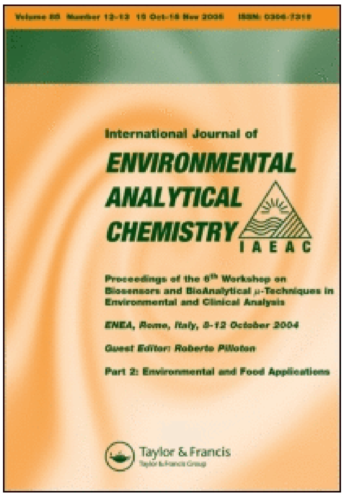

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Behaviour of phenol red pH-sensors in the presence of different surfactants using the sol-gel process

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Phenol red was immobilised into a polysiloxane matrix using a sol-gel process to form pH optical sensors. The sol-gel was obtained by hydrolysis of tetraethoxysilane (TEOS) in the presence of phenol red (PR) and the appropriate surfactant. Different surfactants, namely cetyltrimethylammonium bromide (CTAB), dodecyldimetyl amino-oxide (GLA) and Triton X-100 (TX-100), were employed. Interestingly, the use of surfactants significantly improved the mesostructure of the silica and increased the porosity of the system. The two response pH ranges were shifted to pH 0.0–3.0 and pH 10.5–1.5M [OH^-] compared with those of the free PR (pH 0.0–3.0 and pH 6.5–9.5). It is found that the pH response and the pKa shift of the phenol red were dependent, not only on the silica matrix but also on the ionic properties of surfactants. In the case of ionic surfactants such as CTAB or GLA, there was further shift to more acidic and more basic pH, whereas in the case of non-ionic surfactants such as TX-100 no significant change of the pH curve was observed.

Keywords: sol-gel; phenol red; immobilised phenol red; optical pH sensors

1. Introduction

Immobilised pH indicators and their applications to optical chemical sensors have drawn most attention in the last two decades because of the importance of pH measurements in scientific research and many other practical fields [1–5]. Optical pH sensors are based on changes of the absorption spectra of the doped pH indicator. Silica is considered as one of the best substrates used to host pH indicators [6,7]. Surfactants were used recently to form mesostructure silica and therefore obtained a highly porous nature from these materials to make them excellent hosts for sensing molecules, so the sensing species can easily diffuse towards the sensing centres [8–10].

There are three methods used for the immobilisation of pH indicators: impregnation after calcinations, covalent binding and an entrapment method in which the species were entrapped into the host matrix. Phenol red (phenolsulfonphthalein) and its derivatives were used for the immobilisation into solid supports [11–20]. Wang *et al.* presented a phenol red immobilised sensor based on sol-gel with fast response and long-term stability for pH (6.0–12.0) [11]. Livage and Avnir have immobilised the PR into sol-gel matrices in

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the presence of CTAB for development of optical sensors [10,20]. The effects of the silica matrix and the presence of CTAB on the pH response and pKa shifts were well documented for similar systems [20]. In this work, PR was immobilised into polysiloxane matrix in the absence of the acid catalyst in which phenol red was used as a weak acid catalyst for the sol-gel reaction instead of HCl. Cationic CTAB, zewitterionic GLA and non-ionic TX-100 were used. The pH response ranges and pKa shifts were obtained using three different surfactants. The optical spectra characteristics were used to examine the changes before and after immobilisation, the response pH range and the influence of using different surfactants. An optical polarised microscope was used to provide information about the porosity.

2. Experimental

2.1 *Reagents*

The starting reagents, which include tetraethylorthoslicate, $Si(OEt)_4$ (TEOS), phenol red, $C_{19}H_{14}O_5S$ (PR), cetyltrimethylammonium bromide $C_{19}H_{42}BrN$ (CTAB), and dodecyl dimetyl amino oxide $C_{14}H_{31}NO$ (69%), $C_{16}H_{35}NO$ (25%), $C_{18}H_{39}NO$ (50%) (Genaminox LA, GLA) were purchased from Clariant. Hydrochloric acid, sodium hydroxide, non-ionic Triton X-100 $C_8H_{17}C_6H_4(CH_2CH_2O)_{9.5}O$ (TX-100) and absolute ethanol were purchased from Merck (Darmatadt, Germany) and used as received.

2.2 *Spectra*

The UV/VIS spectra for free and immobilised PR in acid and base solutions were obtained on a Shimadzu -1601 UV/VIS spectrophotometer.

2.3 *Polarisation optical microscopy*

Immobilised monolithic disks were characterised using a Zeiss standard polarisation microscope equipped with a camera.

2.4 *Synthesis*

In a typical preparation of a monolithic disk, 3 mL of a mixture of TEOS : ethanol : water in the following molar ratio 1.0 : 4.0 : 2.0 was used, while the concentration of the dye was maintained at $0.8*10^{-4}$M and the concentration of the surfactant varied from $0.33*10^{-4}$M to $1.33*10^{-2}$M. The mixture was stirred for one minute, and then was left for seven days at an ambient temperature forming monolithic gels. The monolithic materials of the entrapped PR were left for another week to obtain solid transparent crack-free disks with 1.02 mm thickness and 6.3 mm radius. The monolithic disks were washed five times with ethanol/water ($5 \times 5\,cm^3$). The washes were collected and the leaching percentage of PR was examined. It was observed that:

1. No significant leaching of PR was detected.
2. The use of TX-100 surfactant reduced cracking of the monolithic disks.
3. No HCl catalysts were used and the phenol red acts as an acid catalyst.

3. Results and discussion

3.1 *Synthesis*

Monolithic gels of trapped PR were obtained through the sol-gel process by hydrolysis of $Si(OEt)_4$ in which PR acts as an acid catalyst. Ionic surfactants CTAB, GLA and non-ionic surfactant TX-100 were used to modify the matrix structure. It was found that TX-100 surfactant strengthened and reduced cracking of the monolithic disks. No leaching was observed for all samples, this probably occurred because the dimensions of PR molecules adapted to the mesostructured silica pores diameter in the presence of CTAB or GLA surfactants. Moreover, the hydrophilic character of silica favours the adsorption of polar PR molecules through efficient van der Waals and London forces and hydrogen bonding. It was found that the pH of the PR solutions decreased from 4.8 to 3.8 in the presence of TEOS and the pH of the reaction mixture increased from 3.8 to 4.4 in the presence of CTAB and to 6.8 in the presence of GLA. It is possible to suggest that PR was probably acting as an acid catalyst for the hydrolysis and polycondensation of the silane agent. When CTAB or GLA was used, strong electrostatic attraction between the cationic CTAB or zwitterionic GLA and the ionic species of phenol red occurred, thus increasing pH.

3.2 *The spectra*

At normal conditions PR exists in three forms: the acid form (orange-red colour), neutral form (yellow colour) and base form (red-pink colour) which corresponds to the absorptions at about 510 nm, 430 nm and 570 nm, respectively [21].

The absorption spectrum of the free PR is slightly different from that of the immobilised PR (Figure 1). In ethanolic solution (2.5 x 10^{-5} M), two absorption bands were observed at 510 nm and 430 nm, corresponding to the acid and neutral forms

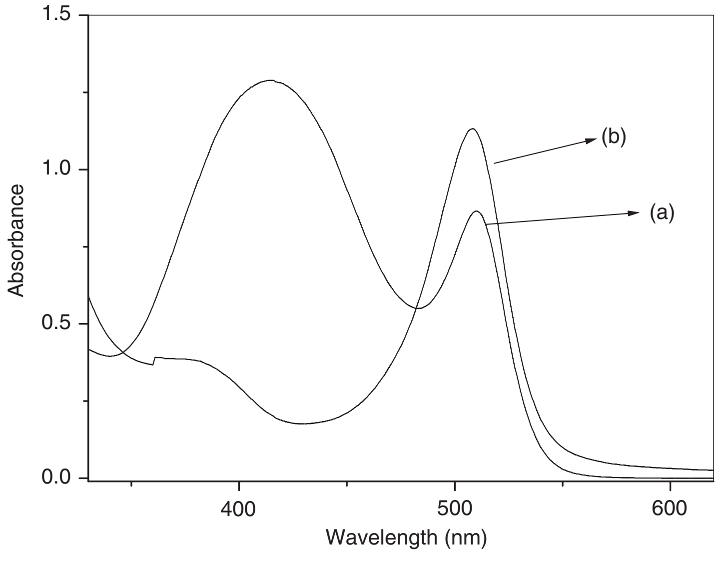


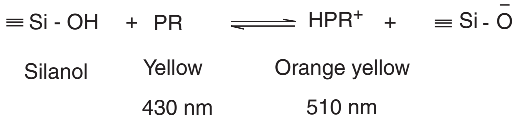
Figure 1. Absorption spectra of: (a) free PR, (b) immobilised PR.

(Figure 1a), whereas only one absorption band at 510 nm was found for the immobilised PR (Figure 1b). This can be explained by the fact that PR molecules were probably protonated by the acidic silanols, when they were immobilised into a siloxane network as shown in Scheme 1.

Only the acid form HPR^+ of phenol red was found when the PR was immobilised into the silica support, indicating that not all PR species were protonated by silica silanols as shown in the systematic diagram (a).

The spectra of the immobilised PR in the presence of different types of surfactants CTAB, GLA and TX-100 are given in Figure 2. Significant changes were noted depending upon the type of surfactant involved. In the presence of CTAB as a cationic surfactant of concentration of 5×10^{-3} M, only one absorption band at 430 nm was observed and no absorption band at 510 nm was shown (Figure 2a). The reason for this is probably that the presence of CTAB has changed the properties of the matrix and acts as a retardation agent for protonation by silanols, yielding the neutral form PR. At higher concentration of CTAB (5×10^{-2}M), the absorption band at 430 nm decreased gradually and a new absorption at 600 nm was developed (Figure 2b). This is probably due to the fact that, above cmc of CTAB, a micelle is formed in which the anion form of phenyl red is localised in the micelle as shown in the systematic diagram (b).

A broad band has been observed in presence of GLA (Figure 2c) with no resolution that can be interpreted as there is a physical and chemical change occurred in the matrix



Scheme 1. Protonation of phenol by acidic silanols.

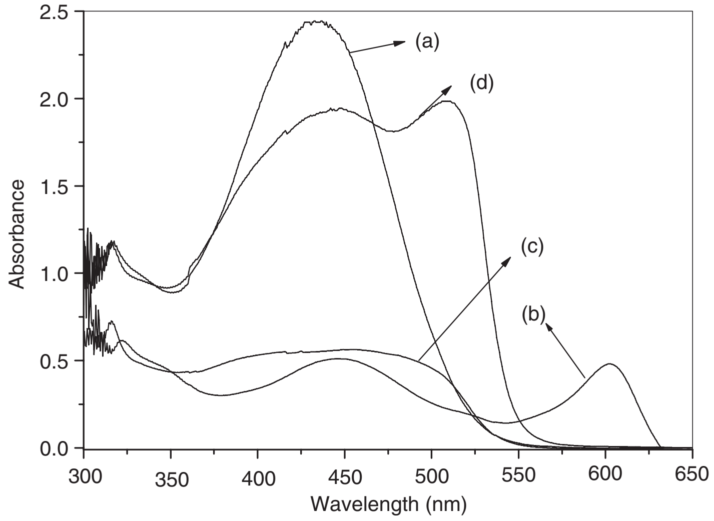


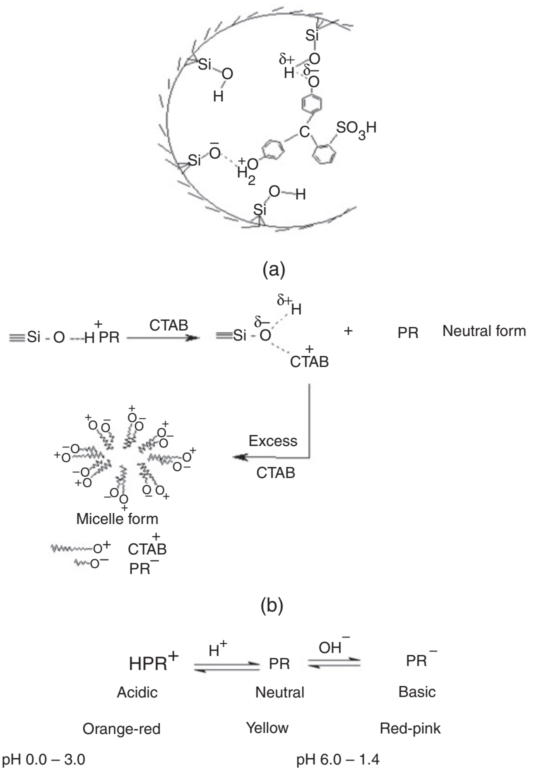
Figure 2. Optical spectra of: (a) immobilised PR/CTAB, 0.005 M, (b) immobilised PR/CTAB, 0.05 M, (c) immobilised PR/GLA, 0.0008 M, and (d) immobilised PR/TX-100, 0.005 M.

properties in the presence of GLA. This can be explained by the strong electrostatic attraction between both the heads positive and negative charges of GLA with the opposite charges of the ionised species of the PR (H^+, PR^-) in the micelle. Thus, neither the acid form nor the base form peaks were clearly shown in the spectra. This was confirmed by the formation of a cluster of associated globules when GLA was used, as discussed in the following section.

In the presence of TX-100, the absorption spectrum shows two absorptions at 510 nm and 430 nm (Figure 2d) which suggests the presence of both acid and neutral forms. The reason for this behaviour is that when the non-ionic surfactant TX-100 was used, London and van der Walls forces were developed between surfactant and PR molecules which results in reducing the protonation of PR by surface silanol groups.

The absorption spectra of free phenol red (PR), the immobilised PR and the immobilised PR/surfactants at different concentrations of [H^+] reveal the presence of three forms of PR (acid, neutral and base forms) in equilibrium with one another (Figures 3–7) (Scheme 2).

Two equilibriums were obtained as pH changes from pH 0.0 to 14, the first equilibrium occurs at a low pH (0.0–3.0) in which the neutral form (yellow colour) was changed into the acidic form (orange-red colour). The second equilibrium occurs at pH (6.0–14) in which the neutral form (yellow colour) was changed into the basic form (red–pink colour) as given in Scheme 2. Reports of similar systems were described by other workers [12,20].



Scheme 2. Systematic diagrams of (a) protonation of PR, (b) deprotonation of PR and micelle formation.

Table 1. pH response ranges and pKa values for free and immobilised PR in different surfactants.

Surfactant	pKa$_1$	pKa$_2$	pH response range	
Free PR	0.87	9.00	0–3.0,	6.5–9.5
Immobilised PR	1.6	12.5	0–3.0,	10.5–1.5M $[OH^-]$
Immobilised PR/TX-100	1.7	12.5	0–3.0,	10.5–1.5M $[OH^-]$
Immobilised PR/CTAB	1.3	13	1.5M $[H^+]$–3.0,	11.7–4M $[OH^-]$
Immobilised PR/GLA	0.5	14	1.5M $[H^+]$–3.0,	2M $[OH^-]$–4M $[OH^-]$

The pH response ranges and pKa values for free, immobilised PR and immobilised PR/surfactants are given in Table 1.

Figure 3 describes the absorption spectra of the free PR versus pH. Two equilibriums were observed, one at low pH 0.0–3.0 (Figure 3a) and the other at high pH 6.5–9.5 (Figure 3b). pKa values (0.87 and 9.0) are close to those reported for similar systems (0.2 and 8.0, respectively) [20]. The absorption spectra of the immobilised PR are given in (Figure 4a and 4b) in which the two pH response ranges occurred at pH 0.0–3.0 and pH 10.5–1.5M $[OH^-]$. The found pKa values, 1.6 and 12.5, were higher than those obtained from the literature, 1.0 and 8.5, respectively [11]. The reason for this variation is that in our preparation of the material the HCl acid catalyst was not used, this of course has changed the microstructure of the silica and thus may result in different pH responses and pKa shift.

The higher pKa values for the immobilised PR (1.6 and 12.5) compared with those of the free PR (0.87 and 9.0, respectively) is probably due to the presence of another proton source from silanols in which the equilibrium is shifted to less acidic and more basic. In the presence of CTAB, there is a further shift in the response pH range to a more acidic and a more basic pH than that of the free and immobilised PR (Table 1, Figure 5a and b). pKa values changed from 1.6 and 12.5 for the immobilised PR to 1.3 and 13.0, respectively, in the presence of CTAB. This is in contrast with the results reported by Rottman *et al.* in which the two pKa values are shifted in the same direction [20]. The acidic shift of pKa value of PR is the same as that reported [11,20] whereas the basic shift of pKa value is found in the opposite way (more basic) as pH increased. The reason for this is that CTAB at the micellar environment favours the anionic hydrophilic species of PR. In the case of using GLA as a surfactant, the spectrum shows only one isobestic point at 470 nm (Figure 6), in which perhaps the two equilibriums obtained are: one equilibrium is between the neutral and acid forms and the other is between the acid and base forms. This was accompanied by a change of pKa values from 1.6 and 12.5 for the immobilised PR to 0.5 and 14.0, respectively, in the presence of GLA. The lower pKa when GLA was used is expected due to strong electrostatic attractions between the zwitterionic surfactant of both heads (negative and positive charges) and the corresponding species of the phenol red.

There was no change either in the response pH range nor in pKa values when TX-100 was used (Figure 7a and 7b) in comparison with the immobilised PR. The explanation for this behaviour is that only van der Waals and London forces are established between PR and the non-ionic surfactant molecules.

At high pH range, the PR molecules were deprotonated which is favoured by the presence of CTAB or GLA forming ion-pairs, e.g. $PR^- - CTAB^+$ localised in the micelle. This explains why there was a shift of the response pH range towards more basic in

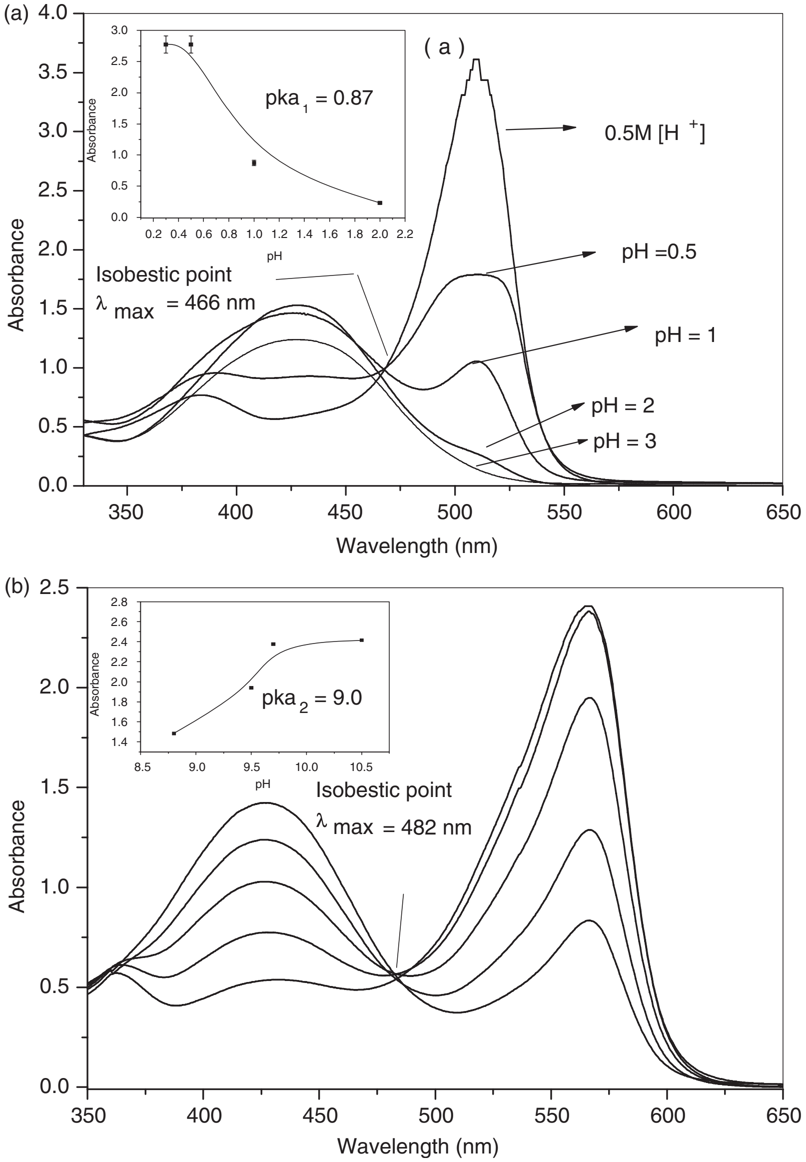


Figure 3. Spectra of PR in solution (2.5×10^{-5} M): (a) at pH 0.0–3.0 (b) at pH 6.0–9.5.

the presence of CTAB or GLA. That was accompanied by the increasing of pKa values from 12.5 for immobilised PR to 13.00 and 14.0 for immobilised PR in presence of CTAB and GLA, respectively (Table 1). At a lower pH range, PR molecules were protonated in which the shape of micelle structure entity may be changed. This may explain why there was a shift of the response pH range towards a more acidic level in the presence of CTAB or GLA (Table 1) and that was accompanied by decreasing pKa values from 1.6 for immobilised PR to 1.3 and 0.5 for immobilised PR, in the presence of CTAB or GLA, respectively (Table 1). The higher shift of the response pH range to more basic and more acidic levels, when GLA was used compared with that of CTAB is probably dependent on

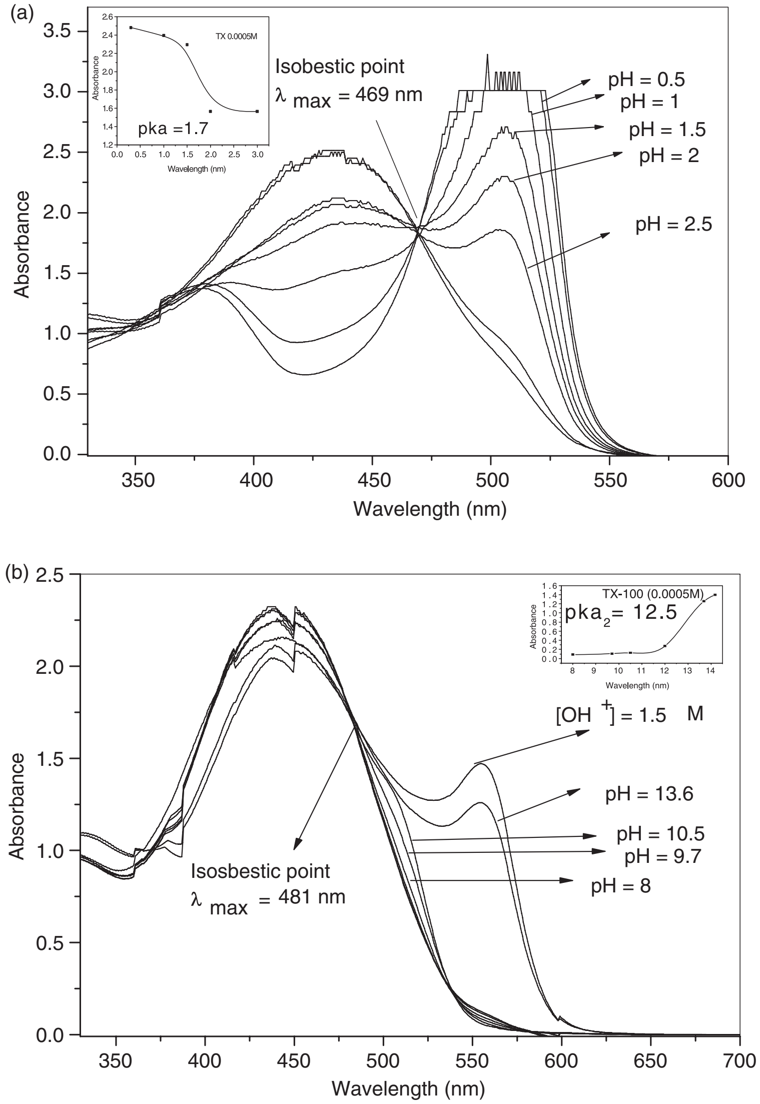


Figure 4. Spectra of immobilised PR (2.5×10^{-5}M): (a) at pH 0.0–3.0 and (b) at pH 6.0–14.

the nature of the used surfactant. GLA has two charges and less bulk than CTAB and therefore a strong electrostatic attraction was expected. We have only tested the PR-gel against pH 1.0–14 using NaOH and HCl. It is found that the PR-gel is sensitive only at high and low pH, but it is not sensitive at a pH of 3.0–10.0.

3.3 *Effect of NaOH*

There were two forms in equilibrium upon treatment of the immobilised PR or the immobilised PR/surfactant with NaOH solution, in which the final form is always the basic form (pink-red), but the initial state is different depending upon the case present.

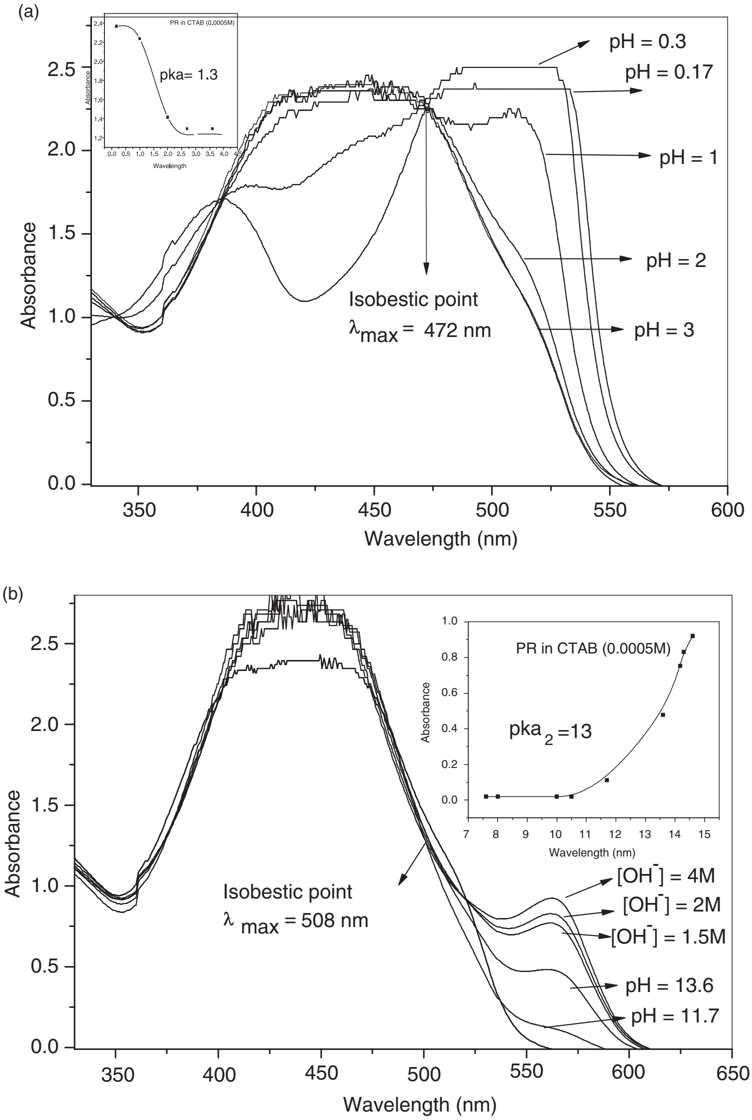


Figure 5. Spectra of immobilised PR/CTAB (0.0005M): (a) at pH 0.0–3.0, (b) at pH 6.0–14.

For example, in the case of immobilised PR the change was between acidic form (orange-red) and basic form (pink-red), whereas in the case of the immobilised PR/CTAB, the change was between neutral form (yellow) to basic form (pink-red). When GLA was used, there was a gradual move from neutral yellow towards the acid form (orange-red), then it changes to the base form (pink-red) (Figure 8). The optical spectra of the immobilised PR treated with 1.5 M NaOH are depicted in Figure 8a. The absorption at 510 nm gradually disappeared and new two absorptions were observed at 570 and 430 nm. Two isobestic points at 538 and 475 nm were found, indicating the presence of only two forms in which the acid form (orange-red) is changed into the base form (pink-red), upon treatment with NaOH solution.

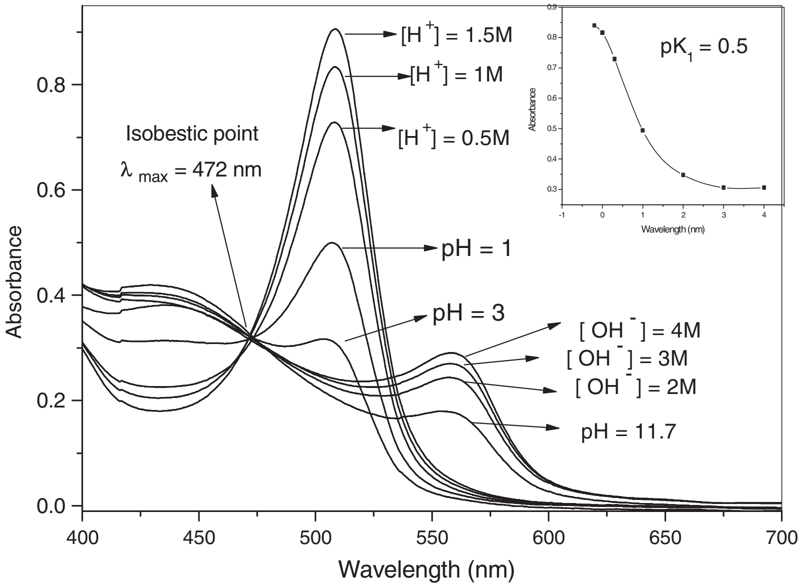


Figure 6. Spectra of immobilised PR/GLA (0.0005M) at pH 0.0–14.

When the immobilised PR/CTAB (5×10^{-3} M) is treated with NaOH solution (1.5 M), a new absorption at 570 nm gradually developed with the presence of two isobestic points at 472 nm and 386 nm (Figure 8b). This may be attributed to equilibrium change from the neutral form (yellow) to the base form (pink-red) upon treatment with NaOH solution.

When the immobilised PR/GLA (8×10^{-4} M) was treated with sodium hydroxide (1.5 M), two absorption bands at 510 nm and 400 nm were obtained. But after a few minutes a new absorption appeared and developed at 570 nm as well as at 430 nm. Therefore the colour changed from yellow to red-pink (Figure 8c).

When the immobilised PR/TX-100 (5×10^{-3} M) is treated with sodium hydroxide (1.5 M), a new absorption band was developed at 570 nm and gradual disappearance of the absorption bands at 510 nm (Figure 8d). The presence of two isobestic points at 530 nm and 475 nm which indicates the presence of two forms in which the neutral and basic forms are in equilibrium.

3.4 *Reversibility of the sensor*

The absorption spectra of the doped PR sensor can be reversed at the two equilibriums pH 3.0–0.0 and 6.5–14 ranges. The maximum absorbance wavelength went back when the pH is changed from 0.0 to 14.

3.5 *Reproducibility (lifetime of the sensor)*

The life time of the sensor was examined for a period of several months. The sensors were stored at ambient temperature in dried conditions. The absorbance response does not change after six months. Therefore, this sensor shows a long-term stability.

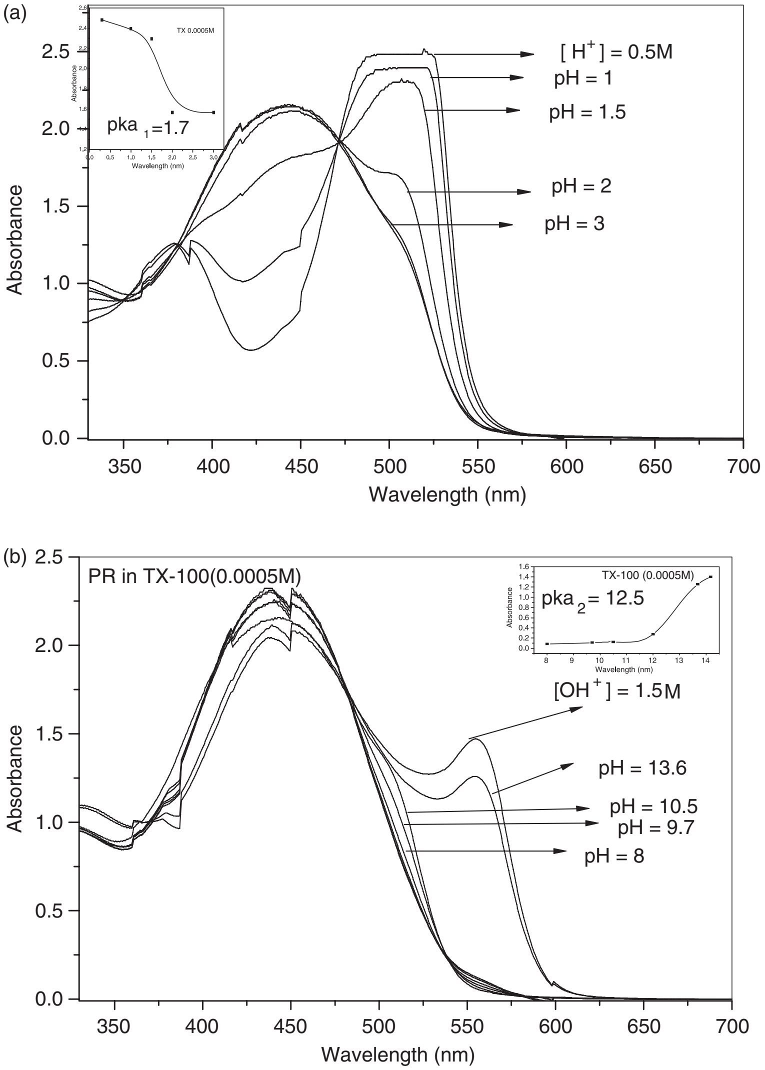


Figure 7. Spectra of immobilised PR/TX −100 (0.0005M): (a) at pH 0.0–3.0 (b) at pH 6.0–14.

3.6 *Optical photograph*

Optical polarised photographs of immobilised PR and immobilised PR/GLA surfactants are depicted in Figures 9a and 9b. The presence of GLA surfactant makes particles more uniform and more particles available, which increases the surface area of interaction (Figure 9b). The photograph shows that with the presence of the GLA surfactant the particles form a cluster of associated globules.

4. Conclusion

Monolithic disks of the immobilised PR in the presence of ionic and non-ionic surfactants were prepared by the sol-gel process in absence of catalysts. It is found that the pH

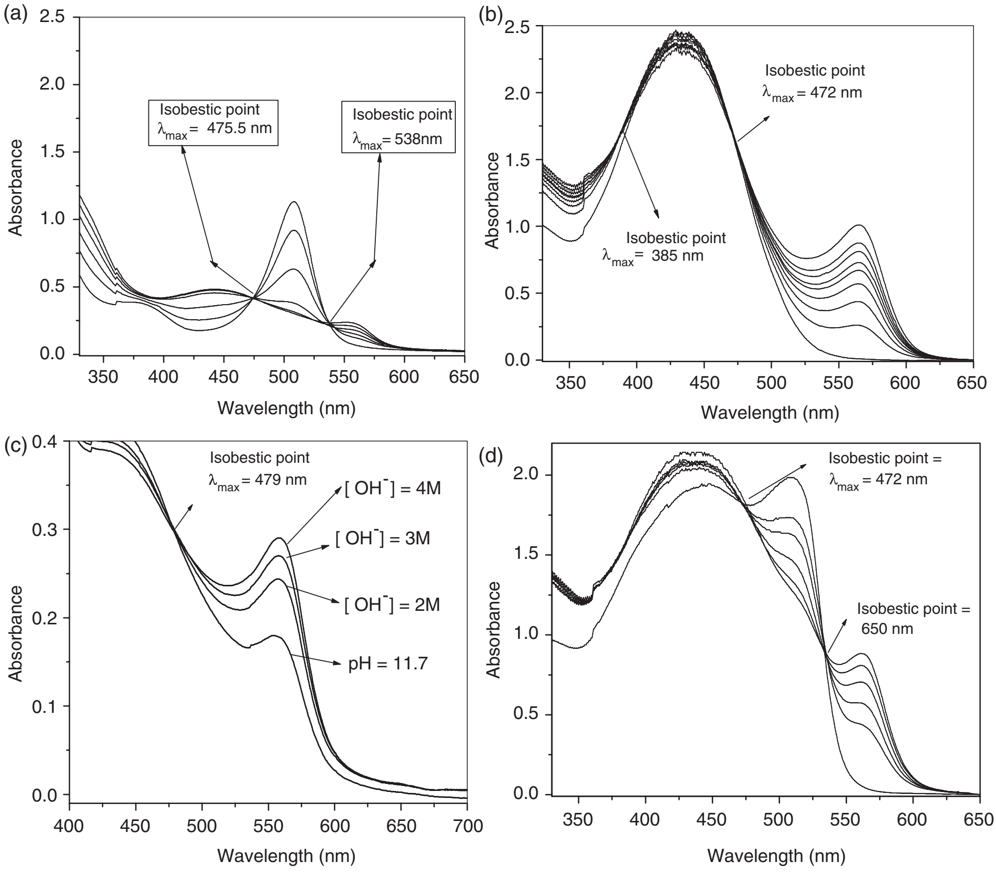


Figure 8. UV/VIS spectra of: (a) immobilised PR (0.00025 M), (b) immobilised PR (0.00025 M)/CTAB, (c) immobilised PR/GLA (0.0005M), and (d) immobilised PR/TX −100, 0.005 M upon treatment with sodium hydroxide solution (1.5M).

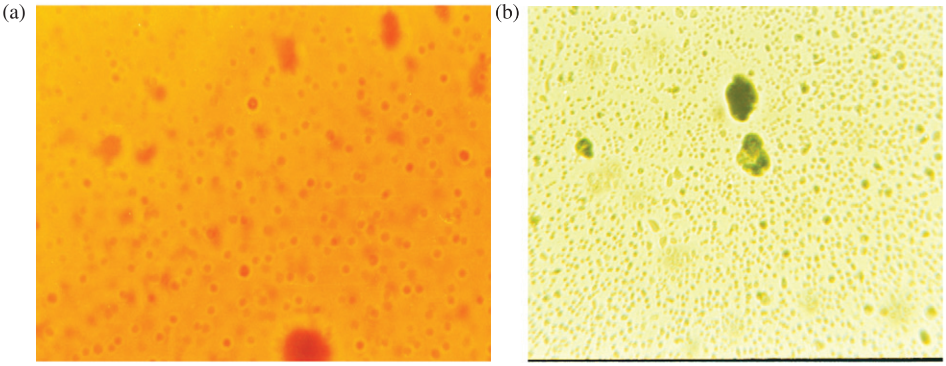


Figure 9. Optical polarised photograph of: (a) immobilised PR (0.001M) and (b) immobilised PR (0.001M)/GLA (0.005M).

response and the pKa of the phenol red were dependent on the silica matrix and the ionic properties and concentration of surfactants. Polarised microscope photographs showed a cluster structure of associated globules being formed in the presence of zwitterionic surfactant as a result of strong interactions between the surfactant and the phenol red species. There was a strong shift of the pH response range towards basic and acidic media in the presence of ionic surfactants. Therefore, these materials can be used as sensors for monitoring reactions at negative pH and pH $>$ 14.

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