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Excitation Wavelength Dependent Fluorescence Anisotropy of Quinine Sulphate Doped in PVA Film

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Abstract

An increase in anisotropy in the fluorescence emission of Quinine sulphate dication (QSD) doped in Polyvinyl alcohol is observed on increasing excitation wavelength in the range of first excited absorption band. The dependence of anisotropy is nonlinear. Orientational micro environmental effects are supposed to be responsible for the observed changes in anisotropy.

Keywords: Fluorescence anisotropy; polymers; excitation wavelength dependence.

Introduction

Fluorescence anisotropy measurements are useful in the study of orientation and molecular dynamics in polymer films and fibers [1, 2]. Such studies render important information about the conformational changes at the microstructural level surrounding the doped fluorescent molecule in the polymer. The photophysics of Quinine sulphate has been extensively studied because of its use as a standard for quantum yield measurements [3-5].Quinine sulphate is present as dication (QSD) in 0.1N H_2SO_4[3,4] Earlier workers have reported that QSD is enveloped by various geometrical configurations in polymeric media as well as in frozen glasses. Its fluorescence characteristics are sensitive to micro environmental polarity and free volume of the polymer matrix. Edge excitation red shift and the corresponding increase in the life time are the main features reported earlier [3, 5].

Earlier Anisotropy studies have shown that 0.1N H_2SO_4 aqueous solution of Quinine sulphate shows no polarisation in the entire emission range [7, 8]. However, in thin films a concentration depolarisation has been reported [6]. In the present work fluorescence anisotropy study of Quinine sulphate dication in polyvinyl alcohol films has been carried out. The excitation wavelength dependence of fluorescence anisotropy has been investigated in detail.

Experimental

Polyvinyl alcohol films doped with Quinine sulphate were prepared by adding one ml of 0.1N H_2SO_4, Quinine sulphate solution (10^{-4}M) to 1gm PVA and dissolving the mixture in added water. The solutions were heated at 70°C for a long time and films were prepared by caste method. Polymer films of thickness approximately 0.3 mm were obtained. They were cut to rectangular size to fit into the sample compartment .The excitation and emission spectra were recorded with the help of Perkin Elmer model LS55 spectrofluorimeter mounted with excitation and emission polarisers. Absorption spectra were recorded with the help of Perkin Elmer Lambda 35 model spectrophotometer. Fluorescence intensities were measured parallel and perpendicular to the direction of polarised excitation light. Four relative intensities of polarised fluorescence viz. I_{VV},I_{VH}, I_{HV} and I_{HH} were recorded where I refers to the peak intensity, the first subscript refers to the direction of polarisation of the excitation polarizer (V-vertical, H-horizontal) and the second subscript refers to the direction of the emission polariser. The emission anisotropy 'r' has been determined by the expression [8, 9].

$$r = \frac{I_{VV} - I_{VH}}{I_{VV} + 2I_{VH}}$$

In order to eliminate the effect of the dependence of exciting light on the state of polarisation (the transmission efficiency of monochromator depends on polarisation of light) a correcting factor.

$$G = \frac{I_{VH}}{I_H}$$

is applied and the resulting expression

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}}$$

has been used to determine the anisotropy.

Results and discussion

Absorption and emission spectra of Quinine sulphate 0.1N H_2SO_4 and PVA films doped with these solutions are shown in Figure 1& 2. In the PVA film containing 0.1N H_2SO_4 Quinine sulphate solution the 0-0 absorption band lies at 346.6nm which is nearly at the same position corresponding to 0.1N H_2SO_4 Quinine sulphate solution. This lies at 348.9 nm. The emission peaks for 0.1NH_2SO_4 solution and corresponding PVA film lie at 446.3 nm and 437.9nm respectively. All these measurements correspond to unpolarised light. These observations clearly show that in 0.1 N H_2SO_4 and its polymer film Quinine sulphate is present as dication as evidenced by earlier observations [5, 6]. QSD exhibits red edge excitation effect in solutions and polymer films. Similar results have been observed in the present investigation. The emission peaks slightly differ in position depending on state of polarisations of excitation and emission monoochromators. The results are given in table 1.

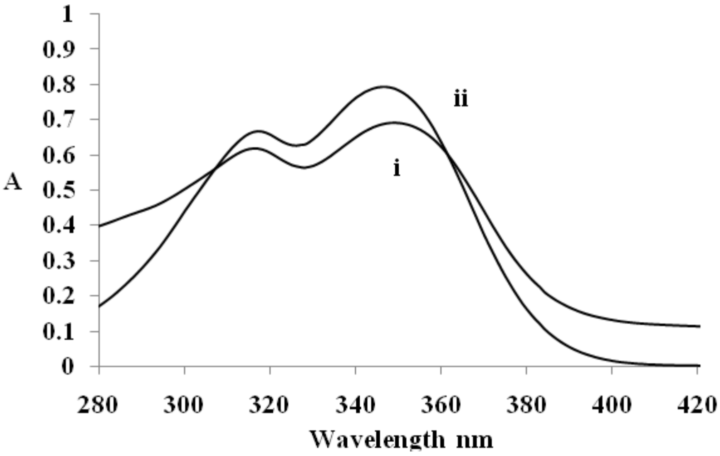

Fig. 1. Absorption spectra of Quinine sulphate in (i) 0.1 N H_2SO_4 (ii) in PVA.

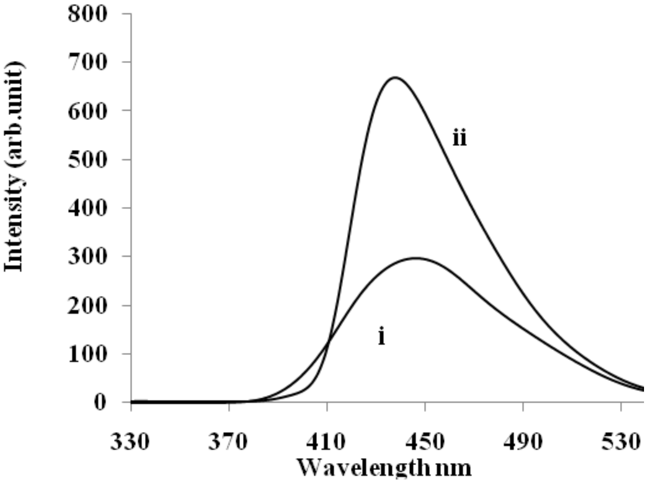

Fig. 2. Emission spectra of Quinine sulphate in (i) 0.1 N H_2SO_4 (ii) in PVA.

Table.1. Positions of emission maxima for QSD in PVA and 0.1N H_2SO_4 for different polariser and analyzer positions.

λ (nm)	PVA(0.1 N H_2S0_4)				0.1 N H_2S0_4			
	λ_{HH}	λ_{VV}	λ_{HV}	λ_{VH}	λ_{HH}	λ_{VV}	λ_{HV}	λ_{VH}
300	438.1	440.5	439.8	438.6	446.7	451.0	451.3	446.1
310	438.5	441.8	439.9	438.4	446.2	451.4	451.2	446.5
330	438.4	439.7	440.2	438.7	446.0	451.0	450.7	445.9
340	438.3	440.1	440.2	438.6	446.2	450.7	450.6	445.9

350	438.4	439.3	440.1	438.4	446.5	451.1	450.5	446.6
360	440.6	442.8	443.5	441.0	447.7	451.8	491.9	447.8
370	440.5	442.0	442.9	440.6	448.9	453.1	453.1	449.4
380	440.4	442.5	443.8	440.8	451.2	455.1	455.3	450.9
390	441.0	443.2	444.3	441.7	453.2	456.9	456.8	454.0
400	442.2	446.1	444.0	442.8	455.4	457.9	458.0	455.2

Figure 3 shows graphs between fluorescence anisotropy vs excitation wavelength for .1NH_2SO_4. Quinine sulphate and its film in PVA. In 0.1N H_2SO_4 solution the anisotropy is very close to zero throughout the range of excitation from 300nm to 400nm. This is an expected observation as QSD solutions are taken as standards to check the accuracy of the anisotropy experiments [8]. On the other hand, the anisotropy for QSD in PVA is different from zero on excitation at 300nm and increase continuously as the excitation wavelength is increased. The behavior of increase in anisotropy in nonlinear. The above observations can be briefed as (i) there is a general red shift in the emission maximum when excited at the red edge 0 the 0-0 absorption band and (ii) polarisation of the emission in the PVA films and its increase with the excitation wavelength. The edge exaction red shift in Quinine sulphate is well known and is attributed to various geometrical configurations in polymeric media [6]. This may give rise to various orientations of the fluophor with respect the polymer microenviroment.

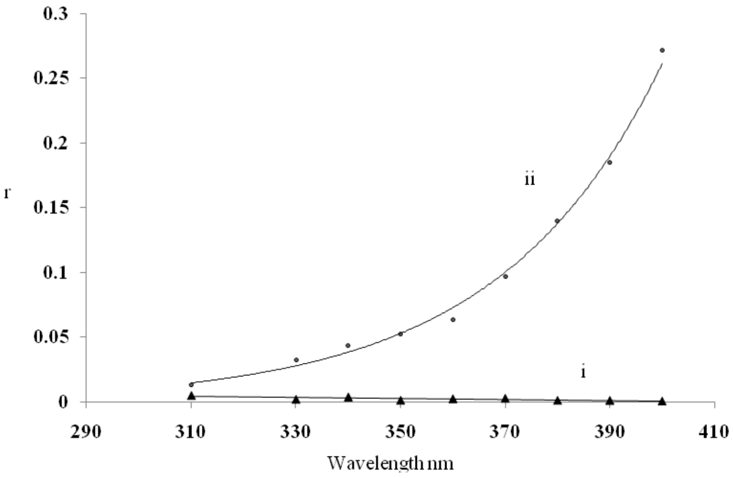

Fig.3 Anisotropy of (i) 0.1n H_2SO_4 Quinine sulphate solution and (ii) in PVA vs excitation wavelength.

At shorter wavelength majority of the molecules having all the possible types of orientations participate in the process of absorption and therefore the emission also corresponds to molecules with all possible orientations. The emission peak corresponding to such environment is due to the ensemble of all types of possible orientations and the resulting emission is unpolarised. However, at longer wavelengths, particularly at the red edge of the 0-0 band, the absorption and emission corresponds to the molecules with selective orientations. This leads to the red shift in the position of the emission peak. The fluorescence of such molecules with selective orientations will show anisotropy which should increase corresponding to excitation very close to the red edge. A correlation between the edge excitation red shift and increase in the lifetime has been reported earlier [6]. The results of the anisotropy studies in the present work also provide evidence of the microenvironmental structures in polymer matrices. Studies of correlation between the anisotropy and the microenvironmental can lead to important information about polymer micro structure.

Conclusion

Quinine sulphate dication (QSD) doped in polyvinyl alcohol shows a nonlinear increase in fluorescence anisotropy with increasing excitation wavelength. A red shift in the emission peak with excitation wavelength has also been observed. The possible explanation to this is the presence of various geometrical configurations in the polymeric media. Study of fluorescence anisotropy measurements in polymeric media doped with Quinine sulphate can play important role in their conformational analysis.

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References

[1] J R Ebdon, B J Hunt, D M Lucar, I Soutar and L S Wauson Com .J.Chem.73 1995(1982)
[2] M A Wannik et,al Photophysical and Photochemical in Polymer Science, conference dynamics. Morpliscopy reidd (1982)
[3] P Gangola, N B Joshi and D D Pant, Chemical Physics Letters, 51 144(1977)
[4] D Pant, U C Tripathi, G C Joshi, H B Tripathi and D D Pant, J. Photochemistry, Photobiology. A Chemistry 51 313(1990)
[5] H C Joshi, A Upadhyaya, H Misra, H B Tripathi, and D D Pant; J. Photochemistry, Photobiology. A Chemistry 122185 (1999)
[6] H Misra, D Pant, T C Pant and H B Tripathi, J. Photochemistry, Photobiology. A Chemistry 177 197(2006)
[7] R F Chan, G G Vurek and N Abxander. Science 156 949(1967)
[8] H Suzuki, M Obara, K Kubo and T Kanazawa.J. Biol.Chem.264 920(1989)
[9] B Valeur. Molecular fluorescence, Principles and application, Wiley VCH Verlag GmbH 3(2001)