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Spectroscopic properties of Na-fluorescein in polyacrylic acid films

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Abstract

Na-fluorescein (NaF), when embedded in thin polyacrylic acid (PAA) films, shows a single absorption band peaking at 444 nm and an emission band peaking at 505 nm. The quantum yield of fluorescence (Q_f) of the NaF/PAA film is 0.65. These spectroscopic properties of NaF in PAA films can be attributed to the existence of a neutral zwitterionic form of NaF with a small percentage of a cationic form of NaF within the PAA film. © 1997 Elsevier Science S.A.

Keywords: Absorption; Fluorescence; Na-fluorescein; Polyacrylic acid

1. Introduction

Na-fluorescein (NaF) is a well-known laser dye belonging to the xanthene series [1] whose molecular structure is shown in Fig. 1. It is also used as a solar energy concentrator [2,3]. Fluorescein derivatives are used as protein tags; they have the same spectroscopic properties as that of the parent compound with the additional capability of binding covalently to proteins [4]. The understanding of the basic photophysical properties of these dyes is very important for their use in various applications. As a continuation of our study on laser dyes and thin film dye lasers [5–9], NaF was embedded in polyacrylic acid (PAA) thin films (thickness, 35 μm) by casting on a quartz plate from a solution of NaF/PAA in methanol (MeOH). The spectroscopic properties shown by NaF in PAA films are different from those of NaF in PAA/MeOH and NaF in MeOH. The properties of NaF/PAA films, e.g. the large Stoke's shift (61 nm) and moderate fluorescence quantum yield (0.65), are useful for applications as lasing media in thin film dye lasers. To understand this different behaviour of NaF in PAA films, a detailed spectroscopic study of NaF was undertaken. As the changes in the spectroscopic properties of NaF in PAA films are the result of the solidification of the NaF/PAA/MeOH solution, the factors which change during the solidification, such as the concentration of PAA, viscosity and pH of the solution, are thought to be responsible for these changes. Therefore, we studied the influence of these factors separately on the spectroscopic properties of NaF. From these studies, it was shown that the changes in pH of the solution during solidification are mainly responsible for the observed spectroscopic properties of NaF in PAA films.

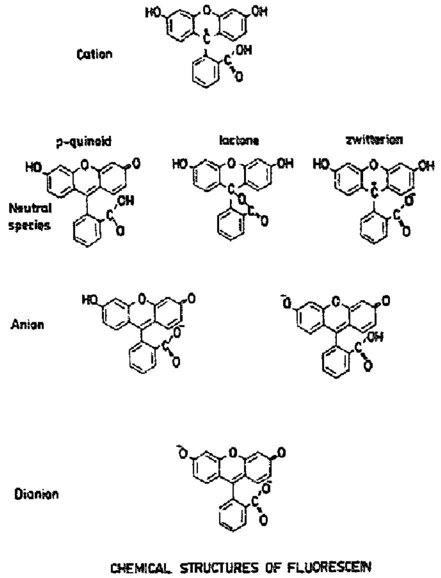

Fig. 1. Molecular structures.

2. Experimental details

The purity of laser grade NaF (Lambda Physik Company) was tested by UV–visible and IR spectroscopy and thin layer

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chromatography. A Milton Roy (model 1201) spectrophotometer was used for absorption measurements. The extinction coefficient of NaF was obtained from absorption measurements in MeOH (reproducible to within ±5% of the reported value [10]). PAA (average molecular weight, 250 000) was obtained from Aldrich Chemical Company. Spectroscopic grade MeOH was obtained from Merck (India). Films of PAA/MeOH were cast by dissolving the desired amount of polymer in MeOH and pouring the film-forming solution onto a horizontal quartz plate. The solvent was allowed to evaporate by air drying at room temperature (RT) (25 °C). The transparency of the films was initially tested by transmission measurements in the 230–650 nm region (about 90% transparency). Films of NaF in PAA were prepared from a solution of NaF/PAA/MeOH containing the desired concentration of NaF (9.7×10^{-5} mol l^{-1}) and 400 mg of PAA in 10 ml of solution (pH 3.0±0.3). Films were cast by solvent evaporation at RT as described above [11].

NaF/PAA films were subjected to absorption, fluorescence and fluorescence quantum yield measurements. The fluorescence spectra of NaF/PAA films were recorded on a fluorometer with excitation/emission grating monochromators of 0.2 m. These measurements were also made for NaF/PAA/MeOH and NaF/MeOH solutions at the same concentration. The fluorescence quantum yields (Q_f) of NaF/PAA films were measured using the front surface excitation/emission geometry. NaF in MeOH (basic) with a Q_f value of 0.93 [12] was used as a standard in a 0.25 cm path length cuvette. The concentrations of the sample and reference were kept very high such that 99% of the excitation light was absorbed. The fluorescence spectra of the sample and reference were scanned by excitation at wavelengths of 430 nm and 480 nm respectively. The recorded emission spectra were corrected for the photomultiplier and monochromator sensitivity and for the refractive index. The absorbed intensity spectra were obtained by overlapping the excitation and absorption spectra. The areas under the emission and absorbed intensity spectra were used to calculate Q_f.

The fluorescence quantum yields of NaF and NaF/PAA in MeOH at various pH values were measured using transverse excitation/emission in dilute solutions (optical density (OD) of less than 0.1 in a 1 cm cuvette). NaF in MeOH (basic) was used as a reference [12]. The fluorescence spectra of the sample and the reference were recorded for the measurement of the Q_f values as described above.

During solidification of the NaF/PAA/MeOH solution, various factors, such as the concentration of PAA with respect to MeOH, viscosity and pH, change simultaneously. To understand the effect of each factor on the spectroscopic properties of NaF, the following experiments were performed.

2.1. *Effect of PAA concentration*

Various solutions of NaF/PAA/MeOH were prepared by keeping the concentration of NaF fixed (9.7×10^{-5} mol l^{-1}) and varying the concentration of PAA from 360 mg to 900 mg in 10 ml of solution. This is the highest limiting concentration possible practically. All solutions containing various concentrations of PAA showed a pH value of 3.0±0.3. These solutions were subjected to absorption/fluorescence measurements.

2.2. *Effect of viscosity*

An NaF/glycerol solution was used containing a fixed concentration of NaF (9.7×10^{-5} mol l^{-1}) at pH 3.0. The appropriate pH of the solution was obtained using a drop of 0.1 N HCl.

2.3. *Effect of pH*

As PAA is a mild acid and an increasing concentration of PAA with respect to MeOH on solidification is thought to lead to a decrease in pH (more acidic), various solutions containing a fixed concentration of NaF (9.7×10^{-5} mol l^{-1}) and PAA (400 mg in 10 ml) were prepared with pH values in the range 3.0–1.6 using HCl. These NaF/PAA/MeOH solutions were subjected to spectroscopic studies.

3. Results and discussion

Fig. 2 shows the absorption spectra of an NaF/PAA thin film and the NaF/PAA/MeOH solution from which it was cast. On the same plot, the absorption spectrum of NaF/MeOH (pH 3.0) containing the same amount of NaF is also shown. From Fig. 2, it is clear that NaF in the PAA film shows one sharp absorption band with a peak at 444 nm, whereas NaF in PAA/MeOH solution shows an absorption spectrum with peaks at 481, 452 and 273 nm. The spectrum of the NaF/MeOH solution also shows these three peaks.

The appearance of various peaks in the spectrum of NaF in MeOH solution (pH 3.0) can be understood if it is assumed

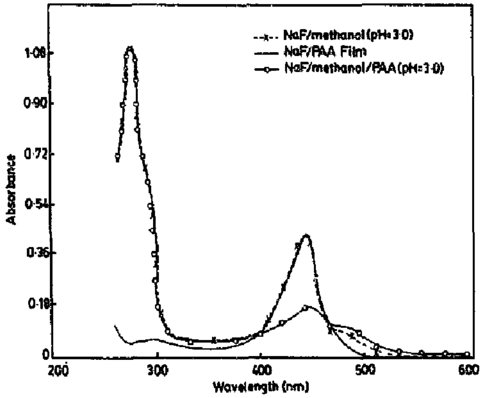

Fig. 2. Absorption spectra of NaF in PAA film, PAA/MeOH and MeOH solution.

that various forms of NaF are present, as reported previously [13–20]. These forms, e.g. cation, neutral (lactone, zwitterion and quinone), anion and dianion, are shown in Fig. 1. As reported by Martin and Lindqvist [14] and Sjoback et al. [20], at pH 3.0, the most probable species is the neutral form of NaF. There are three types of neutral species, namely the quinone, zwitterion and lactone, absorbing at 481 nm (quinone), 452 nm (zwitterion) and 273 nm (lactone). Hence the three absorption bands in the spectra of NaF/PAA/MeOH and NaF/MeOH solutions (Fig. 2) can be attributed to these three neutral species. As shown in Fig. 2, it is clear that, on solidification of the NaF/PAA/MeOH solution, the species present absorbs in the 444 nm region.

Fig. 3 shows the fluorescence spectra of the NaF/PAA film and the NaF/PAA/MeOH solution from which it was cast. The fluorescence spectrum of NaF/MeOH (pH 3.0) is also given. These spectra show two major overlapping bands peaking at 510 and 540 nm. There is a small shoulder at 473 nm. In the NaF/PAA film, the 505 nm fluorescence peak is more intense than the 540 nm peak (intensity ratio, 1.73), whereas in NaF/PAA/MeOH and NaF/MeOH solutions the two peak intensities are comparable. The solution spectra resemble the emission spectrum of the monoanionic species of NaF reported previously [14,20]. As pointed out by Sjoback et al. [20], this is due to the conversion of the cationic or neutral species to the monoanionic species in the excited state, which subsequently decays with its characteristic fluorescence bands. This can be expressed as

$$\begin{tikzcd}
(FH_3^+)^* \arrow[r, dashed] \arrow[d, dashed] & (FH_2)^* \arrow[r, dashed] & (FH^-)^* \arrow[d] \\
(FH_3^+) \arrow[u] \arrow[r, dashed, leftrightarrow] & (FH_2) \arrow[u] \arrow[r, dashed, leftrightarrow] & (FH^-)
\end{tikzcd}$$

Table 1
Spectroscopic properties of NaF in PAA film, PAA/MeOH and MeOH solution

Sample	λ_a (nm)	λ_f (nm)	Q_f
NaF/MeOH	273 452 481	473 510 540	0.20
NaF/PAA/MeOH	273 452 481	473 510 540	0.20
NaF/PAA film	444	473 505 540	0.65

Uncertainty: λ_a/λ_f (±1 nm); Q_f (±0.1).

where FH_3^+, FH_2 and FH^- are the cationic, neutral and monoanionic species of NaF respectively. The asterisk denotes the excited state.

The small contribution at 473 nm is due to an unidentified species (higher cationic) as suggested by Sjoback et al. [20]. The quantum yields (Q_f) calculated are shown in Table 1, together with the other absorption/fluorescence data of NaF in PAA films, PAA/MeOH and MeOH solution. The Q_f values are about 0.20–0.22 for NaF in PAA/MeOH or MeOH solution. However, the Q_f value measured for the NaF/PAA film is 0.65. In order to understand the increase in the Q_f value on solidification and the species responsible for this behaviour, the effect of various factors, which might change on solidification, on the spectroscopic properties was studied.

3.1. Effect of PAA concentration

Fig. 4 shows the absorption/fluorescence spectra of an NaF/PAA/MeOH solution at various concentrations of PAA

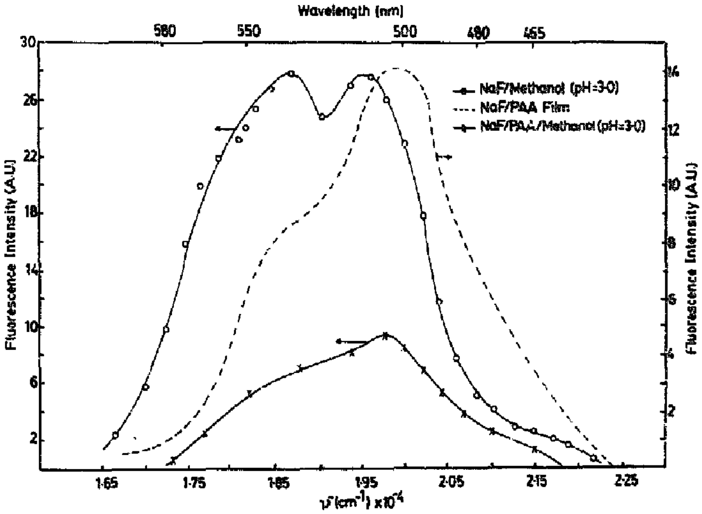

Fig. 3. Fluorescence spectra of NaF in PAA film, PAA/MeOH and MeOH solution.

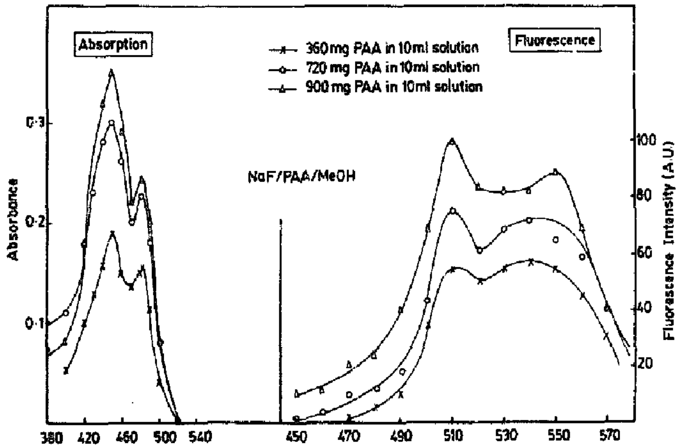

Fig. 4. Absorption/fluorescence spectra of NaF/PAA/MeOH solutions at various PAA concentrations.

but at fixed NaF. It can be seen that, as the concentration of PAA is increased, the shorter wavelength absorption peak (corresponding to the zwitterionic species) increases significantly relative to the longer wavelength absorption peak (corresponding to the quinoid form). Hence an increasing concentration of PAA in solution helps to increase the concentration of the neutral zwitterionic species relative to the quinoid species. The fluorescence spectra show the presence of both peaks (510 and 540 nm) for all the studied concentrations of PAA in solution, with a slight red shift of the longer wavelength emission band with increasing concentration. These fluorescence spectra resemble the fluorescence spectrum of the monoanionic species. This shows that a change in PAA concentration may be effective in increasing the concentration of the neutral zwitterionic species relative to the other neutral species.

3.2. *Effect of viscosity*

The effect of the viscosity on the absorption/fluorescence spectra was studied by preparing a solution of NaF/glycerol at pH 3.0 with the same concentration of NaF as that in the NaF/PAA/MeOH solution used for the preparation of the films. Fig. 5 shows the absorption/fluorescence spectra of NaF/glycerol at pH 3.0, together with the spectra of the NaF/PAA/MeOH solution containing the same concentration of NaF. It can be seen that the absorption spectrum of NaF/glycerol shows two peaks corresponding to the zwitterionic (454.6 nm) and quinoid (481.6 nm) species with nearly the same absorbance values. However, in the NaF/PAA/MeOH solution, the absorption peak of the zwitterionic species (452 nm) is stronger than the longer wavelength peak corresponding to the quinoid species. The fluorescence spectrum of NaF/glycerol shows two peaks, one at 510 nm and the other at 530 nm, with equal intensities. The fluorescence spectra of NaF/glycerol (pH 3) and NaF/PAA/MeOH (pH 3) are almost comparable, except for the slight blue shift of the longer wavelength peak in NaF/glycerol. The Q_f value of NaF/glycerol (pH 3) is about 0.2, i.e. similar to that of the NaF/PAA/MeOH (pH 3.0) solution. From these studies, it can be concluded that the viscosity is not responsible for the changes in the spectroscopic properties of NaF in PAA films.

3.3. *Effect of pH*

NaF/PAA/MeOH solutions containing the same amounts of PAA and NaF as that of the NaF/PAA/MeOH (pH 3.0) solution used for the preparation of the NaF/PAA films were prepared with pH values in the range 3.0–1.6 by the addition of HCl. As PAA is acidic, an increasing concentration of PAA with respect to MeOH, on solidification, is thought to reduce the pH of the solution. Fig. 6 shows the absorption spectra of the NaF/PAA/MeOH solution at various pH values. With decreasing pH of the solution, the zwitterionic absorption band shifts slightly to the blue (452 nm→447 nm). As the pH is decreased, there is an increase in the absorption band peaking at 447 nm and a decrease in the absorption band peaking at 273 nm. In addition, the ratio of absorbance of the 447 nm peak to the 481 nm peak increases as the pH of the solution is decreased, showing that there is an increase in the concentration of the zwitterionic species relative to the other neutral species. A similar behaviour is also observed in NaF/MeOH solution. The fluorescence spectra of the NaF/PAA/MeOH solution at various pH values were also scanned. No change in emission wavelength with pH was observed, although the contribution of the band peaking at 510 nm increased relative to the 540 nm band with decreasing pH of the solution (ratio of the fluorescence intensity at 510 nm to that at 540 nm increased from 1.1 to 1.3 as the pH of the solution was changed from 3.0 to 1.60). The Q_f values show no change with changing pH of the solution.

From these observations, it is clear that the change in pH is, by and large, responsible for the increasing absorbance at shorter wavelength (444 nm) relative to the other absorption

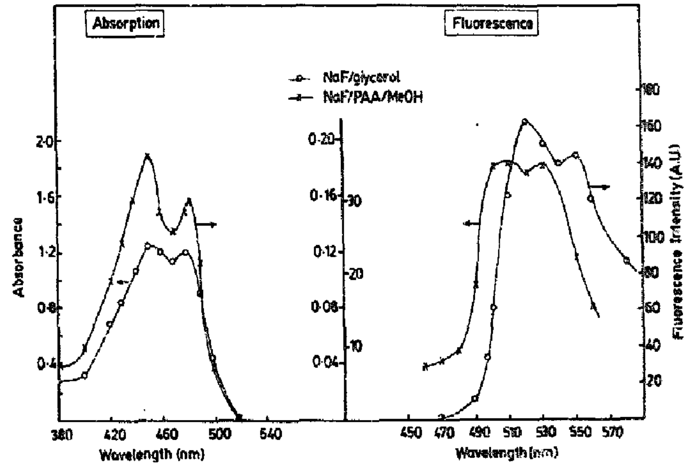

Fig. 5. Absorption/fluorescence spectra of NaF/PAA/MeOH solution (pH 3) and NaF/glycerol solution (pH 3).

peaks, i.e. at 481 and 273 nm. In addition, a change in pH results in a greater fluorescence intensity at 510 nm compared with that at 540 nm, as observed in the NaF/PAA film. If earlier reports on the various forms of NaF are considered [14–20], we can infer that the neutral zwitterionic and cationic species of NaF are responsible for the absorption at 444 nm. At pH 3.0, most of the contribution at 444 nm is due to the neutral form of NaF, but as the pH is decreased there is some contribution from the cationic species.

In solutions of NaF/PAA/MeOH and NaF/MeOH at the various pH values studied, the Q_f value remains almost unchanged. This observation agrees with earlier reports [14,20] and with the above-mentioned scheme of conversion of one form of NaF to another. In solution, the conversion/decay scheme does not end with the monoanion, and there is the possibility of conversion to the dianion. In the NaF/PAA film, once the NaF molecules are separated in the microdomains, as suggested by Jones and Reheman [21,22], the possibility of conversion to another species is reduced. Hence the conversion

$$\begin{tikzcd}
(\text{Cation})^* \arrow[r, "Q_{1c}"] & (\text{Zwitterion, neutral})^* \arrow[r, "Q_{2c}"] & (\text{monoanion})^* \arrow[d, "Q_f"] \\
(\text{Cation}) \arrow[r] \arrow[u] & (\text{Zwitterion, neutral}) \arrow[r] \arrow[u] & (\text{monoanion})
\end{tikzcd}$$

and

$$Q_f(\text{NaF/PAA film}) =$$

$$(1-\alpha)Q_{2c}Q_{f,\text{monoanion}} + \alpha Q_{1c}Q_{2c}Q_{f,\text{monoanion}}$$

takes place, so that emission is observed from monoanionic NaF (in the pH range 3.0–1.6, no possibility of the dianion). In the above equation, α is the fraction of cationic absorbing species relative to zwitterionic species. From the Q_f value of the NaF/PAA film, we can infer that the Q_f value of the monoanion must be very high. In addition, the conversion coefficient (Q_{2c}) of (zwitterion)* → (monoanion)* must be very high (close to unity). Moreover, cation formation must be fairly low (α very small) relative to the formation of the neutral zwitterionic species. Otherwise a moderate value of Q_f in the NaF/PAA film would not be observed. This is because (cation)* → (zwitterion)* → (monoanion)* reduces the conversion yield

$$Q_{c-\text{mna}} = Q_{1c}Q_{2c}$$

Hence most of the species contributing to the 444 nm band are the neutral zwitterionic species of NaF in NaF/PAA films. Some contribution from the cation leads to a moderate value of Q_f. If cationic species were absent, a higher Q_f value would have been observed in NaF/PAA films.

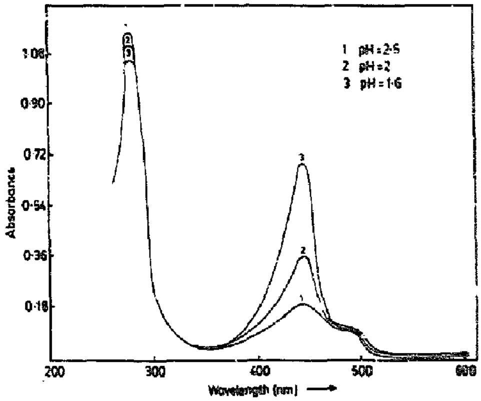

Fig. 6. Absorption/fluorescence spectra of NaF/PAA/MeOH solutions at various pH values.

4. Conclusions

The NaF/PAA film shows a single absorption band peaking at 444 nm, an emission band peaking at 505 nm with a shoulder at 540 nm and a moderate Q_f value of 0.65. These properties are attributed to the existence of the neutral zwitterionic species of NaF in large concentration, with a small contribution of the cationic species, in NaF/PAA films. These properties are very useful for applications as lasing media in dye lasers.

Acknowledgements

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