



Excitation wavelength dependence of emission spectra of polymer films doped with 2-naphthol

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Abstract

The excitation wavelength dependence of emission spectra for the aqueous solution and films of Polymethyl methacrylate (PMMA), Polyvinyl alcohol (PVA) and Polyvinyl acetate (PVAc) doped with 2-naphthol has been studied. It is observed that while for PVA and PVAc films the absorption and emission spectra of 2-naphthol are similar to the corresponding spectrum of 2-naphthol in water. But for PMMA while the absorption spectrum is as similar to absorption spectrum in other polymers and water the emission spectrum differs considerably. Such a difference has been explained on the basis of one to one binding of 2-naphthol with PMMA molecules. The observed excitation wavelength dependence of the emission spectrum is attributed to different conformations present in the polymer matrix.

Keywords: 2-naphthol, PMMA, PVA, PVAc.

Introduction

Polymers doped with fluorescent molecules are being widely investigated because of their numerous applications in science and technology^{1,2}. Polymers doped with fluorescent molecules are used in pigment intensity light emitting diodes, for making spectrally selective surface to increase the efficiency of solar photovoltaic cells and photo thermal concentrations applied switches etc. One of the important applications of doping organic molecules in to a polymer is to study the polymer conformation at the micro level^{3,4}. The absorption, excitation and fluorescence spectra of these organic molecules are dependent upon the polymer composition and the micro environment surrounding the fluophore⁵. The second important application is that the polymers doped with organic fluorescence can be used as pH, humidity, and pressure sensors⁶⁻⁸. They can also be used to ascertain the photo stability of the doped polymers⁹⁻¹³. In the present study absorption and emission spectra of 2-naphthol doped in the aqueous solution and PMMA, PVA and PVAc films has been made. The excitation wavelength dependence of emission of these thin films has also been investigated.

Materials and methods

2-naphthol was procured from Sigma Chemicals (USA) and was used as received without further purification. Films of Polymethyl methacrylate (PMMA), doped with 2-naphthol were prepared by dissolving 1gm of PMMA grains in chloroform. The Polyvinyl alcohol (PVA) films were prepared by dissolving PVA (1gm) in water (double distilled) and Polyvinyl acetate (PVAc) films were prepared by dissolving PVAc (1gm) in

toluene. The solvents chloroform and toluene were used of spectroscopic grade (procured from Merck India Ltd.) and the desired concentration of 2-naphthol was taken 10^{-4} M for experimental purpose. The solutions were kept on flat polypropylene dish and were dried for several hours till the polymers in the form of films of uniform thickness were obtained. The average thickness, measured with the help of screw gauge, was found to be between 0.25mm. The films were cut to the size to fit into the Perkin-elimer, Lambda-35UV-Visible spectrometer and Perkin-elimer LS- 55 fluorescence spectrometer to record absorption and fluorescence spectra respectively.

Results and discussions

Absorption Spectra: Absorption spectra of 2-naphthol in water, PMMA, PVA and PVAc films doped with 2-naphthol (conc. 10^{-4} M) are shown in Figures 1(a), 1(b), 1(c) and 1(d) respectively.

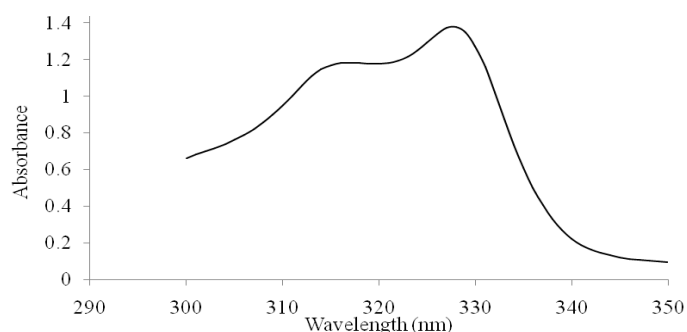


Figure-1a: Absorption spectra of 2-naphthol (10^{-4} M/l) in water.

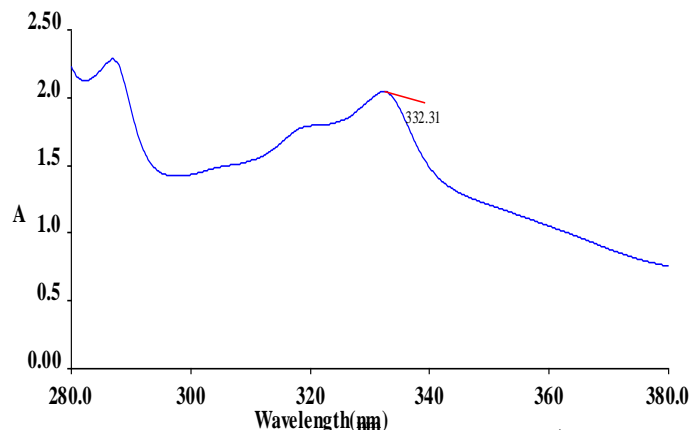


Figure-1b: Absorption spectrum of 2-naphthol (10^{-4} M/l) doped in PMMA.

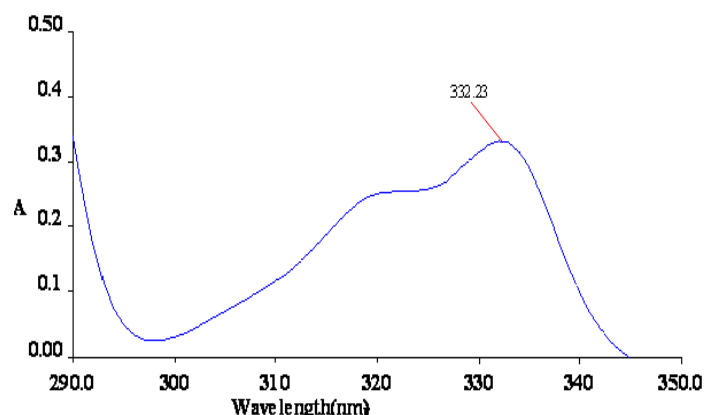


Figure-1c: Absorption spectra of 2-naphthol (10^{-4} M/l) doped in PVA.

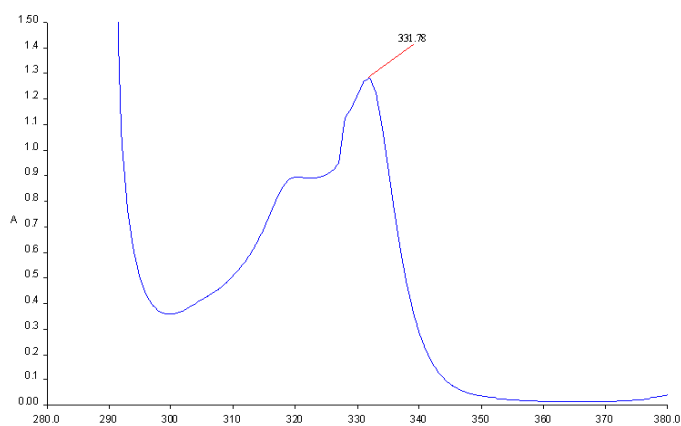


Figure-1d: Absorption spectra of 2-naphthol (10^{-4} M/l) doped in PVAc.

The general nature of the spectra is indicative of the fact that in polymer film 2-naphthol is the absorbing species and there are no signs of naphtholate ion being present. In some experiments carried out by adjusting the pH of the 2-naphthol PMMA solution and then drying it is change has been observed in absorption spectra.

It is observed from the absorption spectra that the absorption peak corresponding to 0-0 band lies at 327.8nm in 2-naphthol water; the 0-0 band is red shifted in polymers; the positions of 0-0 absorption band for PMMA, PVA and PVAc are at 332.31nm, 332.23nm and 331.78nm respectively. This small red shift in the absorption corresponds to the interaction between the polymer matrix and the corresponding fluorophore.

Emission Spectra: The emission spectra of 2-naphthol in water, PMMA, PVA and PVAc are shown in Figure 2(a), 2(b), 2(c) and 2(d) respectively. The emission spectra have been recorded for different wavelengths of excitation viz. 260, 280, 300, and 320nm respectively. In water the peak corresponding of 2-naphthol emission is at 354.20nm corresponding to excitation at 260nm and there is no excitation wavelength dependence in the emission spectra. Similar observations have been obtained for 2-naphthol PVA and 2-naphthol PVAc films (Figure 2(c) and 2(d)). However, the emission peaks lie at 359.2nm and 358.4 nm for PVA and PVAc films respectively.

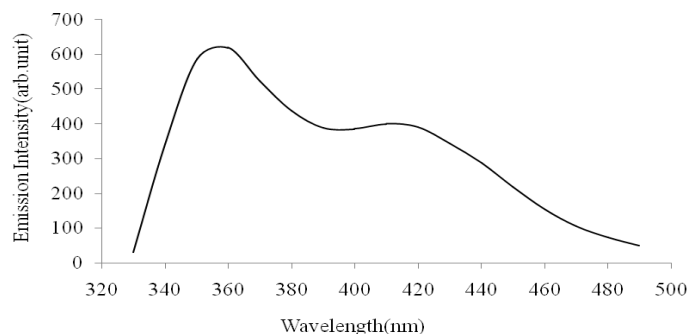


Figure-2a: Emission spectrum of 2-naphthol in water (pH=5).

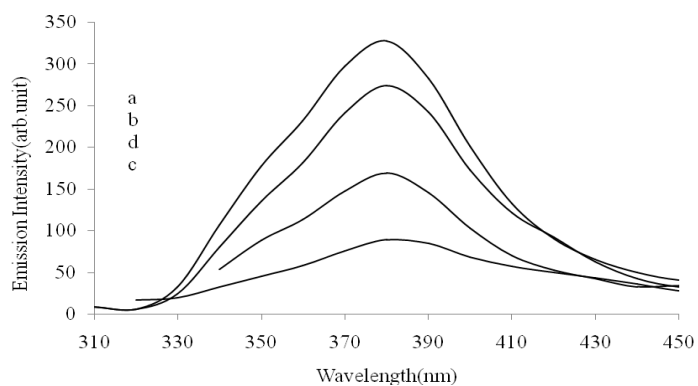


Figure-2b: Emission spectra of 2-naphthol doped in PMMA for λ (excitation) (a)260nm (b)280nm, (c) 300nm and(d)320nm.

The emission spectra of 2-naphthol in PMMA however, shows a marked difference from the corresponding spectra in water, PVA and PVAc. The main differences are: i. Marked red shift is observed in the emission peak in 24nm. ii. A shoulder appears approximately at 354.2nm. iii. There is a red shift in the emission peak corresponding to excitation at longer wavelengths.

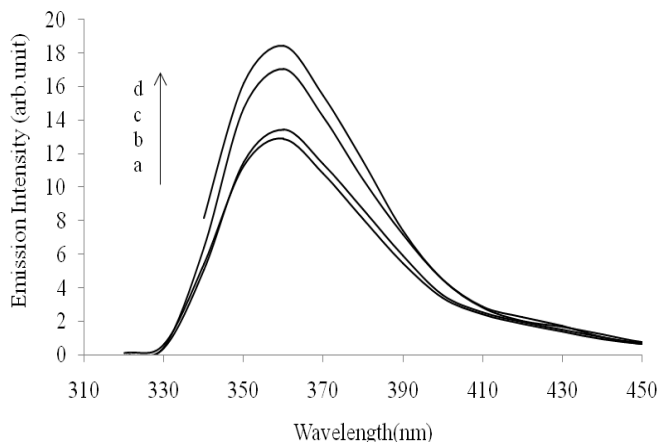


Figure-2c: Emission spectra of 2-naphthol doped in PVA for λ (excitation) 260nm (a) =359.2. 280nm (b) =359.4. 300nm (c) =356.7. and 320nm (d) =357.6.

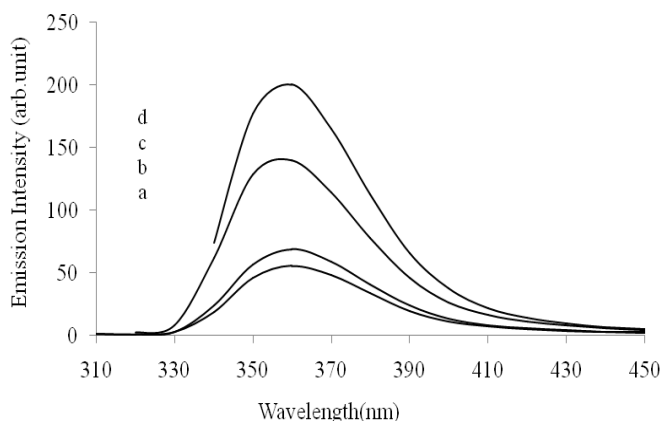


Figure-2d: Emission spectra of 2-naphthol doped in PVAc for λ (excitation) 260nm (a) 280nm (b) 300nm(c) and 320nm (d).

All the results have been summarized in Table-1. In order to investigate the mechanism of interaction between PMMA and 2-naphthol which is responsible for the observed red shift, solutions of 2-naphthol with increasing amount of PMMA have been prepared and the dependence of emission spectra on PMMA concentration was studied. The results are shown in Figure-3. In Figure-3(a) the spectrum corresponds to 2-naphthol in water in the absence of PMMA. Emission from both naphthol and naphtholate ion are observed in a manner similar to the emissions of aqueous solution of 2-naphthol on pH=5.

The emission at 354.2nm is due to naphthol and at 412.3nm due to naphtholate ion formed due to excited state proton transfer. Figure-3(b) shows the emission spectrum of 2-naphthol and 2-ml of PMMA solution. It is seen that the intensity of emission corresponding 2-naphthol as well as naphtholate decreases drastically. However, the intensity of naphtholate ion emission decreases more than the intensity of the naphthol.

This result shows that in presence of PMMA the excited state proton transfer rate decreases. The same is observed in Figure-3(c) when, on increasing the PMMA concentration the excited state proton transfer almost vanishes. On further increasing PMMA (Figure-3d) the emission spectrum changes discontinuously. The emission band at 354nm vanishes and a new band at 379.5nm appears. This band is at the same position as observed in dried polymer films.

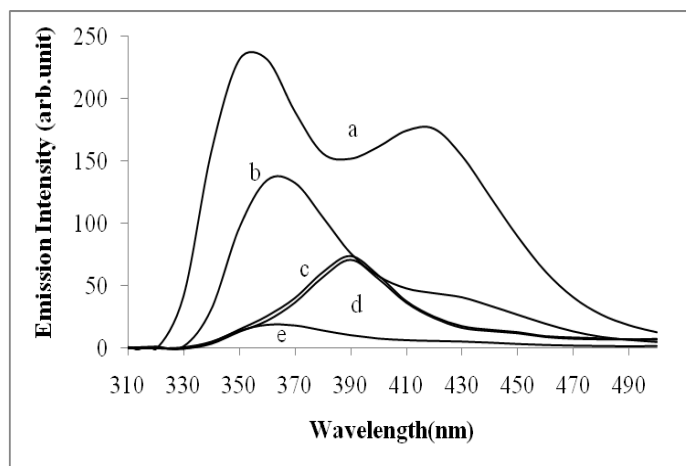


Figure-3: Emission spectra of 2-naphthol doped (a) in water in the absence of PMMA (b) 2MI PMMA (c) 4MI PMMA (d) 6MI PMMA and (e) 8MI PMMA, (excitation wavelength 260nm).

The result show that in PMMA film while the absorption of 2-naphthol is at the same position as in aqueous solution as well as in PVA and PVAc films, the emission shows a marked red shift. The possible explanation to this is the binding of 2-naphthol with PMMA. The interaction between 2-naphthol in PMMA molecules is strong and this results in the spectral shift in 2-naphthol in PMMA films. The excitation wavelength dependence observed for 2-naphthol in PMMA films is given also in Table-1 also noteworthy. It observed that the emission maximum shows a red shift from 378.7nm to 382.4nm when the wavelength of excitation is moved from 260nm to 320nm. The increase in wavelength of the emission peak is gradual. Such a phenomena in polymer films can be explained by the process of molecular relaxation; when a molecule is excited to any of the higher excited energy states it returns immediately to the zero vibration level of the first excitation state. The molecule at that stage occupies same molecular arrangement as that in the ground state. It is accepted that there might be a large number of conformations surrounding the fluorophore, which are in the form of the micro-crystals because there may be a large number of such conformations there excitation energy to the first excited state varies considerably^{6,7}. It is normally observed that such a conformational difference shows a shift of the emission peak towards longer wavelength side when excited at the red edge of the absorption band. The same is observed in present case. In contrast to the red as edge excitation effect observed for 2-naphthol in PMMA in films and solution no such effect has been observed in PVA and PVAc (Table-1).

Table-1: Positions of absorption and emission spectra of 2-naphthol doped in PMMA, PVA, and PVAc films.

Polymers	Absorption maximum (nm)	Emission maximum (nm)			
		$\lambda=260$	$\lambda=280$	$\lambda=300$	$\lambda=320$
2-naphthol in water solution	327.83	354.2	-----	-----	-----
PMMA	323.31	378.2	379.8	379.5	382.4
PVA	332.23	358.5	358.2	358.3	359.4
PVAc	331.78	359.6	359.4	356.7	357.6

Thus the explanation for the extraordinary behavior of 2-naphthol in PMMA solution and films can be given by the formations of one and one complex between 2-naphthol and PMMA. This complex is responsible for the change in emission spectra. From the above observations of the fluorescence of 2-naphthol in PVA, PVAc and PMMA films a general conclusion can be drawn that there is an interaction between the fluorescent moiety (2-naphthol) and the surrounding polymer matrix. The magnitude of interaction varies for different polymers. In the present investigation it is observed that while the interaction of 2-naphthol with PVA and PVAc is weak it is stronger with PMMA. Such studies in detail will be helpful in analyzing the molecular interaction in polymer blends.

Conclusion

Absorption spectra, emission spectra and the excitation wavelength dependence of emission spectra for the films of Polymethyl methacrylate, Polyvinyl alcohol and Polyvinyl acetate doped with 2-naphthol have been studied. It is observed that while for PVA and PVAc films the absorption and emission spectra of 2-naphthol are similar to the corresponding spectrum of 2-naphthol in water. But for PMMA while the absorption spectrum is never less the same as in other polymers and water the emission spectrum differs considerably. Such a difference has been explained on the basis of one to one binding of 2-naphthol with PMMA molecules. The observed excitation wavelength dependence of the emission spectrum is attributed to different conformations present in the polymer matrix.

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