Chemical and optical properties of dye-doped sol-gel films

M. A. VILLEGAS, L. PASCUAL
Instituto de Cerámica y Vidrio, CSIC. Antigua Ctra. Valencia Km. 24,300.
28500 Arganda del Rey, Madrid, Spain
E-mail: MAVILLEGAS@ICV.CSIC.ES

Sol-gel silica coatings doped with an acid indicator were prepared and their behaviour vs pH in aqueous media were studied. Absorption spectroscopy was used to characterize the reversible optical response of doped films both in liquid and gaseous media. Several features such as: a) strong influence of acid concentration on films colour change, b) reversibility without fatigue all over the pH range, and c) spontaneous regain of initial basic absorption when coatings were sensitized under acid vapour; pointed out that dye molecules were incorporated in the surface of the silica films pores. On the other hand, coatings resistance vs alkaline attack showed that damage quickly proceeded if films surface were inhomogeneous, due to direct corrosion of the glass substrate.
© *2000 Kluwer Academic Publishers*

1. Introduction

The most important feature of sol-gel encapsulated organic molecules is the ability to induce optical properties in solid state matrices, depending on the specifically chosen dopant [1, 2]. This is note worthy in the development of photonic materials that may be applied for analytical purposes. Organic dyes can be incorporated into sol-gel matrices which pore network is interconnected. That dyes, effectively trapped within the polymer-like structure of the sol-gel material, maintain its optical properties as a consequence of their *intact* chemical reactivity. This result has had important implications for sol-gel sensor applications [3, 4]. Previous works have pointed out that organic dyes incorporated into sol-gel materials could not be leached by any washing treatment, even if the sample was exposed to extreme pH [5, 6]. The behaviour of the ensemble organic dye/sol-gel matrix against chemical corrosion could provide information about the interaction kinetics between the dye doped material and the leaching sourronding medium, as well as about the organic dye linkage to the matrix. Since few investigations have been focussed to hydrolitic or alkaline durabilities of both sol-gel bulk glasses [7, 8] and thin films [9], unnormalized experimental routes should be explored in order to clarify the attack mechanism. This point performs one of the present paper objectives.

Moreover, another objective to be achieved here was the study of the optical behaviour of the organic dye, when incorporated into sol-gel films silica based. It is known that pH indicators entrapped in sol-gel matrices (monoliths, fibers or films) [10–12] can be performed as optical sensors for pH measurements devices.

As a consequence, an increasing interest arises to entrapp indicators whose sensitive range is located in an extreme pH. This is the case of tris[(4-dimethylamin)-phenyl]carbonium chloride (crystal violet, CV). Optical properties of CV are sensitive to proton transfer phenomena and have been succesfully used in analytical determinations in the very acid pH range. In addition, the colour change of CV with pH is from violet to yellow in solution, which is *a priori* promising from the point of view of the optical study, since the corresponding absorption bands will be separeted enough (150 nm at least).

2. Experimental

Sols prepared from tetramethylsilane (TMS) as a silica source were doped with CV (1 to 3 wt% added to the pure silica sols). The procedure was as follows: hydrolysis of TMS previously diluted with CH_3OH was carried out at acid pH by using concentrated HCl. Molar ratio TMS : CH_3OH : HCl was 1 : 8 : 4. The colour of CV solution in aqueous-methanolic medium (50-50 vol%) was intense violet and turns to deep green when added to the prehydrolysed silica sol. Silica concentration in the sol was finally fitted to 80 g silica per liter. After dopant addition, the sol was kept under stirring during 30 min and then allowed to settle for 15 min. Once TMS polycondensation was initiated in the last step, films were obtained by dip-coating technique upon common soda lime glass slides. The substrates were cleaned and dried before to be immersed into the sol from which they were drawed up at a constant rate. The samples were dried up to 60°C for three days. After that treatment the coatings appeared with an intense blue colouring.

Coatings thickness was measured by interference fringe method. Results indicated a thickness range between 270 and 410 nm (±10 nm), depending on the drawing rate used. Thicker crack-free films cannot be

obtained from the sols here prepared, which indicates that critical thickness was about 420 nm.

Optical behaviour of CV doped coatings was evaluated versus pH when dipped into buffered solutions with a Perkin-Elmer spectrophotometer model Lambda 9. Since pH sensitivity of coatings had proved to be reversible from any pH value to whatever else, succesive cycles from acid to basic pH were tested in order to detect any optical absorption loss. Fatigue in optical response of films is an essential parameter to evaluate suitableness in pH sensing purposes. CV doped coatings were also sensitive to aqueous vapours with acid-basic properties. Coatings were exposed to a saturated acid atmosphere (HCl 6 M) for 5 min and then they were kept to spontaneously regain its initial absorption. Characteristic colour coordinates at each pH were calculated related to illuminant A [13].

Alkaline resistance of coatings was tested by dipping them into a mixture (50-50 vol%) of NaOH 1 M and Na_2CO_3 0.5 M, as is usually standarized [14] to test and classify the resistance of glasses attacked by that solution of mixed alkali. Tests were performed at room temperature in Teflon containers, both by direct immersion of coating into the attack solution and by immersion after hidratation with deionized water. Evolution of optical absorption of coatings versus attack time was recorded. Scanning electron microscopy (SEM) observations of the films surface after the attack run were carried out with a Philips XL30 equipment.

3. Results and discussion

CV doped silica coatings show a transparent homogeneous intense blue appearance when obtained after drying, showing optical quality good enough to be used for sensing purposes. CV coatings change their optical absorption (colour) depending on the pH of the solution in which they are dipped. As Fig. 1 demonstrates,
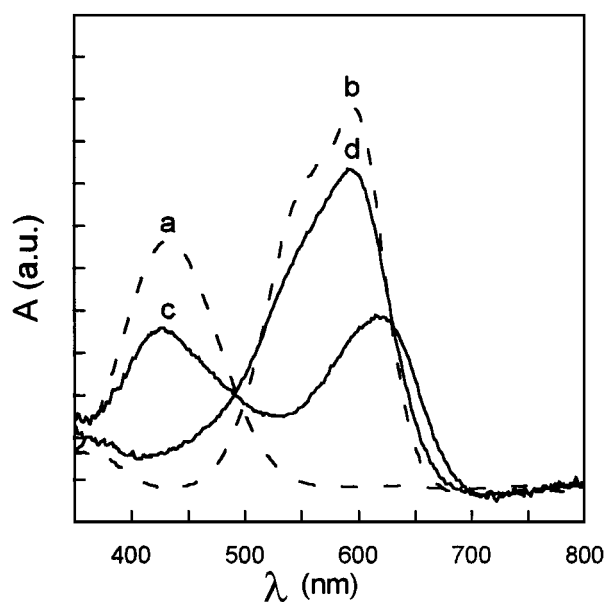
the characteristic absorption bands of CV coatings for both basic (590 nm) and acid (435 nm) pH are the same that for CV in solution, except for the spectrum corresponding to CV coating at acid pH which showed also a residual basic band at 618 nm. CV molecules incorporated to the gel pores are distributed along the whole coating thickness in that way that those inaccesible to the buffered solution remain in its basic form. The simultaneous presence of bands at 435 and 618 nm at acid pH yielded green colouring. CV is commonly used as pH indicator in non aqueous media for titrations in the 0.1–2.0 pH range. Its stable form is the violet basic one (blue for coatings) which turns to yellow (green for coatings) at acid pH.

Fig. 2A depicts the optical spectra evolution of CV coatings for different pH values, showing that both characteristic acid and basic bands maxima shift with pH and also change in intensity. Likewise, maximum
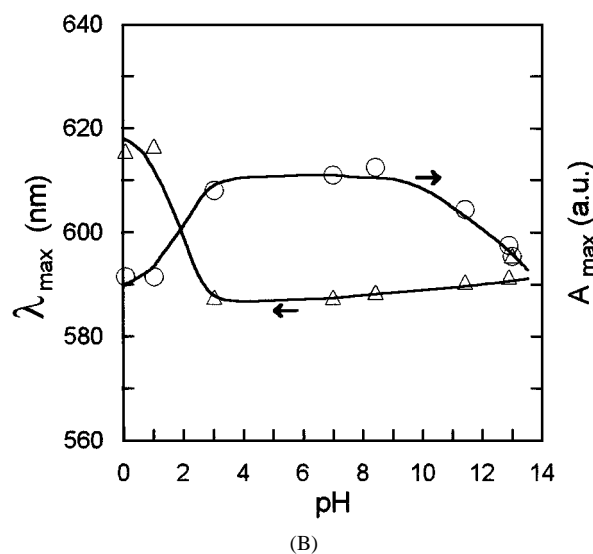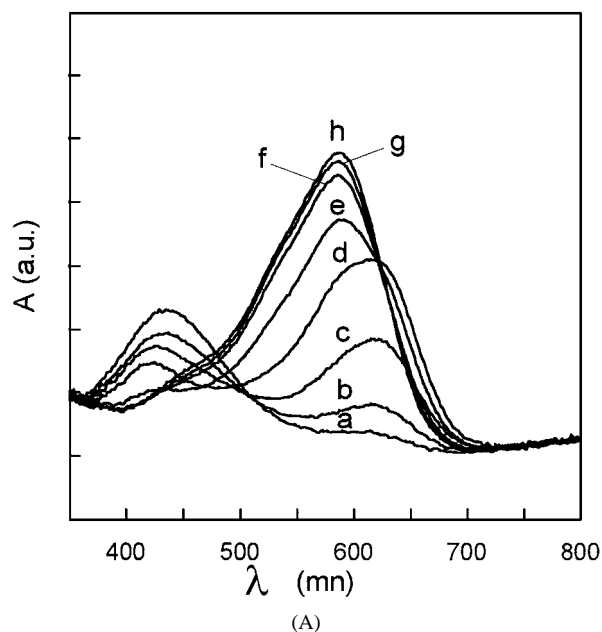
(A)

Figure 1 Normalized optical absorption spectra of CV in: (a) solution at acid pH, (b) solution at basic pH, (c) silica coating at acid pH, (d) silica coating at basic pH.

(B)

Figure 2 (A) Optical absorption spectra of CV doped coatings dipped into solutions: a) HCl 12 M, b) HCl 6 M, c) HCl 3 M, d) pH = 0.06, e) pH = 1.03, f) pH = 3.02, g) pH = 7.00 and h) pH = 8.44. (B) Evolution of both maximum wavelength and maximum intensity of the main absorption band against pH.

absorption intensities and the corresponding wavelengths were plotted in Fig. 2B. This figure could resume the optical behaviour of CV coatings as a tritation curve. pH range of maximum sensitivity is located between 0 and 3, which allows to propose an apparent pK_{Ind} for CV in coatings around 1.5. In addition, absorption intensity considerably increased in that range.

Moreover, CV coatings had proved to be sensitive to the concentration in acid of the solution in which they were immersed (see Fig. 2A). Although CV has not acidic protons, the influence of acid concentration can be easily explained on the basis of the conventional equilibrium of CV as an acid indicator:

$$HInd \rightleftharpoons H^+ + Ind^- \qquad (1)$$
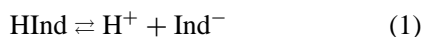
that are displaced to the left only if the H^+ concentration is high enough. In this case the specie HInd, that would be responsible for the yellow band at 435 nm, could be dominant as Fig. 3 shows. When [HInd] is 100 times greater than [Ind$^-$] the band at 435 nm will predominate upon the 590 nm band, and the colour will be yellow (green in CV coatings for the reason explained above). Indeed, for CV the change in optical absorption versus pH is explained by the existence of at least two different forms (probably the neutral and the zwitterionic) [5], which will respectively be the origin for acid and basic dominant species. On the other hand, this accounts for the use of CV as pH indicator in non aqueous media.

Reversibility is another characteristic feature of CV doped coatings. Results of Fig. 4 depict how the sol-gel system behaved along 50 cycles from extreme acid to basic pH. The bands position remain practically unchanged during the runs carried out for a whole of 500 min. Moreover, the band intensities were maintained and is possible to say that the system showed no fatigue in reversible runs, at least for the tested conditions. The quickly response (few seconds) to abrupt changes in pH, without absorbance loss (intensity and colour), could fit well with the pattern of CV incorpora-
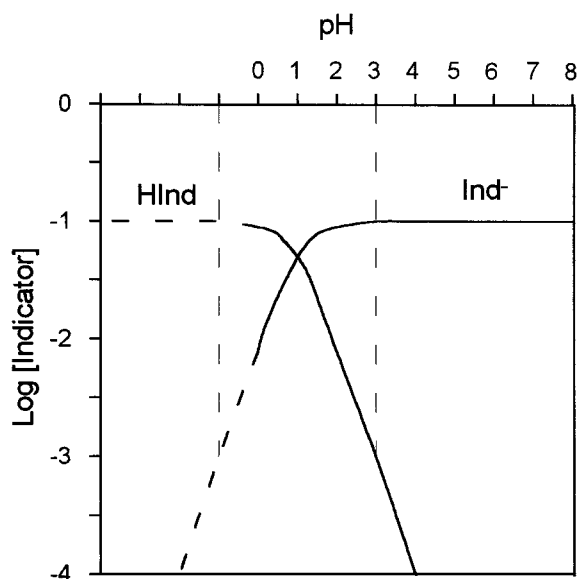

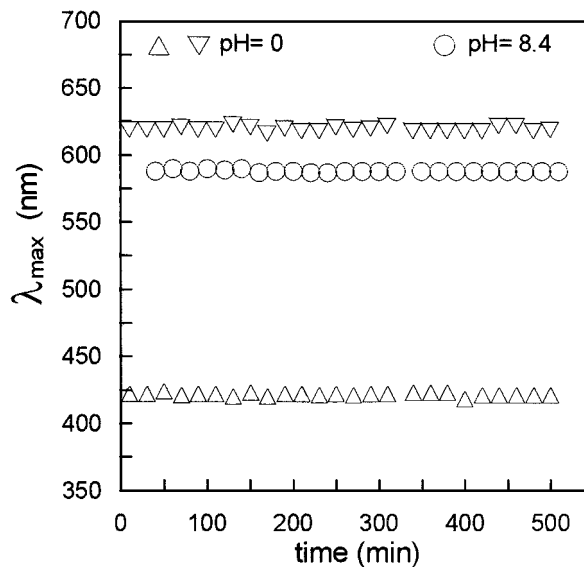*Figure 4* Maximum wavelengths of the main absorption bands recorded for acid (pH = 0) and basic (pH = 8.4) succesive runs.

tion in the interconnected pore surface of gel coatings. This type of linkage, bridging with water molecules and silanol groups from the silica matrix partially densified in the inner surface of open pores, has yet discussed for other dye doped systems [15].

Fig. 5 shows the spontaneous regain of both maximum absorption wavelengths and intensities when doped coatings were exposed to a saturated aqueous HCl atmosphere for 5 min. Once the exposition had finished the regain from the 435 nm (yellow) band to the 590 nm (blue) band quickly proceeded. This mainly occurred during the first 10 min. After 120 min the values recorded for absorption wavelengths and their intensities are close to the standards before the exposition (dashed lines in both figures). This spontaneous regain towards the characteristic basic features of CV coatings can be understood once again as a consequence of the CV pK_{Ind} value, which is close to 1; and, hence, a very high concentration of acid is neccessary to maintain the characteristic acid features (see Fig. 3). Obviously, that high concentration can not be achieved for long time under these conditions.

In an attempt to illustrate the colour change that took place when CV doped coatings were submitted to different pH, Fig. 6 reports on the evolution of trichromatic coordinates with pH inside the chromaticity chart. Colours for basic and neutral pH are located upon the blue region, whereas those from acid pH and concentrated HCl enter into the green domain. As it was indicated above, this is due to the presence of residual basic band, probably promoted by CV molecules entrapped in closed pores of the gel film which had no contact with acid reagents.

Leaching of organic dyes from sol-gel matrices is one important handicap which arises when sensors are the final application [16]. Although CV doped coatings resisted well against chemical reagents all over the pH range, (since no CV molecules were detected in solutions and buffers used after several washing runs), it was interesting to perform some tests that could indicate

Figure 3 Representation of CV concentration vs pH, as acid indicator in solution, taking $pK_{CV} = 1$.
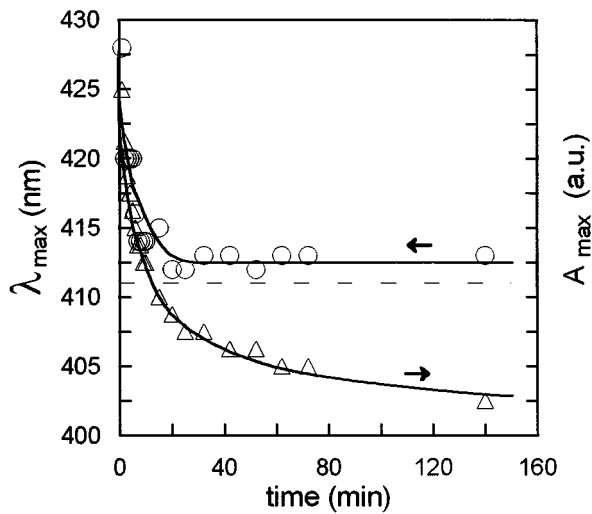
(a)
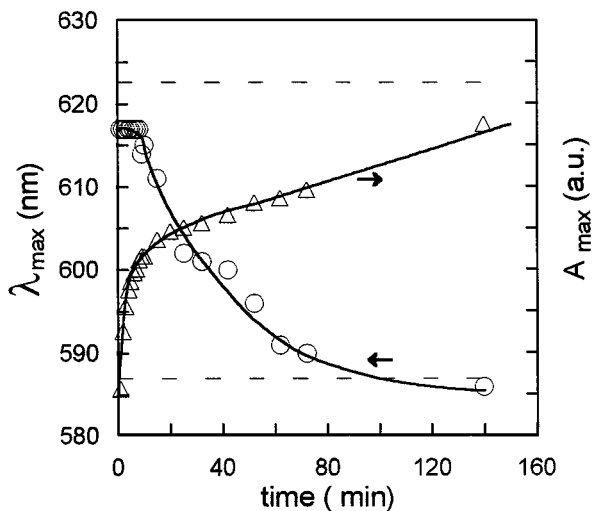
(b)

Figure 5 Spontaneous regain of characteristic optical features of basic pH for coatings sensitized under aqueous acid vapours.
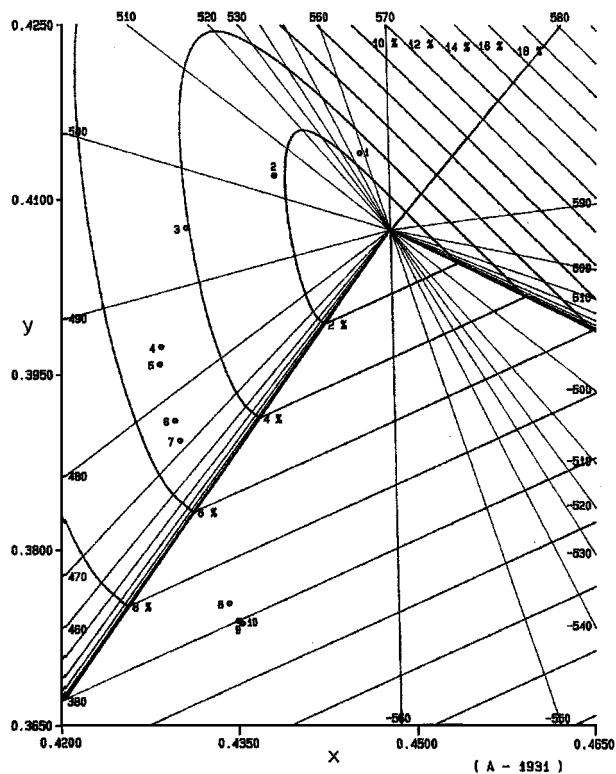

Figure 6 Chromaticity chart showing the evolution of colour coordinates of CV doped films dipped on different solutions: 1) HCl 12 M, 2) HCl 6 M, 3) HCl 4 M, 4) HCl 3 M, 5) HCl 2.5 M, 6) HCl 1.5 M, 7) pH = 0.06, 8) pH = 1.03, 9) pH = 3.02 and 10) pH = 7.00.
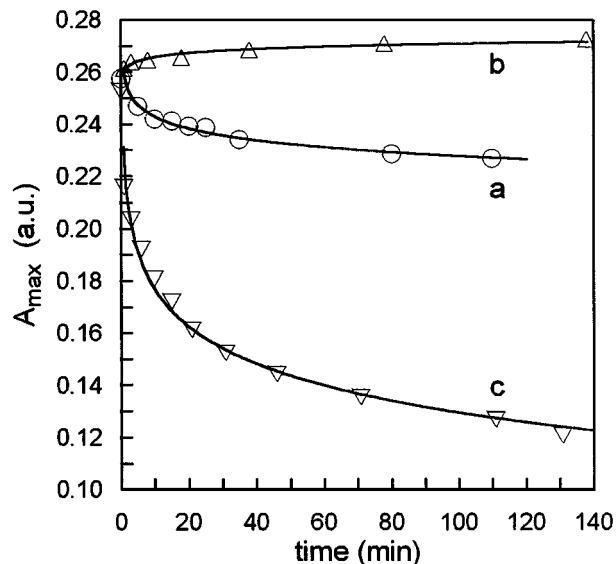

Figure 7 Optical absorption change (related to the maximum of the corresponding main band at each pH) of doped coatings. Curve a: after dipping into the alkaline attack solution. Curve b: after dipping into deionized water. Curve c: prehidrated as in curve b and then dipped into the attack solution.

the ways in which the coatings could be attacked or even destroyed. This is the reason why a solution (pH = 14) commonly used [14] to evaluate alkaline resistance of conventional glasses was chosen. In order to avoid thermal release of CV, the test temperature was here maintained around 20°C.

When CV doped coatings, dried at 60°C for 3 days and stored under anhidrous conditions during one month at room temperature, were submitted to alkaline attack, a light decrease in absorption intensity is recorded (Fig. 7, curve a). SEM observations performed on these samples confirm the formation of cracks at this stage (Fig. 8). Such cracks (5 μm average width) probably appeared as the result of an abrupt humectation-attack mixed mechanism, which was initiated in the nearest of small defects or pits on the coating surface. Once the pit was attacked, the alkaline solution could penetrate into the gel coating or, even the worst, between the coating and the glass substrate. In the late case, alkaline corrosion can quickly advance, favouring the formation of long cracks on the coating. Light dispersion due to the presence of such cracks may account for the decrease of optical absorption recorded (Fig. 7, curve a). Average width for cracks ($\approx$5 μm)

were found to be of the same order of magnitude that cracks formed by corrosion of K-Ca silicate glasses [17] submitted to an acid leaching solution for 24 h at room temperature.

On the other hand, hidratation of coatings (dried and stored by the same way) by dipping them into deionized water, yielded a very weak increase of optical absorption (Fig. 7, curve b), and no cracks generation was observed. That curve can be fitted to a logarithmic
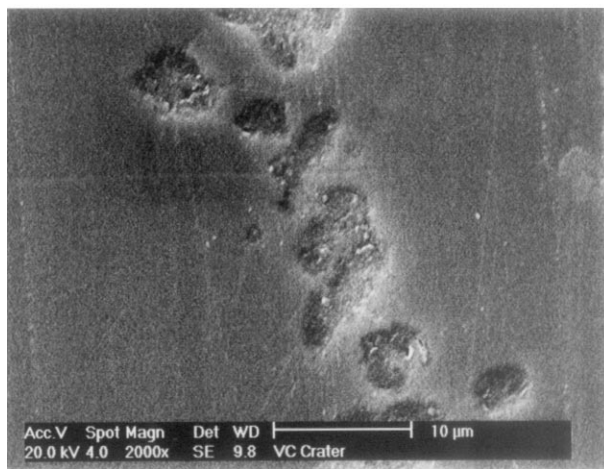
(a)
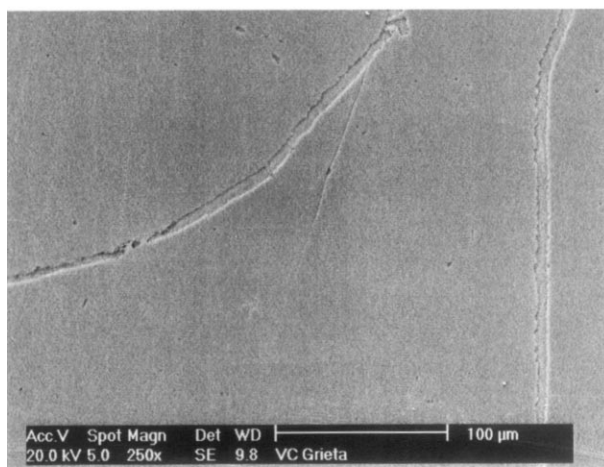
(b)

Figure 8 Scanning electron micrographs of CV doped coatings after being chemically attacked with mixed alkaline solution at room temperature. (a) corrosion beginning, (b) cracks generated by corrosion.

function and could be adscribed to a diffusion pattern. Water penetrated inside the gel coating reaching the farest pores and enhancing CV molecules there located to response against water pH. Once all accesible CV molecules were activated, no further increase in optical absorption was expected, as curve b of Fig. 7 confirms.

Previously hidrated coatings were further submitted to alkaline attack. Results pointed out a decrease in absorption intensity together with a progressive coating corrosion, visually observed (Fig. 7, curve c). When pore channels were well open by hidratation, the attack rate increased, even destroying the coating. Dissolution of the partial densified silica coating rather than leaching of dopant dye is proposed as the main process that took place. As is well known, silicate glasses were strongly damaged by alkaline solutions through network dissolution mechanism. On this basis, the release of the gel film was favoured by the alkaline attack to the glass substrate.

4. Conclusions

CV doped silica films were prepared in such a way that chemical reactivity of the dopant dye was maintained. Coatings were pH sensitive in both aqueous liquid and gaseous media, showing a sensitivity range around the pH value in which CV changes its colour in solution

(pH $\approx$ 1). Optical absorption spectroscopy became a useful tool to characterize the changes that occurred in doped coatings versus pH.

The colour changes produced by pH on the CV doped silica coatings were reversible, at least for 50 cycles. It probably could be extended, since no fatigue was found in the optical response of coatings.

Dye doped films were stable all over the pH range at room temperature, showing no leaching of CV molecules. However, attack with a standard mixed alkaline solution produced cracks. These cracks probably were initiated by chemical corrosion in small defects or pits upon coatings. That yielded a decreasing optical absorption, due to ligth loss by dispersion. More research is overcome to clarify limits in which CV doped silica films are suitable to be used as an optical pH sensor.

References
1. J. I. ZINK and B. DUNN, in "Sol-Gel Optics: Processing and Applications," edited by L. C. Klein (Kluwer Academic Publishers, Norwell, 1994) p. 303.
2. R. ZUSMAN, C. ROTTMAN, M. OTTOLENGHI and D. AVNIR, *J. Non-Cryst. Solids* **122** (1990) 107.
3. B. DUNN and J. I. ZINK, *Chem. Mater.* **9** (1997) 2280.
4. P. LANVIN, C. M. MCDONAGH and B. D. MACCRAITH, *J. Sol-Gel Sci. Technol.* **13** (1998) 641.
5. B. DUNN and J. I. ZINK, *J. Mater. Chem.* **1** (1991) 903.
6. M. A. VILLEGAS and L. PASCUAL, *Thin Solid Films*, in press.
7. M. A. VILLEGAS and J. M. FERNANDEZ NAVARRO, in Proceedings of the 1st International Workshop on Non-Crystalline Solids, San Feliú de Guixols, May 1986, edited by M. D. Baró and N. Clavaguera (World Scientific, Philadelphia, 1986) p. 433.
8. M. A. VILLEGAS and J. M. FERNANDEZ NAVARRO, *J. Non-Cryst. Solids* **100** (1988) 453.
9. T. M. BUTLER, B. D. MACCRAITH and C. MCDONAGH, *ibid.* **224** (1998) 249.
10. J. Y. DING, M. R. SHAHRIARI and G. H. SIGEL, JR., *Electronics Lett.* **27** (1991) 1560.
11. B. D. MACCRAITH, V. RUDDY, C. POTTER, B. O'KELLY and J. F. MCGILP, *ibid.* **27** (1991) 1247.
12. M. R. SHAHRIARI and J. Y. DING in "Sol-Gel Optics: Processing and Applications," edited by L. C. Klein (Kluwer Academic Publishers, Norwell, 1994) p. 279.
13. C. R. BAMFORD, "Colour generation and control in glass" (Elsevier, Amsterdam, 1977) p. 16.
14. ISO 695, Glass, Resistance to attack by a boiling aqueous solution of mixed alkali, Method of Test and Classification.
15. C. ROTTMAN, A. TURNIANSKY and D. AVNIR, *J. Sol-Gel Sci. Technol.* **13** (1998) 17.
16. N. AHARONSON, M. ALTSTEIN, G. AVIDAN, D. AVNIR, A. BRONSHTEIN, A. LEWIS, K. LIBERMAN, M. OTTOLENGHI, Y. POLEVAYA, C. ROTTMAN, J. SAMUEL, S. SHALOM, A. STRINKOVSKI and A. TURNIANSKY, *Mat. Res. Soc. Symp. Proc.* **346** (1994) 519.
17. A. A. SALEM, M. GRASSERBAUER and M. SCHREIMER, *Glass Technol.* **35** (1994) 89.