THE COMPOSITION AND STABILITY OF THE COMPLEX BETWEEN URANYL IONS AND 2,4-DIHYDROXYBENZOIC ACID IN AQUEOUS MEDIUM

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In continuation of our studies[1-3] on chelates formed by 2,4-dihydroxybenzoic acid with various bivalent and trivalent metal ions, it has been found that 2,4-dihydroxybenzoic acid forms an orange water soluble complex with uranyl ions having an absorption maximum at 450 nm and a flat region thereafter. Although Desai and coworkers[4] studied the system at 25°C, they did not maintain the constant ionic strength of the solution. In the present paper the author has determined the stability constant of uranyl-2,4-dihydroxybenzoate complex at various ionic strengths and temperatures with a view to obtain thermodynamic functions like change in free energy, enthalpy and enthropy of the complex formation. The straight line method of Asmus was also used for determination of molecular composition of the complex.

EXPERIMENTAL

A pure sample of uranyl nitrate (B.D.H., L.R.) was used for preparing standard solution. 2,4-dihydroxybenzoic acid was of B.D.H., L.R. quality and was recrystallized before use. Sodium acetate and acetic acid were used to maintain pH of solutions. Sodium perchlorate (E. Merck) was added to adjust ionic the strength.

Absorption measurements were made by Hilger Uvispeck spectrophotometer (Model H 700—308) using one cm effective light path. The cell compartment was fitted with a jacket through which water could be circulated from a thermostat (Townson & Mercer, London). A thermometer inserted into cell compartment and allowed to come to temperature equilibrium, showed a variation of less than 0·1°C over a period of time much longer than needed for measuring the absorbance. Beckman pH meter (Model H2) was used to measure pH of solutions. All solutions and subsequent dilutions were made with doubly distilled water.

RESULTS AND DISCUSSION

Spectral studies: Uranyl nitrate solution (10^{-2}M) and 2,4-dihydroxybenzoic acid were mixed in the ratios of 1 : 1, 1 : 2, and 1 : 3 and absorbances at different wavelengths were recorded. The complex showed maximum absorbance at 450 nm and a flat region thereafter in all the cases, thus indicating the formation of one complex only[5]. The corresponding wavelength 450 nm was used for subsequent work.

Effect of pH. Solutions containing equal concentrations of uranyl and ligand were prepared at various pH values and absorbances were noted at 450 nm. It was found that the complex is stable in the pH range 4·5 to 4·8 and hence a pH of 4·5 was selected for studying complex formation.

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Composition of Complex

Job's method of continued variation. Curves *1*, *2* and *3* Fig. 1 give molecular composition of the complex at pH 4·5 and at ionic strength 0·1 from absorbance measurements at total molarity (X)

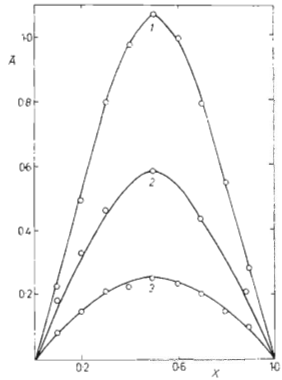

FIG. 1

Job's Method of Continued Variation
$\bar{A}$ the corrected absorbance, X $C_{UO_2^{2+}}$: : $C_{UO_2^{2+}} + C_{acid}$.

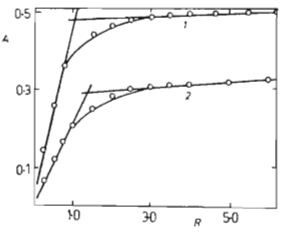

FIG. 2

Mol-Ratio Method
R mol Acid/mol Uranyl

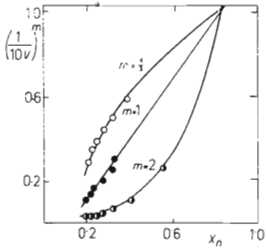

FIG. 3

Straight Line Method

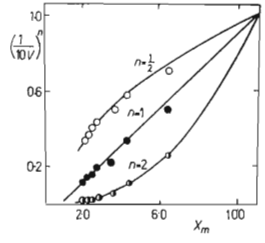

FIG. 4

Straight Line Method

$1{\cdot}0 \cdot 10^{-2}$M, $5{\cdot}0 \cdot 10^{-3}$ and $2{\cdot}5 \cdot 10^{-3}$M respectively. The absorbance A (difference between total absorbance of solution containing uranyl ions and ligand and that which is shown by uranyl ions at the same pH) was plotted against the mole fraction of uranyl ions. The maximum at 0·5 in all the three cases indicate the formation of 1 : 1 complex.

TABLE I

Straight Line Method for the Complex between Uranyl and 2,4-Dihydroxybenzoic Acid in Aqueous Medium

Total volume 10 ml, ionic strength 0·1, pH = 4·5, λ = 450 nm. Concentration of the constant component $5{\cdot}0 \cdot 10^{-3}$ mol l^{-1}.

Concn. of reagent mol $l^{-1} \cdot 10^{-4}$	Corrected absorbance	Concn. of UO_2^{+2}, mol $l^{-1} \cdot 10^{-4}$	Corrected absorbance
2·5	0·091	2·5	0·120
5·0	0·155	5·0	0·180
7·5	0·228	7·5	0·245
1·0	0·284	1·0	0·314
12·5	0·367	12·5	0·378
15·0	0·400	15·0	0·430
17·5	0·445	17·5	0·446
20·0	0·476	20·0	0·495

TABLE II

Effect of Ionic Strength (I) on the Stability Constant K_1 of the Complex between Uranyl Ions and 2,4-Dihydroxybenzoic Acid in Aqueous Medium

λ_{nm} 450, pH 4·5, t 30°C.

I	0·02	0·05	0·10	0·15	0·20
$K_1 \cdot 10^{-4}$	3·10	2·78	2·53	2·43	2·38

TABLE III

Stability Constant of the Complex at Various Temperatures

λ_{nm} 450, pH 4·5, I 0·02.

Temp., °K	293·16	303·16	313·16	323·16	333·16
$K_1 \cdot 10^{-4}$	2·13	3·10	4·08	5·15	6·94

Molar-ratio method: A series of solutions was prepared from $2 \cdot 0 \cdot 10^{-3}$M solutions of uranyl and ligand at pH 4·5 and ionic strength 0·1 varying the mol ratio (R) of uranyl to ligand from 1 : 0·2 to 1 : 5. Curve 1 Fig. 2 shows a break at a ratio of one mole of uranyl to one mol of 2,4-dihydroxybenzoic acid. The same ratio is also obtained using $1 \cdot 0 \cdot 10^{-3}$M of uranyl solution.

Straight line method: The molecular composition of the complex was determined by straight line method as suggested by Asmus[6] and further modified by Klausen and Langmyhr[7]. Thus the plot of $1/v^n$ against X_m for sets of m, n gave straight line cnrresponding to actual values of m and n. Two series of solutions with the sams pH and constant ionic strength were prepared, one with constant concentration of uranyl ions and another with constant concentration of 2,4-dihydroxybenzoic acid. The experimental details are given in the Table I. It was found that the ratio of m and n is one (Fig. 3, 4).

Molecular Extinction Coefficient and Stability Constant

Using absorbances of solutions containing a large excess of acid so that as a first approximation the concentration of the complex may be taken equal to that of uranyl ions added, extinction coefficient of the complex was found to be $3 \cdot 156 \cdot 10^2$. The instability constant of the complex has been calculated at various ionic strengths and at temperatures mentioned in an earlier paper[1] and are reported in the Tables II, III. From the plot of log K against $1/T$, a practically straight line is obtained. The values of ΔH and ΔS have been calculated as 1·6 k cal/mol and 22·6 e.u. respectively.

Attempts have also been made to study complex formation conductometrically. The same ratio is found by performing conductometric titrations of uranyl solutions with 2,4-dihydroxybenzoic acid at various concentrations.

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