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Novel dye + solid polymer electrolyte material for optical humidity sensing

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Abstract

Our experimental observations show that certain dyes when incorporated in solid polymer electrolytes (SPE) can serve as an excellent candidates for optical humidity sensing. Crystal violet (CV) have been incorporated in poly(vinyl alcohol) (PVA)/H_3PO_4, which is known to be a SPE and a good proton conductor. Films of PVA/H_3PO_4 containing CV dye have been studied for use in optical humidity sensing and the interesting results have been discussed here in this paper. We have also tried to give a mechanism for the changes observed in the optical properties of such films by the variation of humidity. © 2001 Published by Elsevier Science B.V.

Keywords: Solid polymer electrolyte; Poly(vinyl alcohol); Crystal violet; Relative humidity; Optical humidity sensing

1. Introduction

Optodes (optical electrodes) are based on analyte-dependent changes of optical properties such as absorbance, reflectance or fluorescence of their receptor part. Optical fiber chemical sensors have attracted increasing interest in the recent years owing to their inherent characteristics such as immunity to electrical noise, ease of miniaturization and the possibility of real-time monitoring and remote sensing. They have many advantages in comparison with electrical sensors. They have very fast response time as compared to electrical sensors and do not need electrical contacts that could be damaged by the sensed substance. For the same reason they are much safer in case of flammable gas or vapors. These features makes optodes a powerful tool for environmental and industrial process monitoring.

The relative humidity (RH) of air is an important parameter which needs to be measured or monitored in various chemical processes, such as in the food, electronics, textile, chemicals and pharmaceutical industries and in the ambient environment. In these respects, different humidity sensors based on measurement of electrical and optical properties have been described. Conductometric humidity sensors based on poly(vinyl

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alcohol) (PVA) and graphitized carbon black were studied by Barkauskas [1]. Humidity sensors based on organic polymeric films have also been constructed [2,3]. Perez and Freyre employed the change in relative permittivity of poly(ethylene terephthalate) to measure RH [2]. Capacitive-type sensors using cross-linked polyimide films were employed by Matsuguch et al. [3] to measure RH. Humidity sensors based on ceramic materials have also been frequently described [4–6]. Inorganic substances are rarely applied for the construction of optical chemo-sensitive membranes. The application of $CoCl_2$ films for optical sensing of humidity can serve as an example [7–10]. The change in color from blue to pink that accompanies the hydration of cobalt chloride is the analytical signal of such optodes. Cobalt oxide films (Co_3O_4) showed absorbance changes in the visible wavelength region when exposed to different RH at room temperature [11].

It is well established that both organic and inorganic polymers constitute important component of optical sensors. A variety of polymers have been used in optical sensors which include silicones, poly(vinylchloride) (PVC), poly(tetrafluoroethylene) (PTFE), nafion, nylon, agarose, sol–gels, etc. [12]. In general, polymers provide good mechanical properties to the sensor design. The chemical sensing and signal processing capability of the chemo-optical interface is generally achieved by the incorporation of a reagent. The reagent layer usually consists of a dye which reversibly reacts with the analyte contended in the sample. Selective complex-forming indicator dyes (chro-moionophores) or acid–base indicator are frequently used [13,14]. Otsuki et al. [15] employed an extremely curved optical fiber covered with a sensing film composed of rhodamine B (RB) and hydroxypropylcellulose to determine RH in the region 0–95%, with a response time of 2.3 min. A fluorimetric sensor based on the entrapment of ethylene glycol and rhodamine 6G (R6G) in gelatin was described by Choi and Tse [16]. Raimundo and Narayanaswamy [17] have used nafion as an ion-exchange matrix for crystal violet (CV) for the determination of RH and used as a suitable matrix for the optical fiber based moisture sensors. Different dyes have been doped in nafion and their optical properties and optical humidity sensing characteristics were studied by different groups [18–21]. The choice of the polymer is governed by its structural characteristics for the reagent immobilization, its stability, its permeability to the analyte and its compatibility for interfacing with fiber optics in the sensor design and fabrication.

In this paper, we are presenting our results on how the CV when incorporated in solid polymer electrolyte (SPE)-like PVA/H_3PO_4 can be used for the optical sensing of the humidity. The optical properties of such polymer–dye composite films have been studied in dry and wet states. We will publish our results on other systems such as methylene blue (MB), RB, R6G doped in SPE for the usage of optical humidity sensing in some of our forthcoming publications.

2. Experimental

Polyvinylalcohol (PVA, MW 10^4, Loba Chemie) films containing phosphoric acid (1:1) from aqueous solution (1 wt.%) which also contained the crystal violet (CV, MW 407.99, Thomas Baker Chemicals) dye having different concentrations has been prepared by dip coating the microscopic grade glass substrate which were cleaned earlier using an ultrasonic cleaner. The films thus obtained are examined for their sensitivity towards humidity. The humidity is varied and measured by standard two temperature method, which is described in brief below. A He–Ne laser beam is allowed to pass through the sample (films), and the output (in the form of transmission of the beam) is measured by using a photodiode which converts the incident light on it to the voltage. The laser beam is incident perpendicular to the surface of the film. The readings in the form of voltage (which is directly a measure of the transmission of the film) are taken with respect to the humidity. Normalized output is plotted with respect to the humidity.

Different saturated solutions of the salts in water are known to give controlled humidity such as saturated solution of NH_4Cl in water is known to give a 77% humidity, likewise K_2CO_3 – 44%, $CaCl_2$ – 30% and H_3PO_4 – 9%. The films under

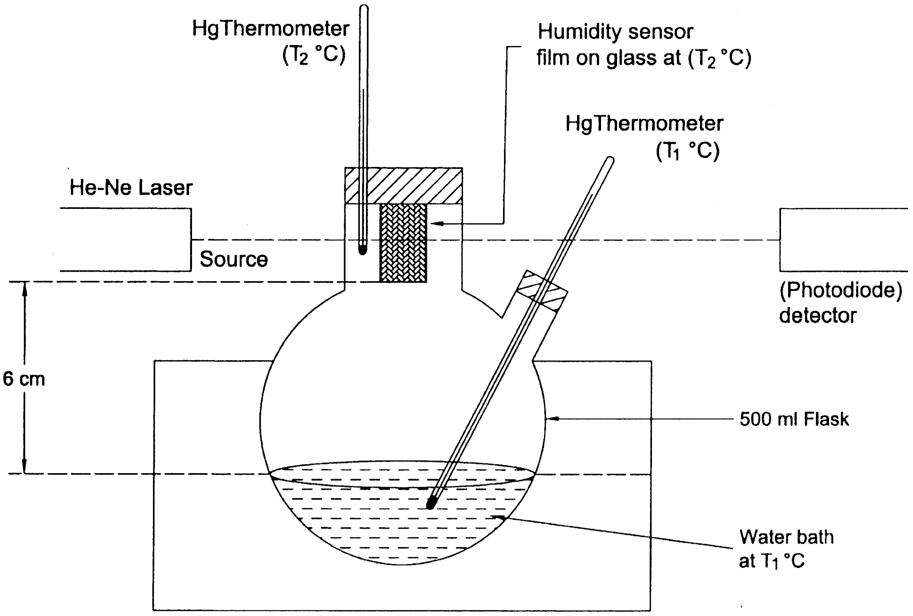

Fig. 1. Schematic of the experimental set up for the measurement of RH (using two temperature method).

study are exposed to different humidity levels in a glass chamber in which the controlled humidity is obtained by using such salt solutions. UV–VIS spectra of the such films (exposed to different humidity levels) are taken on a Shimadzu UV-240 spectrophotometer. The dry state and the wet state of the film means the film kept in the dry box for a long time and the film exposed to 100% humidity and not the film dipped in water.

Fig. 1 shows the schematic diagram of the dynamic humidity chamber used for varying and measuring the humidity by two temperature method. The humidity system used consists of a closed flask (total volume 500 ml), with two necks for inserting thermometers (range −10°C to 60°C with an accuracy of 0.5°C) and the sensor, partially filled with water and kept in a thermocole container. External container is filled to the equal level of water (which is present in the flask) with ice. The temperature of the system is adjusted by mixing ice and water as required. Thus, the water inside the flask can be kept at the required temperature (T_1). The sensor (i.e. the film of CV/PVA + H_3PO_4) is mounted inside the flask at an height of 6 cm from the surface of the water and the temperature of the sample (T_2) is measured with a thermocouple which is placed at an equal height of the sample to be studied. The humidity inside the chamber is calculated by taking the ratio of the saturated water vapor pressure at water temperature (T_1) and the sample temperature (T_2). The values of the saturated vapor pressure are obtained from the CRC manual of chemistry. It is to be noted that the temperature of the sample changes by 3–6°C during the experiment. The %RH in the air of the flask is given by

$$\%\mathrm{RH} = [E_w(T_1)/E_w(T_2)] \times 100, \qquad (1)$$

where $E_w(T_1)$ is the saturated water vapor pressure at the temperature of the water and $E_w(T_2)$ is the saturated water vapor pressure at the temperature of the sensor element. Different RH values are obtained by adjusting the temperature of the water inside the flask, with ice and water mixture from room temperature to 0°C. The system equilibrium time is quite small and stable readings were obtained within 10 minutes [22,23].

3. Results and discussion

Fig. 2 shows the UV–VIS spectra of the CV in an aqueous medium. It shows a peak at around 575 nm with a hump at 530 nm and a small peak at 360 nm. Figs. 3(A) and (B) show the UV–VIS spectra of the PVA + H_3PO_4 + CV (dye concentration 17.6 mM/monomer) film in the dry state (9% humidity) and the wet state (100% humidity) respectively. Spectra at the intermediate humidity levels are not shown here. In the dry state, the color of the film is yellow with a main absorption peak at around 430 nm. As the humidity increases, however, this peak decreases in intensity and a new peak maximum forces at 620 nm. The color of the film in the wet state is violet. The very thin nature of the PVA films (thickness ~1 μm) together with the high sensitivity of the PVA + H_3PO_4 + CV complex, gives rapid and fully reversible changes in the absorbance when exposed to humid conditions.

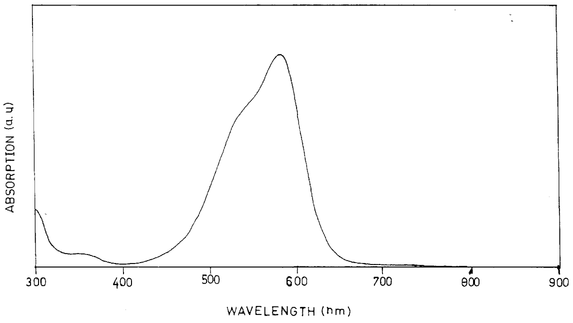

Fig. 2. UV–VIS spectra of CV in distilled water.

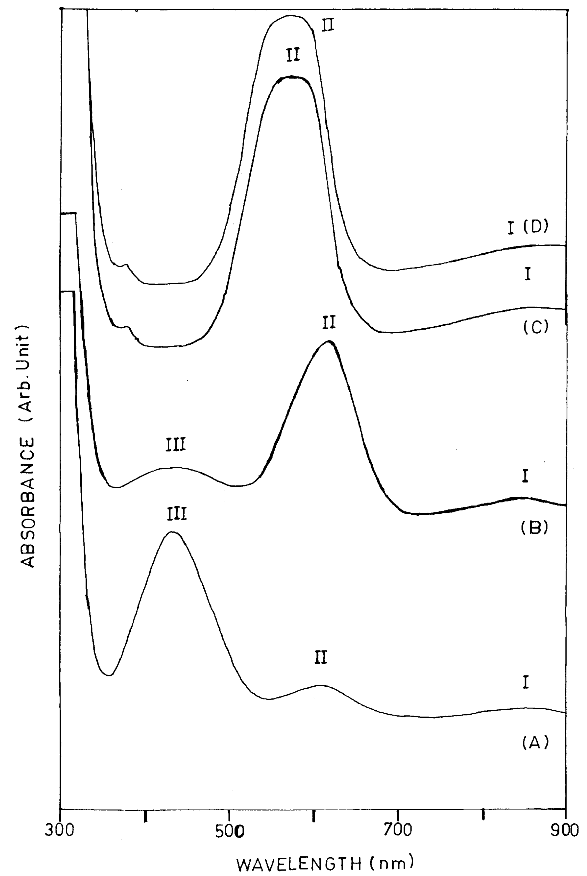

Fig. 3. (A) UV–VIS spectra of the PVA + H_3PO_4/CV dip-coated film on glass at 9% humidity (dye concentration 17.6 mM/monomer). (B) UV–VIS spectra of the PVA + H_3PO_4/CV dip-coated film on glass at 100% humidity (dye concentration 17.6 mM/monomer). (C) UV–VIS spectra of the PVA/CV dip-coated film on glass at 9% humidity (dye concentration 17.6 mM/monomer). (D) UV–VIS spectra of the PVA/CV dip-coated film on glass at 100% humidity (dye concentration 17.6 mM/monomer).

This change in the optical properties of the films by humidity can be possibly due to either association/dissociation complex that the dye (CV) must be forming with the polymer or due to change in the pH value. The peak corresponding to 620 nm in Figs. 3(A) and (B) can be associated with the absorption of the dye. The presence of a new peak at about 430 nm can be associated with the formation of a complex between CV and PVA/H_3PO_4. CV is a cationic dye which contains three *N*-phenyl terminal groups. It is usually found in the form of the chloride salt and, therefore, has two free *N*-phenyl terminal groups that can acts as basic sites. It is well known that CV undergoes solvatochromism in which the color is very sensitive to the acidity of the protons. In water, CV is frequently used as an acid–base indicator, undergoing a color change from yellow to purple in the pH 0.1–2.0 range. PVA doped with phosphoric acid (i.e. PVA + H_3PO_4) is a SPE and a well known proton conductor – extensively studied and used for lithium rechargeable batteries and in all solid state electrochromic display devices, solid state photocells etc. [24–28]. CV is in highly acidic environment when incorporated in SPE (SPE, i.e.

PVA + H_3PO_4). The acidity of the environment around CV depends on the water content in the film. Here, it is worthwhile to mention that PVA doped with phosphoric acid should be treated as a single entity (say as a SPE) as they from a complex with each other which is well known [24–28]. The CV–SPE film has very high acidity (because of the doped phosphoric acid in PVA) and as a consequence, CV must be in a diprotonated form and the film remains yellow – similar to CV in nafion, as reported earlier by many authors. With increasing water content, the film becomes less acidic and the diprotonated CV loses protons, converting it to monoprotonated and non-protonated forms and consequently the color of the film changes. When the water content in the film is very high, CV shows its own optical properties as if it is in water only, giving the film an intense violet color. It is also worthwhile to mention here that PVA is an hydro-gel and hence as such absorbs moisture/humidity heavily.

From Figs. 2 and 3(A), it can be seen that the peak corresponding to the complex formation between the CV and PVA + H_3PO_4 (i.e. peak at 430 nm) decreases in intensity (and at the same time the peak at 620 nm increases in intensity) with increase in the humidity. In other words, it means that as the humidity increases the complex between CV and PVA + H_3PO_4 breaks and that is why the absorption at 430 nm decreases in intensity with the increase in humidity. As the complex dissociates more and more with respect to humidity, the absorption at 620 nm will naturally increase because of the presence of CV in its molecular form. It can be seen from Fig. 3(C) and (D) (dye concentration 17.6 mM/monomer) that the CV does not forms a complex with PVA alone but it forms a complex with PVA/H_3PO_4. PVA films containing CV (without H_3PO_4) are studied for their sensitivity towards humidity. They are observed to be insensitive to humidity [can be seen from Fig. 3(C) and (D), which shows the UV–VIS spectra of such films in the dry and wet state respectively]. The necessarily for the presence of the acidic environment for showing such a chromic effect indicates that the above proposed mechanism must be holding true. Thus, it can be concluded that the change in the optical properties (color) of the PVA + H_3PO_4/CV films with respect to humidity is due to the formation of the association/dissociation complex between the two.

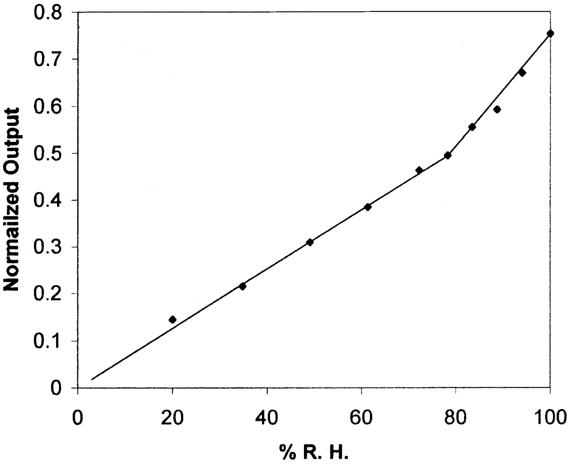

Fig. 4. Variation of the normalized output with respect to the humidity for PVA + H_3PO_4/CV dip-coated film (dye concentration 17.6 mM/monomer) on glass.

Fig. 4 shows the normalized output – which is directly a measure of the absorption of the film at 631 nm with variation in the humidity. It can be seen that as the humidity decreases the normalized output (absorbance at 631 nm) also decreases which is inconsistent with the observed decrease in the intensity of the peak at 620 nm in the UV–VIS of such films. The linearity of the response is an advantage as compared with the CV–nafion system. The response shows (i.e. Fig. 4) two straight lines which can be due to surface dependent and bulk related phenomenon's. The surface dependent phenomenon which occurs by the diffusion of the moisture is a relatively slow phenomenon and hence the response/straight line has a lower slope as compared to the bulk process. Hysteresis is practically absent. However, the material under study suffers a drawback. Since the polymer i.e. PVA is soluble in water, as a result, the sensor fabricated using this material (as a host material) cannot operate in highly humid conditions for a long time or in an atmosphere where it can dew. But the material is highly suitable for 20–80% RH. Similar humido-chromic effect (change in the optical properties i.e. color of the materials by humidity) have also been observed by using RB, MB dyes in SPE. Currently, we are coupling such materials with the optical fibers and studying their response for the humidity. We will be publishing the results of these in detail in some of our forthcoming publications.

4. Conclusions

CV when incorporated in SPE-like PVA/H_3PO_4 can serve as an excellent candidate for optical humidity sensing. The system displays novel color change in the visible region with the variation of the humidity from yellow to violet which can be associated with the formation of association/dissociation complex between the two and consequently the protonation/de-protonation of the CV. The linearity of the response is an advantage of this system over nafion–CV system. Similar humido-chromic effect has also been shown by other dyes-like MB, RB, etc.

References

[1] J. Barkauskas, Talanta 44 (1997) 1107.
[2] J.M.M. Perez, C. Freyre, Sens. Actuators B 42 (1997) 27.
[3] M. Matsuguch, T. Kuroiwa, T. Miyagishi, S. Suzuki, T. Ogura, Y. Sakai, Sens. Actuators B 52 (1998) 53.
[4] C.D. Feng, S.L. Sun, H. Wang, C.U. Segre, J.R. Stetter, Sens. Actuators B 40 (1997) 217.
[5] W. Qu, J.U. Meyer, Sens. Actuators B 40 (1997) 175.
[6] M. Pelino, C. Cantalini, H.T. Sun, M. Faccio, Sens. Actuators B 46 (1998) 186.
[7] A.P. Russel, K.S. Fletcher, Anal. Chim. Acta 170 (1985) 209.
[8] D.S. Ballantine, H. Wohltjen, Anal. Chem. 58 (1986) 2883.
[9] Q. Zhou, M.R. Shahriari, D. Kritz, G.H. Sigel Jr., Anal. Chem. 60 (1988) 2317.
[10] F. Boltinghouse, K. Abel, Anal. Chem. 61 (1989) 1863.
[11] M. Ando, T. Kobayashi, M. Haruta, Sens. Actuators B 32 (1996) 157.
[12] T.E. Brook, R. Narayanaswamy, Sens. Actuators B 51 (1998) 77.
[13] W.R. Seitz, CRC Crit. Rev. Anal. Chem. 19 (1998) 135.
[14] W. Wroblewski, A. Dybko, Z. Brzozka, Chem. Anal. 42 (1997) 757.
[15] S. Otsuki, S. Adachi, T. Taguchi, Sens. Actuators B 53 (1998) 91.
[16] M.M.F. Choi, O.L. Tse, Anal. Chim. Acta 378 (1999) 127.
[17] I.M. Raimundo Jr., R. Narayanaswamy, Analyst 124 (1999) 1623.
[18] Y. Sadaoka, M. Matsuguchi, Y. Sakai, Y. Murata, J. Mater. Sci. 27 (1992) 5095.
[19] S. Otsuki, K. Adachi, J. Appl. Polym. Sci. 56 (1995) 697.
[20] Y. Sadaoka, M. Matsuguchi, Y. Sakai, Y. Murata, Chem. Lett. 4 (1991) 717.
[21] S.A. John, R. Ramaraj, J. Appl. Polym. Sci. 65 (1997) 777.
[22] B.M. Kulwicki, J. Am. Ceram. Soc. 74 (1991) 697.
[23] M.L. Jadhav, S.A. Gangal, R.N. Karekar, Sens. Actuators 8 (1985) 149.
[24] P. Somani, S. Radhakrishnan, Chem. Phys. Lett. 292 (1998) 218.
[25] S. Radhakrishnan, P. Somani, Mater. Lett. 37 (1998) 192.
[26] P. Somani, D.P. Amalnerkar, S. Radhakrishnan, Synth. Metals 110 (2000) 181.
[27] P. Somani, A.B. Mandale, S. Radhakrishnan, Acta Materialia 48 (2000) 2859.
[28] P. Somani, S. Radhakrishnan, Mater. Chem. Phys. 70 (2001) 150.