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Development of Low Cost Optical pH Sensor

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A new low cost pH sensor was developed by immobilizing a direct indicator dye to porous and transparent acetylcellulose film. This sensor was fabricated by binding (Congo red and alizarin red S) to a cellulose acetate film that had previously been subjected to an exhaustive base hydrolysis for 24 h and increase the porosity of the membrane. The cellulose membranes were immediately treated with a mixture of 0.60% (w/v) thiourea and 0.50% (w/v) polyvinyl alcohol solution for 48 h at 25°C. The cellulose membranes were separately treated with 0.1% (w/v) solution of alizarin red S at 35°C and 0.050% (w/v) Congo red at 25°C with magnetic stirring of the solution for 14 h. After washing, the films were dried at 45°C for 20 min. Then the membranes had good durability (> 12 months) and a short response time (< 9 s). The method is easy to perform and uses acetylcellulose as a carrier. The reagents used for the activity of cellulose support are inexpensive, non-toxic and widely available.

Ket Words: **Optrode, pH, Alizarin red S, Congo red, Sensing film.**

INTRODUCTION

Optical pH sensors (optrodes) are based on pH-dependent change of the optical properties of thin and proton-permeable layers in which a pH indicator has been chemically or physically immobilized[1]. Several authors[2–6] have reported the immobilization of calorimetric reagents at various films as an effective approach to construction sensors for pH. Although the properties desired of an immobilized indicator phase would vary depending on the intended application, in general the ideal immobilization techniques should produce a highly stable assembly of molecules that remain strictly accessible to the dissolved dye.

Covalent attachment to a functionalized support[3] and physical entrapment, either in a porous polymer matrix[4] or behind a selectively porous membrane[2] are two commonly employed techniques. Entrapment is the technically simpler technique, but the response is often relatively long.

A method for covalent binding of enzyme to cellulose carrier, which includes activation of the cellulose by urea and formaldehyde, was described previously[3, 7]. The purpose of this work was to investigate the possibility of developing a modification of the above methods for covalent immobilization of new indicators on optically transparent acetylcellulose membrane that has been previously hydrolyzed and activated using thiurea and polyvinyl alcohol.

The characteristics of the membrane produced were investigated and the possibilities for its use in the design of optical pH sensors were evaluated. According to our knowledge, up to now, only dye molecules with amino groups on the ring cycle were used to construct optical pH sensors based on chemical modification of polymer films. In this paper, we used thiourea in linking every type of dye (with or without amino groups on the ring) to cellulose acetate film with satisfactory results. The alizarin red S sensor can be used for direct determination of pH in alkaline media (pH 8.5–13.5) without any alkaline error.

EXPERIMENTAL

Congo red 0.050% solution (Merck) and alizarin red S 0.1% solution (Merck) were prepared by dissolving the dyes in water. Polyvinyl alcohol solution was prepared by dissolving 0.50 g of the reagent (Merck) in 100 mL water. Thiourea solution was prepared by dissolving 0.60 g of the reagent (Merck) in 100 mL water. Solution of known pH was prepared using both analytical grade sodium borate and sodium citrate (Merck) or H_3PO_4 and NaOH with degassed doubly distilled water.

The pH of buffer solutions was measured with a commerical pH meter (Scotte, Model CG 825) calibrated with Merck pH standards of pH 4.00, 7.00 and 10.00 at 25°C. A UV-Visible spectrophotometer (Shimadzu, model 240) was used to acquire absorption spectra.

Preparation of Sensors

The triacetyl cellulose was previously hydrolyzed in order to de-esterify the acetyl groups and to increase the porosity of the membrane. A 2 g amount of transparent film (separate pieces of size 34 × 8 × 0.1 mm) was treated with 0.10 mol/L KOH for 24 h. The film was washed with water. The cellulose membranes were immediately treated with a mixture of 0.60% (w/v) thiourea and 0.50% (w/v) polyvinyl alcohol solution for 48 h at 25°C. The cellulose membranes were separately treated with 0.1% (w/v) solution of alizarin red S at 35°C and Congo red 0.050% (w/v) at 25°C with magnetic stirring for 14 h. After washing, the films were dried at 45°C for 20 min. Then the membranes were washed with distilled water until there was no absorption at the wavelength of the dyes during rinsing. Then the films were dried at 45°C for 20 min.

Spectrophotometric measurements

The measures with immobilized indicator were stretched vertically inside the cuvette using a special frame. The size of its opening was 8.5 × 35 mm. The control sample against which the measurement was performed consisted of triacetylcellulose film treated in the same way but without indicator. The control sample was stretched in the same way inside the cuvette using a frame of the same size. The spectral characteristics of alizarin red S were measured using borate, citrate and phosphate (0.20–0.05–0.10) M buffer in the pH range 7–13 in steps of 0.50 and those of Congo red using (0.20–0.05–0.10) M borate, citrate and phosphate buffer and in the pH range 2–6 in steps of 0.50.

RESULTS AND DISCUSSION

Alizarin red S is a dye without an amino group in the ring, whereas Congo red has one amino group in the ring. These dye molecules can be linked to the cellulose acetate film by special treatment. Kostov and coworkers[3] showed that only the dye with amino group could be linked with cellulose acetate. We find that using thiourea, dyes with or without amino group can be linked to cellulose acetate film. The optical properties of alizarin red S solution and immobilized alizarin red S at hydrolyzed cellulose membrane are a function of pH. As can be seen, a blue shift of the transition interval from the acidic reagent to the neutral reagent occurred for the Congo red and a red shift of the absorption maxima at the hydrolyzed cellulose, in comparison with the free dye in the solution, was observed. For the immobilized alizarin red S, there was a red shift of the transition interval from the neutral region to the basic solution and a blue shift of the absorption maxima at the hydrolyzed cellulose. On the other hand, the change in absorbance is linear only for the pH range from 7 to 13.

The absorption maxima of the immobilized Congo red are located at 485 and 590 nm and those of the free dye at 480 and 570 nm. The absorption maxima of the immobilized alizarin red S are located at 350 and 420 nm, whereas for the free dye they are at 360 and 440 nm. The above results can be interpreted based on the influence of the immobilized procedure on the behaviour of the indicators. Krysteva and coworkers[8] showed that the condensation between the hydroxylmethyl groups of the carrier and the protein is accomplished through the transformation of the amino groups in the alkaline pH region and of the amino group in the acidic pH region. In addition, the reactivity of the activated carrier is so high that it was considered that interaction is possible with low molecular weight compounds that have a free ortho position in the molecule. For this reason, indicators having amino groups of free ortho positions in their structure can be used. For this reason thiorea was used as a bridge to connect the dye molecules to the membrane cellulose acetate film. Possible schemes for the reactions are shown in Fig. 1. This makes it possible to achieve covalent binding to the activated matrix. In the experiments, it was found that a considerable amount of indicators with amino groups was linked to the activated membrane *via* covalent binding. On the other hand, the indicators without amino groups such as alizarin red S can also be linked with cellulose membrane. The fact that the immobilization changes the ratio of the heights and position of the absorption maxima of the indicators shows that the amino groups are auxochrome elements of the molecule and the loss of a proton after the covalent binding influences the charge distribution during the dissociation of the immobilized dye. The reasons for the transitions interval shift are possibly the new covalent binding and the influence of the nearby acetyl cellulose carrier.

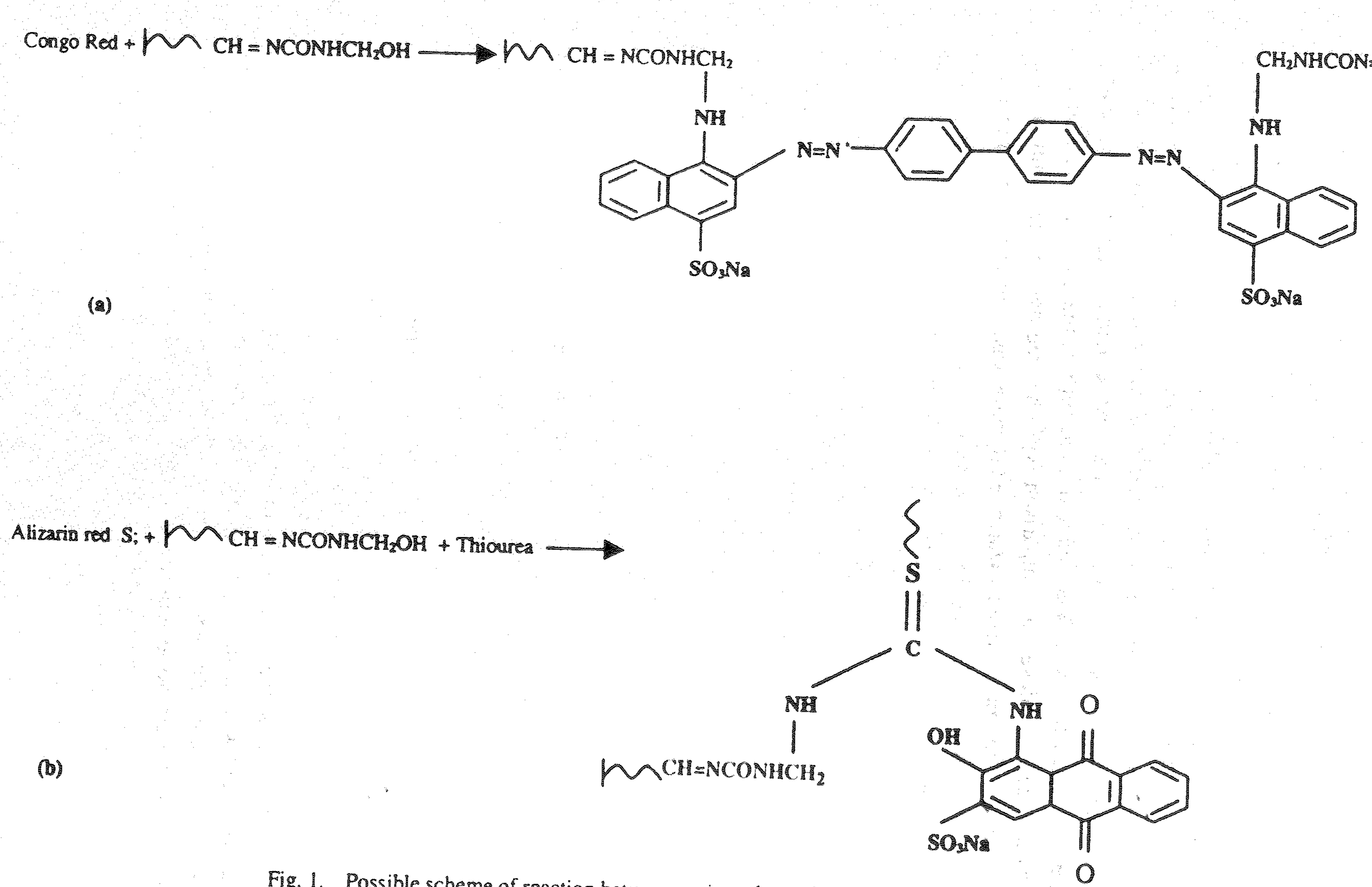

Fig. 1. Possible scheme of reaction between activated membrane and (a) Congo red; (b) alizarin red S

Sensor Stability and Response Time

Repeated measurements showed that the changes in the absorption coefficient after keeping the measurements in aqueous solutions for months were less than 5%.

The stability of the membrane sensors based on a recycled support made from waste films is higher in comparison with other methods in which acetylecllulose is also used for producing optical sensors[2]. This is due to the higher mechanical strength of the carrier and to the covalent binding between the indicator and the change in optical properties of membranes with immobilized alizarin red S and Congo red hydrochloride were measured at 585 and 420 nm, respectively. Fig. 2 shows a typical curve for the transition processes. As shown in the figure, less than 9 s, the output signal reaches 98% of the steady-state response for about 8 s, for two membranes.

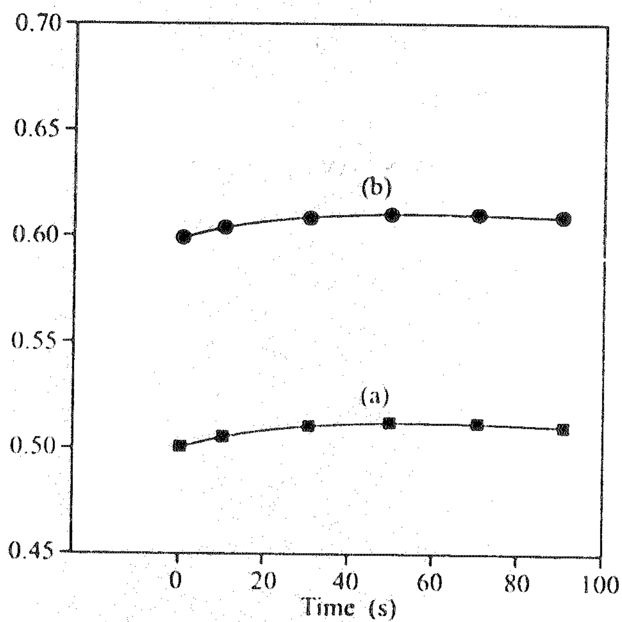

Fig. 2. Transition process of the pH sensor constructed by covalent binding of (a) Congo red and (b) alizarin red s to acetylcellulose. (Conditions: for (a), initial pH was 5.00 and at $t = 0$ the pH was changed to 3.00; for (b) the initial pH was 10.00 and at $t = 0$ the pH was changed to 8.50

Conclusion

The spectra for the alizarin red S and Congo red hydrochloride indicate that these sensors exhibit a dynamic range of more than 7–13 pH and 2–6 pH units respectively.

The described method for producing pH-sensitive optical membranes has the following advantages in comparison with other methods: (a) a waste cellulose material with good optical and mechanical properties is used as a matrix for immbilization; (b) immobilization of the indicators on the membrane's surface reduces the diffusion limitations and allows sensors with short response time, (c) its activation is performed by using non-expensive and available reagents with suitable time stability for large numbers of measurements; (d) the dye without amino groups in the ring can be linked with cellulose acetate membrane *via* thiourea molecule. Also the pH sensor constructed from Congo red has a thin linear dynamic range; the Alizarin Red S sensor is useful for measuring pH values in highly alkaline media (pH 7–13) without any alkaline error, where a glass electrode cannot be used for direct pH determination. The results are shown in Table-1.

TABLE-1
APPLICATION OF THE ALIZARIN RED S pH SENSOR FOR DIRECT DETERMINATION OF pH IN HIGHLY ALKALINE MEDIA

Solution No.	NaOH solution, M[a]	pH found
1.	2.00×10^{-4}	10.27
2.	4.00×10^{-3}	11.56
3.	2.00×10^{-2}	12.26
4.	6.00×10^{-2}	12.73
5.	1.00×10^{-1}	13.06

[a]Sodium hydroxide was added to distilled water.

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