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Spectrophotometric Study of Uranyl Complexes with 4-Methyl- & 4-Phenyl-daphnetins

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Reactions of uranium(VI) with 4-phenyl-7,8-dihydroxycoumarin (4-phenyldaphnetin) and 4-methyl-7,8-dihydroxycoumarin (4-methyldaphnetin) in solution have been studied spectrophotometrically. In each case two mononuclear complexes are formed depending upon the *p*H and the concentration of the ligand. The log *K* values of 1 : 1 and 1 : 2 complexes of 4-phenyldaphnetin and 4-methyldaphnetin are found to be 9·0 and 10·35; and 9·43 and 10·83 respectively.

SUBSTITUTED dihydroxycoumarins have been used as analytical reagents[1-5]. We have now observed that acetone solution of 4-phenyldaphnetin (4-PD) and 4-methyldaphnetin (4-MD) give yellow colour with aqueous solutions of uranyl nitrate. Spectrophotometric study of colour reactions reported in this paper has established the formation of two mononuclear complexes in each case.

Materials and Methods

Stock solution of uranyl nitrate ($M/10$) was prepared by dissolving the required amount of $UO_2(NO_3)_2.6H_2O$ in water. Working solutions were prepared by diluting the standardized stock solution.

Unicam SP600 spectrophotometer and Metrohm *p*H meter model E350 were used in the present studies.

4-Phenyldaphnetin (4-PD, m.p. 190°) and 4-methyldaphnetin (4-MD, m.p. 234°) were prepared and recrystallized from benzene[6,7].

Results and Discussion

Reactions of 4-PD and 4-MD with UO_2^{2+} were found to be reversible in nature. Only mononuclear complexes are formed in the entire *p*H range when excess of ligand is used. The absence of polynuclear species is inferred from the overlapping of *p*H versus (A/C_M) curves for different C_M values.

In all the studies absorbance due to excess ligand was subtracted from the observed value and that due to complexed ligand was ignored. The following two general equilibria (1 and 2) represent the complexation reactions when excess ligand is present.

$$\mathrm{M}+n\mathrm{H}_i\mathrm{R} \overset{K_n}{\rightleftharpoons} \mathrm{MR}_n\mathrm{H}_m+(ni-m)\mathrm{H}^+ \qquad \ldots(1)$$

$$\mathrm{MR}_n\mathrm{H}_m+j\mathrm{H}_i\mathrm{R} \overset{K_J}{\rightleftharpoons} \mathrm{MR}_{n+j}\mathrm{H}_{q+m}+(ji-q)\mathrm{H}^+ \qquad \ldots(2)$$

For the above equilibria following equations (3-5) may be written[8-11]:

$$A=\epsilon_1 C_{\mathrm{M}}-(\mathrm{H}^+)^{ni-m}A/C_R^n.K_n \qquad \ldots(3)$$

$$A=\epsilon_1 C_{\mathrm{M}}+C_R^j(\epsilon_2 C_{\mathrm{M}}-A)K_j/(\mathrm{H}^+)^{(ji-q)} \qquad \ldots(4)$$

$$A=\epsilon_2 C_{\mathrm{M}}-(\mathrm{H}^+)^{ji-q}\,(A-\epsilon_1 C_{\mathrm{M}})/K_j.C_R^j \qquad \ldots(5)$$

In the above equations A represents absorbance, ϵ_1 and ϵ_2 represent molar absorptivities of the two complexes, C_M is concentration of metal ion in the form of complex (since concentration of free metal ion is very small, it has been neglected), C_R is total concentration of the ligand (since amount of ligand complexed is very small in comparison with the free ligand, it has been neglected) and K_n and K_J are equilibrium constants for the two species.

Plots of A versus $A(\mathrm{H})^{ni-m}$, A versus $(C_M-A)/(\mathrm{H}^+)^{ji-q}$ and A versus $(\mathrm{H}^+)^{ji-q}/(A-\epsilon_1 C_{\mathrm{M}})$ were drawn using the *p*H absorbance curves for solutions containing excess ligand, C_R^n or C_R^j. The values of ϵ_1 and ϵ_2 were deduced from the above plots. Since neither of the values of ϵ_1 or ϵ_2 were directly accessible from the curves on account of mutual transition of complexes, these were obtained by extrapolation. The stability constants of the two complexes were obtained from the following Eqs. 6 and 7 using the calculated values of ϵ_1 and ϵ_2.

$$\log A/\epsilon_1 C_{\mathrm{M}}-A=n\log C_R+(ni-m)p\mathrm{H}+\log K_n \qquad \ldots(6)$$

$$\log\,(A-\epsilon_1 C_{\mathrm{M}})/(\epsilon_2 C_{\mathrm{M}}-A) = J\log C_R + (Ji-q)p\mathrm{H}+\log K_j \qquad \ldots(7)$$

The number of protons liberated during complexation and nature of the coordinated ligand species were studied by analysing *p*H-absorbance curves obtained at constant [metal ion] and varying [ligand]. The slopes of the simple logarithmic plots give directly the ratio of the number of coordinated ligands in the complex and the number of protons liberated during the complexation, i.e. n/x and j/y. The following Eqs. 8 and 9 derived from Eqs. 6 and 7 were used for the purpose.

$$p\mathrm{H} = n/(ni-m)\ (-\log C_R)+\text{constant} \qquad \ldots(8)$$

$$p\mathrm{H} = j/(ji-q)\ (-\log C_R)+\text{constant} \qquad \ldots(9)$$

The existence of polynuclear complex, especially dinuclear complex, in the solution containing constant excess of ligand, was examined by slight variations in the concentration of metal ion and finding out the ratio of the number of metal ion complexed and that of protons liberated, using Eq. 10.

$$pH = (m-1)/x(-\log C_M)+\text{constant} \quad ...(10)$$

Eqs. 3-5 were used for the interpretation of the plots of the absorban ceagainst the increasing ligand concentration at constant *p*H. The number of coordinated ligands were obtained from the plots of A versus A/C_R^n and A versus $(A-\epsilon_1\ C_M)/C_R^j$.

A group of curves were obtained by plotting varying [ligand] at different *p*H values (Fig. 1) against a fixed concentration of metal ion. These curves were interpreted using Eqs. 3-5 assuming the general equilibria (1) and (2) (Figs. 2-4). Considering Eqs. 3-5 as the linear equations and the results of logarithmic Eqs. 6 and 7 for particular complexes, two different complexation equilibria (11) and (12) are indicated in the *p*H range studied.

$$UO_2^{2+}+H_2R \rightleftharpoons UO_2(RH)^+ + H^+ \quad ...(11)$$

$$UO(RH)^+ + H_2R \rightleftharpoons UO_2(RH)_2 + H^+ \quad ...(12)$$

Absorbance-ligand concentration plots — In general exponential form is observed with 4-phenyldaphnetin

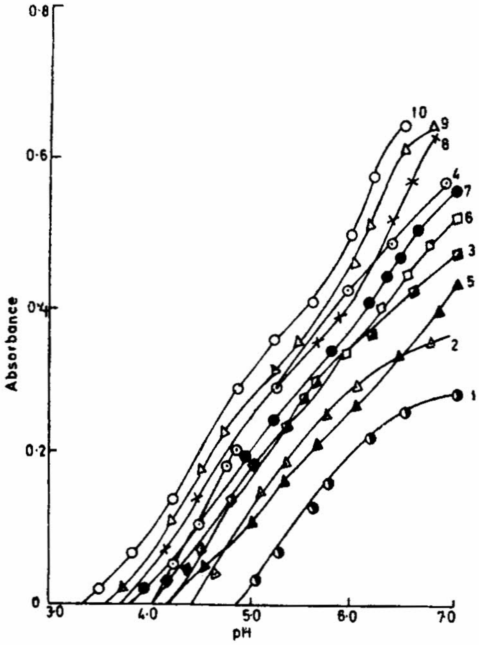

Fig. 1 — *p*H-absorbance curves for UO_2^{2+}-4-methyldaphnetin (curves 1-4) and UO_2^{2+}-4-phenyldaphnetin (curves 5-10) complexes at various ligand concentrations and 400 nm, $C_M = 5\times10^{-5}M$, $I = 0{\cdot}1$ [Curves 1, 5: $C_R = 1{\cdot}25\times10^{-4}M$; curves 2, 6: $C_R = 2{\cdot}5\times10^{-4}M$; curves 3, 7: $C_R = 5\times10^{-4}M$; curves 4, 10: $C_R = 12{\cdot}5\times10^{-4}M$; curve 8: $C_R = 7{\cdot}5\times10^{-4}M$; curve 9: $C_R = 10\times10^{-4}M$]

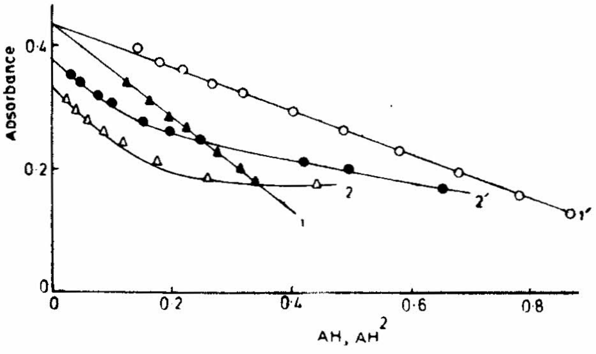

Fig. 2 — Analysis of the *p*H-absorbance curves for UO_2^{2+}-4-methyldaphnetin (curves 1′, 2′) and UO^{2+}-4-phenyldaphnetin (curves 1, 2) complexes at 400 nm, $I = 0{\cdot}1$, $C_M = 5\times10^{-5}M$; $C_R = 10\times10^{-5}M$ [Curves 1, 1′ = AH; curves 2, 2′ = AH²]

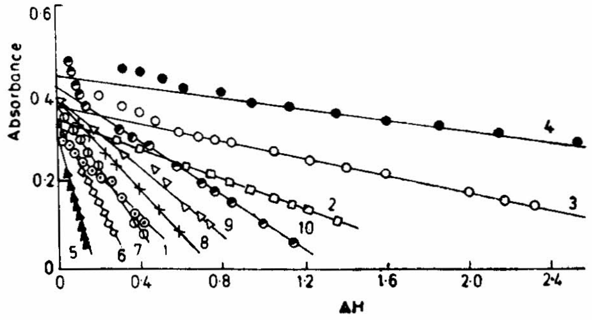

Fig. 3 — Analysis of lower portion of *p*H-absorbance curves for UO_2^{2+}-4-methyldaphnetin (curves 1-4) and UO_2^{2+}-4-phenyldaphnetin (curves 5-10) complexes at 400 nm, $I = 0{\cdot}1$, $C_M = 5\times10^{-5}M$ [Curves 1, 5: $C_R = 1{\cdot}28\times10^{-4}M$; curves 2, 6: $C_R = 2{\cdot}5\times10^{-4}M$; curves 3, 7: $C_R = 5\times10^{-4}M$; curves 4, 10: $C_R = 12{\cdot}5\times10^{-4}M$; curve 8: $C_R = 7{\cdot}5\times10^{-4}M$; curve 9: $C_R = 10\times10^{-4}M$]

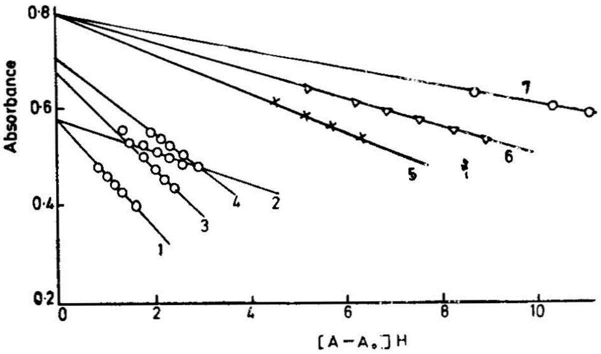

Fig. 4 — Analysis of upper portion of *p*H-absorbance curves for UO_2^{2+}-4-methyldaphnetin (curves 1-4) and UO_2^{2+}-4-phenyldaphnetin (curves 5-7) complexes at 400 nm, $I = 0{\cdot}1$, $C_M = 5\times10^{-5}M$ [Curves 1, 4: $C_R = 5\times10^{-4}M$; curves 2, 7: $C_R = 12{\cdot}5\times10^{-4}M$; curve 3: $C_R = 2{\cdot}5\times10^{-4}M$; curve 5: $C_R = 7{\cdot}5\times10^{-4}M$; curve 6: $C_R = 10\times10^{-4}M$]

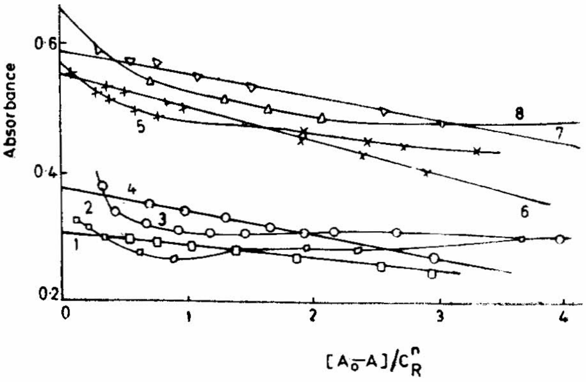

Fig. 5 — Analysis of ligand concentration-absorbance curves for UO_2^{2+}-4-methyldaphnetin (curves 1, 2, 5, 6) and UO_2^{2+}-4-phenyldaphnetin (curves 3, 4, 7, 8) complexes at 400 nm [Curves 1, 4, 6 and 8 are for A_0-A/C_R, $n = 1$; and curves 2, 3, 5 and 7 are for A_0-A/C^2_R, $n = 2$]

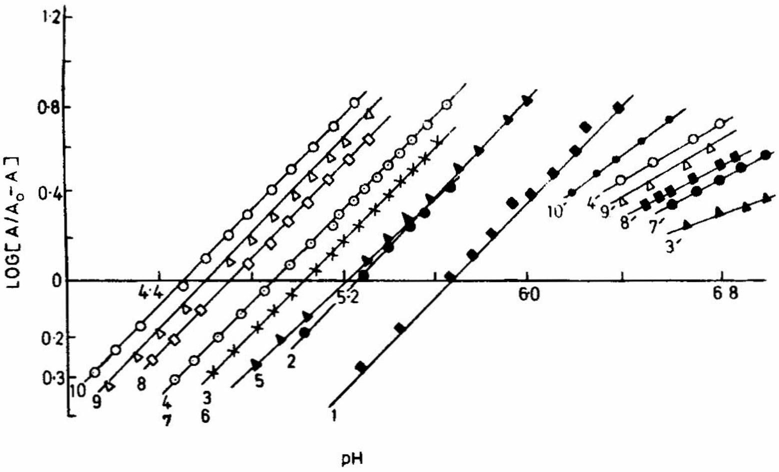

Fig. 6 — Logarithmic analysis of *p*H-absorbance curves for UO_2^{2+}-4-methyldaphnetin (curves 1-4 and 3′, 4′, 7′) and UO_2^{2+}-4-phenyldaphnetin (curves 5-10 and 8′, 9′, 10′) complexes at $C_M = 5\times10^{-5}M$ and 400 nm [Curve 1: $C_R = 1{\cdot}25\times10^{-4}M$; curves 2, 6: $C_R = 2{\cdot}5\times10^{-4}M$; curves 3, 7: $C_R = 5\times10^{-4}M$; curves 4, 10: $C_R = 12{\cdot}5\times10^{-4}M$; curve 8: $C_R = 7{\cdot}5\times10^{-5}M$; curve 9: $C_R = 10\times10^{-4}M$]

and 4-methyldaphnetin at *p*H 4·85, 5·9 and 5·1, 6·0 respectively at 400 nm.

At selected *p*H values, the transition between two particular complexes was examined using Eqs. 3-5 keeping $[H]^{x,y*}$ constant and plotting A versus $(A_{01}-A)/C_R^n$ (Fig. 5). At *p*H 4·9 and 5·1 in the case of 4-phenyl- and 4-methyl-daphenetin, only $UO_2(RH)^+$ is present. Up to *p*H 6·0, formation of both the complexes, viz. $UO_2(RH)^+$ and $UO_2(RH)_2$ is observed depending upon the *p*H and concentration of ligand.

Molar composition of the complexes — The Job's curves at 400, 410 and 420 nm showed the existence of 1:1 complexes at *p*H 4·85, 4·9 and 5·0. The composition at *p*H 6·0 in both the cases by Job's method as well as by Asmus' method is found to be 1:2.

Equilibria constant — The conditional constants of the complexes of both the ligands were calculated from logarithmic plots (Fig. 6) using the following equations (derived from equations 6 and 7):

$$\log\frac{A}{\epsilon_1 C_M - A}\left(1+\frac{K_{ai}}{(H^+)}\right) = pH + \log C_R + \log K_1' \quad \ldots(13)$$

$$\log\frac{A-\epsilon_1 C_M}{\epsilon_2 C_M - A}\left(1+\frac{K_{ai}}{(H^+)}\right) = pH + \log C_R + \log K_2' \quad \ldots(14)$$

($\epsilon_1 C_M$ and $\epsilon_2 C_M$ may be replaced by A_{01} and A_{02}) The values of stability constants (log K) of complexes are found to be 9·0 and 10·35; and 9·43 and 10·83 for uranyl complexes with 4-phenyldaphnetin and 4-methyldaphnetin respectively.

The values of molar absorptivities of two complexes in the case of 4-phenyldaphnetin are $8{\cdot}0\times10^3$ and $15{\cdot}2\times10^3$ while those in the case of 4-methyldaphnetin are $7{\cdot}7\times10^3$ and $11{\cdot}8\times10^3$.

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*x, y = $(ni-m)$, $(ji-q)$.