

FLUORESCENCE SPECTRA OF 3-AMINOCOUMARIN AND ITS ACID-BASE BEHAVIOUR IN THE EXCITED SINGLET STATE

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Summary

The fluorescence spectra of 3-aminocoumarin in rigid glass media at 77 K are reported. The study of the effect of pH on the fluorescence data indicates the presence of three different cations of 3-aminocoumarin in aqueous acidic solutions. The quantum yields for various cations are found to be very low. The acidity constants for the various prototropic equilibria of the dissociation reaction in solution are evaluated.

1. Introduction

Coumarin is widely distributed in nature and some of its derivatives are of importance in chemistry and medicine [1]. The prototropic behaviour of methyl-, hydroxy- and phenyl-substituted coumarins is well documented in the literature [1 - 7]. Many coumarins are markedly fluorescent and are useful as fluorescent indicators and as laser-dye solutions [3 - 7]. Coumarin, however, is reported to be non-fluorescent [1, 8] over a wide range of pH. Recently we have reported the acid-base behaviour of some carbocyclic [9, 10] and heterocyclic [11 - 13] amines. As a continuation of the above study we observed that 3-aminocoumarin (AC) is non-fluorescent, similar to the parent coumarin at 298 K. The prototropic equilibria of AC has now been detected by absorption and fluorescence spectroscopy and the acidity constants for the different equilibria have been determined. In addition, the fluorescence spectra of AC in rigid glass media at 77 K are also presented.

2. Experimental details

AC (ICN Pharmaceuticals) was recrystallized twice from hot water. Its purity was further checked by obtaining the same fluorescence maximum with different excitation wavelengths. Cyclohexane (BDH) and ether (Merck) were purified by standard methods [14]. Spectroscopy grade methanol (BDH) was used as received. Analytical grade sulphuric acid and sodium

hydroxide (both BDH) and triply distilled water were used for the preparation of solutions of different acidities. Solutions of high acid concentration were prepared using Jorgenson's method [15] and the pH measurements were made using a model CL-44A Toshniwal pH meter.

The absorption spectra were recorded using a Shimadzu UV-190 spectrophotometer and the fluorescence spectra using a laboratory-made scanning fluorometer [16]. Isosbestic wavelengths were chosen for excitation in fluorometric titration. The spectra at 77 K were recorded using an Aminco-Bowman low temperature accessory in our fluorometer. The fluorescence spectra were corrected, and quantum yields and pK_a values were determined as mentioned in our previous papers [10 - 13].

3. Results and discussion

The absorption and fluorescence maxima of AC in various solvents are compiled in Table 1. The data indicate that all the absorption bands are

TABLE 1

Absorption and fluorescence maxima of the prototropic species of 3-aminocoumarin at 298 K

<i>Species</i>	<i>Solvent or pH or H_0</i>	λ_a^a (nm) ($\epsilon(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$)	λ_f^b (ϕ_f)
Neutral	Cyclohexane	319 (4.29)	378 (0.04)
		241 (3.78)	
		210 (4.35)	
Neutral	Ether	321 (4.31)	380 (0.01)
		238 (3.77)	
		213 (4.16)	
Neutral	Acetonitrile	322 (4.14)	—
		242 (3.63)	
		203 (4.38)	
Neutral	Methanol	324 (4.14)	—
		244 (3.65)	
		204 (4.35)	
Neutral	pH 6	322 (4.03)	—
		241 (3.56)	
		201 (4.40)	
Monovalent	$H_0 = -3$	307 (3.88) s	401 (0.05)
		282 (4.04)	
		198 (4.39)	
Divalent	$H_0 = -7$	325 (3.63) s	462 (0.09)
		294 (4.05)	
		194 (4.46)	
Trivalent cation	$H_0 = -10$	—	477 (0.10)

^as, shoulder.

^bValues at 77 K are given in parentheses.

slightly red shifted in polar solvents in comparison with cyclohexane. In water, however, the band maxima are slightly blue shifted in relation to methanol, but red shifted with respect to cyclohexane. The molecule is non-fluorescent in polar solvents and the fluorescence intensity is much less in ether. A red shift in the fluorescence maximum, similar to that in the absorption maximum, is noticed in going from cyclohexane to ether. In coumarins [1 - 5] the longest wavelength transition is established to be $\pi \rightarrow \pi^*$. The data of AC also confirm this and indicate that dispersive interactions of AC are very important in all the solvents, except water, where AC may also act as a proton acceptor. The non-fluorescent nature of the neutral AC in polar solvents may be due to the greater rate of non-radiative processes than the radiative processes. At 77 K, AC is found to exhibit fluorescence with a fluorescence maximum at 388 nm and the fluorescence is similar to that obtained in cyclohexane and ether at 298 K. The fluorescence spectra of the neutral AC in different solvents are recorded in Fig. 1.

The blue shift followed by the red shift in the absorption spectra of AC in acid solutions indicates that the monovalent cation is formed by protonation on the amino group and the divalent cation by protonation on the carbonyl group, similar to that reported on other compounds containing amino [7 - 13] and carbonyl [17] groups. The absorption and fluorescence maxima of the prototropic forms of AC are recorded in Table 1.

The fluorescence data also indicate that similar prototropism occurs in the excited singlet state. The fluorescence spectra with a band maximum at 401 nm in solutions from $H_0 = -1$ to $H_0 = -5$ resemble the spectrum of the parent molecule [1] and confirm the formation of the monovalent cation. The monovalent cation has a fluorescence maximum of 380 nm at 77 K. The large blue shift (about 20 nm), compared with that at 298 K, is expected because of the minimum of solvent relaxation at low temperature. In such a case, if the neutral AC fluoresces at all, its maximum is expected to be at a wavelength longer than 401 nm at 298 K, which is reasonable as the amino

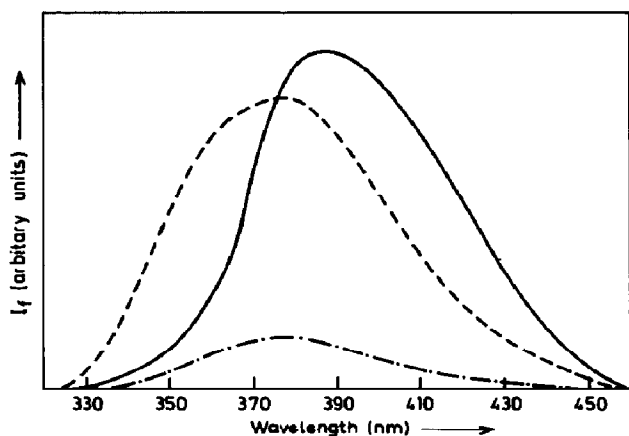


Fig. 1. Fluorescence spectra of the neutral AC: — — —, in cyclohexane at 298 K; — · —, in ether at 298 K; —, in water at 77 K.

substituent will shift the transition of the parent coumarin to the lower energy region. The blue shift in the fluorescence maximum observed in going from the neutral AC to its monovalent cation at 77 K is consistent with the change observed in the absorption spectra at 298 K.

The fluorescence maximum of 462 nm in high acid concentrations is also due to the formation of the divalent cation, as the protonation on the carbonyl group will lead to a red shift in the fluorescence maximum. A further red shift, observed in the fluorescence spectra at $H_0 = -10$, is due to the formation of the trivalent cation. The protonation could be on the carbon centre of the carbocyclic ring, analogous to the protonation in the benzene ring [18]. The fluorescence spectra of the different cations are recorded in Fig. 2.

A scheme for the acid-base equilibria of AC in aqueous solutions is illustrated in Fig. 3. The acidity constants in the ground state are calculated by absorptiometric titration and are recorded in Table 2. The values are 1.0 and -6.0 , for the equilibria between the monovalent cation and the neutral molecule and between the divalent cation and the monovalent cation respectively.

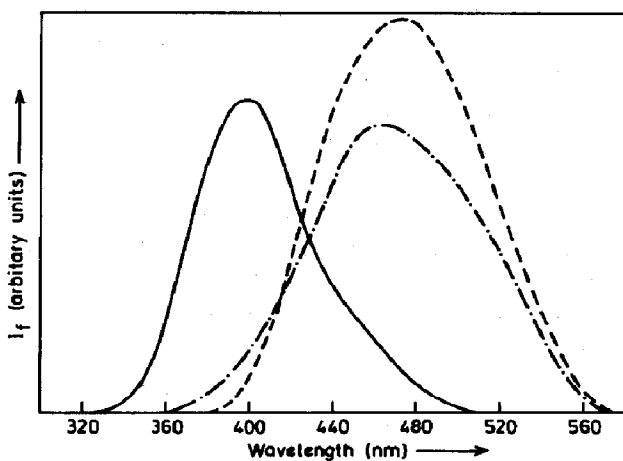


Fig. 2. Fluorescence spectra of the cations of AC at 298 K: —, monovalent; - - -, divalent; - · -, trivalent.

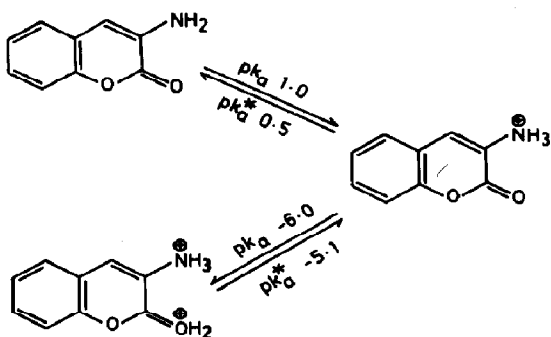


Fig. 3. Scheme for the acid-base equilibria of AC.

TABLE 2

pK_a values for the various prototropic equilibria of 3-aminocoumarin in the ground and excited singlet states

Equilibrium	$pK_a(S_0)^a$	$pK_a(S_1)^b$	$pK_a(S_1)^c$	$pK_a(S_1)^d$
Trivalent cation to divalent cation	—	—	1.43 ^e	—
Divalent cation to monovalent cation	-6.0	-2.21	0.91	-5.1
Monovalent cation to neutral molecule	1.0	-2.19	-0.14 ^f	0.5

S_0 , ground state; S_1 , excited singlet state.

^aSpectrophotometric titration.

^bFörster cycle method using absorption data.

^cUsing fluorescence data.

^dFluorometric titration.

^e ΔpK_a .

^fFrom the data at 77 K.

The pK_a values for the respective equilibria in the excited singlet state, calculated from the fluorometric titration curves of Fig. 4, are 0.5 and -5.1. The pK_a values for the equilibrium between the monovalent cation and neutral AC are less compared with such equilibria of other amines [9 - 13] owing to the presence of an electron-withdrawing substituent at the ortho position.

Although there is a trend indicating that the amino group becomes less basic and the carbonyl group less acidic on excitation, the difference in the

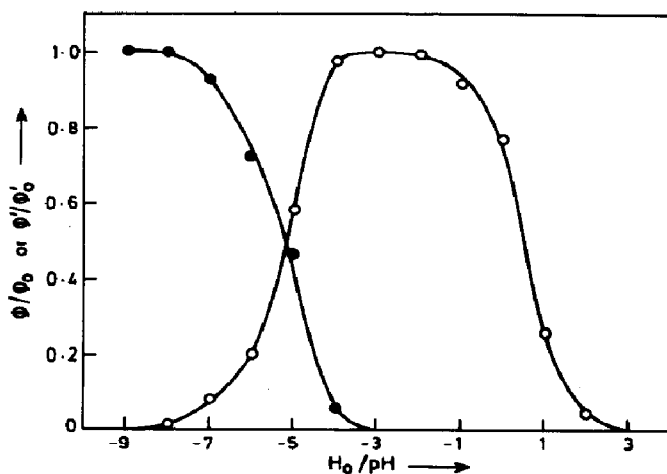


Fig. 4. Plot of ϕ/ϕ_0 or ϕ'/ϕ_0' vs. H_0 or pH. 300 nm and 320 nm are used as λ_{ex} for the equilibria between the monovalent cation and the neutral molecule (pH 10 to $H_0 = -3$) and between the divalent cation and the monovalent cation ($H_0 = -2$ to $H_0 = -9$) respectively.

basicity of both groups in the ground and excited singlet states is not that large, as is normally observed in other similar aromatic compounds [9 - 11, 17]. In reality the pK_a values in the excited singlet state are closer to the ground state values, indicating that the lifetimes of the species are very short and that the prototropic equilibria are not well established in the excited singlet state.

The pK_a values calculated with the help of the Förster cycle method [19, 20] using the spectral data are also listed in Table 2. These values also indicate the normal trend reported for similar molecules. The difference between the values obtained using the absorption and fluorescence data is due to the difference in the solvent relaxation of the species in the two states, as well as to the fact that the band maximum is used instead of the 0-0 transition. The acidity constant for the formation of the trivalent cation cannot be calculated because no change is noticed in the absorption spectra even at $H_0 = -10$. However, this does suggest that the pK_a value is less than -10 . The high acidity associated with the protonation of the carbon centre of AC compared with that of benzene is due to the presence of the positive charge on the molecule. Although the trivalent cation is indicated by the fluorescence spectra, the pK_a values in the excited singlet state cannot be determined as the change is observed only at $H_0 = -10$, the highest acid concentration studied. However, the ΔpK_a values (the difference in the pK_a values between the excited singlet and ground states) obtained by Förster's method using the fluorescence data do indicate that the carbon centre becomes more basic on excitation, similarly to previously reported results [13].

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