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Design and fabrication of optical chemical sensor for detection of nitroaromatic explosives based on fluorescence quenching of phenol red immobilized poly(vinyl alcohol) membrane



Ali Reza Zarei*, Behnam Ghazanchayi

Faculty of Chemistry and Chemical Engineering, Malek Ashtar University of Technology, P.O. Box 15875-1774, Tehran, Iran

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ABSTRACT

The present study developed a new optical chemical sensor for detection of nitroaromatic explosives in liquid phase. The method is based on the fluorescence quenching of phenol red as fluorophore in a poly (vinyl alcohol) (PVA) membrane in the presence of nitroaromatic explosives as quenchers, e.g., 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 4-nitrotoluene (4-NT), 2,4,6-trinitrobenzene (TNB), and nitrobenzene (NB). For chemical immobilization of phenol red in PVA, phenol red reacted with formaldehyde to produce hydroxymethyl groups and then attached to PVA membrane through the hydroxymethyl groups. The optical sensor showed strong quenching of nitroaromatic explosives. A Stern–Volmer graph for each explosive was constructed and showed that the range of concentration from 5.0×10^{-6} to 2.5×10^{-4} mol L⁻¹ was linear for each explosive and sensitivity varied as TNB > TNT > 2,4-DNT > NB > 4-NT. The response time of the sensor was within 1 min. The proposed sensor showed good reversibility and reproducibility.

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1. Introduction

Nitroaromatic explosives are used in munitions such as landmines and bombs [1,2]. There have been large increase in the development of trace explosive detection in the last decade in response to globalization of terrorist acts and to reclamation of contaminated land previously used for military purposes [3]. Quick and reliable sensors for the detection of high explosives have generated interest as tools to protect societies from terrorism and control environmental pollution [4,5]. From the environmental perspective, such explosives present in undetonated landmines and unexploded ordnances (UXO) can leach into and persist in the soil and groundwater, posing a threat to the environment and living inhabitants [6,7]. It is clear that sensitive and reliable methods are needed to monitor nitroaromatic explosives.

Although explosive detection technologies, such as sniffer dogs or sophisticated instruments are common, these techniques are expensive and may not be easily accessible [8–12]. Among the current methods for explosive detection, fluorescence-based chemical sensors have shown high sensitivity and detection simplicity [13–17]. Because most explosives are electron deficient nitroaromatic compounds, they can efficiently quench fluorescence

emissions of a π -electron rich fluorophore compound by photo-induced electron transfer and provides a simple application for explosive detection [18–25].

Chemical sensors for fast and highly-selective detection of high explosives have attracted attention for security and have environmental and humanitarian implications [26,27]. There is a growing need for construction of chemical sensors for fast and economical monitoring of environmental samples. A suitable sensor should be able to analyze samples in a relatively short period of time. A variety of chemical sensors have been developed using different transductions. Optical chemical sensors are those using advanced techniques in analytical chemistry and have been accepted as advantageous because they can be miniaturized and manufactured at low cost [28].

The immobilization of sensing reagents onto membranes is an important step in the preparation of optical chemical sensors for practical applications. The methods developed for immobilization of a sensing reagent are adsorption, entrapment, and covalent binding. Both adsorption and entrapment methods are relatively easy for preparation, but leakage of the sensing reagents makes long-term use of the sensor impractical. The chemical binding method is relatively complicated and time-consuming, but the good stability and long life of sensors can be acquired because the reagents are not likely to leak [29]; thus, the chemical binding method is more common.

Various polymeric membranes have been used as a supporting

* Corresponding author.

E-mail address: zareei1349@gmail.com (A.R. Zarei).

matrix for preparation of optical sensors. The rapid response results from the porous structure of the polymeric support, which minimizes barriers to mass transport between the analyte and immobilized sensing reagent. Poly(vinyl alcohol) (PVA), poly(vinyl chloride) (PVC), and hydrolyzed cellulose film are examples of polymeric membranes used for the preparation of optical sensors [30–39].

The present study developed a phenol red immobilized PVA membrane as a fluorescence sensor for detection of nitroaromatic explosives. This method is based on the formation of hydroxymethyl groups in the phenol red by condensation reaction with formaldehyde, which are then attached to the PVA membrane. Fluorescence spectral characteristics, quenching constants, response time, reproducibility, and long-time stability of the sensor membrane are discussed.

2. Experimental

2.1. Materials

All chemicals used were of analytical-reagent grade. All solvents used were of spectroscopic grade. Phenol red was obtained from Sigma. Poly(vinyl alcohol) (approximate molecular weight of 49,000) and formaldehyde solution (37% w/w) were obtained from Merck. A stock solution of 1.0 mmol L^{-1} of nitroaromatic compound (TNT, TNB, 2,4-DNT, NB, and 4-NT) were prepared separately by dissolving the appropriate weight of each explosive in methanol and diluting it to 100 ml in a volumetric flask. Working standard solutions were obtained by appropriate dilution of the stock standard solution of each explosive with distilled water. The pH was adjusted to a desirable level (pH 4.0) by dissolving appropriate amounts of sodium acetate trihydrate (Merck) in water (0.05 mol L^{-1}) and adding acetic acid (Merck) solution.

2.2. Apparatus

A LS-50B luminescence spectrophotometer with a xenon lamp as the light source and a 1.00 cm quartz cell was used to record the fluorescence spectra. A spin-on EC101DT photo resist spinner (Headway Research) was used to spin-coat the PVA film onto glass plate.

2.3. Preparation of sensor film

Film preparation was carried out according to the method described by Liu et al. [35] as follows. First, 35 mg phenol red (1.0 mmol), 1.0 ml 37% (w/w) formaldehyde aqueous solution (12.35 mmol), 0.25 g sodium hydroxide, and 6.0 ml distilled water were added to a three-neck flask equipped with a mechanical stirrer, a N_2 inlet, and a condenser. The mixture reacted at the boiling temperature under nitrogen atmosphere for 4 h, when another 2.0 ml of formaldehyde aqueous solution was added. After 4 h of reaction, the concentrated hydrochloric acid solution was added stepwise to precipitate the reaction product. The precipitate phenol red-formaldehyde (PRF) was dried in a vacuum oven at ambient temperature for 24 h.

Next, 2.0 g PVA was dissolved in 20 ml dimethyl-sulfoxide (DMSO) at 100°C under N_2 atmosphere. Then, 50 mg of PRF was added and the mixture was stirred for 2 h. For spin-coating, a clean glass plate was mounted on the spin-on device and rotated at a frequency of 800 rpm. Using a syringe, 200 μl of membrane solution was sprayed toward the center of the plate. After a spinning time of 5 s, the film had coated the plate, which was then placed into an oven at 90°C for 30 min and 120°C for 2 h. The glass plate was then immersed in 0.1 mol L^{-1} NaOH for 1 d to

remove unreacted PRF.

2.4. Fluorescence spectral characteristics of sensor

The excitation and fluorescence emission spectra of PVA membrane were recorded in 1 cm quartz cells filled with aqueous solution containing nitroaromatic explosive quencher and acetate buffer at pH 4.0. The coated glass plate was placed diagonally into the quartz cell. The advantage of this kind of placement was to guarantee the detection of fluorescence emission intensity without interference from the excitation source. The fluorescence intensity was measured at $\lambda_{ex}=386 \text{ nm}$ and $\lambda_{em}=578 \text{ nm}$. The data was reported as the initial intensity before quencher had entered the membrane (F^0) divided by the intensity in the membrane of quencher F . The data increased linearly versus quencher concentration.

3. Results and discussion

3.1. Preliminary investigation

The phenol-formaldehyde reaction is a well-known reaction; the formaldehyde primarily attacks the phenol at the ortho and para positions of the phenolic hydroxyls and not the phenolic hydroxyls themselves [40]. The phenolic hydroxyl remains in the molecular structures after the reaction. They can be covalently bound to the PVA membrane through the numerous newly-produced hydroxymethyl groups [35,36]. The reaction involving the formation of phenol-formaldehyde and immobilization of the product on the PVA membrane is shown in Scheme 1 [41,42].

3.2. Excitation and emission spectral characteristics of sensor

The excitation and emission spectra of the phenol red fluorophore were recorded in the methanol solution phase and PVA matrix (Fig. 1). The fluorophore exhibited excitation and emission at longer wavelengths and at a higher fluorescent intensity in the PVA matrix compared to that in the solution phase. The immobilization of fluorophore molecules in the solid matrix may reduce intramolecular motion and rearrangement (restriction of vibrational rotational motion), leading to red shift in wavelengths and enhanced fluorescence capability. The PRF-PVA membrane showed one emission at 578 nm when it was excited at 386 nm.

The fluorescence characteristics of PRF-PVA film in solvent was studied at different polarities. Fig. 2 shows that the sensor film gives better intensity fluorescence in methanol solvent than in other solvents because of the improved swelling of the PVA film in polar solvents. Although PVA film swells more in water than in methanol medium, the fluorescence intensity of the sensor in water is lower for methanol because of the lower quantum yield of the PRF-PVA membrane in water.

The effect of solution pH on the fluorescence response of the proposed sensor was investigated at a range of 2.0 to 9.0 using 0.01 mol L^{-1} HCl or NaOH solution for pH adjustment. The fluorescence intensity increased as the pH increased up to 4.0 and decreased at higher pH values (Fig. 3). This could be in response to the molecular structure of the phenol red in acidic media for electron transition of $\pi-\pi^*$ is desirable in comparison with electron transition of $n-\pi^*$ occurring in basic media. The pH of 4.0 was adjusted using 0.05 mol L^{-1} acetate buffer solution.

3.3. Quenching of sensor in the presence of nitroaromatic compounds

One promising approach for explosives detection is

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