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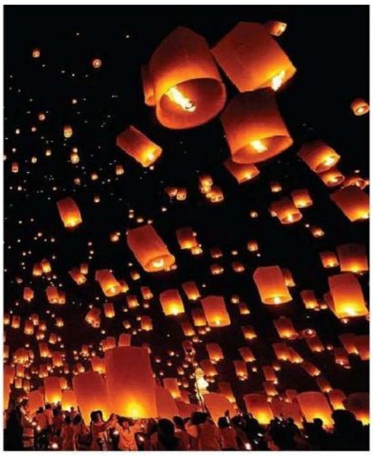

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Optical pH Sensor Using Alizarin Yellow R Immobilized on Hydrolyzed Cellulose Acetate Membrane

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Abstract

Optical pH sensing material was prepared using alizarin yellow R (AY) immobilized onto a hydrolyzed cellulose acetate (CA) membrane. Used photographic film was color-bleached with sodium hypochlorite and hydrolyzed with sodium hydroxide to obtain the hydrolyzed membrane. AY was immobilized onto the hydrolyzed membrane from methanol solution. AY was strongly fixed on the CA membrane and not washable by water. UV-visible spectrometer was used to measure the absorption intensity of the immobilized dye (at wavelength 382 nm) as a function of solution pH (7 - 14). It was found that a linear correlation (between pH and absorption intensity) was obtained at pH = 8 – 12, with a response time of less than 4 min. At pH > 12, the sensing membrane cannot be used due to the formation of white precipitates on the CA membrane.

Keywords: Optical pH sensor, Hydrolyzed cellulose acetate membrane, Alizarin yellow R

Introduction

Developments of pH sensors have grown rapidly because so many chemical process, biological process, and practical applications such as clinical analysis, environmental analysis and process control are dependent on pH [1, 2]. Measuring methods for pH values can be divided into 5 categories: pH indicator reagents, pH test strips, hydrogen electrode, glass electrode, metal electrodes and optical pH sensor [1].

Most optical pH sensors are usually based on acid–base indicators. The pH indicator dyes can be immobilized on the surface of supporting materials (such as polymeric or sol-gel) to obtain the pH sensor membrane. The diffusion of acid/base solutions into the sensor membrane causes the change of absorbance or luminescence of certain indicator molecules.

The construction of an optical pH sensor based on several dyes immobilization of transparent cellulose acetate (CA) was described [2-4]. CA membrane was prepared from used photographic film whose original color layer was bleached out. Suitable type of indicator dye can be chosen such that the membrane sensor can effectively measure pH at high and low pH ranges, where common pH electrodes encounter alkaline and acid errors [3-5]. In addition, the mixing of multiple indicator dyes (with different pK_a or pK_b values) on the same sensor membrane can be done to extend the working detection range [2-3].

Our previous work was performed on the immobilization of various indicator dyes (methyl orange, phenolphthalein, thymol blue, bromothymol blue, and alizarin yellow R) onto the hydrolyzed CA membrane obtained from used photographic film. It was found that alizarin yellow R (AY) gave the best result. AY was strongly fixed onto the membrane and not washable by water. Thus, AY immobilized CA membrane was selected as a sensing material for development of optical pH sensor. This paper involves the study of UV-Vis absorption behavior of immobilized AY as a function of pH and sensor characteristics of the immobilized CA membrane.

Experimental

Reagents

All reagents used in this work were of analytical grade. AY was purchased from Sigma-Aldrich. 0.1% w/v solution of AY was prepared by dissolving AY in methanol. Commercial sodium hypochlorite was used as a bleaching agent. 0.1 M sodium hydroxide was used for hydrolyzing CA membrane. All aqueous solutions were prepared with deionized water.

Instrumentation

An AvaSpec-2048 portable fiber optic spectrometer from Avantes was used for recording absorbance and UV-Vis spectra. Setup for the spectrometric measurements was shown in Figure 1. A Metrohm 744 digital pH-meter was used for measuring pH value.

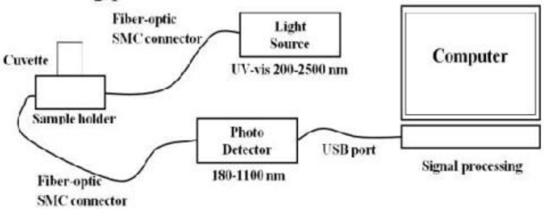

Figure 1. Set-up of measuring system

Preparation of AY-immobilized CA membrane

The transparent CA membrane was prepared from used photographic film. Used film strip was cut into a rectangular shape (1 x 6 cm^2). The used film was treated with commercial sodium hypochlorite for 24 h in order to remove the colored gelatinous layers. The obtained film was then treated with 0.1 M sodium hydroxide solution for 2 h to obtain the hydrolyzed membrane. This hydrolyzing step causes removal of the acetyl groups and increase of the membrane porosity. The hydrolyzed film was rinsed a few times with water and kept in distilled water for 24 h prior to use. Dye immobilization was performed by immersing the hydrolyzed film in a 0.1% w/v AY solution for 1 h. The immobilized film was washed several times with water to remove loosely trapped dyes and kept in distilled water when not in use.

Optical properties of the immobilized membrane

Acid-based behaviors of AY in solution and AY immobilized films were studied by spectrometric measurements. A strip of immobilized film was placed inside a quartz cuvette where a solution with a desirable pH was previously filled. Solutions with various pH from 7.0-14.0 was adjusted by addition of 1 M sodium hydroxide solution into a solution initially at pH 7.0. All of the solution pH was measured by the digital pH meter. The absorption spectra were taken using a cuvette filled with water as blank.

Results and Discussion

Optical property of AY indicator in solution

Effect of pH on the AY in methanol solution and AY immobilized on the hydrolyzed CA membranes was studied in the solution pH between 7 and 14. The basic pH range was used because AY indicator changes color from yellow to red at pH around 10-12. The spectral change, thus, corresponds to an acid-base equilibrium of the indicators.

The absorption spectra of AY in methanol solution as a function pH are shown in Figure 2. Two absorption maxima at 367 and 490 nm can be seen from the spectra. Peak at 367 nm corresponds to the yellow form while that at 490 nm represents the red form. At pH < 10, solution color was yellow and only the peak at 367 nm (yellow form) was found. When the pH got higher, solution color gradually changed from yellow to red as the yellow peak was decreasing in intensity while a new peak at 490 nm (red form) was emerging. At pH > 10, the yellow peak disappeared and only the red peak remained. Plot of peak intensity at 367 and 490 nm against solution pH (in Figure 3) showed the reversible yellow-red transition with the equilibrium pH (end-point of indicator) ~ 11-12. The presence of characteristic *isobestic* point (region where all of the spectrum lines are intercept) at around 410 nm indicates the fully reversible, equilibrium between protonated (yellow) and deprotonated (red) forms of this pH indicator [5].

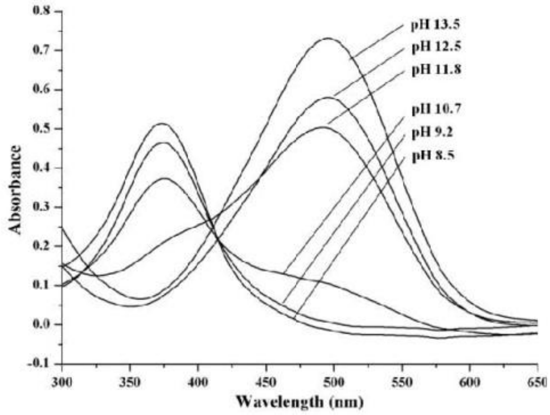

Figure 2. Absorption spectra of AY in methanol solution

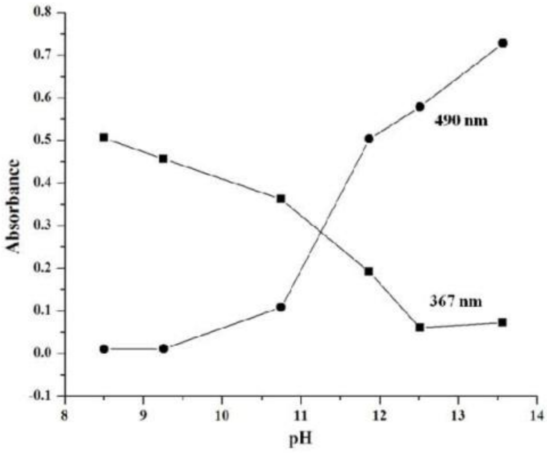

Figure 3. Effect of pH on absorbance of AY solution at 367 nm (yellow form) and 490 nm (red form)

Optical property of immobilized AY in hydrolyzed CA film

After immobilization, colorless CA film turned yellow. It was found that the yellowish AY color was strongly fixed on the CA membrane and not washable by water. After treating with basic pH from 8 to 13, it was observed that the film color was almost unchanged (remained yellow, with slightly stronger color at higher pH). Absorption spectra of AY immobilized onto hydrolyzed CA film as a function pH are shown in Figure 4.

Two obvious differences were found in the spectra of immobilized AY, as compared to those of the AY solution. First, spectra of the immobilized AY only showed one absorption maxima at 382 nm (yellow form) and its yellow peak was also red-shift (from 367 nm to 382 nm). Second, peak intensity of the yellow form was increasing as higher pH while intensity of the solution peak was decreasing as the solution color changes from yellow to red.

The above results indicated that the immobilized AY molecules should form strong interactions (possibly chemical bonding) to the CA surface in such the way that their structural conformations were fixed in a restricted yellow form. The structural restriction of the immobilized form gives rise to the marked differences in both optical property and acid-base reactivity as compared to the dissolved form in the solution. The strong interactions are also contributed to the good film-dying property and stability of the immobilizing film.

Since the film color does not change when exposed to different solution pH, the AY immobilized film cannot be used as a pH sensor in the conventional fashion. Nevertheless, it was observed that color intensity of the immobilized film increases with solution pH and the change is reversible. This intensity change could be useful as pH sensor signal, as oppose to the color change found in most indicator dye systems.

Figure 5 shows a plot between peak intensity of the immobilized yellow form at 382 nm and solution pH. The good linear relation (with an R^2 value of 0.9982) was found in the pH range between 8 to12.

It was found that absorption intensity increases drastically when the solution pH > 12. It was also observed

A small amount of white deposits was also observed in the CA membrane. These deposits remained on the film and reversibility of the film signal was lost. Therefore AY immobilized CA film can be useful as pH sensing material only when solution pH is less than 12.

Sensor response of the AY-immobilized CA film

To determine the response time, the immobilized film was placed in a solution pH 7 for a few minutes to get equilibrium intensity. Then, pre-determined amount of NaOH solution was quickly added and stirred to get a solution pH = 12 and peak intensity was monitored as a function of time until signal reaches equilibrium values.

As seen in Figure 6, the absorption intensity reaches equilibrium within about 5 minutes and the response time from 0% to 95% of the steady state signal is about 3 minutes. Note that several experiments were done and found that the 95% response time was less than 4 minutes

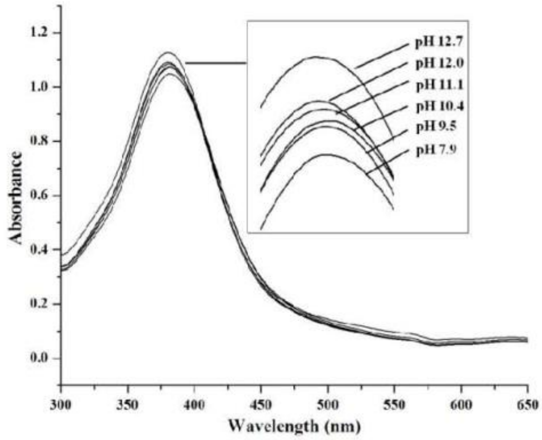

Figure 4. Absorption spectra of immobilized AY on hydrolyzed CA film

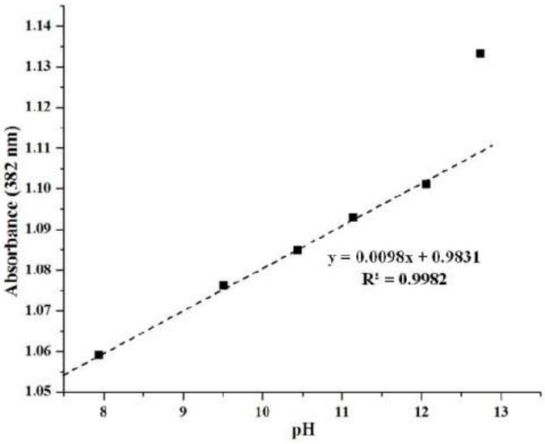

Figure 5. Plot of absorbance at 382 nm of the immobilized membrane against solution pH, showing a linear relation in the pH range of 8-12

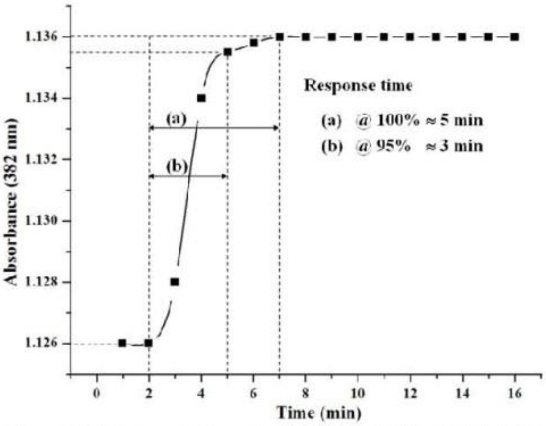

Figure 6. Response time for AY immobilized CA film when solution was change from pH = 7 to 12

Conclusions

A used cellulose acetate film was used as a matrix for immobilization of AY dye. It was found that optical property of the immobilized dye was different from its dissolved form in solution. While the color of the immobilized dye was not unchanged, its color intensity was linearly changed with pH. The AY-immobilized CA film can be useful as a sensor material with a pH working range from pH 8 to 12 and a response time (95% signal) of less than 4 minutes. The sensing membrane cannot be used at pH > 12 due to the formation of white precipitates on the CA membrane.

Acknowledgments

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