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Optical pH sensor based on spectral response of newly synthesized Schiff bases

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Abstract

In most of the common designs, pH optodes rely on weak acidic dyes whose dissociated and undissociated forms have different absorption or emission maximums. In this work the newly synthesized Schiff bases; *N*,*N*′-bis(4-diaminobenzyliden)-1,2-cyclohexandiamine [I], *N*,*N*′-bis(4-diaminobenzyliden)-1,2-ethanediamine [II] and 2,6-bis[(4-dimethylaminophenylimino)ethyl]pyridine [III], have been used for pH sensing in four different plasticized PVC matrices. The Schiff bases exhibited absorption and emission based optical responses to protons in the pH range of 3.0–7.8, and, therefore, can be used as an optical pH sensor for near neutral region of pH scale. The absorption and emission spectra were recorded by preparing thin films on a Mylar polyester support. Responses of the sensor slides were fully reversible within the dynamic range and the response time was approximately 3 min under batch conditions. All of the compositions exhibited a significant absorption based response to pH in immobilized form. Throughout spectroscopic studies, relative signal change of 79% has been achieved for sensor dye (I). In contrast to the weak emission peaks of (I) and (II), the sensor dye (III) exhibited a significant emission based response and is evaluated in a different category.

Keywords: Optical pH sensing; pH sensing with Schiff bases; PVC doped Schiff bases

1. Introduction

Optical pH sensors are based on pH dependent changes of the optical properties of thin and proton-permeable layers in which a pH indicator has been chemically or physically immobilized. Organic dyes such as phenol red; (α-hydroxy-αα-bis[4-hydroxyphenyl]-*o*-toluenesulphonic acid, γ sultone), bromthymol blue; (αα-bis[3,5-dibromo-4-hydroxyphenyl] - α - hydroxy - *o* - toluenesulphonic acid, γ sultone) and derivatives, bromophenol blue; (αα - bis(6 - bromo - 5 - hydroxycarvacryl)α - hydroxy-*o*-toluenesulphonic acid γ sultone), thiazole yellow (C.I. Direct Yellow 9) and cresol red (3′,3″ - bis[*N* - (carboxymethyl) - *N* - methylaminomethyl] - *o* - cresolsulfonphthalein), have been reported as absorbent or fluorescent pH indicators [1–3]. Certain conductive polymers change their colours as a function of pH and thus can be used for pH sensing. Polyaniline [4,5], substituted

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polyaniline [6], and polypyrolle [7] have been used in the development of optical and fiber optic pH sensors based on their absorption both in the visible and near IR regions.

An azlactone derivative embedded in plasticized PVC polymer film is used as a fully reversible pH sensor in the pH range of 1–7 [8]. Prussian blue; (C.I. Pigment blue 27) [9], bromo fluorescein; (C.I. Acid red 87) and its related compounds [10–13] were used as absorption and emission based new optochemically sensitive materials in chemical sensors. Hydroxypyrenetrisulfonic acid is another class of dye commonly used for pH sensing [14,15].

In most of the common designs, sensing parts of pH optodes contain weak acidic dyes whose dissociated and undissociated forms have different absorption or emission in the pH range of interest [1,2,10,11–16]. The aim of this work is to assess the performances of these novel Schiff bases in plasticized PVC matrices as optical pH sensors in terms of response time, dynamic working range, and sensor stability. In our early laboratory experiments, newly synthesized Schiff bases [I], [II] and [III], exhibited a high sensitivity to pH in near neutral region. In contrast to the weak emission peaks of [I] and [II], the sensor dye [III] exhibited a strong emission band at $\lambda_{\max} = 607$ nm, and is evaluated in a different category.

2. Experimental

2.1. Reagents

N,*N*′-Bis(4-diaminobenzyliden)-1,2-cyclohexandiamine[I], *N*,*N*′-bis(4-diaminobenzyliden)-1,2-ethanediamine [II] and 2,6-bis[(4-dimethylaminophenylimino)ethyl]pyridine [III], were synthesized and purified according to literature [18]. Chemical structures of Schiff bases I, II and III are shown in Fig. 1. The membrane components, PVC (high molecular weight) and the plasticizers, bis-(2-ethylhexyl)phtalate (DOP), bis-(2-ethylhexyl)-sebacate (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. Butylhydroxytoluene, hydrochloric acid and the regeneration buffer (titrisol, pH = 7 ± 0.02) were from Merck. Buffer solutions were prepared with *N*,*N*-bis(2-hydroxyethyl)-2-amino-ethanesulfonic acid (BES) from Sigma. Acid solutions and buffers were prepared with pure water obtained from an apparatus working with reverse osmosis principle from Elga. The polyester support (Mylar type) was provided from Du Pont Istanbul, Turkey.

2.2. Instrumentation

The absorption spectra of the polymer films were measured at Jasko V-530 UV–VIS spectrophotometer. The fluorescence emission spectra were recorded using a PTI-QM1 fluorescence spectrophotometer. pH measurements were performed with a pH meter Jenway 3040 Ion Analyser.

2.3. Polymer film preparation

The optode membranes were prepared to contain 120 mg of PVC, 240 mg of plasticizer, 20 mmole dye kg^{-1} polymer, the equal mole number of dye of potassium tetrakis (4-chlorophenyl) borate and 1.5 ml of THF. The prepared mixtures contained 33% PVC and 66% plasticizer by weight which is in accordance with literature [16,17]. The absorption spectra were recorded on thin films. For this purpose the resulting mixtures were spread onto a 125 μm polyester support (Mylar TM type), by means of a spreading device. Thin films were kept in a desiccator in the dark to ensure the photostability of the membrane and avoid the damage from ambient air of the laboratory. The polyester support was optically fully transparent, ion impermeable and exhibited good adhesion to PVC. The most important function of the polyester was to act as a mechanical support because the thin PVC films are difficult to handle. Once dried, the film was insoluble in water and could be cut into pieces of appropriate size. Film thickness of the sensing slides was measured with a Tencor Alpha Step 500 Prophylometer and found to be 5.10 μm. This result was an average of eight

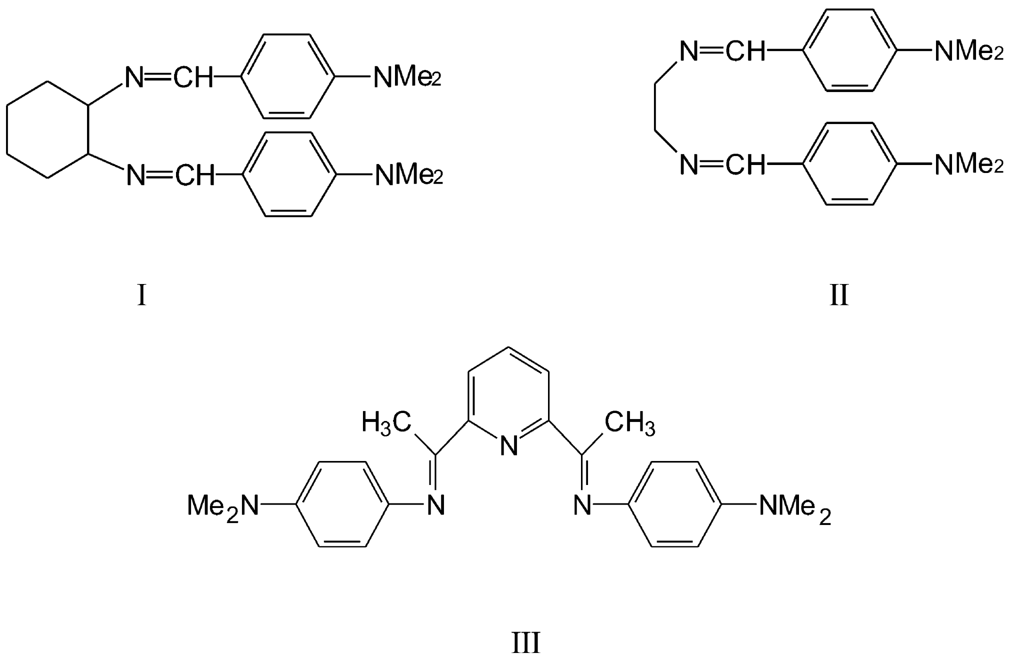

Fig. 1. Schematic representation of structures of the Schiff bases [I], [II] and [III].

measurements and exhibited a standard deviation of ±0.081. Each sensing film was cut to 1.2 cm width, fixed diagonally into the sample cuvette, and the absorption or emission spectra were recorded.

3. Results and discussion

3.1. Choice of indicator and matrix

The Schiff base structures contain active centres for proton attacks on the dimethylamino group and hence are pH sensitive. They easily dissolve in organic solvents or suitable solvent–water mixtures, undergo protonation reactions, and do not reversibly work in the solvent phase. The Schiff base doped polymer films respond to protons by a decrease in absorbance or emission intensity that is used as the analytical signal. In contrast to the results of the solution phase, absorption and emission spectra of the structures are expected to be reversibly pH dependent in solid matrices and our further experimental results proved this idea.

The sensor dyes [I], [II] and [III] exhibited excellent solubilities and quite good stabilities in plasticized PVC matrix. In order to decrease the cross sensitivity to oxygen and provide a better long-term stability, the antioxidant agent, butylhydroxytoluene (BHT) was added into the membrane composition III. In this way, storage stability of the Schiff base III increased from several days to more than six months.

Films were fully transparent, ion-permeable and the chosen dyes exhibited good compatibility to PVC. Plasticized PVC membranes are believed to be useful as matrix materials for analytical applications because of their optical transparency [19], simplicity of preparation, good mechanical properties and homogeneity [20–23] and, therefore, have been chosen as the matrix material for Schiff bases. The absorption spectra of the three different Schiff bases were recorded in presence of four different types of plasticizers. A representative absorption spectrum of immobilized Schiff base-I, in presence of the plasticizers of DOP, DOS, DOA and NPOE at pH = 6.8 is shown in Fig. 2. Since the highest signal intensities were obtained in

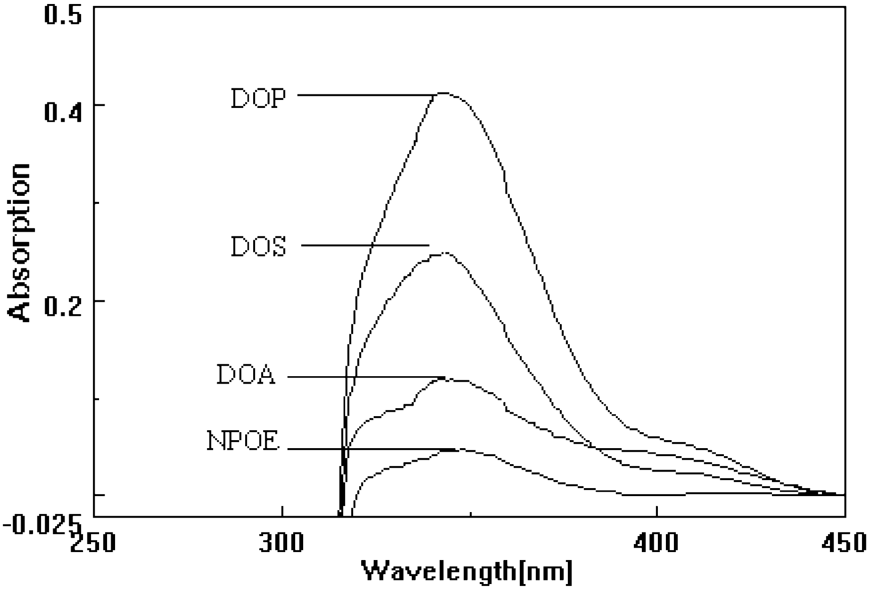

Fig. 2. Effect of different plasticizers; bis-(2-ethylhexyl)phtalate (DOP), bis-(2-ethylhexyl)sebacate, (DOS) bis-(2-ethylhexyl)adipate (DOA), and 2-nitrophenyl octyl ether (NPOE) on the response of immobilized sensor dye (I), at pH = 6.8.

presence of plasticizer of DOP, in further studies, DOP doped membranes were used.

3.2. Spectroscopic measurements

When immobilized in plasticized PVC matrices, the Schiff base structures, I II and III exhibited high molar absorptions; $\epsilon = 27\,000$ l mol^{-1} cm^{-1} at 348 nm, $\epsilon = 21\ 300$ l mol^{-1} cm^{-1} at 346 nm and $\epsilon = 28\ 300$ l mol^{-1} cm^{-1} at 495 nm respectively. The absorption spectrum of Schiff base II is very similar to the spectrum of Schiff base I. Given data were extracted from absorption spectra of Schiff bases at neutral pH values (see Fig. 3). The absorption maximum of immobilized Schiff base III is in the visible region of electromagnetic spectrum. In contrast to the weak emission bands of Schiff bases I and II, the Schiff base III, yielded a strong emission band at 607 nm when excited at 417 nm (Fig. 3a). The broad absorption band of the Schiff base III (410–610 nm), matches the emission of blue LED, which makes the dye LED compatible. Quite large Stokes' shift value (190 nm) of compound III also makes the usage of optical fibers and other solid-state components possible.

3.3. pH induced measurements

The sensor membranes reversibly respond to H^+ ions. They exhibit a decrease in absorption or emission intensity in the direction of protonation and an increase in the opposite way. Upon exposure to the solutions between pH 7.0–3.0, the M−1 exhibited a 79% relative signal change in direction of decrease in absorbance intensity. The pH induced absorption characteristics of Schiff base II is very similar to the Schiff base I (see Fig. 3a and b).

The pH induced emission spectrum of Schiff base III, and the dependence of the relative emission intensity on pH are shown in Fig. 4a and b respectively. For all sensor types, the plots of the absorption or emission based intensities versus pH exhibited "S" shaped calibration graphs with one inflection point.

pK_a values were calculated via equation

$$pK_a = pH + \log (A_x - A_b)/(A_a - A_x)$$

where A_a and A_b are the absorbance values of dye in its acid and conjugate base form respectively

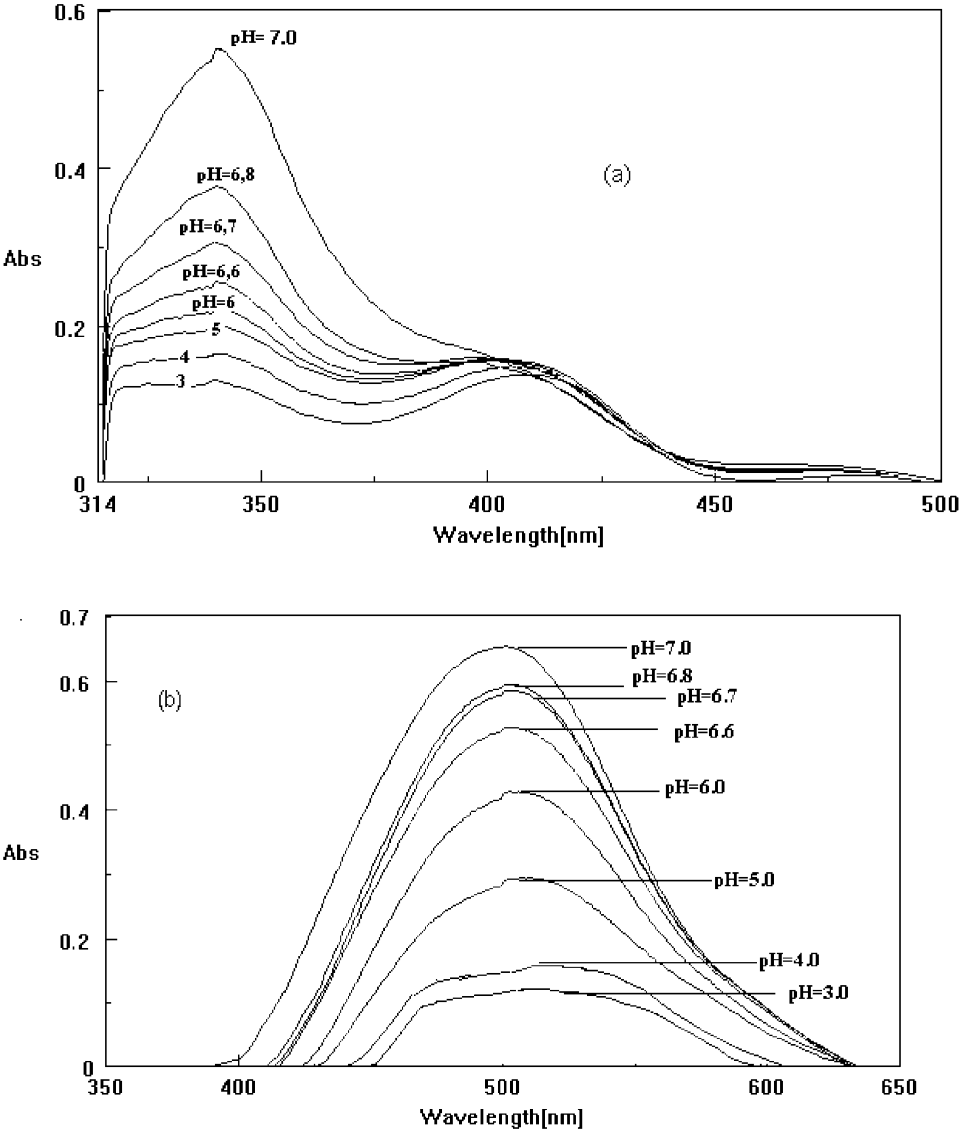

Fig. 3. (a) Dependence of absorption spectrum on pH of sensor membrane I at $\lambda_{max} = 348$ nm; (b) sensor membrane III at $\lambda_{max} = 346$ nm; in BES buffered solutions between pH 7.0 and 3.0.

and A_x is the absorbance measured at a pH around of pK_a of the dye [24].

From the equation the pK_a value of the immobilized Schiff base III is calculated as p$K_a = 6.28$. In a similar way, from the pH-induced absorption spectra, pK_a values of immobilized Schiff bases I and II were found to be 6.41 and 6.62 in the DOP containing PVC matrices respectively.

3.4. Response and reproducibility

The sensor slides were found to give reproducible results on absorption and fluorescence emission measurements when pH was varied from 7.0 to 3.0. The responses of pH sensors of I to III to protons were investigated in BES buffered solutions. Regeneration was accomplished with

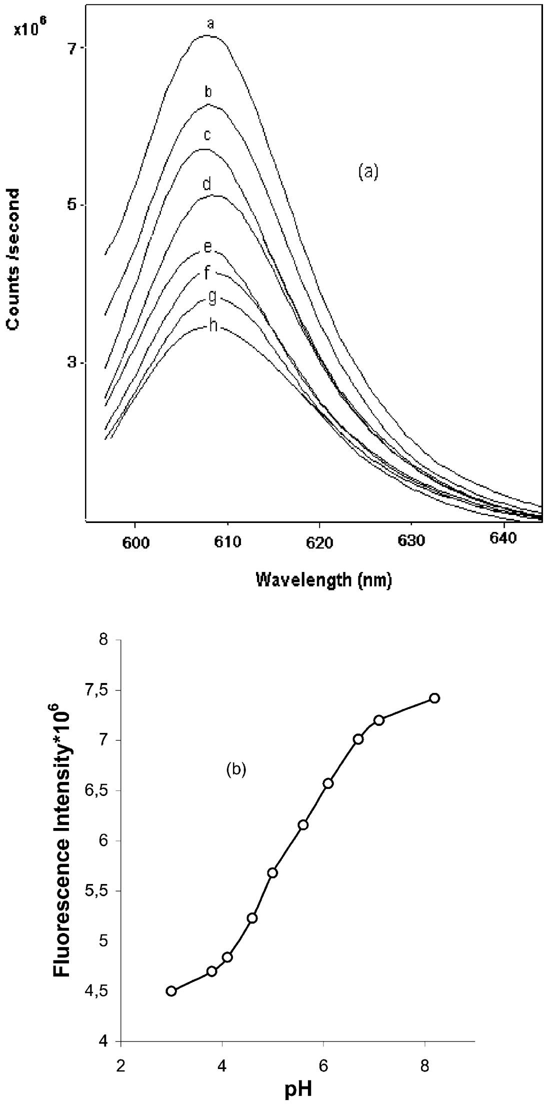

Fig. 4. (a) Dependence of emission spectrum of Schiff base III on pH in different pH buffers, [a] pH = 8.2, [b] pH = 7.1, [c] pH = 6.7, [d] pH = 6.2, [e] pH = 5.6, [f] pH = 5.0, [g] pH = 4.2, [h] pH = 3.2; (b) emission based sigmoidal response of Schiff base III to pH.

concentrated titrisol buffer solutions at pH = 7.0 ± 0.02. Fig. 5 shows the relative signal change, and reversibility of the sensor membrane III. The optode membranes of Schiff bases are found to reach 90% of the signal intensity (τ_{90}) between 2.7 and 3.2 min. Since the ion binding process is faster than that of unbinding, the regeneration time for all sensors was found to be approximately 15 min in $H_2PO_4^-/HPO_4^{2-}$ buffer. However the upper limit of response time can be improved. In our case, film thickness is approximately 5 μm, which can be reduced and shorter response times can be reached.

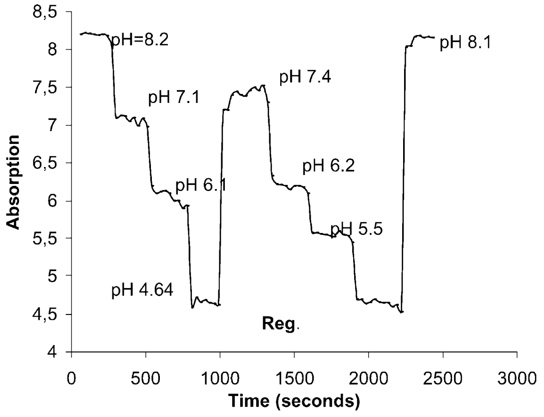

Fig. 5. Absorption based response curve of Schiff base III.

The absorption based pH induced relative signal change of Schiff base I and Schiff base II were found nearly same and are 79% and 80% respectively. Responses of the all sensor compositions were fully reversible in the pH range of 7.8 and 3.0. The reproducibility of the optical responses was assessed by repeatedly introducing a sample of pH = 4.6 in 0.02M BES buffer and a 0.2 M Titrisol buffer at pH 7.0. Between the first and fourth cycles, the level of reproducibility achieved was quite good with a RSD of 2.2%.

3.5. *Effect of ionic strength*

The dynamic working ranges of the sensors also cover the physiologically important range. For this reason, we compared the pH-induced responses of the sensor compositions in buffered, unbuffered and salty-buffered solutions. The chosen ionic strength was the same as the ionic strength of blood. The pH dependence of the membrane was affected by the ionic strength of the buffer solutions. In unbuffered solutions, within the dynamic working range of the sensor, the pH induced relative signal change was high. When the pH values of unbuffered solutions were plotted versus to the normalized absorbance (which is the ratio of absorbance at any point to the maximum absorbance value, $(A/A_{\max})$, exhibited more sigmoidal (S-shaped) curves, but the stability and reproducibility of the measurements became poor. In buffered solutions, reproducibility was satisfactory; response was more linear than that of the unbuffered ones, but relative signal change dropped from 80 to 70%. In presence of 135 mM NaCl, the pH-induced response of buffered solutions exhibited a 21% of decrease in the relative signal change in comparison with the responses of the unbuffered solutions. In order to acquire stable and reproducible data, all of the spectra have been recorded in BES buffered solutions which provides a similar medium to physiological liquids.

4. Conclusion

We demonstrate that, newly synthesized Schiff bases [I], [II] and [III], can be used for reversible pH sensing in the plasticized PVC matrix. In the present absorption and emission based studies, the dynamic working range has been determined as pH = 7.0–3.0. The compatibility of the sensor dye III with the solid-state optical components (in particular LED's) can be useful in construction of inexpensive and field available instrumentation. Our work along these lines but on different matrix is in progress.

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