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Chromophoric thin film based on cellulose triacetate blends for sensing metal ions

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ARTICLE INFO

Article history:

Received 22 June 2013

Accepted after revision 9 October 2013

Available online 22 February 2014

Keywords:

Cellulose triacetate

PEG 600

8-Hydroxyquinoline

Fluorescence

Optical sensor

Metal ions

ABSTRACT

Chromophoric sensors were made based on 8-hydroxyquinoline immobilized onto a thin film of a polymer blend matrix. The thin films were made by the solution casting method using cellulose triacetate and polyethylene glycol (PEG 600) as plasticizer and pore-forming agent. Different contents of PEG 600 additive were investigated. The prepared films were characterized by FTIR and thermal analysis. The absorption and fluorescence spectra of different films were dependent on the content of PEG 600 with clear quenching of the fluorescence of the film that contains PEG 600 compared to that with zero content. This behavior was attributed to the collective effect of hydrogen bonding (intra- and intermolecular hydrogen bonding) that enhances the process of excited-state proton transfer. This result is favorable to a responsive sensor that shows fluorescence off in the absence of metal ions and fluorescence on upon metal ion chelation. The detection of 5×10^{-5} M of Al^{3+} , Zn^{2+} and thallium (I) in aqueous solution has been observed with the fluorescence method. The result obtained is consistent with the enhancing effect of PEG 600 in the detectability of metal ions. Compared with the detection of Al^{3+} and Zn^{2+} , the sensor shows better detection of thallium (I), with clear fluorescence spectra.

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1. Introduction

The development of fluorescent sensors for the detection of heavy metal ions in aqueous solutions that are harmful for the environment is of increasing interest [1–4]. In this rapidly developing field, fluorescent detection has become one of the most exploited techniques owing to its high sensitivity and ease of operation [5,6]. It is worth to mention that the word “sensor” refers to a device that is capable of responding to the presence of an analyte such as a metal ion in a reversible and continuous manner. Sensors producing an irreversible response to the presence of heavy metal ions are called probes. The detection of heavy metal ions is mainly based on the use of a chromophore capable of

binding with the ions upon which a fast response by a change in the absorbance or fluorescence of such chelators takes place. This means that the chromophore acts as a transducer for the chemical species that cannot be determined directly by optical means [7–9]. Thus, sensors based on ion-induced changes in fluorescence appear to be particularly attractive due to their simplicity, high sensitivity, high selectivity, and instantaneous response [10].

The immobilization of a fluorescent chromophore (fluorophore) onto a solid support such as a polymer matrix has advantages for practical applications due to easy recovery and reusability. Various polymeric membranes have been used as supporting matrices for the preparation of optical chemical sensors in the literature. In principle, the immobilization of a fluorophore either by chemical or physical bonds with a plasticized polymer facilitates sensor–analyte interactions and produces a distinctive change in the optical signal. The selection of the

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polymer matrix for the ion-sensitive thin film is governed by parameters such as permeability of the analyte, mechanical stability, and its suitability for chromophore immobilization [11]. Basic principles, techniques, and recent studies of optical ion sensing have been described [12,13] and reviewed [14–17].

Cellulose triacetate (CTA) is a transparent semi-synthetic biodegradable biopolymer, widely used in different applications such as hemodialysis, reverse osmosis membranes, and liquid crystal displays [18]. Previous studies have shown that CTA is an effective polymer matrix for the transport of some transition metal ions after being blended with a plasticizer and an ionophore [19–21]. It has been reported that the use of PEG 600 as an additive for CTA membranes promoted a higher resistance to pressure of the prepared membranes and increased pure water flux through the membranes, as well as the ion diffusion coefficient [22]. Therefore, it was hypothesized that mixing PEG 600 as the plasticizer with CTA would help better ion-sensor interaction by increasing the polarity of the polymer matrix.

8-Hydroxyquinoline (8-HQ) was selected in this study owing to its on-off fluorescence response upon metal ion binding [23]. Sensors based on 8-HQ moiety have recently been reported [24–26]. Recent studies indicated that the on-off fluorescence of 8-HQ upon its interaction with metal ions has been attributed to a proton transfer mechanism in which 8-HQ is weakly or nonfluorescent (off) due to an excited-state proton transfer (ESPT); upon binding with the metal ion, fluorescence appears (on), due to the inhibition of the ESPT process [27]. To the best of our knowledge, a chromophoric thin film based on CTA-immobilized 8-HQ has not been reported. In this work, chromophoric thin films composed of CTA as the polymer matrix, PEG 600 as the plasticizer and 8-HQ as the chromophore are investigated. These films were characterized by thermal analysis (TGA), FTIR, UV-visible and fluorescence spectra before and after metal ion binding.

2. Experimental

2.1. General

Cellulose triacetate (CTA), polyethylene glycol 600 (PEG 600), 8-hydroxyquinoline (8-HQ), dichloromethane (DCM), $\text{AlCl}_3 \cdot \text{H}_2\text{O}$, ZnCl_2 , and TlCl (thallium (I) chloride) were of the highest purity available, purchased from BDH Chemicals Ltd Poole, England, and used as received.

2.2. Thin film preparation

Six thin films, referred to as CTA, CTA-PEG1, CTA-PEG2, CTA-8-HQ, CTA-PEG1-8-HQ, and CTA-PEG2-8-HQ with the composition shown in Table 1, have been prepared by the solution casting method. The first set of films (CTA, CTA-PEG1, and CTA-PEG2) and the second set of films (CTA-8-HQ, CTA-PEG1-8-HQ, and CTA-PEG2-8-HQ) were prepared at different PEG 600 contents and in the absence and presence of 8-HQ, respectively as follows. The film solutions for the first set were prepared by dissolving 1000 mg of CTA and

Table 1
Sample description.

Film	Composition
CTA	1000 mg CTA/32 mL DCM
CTA-PEG1	1000 mg CTA + 500 mg PEG/32 mL DCM
CTA-PEG2	1000 mg CTA + 1000 mg PEG/32 mL DCM
CTA-8-HQ	The composition of all films are the same
CTA-PEG1-8-HQ	as above but in the presence of 8-HQ
CTA-PEG2-8-HQ	(0.58% w/w of polymer matrix)

different PEG 600 (0, 500, and 1000 mg) in 32 ml of DCM for making films CTA, CTA-PEG1 and CTA-PEG2, respectively. Similarly, the film solutions for the second set were prepared by dissolving 1000 mg of CTA, different PEG 600 (0, 500, and 1000 mg) and different 8-HQ (5.8, 8.7, and 11.6 mg) in 32 mL of DCM for making films CTA-8-HQ, CTA-PEG1-8-HQ, and CTA-PEG2-8-HQ, respectively. The different amounts used from 8-HQ produced the same fluorophore concentration (0.58% w/w based on the weight of polymer matrix). All solutions were homogenized at room temperature after having been stirred for one hour. The films were made by casting ca. 20 g of the homogenized mixture in a Petri dish (80 × 10 mm). The solution was dried at 50 °C overnight and the films obtained were of thickness ca. 0.15 mm. The films were cut into strips of dimension 9 × 30 mm so as to be used for UV-visible and fluorescence measurements.

2.3. Absorption and fluorescence spectra

Absorption and fluorescence emission spectra of films were recorded in quartz cells. The films were placed in diagonal position in the quartz cell. For the fluorescence measurements, the quartz cell was filled with the salt solution (5×10^{-5} M) and the strip was immersed, then the fluorescence was measured after 5 min as a constant response time. The excitation wave length was 350 nm and the slit width was set at 5.0 nm for both excitation and emission. Absorption spectra were measured on a UV-1650 PC Shimadzu spectrophotometer. Fluorescence spectra were measured on a RF-5301 PC Shimadzu spectrofluorophotometer and are uncorrected.

2.4. ATR-FTIR

The Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectra of thin films were measured in the 4000–650 cm^{-1} regions using a PerkinElmer spectrum 100 FTIR spectrometer.

2.5. Thermal analysis

Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50H thermogravimeter analyzer and the samples were heated from room temperature to 650 °C at a rate of 20 °C/min under an inert nitrogen atmosphere.

3. Results and discussion

3.1. ATR-FTIR

Infrared spectra showed the following characteristics bands of cellulose triacetate (CTA) in Fig. 1: –OH stretch at

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