenum (VI) and thorium (IV) were prepared by dissolving ammonium molybdate and thorium nitrate (A.R., B.D.H.) in double distilled water. A standard solution of zirconium was prepared by dissolving zirconium oxychloride (E. Merck, G.R.) in HCl (conc.), boiling the solution for ½ hr., and diluting to a known volume with HCl (dil.). All the solutions of these metal ions were standardised gravimetrically.

Molybdenum Complexes

The absorption spectrum of molybdenum complex with ∝-carboxy-β-methyltropolone was studied as a function of *p*H. The complex has maximum absorption at 385 mμ at all *p*H values. The absorbance readings at 385 and 410 mμ at different *p*H values are plotted in Fig. 1. The absorbance was found to be approximately constant in the

1. Oka and Umehara, *Nippon Kagaku Zasshi*, 1963, **84**, 928.
2. Dyrssen, *Acta Chem. Scand.*, 1955, **9**, 1567.

*p*H range 1.0-5.0 at 385 mμ, whereas there was a sharp fall in absorbance at 410 mμ after *p*H 3.0. At higher wave lengths the absorption characteristics of the system were similar to those at 410 mμ. This shows the formation of more than one complex in this system.

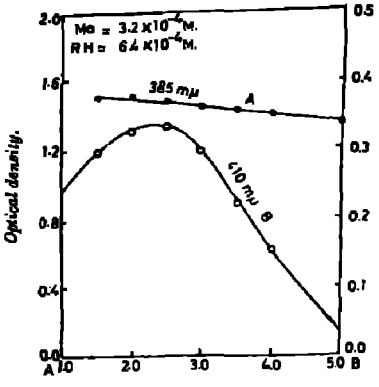


FIG. 1

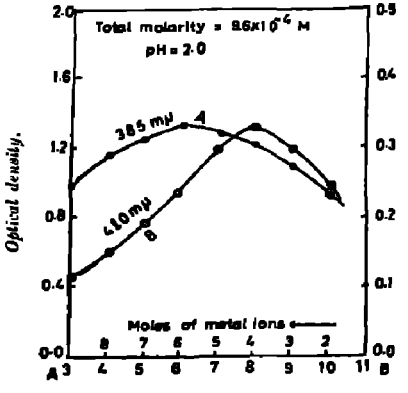


FIG. 2

Job's method of continued variations was used to study the composition of the complexes formed in solution (Fig. 2). At *p*H 2.0, using the wave length 380 mμ, the metal: ligand ratio in the complex was found to be 1:1, but at 410 mμ, the maximum in Job's curve corresponded to the formation of a 1 : 2 complex. These observations show that molybdenum forms both 1:1 and 1:2 complexes with ∝-carboxy-β-methyltropolone.

Zirconium Complexes

The absorption spectrum of solutions containing zirconium and the reagent in the ratio 1:4 was studied at different concentrations of HCl. Maximum absorption due to the complex took place at 377 mμ at all acidities. Increase in concentration of the acid decreased the extinction of the complex (Fig. 3).

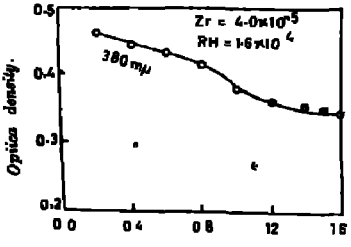


FIG. 3

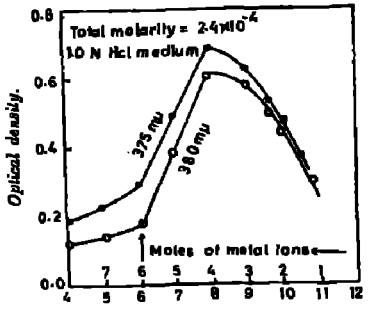


FIG. 4

Job's method of continued variations was used to find out the composition of the complex (Fig. 4). The maximum in Job's curve corresponded to the formation of 1:2 complex, but there was a sharp break in the curve at zirconium: reagent ratio of 1:1. A complex having zirconium and the reagent in the ratio 1:1 was also formed simultaneously, but it could not be detected directly because of its absorbance being much less than the 1:2 complex at the wave lengths used.

Thorium Complexes

The absorption spectrum of solutions containing thorium and the reagent in the ratio of 1:4 was studied as a function of *p*H. The absorbance due to the complex was maximum at 377 mμ at all *p*H values. The absorbance reading at 380 and 390 mμ at different *p*H values are plotted in Fig. 5. The optical density of the complex at 380 mμ was found to be practically constant in the *p*H range 3.5-5.0 and fall sharply below *p*H 3.0. The absorbance at 390 mμ was practically constant in the *p*H range 2 0 to 4.0. and increased after *p*H 4.0. This indicates the formation of more than one complex in this system. Since optical density at 390 mμ increased sharply beyond *p*H 4.0, it was concluded that a new complex having the same absorption at 380 but a higher absorption at 390 mμ than the other complex, was being formed.

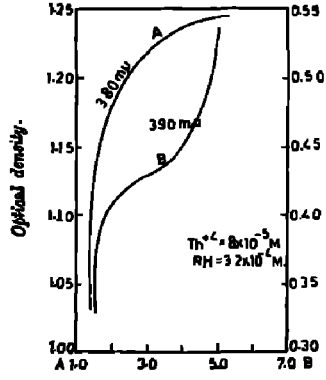
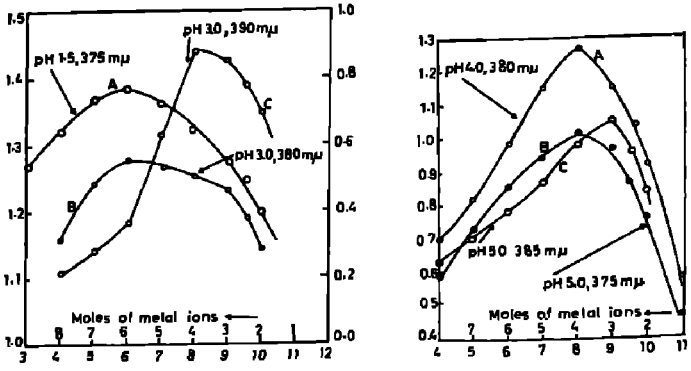


FIG. 5

Continued variations method was used to determine the composition of the complexes formed at different *p*H values (Fig. 6). Using a wave length of 375 mμ at *p*H 1.5, the composition of the complex was found to be 1:1. Composition of the thorium complex at 380 mμ and at *p*H 3.0 was found to be 1:1, whereas at 390 mμ, the maximum in Job's curve showed presence of a 1:2 complex as well.

Using Job's method at *p*H 4.0, the composition of the complex was found to be 1:2 at all wave lengths. At *p*H 5.0, using the wave length 375 mμ, the composition corresponded to that of 1:2 complex, but at 385 and 390 mμ, the maximum in Job's curve show-

ed the formation of a 1:3 complex. The formation of this new complex explains the effect of *p*H on the absorbance of the complex at 380 and 390 mμ, as described earlier.



B A & C

FIG. 6

Thus in the thorium—α-carboxy-β-methyltropolone system, three complexes having the composition of 1:1, 1:2, and 1:3 are formed stepwise with increasing *p*H values.

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Total molarity at *p*H 3.0=9.6×10⁻⁴*M*; at other *p*H values=3.84×10⁻⁴*M*.