A Study on the Uranyl Complexes of Acetyl-p-Cresotic Acid

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With 6 Figures

Summary

The complex compound formation in the sytem $UO_2(NO_3)_2 - C_6H_3(CH_3)\begin{smallmatrix} O \cdot COCH_3 \\ COONa \end{smallmatrix} - H_2O$ has been investigated spectrophotometrically, following the continued and monovariation methods. Only one complex viz. 1:1 has been found to be formed in the above sytem by both the techniques. p_H studies of the above system indicate the 1:1 complex to be a chelate.

From spectrophotometric data, the value of formation constant has been calculated which works out to be $5 \cdot 10 \times 10^2$.

Introduction

In previous communications, the complexes of acetyl-p-cresotic acid with Fe(III)[1] and Cu(II)[2] ions were investigated spectrophotometrically. These investigations have now been extended to the uranyl complexes of the above chelating agent. Uranyl complexes of sulfo salicylic acid and 1-hydroxy 2-napthoic acid have been investigated earlier by Foley and Anderson[3] and by Prakash and Tripathi[4] respectively.

Experimental

Stock solutions of uranyl nitrate and mono sodium acetyl-p-cresotate — the reagent (hereafter to be designated by R) were prepared, the former by the direct weighing of the B.D.H. (A.R.) grade material and the latter as described earlier[1]. Spectrophotometric and p_H measurements were carried out as described in our earlier communication[1]. The results obtained from the spectrophotometric and electrometric studies are represented graphically in figures.

[1] R. C. Aggarwal, S. P. Agrawal and T. N. Srivastava, Z. anorg. allg. Chem. (under publication).

[2] R. C. Aggarwal, S. P. Agrawal and T. N. Srivastava, Z. anorg. allg. Chem. (under publication).

[3] R. T. Foley and R. C. Anderson, J. Amer. chem. Soc. 71, 709 (1949).

[4] S. C. Tripathi and Satya Prakash, J. Indian chem. Soc. 36, 19 (1959).

Selection of the p_H for Maximum Absorption

For finding the p_H at which the absorption is maximum three different series of solutions of graded p_H were prepared in which $UO_2(NO_3)_2$ and R were in the ratio of 1:1, 1:2 and 1:3 respectively. In these series of solutions the p_H was varied by the addition of a systematically increasing amount of sodium hydroxide. Optical density and p_H of
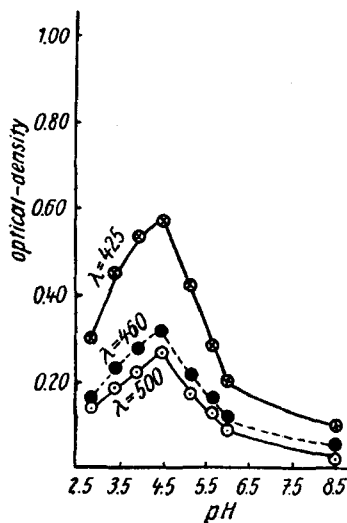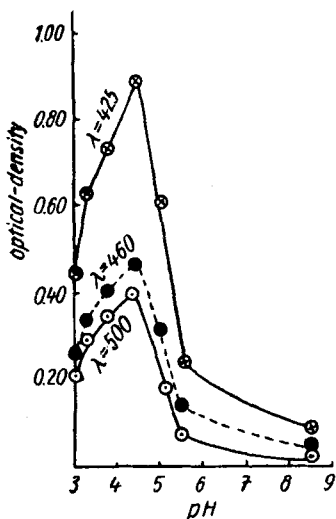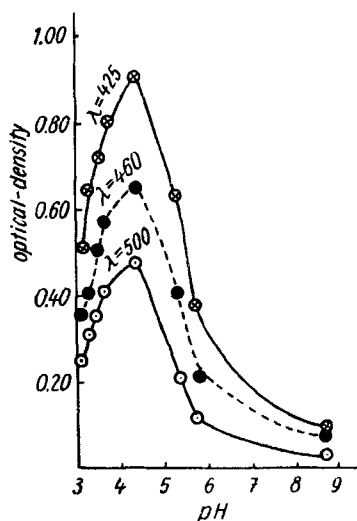

Fig. 1

Fig. 2

Fig. 3

Fig. 1—3. System Uranyl-nitrate and monosodium-acetyl-p-cresotate. Optical density measurements of 5 c.c., 0.2 M Uranyl-nitrate with 5 c.c. (Fig. 1), 10 c.c. (Fig. 2) and 15 c.c. (Fig. 3) of 0.2 M monosodium-acetyl-p-cresotate at different p_H values

all the solutions in the three series was determined. From the plots of optical density against p_H the value of p_H for maximum absorption was found (Figures 1—3). From the above figures this value of p_H has been found to be 4.4.

Formulae of the Complexes Formed

The composition of the complexes existing in the ystem UO_2^{++}— R—H_2O has been investigated by continued and mono variation methods. For the continued variation method of Job two series of solutions with different initial concentrations of UO_2^{++} and R were prepared. In these series of solutions the concentrations of UO_2^{++} and R were systematically varied — p_H was brought to about 4.4 in each solution by the addition of the requisite amount of sodium hydroxide solution — 10 c. c. of molar potassium nitrate was added to each solution to get a practically constant value of the inonic strength and finally all solutions were made up to a constant volume (50 c. c. with water. Optical density of all the solutions in the two series was determined in a thermostatically controlled room (maintained at 30 °C) at three different wave lengths
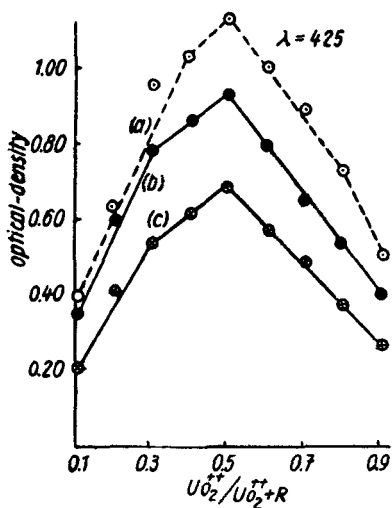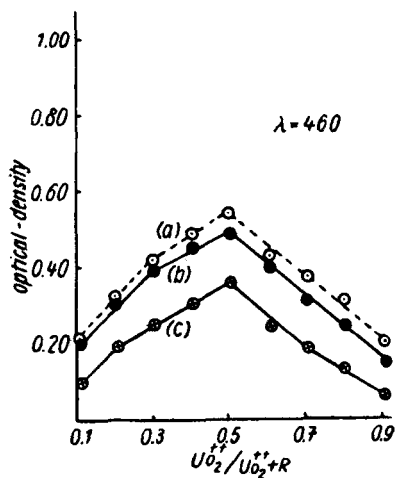

Fig. 4   Fig. 5

Fig. 4 and 5.   System   Uranyl-nitrate—monosodium-acetyl-p-cresotate—water.   In curves a, b and c initial concccutrations of $UO_2(NO_3)_2$ acetyl-p-cresotate arc 0.1, 0.2 and 0.33 M respectively p_H 4.4

viz., 425, 460 and 500 mμ. On plotting the values of optical density against the mole fraction of UO_2^{++}, peaks are obtained corresponding to the formation of 1 : 1 complex in both the series (figures 4 and 5). As there

is no shift in the position of the peaks with the wave lenght, it may be concluded that only one complex exists in the system under investigation. For the investigation of the complex formation by the mono variation method, a series of solutions was prepared in which the concentration of R, was kept constant, while that of $UO_2(NO_3)_2$ was systematically varied. The volume in each solution was made up to 50 c. c. with water after adding requisite amount of alkali and 10 c. c. of molar potassium nitrate. In this way a practically constant value of p_H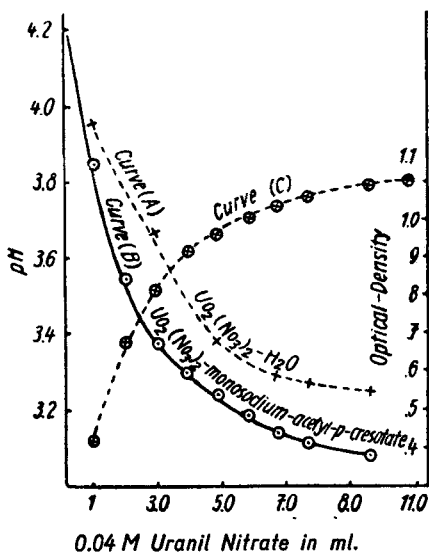 (about 4.4) and ionic strenght was achieved throughout. Optical density of all the solutions prepared as above was determined. The values of optical density were plotted against the concentration of uranyl nitrate, the varying componnent (figure 6 curve c). The fact that the optical density in the above figure goes on increasing till the molar ratio 1:1 (of UO_2^{++} and R) and thereafter becomes practically constant, indicates the formation of the 1:1 complex. The results obtained by the mono variation method are thus in conformity with those obtained by JOB's method.

Fig. 6. Elektrometric titrations of water (Curve A) and 5 c. c. reagent 0.04 M (Curve B) containing different amounts of 0.04 M $UO_2(NO_3)_2$ — total volume made up to 50 c. c. Curve C: Spectrophotometric measurements of solutions containing 5 c. c. 0.04 M reagent and different amounts 0.04 M $UO_2(NO_3)_2$ — total volume made up to 50 c. c.

Nature of the 1:1 Compound

With a view to find out the nature of the 1:1 compound existing here electrometric titrations of (1) water and (2) the reagent were carried out against uranyl nitrate. The results are represented graphically in figures 6 (curve A—B). The fact that the Curve B for the system UO_2^{++}—R lies below the curve A for the system UO_2^{++}—H_2O shows that chelation takes place between UO_2^{++} and R. The 1:1 chelate may be represented as

$$\left[C_6H_3(CH_3) \underset{\underset{\overset{\|}{O}}{C-O}}{\overset{\overset{CH_3}{O\diagup}}{\diagup}} UO_2 \right]$$
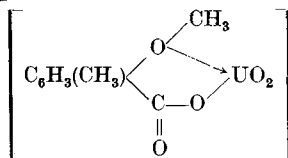
From the spectrophotometric data, the value of the formation constant has been calculated for the above chelate following the method of TURNER and ANDERSON[5]). The value of K works aut to be $5 \cdot 10 \times 10^2$.

[5]) S. E. TURNER and R. C. ANDERSON, J. Amer. chem. Soc. 7, 1912 (1949).

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