Spectral pH dependence of erythrosin B in sol-gel silica coatings and buffered solutions

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Thin coatings optically sensitive against pH are obtained by entrapping erythrosin B molecules in a sol-gel silica matrix. Comparisons between optical spectra of erythrosin B in solutions and those once entrapped in silica coatings are performed for pH ranging from 0.5 to 12.0. Significant differences between both kinds of spectra (solutions and coatings) of erythrosin B are observed. Main changes are displayed in the absorption spectra for neutral to basic pH. Furthermore, the erythrosin B doped coatings show memory effect or hysteresis in their spectral response against pH. This means that absorption spectra depend on the direction of the pH change. Likewise, the photoluminescent spectra of erythrosin B in buffered solutions exhibit pH dependence and a maximized response in the basic pH range. On contrast, no significant photoluminescence from the erythrosin B entrapped in the silica coatings is observed.
Results are mainly discussed on the basis of different optical response of polyprotic forms of erythrosin B and possible interactions between the molecule and oxygen as well as the porous walls of the sol-gel silica matrix. In addition, the presence of diffusional barriers, which hamper the flowing of protons and other associated ions, is taken into account. Good agreement with previous observations about low absorption of polyprotic cationic and neutral forms of erythrosin B is found.

Keywords: A. Optical materials, B. Glassy coatings, C. Sol-gel chemistry, D. Optical properties, D. Luminescence

Dependencia espectral de la eritrosina B con el pH en soluciones tampón y en recubrimientos sol-gel de silice.

Se han obtenido recubrimientos delgados ópticamente sensibles al pH mediante atrapamiento de moléculas de eritrosina B en matrices de sílice obtenidas por sol-gel. Se compara la respuesta espectral de la eritrosina B en solución y atrapada en los recubrimientos de sílice para un intervalo de pH comprendido entre 0,5 y 12. Se observan apreciables diferencias entre ambos tipos de espectros (en solución y en recubrimiento) de la eritrosina B. Los principales cambios aparecen en los espectros de absorción para el intervalo neutro y básico de pH. Además, los recubrimientos dopados con eritrosina B muestran respuestas espectrales frente al pH con efecto de memoria o histéresis. Esto significa, que el espectro de absorción depende del sentido del cambio del pH. De forma análoga se ha visto que los espectros de fotoluminiscencia para la eritrosina B en soluciones tampón dependen del pH, mostrando su máxima respuesta en el intervalo básico de pH. Por el contrario, para la eritrosina B atrapada en los recubrimientos de sílice no se observa señal de fotoluminiscencia.
Se discuten los resultados teniendo en cuenta principalmente, la diferente respuesta óptica de las formas poliproticas de la eritrosina B y sus posibles interacciones con el oxígeno así como con las paredes de los poros de la matriz sol-gel. Además, se considera la presencia de barreras difusionales hacia la molécula que impiden el flujo de protones y otros iones asociados. Se encuentra un buen acuerdo con observaciones previas sobre la baja absorción óptica de las formas poliprótica cationica y neutra de la eritrosina B.

Palabras clave A. Materiales ópticos, B. Recubrimientos vítreos, C. Química del sol-gel, D. Propiedades ópticas, D. Luminiscencia.

1. INTRODUCTION

Sol-gel glasses are currently used as suitable host matrices for a great variety of organic molecules that can be incorporated in the micro porous structure of the glass network (1-10). In fact, there are a wide variety of dye molecules and novel sensors, which are being investigated and developed on the basis of the sol-gel method (11-16). One benefit of this procedure is related with the fact that the method involves low temperature process from liquid phase, which prevents the pyrolysis of organic molecules. Furthermore, provides a chemically inert enclosed space at high concentrations of the dye molecules without aggregation. Sol-gel thin coatings technology shows some other advantages such as complex shape deposition, easy handling of chemical composition and suitable coating thickness. This technology is also used for obtaining advanced ceramics, electroceramics and composites (17,18).

In the current study the incorporation of organic molecules and particularly erythrosin B into the thin silica coatings is

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carried out as a mean to sensitise optically the coatings against pH.
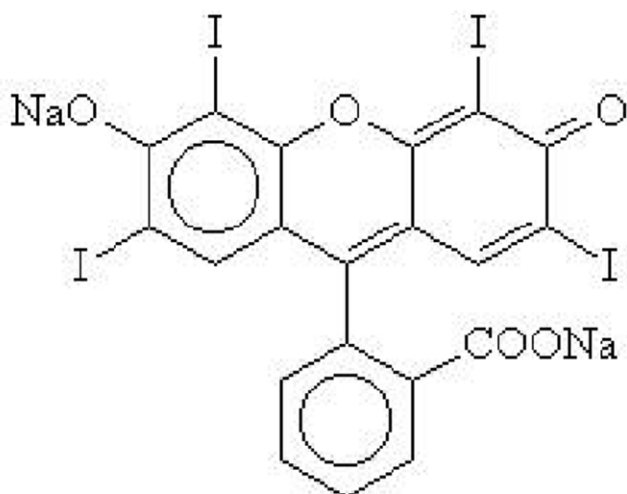

Fig. 1- Structure of Erythrosin B (2', 4', 5´, 7' tetraiodofluorescein disodium salt).

Erythrosine B is an iodo derivative of fluorescein and it is used in a variety of applications in colouring cosmetics and food, in printing inks, as a biological stain and as a radiopaque medium. Fig. 1 show structure of Erythrosin B (2', 4', 5´, 7' tetraiodofluorescein disodium salt) employed in the present work. Its use in this investigation is partially motivated because the optical pH sensitivity of erythrosin B in buffered solutions. This sensitivity has been established long time ago by various research workers (19-21). However, their application as sensor in sol-gel matrices has been poorly investigated or only focused from the point of view of phosphorescent properties to be applied to oxygen sensors (22-24).

The current study is a part of a wider research designed to obtain suitable pH sensors by sol-gel method. In this way, the main purpose of the present work is to combine both pH sensitivity and optical response for short times in the same sol-gel system. With this end, we take into account the adequate optical behaviour of the dye in solution, the ability to be incorporated in the sol-gel system as well as the photostability of the dye doped coating and its reactivity into the coating network.

2. EXPERIMENTAL

In this work we used optical spectroscopy (absorption and photoluminescence) to evaluate the optical response versus pH of erythrosin B entrapped in sol-gel silica glasses, and we compared with those of erythrosin B in methanol-buffered solutions for a same concentration. Commercial buffered solutions between pH 2.0 and 12.0 from pHydrion Buffers, Micro Essential Laboratory were used. Adding $1.9x10^{-4}$ M in methanol to the corresponding pH buffered solution, with a volume ratio of 1:4 respectively made Erythrosin B solutions with different pH. Dye-doped silica coatings were prepared as follows: 2.5 wt% of erythrosin B (previously dissolved in methanol) was added to a methanol solution of hydrochloric acid (3M) and tetraethoxylane (TEOS) in a

molar ratio TEOS:MeOH:HCl of 1:4:8. Once homogenised, the coating was obtained by dip-coating soda lime silicate substrates (microscope slides) into the previous solution with a withdrawal rates in the 5-25 cm min^{-1} range. Then, after drying at room temperature for 10 min, the samples were maintained at 60 ^{0}C for three days in a drying chamber. Thickness of the coatings was measured from the reflectance spectra by the interference fringe method to be in the 200-450 nm ranges. Optical response was monitored for absorption and reflectance spectra by means of a double beam spectrophotometer Shimadzu 3100 attached with an integrating sphere, whereas for photoluminescence spectra (emission and excitation) a Perkin-Elmer LS5 fluorometer was used. The fluorometer provides corrected excitation and emission spectra in the 250-700 nm range. Thus, it eliminates band-shape distortions and errors in peak heights and wavelengths. Before the spectra recording, the doped coatings were immersed in the corresponding pH buffered solution for 5 min and then carefully dried with a soft tissue at room temperature.

3. RESULTS AND DISCUSSION

3.1 Absorption-pH dependence

Absorption spectra from as prepared erythrosin B pH buffered solutions in the 330-700 nm range consist in three well-defined peaks. The shape, intensity and peak position of those spectra are pH dependent as is shown in Fig. 2. Thus, for pH between 12.0 and 4.0 the spectra are dominated by a peak close to 530 nm, together with a shoulder at about 500 nm, and a secondary band -less intense- peaked at about 355 nm. The main peak appears more intense for pH in the basic and neutral ranges and strongly decreases in intensity in acid range, especially for pH between 3.5 and 0.5. Actually, the main peaks shift gradually from 5 to 10 nm towards long wavelength as the pH decreases from 3.5 to 0.5. In addition, the 355 nm peak vanishes and a very broad band centred at about 415 nm, whose intensity remains practically constant against pH, appeared (see Fig.2a). The marked changes displayed between pH 4.0 and 3.5 in the absorption spectrum, strongly suggest that a polyprotic transformation takes place. Fig.2b represents the pH dependence in intensity of the two main peaks at about 530 and 500 nm. As can be seen in the figure, these results are in good agreement with the value of pK_a ~ 3.8 given in the literature for the equilibrium between monoanionic and dianionic forms.

$$HEB^- \leftrightarrows EB^{2-} + H^+ \qquad (1)$$

Therefore, for pH>4 the dianionic form (EB^{2-}) would be involved as main responsible in the absorption spectra. Likewise, for pH<3.5 the spectra would be mainly related to the monoanionic form (HEB^-). This is partially supported because the presence of the four iodine atoms in the erythrosin B gives rise to a significant decrease in the protonation trend of the molecule. All that results confirm that the polyprotic cationic and neutral forms of the molecule show low values for the molar extinction coefficient in difference with the dianionic form.

On contrast co erythrosin B in the buffered solutions, this molecule behaves differently when entrapped in the sol-gel matrix. As can be seen in Fig.3, the erythrosin B coatings
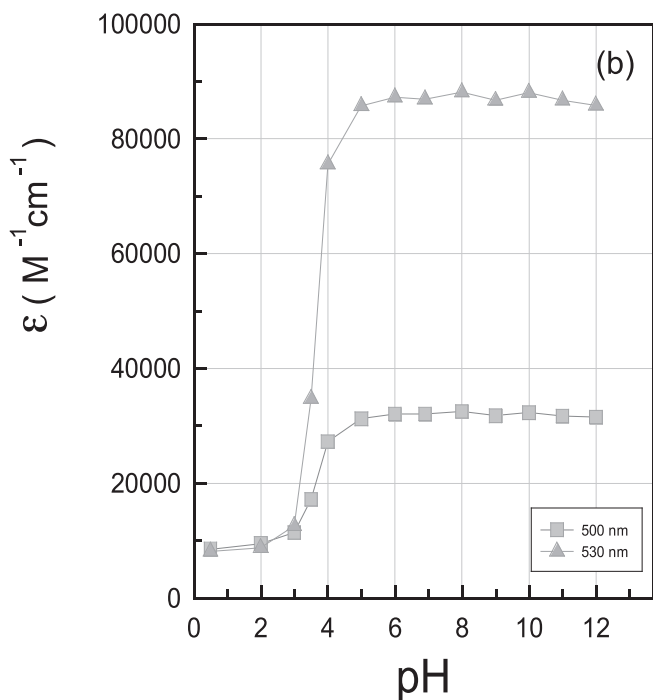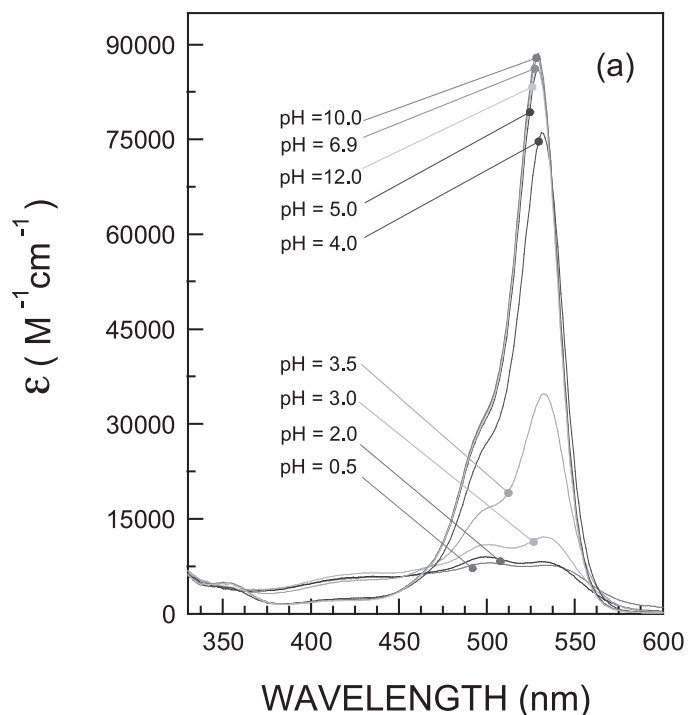
Fig. 2- (a) Absorption spectra of erythrosin B in different pH methanol-buffered solutions, (b) pH dependence of the main peak intensities.

is displayed in the absorption spectra. In this case, the peak appeared strongly overlapped with the absorption spectrum tail of the soda lime silicate glass substrate. Absorption spectra of the buffered solutions in which coatings were immersed, were registered in order to assure that erythrosine B was not released from the matrix. These facts indicate that, in addition to immobilization of the molecule, the wall of porous in which the molecule is enclosed, interacts and modifying clearly their electronic transitions. Usually it is assumed that the dye may interact with the surface groups, mainly silanols that form the pore walls. As a consequence, the dye molecules relax and the energy between electronic levels, in which absorption transitions take place, decreases. Then red shifts occur in the optical spectra. This energy decreasing associated with the red shifts may be also considered as a consequence of an increasing in the effective length of conjugate electron path for the entrapped molecule.

On the other hand, for pH < 4 the spectra change slightly and the peaks at 550 and 510 nm appear less intense (see Fig.3). The decreasing in intensity of both peaks in the acid range, as occur from the erythrosin B in the buffered solutions, partially supports their ascription to the dianionic form of erythrosin B, which would be then in low concentration. Furthermore, for the whole pH range studied, the coatings exhibited a broad absorption band centred at about 415 nm, whose intensity remains practically constant. The band shape seems to be quite similar to that displayed at about 415 nm in the spectra of erythrosin B for acid pH solutions (see Fig.2). Contrary, the undoped coatings show no structure absorption spectra, which discard an origin from the matrix. These facts strongly suggest a band origin from acid forms of erythrosin B molecules placed in the closed pores of the coatings. In this
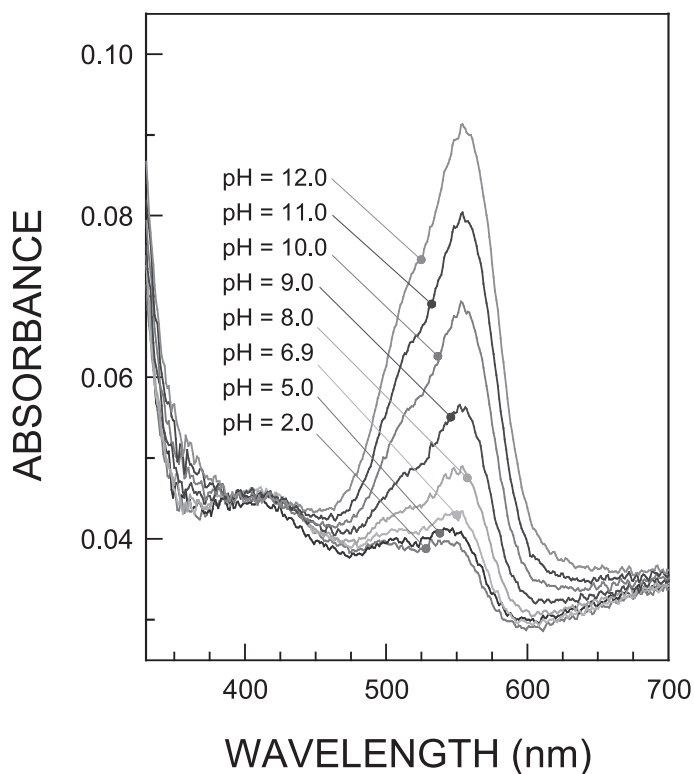

Fig. 3- Absorption spectra taken for increasing pH of a coating doped with 2.5 wt % erythrosin B. Spectra are not corrected by the thickness oscillations.

show some spectral resemblance with those displayed in the buffered solutions. Thus, the main peaks for pH ≥ 4.0 increase gradually in intensity with pH, and then the most intense peak occurs for pH 12.0. Furthermore, the main absorption peaks of erythrosin B in the coatings respect to those observed in the solutions appear shifted towards longer wavelength, consequently both peaks occur in the coating at about 550 and 510 nm. Moreover, less intense peak respect to those observed in the doped buffered solutions, at about 355 nm,

way, the molecules practically cannot interact with the buffered solutions in which the coatings were immersed. Consequently, their optical response did not change substantially for the different pH buffered solutions. Thus, the use of absorption response at 415 nm may be useful for calibration purposes of a possible optrode application, since it remains essentially independent of pH. A similar phenomenon has been already observed in the spectral pH dependence of sol-gel fluorescein doped coatings (24).

In order to have a hint about the homogeneous distribution of the dye over the coating, we studied the optical absorption of a series of five samples as a function of thickness. Prior to the absorption measurements, the samples (containing 2.5 wt% erythrosin B) were immersed in a pH 12.0-buffered solution for 5 min. Fig.4 shows the main peak absorption response taken from different areas of each coating as a function of thickness. Special attention has been paid to the transmission (absorption), which varies periodically with λ^{-1} and hence may affect the absorbance values. Then, to avoid partially this effect, the absorption spectra were corrected by using a sinusoidal function. The dispersion in the absorption values related to thickness displayed in Fig. 4 is mainly explained by surface irregularities, pore-size distribution and corrections from thickness oscillating effects (2, 26). It is well established that the density of silanols is greater in concave surfaces than in flat or convex ones. Hence the different interaction of the dye with the matrix and the diversity in the coatings optical response from area to area, which is, reflected in the error bars of Fig.4. Nevertheless, as can be seen in the figure, the experimental points were fitted satisfactorily to a linear

regression, which is important for potential applications. Therefore, the erythrosin B distribution over the coatings thickness seems to be reasonably homogeneous.

Fig. 5- Absorption dependences for increasing pH ($\triangleright$ pH up) and then for decreasing pH ($\blacktriangledown$ pH down) of a 2.5 wt% erythrosin B doped coating: (a) Main peak intensity and (b) Wavelength main peak position.
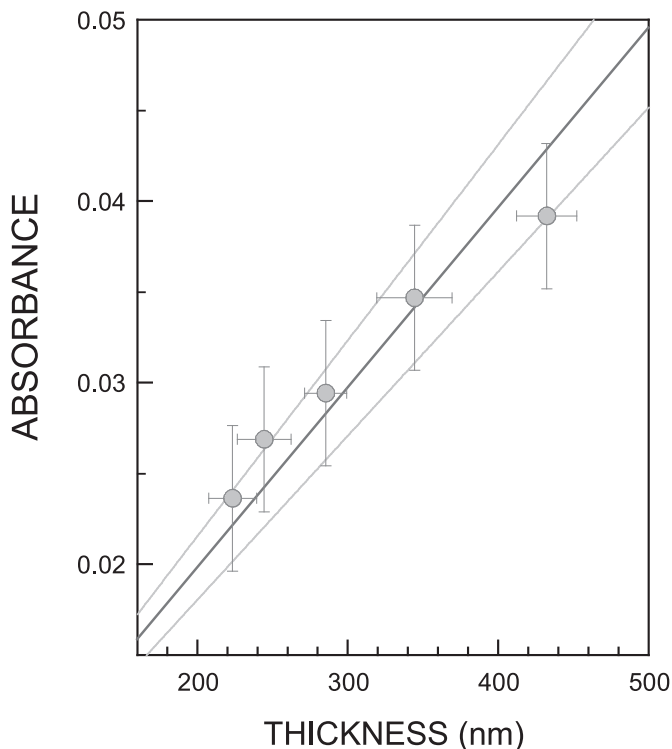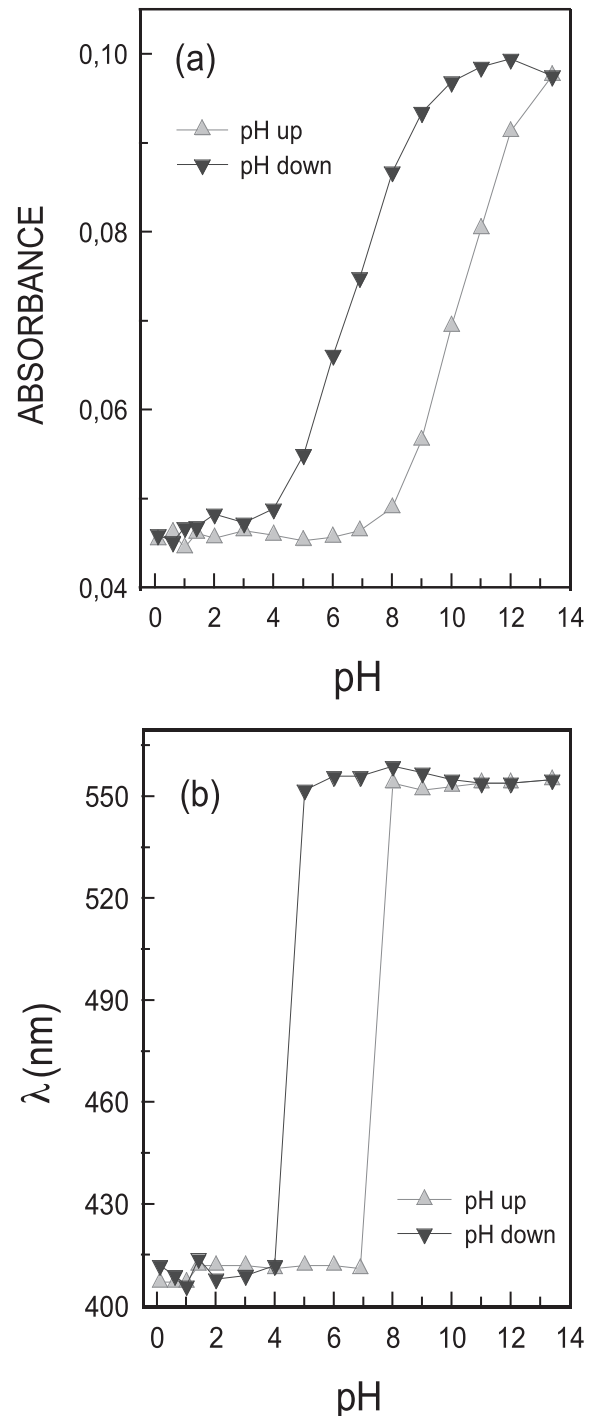

Fig. 4- Main absorption peak intensity as a function of thickness for a series of five different coatings doped with 2.5 wt % erythrosin B at pH 13.4. Solid line through the experimental data was least square fitted. Gray solid curves represent 95% confidence intervals.

In this work, erythrosin B doped coatings show a clear memory effect or hysteresis in their spectral response against pH. Thus, the corresponding absorption spectrum depends on the direction of the pH change. This means that the spectra from increasing pH from 0.5 to 13.4 do not match with those taken for decreasing pH from 13.4 to 0.5, as is shown in Fig.5. In

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particular, the main peak intensity shows a marked increase for pH >7 in the pH up-branch, whereas for pH down-branch the marked decrease appears in the pH range between 4 and 10 (see Fig.5a). Likewise, as Fig.5b shows, both branches exhibit marked differences in the main peak position between pH 4 and 8. Therefore, the protonation and deprotonation processes for these coatings showed a somewhat sluggish behaviour, which indicates the presence of diffusional barriers hampering the flow diffusion of protons and other associated ions. Apart from this, it is important to take into account that any proton diffusion must be accompanied by either counter anion diffusion or cation exchange to maintain the electrical neutrality of the matrix. This means that the diffusion of counter ions may be an additional factor to explain the sluggish pH time response of coatings.

In order to determine fatigue effects on the optical response of coatings they were successively immersed in buffered solutions of extreme pH. Thus, coatings were immersed firstly for 5 min in a very acid solution, pH 0.5, and then in a very basic solution, pH 13.4, and so forth and so on, up to 20 times. After each immersion the optical response was monitorised. Fig.6 shows the evolution of the main absorption peaks at 510 nm (a) and 550 nm (b) for pH 0.5 and 13.4, respectively. As can be seen in the figure, there are an increasing in the response for both peaks at pH 13.4 and a decreasing at pH 0.5, especially for the first immersion cycles. For a larger number of immersions the response tends to be stabilised. Therefore, this procedure indicates a simple and easy method to improve the optical response of erythrosin B doped coatings.
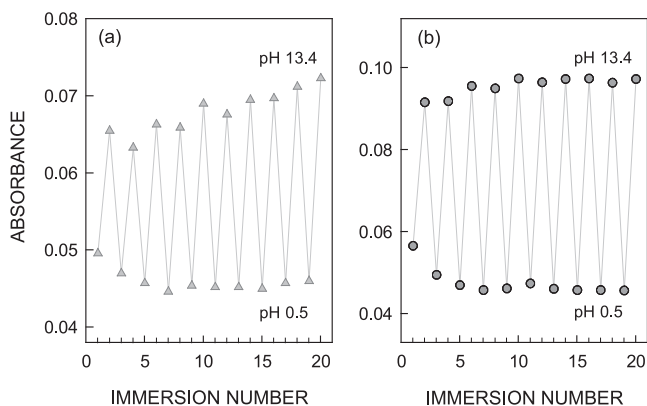

Fig. 6- Evolution of main absorption peaks of spectrum as a function of immersion cycles in extreme pH (0.5 and 13.4) for 2.5 wt% erythrosin B doped coating. Wavelength peak positions at: (a) 510 nm and (b) 550 nm.

3.2 pH dependence on photoluminescence

Erythrosin B doped sol-gel coatings show no significant photoluminescence (PL) (fluorescence and phosphorescence) on contrast co erythrosin B in solutions. The lack of photoluminescence in the coatings seems to be related to quenching effects from interaction of the organic dye with oxygen and with the porous wall in the silica matrix. The first is supported in part from the well know quenching effect of oxygen on the luminescence and especially in the phosphorescence at about 680-690 nm and E-type delayed fluorescence at about 560-570 nm (22-24, 28, 29). On the other

hand, the return to the ground state in a nonradiative way, such as intersystem crossing or multiphonon relaxation, would be favoured by the presumably interaction with the walls of porous matrix, as occur for some inorganic ions from rare earths elements (2, 27).
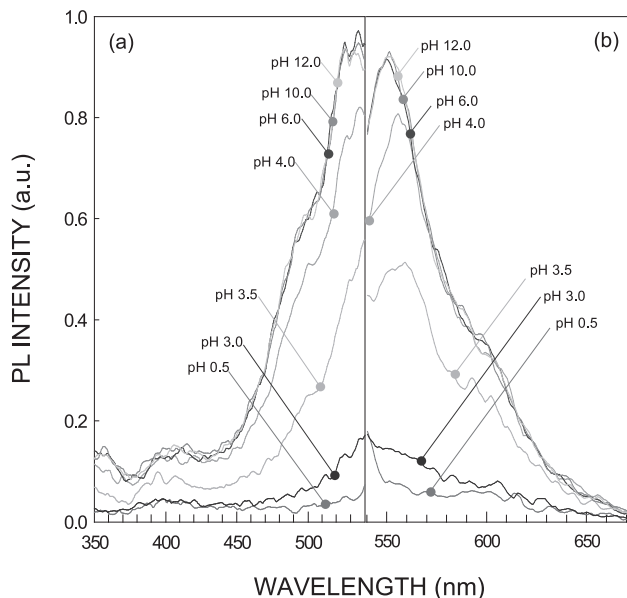

Fig. 7- Normalized photoluminescent spectra of erythrosin B buffered solutions: (a) Excitation spectra for emission at 555 nm, and (b) Emission spectra upon excitation with 535 nm photons.

As for erythrosin B in buffered solutions, the fluorescence spectra is dominated by a broad main emission peaked at about 555 nm, under excitation with photons in the main peak of excitation spectrum at about 535 nm (see Fig.7). Excitation spectra show essentially similar shapes to that exhibited by the absorption spectrum, but with bands at 268 and 321 nm, which are slightly shifted (7 nm) towards longer wavelength, versus those of absorption spectrum (not showed in the figures). As Fig.7 shows for the doped pH buffered solutions, the emission spectra upon excitation with 535 nm photons is maximized in intensity for the neutral-basic ranges (pH between 6.0 and 12.0). Furthermore, the spectra exhibit a weak shoulder peaked at about 600 nm. In the acid range the emission peak shifts progressively towards longer wavelength and decreases in intensity. This behaviour is similar to that described above for the absorption spectra of buffered solutions in the acid pH range and partially supports a dianionic nature for the main peak. Thus, for pH< 3.5 there is not significant emission. This is in good agreement with the polyprotic transformation given above in eq. (1), with a pK_a close to 3.8, as well as for the low absorption of the polyprotic cationic and neutral forms of erythrosin B.

4. CONCLUSIONS

Optical absorption analysis confirms that cationic and neutral forms of erythrosin B have low molar extinction coefficients, in contrast with the dianionic form. The latter form maximizes the emission of erythrosin B in solutions. Interaction between the dye molecule and the porous sol-gel glassy matrix

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gives rise to additional red shifts in the absorption spectra and quenches together with oxygen presence the luminescence of the dye in the coatings. Acceptable homogenous distributions of erythrosin B molecules over the whole coatings thickness are obtained. Both the slow responses versus pH and the hysteresis effects indicate the presence of diffusional barriers, which hamper the flow diffusion of protons and other associated ions.

The use of erythrosin B entrapped in glassy sol-gel silica coatings seems to be quite attractive for the design of absorption pH sensors. However, to obtain a suitable pH optrode, it is essential to improve its optical response time and reversible behaviour.

ACKNOWLEDGEMENTS

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