Fluorescence Sensor for Water Content in Organic Solvents Based on Covalent Immobilization of Benzothioxanthene

Zhi-Zhang Li,[1] Cheng-Gang Niu,*[2] Guang-Ming Zeng,[2] and Pin-Zhu Qin[2]
[1]*Hunan University of Science and Engineering, Yongzhou 425100, P. R. China*
[2]*College of Environmental Science and Engineering, State Key Laboratory for Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, P. R. China*

(Received March 31, 2009; CL-090319; E-mail: cgniu@hnu.cn)

A derivative of benzothioxanthene, *N*-(2-methacryloxyethyl)benzo[*k*,*l*]thioxanthene-3,4-dicarboximide (MBTD), was used as a fluorescent indicator for determination of water content in organic solvents. MBTD was photocopolymerization-immobilized on a glass surface. The prepared sensor system possesses relatively long lifetime, short response, and recovering time. The reversibility and reproducibility are also adequate for practical measurement.

Monitoring and controlling water content are quite important in several fields of chemistry and industry. Recently, optical sensors have been widely developed because they are of inexpensive, miniature, robust, and easy to fabricate.[1–4]

In the fabrication of fluorescence sensors, the most important step is to choose a suitable fluorescent dye. Fluorescent molecules, whose fluorescence lifetime, spectra, and/or intensity are markedly sensitive to solvent polarity, are widely used as reporter probes or sensors for monitoring water content in organic solvents.[5–9] Naphthalimide derivatives are one of such attractive polarity-sensitive fluorophores since they possess excellent photophysical and photobiological properties.[10–12] Meanwhile, immobilization of a fluorescent dye is another important step in the fabrication of a fluorescence sensor and will largely affect the performance of the sensor in terms of sensitivity and stability. As demonstrated in our previous papers,[9,13,14] covalent immobilization seems to be the most efficient method which can effectively prevent the leakage of the fluorescent dye from the sensor membrane, a phenomenon that shortens the long-term stability of many optical sensors.

In this paper, the authors prepare a fluorescence water sensor for the determination of water content in organic solvents. A benzothioxanthene derivative, MBTD (Figure 1), was used as a fluorescence indicator owing to its favorable sensitivity to its surroundings. MBTD with a terminal double bond was photocopolymerized with acrylamide, 2-hydroxyethyl methacrylate, and triethylene glycol dimethacrylate on a glass surface treated with a silanizing agent, for experimental details see Supporting Information.[15] The proposed sensor possesses high sensitivity and selectivity, good reversibility, and rapid response. And the fluorescence intensity of MBTD changed as a linear function of water content in a certain range. The proposed sensor provides an alternative simple approach for determination of water content in organic solvents.

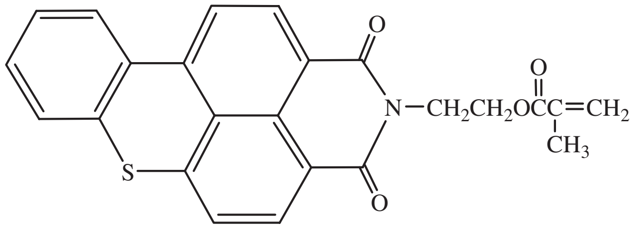

Figure 1. Structure of MBTD.

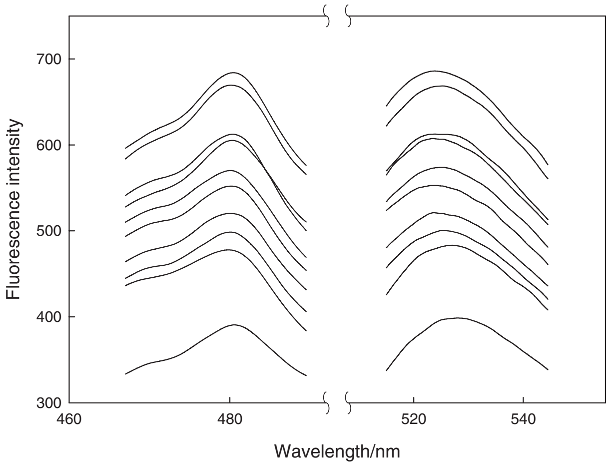

Figure 2. Fluorescence excitation (left) and emission (right) spectra of the sensing membrane on exposure to different solvents (from top to bottom: tetrachloromethane, methylene chloride, ethanol, chloroform, dioxane, acetone, acetonitrile, DMF, methanol, and water).

Fluorescence spectra of the sensing membrane were recorded in various solvents of different polarity and are displayed in Figure 2. The solvent exerted an evident influence on the fluorescence intensities (from 686 in tetrachloromethane to 399 in water). Changing from a nonpolar to a polar solvent increases the solvent interaction with both the ground state and the excited state, but the interaction is greater for the excited states resulting in shifts of the emission spectrum to longer wavelengths (red shift). However, the Stokes shifts in acetone, acetonitrile, ethanol, and methanol generated deviations from the correlations, for experimental details see Supporting Information.[15] These variances may be due to the effect of the formation of hydrogen bonding as well as the glass support and polymer backbone.

The prepared fluorescence sensor seems useful in the determination of water content in organic solvents. The fluorescence spectra of MBTD in the sensing membrane contacted with ethanol solutions of different water content are displayed in Figure 3. With the increase of water content from 0.00 to 100.0% (v/v), the fluorescence intensity of MBTD decreased dramatically and the emission peak underwent a red shift.

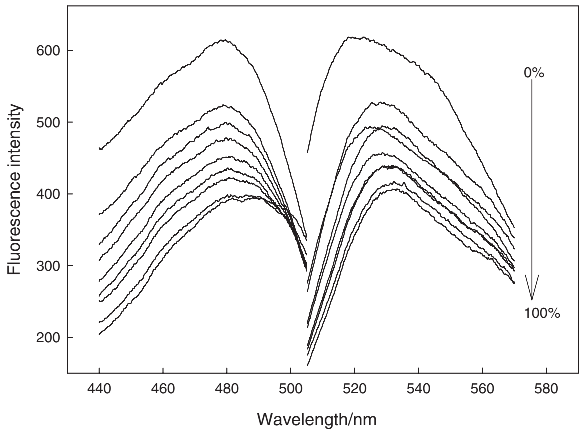

Figure 3. Fluorescence excitation (left) and emission (right) spectra of the sensing membrane contacted with different water content in ethanol in the range of 0 to 100% (v/v) (ex. 479 nm, em. 518 nm): (1) 0.0%, (2) 5.0%, (3) 6.0%, (4) 7.0%, (5) 8.0%, (6) 9.0%, (7) 10%, (8) 50%, and (9) 100%.

The effect of pH on the fluorescence intensity of the MBTD-immobilized sensor was also investigated in aqueous solutions of different pH. The fluorescence intensity of the sensing membrane reduced mildly when pH was below 3.0. But the fluorescence intensity is essentially independent of pH in the range 3.0 to 12.0, and the variation of fluorescence intensity was within 0.81%, for experimental details see Supporting Information.[15] This favorable characteristic was mainly related to the fact that the fluorophore of choice itself is pH-insensitive.

The sensing membrane was equilibrated with ethanol samples with different water content to investigate the response time, reversibility, and reproducibility of the sensor. The sensing membrane consisting of MBTD was alternately exposed to water content of 3.0, 7.0, and 60.0% (v/v) in ethanol. The confidence intervals of mean fluorescence intensity were found to be 567.1 ± 1.9 ($n = 10$), 461.9 ± 1.2 ($n = 5$), and 401.6 ± 1.7 ($n = 4$) for water contents of 3.0, 7.0, and 60.0%, respectively (n is times of sensing membrane exposed to the three different solutions, respectively, the confidence intervals were all calculated for a probability of 0.95). The recovery time was independent of the order of water content change, i.e., it remained the same no matter whether one switched from low to high water content or the reverse. The response time, t_{99} (i.e., time required for 99% of the total signal changes to occur) was of the order of 60 s, for experimental details see Supporting Information.[15] All these results imply that the reproducibility and reversibility of the proposed sensor were satisfactory.

The sensing membrane was exposed to flowing ethanol sample with a water content of 10.0% (v/v) over a period of 8 h under continuous irradiation to investigate the stability of the sensor. The fluorescence intensity was recorded at intervals of 30 min. A relative standard deviation of 1.86% was obtained and no photodecomposition of MBTD was observed. The stability of the sensor over short time periods is reasonable. The membrane exhibited good stability and maintained its function for at least three months of use. Immobilization of MBTD by covalent polymerization can substantially prevent leaching effects and prolong the lifetime of the sensor.

The experimental response curves of the sensing membrane for water content in three different organic solvents (acetonitrile, acetone, and ethanol) were investigated, for experimental details see Supporting Information.[15] The linear response of the sensing membrane covered water content from 0.00 to 20.00% (v/v) for acetonitrile and acetone, and 0.00 to 12.00% (v/v) for ethanol. The following equations were obtained by fitting the experimental data obtained:

$$\text{Acetonitrile: } F/F_0 = -0.0072[\mathrm{H_2O}] + 0.9955 \quad (R = 0.9949) \qquad (1)$$

$$\text{Acetone: } F/F_0 = -0.0041[\mathrm{H_2O}] + 0.9962 \ (R = 0.9908) \qquad (2)$$

$$\text{Ethanol: } F/F_0 = -0.0283[\mathrm{H_2O}] + 0.9920 \ (R = 0.9955) \qquad (3)$$

These calibration equations can serve as a quantitative basis for the determination of trace water content in some organic solvents. The detection limits were of 0.088, 0.144, and 0.019% for acetonitrile, acetone, and ethanol, respectively. The relative standard deviation for the water concentration from the calibration curve is less than 0.13%.

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15 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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