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Investigation of the Uranil(II) – 3-Hydroxyflavone Complex

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Summary. By the application of suitable spectrophotometric methods and *pH*-metric measurements it has been established that uranyl ion and 3-hydroxyflavone form a $[UO_2(C_{15}H_9O_3)]^+$ complex. The concentration stability constant of the complex was determined by Bent-French's ($\beta_1 = 8.59$ at $pH = 3.5$) and Bjerrum's (from 8.68 at $pH = 4$ to 6.14 at $pH = 7$) methods. Conditions are given for the spectrophotometric determination of 3-hydroxyflavone by means of the complex. The regression equation is calculated and the accuracy of the method is determined. All investigations were carried out with 80% ethanolic solutions at room temperature (20°), the spectrophotometric measurements being performed at a constant *pH* (3.5) and a constant ionic strength (0.01 *M*).

Keywords. Spectrophotometric methods; *pH*-metry; 3-Hydroxyflavone; Uranyl(II) nitrate.

Untersuchung des Uranil(II) – 3-Hydroxyflavon-Komplexes

Zusammenfassung. Unter der Anwendung von geeigneten spektrophotometrischen Methoden sowie *pH*-metrischen Messungen wurde gefunden, daß das UO_2^{2+}-Ion und 3-Hydroxyflavon den Komplex $[UO_2(C_{15}H_9O_3)]^+$ bilden. Die Stabilitätskonstante des Komplexes wurde nach Bent und French ($\beta_1 = 8.59$ bei $pH = 3.5$) und nach Bjerrum (von 8.68 bei $pH = 4$ bis 6.14 bei $pH = 7$) bestimmt. Es werden die Bedingungen für die spektrophotometrische Bestimmung des 3-Hydroxyflavons mit Hilfe des Komplexes angegeben, die Regreßgleichung berechnet und die Genauigkeit der Methode ermittelt. Alle Untersuchungen wurden in 80proz. Ethanol bei Raumtemperatur (20°), die spektrophotometrischen Untersuchungen bei konstantem *pH*-Wert und Ionenstärke (0.01 *M*) durchgeführt.

Introduction

3-Hydroxyflavone belongs to the group of flavones containing one hydroxyl group. It is distributed among plants and exhibits a significant physiological and pharmacological activity. 3-Hydroxyflavone forms complex compounds with many metal ions. Besides other authors [1–4], we have also investigated some of these complexes [5, 6].

Experimental

Spectrophotometric measurements were performed on a Unicam SP 600 spectrophotometer by using 1 cm quartz cells. For *pH*-metric measurements a Radiometer pH 28 *pH*-meter was used.

The reagents used were: uranil(II) nitrate, abs. ethanol (both "Merck"); 3-hydroxyflavone ("Aldrich-Chemie") recrystallized several times from absolute ethanol; and hexamethylenetetramine buffer $c = 0.1\,M$ ("Carlo Erba").

Results and Discussion

Composition of the Complex

The complex formed is brown colored with an absorption maximum at 395 nm (Fig. 1). The composition of the complex was determined by application of the method of continuous variations of equimolar solutions [7], by the molar ratio method [8] and by the Bent-French method [9].

According to the first method [7] solutions obtained by mixing $UO_2(NO_3)_2$ and 3-hydroxyflavone solutions having total concentrations $c_{UO_2} = c_{3\text{-}hf} = 5 \cdot 10^{-4} M$ were used. As blank, 3-hydroxyflavone solutions having the same concentrations as the mixed solutions were used. The obtained curve $A = f(x_{UO_2})$ had a maximum absorbance at $x_{UO_2} = 0.5$ (Fig. 2), which shows that the stoichiometric ratio of components in the complex is $UO_2^{2+} : 3\text{-}hf = 1:1$.

According to the second method [8], solutions containing a constant $UO_2(NO_3)_2$ concentration ($5 \cdot 10^{-4} M$) and varied 3-hydroxyflavone concentrations ($2.5 \cdot 10^{-4} - 1.25 \cdot 10^{-3} M$) were prepared. As blank, 3-hydroxyflavone of the same concentrations as the mixed solutions were used. A straight line $A = f(c_{3\text{-}hf}/c_{UO_2})$

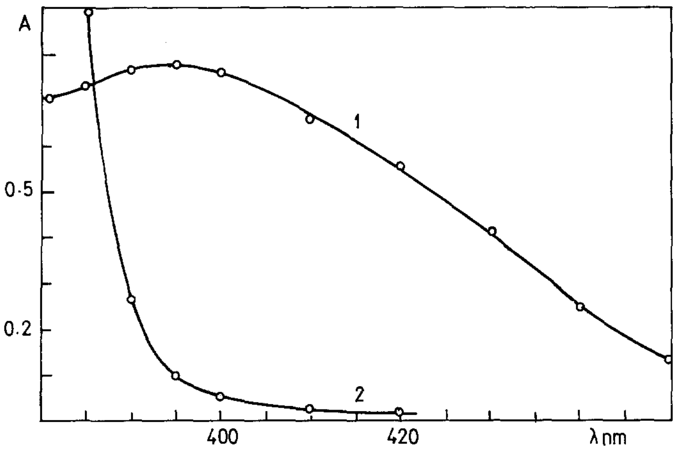

Fig. 1. UV-Vis spectra of the complex (1) and 3-hydroxyflavone (2)

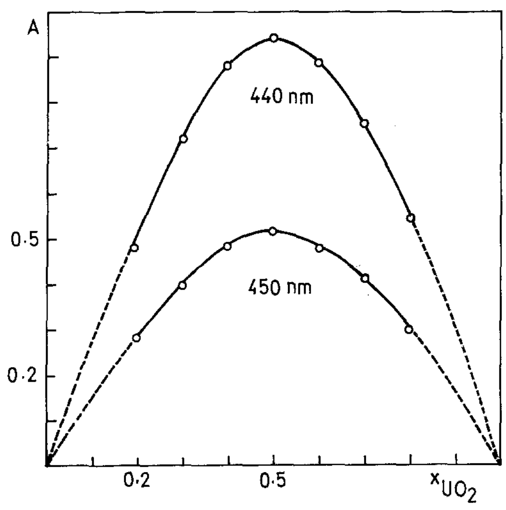

Fig. 2. Method of continuous variations of equimolar solutions: $c_{UO_2} = c_{3\text{-}hf} = 5 \cdot 10^{-4} M$

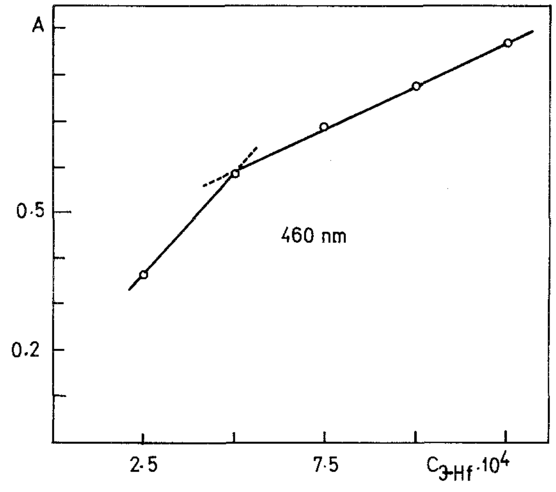

Fig. 3. Method of molar ratios: $c_{UO_2} = 5 \cdot 10^{-4} M$, $c_{3\text{-}hf}$ from $2.5 \cdot 10^{-4}$ to $1.25 \cdot 10^{-3} M$

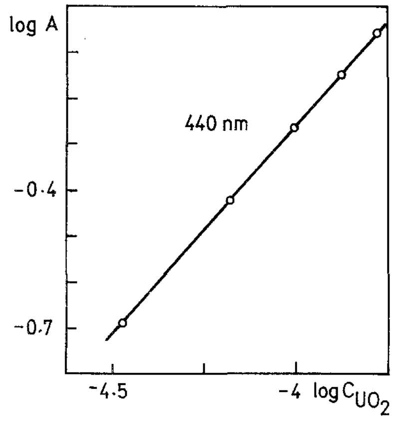

Fig. 4. Bent-French's method: $c_{3\text{-}hf} = 2.3 \cdot 10^{-3} M$, c_{UO_2} from $3.33 \cdot 10^{-5}$ to $1.67 \cdot 10^{-4} M$

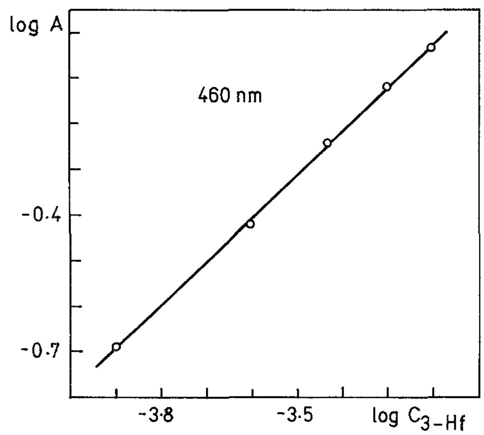

Fig. 5. Bent-French's method: $c_{UO_2} = 2 \cdot 10^{-3} M$, $c_{3\text{-}hf}$ from $1.25 \cdot 10^{-4}$ to $6.25 \cdot 10^{-4} M$

with an interception at $c_{3\text{-}hf} : c_{UO_2} = 1$ was obtained, and that confirms that the ratio of uranil(II) to 3-hydroxyflavone in the complex is 1 : 1 (Fig. 3).

According to the third method [9] two kinds of solutions were prepared:

1. Solutions containing a constant 3-hydroxyflavone concentration ($2.3 \cdot 10^{-3} M$) and varied $UO_2(NO_3)_2$ concentrations ($3.33 \cdot 10^{-5} - 1.67 \cdot 10^{-4} M$).

As blank, a $2.3 \cdot 10^{-3}\,M$ solution of 3-hydroxyflavone was used. A straight line $\log A = f(\log c_{UO_2})$ was obtained with a slope $m = 0.90$, which gives the number of UO_2^{2+} ions in the complex unit (Fig. 4).

2. Solutions containing a constant $UO_2(NO_3)_2$ concentration ($2 \cdot 10^{-3}\,M$) and varied 3-hydroxyflavone concentrations ($1.25 \cdot 10^{-4} - 6.25 \cdot 10^{-4}\,M$). As blank, a $2 \cdot 10^{-3}\,M$ $UO_2(NO_3)_2$ solution was used. The straight line obtained $\log A = f(\log c_{3\text{-}hf})$ had a slope $n = 0.95$ (number of 3-hydroxyflavone molecules) (Fig. 5). The ratio $m \approx n \approx 1$ confirmed the results on the complex composition obtained by the two previous methods.

Reaction of Complex Formation

Solutions having the same concentrations of $UO_2(NO_3)_2$ and 3-hydroxyflavone were prepared. By mixing the same volumes of $UO_2(NO_3)_2$ and 3-hydroxyflavone

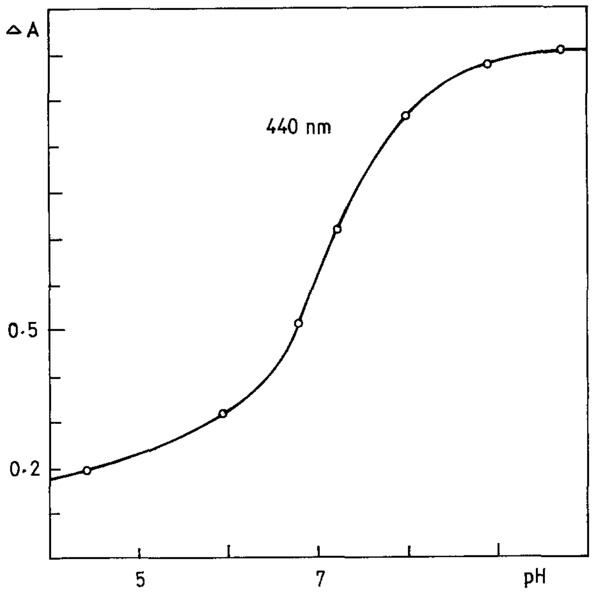

Fig. 6. Bjerrum's method: $c_{UO_2} = 3.3 \cdot 10^{-5}\,M$, $c_{3\text{-}hf} = 1.7 \cdot 10^{-3}\,M$

Table 1. The stability constant of uranil(II) − 3-hydroxyflavone complex ($a_{440} = 33\,485\,cm^{-1}\,mol^{-1}\,l$)

pH	Bent-French's method		Bjerrum's method
	β_1'	$\log \beta_1$	$\log \beta_1$
3.5	69.37	8.59	
4.0			8.68
4.5			7.87
5.0			7.44
5.5			7.02
6.0			6.64
6.5			6.32
7.0			6.14

solutions, of $UO_2(NO_3)_2$ and the solvent, and of 3-hydroxyflavone and the solvent, three mixed solutions in which $c_{UO_2} = c_{3\text{-}hf} = 2 \cdot 10^{-3}\,M$ were obtained. The results of the *pH* measurements of these mixtures (3.65, 4.40, and 6.72, respectively) showed that the *pH* of the mixed solution containing both components was the lowest. A higher H^+ ion concentration in the solution containing both components relative to the sum of H^+ ion concentration in the solution containing both components relative to the sum of H^+ ion concentrations in the other two mixed solutions ($\Delta H^+ = 1.84 \cdot 10^{-4}$ g ions/l) [10], can be explained by the formation of the complex according to the following equation,

$$UO_2^{2+} + C_{15}H_9O_3H \rightleftharpoons [UO_2(C_{15}H_9O_3)]^+ + H^+,$$

where UO_2^{2+} is linked to 3-hydroxyflavone through the 3-hydroxyl group and the carbonyl [2].

Stability Constant of the Complex

The relative stability constant of the complex, β_1', was calculated from Bent-French's method [9], where $c_{3\text{-}hf} = 2.3 \cdot 10^{-3}\,M$, and the corresponding values for A and c_{UO_2} were taken from the straight line $\log A = f(\log c_{UO_2})$ (Fig. 4). The molar absorptivity was calculated from the "s" curve obtained by Bjerrum's method [12]. The concentration stability constant was calculated from the expression [11],

$$\beta_1 = \frac{[[UO_2(C_{15}H_9O_3)]^+]}{[UO_2^{2+}][C_{15}H_9O_3H]} \cdot \frac{[H^+]}{k_d} = \beta_1' \cdot \frac{[H^+]}{k_d},$$

where the dissociation constant of 3-hydroxyflavone $k_d = 5.6 \cdot 10^{-11}$ [4] and $[C_{15}H_9O_3H]$ denotes the equilibrium concentration of 3-hydroxyflavone which is approximately equal to the total concentration ($2.3 \cdot 10^{-3}\,M$) (Table 1).

The concentration stability constant was calculated by using Bjerrum's method [12] according to which the absorbances of the solution containing $3.3 \cdot 10^{-5}\,M$ of $UO_2(NO_3)_2$ and $1.7 \cdot 10^{-3}\,M$ of 3-hydroxyflavone, and those of the solution containing $1.7 \cdot 10^{-3}\,M$ of 3-hydroxyflavone, were measured at different *pH* values. In all cases as blank, 80% ethanol was used. From the difference between the

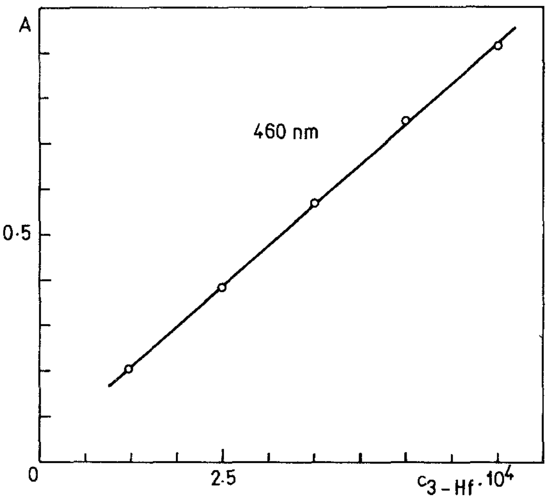

Fig. 7. Determination of 3-hydroxyflavone: $c_{UO_2} = 2 \cdot 10^{-3}\,M$, $c_{3\text{-}hf}$ from $1.25 \cdot 10^{-4}$ to $6.25 \cdot 10^{-4}\,M$

Table 2. Spectrophotometric determination of 3-hydroxyflavone ($n = 10$)

Taken (mg/ml)	Found (mg/ml)	SD	CV (%)
0.02978	0.02917	0.00133	4.56
0.08934	0.09022	0.00288	3.19
0.14890	0.14782	0.00420	2.84

absorbances of these solutions and their *pH* values, the curve "s" $A = f(pH)$ was constructed (Fig. 6); from the latter the molar absorptivity of the complex and its concentration stability constants at different *pH* values were calculated. Numerical values for β_1 at *pH* higher than 7 are not given, since they are unreliable due to the possibility of simultaneous formation of metal hydroxy-complexes (Table 1).

Determination of 3-Hydroxyflavone

Solutions containing a constant $UO_2(NO_3)_2$ concentration ($2 \cdot 10^{-3} M$) and varied 3-hydroxyflavone concentrations were prepared. As blank a $2 \cdot 10^{-3} M$ $UO_2(NO_3)_2$ solution was used. A linear dependence $A = f(c_{3\text{-}hf})$ was obtained for the range of 3-hydroxyflavone concentrations from $1.25 \cdot 10^{-4}$ to $6.25 \cdot 10^{-4} M$ (Fig. 7). By the application of the method of least squares the regression equation was calculated: $y = 6.007x + 0.0285$ ($n = 5$) with a correlation coefficient $r = 0.99987$. The accuracy of the method was determined at three different 3-hydroxyflavone concentrations (Table 2). On account of the formation of complexes with a great many of metal ions, 3-hydroxyflavone cannot be quantitatively determined in the presence of more than one kind of metal ions.

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