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Investigation of the Molybdate(II)-3-hydroxyflavone Complex

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Summary. Investigations on the composition of the molybdate(II)-3-hydroxyflavone complex and its stability constant have been carried out in 70% ethanolic solutions at room temperature (20°C), in the presence of a buffer at *pH* 6.30 ± 0.05 and ionic strength 0.015. It has been found that a complex $[MoO_3(C_{15}H_9O_3)_2^{2-}]$ whose stability constant ranges from 15.13 at *pH* 6.25 to 13.02 at *pH* 7.00 is formed. Conditions are given for the determination of 3-hydroxyflavone by means of the reaction of complex formation in 50% ethanol at *pH* 6.60 ± 0.05 and an ionic strength of 0.0225.

Keywords. Spectrophotometric methods; pH-metry; 3-Hydroxyflavone; Natrium molybdate.

Untersuchung des Molybdat(II)-3-hydroxyflavon-Komplexes

Zusammenfassung. Die Untersuchungen der Zusammensetzung des Komplexes und seiner Stabilitätskonstante wurden in 70% Ethanol, bei Raumtemperatur (20°C), in Anwesenheit von Puffer bei *pH* = 6.30 ± 0.05 und der Ionenstärke 0.015 ausgeführt. Es wird der Komplex $[MoO_3(C_{15}H_9O_3)_2^{2-}]$ gebildet, die Stabilitätskonstanten reichen von 15.13 bei *pH* 6.25 bis zu 13.02 bei *pH* 7.00. Es wurden die Bedingungen zur quantitativen Bestimmung von 3-Hydroxyflavon mittels des Molybdenkomplexes in 50% Ethanol, bei *pH* = 6.60 ± 0.05 und der Ionenstärke 0.0225 ermittelt.

Introduction

3-Hydroxyflavone belongs to the group of flavones containing one hydroxyl group. It is distributed among plants and exhibits a significant physiological activity. 3-Hydroxyflavone forms complex compounds with many metals. Besides other authors [1–4], we have also investigated some of these complexes [5–7].

Experimental

The reagents used were: Na_2MoO_4, abs. ethanol (both Merck); 3-hydroxyflavone (Aldrich-Chemie) recrystallized several times from absolute ethanol; hexamethylenetetramine buffer, $c = 0.1\ M$ (Carlo Erba).

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

Results and Discussion

Composition of the Complex

Molybdate ion, MoO_4^{2-}, and 3-hydroxyflavone (3-*hf*) form a complex of green yellow color with an absorption maximum at 395 nm (Fig. 1).

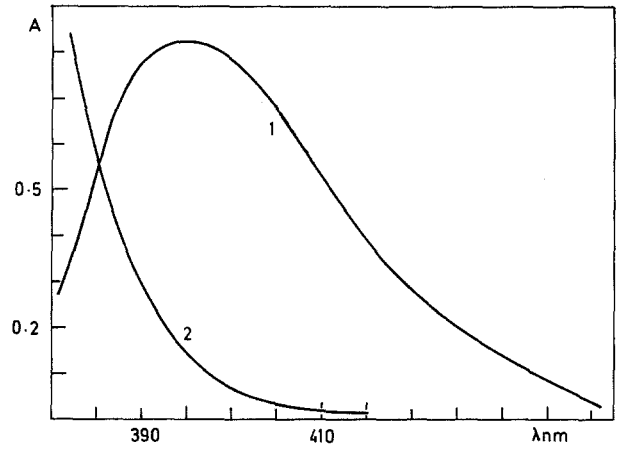

Fig. 1. Spectrophotogram of the complex. Curve 1: absorption curve of the complex ($c_{MoO_4} = 5 \cdot 10^{-5}$ mol/l, $c_{3\text{-}hf} = 1.75 \cdot 10^{-3}$ mol/l). Curve 2: absorption curve of 3-hydroxyflavone ($c_{3\text{-}hf} = 1.75 \cdot 10^{-3}$ mol/l)

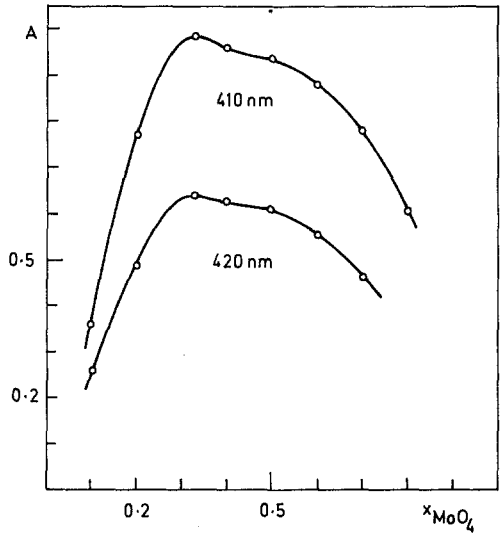

Fig. 2. Method of continual variations of equimolar solutions; $c_{MoO_4} = c_{3\text{-}hf} = 5 \cdot 10^{-4}$ mol/l

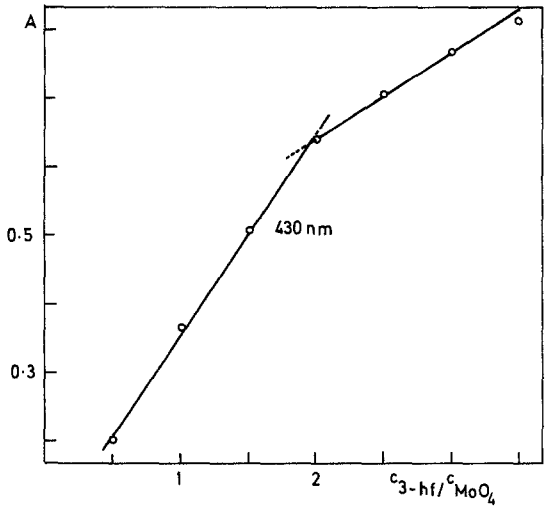

Fig. 3. Method of molar ratios; $c_{MoO_4} = 2.5 \cdot 10^{-4}$ mol/l

The composition of the complex was determined by the application of the method of variations of equimolar solutions [8] and by the molar ratio method [9].

According to the first method [8], mixtures of solutions of Na_2MoO_4 and 3-*hf* having total concentrations $c^0 = 5 \cdot 10^{-4}\,M$, were used. The curve obtained had a maximum at $x_{MoO_4} = 0.33$ which denoted the formation of a MoO_4^{2-} : 3-*hf* = 1 : 2 complex (Fig. 2).

According to the second method [9] solutions containing a constant Na_2MoO_4 concentration ($2.5 \cdot 10^{-4}\,M$) and varied concentrations of 3-*hf* ($1.25 \cdot 10^{-4}$–$8.75 \cdot 10^{-4}\,M$), were prepared. A straight line with an interception at $c_{3\text{-}hf}/c_{MoO_4} = 2$ was obtained and this proves that the stoichiometric ratio of MoO_4^{2-} to 3-*hf* in the complex is 1 : 2 (Fig. 3).

The Reaction of Complex Formation

Three kinds of solutions were prepared: the first solution was a mixed solution containing $c_{Na_2MoO_4} = 1.75 \cdot 10^{-3}\,M$ and $c_{3\text{-}hf} = 3.5 \cdot 10^{-3}\,M$; the second solution contained $1.75 \cdot 10^{-3}\,M$ Na_2MoO_4, whereas the third one contained $3.5 \cdot 10^{-3}\,M$ 3-*hf*. The results obtained by measuring the *pH* of these solutions are given in Table 1.

Our previous investigations [5–7] have shown that metal ions link to the ionic form of 3-hydroxyflavone, whereby H^+ is liberated. Therefore the *pH* of the mixed solution was significantly lower than the *pH* of the 3-*hf* solution. In the present case however, an opposite *pH* effect was observed, which can be explained by the following reaction [10]:

$$MoO_4^{2-} + 2C_{15}H_9O_3H \rightleftharpoons [MoO_3(C_{15}H_9O_3)_2^{2-}] + H_2O\,.$$

The first step involves the formation of molybdenum trioxide,

$$MoO_4^{2-} + 2H^+ \rightleftharpoons MoO_3 + H_2O\,,$$

which links to two ions of 3-*hf* through the 3-hydroxyl and the carbonyl groups [2].

According to data in the literature [11, 12] the *pH* increase of the mixed solution may be due to the following concurrent reactions

$$2H^+ + MoO_4^{2-} \rightleftharpoons H_2MoO_4\,,$$

$$7H^+ + 6MoO_4^{2-} \rightleftharpoons HMo_6O_{21}^{5-} + 3H_2O,$$

which proceed with the formation of molybdenic acid or the corresponding polyanions. Since these products are colorless, their formation either does not take place within the range of maximum complex formation (*pH* range from 4 to 6, Fig. 4), or it occurs parallel with the complexation reaction.

Table 1. pH of substrate-molybdate solutions

Solution	Na_2MoO_4, 3-*hf*	Na_2MoO_4	3-*hf*
pH	8.60	8.70	7.32

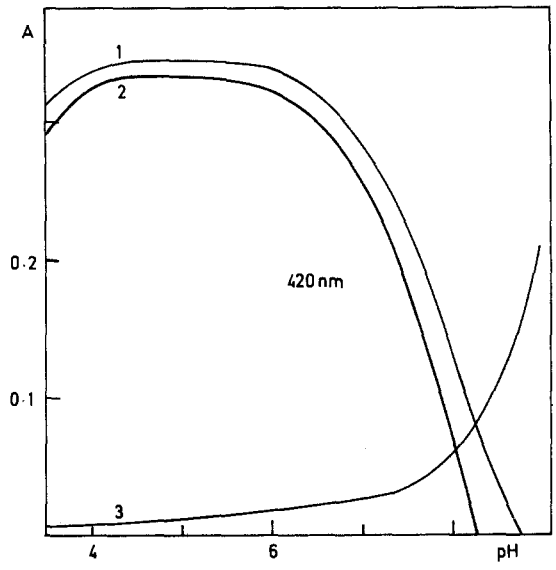

Fig. 4. Bjerrum's method. Curve 1: $c_{MoO_4} = 5 \cdot 10^{-5}$ mol/l, $c_{3\text{-}Hf} = 1 \cdot 10^{-3}$ mol/l. Curve 2: $\Delta A = f(pH)$. Curve 3: $c_{3\text{-}Hf} = 1 \cdot 10^{-3}$ mol/l

Stability Constant of the Complex

The stability constant was determined by the application of Bjerrum's method [13] according to which the absorbances of solutions containing $5 \cdot 10^{-5}$ *M* Na_2MoO_4 and $1 \cdot 10^{-3}$ *M* 3-*hf*, and of solutions containing $1 \cdot 10^{-3}$ *M* 3-*hf* were measured at different *pH* values. In both cases 70% ethanol was used as blank. Two curves were obtained and from these the curve $\Delta A = f(pH)$ (Fig. 4) was calculated. The highest complex concentration was found in the *pH* range from 4 to 6. Within this *pH* range the complex concentration is approximately equal to the total molybdate concentration $[MoO_4^{2-}]^0 = c^0$ and the molar absorptivity could be calculated from the expression $a = A/c^0$. In acid media ($pH < 4$) the complex absorbance decreased abruptly which can be explained by the decomposition of the complex due to the protonation or the formation of molybdenic acid or the corresponding polyanions. The concentration stability constants, β_2, were calculated for the segment of the curve from *pH* 6.25 to 7.00; the results obtained at higher *pH* values are unreliable on account of the possibility of parallel hydroxo-complex formation.

For the calculation of the concentration stability constant the following equations were used [14]:

$$[MoO_3L_2^{2-}] = A/a,$$

$$[HL]^0 = [HL] + [L^-] + 2[MoO_3L_2^{2-}],$$

$$[MoO_4^{2-}]^0 = [MoO_4^{2-}] + [MoO_3L_2^{2-}],$$

$$[H^+] = [L^-] + 2[MoO_3L_2^{2-}],$$

$$k_d = \frac{[H^+][L^-]}{[HL]},$$

$$\beta_2 = \frac{[MoO_3L_2^{2-}]}{[MoO_4^{2-}][L^-]^2},$$

in which HL denotes $C_{15}H_9O_3H$, whereas $k_d = 5.62 \cdot 10^{-11}$ is the dissociation constant of 3-*hf* [4] (Table 2).

Table 2. The concentration stability constant of the complex ($a_{420} = 6\,660\,cm^{-1}\,mol^{-1}\,l$)

pH	6.25	6.50	6.75	7.00
$\log \beta_2$	15.13	14.46	13.75	13.02

Determination of 3-Hydroxyflavone

The stability of the complex allows the quantitative determination of microamounts of 3-*hf*. Solutions containing a constant Na_2MoO_4 concentration ($2.5 \cdot 10^{-3}\,M$) and varied 3-*hf* concentrations were prepared; a $2.5 \cdot 10^{-3}\,M$ Na_2MoO_4 solution was used as blank. All solutions were prepared with 50% ethanol which was found to be the optimum solvent for a complete dissolution of both components. The ionic strength 0.0225 was adjusted by means of a buffer.

A linear dependence of the absorbance on the concentration was obtained for the concentration range of 3-*hf* from $6.25 \cdot 10^{-5}$ to $5 \cdot 10^{-4}\,M$ (Fig. 5). By the application of the method of least squares the regression equation: $y = 4.738x +$

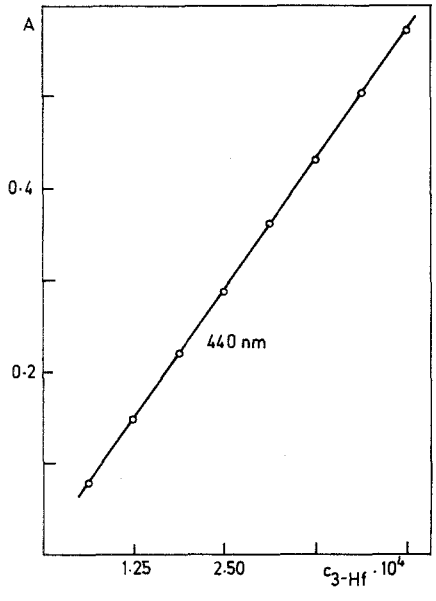

Fig. 5. Spectrophotometric determination of 3-hydroxyflavone; $c_{MoO_4} = 2.5 \cdot 10^{-3}$ mol/l

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

Taken (mg/ml)	Found (mg/ml)	SD	CV (%)
0.02978	0.03119	0.00105	3.36
0.05956	0.06045	0.00081	1.34
0.08934	0.09050	0.00088	0.98
0.11912	0.11996	0.00091	0.76

0.0060 ($n=8$) was calculated with a high correlation coefficient of 0.99999. The accuracy of the method was determined for four different 3-*hf* concentrations (Table 3).

3-Hydroxyflavone form complexes with a great many of metals and therefore its quantitative determination is not possible in the presence of more than one complexing species.

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