



Optical humidity sensor using methylene blue immobilized on a hydrophilic polymer



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ABSTRACT

An optical humidity sensor based on a membrane of hydrophilic polymer has been developed. It is a solid state sensor where the components of the membrane are hydrophilic polymer hydroxypropyl methylcellulose (HPMC), methylene blue to indicate humidity changes and a non-ionic surfactant. The mechanism of the sensor is based on the methachromasy related to the dimerization of methylene blue observed upon exposure to humidity. Measurement were carried out in the range of 0–99.5% relative humidity with a detection limit of 0.034%RH, showing a linear response, with good reproducibility (S.D. 0.27 at 1.78%RH, $n = 5$) and stability, fast response and recovery times (60 and 90 s, respectively) and reversibility up to 50% at room temperature (291 K). This sensor displayed sufficient sensitivity that it could be used to detect low RH in environmental applications. Possible interferences were studied such as O₂, CO₂, CH₄ and H₂ gases, which did not show any interference whereas SO₂ and H₂S cause serious interferences on the humidity sensor.

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1. Introduction

The measurement and control of humidity is common in many areas for weather observation [1,2], agricultural industries [3], forest industries, and most importantly in the manufacturing of chemicals, food products, paper and textile production, and electronic components where air-conditioning control is decisive in maintaining a good production process [4].

Since conventional electronic RH sensors are based on picking up the changes in electric conductivity or capacitance [5–8], electrical-resistance [9,10] and surface acoustic wave types [11], among others [4], there are some difficulties in highly humid conditions. Moreover, an inevitable problem is the fact that the sensor head has to be an electrically powered device. Therefore, places like storehouses holding inflammable and explosive materials are unable to utilize these kinds of humidity sensors.

One alternative to this type of humidity sensor are optical sensors because of their many advantages, including being free from electrical interference, the possibility of remote sensing, small size, and safety, even in flammable gas atmospheres.

Optical humidity sensors are based on the use of inorganic salts or organic dyes, which show a chromatic transition depending on

the relative humidity (RH) in the ambient atmosphere [12–14]. In addition to inorganic salts, different organic dyes exhibit reversible colour change as a result of a change in relative humidity, such as thiazine and flavylum salts in gels [15], crystal violet in Nafion [16] or sol-gel [13], rhodamine B in hydroxypropyl cellulose [17], the thiazinic dye methylene blue in zeolites [17,18] or encapsulated within hydroxyethyl cellulose (HEC) in the presence of urea [19] or the mixture of crystal violet and methylene blue in composites containing poly (vinyl alcohol) as solid electrolyte [20].

To prepare humidity sensors, different materials have been used as the host material such as zeolites, which exhibit a higher stability against organic solvents, acids and bases as well as a high resistance to temperature and radiation [21], or silica xerogel films [22] as well as different organic polymers: silicones, hydroxypropyl cellulose, gelatine, polymethyl methacrylate, poly (tetrafluoro ethylene), nafion, nylon, agarose, etc. [23]. The hydrogels such as polyhydroxyethyl methacrylate, polyacrylamide, poly-*N*-vinyl pyrrolidinone and agarose are suitable for their application in humidity sensors and as a generic rule, the bigger the pore size, the higher the dynamic range and the shorter the response time. Among these hydrogels, the hydrogel with a less stable response is the poly-HEMA and the hydrogel with the best performances over time is the agarose gel with a response time of around 90 s with a range of application from 10 to 100%RH [24].

Methylene blue (MB) is a blue cationic dye that belongs to the phenothiazine family. In diluted aqueous solutions, the dye

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forms face-to-face dimers, while increasing the dye concentration causes the appearance of higher aggregates. This association occurs with metachromasy upon MB absorption into organic and inorganic solids too. The humidity dependence on metachromasy of MB has been observed and discussed on the basis of dye protonation [21] or MB adsorption on the surface of titanate revealing that the metachromasy observed upon exposure to humidity is related to a change in the MB molecular configuration [14].

In this work, a humidity sensor based on a hydrophilic polymer is presented; this sensor is based on a sensing film formed by hydroxypropyl methylcellulose polymer and methylene blue. The preparation of this sensor is very simple; it is just an aqueous solution of this polymer, along with the dye and a surfactant. Cellulose ethers are water-soluble polymers with interesting properties such as thickeners, binders, film formers, and water-retention agents widely used in foods, cosmetics, pharmaceuticals, construction products, and a host of other applications, but to the best of our knowledge hydroxypropyl methylcellulose has never been used as a polymer in humidity sensors.

2. Experimental

2.1. Materials

Methylene blue was obtained from Sigma (Sigma-Aldrich Quimica S.A., Madrid, Spain) and the polymer hydroxypropyl methylcellulose (HPMC) (Methocel E-5, LV USP/EP premium grade) from Dow Chemical Iberia S.L. (Tarragona Spain). Sheets of Mylar-type polyester from Goodfellow (Cambridge, UK) were used as a support for membranes. The surfactants tested were: Tween 20, polioxethylene 23 lauryl ether, Brig 35 and Brig 56 all from Sigma, Mighty PSP from Kao Chemical GmbH (Emmerich am Rhein, Germany) and Melflux 2651 from Basf Chemical Company (Tarragona, Spain). The nitrogen gas used was of a high purity (>99%) and was supplied in gas cylinders by Air Liquid S.A. (Madrid, Spain). The water used was reverse-osmosis type quality from Milli-RO 12 plus a Milli-Q purification system (Millipore, Bedford, MA, USA).

2.2. Instrumentation

A homemade climate chamber made of a matte black painted plastic block, 4.4 cm high, 1.2 cm wide and 3.0 cm long with an upper inlet for steam and a small hole in the bottom to prevent overpressure was used as a cell holder for sensor absorbance measurements with a Hewlett Packard HP-8453 diode array spectrophotometer (Nortwalk, CT, USA).

Through climatic chamber, using an inlet pipe, mixtures of different moistures produced by a controlled evaporator and mixer (CEM) system (Bronkhorst HighTech, AK Ruurlo, The Netherlands) are passed. This system consists of a mass flow controller for measurement and control of the carrier gas flow (N_2), a Cori-flow, which enables measurement of mass flow for liquids (water in this case), and a CEM three-way mixing the liquid with the carrier gas flow resulting in total evaporation. In addition, a temperature-controlled heat exchanger was used to ensure complete evaporation of the liquid and enable the preparation of mixtures with relative humidity (RH) between 0 and 100%.

In order to directly relate the experimental variables, gas flow, liquid flow and temperature, with the analytical variable, the relative humidity (RH), a Microsoft Excel spreadsheet was designed where by simply introducing the flow of the air channel and the water channel, it was possible to directly show the RH value. This spreadsheet was made based on the free software pSICRO, ver. 1.5.1, based on an ASHRAE diagram.

In this work, all the relative humidity values were measured at room temperature (291 K) and ambient pressure and all measurements were repeated three times to check for experimental error.

2.3. Sensing membrane preparation

In order to prepare the sensing membranes all the components of the cocktail were dissolved in water. The optimum composition of the cocktail was 2% HPMC, $2 \times 10^{-2}\%$ MB and $5 \times 10^{-2}\%$ Brij 35 in a final volume of 1 ml of water. In order to prepare the sensing membrane, 20 μ l of this cocktail was cast onto an inert Mylar polyester substrate by a spin-coating technique working at 150 rpm for 1 min. All cocktails were prepared by weighing the chemicals in a 4 ml flask with a DV215CD balance (Ohaus Co., Pine Brook, NJ, USA) with a precision of ± 0.01 mg. Following the drying of the film at room temperature for 5 min, a blue film appears under ambient conditions of around 2 μ m thick.

3. Results and discussion

Methylene blue (MB), which belongs to the thiazine class, is a cationic symmetric dye with an approximately planar aromatic skeleton that justifies its interesting redox, photo-physical and aggregation properties. In addition, MB is an H-bond acceptor but very weak H-bond donor, able to bind aromatic molecules by means of heteroassociation [25]. The well-known intermolecular aggregation of MB causes remarkable spectral changes due to the strong coupling of the molecular transition dipoles that result in an excitonic absorption band different from the absorption band of the monomer [26], an example of metachromasy, the change of the absorption spectra of dyes without modification of the structural skeleton of the molecule [14]. MB forms both head-to-head aggregation (J type) with red-shift displacement and side-by-side aggregation (H type) with blue-shift displacement [27]. In aqueous solution the hypochromic and bathochromic effects observed as the MB concentration increases along with the presence of an isobestic point is ascribed to a dimerization process by means of stacking [28] although some authors disagree [29].

The dimerization equilibrium is profoundly affected by the presence of water, which is why it is the basis of humidity sensors when the dye is incorporated in a membrane. However the simple inclusion of MB in a membrane, i.e. sol-gel [30], polyvinyl acetate (PVA) [31], pectin or methylcellulose [27], leads to small band shifts with humidity and high response time. Different strategies have been devised to improve sensing ability. Somani et al. [20] include MB in an anionic solid polymer electrolyte as PVA/ H_3PO_4 which forms a charge transfer complex with the cationic dimer MB that in the presence of water breaks, causing the deprotonation of the N-phenyl group and the displacement of the dimerization equilibrium to the monomer and a concomitant change in colour from yellow to violet. A similar base underlies the use of anionic Nafion film [28,32] or polysaccharide gel film, such as agar, agarose, sodium alginate or κ -carrageenan [27] containing MB in which the electrostatic interaction between opposite charged polymers is strong enough to retain the self-assembled dyes. Sohrabnezhad et al. [18,21] propose the inclusion of MB and new MB in zeolites in which the protons generated by the dissociation of water molecules upon dehydration of the zeolite are the key for the subsequent protonation and dimerization equilibria of dye. For their part, Horváth et al. [14] propose the use of MB adsorbed on protonated titanate nanowire-based thin films in which the colour change caused by dimerization is induced by water adsorption. Finally, Mills et al. [19] use the deliquescent urea encapsulated within hydroxyl ethyl cellulose with

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