

Complexation Reaction of Dihydroxycoumarins: Studies on the Reaction of Ti(IV) with 7,8-Dihydroxy-4-methylcoumarin (4-Methyl-daphnetin)

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The reaction of Ti(IV) with 7,8-dihydroxy-4-methylcoumarin (4-methyl-daphnetin) has been studied spectrophotometrically. Three mononuclear complexes $\text{TiOH}(\text{RH})^+$, $\text{TiO}(\text{RH})_2$ and $\text{TiO}(\text{RH})_3^+$ are formed in solution depending on pH and the concentration of ligand. The log values of stepwise stability constants and the values of molar extinction coefficients are found to be 8.37, 7.33 and 5.70; and 3.2×10^3 , 6.05×10^3 and 8.85×10^3 respectively.

STEPWISE formation of 1:1, 1:2 and 1:3 complexes of titanium with *o*-diphenols with increase in pH is well known¹. Amongst various *o*-dihydroxycoumarins, only daphnetin² and 4-methyl-esculetin³ have been studied earlier, and formation of 1:3 complexes reported. This paper describes the results of a detailed study of titanium complex with 7,8-dihydroxy-4-methylcoumarin (4-methyl-daphnetin).

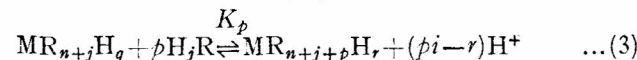
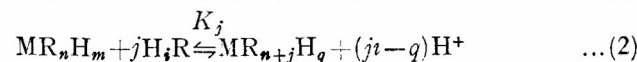
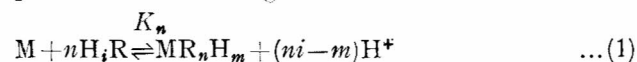
Potassium titanyl oxalate (3.54 g) (AR, BDH) was dissolved in water (1 litre) and then precipitated with ammonia. The precipitate was dissolved in minimum quantity of HClO_4 and diluted to the required volume. The ionic strength was maintained constant by adding sodium perchlorate.

4-Methyl-daphnetin⁴ (m.p. 276-78°) was prepared and crystallized from ethyl alcohol.

A Beckman pH meter, type zeromatic and a Coleman spectrophotometer model 14 were used.

All the experiments have been carried out in 50:50 (v/v) aq. ethanol medium.

Method of calculations—Three general equilibria (1-3) were used for expressing complexation in the presence of excess ligand:



For the above equilibria following equations (4-8) may be written⁵⁻¹⁰

$$A = \epsilon_1 C_m - [H]^{(ni-m)} A / C_R^n K_n \quad \dots(4)$$

$$A = \epsilon_1 C_m + C_R^j (\epsilon_2 C_m - A) / K_j [H]^{(ji-q)} \quad \dots(5)$$

$$A = \epsilon_2 C_m - [H]^{(ji-q)} (A - \epsilon_1 C_m) / K_j C_R^j \quad \dots(6)$$

$$A = \epsilon_2 C_m + C_R^p (\epsilon_3 C_m - A) / K_p [H]^{(pi-r)} \quad \dots(7)$$

$$A = \epsilon_3 C_m - [H]^{(pi-r)} (A - \epsilon_2 C_m) / K_p C_R^p \quad \dots(8)$$

In the above equation A represents absorbance, ϵ_1 , ϵ_2 and ϵ_3 represent molar absorptivities of the three complexes, C_m is the total concentration of

metal ion (concentration of free metal ion being small has been neglected), C_R is the total concentration of the ligand (amount of ligand complexed being very small in comparison to the free ligand has been neglected), and K_n , K_j and K_p are equilibrium constants of three species.

The following method is used for evaluating the values of ϵ_1 , ϵ_2 and ϵ_3 .

Functions A versus $(A/[H]^{(nj-m)})$, A versus $(\epsilon_2 C_m - A) / [H]^{(ji-q)}$ and A versus $(\epsilon_3 C_m - A) / [H]^{(pi-r)}$ were plotted, which in turn were obtained from the pH absorbance curves at different pH values and different ligand concentrations, recorded at suitable wavelength. The values of ϵ_1 , ϵ_2 and ϵ_3 at this wavelength were then deduced from the above plots. Consequently these values of ϵ_1 , ϵ_2 and ϵ_3 were substituted in the logarithmic transformations (9)-(11).

$$\log \frac{A}{\epsilon_1 C_m - A} = n \log C_R + (ni-m) \text{pH} + \log K_n \quad \dots(9)$$

$$\log \frac{A - \epsilon_1 C_m}{\epsilon_2 C_m - A} = j \log C_R + (ji-q) \text{pH} + \log K_j \quad \dots(10)$$

$$\log \frac{A - \epsilon_2 C_m}{\epsilon_3 C_m - A} = p \log C_R + (pi-r) \text{pH} + \log K_p \quad \dots(11)$$

From the slopes of the linear plots obtained using Eqs. (9) to (11) the values of $(m-m)$, $(ji-q)$ and $(pi-r)$ were obtained. The equilibrium or stability constants have then been calculated from the plot of pH versus $-\log C_R$, for the equation with the left hand side being zero, and also by plotting $\log A / (\epsilon_1 C_m - A)$ vs pH and other similar terms vs pH.

Determination of the number of ligand species in the complex and proton liberated during complexation—A set of pH-absorbance curves for solutions containing a constant excess of ligand were analysed (Eqs. 12-14) in corresponding solutions i.e. for solutions having same values of $\epsilon = A - A_{OR} / C_m$ (A_{OR} = absorbance of the ligand). Under such conditions simple logarithmic plots are valid whose slopes give directly the ratio of the number of coordinated ligand molecules and that of the protons liberated during the complexation.

$$pH = \frac{n}{(ni-m)} (-\log C_R) + \text{constant} \quad \dots(12)$$

$$pH = \frac{j}{(ji-q)} (-\log C_R) + \text{constant} \quad \dots(13)$$

$$pH = \frac{p}{(pi-r)} (-\log C_R) + \text{constant} \quad \dots(14)$$

To know the existence of polynuclear complexes, especially dinuclear complexes, solutions containing a constant excess of ligand were examined varying the concentration of metal ion and determining the ratio of the number of metal ions complexed to that of protons liberated, using Eq. (15).

$$pH = \frac{m-1}{m} (-\log C_M) + \text{constant} \quad \dots(15)$$

Eqs. (4) to (8) were used for the interpretation of plots of absorbance versus the increasing [ligand] at constant pH.

Characteristics of Ligand

4-Methyl daphnetin behaves as a dibasic acid. The dissociation constant of 4-methyl daphnetin was determined pH-metrically. The values of pK_1 and pK_2 are found to be 8.2 and 11.4 respectively. In UV and visible region the ligand exhibits¹¹ λ_{max} at 261, 321 and 370 nm ($\log \epsilon_{max}$ 4.14, 4.8 and 3.7).

Results

A deep orange colour appeared in solution of TiO^{2+} with 4-methyldaphnetin in excess. The reaction between TiO^{2+} and 4-methyldaphnetin was reversible in nature in the pH range 2-5. Only mononuclear complexes are formed in solution with excess of ligand in the entire pH region. Absence of polynuclear complexes is inferred from the overlapping of pH versus (A/C_R) curves at different C_M values.

Absorbance-pH curves — A family of curves were obtained at 380 nm with varying ligand concentrations and pH, maintaining a fixed concentration of the metal ion (Fig. 1). The curves indicated

that at the same pH value the absorbance increases if the ligand concentration is raised.

Absorbance-pH curves have been interpreted in two ways: (i) logarithmic method of analysis; and (ii) corresponding solutions method.

(i) Assuming general equilibria (1-3) the following results are obtained on the basis of transformations (4)-(8) as well as on the results of logarithmic analysis according to (9)-(11).

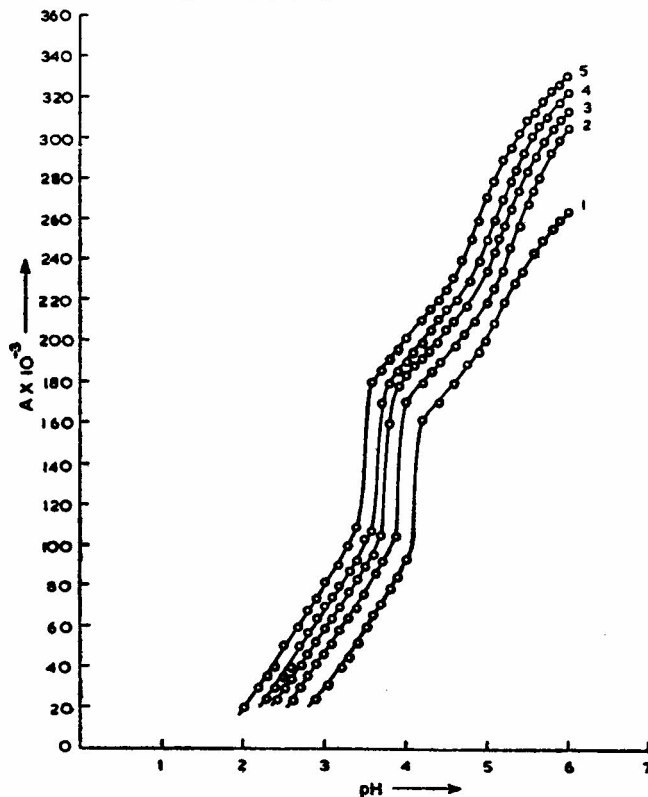


Fig. 1 — pH versus absorbance curves of titanium-4-methyldaphnetin complex at various [ligand] [Wavelength, 380 nm; $C_M = 4 \times 10^{-5} M$; for curves 1-5, C_R values are 2, 4, 6, 8, 12 $\times 10^{-4} M$ respectively]

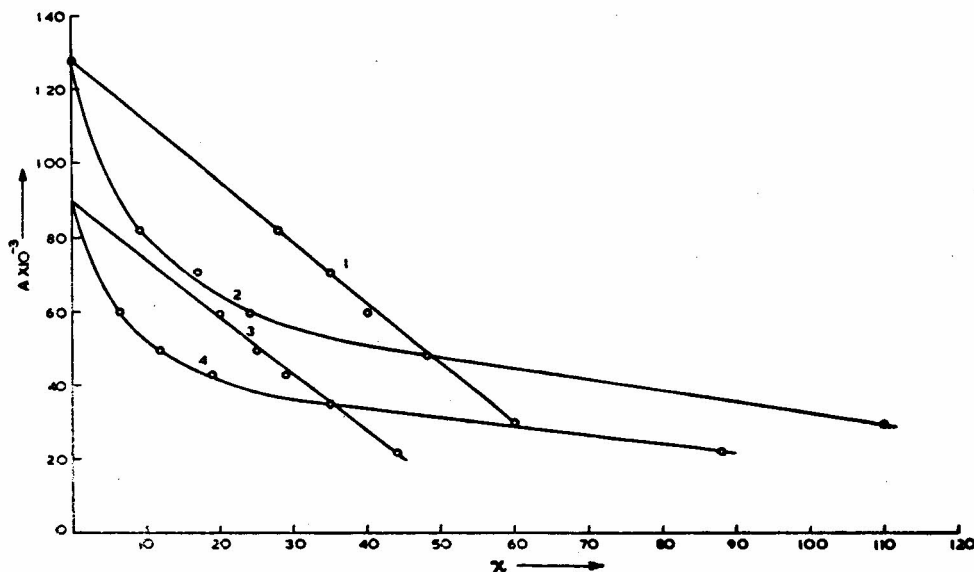


Fig. 2 — Analysis of ligand concentration versus absorbance curves [pH 3.0; $C_M = 4 \times 10^{-5} M$; curves 1, 2 at 380 nm and 3, 4 at 400 nm. x represents A/C_R for curves 1 and 3 and A/C^2_R for curves 2 and 4]

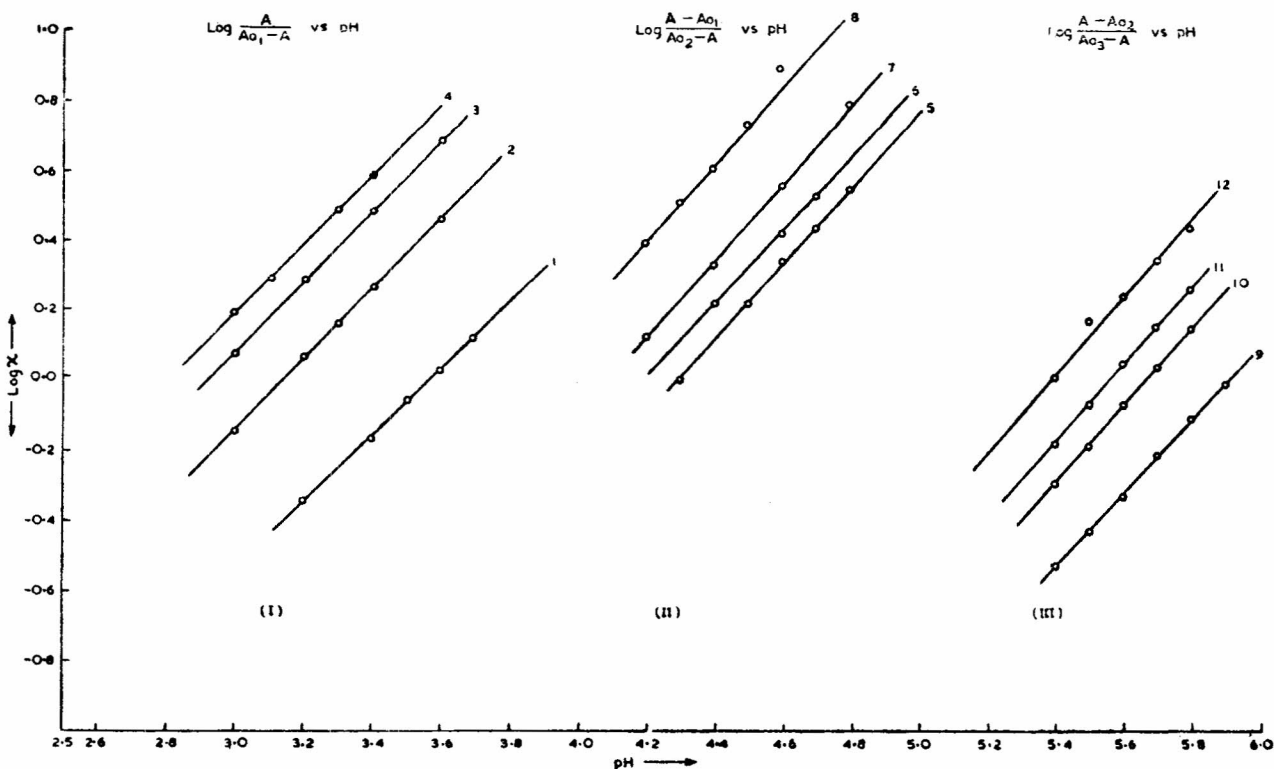


Fig. 3 — Analysis of pH versus absorbance curves according to Eqs. (5), (7) and (8) [Wavelength, 380 nm; C_R values of curves 1, 5, 9 = $4 \times 10^{-4}M$; for curves 2, 6, 10 = $6 \times 10^{-4}M$; for curves 3, 7, 11, $8 \times 10^{-4}M$; and for curves 4, 8, 12 = $12 \times 10^{-4}M$]

At 380 nm the plots of A vs A/C_R (curve 1, Fig. 2) at pH 3.0 and $\log A/(A_{01}-A)$ vs pH [Fig. 3-(I)] in the pH region 2.5 to 3.8 were linear with a slope of unity. The plots of A vs A/C_R^2 at 380 and 400 nm respectively, (Fig. 3, curves 2 and 4) cannot be considered in view of the non-linear nature of these curves. So the following equilibria can be assumed in the above pH region:



Similarly at pH 4.2 and 5.8 at 380 nm the plots of A vs $(A - A_{01})/C_R$ and A vs $(A - A_{02})/C_R$ were drawn (Fig. 4, II and III) to obtain the values of A_{01} and A_{02} . With the help of these values, plots of $\log (A - A_{01})/(A_{02} - A)$ vs pH (Fig. 3, II) in the pH region 4.0 to 4.8 and plots of $\log (A - A_{02})/(A_{03} - A)$ vs pH (Fig. 3, III) in the pH region 5.1 to 5.8 have been obtained. The plots indicated that only one molecule of 4-methyldaphnetin is successively coordinated and only one proton liberated in each step of complexation in solution with large excess of ligand. Therefore, the equilibria (16 and 17) can be assumed in the pH regions 4-4.8 and 5.1-5.8 respectively.



(ii) In this case $-\log C_R$ vs pH was plotted and linear plots of unity slope in different pH regions were obtained, confirming the existence of 1:1, 1:2 and 1:3 complexes in different pH regions. However, a mixture of 1:2 and 1:3 complexes cannot be ruled out in intermediate region of pH.

Method of continuous variations — The Job curves at 400 and 450 nm provided evidence for the

existence of 1:1 complex at pH 3.0, 1:2 complex at pH 4.2 and 1:3 complex at pH 5.5.

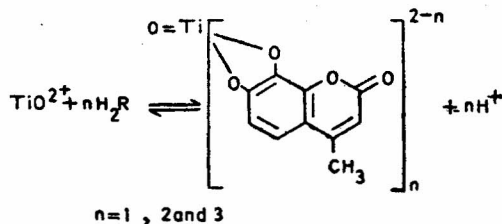
Discussion

The stepwise formation of three complexes of Ti(IV) with 4-methyldaphnetin has been established depending upon the concentration of ligand and pH. The liberation of one proton in different pH ranges indicates the stepwise formation of three protonated complexes.

All the three complexes formed are mononuclear, viz. $TiO(RH)^+$, $TiO(RH)_2$ and $TiO(RH)_3$. The 1:1 complex prevails in acidic solutions and 1:3 complex formed at pH > 5.0, while 1:2 complex is present in the intermediate pH range.

The difference in the reactivity of the two hydroxyl groups has been reported by Rastogi¹². They found that the 7-hydroxyl group is more reactive but not significantly.

Hence the following reaction is suggested:



Stability constants of the complexes — The stability constants K_1 , K_2 and K_3 of the three complexes were calculated from Eqs. (18)-(20).

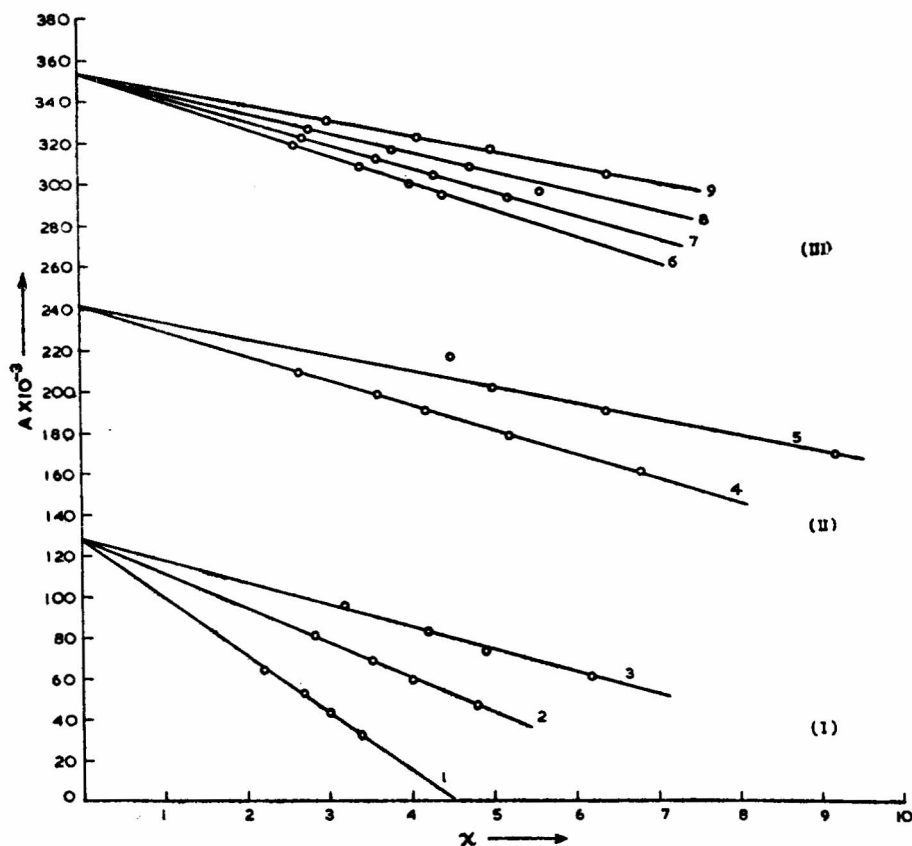


Fig. 4—Logarithmic analysis of pH-absorbance curves [Wavelength, 380 nm; $C_M = 4 \times 10^{-5} M$; $C_R = 2, 4, 6, 8, 12 \times 10^{-4} M$. pH 2.75, 3.0, 3.25 for curves 1-3; 4.2, 4.5 for curves 4, 5; 5.7, 5.8, 5.9, 6.0 for curves 6-9 respectively. X-axis = (I) A/CR ; (II) $A-AO_1/CR$; and (III) $A-AO_2/CR$]

$$\log \frac{A}{\epsilon_1 C_M - A} \left(1 + \frac{K_{a1}}{H}\right) = pH + \log C_R + \log K_1 \quad \dots (18)$$

$$\log \frac{A - \epsilon_1 C_M}{\epsilon_2 C_M - A} \left(1 + \frac{K_{a1}}{H}\right) = pH + \log C_R + \log K_2 \quad \dots (19)$$

$$\log \frac{A - \epsilon_2 C_M}{\epsilon_3 C_M - A} \left(1 + \frac{K_{a1}}{H}\right) = pH + \log C_R + \log K_3 \quad \dots (20)$$

The log values of stepwise stability constants of the three complexes were found to be 8.37, 7.33 and 5.70 respectively.

Also the values of molar absorptivities of ϵ_1 , ϵ_2 and ϵ_3 of three complexes were found to be 3.2×10^3 , 6.05×10^3 and 8.85×10^3 respectively.

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