Influence of pH on the Absorption and Fluorescence Spectra of 6,7-Dihydroxycoumarin in Aqueous Solution

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Absorption and emission spectra of 6,7-dihydroxycoumarin [6,7-DHC] in aqueous solution over a wide pH range are reported. The absorption spectra proved to be strongly sensitive to the pH-value of the solution, whereas the emission spectra change in this range only insignificantly.

An interpretation is attempted on the basis of the differences of the acid-base properties of the 6,7-DHC molecule in its ground and excited singlet state. For this purpose the pK_a's and pK_a^x's values have been calculated. It has been stated that in the excited state the phototautomer form is very unlikely.

1. Introduction

Coumarin derivatives are of great interest in view of their intense fluorescence and exellent laser properties [1—10].

Some of them have been studied for possible phototautomer structures [2, 4, 8, 11—14]. It has been found that the essential factors enabling phototautomerism are water as a solvent component and a free hydroxyl group in position 7 (Fig. 1) [8, 14—16]. Wolfbeis has also found that the occurrence of phototautomerism depends on the steric and electronic properties of the substituents in position 3 and 4 of the umbelliferone [17—19].

It was deemed interesting to investigate the influence of an additional hydroxyl group situated in the immediate vicinity of position 7 of the substituted OH group responsible for the phototautomerism of the umbelliferone (7-hydroxycoumarin). Contrary to other hydroxycoumarines, 6,7-dihydroxycoumarin (6,7-DHC) has received little attention so far [8], in particular its the exact and full acidity dependence in aqueous solution has not been reported up to now. According to their two OH groups and two oxygen atoms (Fig. 1) the electronic spectra of 6,7-DHC ought to be pH-dependent.
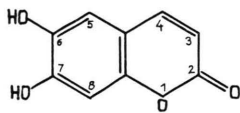

Fig. 1. Chemical structures of 6,7-dihydroxycoumarin.

The aim of the present paper was to examine the existence of the species of 6,7-DHC in aqueous solution in several pH-intervals as well as possible phototautomerism in the excited state.

2. Experimental

6,7-DHC (pro analysi) was obtained from the Eastman Kodak Company and used without further purification. An aqueous solution of 6,7-DHC $(5 \cdot 10^{-4}$ M) was prepared using bidistilled water and adding buffers after Britton and Robinson. The pH-values were measured with a Meratronik N 517 pH-meter.

Absorption measurements were made using a Zeiss Specord UV-VIS spectrophotometer, and fluorescence spectra were obtained by the experimental arrangement described in [20] with an RCA 5819 photomultiplier in lock-in system. The samples were excited with a XHP-150 Xenon lamp and a Zeiss SPM-1 monochromator at 355 nm. A quartz cell of 1 mm thickness was used. All samples were stored in darkness.

3. Results of Measurements

Figures 2—4 show the absorption and emission spectra of 6,7-DHC in aqueous solution in the pH-range $1.5 < \mathrm{pH} < 11.8$ at room temperature, measured immediately after the preparation of the samples. The emission spectra are normalized to unity.

With increasing pH the maximum of the absorption shifts regularly towards longer wave lengths from $\lambda_{\max}^a = 345$ nm for pH 1.5 to $\lambda_{\max}^a =$
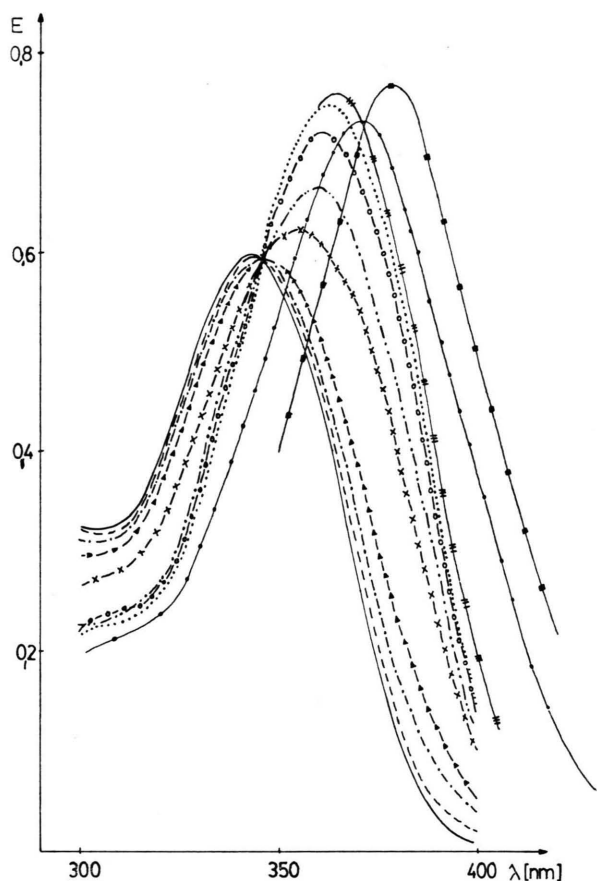
Fig. 2. Absorption spectra of 6,7-DHC at various pH: —— pH 2—3; ----- pH 4; —●—●— pH 4.5; —▲— pH 5; —×— pH 5.5; —··— pH 6; —○— pH 6.5; ········ pH 7; —|||— pH 8; —●— pH 10.5; —■— pH 11.
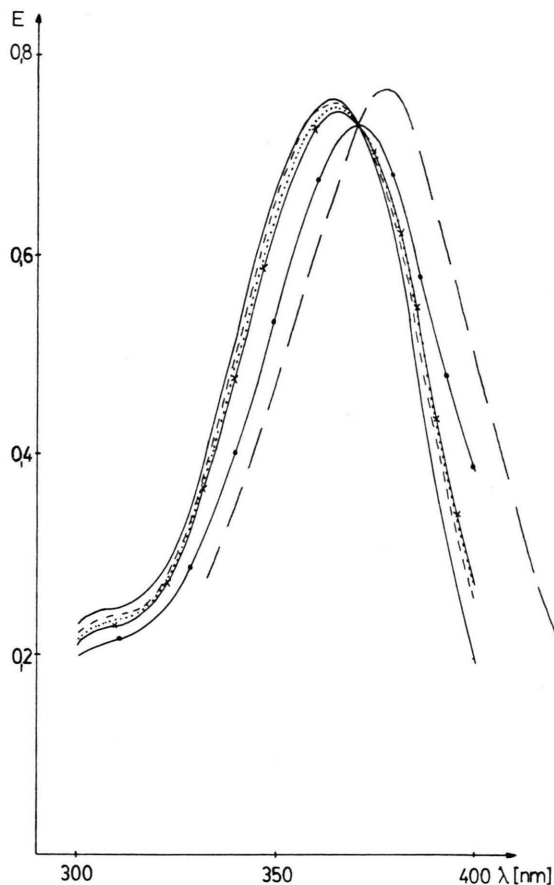

Fig. 3. Absorption spectra of 6,7-DHC in the interval of pH between 8 and 11, —— pH 8; ----- pH 8.5; ········ pH 9; —×— pH 10; —●— pH 10.5; —— pH 11.
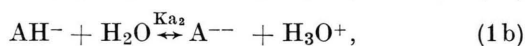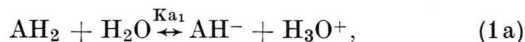
390 nm for pH 11.8. Two isosbestic points are observed at $\lambda_1^i = 347$ nm and $\lambda_2^i = 376$ nm.

On the other hand, the emission spectra (Fig. 4) depend only slightly on the pH-value of the solution. The emission maximum also shifts towards longer wave lengths, but only by about $\Delta\lambda_{max}^e = 15$ nm (from $\lambda_{max}^e = 460$ nm for 1.5 to $\lambda_{max}^e = 475$ nm for pH 11.8), moreover, the character of the shift is irregular: the spectra shift in the range $1.5 < \text{pH} < 6.5$ only, whereas for pH > 7 they remain practically unshifted.

It should be mentioned that in strongly alkaline solutions the 6,7-DHC molecule is unstable: the long wave absorption band diminishes with time after the preparation of the solution (Fig. 5); this is probably due to the ring opening in the 6,7-DHC molecule.

4. Discussion

The analysis of the absorption spectra (Fig. 2, 3), e.g. the shifts of the absorption maximum with increasing pH-values and the existence of two isosbestic points, leads to the conclusion that in the investigated pH-range three species of 6,7-DHC occur at equilibrium in their ground state: neutral, anion and dianion. On the assumption that according to the structure of the 6,7-DHC molecule (Fig. 1) the general reactions in aqueous solutions may be considered as

$$\mathrm{AH_2 + H_2O \overset{Ka_1}{\leftrightarrow} AH^- + H_3O^+}, \qquad (1\,a)$$

$$\mathrm{AH^- + H_2O \overset{Ka_2}{\leftrightarrow} A^{--} + H_3O^+}, \qquad (1\,b)$$

$\mathrm{AH_2}$-neutral molecule; $\mathrm{AH^-}$-anion; $\mathrm{A^{--}}$-dianion. Ka_1, Ka_2 denote chemical equilibrium constants.
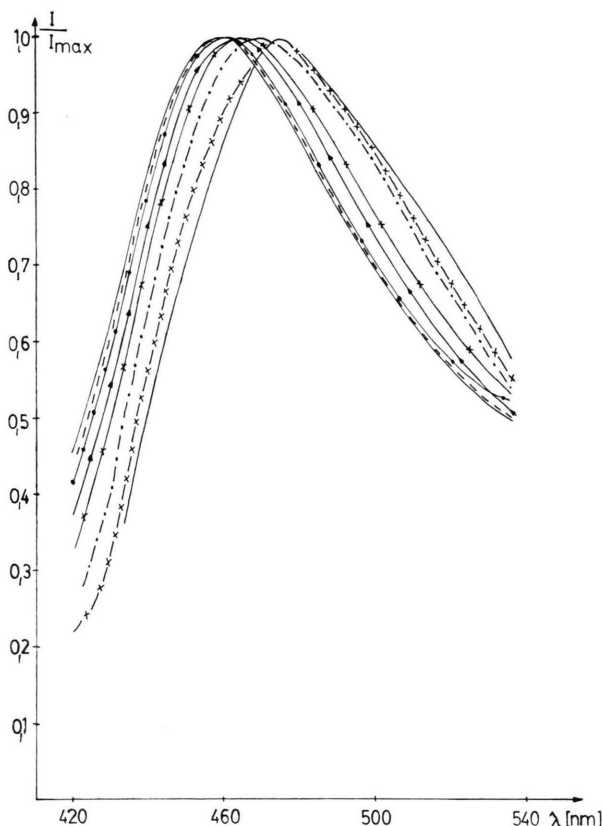
Fig. 4. Emission spectra of 6,7-DHC at various pH.
———— pH 2; – – – – pH 2.5; —●— pH 3; —▲— pH 3.5;
—×— pH 4; —●— pH 5; —×— pH 6; ———— pH $\geqq$ 7.

The acid-base properties of the 6,7-DHC molecule in the system with water are due to protolytic
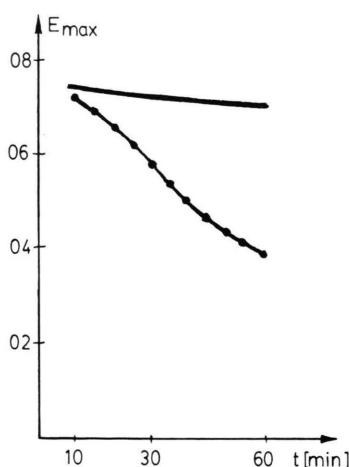

Fig. 5. Decrease in time of the extinction maximum of 6,7-DHC in aqueous solution. Curves for pH 11 ———— and for pH 11.8 —●—.

reactions. For that reason we use the Brönsted definition for acidity and basicity. In our case of dilute solutions, the acid-base equilibrium constant Ka is given by the respective concentrations:

$$K_a = c_A\, c_{H_3O^+}/c_{AH}. \qquad (2)$$

The acidity and basicity of the compound are commonly expressed by $p\,K_a$ values which, using the spectroscopic method, can be obtained on the basis of (1) from the relation

$$p\,K_a = pH - \log\{(E - E_{AH})/(E_A - E)\} \quad (3)$$

for a given wavelength λ. E_{AH}, E_A are the extinctions (optical densities) of the respective pure form, and E is the extinction for a solution measured at the pH-value given in (2) (mixture of both forms).

The analysis of the absorption spectra allows us to assume the existence of only one pure form in the vicinity of the pH values: 2–3; 7.5–8.5; 10.9–11.8; since near these values the absorption spectra do not change.

The mean $p\,K_a$ value calculated from (3) for the wavelengths: 330, 360, 370 and graphicly for 380 nm amounts to 5.4 ± 0.1.
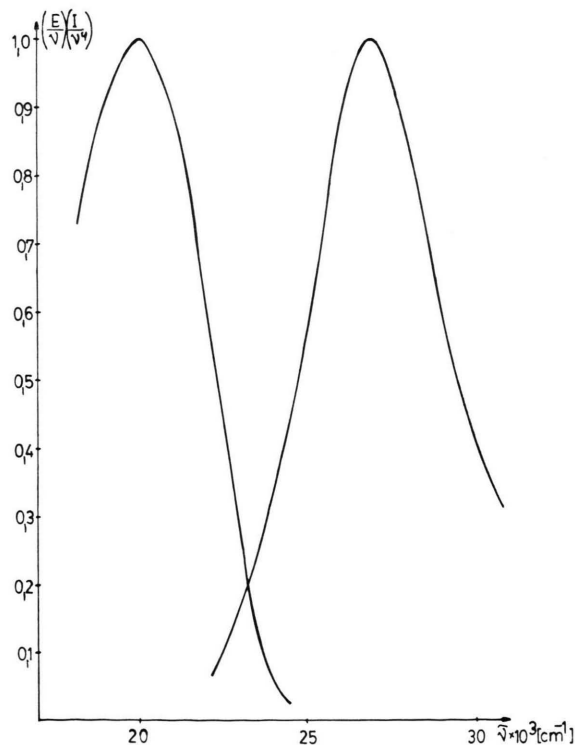

Fig. 6. Emission $I(\nu)/\nu^4$ and absorption $E(\nu)/\nu$ spectra of 6,7-DHC for pH 10.5 (normalized to unity) versus $\tilde{\nu}$.

There is no doubt that in the system 6.7-DHC-water the difference in behaviour of the absorption and emission spectra in dependence of the pH-value of the solution is due to the differences of the acid-base properties of the 6,7-DHC molecule in its ground and excited singlet states.

In order to recognize the differences in acidity of the 6,7-DHC molecule in its ground and excited singlet state the acid-base equilibrium constant of the first excited singlet state $p\mathrm{K_a^\times}$ must be known. Using the so called Förster cycle, $p\mathrm{K_a^\times}$ was calculated at 295 K from the Weller equation [21]

$$p\mathrm{K_a^\times} = p\mathrm{K_a} - 2.1 \cdot 10^{-3} \Delta\tilde{\nu} \qquad (4)$$

with $\Delta\nu = \tilde{\nu}_{\mathrm{AH}}^{00} - \tilde{\nu}_{\mathrm{A}}^{00}$, where $\tilde{\nu}_{\mathrm{AH}}^{00}$, $\tilde{\nu}_{\mathrm{A}}^{00}$ denote the wave numbers corresponding to the 0–0 transitions in the AH and A species, respectively. The 0–0 transitions have been obtained from the intersec-

tion point of the curves $I(\nu)/\nu^4$ and $E(\nu)/\nu$ of the required species (Figure 6). The resulting values amount to $p\mathrm{K_{a_1}^\times} = 2.15 \pm 0.15$ and $p\mathrm{K_{a_2}^\times} = 7.7 \pm 0.2$.

Comparing the $p\mathrm{K_a}$ and $p\mathrm{K_a^+}$ values we can state that the 6,7-DHC molecule becomes much more acidic at the hydroxyl group in its excited state. It is clear now why we have found from the emission spectra only two species in the investigated range of pH, namely anion and dianion.

On the other hand, the existence of the phototautomer form in the excited state is very unlikely, because we have not observed a characteristic unusual Stoke's shift of the emission band, as we did for umbelliferone [20].

Acknowledgement

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