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Fluorescence emission studies of an azlactone derivative embedded in polymer films
An optical sensor for pH measurements

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Abstract

Azlactone molecules can be protonated in acidic media, and the process of protonation is irreversible due to ring opening in solutions. A new fully reversible pH sensor has been developed 4-(*p*-*N*,*N*-dimethylamino phenyl methylene)-2-phenyl-5-oxazolone (DPO), an azlactone derivative, embedded in a plasticized PVC polymer film. The sensor membrane is completely transparent and exhibits pH induced color change which is capable of measuring of pH in the range 1–7 and has a pK_a value of 3.4. In agreement with crystal phase studies, DPO displays enhanced fluorescence emission quantum yield, $Q_f = 0.52$, and fluorescence emission lifetime, $\tau_f = 1.35$ ns, in immobilized PVC film matrix, compared to $Q_f \cong 0.03$ and $\tau_f = 0.02$–0.03 ns in solutions. Stokes shift decreased to 46 nm in plasticized PVC film, with respect to Stokes shift of 81 nm in acetonitrile solution. Singlet energy, $E_s = 60.4\,\mathrm{kcal\,mol^{-1}}$, of DPO in PVC film, which is 1.1–1.4 $\mathrm{kcal\,mol^{-1}}$ lower with respect to solutions, is taken as evidence of lessened singlet–triplet crossings in excited state of DPO in immobilized phase, and result in enhanced fluorescence emissions.

Keywords: Optical sensor; Fluorescence emission; Azlactone; pH; Polymer film

1. Introduction

Extensive studies on 4-arylene-2-aryl-5-oxazolones (azlactones) [1–8] proved that in liquid state:

1. hetero ring is unstable, ring opening occurs in acidic–basic media, at sensitized photo-oxidations and at chemical electron transfer reactions,
2. fluorescence quantum yields, Q_f, are very low ($\sim 10^{-2}$–10^{-4}),

but in solid state:

1. molecular structure is photostable and fluorescence emission is enhanced ($Q_f \approx 10^{-1}$–1.0),
2. favored photophysical and photochemical properties resulted in use of azlactones at semiconductor devices, at electrophotographic photoreceptors and at non-linear optical materials.

An efficient hydrogen abstraction of azlactone (4-benzal-2-phenyl-5-oxazolone) from solvent molecules is demonstrated by Baumann [3,4] in solutions. The rate of hydrogen abstraction was higher in protic solvents (in alcohols) with respect to aprotic solvents. Another photochemical process is geometrical isomerization on 4-arylidene part of the molecule, where *Z* (or *syn*) isomeric form is reported to be more stable [3,4,7,8]. Baumann also reports concentration quenching as a competing photochemical process to hydrogen abstraction. Hydrogen abstraction rate from solvent was decreased by the increase of concentration of 4-benzal-2-phenyl-5-oxazolone in *iso*-propanol. Based on the observed photochemical processes, it is suggested that hydrogen abstraction occurs from $T_2(n,\pi^*)$ and geometrical isomerization from $T_1(\pi,\pi^*)$. This result leads to the conclusion that the life time of $T_2(n,\pi^*)$ should be long. An efficient intersystem crossing from singlet (S_2) to T_2 and singlet (S_1 or S_2) to T_1 have to occur in solutions of azlactone molecule.

Under the light of literature, one would study the fluorescence emission of azlactone molecule in an immobilized phase, where higher yield of fluorescence emission and improved stability toward chemical and photochemical environment could be reached. Thin polymer films of pigments are known to be applied for photophysical and photochemical studies. Our earlier studies revealed that 4-(*p*-*N*,*N*-dimethylbenzal)-2-phenyl-2-oxazolone, 4-(*p*-*N*,*N*-

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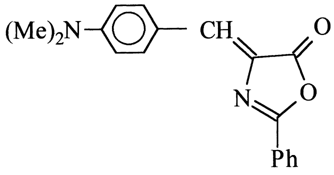
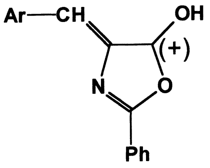
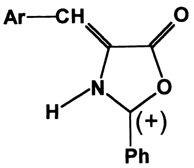
dimethylamino phenyl methylene)-2-phenyl-5-oxazolone (DPO), gives better fluorescence quantum yields, Q_f, in solution and in solid state in comparison to other benzal oxazolones. In fact in solid state Q_f is about unity. The color of DPO is bright red in crystal form, in contrast to pale yellow–orange colors of other azlactone crystals. Long wavelength absorption of DPO (465 nm) in liquid phase, may display a color change in polymer film if protonated in an acidic medium, which may be used as a practical visual observation.



DPO

Because of the presence of carbonyl oxygen and nitrogen atom in hetero ring of azlactones, protonation would occur in acidic medium and would alter the absorption bands. π-Bonds of hetero atoms would open in protonated forms of azlactone, that would result in loss of absorption at longest wavelength band. Oxazolone ring opens in liquid state in acidic medium, but in immobilized phase of polymer film hetero ring is expected to be stable and one may be able to achieve reversible process of protonation. Then one may be able to study pH dependent absorption and fluorescence emission spectra of azlactones.





Glass pH electrodes are the most widely used instruments in all kinds of sciences including chemical, biochemical and environmental. But glass electrodes show poor performance at low (0–2) and high (12–14) pH values. In order to overcome this handicap numerous chemical sensor systems have been developed in recent years [9]. Because of different operating principle, pH optrodes (optical electrod) and optodes (optical sensor) offer new possibilities and overcome some of the limitations of pH electrodes. The usage of optrodes in industrial hazardous environments is easy and safe for physiological and biological systems. A number of optical sensors for pH have been described, each differing in the chemical transducer and the optical principle employed [10–13]. The determination of pH with fluorescence-based optosensing techniques have advantages over methods based on spectrophotometric sensing owing to the sensitivity of fluorescence. Wolfbeis et al. [14] have used certain coumarins and trisodium salt of 8-hydroxy-1,3,6-pyrenetrisulfonate (HTPS) for measuring near neutral pH values. Zhujun and Seitz [12] prepared a pH sensor by electrostatic immobilization of HPTS on an anion exchange membrane. This sensor allowed the measurements of pH in the range 6–8. Kawabata et al. [15] immobilized a monolayer of fluorescein directly to surface of a modified optical fiber. Jordan and Walt [16] developed an energy transfer-based sensor using eosine and phenol red combination for physiological ranges. Werner and Wolfbeis presented a pH sensitive membrane for the pH 10–13 range. They covalently immobilized the N8 dye to cellulose on a polyester support. They measured the pH dependent absorption of the membrane at 555 nm via optical fibers [17]. Wolfbeis reports quenching effect of widely used 2-nitrophenyl octyl ether plasticizer on fluorescence emission of porphyrines in plasticized polymer films [18].

The azlactone derivative DPO contains available active centers for proton attacks and it is appropriate for use as a optode pH sensor.

2. Experimental details

2.1. Materials

DPO was synthesized and purified as described [7]. The membrane components, PVC (high molecular weight) and the plasticizers bis-(2-ethylhexyl)phtalate (DOP), bis-(2-ethylhexyl)sebecate (DOS) and 2-nitrophenyl octyl ether (NPOE) were supplied from Fluka, bis-(2-ethylhexyl)-adipate (DOA), the lipophilic anionic additive potassium tetrakis-(4-chlorophenyl)borate (PTCPB) and tetrahydrofuran (THF) were obtained from Aldrich, the acids used (HNO_3 and HCl) and the regeneration buffer (titrisol, $pH = 7 \pm 0.02$) were from Merck. Studies performed in buffered solutions of acids were carried out with *N*,*N*-bis(2-hydroxyethyl)-2-amino-ethanesulfonic acid (BES) from Sigma. Acid solutions and buffers used, for investigation of pH effects, were prepared with a high quality pure water. Pure water was obtained from an apparatus working with reverse osmosis principle from Elga. All the other chemicals were obtained from Fluka and Merck, and were used as supplied. The organic solvents used (acetonitrile, chloroform, THF) were all of spectrophotometric grade, and were used as supplied. The polyester support (Mylar type) was provided from DuPont, Switzerland.

2.2. Polymer film preparation

The optode polymer films were prepared from a mixture of 120 mg of PVC, 240 mg of plasticizer, equimolar PTCPB to dye DPO and 1.5 ml of THF (dry). The concentration of DPO in mixture was in the range 10^{-3}–10^{-4} M (about 20 mmol dye kg^{-1} polymer). Fluorescence emission of DPO was lost at lower than 10^{-4} M concentrations, in plasticized PVC. The resulting cocktails were spread onto a 125 μm polyester support (Mylar type), by means of a spreading device (from Heidelberg, Germany). PVC films were kept in a THF containing dessicator and in the dark for the photostability of the membrane and the damage from the ambient air of laboratory was avoided. Each sensor PVC film was cut with a width of 120 mm and located diagonally into the sample cuvette. The advantage of this kind of a placement was to improve the reproducibility of the measurements. The films were photographed under Leitz ortopcan polarise microscope, connected to a computer and thicknesses were measured in reference to thickness of Mylar type polyester support. PVC film thicknesses were found to be in the range 5–10 μm.

2.3. Spectroscopic measurements

The absorption spectra of the polymer films were measured at Jasko V-530 UV–Vis spectrophotometer, the fluorescence emission spectra was recorded at PTI-QM1 fluorescence spectrophotometer. pH measurements were performed with a pH meter Jenway 3040 Ion Analyzer calibrated with Merck pH standards of pH 7.00 (titrisol buffer) and 4 at 20°C. Fluorescence quantum yield of DPO was measured in reference to absorption and fluorescence emission of *n*-dodecyl perylene diimide, $\lambda_{exc} = 485$ nm. Absorption and fluorescence emission spectra of polymer films were measured in quartz UV cells, which were filled with water, and polymer films were placed in diagonal positions. For pH induced measurements, neutral water was replaced with buffered (with BES) or unbuffered solutions at various pHs. Preference of BES is due to its adoptance to human serums.

3. Results and discussion

3.1. UV–Vis and fluorescence emission spectroscopy studies

Absorption and fluorescence emissions of DPO both in THF solution and in plasticized PVC film had shown similar spectra (Fig. 1 and Table 1). Wavelength of absorption, λ_{max}, in film is seen to be shifted about 10 nm compared to absorption λ_{max} in THF solution. Red shift of absorption of DPO may be related to enhanced conjugation in immobilized polymer phase by hindrance of vibrational rotational motions. A decrease of Stokes shifts ($\Delta\nu$), in the order of

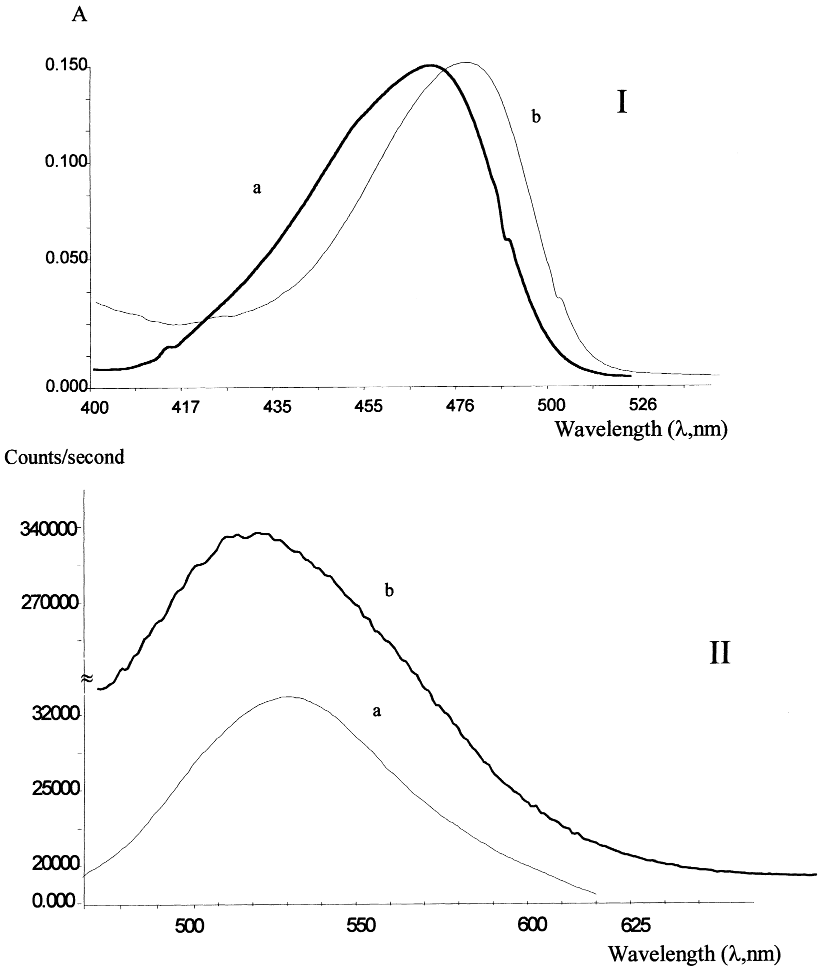


Fig. 1. Absorption (I) and fluorescence emission spectra (II) of DPO in: (a) THF solution, 5.5×10^{-6} M, $\lambda_{max} = 463$ nm; (b) polymer film, 1.1×10^{-3} M, $\lambda_{max} = 478$ nm.

Table 1

UV–Vis spectroscopy data (λ, nm and ε, $\mathrm{l\,mol^{-1}\,cm^{-1}}$), Stokes shifts, $\Delta\nu$ ($\mathrm{cm^{-1}}$), fluorescence quantum yield, Q_f, radiative lifetime, τ_0 (ns), fluorescence lifetime, τ_f (ns), fluorescence rate constant, k_f ($10^9\,\mathrm{s^{-1}}$), and singlet energy, E_s ($\mathrm{kcal\,mol^{-1}}$) of synthesized DPO in solutions and in PVC polymer film

Solvent	λ_{max}^{ab}	ε_{max}	λ_{max}^{f}	$\Delta\nu$	Q_f	τ_0	τ_f [a]	k_f [b]	E_s
CAN	465	51000	546	3190	0.0027	7.2	0.02	52.6	61.5
THF	463	21000	525	2623	0.0025	11.4	0.03	34.5	61.8
PVC film	478	200000	520	1873	0.52	2.6	1.35	0.4	60.4

[a] $\tau_f = \tau_0 Q_f$.

[b] $k_f = 1/\tau_0$.

acetonitrile, THF solutions and PVC film, 3190, 2623 and $1873\,\mathrm{cm^{-1}}$, respectively is evident. Difference between acetonitrile and THF solutions can be related to differences in solvent polarities, but the decrease of Stokes shift in polymer film would arise from lowered difference of equilibrium geometries between ground and excited states in immobilized phase with respect to solutions.

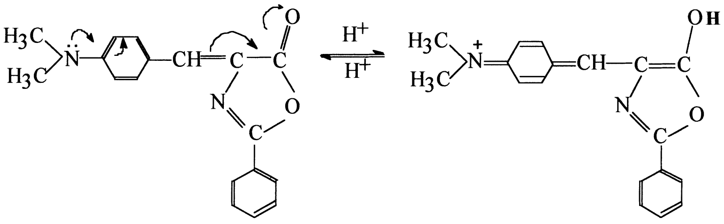
The radiative lifetimes, τ_0, were calculated by the formula [19,20]: $\tau_0 = 3.5 \times 10^8/\nu_{max}^2 \varepsilon_{max} \Delta\nu_{1/2}$, where ν_{max} is the wavenumber in $\mathrm{cm^{-1}}$, ε_{max} the molar absorption coefficient at the selected absorption wavelength, and $\Delta\nu_{1/2}$ the half-width of the selected absorption in wavenumber units of $\mathrm{cm^{-1}}$. In agreement with crystal phase studies [8], fluorescence quantum yield of DPO in polymer film matrix, $Q_f = 0.52$, has increased about 200-fold, with respect to Q_f of DPO in solutions, and fluorescence lifetime of DPO in polymer film matrix, $\tau_f = 1.35$ ns, has increased about 50-fold, with respect to τ_f of DPO in solutions. These data can be taken as proofs that azlactone molecule DPO fluoresces better in immobilized PVC matrix. Singlet energy of DPO in polymer film matrix, $E_s = 60.4\,\mathrm{kcal\,mol^{-1}}$, is observed to be lowered about $1.1–1.4\,\mathrm{kcal\,mol^{-1}}$, with respect to E_s of DPO in solutions. This result may be taken as an evidence of lessened singlet–triplet intersystem crossings of azlactones in polymer film matrix, with respect to in solutions, in support of enhanced fluorescence emission. Induced steric effect in immobilized phase, with respect to solvated molecule in solution, may endorse enhancement fluorescence emission. Azlactone molecule is expected to lie in planar form in polymer film matrix, as suggested for in crystalline structure [8].

3.2. Studies in polymer film matrices

3.2.1. Choice of indicator

DPO was selected among the oxazolone derivatives, because of its longest wavelength absorption (λ_{max} = 465 nm) in visible region, and highest fluorescence quantum yield ($Q_f \cong 0.003$, Table 1) compared to all of the azlactones studied earlier [7,8]. Also it is observed that the dye DPO has an excellent solubility in plasticized PVC matrix. High molar absorption coefficient ($\varepsilon = 2\times10^4–5\times10^4\,\mathrm{M^{-1}\,cm^{-1}}$ in liquid phase) of DPO is another parameter of advantage of selection in polymer film matrices [9].

UV absorptions of DPO were recorded in acetone and dimethylformamide solutions, and $\lambda_{max} \cong 465$ nm absorption was found to be unchanged on titration with perchloric acid dissolved in glacial acetic acid. But when DPO solution was titrated with tetrabutylammoniumhydroxide solution in 2-propanol, it was found that $\lambda_{max} \cong 465$ nm absorption disappeared and an intense band appeared at $\lambda_{max} \cong 360$ nm, and a color change from orange to yellow occurred irreversibly. 5-Oxazolone ring is known to open in the presence of a weak base, such as ammonia [21]. Acidification with glacial acetic acid, did not changed the color either. In general, it appears that non-aqueous solutions of DPO is in part stable in acidic medium, but unstable in basic medium. On the other hand DPO embedded in PVC undergoes a protonation–deprotonation equilibria when exposed to acid solutions. This reversible equilibria is shown below. Probably resonance contribution from methylated aniline ring contributes to the formation of enol form in hetero ring.



3.2.2. Choice of polymer and plasticizer

Organic pigments are advised to be inserted in polymer matrices of polyvinylchloride (PVC) and ethyl cellulose. Our experiments with PVC and ethyl cellulose proved that PVC matrices give better and faster responses to both absorbance and fluorescence emission measurements at various pH values with DPO. A comparative study on the effect of different plasticizers and matrix materials on the performance of pH sensor also is performed. The polymer film matrix

Table 2
Polymer film matrices of DPO prepared with plasticizers of DOP, DOA, DOS, NPOE in polymers of PVC and ethyl cellulose

	Polymer (mg)	Solvent (ml)	Plasticizer (mg)	Anionic lipophilic additive	Dye	Notes
PF-1	PVC, 120	THF, 1.5	DOP, 240	PTCPB, 20 mmol kg^{-1} polymer	DPO, 20 mmol kg^{-1} polymer	Transparent, $\lambda_{max} = 478$ nm
PF-2	PVC, 120	THF, 1.5	DOA, 240	PTCPB, 20 mmol kg^{-1} polymer	DPO, 20 mmol kg^{-1} polymer	Transparent, $\lambda_{max} = 474$ nm
PF-3	PVC, 120	THF, 1.5	DOS, 240	PTCPB, 20 mmol kg^{-1} polymer	DPO, 20 mmol kg^{-1} polymer	Transparent, $\lambda_{max} = 480$ nm
PF-4	PVC, 120	THF, 1.5	NPOE, 240	PTCPB, 20 mmol kg^{-1} polymer	DPO, 20 mmol kg^{-1} polymer	Transparent, $\lambda_{max} = 480$ nm

components were mixed according to the amounts given in Table 2.

The effect of the plasticizer type in polymer matrix on the pH induced fluorescence emission measurements was tested with four different plasticizers in ratios of 1/2, polymer/plasticizer, respectively. Fluorescence emission spectra in 10^{-8}–10^{-1} M HCl solutions, were recorded for each compositions above. It was found that the best resolved emission spectra, relative signal change, fast response time and good reproducibility were obtained with DOP plasticizer in composition of PF-1. Fig. 2 shows the resolution differences of DPO fluorescence emission in DOP (PF-1) and in DOA (PF-2) plasticizers, in PVC polymer film matrices. As seen fluorescence emission resolution is lost in DPO/DOA (PF-2) composition, from neutral to acidic solutions. Fluorescence emission resolution is again found to be lost in DPO/DOS (PF-3) composition, from neutral to acidic solutions. NPOE plasticizer (PF-4) is detected to quench DPO fluorescence emission, as reported in literature [18].

3.2.3. pK_a value of DPO

pK_a value of DPO were calculated in polymer film matrices. UV absorption of DPO were recorded in buffered, BES/HCl solutions, and in unbuffered HCl solutions (Fig. 3). The buffer capacity of the sample matrix is seen to

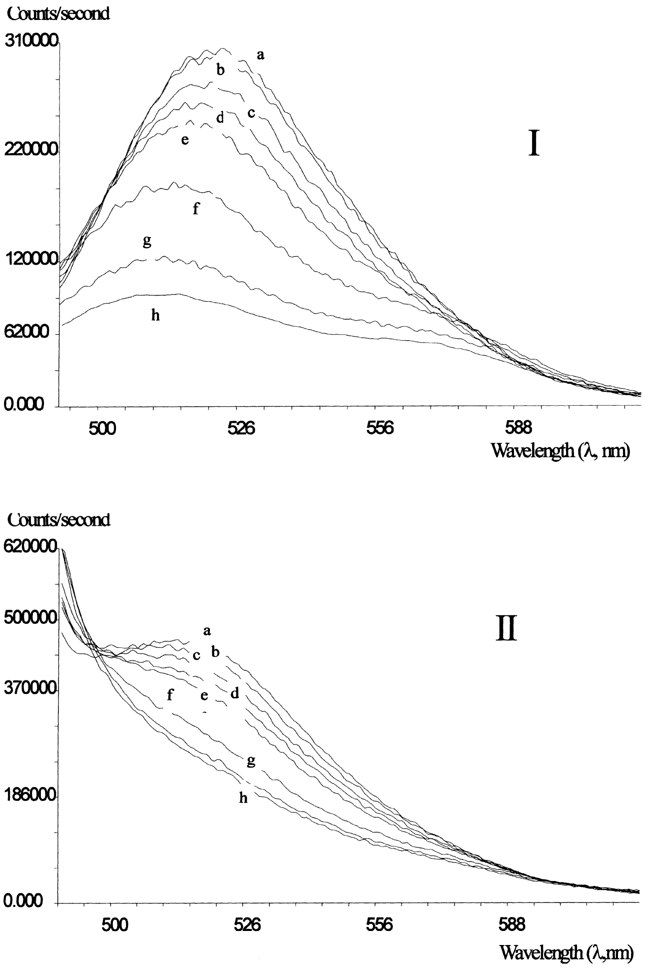


Fig. 2. Fluorescence emission spectra ($\lambda_{exc} = 474$ nm) of DPO in plasticized PVC film (I) with DOP and (II) with DOA plasticizer at pH values of: (a) 7.0; (b) 6.0; (c) 5.0; (d) 4.0; (e) 3.0; (f) 2.0; (g) 1.3; (h) 1.0.

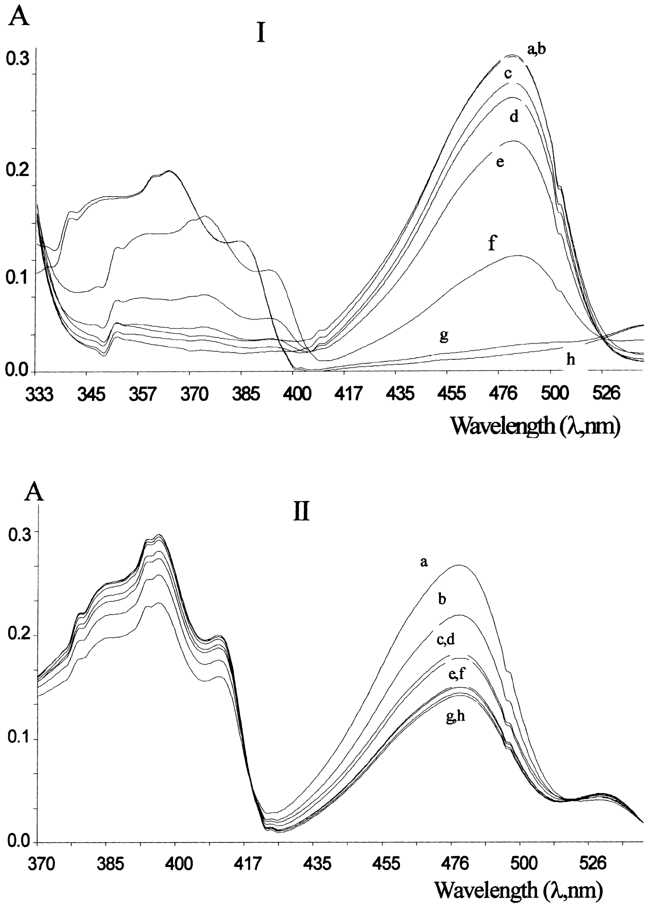


Fig. 3. Absorption spectra ($\lambda_{max} = 474$ nm) of DPO in plasticized PVC film (I) in unbuffered aqueous solution and (II) in BES/HCl buffered aqueous solution at pH values of: (a) 7.0; (b) 6.0; (c) 5.0; (d) 4.0; (e) 3.0; (f) 2.0; (g) 1.3; (h) 1.0.

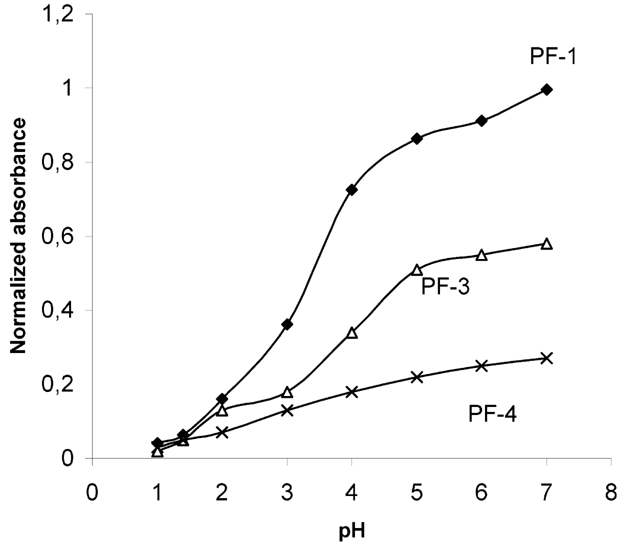


Fig. 4. Plot of pH versus normalized absorbance of DPO in plasticized PVC film.

influence the sensor response strongly. Normalized absorption parameters (A_x/A_0) are calculated by division of measured absorption to absorption at neutral pH as A_0 (pH $\cong$ 7). Fig. 4 shows the plot of normalized absorbance, A_x/A_0 versus measured pH values in buffered solutions. pK_a value was found as 3.4, pH value at half of the normalized absorption. pK_a was also calculated by using non-linear fitting algorithm of Gauss–Newton–Marquardt method [17],

$$\mathrm{p}K_\mathrm{a} = \mathrm{pH} + \frac{\log(A_x - A_\mathrm{b})}{A_\mathrm{a} - A_x}$$

where A_a and A_b are absorbances of acidic and basic forms and A_x is the absorbance at a pH near to the pK_a.

In accordance with direct measurement, p$K_\mathrm{a} = 3.42$ value was calculated from the above equation. This result points that DPO may be an effective pH sensor in acidic region of pH 1–7.

3.2.4. DPO as an optode pH sensor

DPO in composition of PF-1 polymer matrix was found to give reproducible results on fluorescence emission measurements when pH was varied from 7 to 1 and from 1 to 7. Dynamic pH range 7–1 corresponds to HCl concentrations of 10^{-8}–10^{-1} M, respectively. The detection limit was observed to be 10^{-9} M HCl concentration. It was also observed that the color of the polymer film was orange at pH = 7, but gradually changed to pink as it reached to pH = 1, and reverse color change was observed opposite pH change. Proton binding was seen to be faster than that of unbinding. The regenaration time of DPO pH sensor was found to be 30 min in $H_2PO_4^-/HPO_4^{2-}$ buffer solution, that gives a pH of 7 ± 0.02.

Plot in Fig. 5 outlines the pH induced absorbance variation versus time. It is apparent in Fig. 4 that the response time (τ_{90}) is 4–4.5 min under batch conditions. Absorbance of DPO is found to decrease (or drift) about 2% after third cycle. Fig. 4 also points a pH induced relative signal intensity change of 83.5 in unbuffered solution. pH induced relative signal intensity change is observed to be 73.9% in BES/HCl buffered solution. Dynamic range of DPO polymer matrix is detected to be at pH of 6.8–2 in BES/HCl buffered solution.

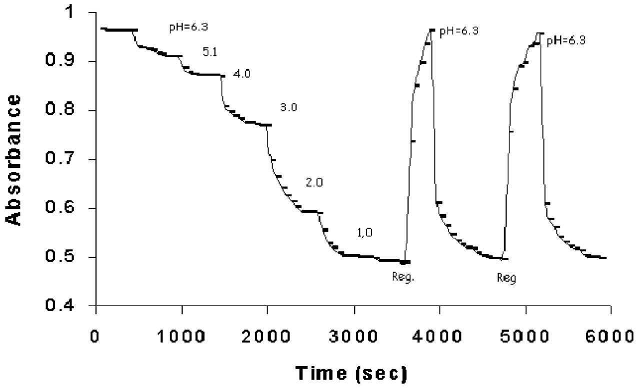


Fig. 5. Plot of pH induced normalized absorbance of DPO in plasticized film versus time.

4. Conclusion

It is proved that azlactone molecules would exhibit much higher fluorescence emissions in immobilized polymer film matrices with respect to solutions, studied for 4-(*p*-*N*,*N*-dimethylbenzal)-2-phenyl-2-oxazolone, DPO, molecule. pK_a value of DPO in PVC matrix, calculated from absorption spectra, is found to be 3.4, pointed a protonation process in acidic medium. Completely reversible protonation–deprotonation of plasticized PVC film of azlactone DPO, detected both in fluorescence emission and absorption spectra, allowed us to develop an optode pH sensor of pH 1–7 range. The optode pH sensor of DPO is found to reach 90% of the signal intensity in less than 5 min (τ_{90}). High performance with respect to response time, reproducibility, dynamic pH range 1–7, and the visible color change are the main advantageous parameters for this new optical sensor of pH measurements.

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