

Incorporation and optical behaviour of 4-dimethylaminazobenzene in sol-gel silica thin coatings

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Abstract

Various percentages of 4-dimethylaminazobenzene (dimethyl yellow, DY) have been incorporated into silica sol-gel coatings prepared from tetraethylorthosilicate and methyltriethoxysilane. The dye was entrapped in the sol-gel layer maintaining its acid-basic properties. Sensitivity of coatings against pH in aqueous media was evaluated by absorption spectrophotometry for each type of samples, including one pre-treated at low temperature. The response time of coatings from acid pH to neutral conditions and *vice versa* allows to propose the use of this system as a pH optical sensor. On the other hand, several tests oriented to point out the behaviour of coatings during chemical attack were performed: firstly by dipping the samples in distilled water for different lengths of time and, secondly, submitting them to reiterated cycles at 60 °C in a washing machine using conventional abrasive detergent. Results obtained in both cases indicated good resistance, especially for those hybrid films prepared from tetraethylorthosilicate and methyltriethoxysilane doped with 5 wt.% DY. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The advantage of using porous materials as matrices for chemical reagents immobilization were pointed out by Tobacco et al.¹ Microporous and partially densified sol-gel materials prepared from alkoxides or alkylalkoxides offer the possibility of obtaining, at low temperature, many interesting materials useful as waveguides,² non-linear opticals,³ pigments,⁴ sensors,^{5,6} hydrophobic thick films,⁷ mechanically improved coatings,⁸ etc.

Sol-gel thin films have proved to be adequate hosts for organic dyes, such as common pH indicators,^{9–11} among other type of dopants capable of forming systems for sensing purposes.¹²

Reactivity and physico-chemical properties of some azo dyes when entrapped inside sol-gel materials have been studied both for monolithic specimens¹³ and thin film coatings.¹⁰ In the case of coatings, immobilization of dyes is explained by weak linkages between dye molecules and superficial silanol groups (in the case of

silica matrices) by means of hydrogen bonds. This occurs in the presence of water molecules, which behave as a bridge and transport medium for H⁺ and OH⁻. Aqueous acid and basic ions move freely in the micropores of the sol-gel coating surface when dipped into liquids at different pH. Then, the tautomeric forms of the organic dye responsible for variation in the optical absorption of the whole system are changing. Chemical reactions at the coating micropores occur reversibly from acid to basic pH and vice versa. On the other hand, photostability, mechanical and chemical resistance of some dye-doped films are good enough to be used as intrinsic pH optical sensors. Thermal release of dye molecules above 120 °C, approximately, arise as a limiting factor for the use of such a type of sensor.

In order to increase the absorption intensity of doped coatings and to make them more useful, even by visual observation, two routes seem to be easily testable. First, increasing film thickness and second increasing dye concentration in the sol. Apart from the possibility of preparing multilayer coatings, the first route for monolayer films depends on the rheological parameters of the sol, i.e. concentration, density, viscosity, surface tension,

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etc. which determine film adherence to the substrate. Modification of such parameters could lead to a critical thickness overflowing (maximum thickness without cracks). Thus, the increase of dye concentration in the sol could be a promising way to intensify the optical absorption of coatings. However, a limitation arises from the porous microstructure of the gel coating, in which dye molecules have to be linked. Those dye molecules that are not completely incorporated into the gel film could be easily leached, when the doped coatings are dipped into solutions at different pH. Moreover, problems derived from the scarce solubility of such organic dyes in the alcohol-aqueous medium of the starting sol could be a handicap to increasing dye concentration.

Modification of the silica matrix by using an alkoxide-alkylalkoxide mixture as precursor deals with an increased microporosity which, probably, enhances the incorporation of dye molecules in the gel film.

In the present work, objectives are focussed on the preparation of sol-gel films doped with an azo dye, usually used as an acid pH indicator, in different concentrations and two different silica matrices obtained from alkoxide/alkylalkoxide precursors. Optical absorption response as a function of pH is evaluated as well as chemical resistance.

2. Experimental

One, 3 and 5 wt.% of DY were added to pure silica sols prepared starting from tetraethoxysilane (TEOS). A fourth sol was obtained from a mixture of TEOS and methyltriethoxysilane (ME₃S) doped with 5 wt.% DY (hybrid sample). The alkoxide or alkoxide-alkylalkoxide mixture were previously hydrolyzed in aqueous-alcoholic medium at pH = 2. Molar ratio TEOS/ME₃S:H₂O:CH₃CH₂OH was 1:4:8.

Coatings were deposited at room temperature upon common soda lime glass slides by dipping at a withdrawal rate in the 5–25 cm min⁻¹ range. Thickness of films after heat treatment at 60 °C for 3 days is in the 270–310 nm (±10 nm) range, as was estimated by the interference fringe method.

The as-prepared samples are transparent, crack-free coloured coatings, capable of changing their optical absorption when in contact with aqueous solutions at different pH. Such a change is reversible and visually perceptible.

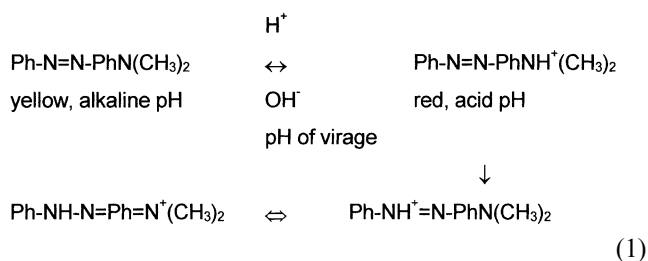
Scanning electron microscopy observations of the substrate-film profile were performed without success, due the scarce textural differences between both the glassy coating and glass substrate. Optical response of coatings against pH change in liquid media (buffered solutions) was monitored by using both spectrophotometers Perkin-Elmer Lambda 9 and Shimadzu

model 3100. A sample prepared from TEOS doped with 1 wt.% DY was maintained at -5 °C for a maximum of 3.5 months. Then, the optical response was checked after dipping in buffered solutions at different pH.

With the aim to prove the chemical durability of the films as a function of the dopant concentration, hydrolytic tests were carried out. Samples were immersed into Teflon vessels with distilled water at room temperature for different periods of time. On the other hand, successive cycles of 30 min each one in a conventional tableware washing machine using common abrasive detergent (alkaline pH) were run, in an attempt to test adherence and scratching resistance of coatings.

3. Results and discussion

4-Dimethylaminazobenzene (dimethyl yellow, DY), is an azo dye commonly used as acid pH indicator. In aqueous medium the pH virage range is between 2.9 and 4.0. The change of colour with pH (yellow/red) is due to several intramolecular changes that can be written as follows:¹⁴



DY molecules can be introduced into the cross-linked network of the sol-gel film, remaining entrapped inside micropores and interstitial sites. Such positions could respectively hinder or allow dye molecules to be in contact with aqueous species and, thus, govern DY reactivity when introduced in the film. Scanning electron microscopy observations of the samples profile pointed out almost the same texture of both glass substrate and sol-gel film, in such a way that for the major part of the studied samples the microstructures are practically indistinguishable. Glassy sol-gel coatings form stable chemical bonds with the common glass slides via silanol groups (Si-OH) that are present in both the glass surface and the deposited film. This similar chemical nature ensures a priori good adherence and stability versus external physicochemical attack agents.

In Fig. 1 optical absorption spectra corresponding to DY in solution and DY incorporated into the silica sol-gel film at two extreme pH are shown (pH = 0.50 and pH = 12.99). Deconvoluted Gaussian shapes are also displayed to clarify the wide absorption bands recorded. Contribution of the glass substrate to the whole spectra were subtracted in all cases. Spectra corresponding to

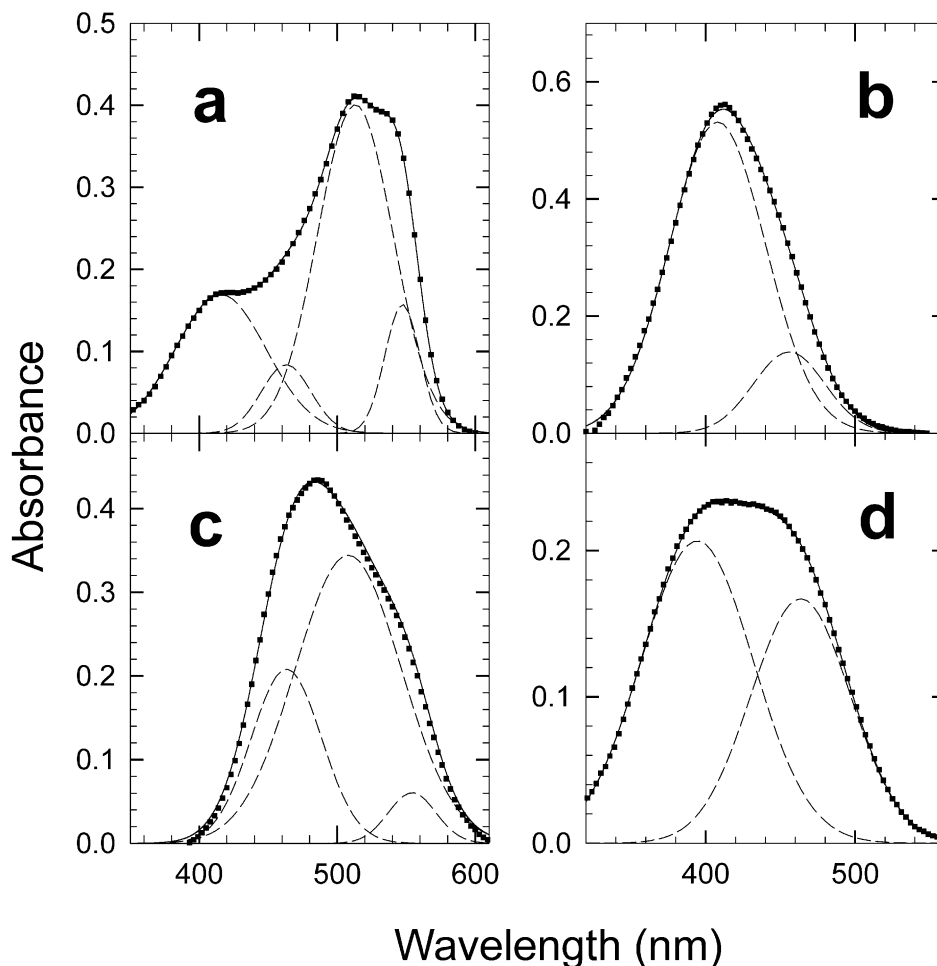


Fig. 1. Optical absorption spectra of DY in (a and b) solution and (c and d) DY incorporated into the sol-gel film at (a and c) pH = 0.50 and (b and d) pH = 12.99. Symbols represent experimental data, solid lines the fits and dashed lines the Gaussian shapes.

DY doped coating are wider than those of DY in aqueous solution, for both acid and basic pH. This can be explained, bearing in mind that in aqueous medium all DY molecules have the same or very similar surrounding conditions; while for the case of the DY molecules inside the coating, a variety of sites in the sol-gel network can be occupied. Moreover, for a given pH, part of the DY molecules are well accessible to aqueous species H^+ and OH^- , thus reacting and changing their optical absorption. However, dye molecules entrapped inside closed micropores could not be attained by reagents and, therefore, their absorption would remain unchanged. The sum of all the contributions from DY molecules in different sites results in a wide absorption band.

As can be seen in Fig. 1 acid bands could be assigned to the spectral components at 508 nm (B3) and 550 nm (B4), approximately; and the basic one at around 400 nm (B1). Another band centered at about 460 nm (B2) is present in all spectra both for acid and basic pH. It could be attributed to the contribution of DY molecules located in the less attainable sites of the gel network, which are submitted to an intermediate pH in the range

tested. These DY molecules would remain as one of the tautomeric forms of Eq. (1) without any change, since they are not affected by the liquid environment. The basic band B1 appears in Fig. 1b and d at a similar peak wavelength: a shift (<10 nm) of the 400 nm band to shorter wavelength is observed when DY are in the sol-gel film. On the other hand, a small shift of the band at 460 nm to a longer wavelength is recorded in the spectrum of the doped film. These facts can be explained if one takes into account the different sites occupied for DY molecules in the coatings. Thus, the peak shifts seem to be promoted by small variations in the pH at which all DY molecules were submitted into the coatings.

As for acid pH spectra (Fig. 1a and c), it is to note that the band at 460 nm appears together with the acid bands. Moreover, in Fig. 1a the characteristic band at 400 nm is also present. In this latter case it could be due to an effect of partial dimerization of DY molecules at pH = 0.50, which hinders all neutral DY forms in Eq. [1] (yellow at basic pH) to change to the ionic form in Eq. (1) (red at acid pH). In addition, for DY entrapped in the sol-gel film (Fig. 1c), the presence of the 460 nm band is

probably due to absorption from dye molecules located in sites out of contact of H_3O^+ ions. On the other hand, the densification degree of the gel network attained in the dried films determines the residual free volume of such a matrix for dye molecules and, hence, the degree of freedom and reactivity of the entrapped DY.

The optical absorption spectra corresponding to the samples doped with 1, 3 and 5 wt.% DY and the hybrid sample doped with 5 wt.% DY, for different pH show a decrease of the intensity of the characteristic acid bands as the pH increases up to 4.64, for which the basic band dominates. In Fig. 2 the evolution against pH of the intensity of the deconvoluted Gaussian shapes is shown for each sample. As can be seen in Fig. 2 bands at 400, 508 and 550 nm (labeled above B1, B3 and B4, respectively) show a clear pH dependence, whereas the band at 460 nm (band B2) does not show a defined evolution with pH, probably due to the reasons stated before. Band B1, characteristic for basic pH, undergoes an intensity increase, especially in the range of pH between 0 and 2 and for $\text{pH} \geq 10$. This increase is found more remarkable for the hybrid sample doped with 5 wt.% DY, while for the other samples prepared from non-hybrid precursors the intensity variations are smaller, apart from the changes in the very acid region and those due to the different DY concentration (1, 3 and 5 wt.%).

The intensity of the bands B3 and B4 in Fig. 2 sharply diminishes in the acid pH range and, after a slight stabilization, it continues to drop up to $\text{pH} = 10$ where it practically disappears from the spectra. In this case, data corresponding to the hybrid sample also show the higher intensity values. Results from Fig. 2 suggest that the sample prepared from hybrid precursor contains more available sites for DY molecules attainable to reagents, when compared to that obtained from non-hybrids precursors for the same dye percentages. According to Innocenzi et al.¹⁵ and former research about hybrid coatings,¹⁶ the mixture of alkoxides and alkylalkoxides deals with thicker and more microporous films than non-hybrid systems. This allows for a soft microstructure adequate for a proper entrapment of organic molecules.

Similarly to Fig. 2, in Fig. 3 intensity changes with pH for the deconvoluted Gaussian shapes, corresponding to the sample pre-treated at low temperature, are displayed. Evolution of band B1 (characteristic for basic pH at 400 nm) is almost the same as that observed in Fig. 2 for the samples obtained from a non-hybrid precursor. However, both characteristic acid bands (B3 and B4) display an evolution comparable to that shown in Fig. 2 for the hybrid coating. Finally, the 460 nm band also shows similar behaviour against pH as that for the spectra of coatings not pre-treated at low temperature (see Fig. 2), i.e. no clear tendency. These results indicate that pre-treatment at low temperature enhances the behaviour of the doped coating in the acid pH range.

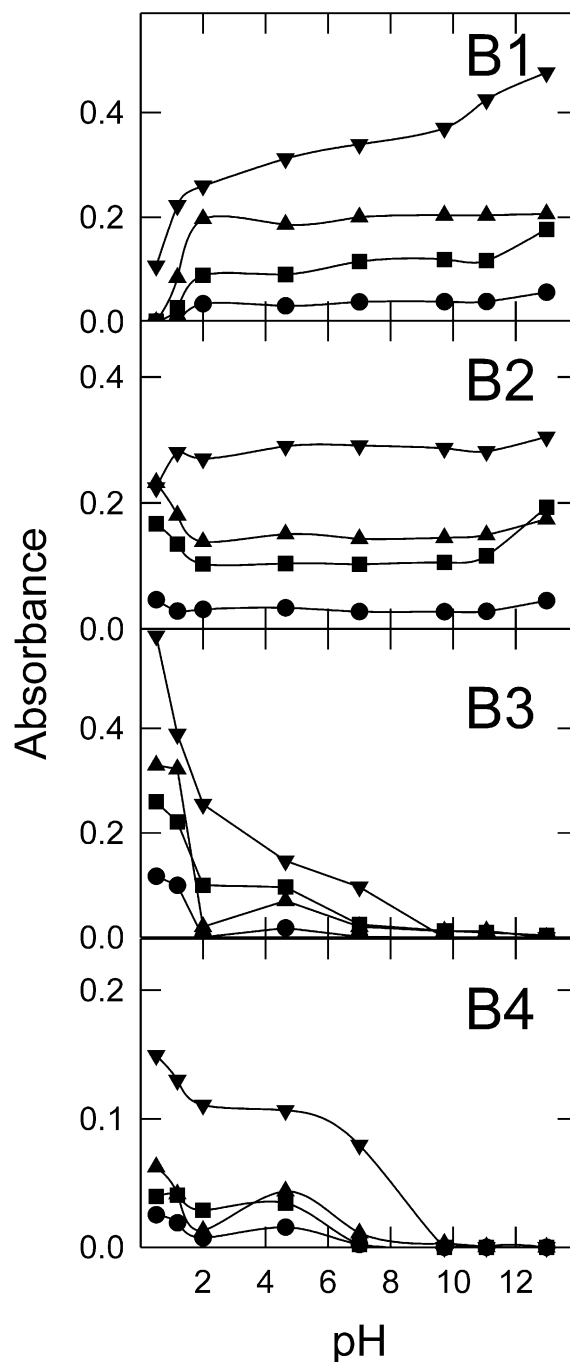


Fig. 2. Evolution with pH of the deconvoluted Gaussian shape intensities corresponding to coatings doped with: 1% (circles), 3% (squares), 5% (upright triangles) and 5% DY hybrid sample (inverted triangles). Lines are drawn as a guide for the eyes.

Low temperatures did not affect the standard reactivity of the doped coating, but improved it. Such treatment could preserve the open micropores against the network collapse and/or progressive densification (that could create closed micropores), thus favouring DY molecules to remain in contact with reagents, especially for $\text{pH} \leq 3$.

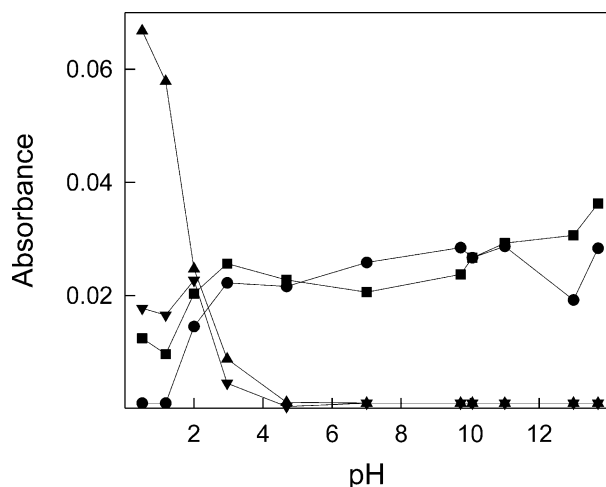


Fig. 3. Evolution with pH of the deconvoluted Gaussian shape intensities from the absorbance spectrum of the sample pre-treated at low temperature: band B1 (circles), B2 (squares), B3 (upright triangles) and B4 (inverted triangles). Lines are drawn as a guide for the eyes.

Optical response of the hybrid dye doped coating (5 wt.% DY) was studied from the absorption spectra successively recorded after several dipping times into solutions at different pH. Firstly, the sample was immersed in a buffered solution at pH = 0.50 and its absorption spectrum was recorded as the initial one (Fig. 4a). The second spectrum was taken after the sample was dipped into a pH = 7 buffered solution for 10 s. For the third spectrum, the sample was once again submitted to the acid solution and, after that, dipped in the neutral solution for 20 s, etc. In Fig. 4b the response test was scheduled as in Fig. 4a, starting from the neutral pH and recording

absorption spectra after different times of dipping into the solution at pH = 0.50.

Intensity of the acid 508 nm band was selected to monitor the sensitivity of the film with pH. Fig. 4c displays the evolution of the band intensity as a function of time, from acid to neutral pH and vice versa (note different time scale for both curves). Whole response time from neutral to acid pH is approximately one order of magnitude smaller than those from acid to neutral pH. For instance, after 1 min of immersion in the corresponding solution, the optical absorption of the coating from neutral to acid pH is changed over $\Delta A \approx 0.43$; whereas after the same time, the optical absorption of the sample from acid to neutral pH is changed over $\Delta A \approx 0.17$. Moreover, DY doped coating spend 200 s to stabilize the optical absorption when it change from neutral to acid pH; while it needs ten times more (2000 s) to stabilize the optical absorption when it change from acid to neutral pH (see Fig. 4c).

These different response times for reversible reactivity in liquid media seem to be related to the different stability of the tautomeric forms of DY into the gel film at a given pH. DY is considered as an acid indicator for neutralization titrations with a virage range $2.9 \leq \text{pH} \leq 4.0$. When DY molecules are entrapped in the sol-gel network such virage range is slightly shifted towards the acid region ($1 < \text{pH} < 3$), as can be deduced from Fig. 2 (band B3). This implies that higher H_3O^+ concentration is necessary to change the absorption spectrum, that is, to displace the equilibrium of the corresponding tautomeric forms towards the red protonated one of Eq. (1). This agrees well with the fact that part of DY molecules can be located in closed micropores and/or in less

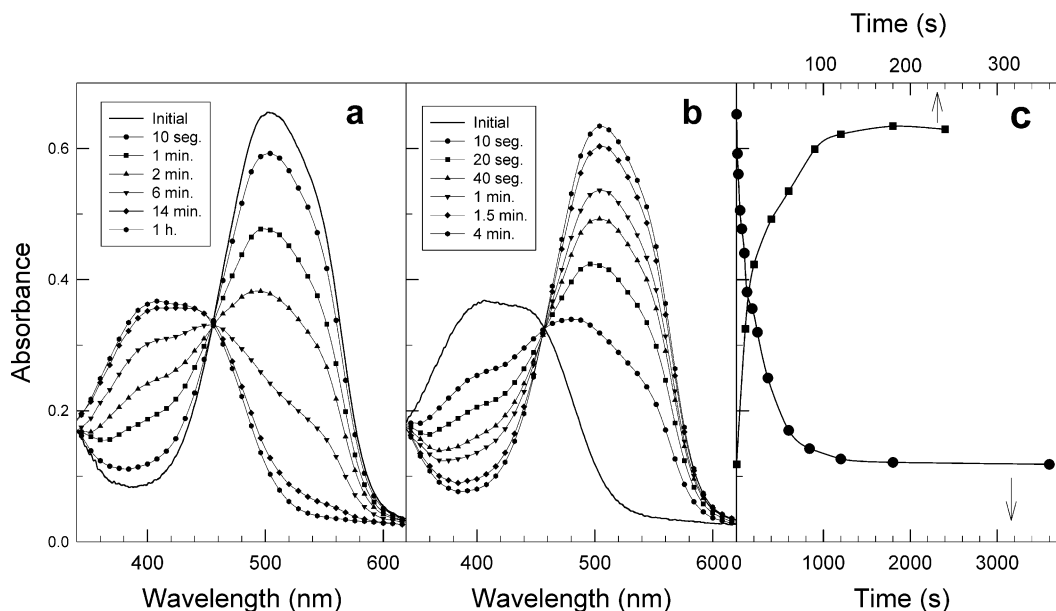


Fig. 4. Optical absorption spectra of hybrid sample doped with 5% DY, recorded after several dipping times (a) from acid to neutral pH, (b) from neutral to acid pH. (c) Change of the absorption intensity of band B3 at 508 nm from acid to neutral pH (circles) and from neutral to acid pH (squares).

attainable sites of the sol-gel network. Such molecules are not sensitive to reagents at any pH and give an absorption background to be compensated by the optical absorption contribution of the other sensitive DY molecules incorporated to the film in open micropores and interstitial sites. Fig. 5 shows the time evolution of the relative intensity of deconvoluted components from spectra displayed in Fig. 4a. The acid bands at 505 and 550 nm have a decreasing slope as the time increases, i. e. as the pH moves from acid to neutral conditions. In turn, the basic band at 400 nm rises with time for the same pH variation. However, the 460 nm band does not undergo significant changes, in agreement with results of Fig. 2 (band B2). Moreover, that component is directly related to the isobestic point shown in Fig. 4a and b, at 460 nm. This is likely due to the tautomeric equilibrium between two or more DY forms, which remain constant all long the pH range.

Hydrolytic resistance tests showed no band wavelength shift in the corresponding absorption spectra recorded after different dipping times, but a loss in intensity more important for periods of time longer than 17 h of continuous immersion. In Fig. 6 the loss of intensity of the 508 nm band for each case is drawn against attack time. The higher the concentration of DY in the doped non-hybrid coatings, the higher is the loss in intensity for such band. This indicates that the number of DY molecules that can be entrapped in the gel network is limited to those that are located in micropores and interstitial gaps. The other ones can be physically adsorbed upon the coating surface and, therefore, are easily leachable. The first step of hydrolytic attack after 1 min causes abrupt fall down of the absorbance. In this respect it is noteworthy that some small change of the pH of the coating could contribute to such diminishing, since pH of the attack medium (distilled water) is not exactly the pH of the coatings previously submitted to a neutral buffered solution. In any case, the results shown in Fig. 6 indicate that after 135 min of hydrolytic attack,

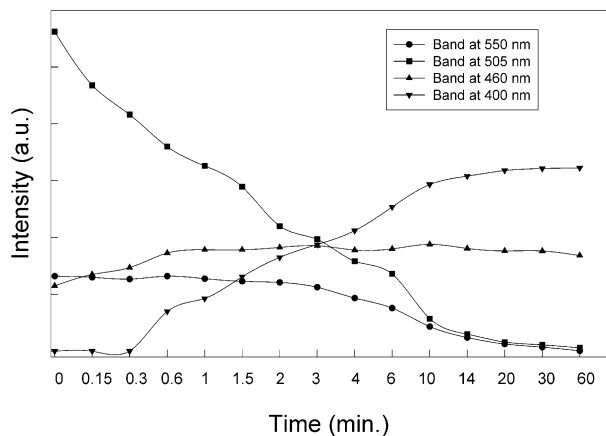


Fig. 5. Time evolution of the relative intensity of deconvoluted components from spectra displayed in Fig. 4a.

the coatings diminished their optical absorption quickly. This means there is continuous water penetration into the gel network that rehydrates the porous microstructure as a sponge and maintains it as a liquid medium capable of redissolving DY molecules by leaching.

As can be seen in Fig. 6, hydrolytic resistance of the hybrid coating doped with 5 wt.% DY is quite different from that of the former samples. Absorption intensity loss is smaller for the same times of attack, which proceeds slowly. In this case, DY molecules have more possibilities for entrapment according to the higher thickness and microporosity of the film, as was demonstrated before.^{15,16} Whole hydrolytic resistance results allow the conclusion that a more adequate microstructure must be performed during coatings preparation, in order to incorporate higher dye amount, rather than a linear increase of dopant percentage in a properless matrix.

Qualitative scratching resistance of doped films was tested by means of washing cycles with conventional abrasive detergent. In Fig. 7 the intensity of the 508 nm band, corresponding to the spectra recorded after each cycle, is drawn versus the washing cycles. It is to note that neither scratches nor delamination were observed. Absorbance intensity falls down at about 50% after 5 washing cycles and then a slow diminishing of absorbance percentage takes place up to visual fading after 14 cycles. Chemical attack performed during washing cycles

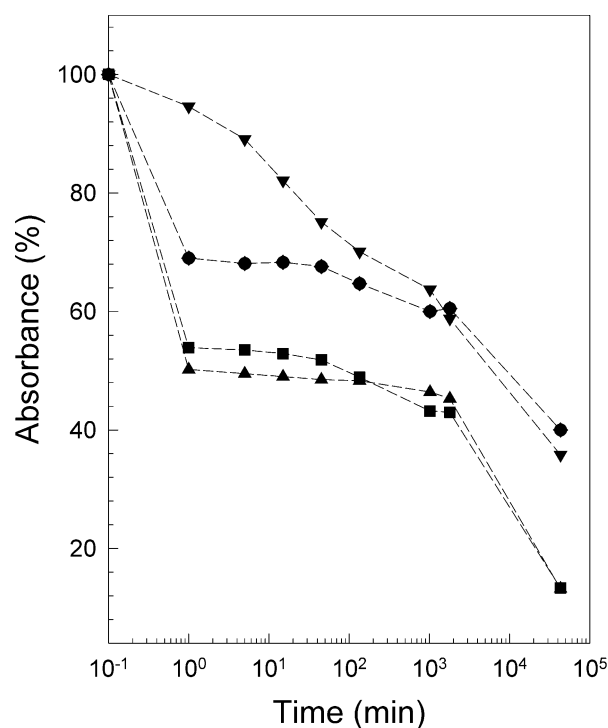


Fig. 6. Intensity loss of band B3 as a function of hydrolytic attack time for coatings doped with: 1% (circles), 3% (squares), 5% (upright triangles) and 5% DY hybrid sample (inverted triangles). Lines are drawn as a guide for the eyes.

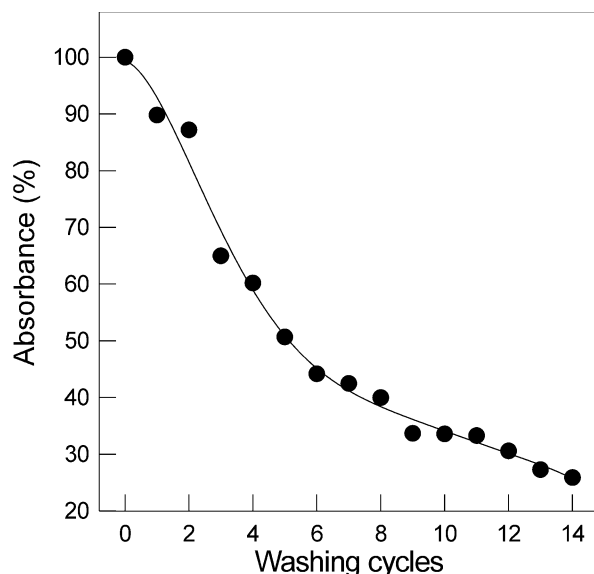


Fig. 7. Intensity loss of band B3 corresponding to sample doped with 3% DY after washing cycles with a common abrasive detergent at basic pH. A line is drawn as a guide for the eyes.

corresponds to an alkaline leaching, which is the attack type the more aggressive for glassy materials, since it destroys the silica network via the rupture of siloxane Si–O–Si bonds. Thus, although during each cycle DY molecules are leached together with silica, no cracks and delamination were observed all over the surface, even after 14 cycles. Such results demonstrate that doped silica coatings have good adherence properties, enough to be used as a pH optical sensor.

4. Conclusions

Sol-gel coatings doped with different percentages of 4-dimethylanilazobenzene (DY) have been obtained upon common glass slides. Both samples prepared from hybrid organic–inorganic and non-hybrid precursors showed reversible optical absorption changes when dipped into aqueous solutions at different pH. DY molecules remain entrapped in the micropores of the gel network, in such a way that, those located in open micropores and adsorbed superficially, can easily react vs pH changes. Optical absorption of DY molecules located in non-attainable sites remain unchanged against pH changes. Coatings pre-treated at low temperature maintain pH sensitivity and even improved it, since gel network densification was delayed. Different time response was measured for coatings sensitivity from acid to neutral pH and vice versa. The latter is approximately one order of magnitude smaller than the former. Chemical resistance of DY doped coatings submitted to neutral hydrolytic attack and to washing cycles at basic pH was particularly good for hybrid samples. The higher the

concentration of dopant in non-hybrid coatings, the higher was the leaching of DY during hydrolytic tests; which is indicative for a limited number of positions for DY entrapment in the gel network. In order to increase the amount of incorporated dye, a microporosity improvement (as is the case of hybrid samples), seems to be the route for a proper texture.

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